

**Study of chemically reactive surfaces of TiO₂ and Ag/TiO₂ for adsorptive desulfurization of
liquid fuels and photocatalysis applications**

by

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Abstract

The first part of this study focuses on the mechanisms study of UV photo-induced adsorptive desulfurization of liquid model fuels on anatase TiO_2 adsorbents. Previous studies showed UV irradiation during or prior to the desulfurization breakthrough experiment can improve the sulfur removal breakthrough capacity of anatase TiO_2 by up to 65%. To further improve the sulfur removal efficiency of the adsorbent, it's of primary importance to understand the surface alteration mechanism caused by UV irradiation. X-ray photoelectron spectroscopy (XPS) is a surface analytical instrument that can reveal surface chemical properties of solid samples. By comparing the XPS spectral change of Titanium, O, Ag, and C elements before and after UV treatment, XPS can provide us a scheme of the surface chemical composition alteration caused by UV irradiation. In situ XPS technique can further assist us to access the reaction mechanisms by showing the chemical property changes during the reaction procedure. In this study, XPS and in situ XPS spectral results illustrate that UV irradiation converts lattice oxide oxygen into surface hydroxyl groups, and those photo-generated surface hydroxyl groups are essential factors for the improvement of sulfur removal capacities. Qualitative and quantitative analysis showed the ratio between the rate of hydroxyl production and lattice oxide oxygen consumption is 2:1. Thus, the mechanism of UV photo-induced adsorptive desulfurization is UV irradiation converts one oxide oxygen into two surface hydroxyl groups on anatase TiO_2 and the additional hydroxyl groups improved the desulfurization capacity of anatase TiO_2 adsorbent.

To further understand and estimate the mechanisms of UV irradiation on TiO_2 adsorbent, two different types of anatase TiO_2 adsorbents were applied to XPS characterization. It is proposed that UV photo-catalytic reaction of anatase TiO_2 is influenced by adsorbed H_2O , so

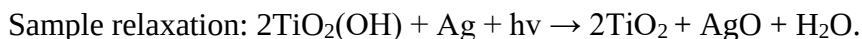
XPS measurements were conducted on UV treated and untreated TiO₂ adsorbents that were prepared at 110 °C and 450 °C, respectively. Temperature has a significant effect on the relative amount of H₂O can be adsorbed on TiO₂ samples as it is indicated by TGA (Thermogravimetric Analysis). XPS spectra showed that UV treatment on 110 °C prepared TiO₂ can produce more hydroxyl groups than TiO₂ prepared at 450 °C. XPS spectral results also showed that UV irradiation on TiO₂ with higher surface area produced more additional hydroxyl groups. The results illustrated that the reactions caused by UV irradiation were that one adsorbed H₂O and one lattice oxygen in anatase TiO₂ went through photo-catalytic reactions under UV treatment to form two additional surface hydroxyl groups.

The second part of this study investigated the reaction mechanism for the UV induced decomposition of carbon contaminants on anatase TiO₂. Earlier research efforts showed hydrocarbon contaminants inevitably present on the surface of every catalyst during the preparation and transfer procedure and they could affect the overall catalytic efficiency of the catalyst. Besides, the hydrocarbon layer could be removed by UV irradiation as indicated by their spectral results. The current presents valuable evidence to qualitatively explore the potential reaction mechanism of UV induced carbon contaminant decomposition on anatase TiO₂ and quantitatively estimate the reaction stoichiometry and quantum efficiency of UV photons at various irradiation intensities within natural sunlight intensity range by means of in situ Fourier-transform infrared spectroscopy (FTIR) and in situ X-ray photoelectron spectroscopy (XPS) coupled with a 375 nm UV laser diode. In situ FTIR spectral change between untreated TiO₂ sample and after 2 hours UV treated TiO₂ sample showed decomposition of carbon contaminant with consumption of adsorbed water and formation of oxidant carbon and isolated surface hydroxyls. UV induced decomposition of carbon species associated with consumption of oxygen

species was also observed by tracking the XPS spectral change of UV irradiated spot comparing to the dark reference spot. The stoichiometry ratio between the decomposition of carbon species and consumption of oxygen species was 2:1. Which implies a potential reaction pathway where the UV irradiation initiated a photocatalytic reaction on anatase TiO_2 surface between one adsorbed oxygen/water and two carbon species and caused decomposition of two carbon contaminant species. Eight different reaction cases were examined using eight TiO_2 specimens treated by UV at four different intensities within natural sunlight radiation intensity range repeated twice each. The measured stoichiometry for the above noted conversion varied from 2.09 to 1.72 with an average value of 1.92 and a standard deviation of 0.11. The photon efficiency was estimated based on the number of carbon species decomposed by one UV photon, and the results showed the highest photon efficiency was obtained as 0.181 % from 5-10 minutes UV exposure at 1.5 mW/cm^2 . All the reaction cases showed a significant efficiency drop after 30 minutes of UV irradiation due to the consumption of adsorbed reactant species. UV irradiation showed a high selectivity of hydrocarbon decomposition, which was $75\% \pm 5\%$ for all the reaction cases.

Earlier research on Ag/TiO_2 adsorptive desulfurization showed 450°C calcined 4wt% Ag/TiO_2 adsorbent had a supreme sulfur removal capacity. It is proposed the capacity enhancement was due to the additional surface hydroxyl groups created by Ag_2O on TiO_2 . However, upon UV irradiation treatment, the desulfurization capacity was significantly decreased. In the current investigation, in-situ time-resolved XPS characterization was carried out to understand the mechanisms of the photo-induced chemical reactions on 4wt% Ag/TiO_2 adsorbent. When compared with the XPS spectral results from pure TiO_2 and 4wt% $\text{HNO}_3/\text{TiO}_2$ samples, a pair of anomalous $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$ peaks were observed by XPS

characterization of 4wt% Ag/TiO₂, which can be identified as Titanium hole species. It is also envisioned from high-resolution O 1s spectra that the Titanium hole species were stabilized by hydroxyls. High-resolution Ag 3d spectra showed Silver Oxide was reduced to Silver metal accompanied by the color of the white sample was turned into black. Time-resolved XPS characterization showed a conversion of Titanium hole, hydroxyls, and Silver metal into Ti⁴⁺, lattice Oxygen, and Silver oxide (sample color was less dark by this procedure). UV irradiation accelerated the conversion of Titanium hole species into Ti⁴⁺. After all the Titanium hole species was converted into Ti⁴⁺, further XPS/UV irradiation would not cause any spectral change to the sample. To observe again the spectral changes, the sample has to be re-calcined at 450 °C in flowing air. By quantitatively analyzing the deconvolution details of the photoelectron peaks, the reaction mechanism is proposed according to the following stoichiometry:



Previous XPS studies on the state of dispersion and growth of Ag on TiO₂ have shown that Ag/Ti intensity ratios increased linearly with Ag content up to 4 wt% and increased less significantly thereafter from 8 wt% to 20 wt% indicating nucleation and growth of Ag crystallites. Based on the earlier observations, the peak intensity of Titanium hole species at the first XPS characterization (exposed to X-ray irradiation for 2 minutes) and its relaxation period should also be dependent on the weight percentage loading of Ag on TiO₂. Silver loading from 1wt% to 20wt% on 169 m²/g Titania was investigated. The Titanium hole species peak intensities at 2 minutes of X-ray exposure increased linearly with silver content up to 4wt% and increased less significantly thereafter. The relaxation period for all the Titanium hole species to be converted into Ti⁴⁺ was increased linearly from 1wt% to 4wt% but increased less significantly

thereafter. All the above observations indicated that the dispersion of Ag on Titania support determines the Titanium hole species peak intensity at 2 minutes X-ray exposure. Therefore, it is proposed that the sample preparation procedure (incipient wetness impregnation and 450 °C calcination in flowing air) created Oxygen vacancies on Titania supports which are occupied by Silver and hydroxyls. With Silver and hydroxyls on Oxygen vacancies, photo irradiation created holes and electrons can be transferred to the Titanium bonded Silver and Titanium holes were stabilized by hydroxyls. Once Silver received electron to be reduced into isolated Ag metal, holes and electrons created by further photo irradiation would recombine and no more Titanium hole peak intensity would be observed. Under ultrahigh vacuum condition, photo irradiation would cause desorption of hydroxyls (in form of adsorbed H₂O) and caused a decrease of Titanium hole species and hydroxyl peak intensity. Thus, the relaxation reaction occurred.

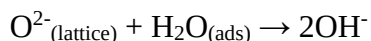
In the first Chapter, in-situ time-resolved XPS will be introduced, including how it is organized and how it functions. Typically, an XPS system contains a load-lock, a sample treatment chamber (STC), and a sample analysis chamber (SAC) ^[2]. To eliminate the influence of electrons and impurities in ambient atmosphere, these chambers need to be under ultra-high vacuum condition (as low as $\sim 10^{-9}$ to 10^{-10} torr). Under ultra-high vacuum condition, only solid surface characterizations can be tested. On load-lock section, there is a sapphire window that is diaphanous for UV light. This sapphire window makes the in-situ XPS study of UV induced catalytic reactions possible. For a certain sample surface, time-resolved XPS is capable to take both survey and narrow scans during a certain time interval. As for snapshot scans, the time interval can be as short as microseconds.

Chapter 2 introduces the desulfurization performance of TiO₂ and Ag/TiO₂ absorbent. Based on the previous observations ^{[1], [3], [4], [5]}, the saturation capacity for sulfur heterocycle removal of

TiO₂ and Ag/TiO₂ have been improved significantly. Especially Shelly's supreme research has proven that UV treatment can make a huge enhancement for the desulfurization capacity of TiO₂. It has been proven that 4wt% Ag/TiO₂ has the highest desulfurization efficiency among all the weight loadings of Ag/TiO₂ absorbent. However, when UV irradiation was applied to 4wt% Ag/TiO₂, the sulfur removal capacity was decreased. Such an interesting observation motivates the study of the mechanism study for photo induced chemical reactions on Ag/TiO₂.

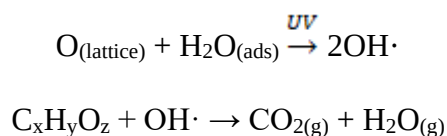
Chapter 3 presents XPS study of two different types of anatase TiO₂ adsorbents. XRD characterization showed the two TiO₂ adsorbents had the same XRD pattern. The two TiO₂ adsorbents are anatase TiO₂. BET results showed that one TiO₂ adsorbent had a higher surface area and larger pore volume. To estimate the effect of adsorbed H₂O on TiO₂ desulfurization, both two TiO₂ samples were prepared at 110 °C and 450 °C, respectively. XPS measurements were conducted for UV treated and untreated TiO₂ adsorbent samples. The XPS spectral results showed in all the eight different reaction cases that the UV irradiation converted lattice oxygen into additional surface hydroxyl groups. By analyzing the deconvolution details of the photoelectron peaks, it is demonstrated that UV irradiation on 110 °C prepared TiO₂ can produce more hydroxyl groups. It's also revealed that TiO₂ sample with higher surface area and higher pore volume can produce more hydroxyl groups by UV irradiation under the same experimental conditions. It is envisioned that adsorbed H₂O reacted with anatase TiO₂ under UV irradiation and produced additional hydroxyl groups. And the photo-generated surface hydroxyls enhanced the sulfur heterocycle removal capacity of anatase TiO₂ sorbents. Sample removed from XPS chamber and stored in laboratory conditions showed UV generated surface hydroxyls can persist for over two weeks with or without handling. The deconvolution details of the photoelectron peaks revealed the reaction mechanisms.

Chapter 3 also presents the results analysis and discussion of XPS study of UV treated and untreated TiO₂ adsorbents. All the XPS spectral results showed part of lattice oxide oxygen was converted to hydroxyl groups. The additional hydroxyl groups created by UV irradiation on the TiO₂ adsorbent can be maintained for up to two weeks. It has been proven that surface hydroxyl groups are essential for the enhancement of sulfur removal capacity of TiO₂ adsorbent []. The quantitative analysis of the deconvolution details of eight different reaction cases indicated the conversion stoichiometry of lattice oxygen into surface hydroxyls varied from 1.83 to 2.15 with an average of 1.98 and a standard deviation of 0.10. Thus, the mechanism for the UV induced enhancement for sulfur heterocycle removal capacity of anatase TiO₂ is that UV irradiation produces additional hydroxyl groups by converting one lattice oxide oxygen and one adsorbed H₂O into two active sulfur removal sites (surface hydroxyl groups) on TiO₂ surface. The reaction stoichiometry is shown as following:



Chapter 4 illustrates the the transient photocatalytic oxidation mechanism of carbon contaminants from a high surface area anatase TiO₂ pellet under starved water/oxygen reaction conditions created when specimens are irradiated via a 375 nm UV laser inside the UHV analysis chamber of an XPS spectrometer. Complementary results are also provided following similar UV irradiations and reaction procedures in an evacuated *in situ* reaction cell of a Fourier-transform infrared spectrometer (FTIR). An interactive and non-steady state transient photocatalytic reaction is observed between surface carbon species and strongly adsorbed H₂O brought to the exterior surface of the pellet via UV photodesorption from within the deeper lying pores of the pellet. The reaction stoichiometry and quantum efficiency of the reaction are reported at various irradiation intensities. Heating the sample specimen to 100 °C for 2-hour

inside the XPS-UHV analysis chamber prior to UV illumination was effective in eliminating photocatalytic oxidation and carbon removal from the surface thereby demonstrating that strongly adsorbed water (prior to heating in vacuum) was a critical and limiting reagent in the overall H₂O transport and reaction process. The reaction stoichiometry and mechanism is proposed by the FTIR and XPS analysis as following:



Chapter 5 demonstrates the observation of an anomalous and unique time dependent spectral change and a color change of 4wt% Ag/TiO₂ sample during time dependent XPS characterization. A time-dependent observation of a stabilized chemical species of titanium at 1.5 eV binding energy higher compared with Ti⁴⁺ in TiO₂ was observed from XPS for the first time. Notably it was identified as the TiO₂^{+(hole)} species generated by X-ray photon on 4wt% Ag/TiO₂ sample. The species was stabilized by hydroxyls under ultrahigh vacuum (UHV) conditions. Surface charging effect was examined by analysis using sample mounting method, sample particle size, neutralizer, and X-ray induced Auger spectra and Auger parameters. The results showed that the time dependent spectral change observed from XPS was caused by chemical reactions. X-ray photon quantum efficiency analysis showed that one X-ray photon was able to create at least 17 TiO₂^{+(hole)} species, which indicates that hole carriers were transferred to the sample surface from the bulk. 4wt% Ag/TiO₂ sample could be recharged by pulling the relaxed sample out from the UHV chamber and re-calcined the sample in flowing air at 450 °C for 2 hours.

Chapter 6 presents X-ray and UV irradiation effects on in-situ time-resolved XPS characterization of photo-induced chemical reaction study on TiO₂ and 4wt% Ag/TiO₂ samples.

The variation of X-ray irradiation flux made a significant difference to the XPS spectral change rate (reaction rate). There is almost a linear relationship between the X-ray irradiation flux and the reaction rate in terms of X-ray exposure time from six experiments with three different X-ray irradiation intensities repeated twice each. By quantifying the amount of X-ray photons hit the sample surface, the reaction rate was found to be related to the X-ray photon fluence. The dependence of the reaction rate on the X-ray photon fluence is almost identical for all the reaction cases. Besides, UV irradiation was also investigated by coupling a 375 nm UV laser diode on the SAC chamber of the XPS. And the results showed UV irradiation prior to or during the time dependent XPS experiment made a significant difference to the XPS spectral changes. Different UV irradiation intensities and UV exposure time were also examined, and the results showed that the reaction rate (spectral change rate) was also linearly related to the UV irradiation fluence. But the UV irradiation could not relax all the titanium hole species, which is potentially because of the UV photons were not able to reach the deep layers of the Titania support due to its limited penetration depth when compared with X-rays. X-ray and UV have different photon efficiencies and it was related to their photon energy and transmission depth on 4wt% Ag/TiO₂ sample.

Chapter 7 shows the study of different weight percent loading of Ag on TiO₂ and its effect on the stabilized Ti(hole) phenomenon. Other transition metal ions doped on TiO₂, and Ag doped on other semiconductor support (i.e. SiO₂ and Al₂O₃) was also investigated and the results showed the Ti(hole) phenomenon was not generalized for all the transition metal ions doped on TiO₂ or other semiconductor supports. Different weight percentage of silver loading onto anatase TiO₂ support were prepared and examined by XPS to reveal the impact of silver loadings on the stabilized hole species phenomenon. The results showed the titanium hole species concentration

was determined by the dispersion of silver atoms on Titania support until a saturated dispersion of one monolayer of silver was reached (4wt%). From 1wt% to 4wt% loading of silver, the amount of titanium hole species generated by X-ray irradiation was proportional to the surface concentration of silver atom. After 4wt%, silver becomes to aggregate on TiO₂ surface, and so that the amount of titanium hole species generated by X-ray irradiation did not show any significant increase. The results potentially indicate only up to one monolayer of ionic Ag(I) was directly involved in the photocatalytic reactions due to their direct interaction with photoelectrons.

Besides silver, other transition metal ions and other semiconductor support materials were also investigated and similar spectral change was only observed for Cu/TiO₂ sample. Experiments on Ni/TiO₂ and Pd/TiO₂ did not show any evidence of the generation of stabilized hole species on TiO₂ from in situ time dependent XPS characterizations. Time dependent XPS characterization of Pt/TiO₂ sample showed a small portion of stabilized hole species were generated by X-ray irradiation. The same XPS study on Ag/SiO₂ and Ag/Al₂O₃ samples did not show any time dependent spectral change nor the generation of hole species, which indicates the unique photoelectrical properties of the redox Ag(I) ion and the band structure of anatase TiO₂ with surface defective sites were the key factors for the stabilized hole species phenomenon. The current study potentially provides direct evidence to explore the capacity and efficiency of different transition metal ions to transfer and separate electrons and holes on anatase TiO₂.

Chapter 8 illustrates the effect of hydrogenated species (i.e. adsorbed H₂O/OH-) on the stabilized Ti(hole) phenomenon by varying the hydration levels of 4wt% Ag/TiO₂ sample. Both neat TiO₂ and 4wt% Ag/TiO₂ were investigated at different hydration levels as determined by Thermogravimetric Analysis (TGA). 4wt% Ag/TiO₂ samples were prepared in flowing air and

flowing oxygen environments and the as prepared 4wt% Ag/TiO₂ samples showed different colors. The 4wt% Ag/TiO₂ sample prepared in flowing oxygen showed black color and there was almost no adsorbed H₂O as well as no hole species observed by XPS. For the 4wt% Ag/TiO₂ sample prepared in air, time dependent spectral change associated with the generation and relaxation of titanium hole species was observed. Vacuum heating of this sample at 400 °C for 2 hours in the UHV chamber caused color change from white to black as well as significant desorption of adsorbed H₂O/OH. And the following in situ time dependent XPS characterization showed significantly reduced amount of titanium hole species, which indicates the adsorbed H₂O/OH was the essential component for the generation and stabilization of the hole species on 4wt% Ag/TiO₂ sample under UHV conditions. Further X-ray exposure caused desorption of hydroxyls in form of H₂O so that the relaxation of hole species was triggered as indicated by the XPS quantitative analysis results.

Finally, this study provides insightful evidence and contribution to the development of process modified adsorptive desulfurization for liquid hydrocarbon fuels. By introducing a one-time ex-situ or in-situ UV irradiation or introducing Ag on Titania sorbents, additional surface hydroxyls were created and the sulfur heterocycle removal saturation capacity and selectivity of TiO₂ sorbents were enhanced. A special state of titanium was observed through XPS characterization of 4wt% Ag/TiO₂ and a time-resolved relaxation reaction mechanism was proposed based on the quantitative analysis of the spectral changes. The current observation sets a promising prospect for the reaction mechanism of TiO₂ photocatalysis and provides potential applications of TiO₂ materials for industrial applications.

Chapter 9 sets an expectation for the future work and applications of the current study. Microsecond time resolved XPS analysis has a huge potential to study the photocatalytic reaction

mechanisms and kinetics on a microsecond time scale. Finding the suitable materials as well as increase the resolution of the resulting spectra would be challenging. Besides, the current study provides a great perspective for the application of the Ag/TiO₂ material as a key component for sunscreen products and some energy efficient build material such as glass. The progress will be reported in future works.

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List of Abbreviations

XPS	X-ray Photoelectron Spectroscopy
FTIR	Fourier-transform infrared spectroscopy
PAD	Photo-assisted Adsorptive Desulfurization
STC	Sample Treatment Chamber
SAC	Sample Analytical Chamber
UV	Ultraviolet
BET	Brunauer-Emmett-Teller
XRD	X-ray Diffraction
UV-Vis	Ultraviolet Visible spectroscopy
TGA	Thermogravimetric Analysis

Chapter 1 Introduction and background

1.1 Introduction to XPS

X-ray photoelectron spectroscopy (XPS), often referred to as electron spectroscopy for chemical analysis (ESCA), is a surface analytical technique that has matured into an essential tool for many material characterization laboratories since the introduction of the first commercial instrument in the late 1960's [1].

There are many excellent textbooks available which review the basic principles of XPS like Vickerman [2], Briggs and Seah [3] and Briggs and Grant [4]. The popularity of the technique when compared with other surface analytical techniques can be attributed to a unique combination of surface and chemical sensitivity as well as relatively straightforward means of quantification.

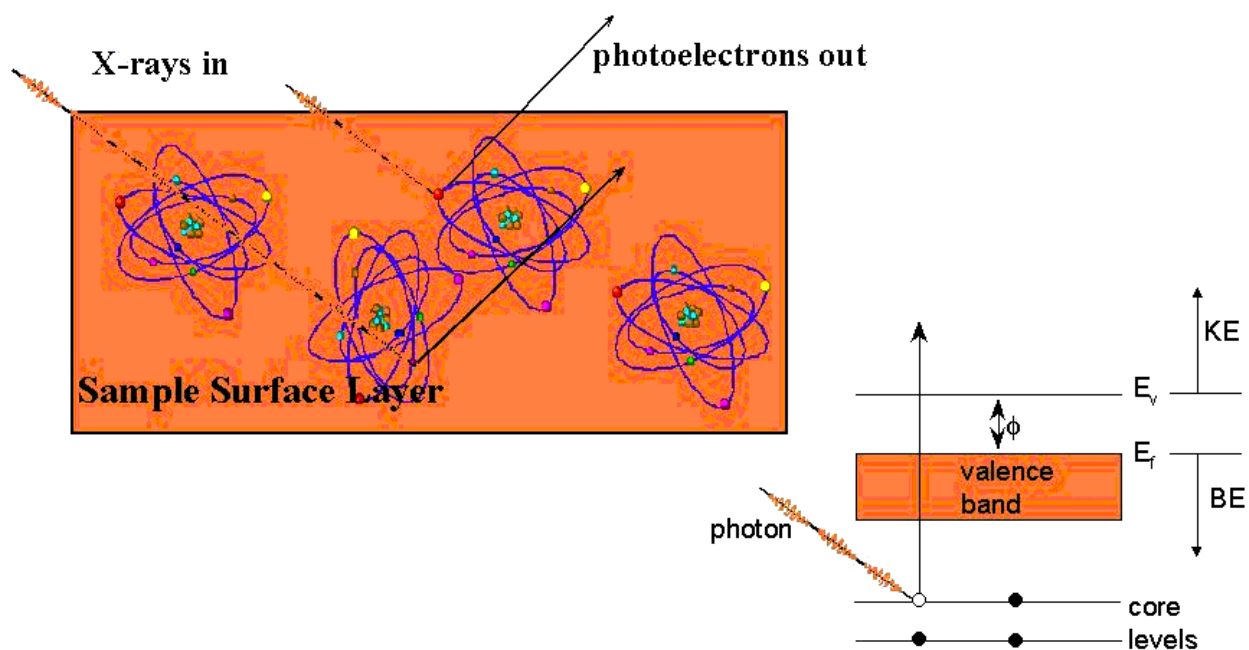


Figure 1.1 The photoemission process

Figure 1.1 shows a sample surface illuminated with X-rays of energy $h\nu$. Photoelectrons of kinetic energy (KE) are emitted from the sample surface via the photoemission process. In the

photoelectron spectrometer, the kinetic energy of the photoelectron is measured to give the binding energy (BE) with which the electron was bound to the nucleus via the relationship given by Equation 1. ϕ represents the combined electron spectrometer and sample work functions and is an instrument dependent factor normally derived for each instrument as part of a calibration procedure.

$$\text{Eqn (1) BE (eV)} = h\nu - \text{KE} - \phi$$

The technique derives its chemical sensitivity from the fact that nearest neighbor atoms will have a direct effect upon the binding energy of the core level electrons. Therefore, any change in the chemical environment such as oxidation state will lead to a modification of the KE. The surface sensitivity of the technique can be explained by the fact the relatively low energy photoelectrons can travel only a short distance through the solid without undergoing inelastic scattering. The average distance the photoelectron can travel without energy loss is defined as the inelastic mean free path (IMFP) [5]. The sampling depth, d from which 95% of all photoelectrons are detected is given by the relationship:

$$\text{Eqn (2) } d = 3\lambda$$

1.2 Introduction to desulfurization

Desulfurization of liquid fuels has gained significant importance in recent years due to the requirement for clean energy along with environmental concerns, and stringent regulations have been applied to limit the maximum sulfur emissions in many countries around the world. The most prevailing and commonly used technique in industry is Hydro Desulfurization (HDS) [6-10]. Alternative processes include catalytic oxidation [11-13], biological removal [14-16], and membrane separation [17,18]. These techniques are used more frequently when HDS can't achieve the optimum level or cost prohibitive. Taking advantage of its inexpensive cost, low

energy requirement and scalability, adsorptive desulfurization is a promising and feasible application [19-22]. The Center for Microfiber Material Manufacturing (CM3) research group has been studying adsorptive desulfurization for over a decade, and the sulfur heterocycle removal saturation capacity has been enhanced significantly by continuously modification for the desulfurization procedure as well as the sorbents [21,23-37]. To further improve the capacity and efficiency, the mechanism study is of primary importance. In the current study, the surface alteration mechanism of anatase TiO_2 sorbents has been investigated to understand the process modified UV assisted adsorptive desulfurization capacity enhancement. And it is attributed to the additional surface hydroxyls created by one-time UV treatment. Besides, the surface modification of TiO_2 by loading ionic silver was also investigated to illustrate the mechanism for enhanced sulfur heterocycle removal selectivity and saturation capacity in liquid hydrocarbon fuels of 4wt% Ag/ TiO_2 sorbents.

1.3 Introduction to in-situ time-resolved XPS (ISTR XPS)

The current XPS characterization is carried out on an AXIS Ultra DLD (delay lines detector) X-ray photoelectron spectrometer (XPS) from Kratos Analytical Ltd. The instrument is majorly composed of a fast entry load lock, a sample treatment chamber (STC) and a sample analysis chamber (SAC) as shown in Figure 1.2. TiO_2 and Ag/ TiO_2 samples were analyzed in SAC under ultra-high vacuum conditions (less than 10^{-9} Torr). To achieve in-situ XPS experiment, the pressure in load-lock needs to be pumped down to 10^{-7} to 10^{-8} torr after the sample is introduced into load-lock. The UV light directly irradiates on the sample surface through the sapphire DUV window on the load-lock section. After a certain period of UV irradiation, sample will be transferred to SAC chamber immediately. This “in-situ” treatment makes the XPS characterization more accurate by eliminating the atmospheric interactions. A UV laser diode

(Oxiuss 375) was installed on a side sapphire DUV window of the sample analytical chamber (SAC) of the XPS system. The UV irradiation focus point was aligned with X-ray focus point. In-situ time-resolved XPS characterization was conducted for UV induced chemical reactions on photo active surfaces. By quantitatively controlling the UV flux on sample surface, the UV induced reaction dynamics could be adjusted, and the consequence could also be monitored by XPS spectral results.

1.4 Motivation of research

One-time UV treatment on anatase TiO_2 has been proven to be capable of significantly enhancing the sulfur heterocycle removal capacity of TiO_2 sorbents. The desulfurization saturation capacity study also showed Ag/ TiO_2 sorbents without UV treatment had an enhanced capacity than neat TiO_2 sorbents. However, UV treatment on Ag/ TiO_2 sorbents had a negative effect for the desulfurization capacity. Such an interesting phenomenon caused our curiosity to investigate the reason and the mechanism behind the phenomenon. Material characterization could provide essential chemical and physical properties of the sorbents and hence indicate the surface alteration caused by the modification methods. XPS is a perfect instrument to investigate the surface modification mechanism qualitatively and quantitatively before, during, and after reactions. By analyzing the deconvolution details of the photoelectron peaks, the changes caused by different treatment on TiO_2 surface could be revealed and the mechanism can be proposed according to the conversion stoichiometry.

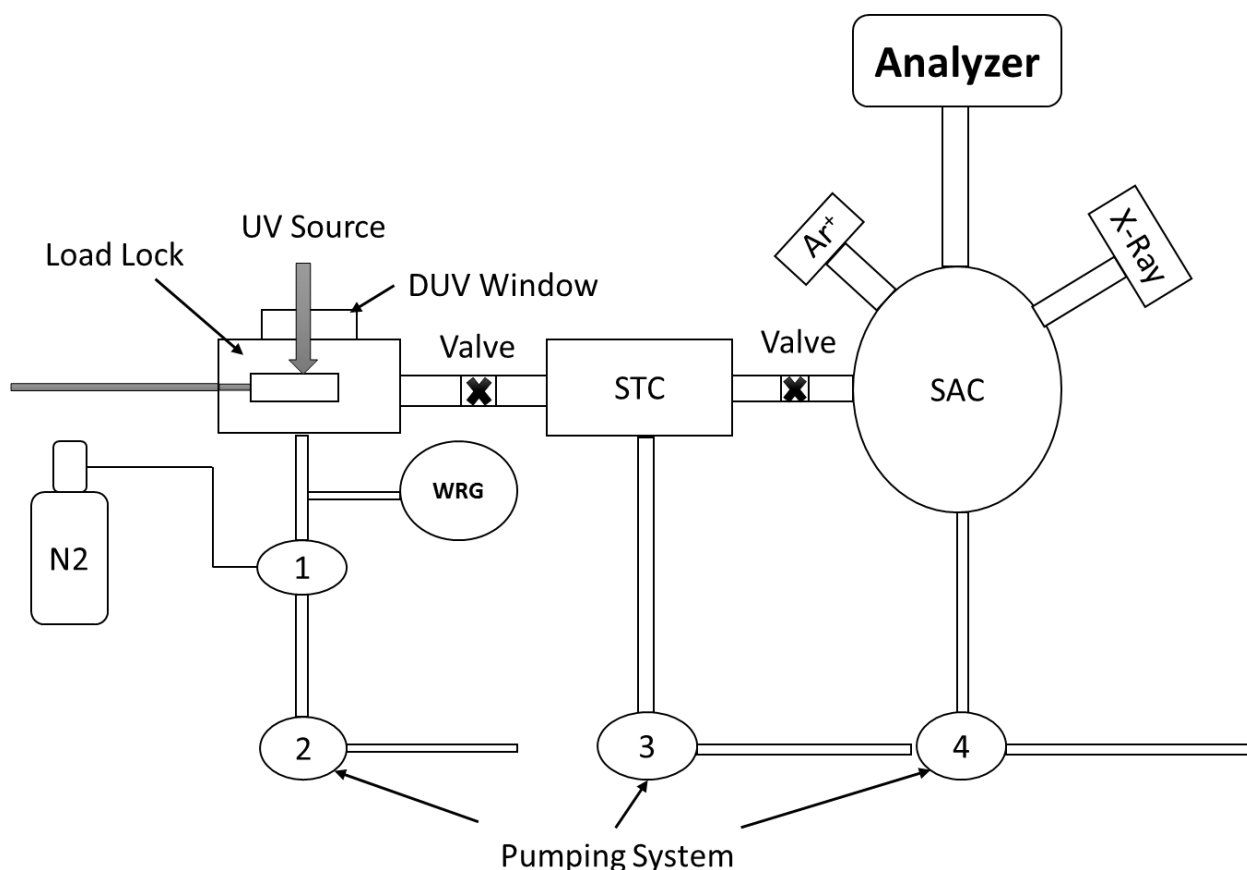


Figure 1.2. Schematic configuration of XPS apparatus with UV light.

The color change during the photon irradiation on Ag/TiO₂ sorbents also drew my interest. Either XPS, XRD, and UV-Vis spectroscopy characterization with pulsed photon irradiation could cause a color change of Ag/TiO₂ material from white to black. The time-resolved XPS characterization was also accompanied a time-resolved color change of the Ag/TiO₂ sample. The color of the Ag/TiO₂ sample came from white to black and less dark, finally it appeared as gray color.

All the above observations motivate this research study to focus on the mechanism studies of chemically reactive surfaces. Taking use of several sample characterization tools such as XPS, XRD, FTIR, BET, TGA, and UV-Vis, the chemically active surface functional groups such as surface hydroxyls and ionic metal compounds can be qualitatively revealed and quantitatively

studied. By understanding the reaction mechanisms, further enhancement for the sulfur heterocycle removal saturation capacity can be achieved. By synthesizing advanced materials with specific functional groups, potential applications and goals for industrial purposes can be realized.

To sum up, the current research is aimed at investigating the active functional groups on TiO_2 and Ag/TiO_2 materials for the photo assisted adsorptive desulfurization applications and providing valuable insights to advance the development of various potential applications.

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Chapter 2 Photo assisted TiO₂ and Ag/TiO₂ adsorptive desulfurization

2.1 Abstract

This work majorly investigates process modified UV assisted adsorptive desulfurization (ADS) using TiO₂ and Ag/TiO₂ sorbents of hydrocarbon fuels at ambient conditions. Commercial anatase TiO₂ was used as the sorbent material, and process modified adsorptive desulfurization was carried out by introducing one-time UV irradiation or by introducing silver on Titania adsorbent. Both modification methods were proven capable of enhancing the sulfur heterocycle removal capacity of TiO₂ sorbents. UV irradiation was firstly introduced into ADS and directly applied on fixed bed reactor using dynamic adsorption experiments. The current research was also focused on ultra-deep removal of benzothiophene in model fuel over modified TiO₂. UV irradiation before and during desulfurization breakthrough experiments both enhanced TiO₂ sulfur removal capacities significantly. The addition of 4wt% silver on Titania support showed an even higher breakthrough capacity enhancement than one-time UV irradiation treatment. However, the presence of H₂O in the model fuels played an important role on affecting the sulfur heterocycle removal capacities of Ag/TiO₂ adsorbent when UV was applied to the adsorptive desulfurization applications. UV irradiation on Ag/TiO₂ with the presence of H₂O in the liquid fuels enhanced the breakthrough capacity of the adsorbent, but the opposite effect was observed when UV irradiation was carried without the presence of H₂O in the liquid fuels. The current study provides us a promising prospective that the involvement of H₂O and potential UV induced reactions on TiO₂ promoted the desulfurization capacities of TiO₂ sorbents.

2.2 Introduction

Titanium dioxide (TiO_2) materials are widely used as catalysts, semiconductors and adsorbents in many application areas including energy field, water splitting, air and water purification, and the degradation of organic compound [1-8]. Nowadays, TiO_2 is largely used as the photo-catalyst for photo-oxidative desulfurization (PODS) from liquid fuels in presence of UV irradiation [9-11]. And TiO_2 /UV system has shown a promising desulfurization result in oxidative removal of various organic sulfur compounds [10,12]. Moreover, TiO_2 and TiO_2 supported materials have been studied and evaluated to remove organic sulfur by adsorptive desulfurization (ADS) from liquid transportation fuels [13-18]. Recently, silver supported on TiO_2 and $\text{TiO}_2\text{-Al}_2\text{O}_3$ adsorbents with advanced sulfur adsorption capacities for logistic and commercial fuels have been developed in our CM3-adsorption lab [19-21]. The desulfurization performance was depended on surface acidity which was also related to photocatalytic activity of TiO_2 [20].

2.3 Experimental

2.3.1 Sample preparation

Anatase TiO_2 supports were obtained from Saint Gobain Norpro (ST61120) as 3.2 mm pellets. The pellets were crushed and sieved to 850–1400 μm followed by drying in a convection oven for at least 6 h at 110 $^\circ\text{C}$. Neat TiO_2 sorbent used in desulfurization experiments were calcined in flowing air at 450 $^\circ\text{C}$ prior to use. For XPS characterization, the pellets were crushed and sieved further to 75-125 μm .

For 4wt% Ag/ TiO_2 sorbents, the 3.2 mm as received TiO_2 pellets were crushed and sieved to 850-1400 μm followed by drying in a convection oven for at least 12 h at 110 $^\circ\text{C}$. Silver (Ag) was introduced by incipient wetness impregnation using AgNO_3 solution followed by drying in a convection oven for another 12 h at 110 $^\circ\text{C}$. After that, sample was calcined at 450 $^\circ\text{C}$ in flowing

air for 2 h followed by in situ cooling in flowing air for another 2 h. The as prepared Ag/TiO₂ particles appeared as white pellets. For XPS characterization, the Ag/TiO₂ pellets were further crushed and sieved to 75-125 μ m powders.

2.3.2 Model fuels

All the model fuels used for the desulfurization breakthrough experiments were prepared by mixing Benzothiophene (from Alfa Aesar) and n-octane (from Acros Organics). Typically, for a fixed bed reactor breakthrough experiment, 3500 ppmw total sulfur was included in the model fuel. The effect of H₂O was estimated by adding 1000 ppmw distilled water into the model fuel.

2.3.3 UV light sources

A compact ultraviolet lamp (UVP) was applied to the UV assisted adsorptive desulfurization breakthrough experiments. The power output of the UV source was 8 watts and the wavelength was 365 nm. A digital UV radiometer (UVX-36, UVP) was applied to measure the UV lamp irradiance at 365 nm wavelength. To measure the light intensity, UVX radiometer was applied to place at a fixed distance from the UV lamp. The measured light intensity at 5 cm from light source was ca. 2.0 mW/cm², at 8 cm from the light source was ca. 1.2 mW/cm². For the desulfurization breakthrough experiment, the UV lamp was fixed at 5 cm distance from the reactor bed.

2.3.4 Breakthrough desulfurization experiments

Dynamic sulfur adsorption breakthrough experiments were carried out to investigate the effects of UV irradiation and the impact by H₂O. A quartz tube reactor with inner diameter of 16 mm and length of 62 mm was applied to load 10.0 g of adsorbents for each test. Before breakthrough experiment, the reactor bed was treated by dry N₂ for 1 h to remove moisture and impurities. After that, model fuel was introduced into the reactor bed by a peristaltic pump at a

flow rate of 0.5 mL/min and WHSV of 2.5 h⁻¹ (LHSV ~ 2h⁻¹) with or without UV irradiation. The outlet fuels were collected and analyzed via an Antek 9000S total sulfur analyzer at regular time intervals. The low detection limit was 200 ppbw. The instrument calibration was carried out by testing the standard samples of real fuels and model fuels.

2.3.5 Adsorbent regeneration experiments

After breakthrough experiments, the used adsorbent bed was treated by flowing air at 220 °C for 2 h and further heated up to 450 °C for another 2 h in flowing air followed by in-situ cooling in flowing air for at least another 2 h. Previous studies have shown this procedure ensured the removal of fuels and sulfur compounds from the adsorbents. Another breakthrough experiment was conducted to the regenerated adsorbent thereafter.

2.4. Results and discussion

To evaluate the breakthrough and saturation capacities of the adsorbents, the breakthrough curves were plotted by normalizing the outlet total sulfur concentration (C) by initial sulfur concentration (C₀) versus breakthrough time (minutes).

2.4.1 Breakthrough results for TiO₂ adsorbents

Table 2.1 Breakthrough results of sulfur heterocycle removal capacities for TiO₂ using model fuels (containing 3500 ppmw sulfur)

Conditions	Without H ₂ O		With 1000 ppmw H ₂ O	
	No UV	With UV	No UV	With UV
Breakthrough capacity (mg S/g)	2.51	4.15	1.55	4.95
Saturation capacity (mg S/g)	3.95	5.66	3.24	6.22

The results of breakthrough capacities for TiO₂ adsorbents are summarized in Table 2.1, without H₂O in the model fuels, the breakthrough capacity of neat TiO₂ without UV treatment

was 2.51 mg S/g adsorbent and 4.15 mg S/g adsorbent for UV pretreated TiO₂. The breakthrough curves for UV pretreated TiO₂ and in-situ UV treated TiO₂ adsorbents were very close as it is shown in Figure 2.2. The breakthrough curves for neat TiO₂ under dark and treated by UV are shown in Figure 2.1. The saturation capacities of neat TiO₂, UV pretreated TiO₂, and in-situ UV treated TiO₂ were 3.95, 5.66, and 5.63 mg S/g adsorbent, respectively.

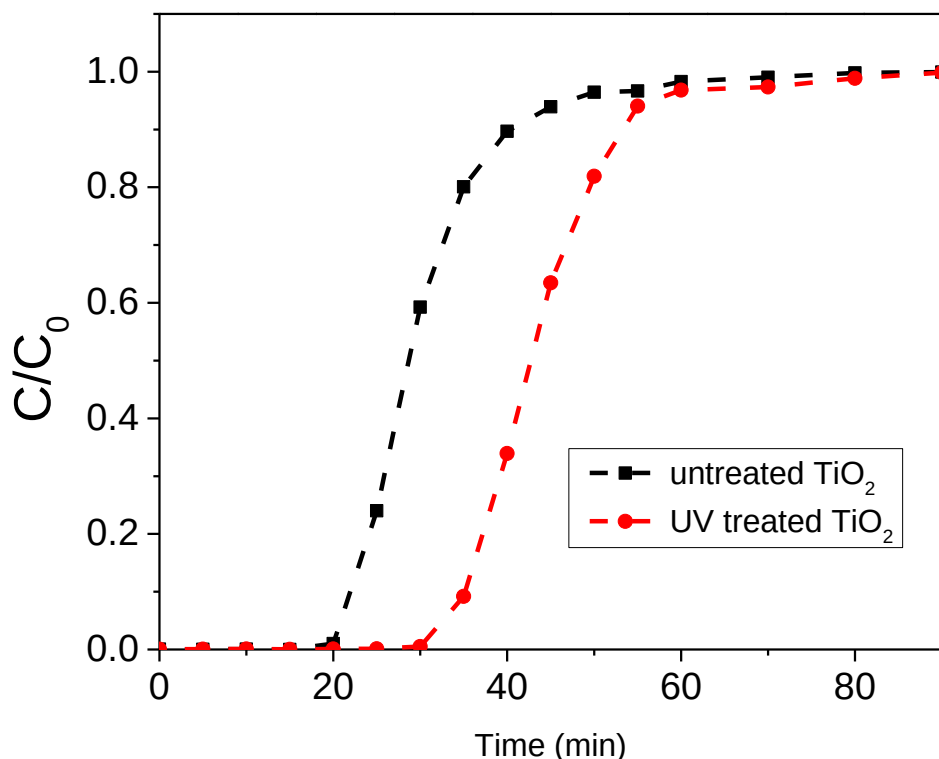


Figure 2.1 Breakthrough desulfurization curves for untreated and UV treated TiO₂ without H₂O in model fuels

With H₂O in the model fuels, the breakthrough and saturation capacities of neat TiO₂ without UV treatment were 1.55 and 3.24 mg S/g adsorbent. For UV pretreated TiO₂, the breakthrough and saturation capacities were 4.95 and 6.22 mg S/g adsorbent. Therefore, UV irradiation on commercial anatase TiO₂ adsorbents significantly increased the breakthrough

capacities. However, H_2O is a very important factor for TiO_2 adsorptive desulfurization. As it is shown in Figure 2.3, without UV treatment, H_2O itself decreased TiO_2 breakthrough and saturation capacities. But with UV treatment, H_2O increased TiO_2 breakthrough and saturation capacities significantly.

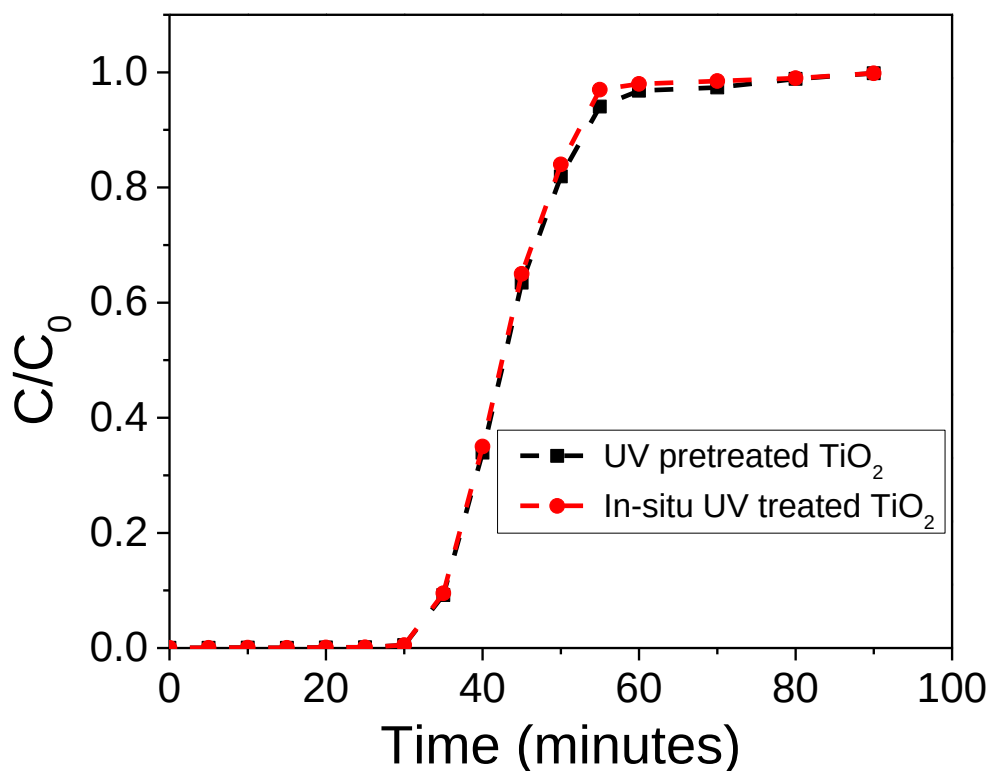


Figure 2.2 Breakthrough desulfurization curves for UV pretreated and in-situ UV treated TiO_2 without H_2O in model fuels

2.4.2 Breakthrough results for 4wt% Ag/TiO_2 adsorbent

For 4wt% Ag/TiO_2 adsorbents, the breakthrough and saturation capacities under various conditions results are summarized in Table 2.2. As it is shown in Table 2.2, the breakthrough and saturation capacities of 4wt% Ag/TiO_2 without UV treatment and without the presence of H_2O

was 4.45 and 5.88 mg S/g adsorbent. The results indicated the addition of silver on TiO₂ enhanced the desulfurization capacities of TiO₂ adsorbents.

Table 2.2 Breakthrough results of sulfur heterocycle removal capacities for 4wt% Ag/TiO₂ using model fuels (containing 3500 ppmw sulfur)

Conditions	Without H ₂ O		With 1000 ppmw H ₂ O	
	No UV	With UV	No UV	With UV
Breakthrough capacity (mg S/g)	4.45	2.55	3.05	4.82
Saturation capacity (mg S/g)	5.88	3.70	4.60	6.33

However, as it is indicated by Figure 2.4, in-situ UV irradiation on 4wt% Ag/TiO₂ made a significant difference of the breakthrough capacities based on the presence of H₂O in the model fuels. With 1000 ppmw H₂O, in-situ UV irradiation during the breakthrough experiment enhanced the breakthrough and saturation capacities of 4wt% Ag/TiO₂ from 3.05 mg S/g adsorbent and 4.60 mg S/g adsorbent to 4.82 mg S/g adsorbent and 6.33 mg S/g adsorbent. When compared with the results from model fuels without H₂O, H₂O by itself decreased the breakthrough capacity of 4wt% Ag/TiO₂ adsorbent. However, UV irradiation with the presence of H₂O in model fuel increased the breakthrough and saturation capacities of 4wt% Ag/TiO₂. Moreover, UV irradiation without the presence of H₂O in model fuel dropped the breakthrough and saturation capacities of 4wt% Ag/TiO₂ from 4.45 and 5.80 mg S/g adsorbent to 2.55 and 3.70 mg S/g adsorbent (as it is shown in Figure 2.5). In both cases, UV irradiation caused a color change of the adsorbent from white to black indicating the conversion of chemical states of silver ions into metallic silver.

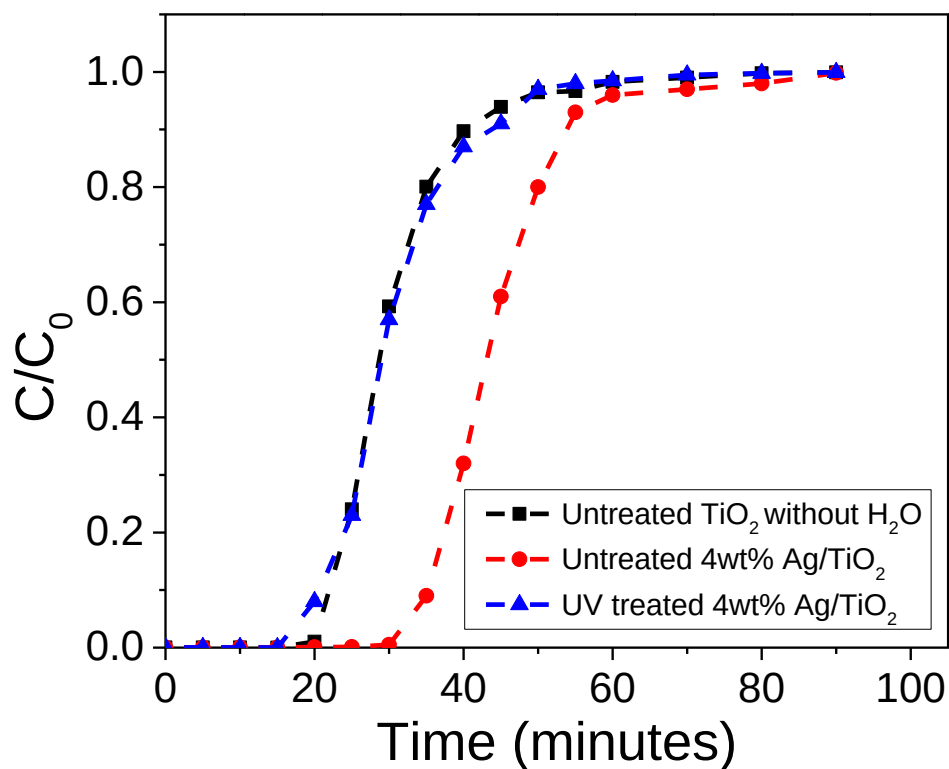


Figure 2.4 Breakthrough desulfurization curves for untreated TiO₂ without H₂O in model fuel and untreated and UV treated 4wt% Ag/TiO₂ without H₂O in model fuels

2.4.3 Breakthrough results for regenerated TiO₂ and 4wt% Ag/TiO₂ adsorbents

The sample regeneration breakthrough curves are shown in Figure 2.5 and Figure 2.6. The results showed the desulfurization capacities of TiO₂ and 4wt% Ag/TiO₂ adsorbents are stable over several adsorption and desorption cycles.

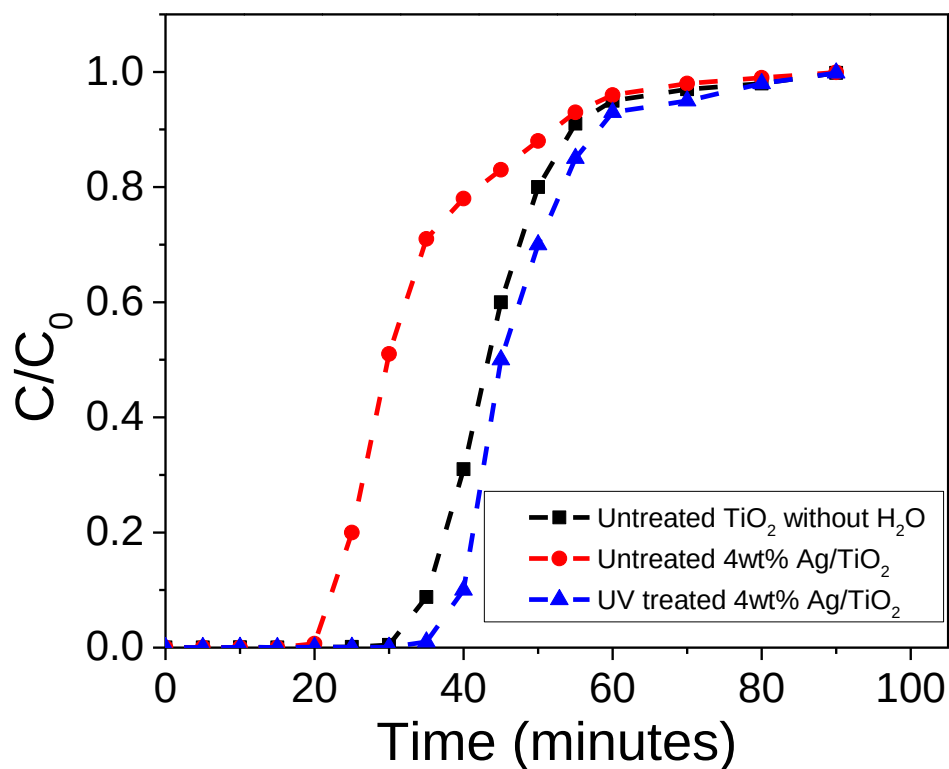


Figure 2.5 Breakthrough desulfurization curves for untreated TiO₂ without H₂O in model fuel and untreated and UV treated 4wt% Ag/TiO₂ with 1000 ppmw H₂O in model fuels

Based on the above observations, the sulfur heterocycle removal saturation capacities of TiO₂ are affected by UV irradiation, loading of silver, and the presence of H₂O. The reaction mechanisms for these results will be studied and discussed in the following chapters.

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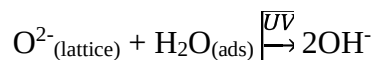
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Chapter 3 Mechanism study of process modified TiO₂ adsorptive desulfurization

3.1 Abstract

UV pretreatment has proven effective in enhancing the sulfur heterocycle specificity and saturation capacity of TiO₂ adsorbents. Previous efforts in our laboratory have shown this effect to persist for over two weeks and were attributed to increased densities of surface hydroxyl groups as assessed by XPS and FTIR evaluations. This paper presents further evidence of the previous assertion by tracking the UV-induced conversion of adsorbed water and lattice oxygen into surface hydroxyls as monitored by XPS. Two different commercial TiO₂ adsorbents (@ 163 and 70 m²/g) were investigated at various hydration levels as determined by TGA. Deconvolution of the XPS spectra demonstrated both the qualitative nature and quantitative conversion of adsorbed water and lattice oxygen according to the following stoichiometry, where one lattice oxygen is converted into two surface hydroxyls.



Eight different reaction cases were examined using the 163 and 70 m²/g supports at four different hydration levels each. The measured stoichiometry for the above-noted conversion varied from 1.83 to 2.15 with an average value of 1.98 and a standard deviation of 0.10.

Samples removed from the XPS chamber and stored in laboratory conditions showed that photo-generated surface hydroxyls could persist for over two weeks with or without handling.

Keyword: Photo-assisted adsorptive Desulfurization, Titanium dioxide, Hydroxyl group, UV, XPS, TGA

3.2 Introduction

Sulfur compounds are toxic and corrosive for fuel cell electrodes and catalysts. Researchers have strived to develop an efficient and convenient technique to remove sulfur compounds in

liquid fuel cells for decades [1-4]. Due to the stringent requirements on maximum sulfur emissions that have been put into effect by governments, ultra-deep desulfurization has been paid more and more attention recently [5-9]. A variety of desulfurization methods such as hydrodesulfurization [10-14], catalytic oxidation [15-17], biological desulfurization [18-21], and membrane separation desulfurization [22, 23] have been developed. Taking advantage of its inexpensive cost, low energy requirement and scalability, adsorptive desulfurization is a promising and feasible application [24-27]. Recently, it has been established that UV photo-assisted adsorptive desulfurization can significantly enhance the desulfurization capacity of anatase TiO_2 adsorbent by up to 65% using UV irradiation during or before the desulfurization breakthrough experiment [28].

Understanding the surface alteration mechanism caused by UV pretreatment is of primary interest to optimize the UV induced photo-assisted adsorptive desulfurization applications. In previous studies [28,29], commercial anatase TiO_2 with the high surface area and large pore volume were investigated for UV induced photo-assisted desulfurization applications and characterized by X-ray photoelectron spectroscopy (XPS). Previous studies [30,31] have shown that additional surface hydroxyl groups have a significant enhancement for sulfur heterocycle removal capacity on the TiO_2 adsorbent. Our earlier observations [28] showed us a promising result suggesting UV photo-induced chemical reactions between anatase TiO_2 and adsorbed H_2O produced additional surface isolated hydroxyl groups, which enhanced sulfur adsorption capacity. Further characterization of the adsorbents is necessary to investigate the effect of adsorbed H_2O , which is also related to experimental conditions and TiO_2 textural properties. Fujishima and Honda achieved UV light-induced water cleavage using a TiO_2 photoanode in combination with a Pt counter electrode immersed in an aqueous electrolytic solution [32]. Kurtz

R L et al. [33] demonstrated in a synchrotron photoemission study that surface hydroxyl groups are present after H₂O adsorption at 300 K on defective TiO₂ (110) surface with photoemission. It was proposed that an adsorbed H₂O molecule reacts with a bridging-oxygen atom to form two OH groups during the photoemission procedure. Furthermore, Nakamura, Ryuhei, and Yoshihiro Nakato [34] also proposed a form of surface hydroxyl groups by photocatalytic reactions on the TiO₂ surface through in situ FTIR absorption and photoluminescence measurements. In a study by Akihito, I. et al. [35], the energy levels of the O 2p orbitals for H₂O and OH from the reported photoelectron emission spectra and of Ti–OH at the TiO₂/water interface were estimated from the respective UV photoelectron spectra. The authors also revealed the production of surface hydroxyl groups bonded to Ti⁴⁺ species by the photooxidation reaction of water on TiO₂.

X-ray photoelectron spectroscopy (XPS) is a perfect technique to study the mechanisms of adsorption, desorption, and surface chemical reactions [36-39]. With the booming development of XPS technology, some in situ measurements have already been carried out to characterize the real-time reaction procedures [40,41]. By measuring the surface compositions before and after chemical reactions, the reaction mechanism can be revealed. The “in-situ” measurements can even monitor the reaction pathways by recording the species’ peak position and intensity changes during and after reactions. Ohtsu, Naofumi, et al. [42] used an “in-situ” XPS setup to study the removal of a contaminant hydrocarbon layer adsorbed on a photocatalytic TiO₂ film. It was considered as an “in-situ” XPS analysis in their study which assumed that sample transfer in XPS ultrahigh vacuum chambers would not affect the sample surface after UV irradiation. Lampimäki, Markus, et al. [43] studied the photochemistry formation of nitrogenated organic species on TiO₂ (110) surface using an “in-situ” XPS setup. The TiO₂ sample was treated by a UV laser diode module (Oxxius LBX 375) mounted on the viewport at the top of the

hemispherical analyzer. Switching the laser on and off at different spots on the sample made the “in-situ” XPS measurements under illumination and reference measurements on unexposed spots on the sample. The “in-situ” XPS studies provide crucial evidence for the reaction mechanisms and pathways.

The current work takes uses of BET, XRD, XPS, and TGA techniques to study and reveal the potential mechanisms for photo-assisted adsorptive desulfurization applications. With a better understanding of the reaction mechanisms, further adsorption efficiency enhancement can be expected.

3.3 Experimental

3.3.1 Sample preparation

Two kinds of commercial anatase TiO_2 samples were purchased from Saint-Gobain Norpro in 2010 and 2013. Both samples have the same product code “ST61120”, but they have different textural properties due to the manufacturing technique was changed. The as-received 3.2 mm pellets were crushed and sieved to 80-120 μm followed by drying in a convection oven at 110 $^{\circ}\text{C}$ for 24 h. Some of the samples were calcined in flowing air for 2 hours at 450 $^{\circ}\text{C}$ followed by in-situ cooling in flowing air for another 2 hours. For the “ex-situ” XPS experiments, TiO_2 samples were treated by UV irradiation in dark atmospheric conditions for 2 hours before XPS measurements. For the “in high vacuum” XPS experiments, the sample was first loaded into XPS load-lock chamber and was then treated by UV irradiation under vacuum for 2 hours directly followed by XPS measurements.

3.3.2 UV source

A compact ultraviolet lamp (UVP) was used for UV irradiation. The power output of the UV source was 8 watts, and the wavelength was 365 nm. A digital UV radiometer (UVX-36, UVP)

was applied to measure the UV lamp irradiance at 365 nm wavelength. UVX radiometer was placed at a fixed distance from the UV lamp to measure the light intensity. The light intensity at 5 cm from light source was ca. 2.0 mW/cm², at 8 cm from the light source was ca. 1.2 mW/cm². For the “in high vacuum” experiments, the light intensity at 5 cm from light source was reduced to ca. 1.2 mW/cm² due to the light penetration through the DUV sapphire window of XPS load-lock chamber.

3.3.3 Textural properties characterization

3.3.3.1 BET measurements

BET surface areas of the catalysts were determined by N₂ adsorption at −196 °C using a Micromeritics Tristar II surface area analyzer. The pore size distribution was calculated from the BJH desorption branch of the isotherm. Before analysis, all samples were degassed at 350 °C for 4 h under a flow of helium.

3.3.3.2 XRD measurements

XRD measurement was carried out in a Bruker D-8 X-ray diffractometer equipped with a CuK α (40 KV/40 mA) source. The XRD scan range was 20-90 degrees, and scan speed was 0.1 s/step (~5.85 degrees/min).

3.3.4 Thermogravimetric analysis

Thermogravimetric Analysis (TGA) measurements were carried out to understand the effect of adsorbed H₂O. TGA measurements were performed on a TA Instrument TGA-Q500. First, 80-120 μ m TiO₂ powder samples were pretreated at 110 °C in a convection oven for 24 h. For TGA measurements, 30 mg of TiO₂ samples were heated from 25 °C to 700 °C at a rate of 20 °C/min followed by cooling from 700 °C to 100 °C at a rate of 25 °C/min in flowing N₂ at 40 ccs/min.

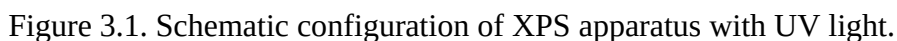
3.3.5 XPS analysis

XPS measurements were conducted on a Kratos Analytical Ltd. AXIS Ultra DLD (delay lines detector) X-ray photoelectron spectrometer (XPS) with a monochromatic Al K α X-ray source (1486.6 eV). The end station consists of a fast entry load lock, a sample treatment chamber (STC) and a sample analysis chamber (SAC) as shown in Figure 1. The X-ray spot size was about 300 $\times$ 700 μm^2 , and the angle between the sample holder and X-ray source was 35 degrees. Pass energy of 20 eV was used to measure the high-resolution spectra of Ti 2p, O 1s, and C 1s narrow scans. The binding energy shifts due to surface charging were corrected by constraining C 1s peak at 284.8 eV. No surface cleaning treatment was used to remove surface adsorbates during this experiment. Deconvolutions of the peaks using XPSPEAKS 4.1 software were conducted to obtain the relative atomic density of each species. Core level peaks were deconvoluted by fixing the binding energy at suggested values using Gaussian-Lorentzian (20%) method. The atomic sensitivity factors provided by the standard XPS handbook were used for the calculation.

3.3.5.1 Ex-situ XPS measurement

In the current study, “ex-situ” XPS measurements were carried out on two TiO₂ samples prepared at 110 °C and 450 °C to contrast and understand the effect of UV irradiation and adsorbed H₂O. TiO₂ samples were loaded onto XPS sample support bar. UV irradiation was carried out by fixing the UV lamp at 8 cm on the top of the XPS sample bar for 2 hours. UV treatment procedure was carried out under a dark atmospheric condition. After 2 h UV irradiation, the sample was loaded into the XPS system for further analysis. In a separate experiment, the other TiO₂ sample was directly loaded into XPS system without exposure to any light source.

TiO₂ adsorbents were directly loaded into XPS system without exposure to any light source. The experimental condition was XPS high vacuum ($\sim 5 \times 10^{-7}$ torr) conditions. 2 h UV irradiation



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conditions ($\sim 5 \times 10^{-7}$ torr), and the XPS examinations were conducted in the analytical chamber under ultrahigh vacuum conditions ($\sim 5 \times 10^{-10}$ torr). Our previous study showed that the sulfur heterocycle removal saturation capacity enhancement of anatase TiO_2 could be maintained for up to two weeks before a breakthrough experiment [28]. Another XPS experiment was conducted on the same TiO_2 sample that has been removed from the XPS and stored in a vial under laboratory conditions for two weeks after UV irradiation treatment.

3.4 Results and discussion

3.4.1 Physical properties characterization of TiO_2 samples

3.4.1.1 BET analysis

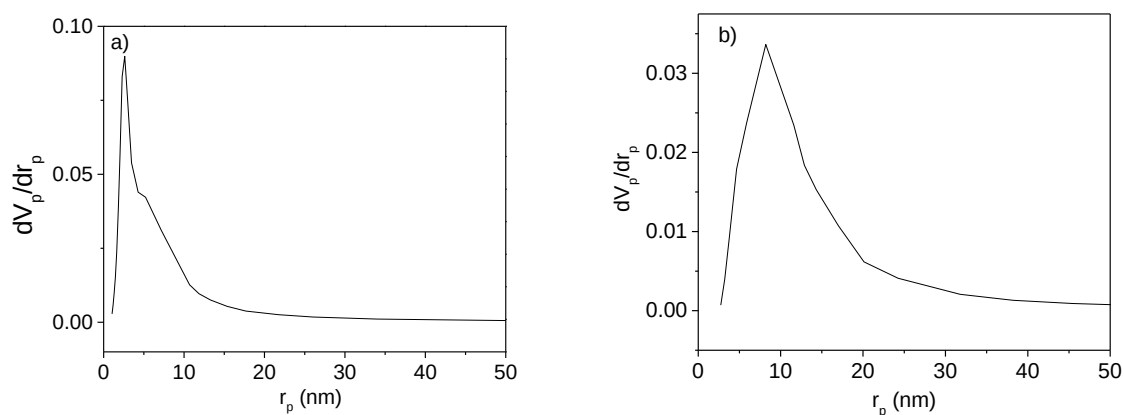


Figure 3.2. BJH pore-size distribution of a). TiO_2 (I) adsorbent; b). TiO_2 (II) adsorbent. r_p : pore radius (nm).

BET surface areas and pore volumes are illustrated in Table. 3.1. It is clearly shown that sample 1 has a higher BET surface area and a higher pore volume than TiO_2 Sample 2. Reports suggested that adsorbent with the higher surface area can absorb more H_2O [44, 45]. TiO_2 samples were defined as TiO_2 (I): with the higher surface area and higher pore volume; TiO_2 (II): with the lower surface area and lower pore volume. Figure 3.2 illustrates the pore size distributions of TiO_2 (I) and TiO_2 (II). The average pore diameter is 10.93 nm for TiO_2 (I) and

20.84 nm for TiO₂ (II). The average pore diameter for both TiO₂ (I) and TiO₂ (II) samples are sufficient for H₂O adsorption [46-48].

Table 3.1. BET parameters of two TiO₂ adsorbents

	TiO ₂ (I)	TiO ₂ (II)
Textural Properties	From Saint-Gobain 2010	From Saint-Gobain 2013
Surface area (m ² /g)	162.90	70.40
Pore Volume (cm ³ /g)	0.47	0.38
Average Pore radius (nm)	10.93	20.84

3.4.1.2 TiO₂ phase identification

Figure 3.3 shows the XRD spectra of 110 °C treated TiO₂ samples. As it is shown in Figure 3.3, all the peaks indicate anatase phase TiO₂. Peaks at 25, 38, 48, 54, 56, 63, 69, 71, 75, 83 degrees indicate (101), (004), (200), (105), (211), (204), (116), (220), (215), (303) anatase TiO₂ phases [49-56]. Both samples are photo-active under UV irradiation due to the band gap of anatase TiO₂ being 3.2 eV (387 nm in wavelength). There is no significant difference in XRD patterns for the samples after calcination at 450 °C or UV irradiation pretreatment.

3.4.2 Thermogravimetric analysis (TGA) of adsorbed H₂O

Thermogravimetric Analysis (TGA) was conducted to measure the relative amount of H₂O adsorbed on TiO₂ samples. The TGA results of TiO₂ (I) and TiO₂ (II) samples from 25 °C to 700 °C under flowing N₂ are presented in Figure 3.4. When the temperature was raised from 25 °C to 100 °C, both samples showed a significant weight loss due to the desorption of moisture. The

weight percentage drop of TiO₂ (I) adsorbent is larger than TiO₂ (II). It means TiO₂ (I) adsorbs more H₂O from the atmosphere than TiO₂ (II). Figure 3.4 also illustrated that from 100 °C to 700 °C region, there is only strongly adsorbed H₂O in TiO₂ pores. At this scan range, TiO₂ (I) dropped a higher weight percentage than TiO₂ (II), which means high surface area TiO₂ (I) has more H₂O

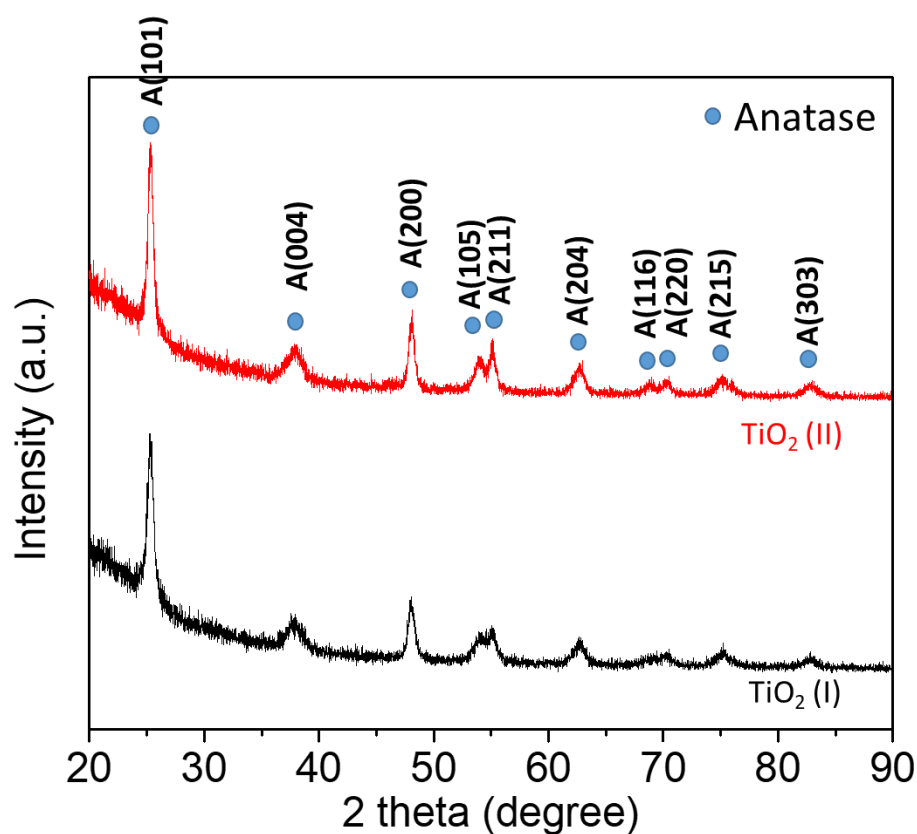


Figure 3.3. XRD patterns of TiO₂ (I) and TiO₂ (II) adsorbents

desorbed than TiO₂ (II). The rates of weight percentage loss of both samples were reduced above 450 °C, which indicates most of the adsorbed H₂O in TiO₂ samples can be driven off at 450 °C. Only a small amount of adsorbed H₂O can still exist above 450 °C.

In summation, TGA analysis indicated: 1) TiO₂ (I) has more physisorbed H₂O; 2) TiO₂ (I) has more chemisorbed H₂O; 3) Dried TiO₂ has more adsorbed H₂O than calcined TiO₂.

3.4.3 XPS analysis of active surface hydroxyl groups

The high-resolution Ti 2p XPS spectra of UV treated, and no UV treated TiO₂ (I) sample is shown in Figure 3.5. TiO₂ can be identified by Ti 2p_{1/2} and Ti 2p_{3/2} peaks at binding energies of 464.3 eV and 458.5 eV respectively [57-60]. No difference was shown on Ti 2p high-resolution XPS spectra which suggest based on our experiment, no change for the chemical state of Ti⁴⁺

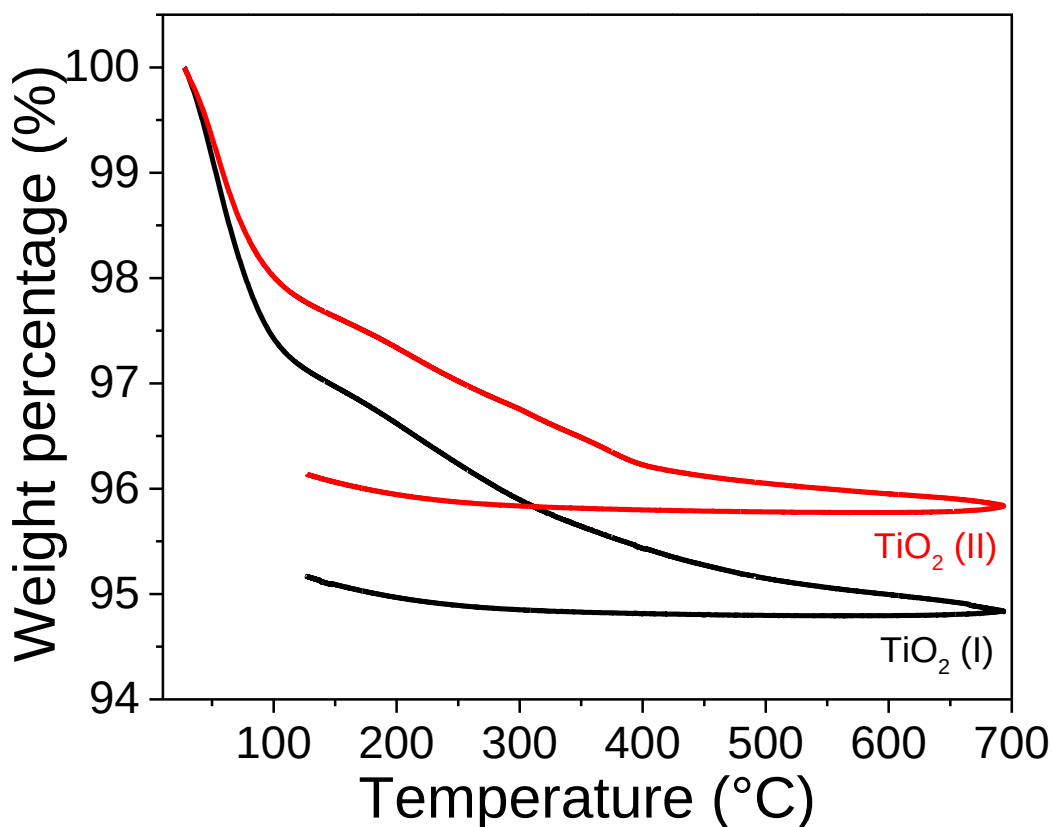


Figure 3.4. TGA results of TiO₂ (I) and TiO₂ (II) samples from 25°C to 700 °C in flowing N₂ conditions.

was observed. The same result was obtained from TiO₂ (II) adsorbent. Figures 3.6a)-3.6b) present the high-resolution XPS O 1s region scan of UV treated and no UV treated TiO₂ (I) sample. A significant difference was observed at the O 1s peaks of the O²⁻ species at a binding

energy of 529.8 eV and the OH species at a binding energy of 531.0 eV [28, 43, 61,62]. Table 2 shows the peak area percentage of each O species calculated from the deconvoluted XPS spectral results. As is shown in Table 2, UV treatment increased the intensity of OH peak and decreased the intensity of lattice O^{2-} peak. The same phenomenon was observed on TiO_2 (II) sample as shown in Figures 6c)-6d) respectively. There was no significant difference on XPS O 1s spectra when anatase TiO_2 sample was placed in XPS SAC chamber for two weeks after UV irradiation (Figure 7), which means the UV photo-generated additional hydroxyl groups can be maintained for up to 2 weeks.

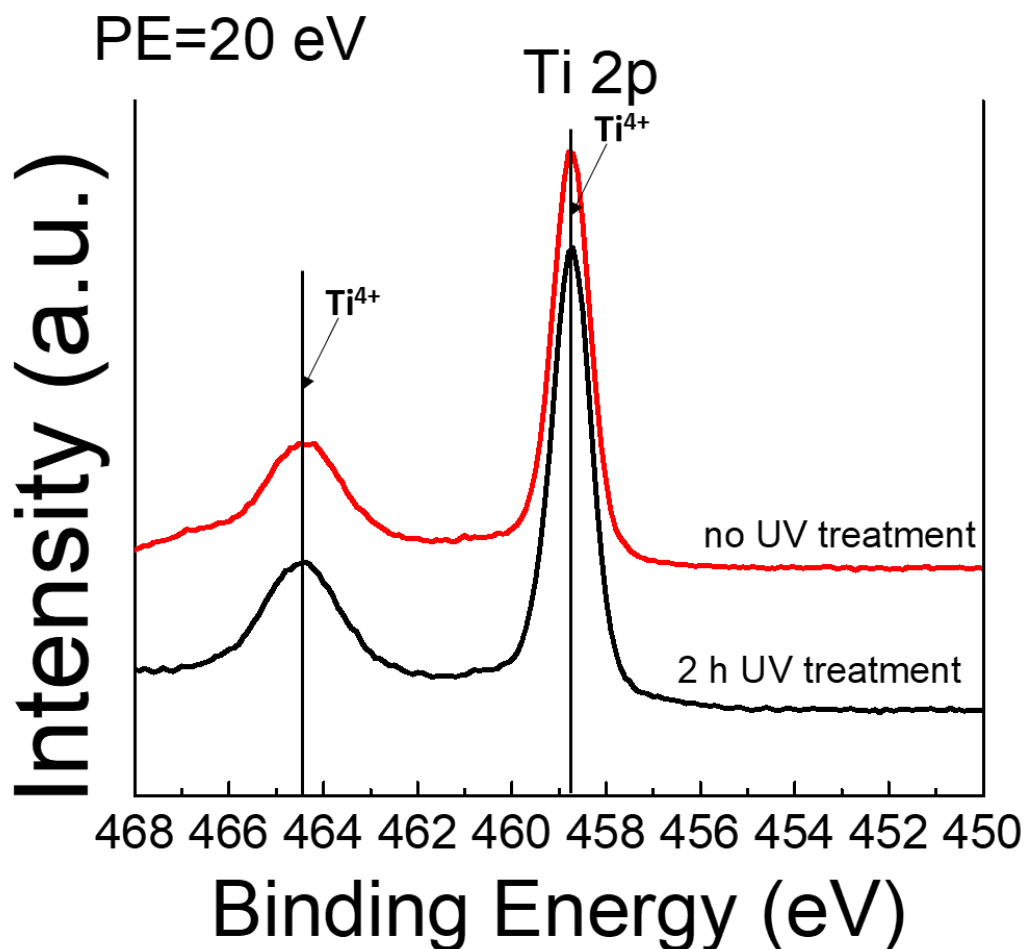


Figure 3.5. High resolution XPS spectra of Ti 2p for TiO_2 (I) sample

Figure 3.8 and 3.9 show the peak area ratios of OH and O²⁻ to Ti⁴⁺ from XPS O 1s spectra of 110 °C and 450 °C prepared TiO₂ samples treated by UV and no UV irradiation. There is no change in the Ti 2p spectra caused by UV irradiation. The peak area of Ti 2p can be viewed as a reference value. The relative amount of OH and O²⁻ can be determined by the ratio of OH and O²⁻ peak area to Ti 2p peak area.

Based on the nature of anatase TiO₂ material, the number of Ti atoms per nm³ based on 1 g of TiO₂ can be determined by the following equation.

$$N(\text{Ti})/\text{m}^3 = \frac{N_A \cdot n(\text{Ti})}{V(\text{TiO}_2)} \quad (1)$$

$N(\text{Ti})$ is the number of Ti atoms; N_A is the Avogadro constant (atoms/mol); $n(\text{Ti})$ is the mole of Ti (mol); $V(\text{TiO}_2)$ is the volume of 1 g anatase TiO₂ (m³).

$$\text{The volume of 1 Ti atom} = \frac{1}{N(\text{Ti})}$$

Assuming Ti atoms are spherical, the volume of 1 Ti atom = $\frac{4}{3} \pi r^3$. The surface area of 1 Ti atom is equal to πr^2

$$\text{The number of Ti atoms/nm}^2 = \frac{1}{\pi r^2}$$

Similarly, the number of OH atoms per nm² is calculated from the ratio of OH peak area to Ti peak area.

$$I = I_0 n \sigma \lambda(\epsilon) D(\epsilon) \int_0^t e^{-t/\lambda} dt \quad (2)$$

$$\frac{n(\text{OH})}{n(\text{Ti})} = \frac{I(\text{Ti}) \sigma(\text{Ti}) \lambda(\epsilon_{\text{Ti}}) D(\epsilon_{\text{Ti}}) \int_0^t e^{-t/\lambda} dt}{I(\text{OH}) \sigma(\text{OH}) \lambda(\epsilon_{\text{OH}}) D(\epsilon_{\text{OH}}) \int_0^t e^{-t/\lambda} dt} \quad (3)$$

$$\frac{n(\text{O}^{2-})}{n(\text{Ti})} = \frac{I(\text{Ti}) \sigma(\text{Ti}) \lambda(\epsilon_{\text{Ti}}) D(\epsilon_{\text{Ti}}) \int_0^t e^{-t/\lambda} dt}{I(\text{O}^{2-}) \sigma(\text{O}^{2-}) \lambda(\epsilon_{\text{O}^{2-}}) D(\epsilon_{\text{O}^{2-}}) \int_0^t e^{-t/\lambda} dt} \quad (4)$$

Where I_0 : X-ray flux; N : Density of atoms; σ : Photoelectron cross-section; I : XPS peak intensity (peak area); $\lambda(\epsilon)$: Mean free path of energy(ϵ); $D(\epsilon)$: Fraction of electrons detected by the analyzer; t : The sampling depth

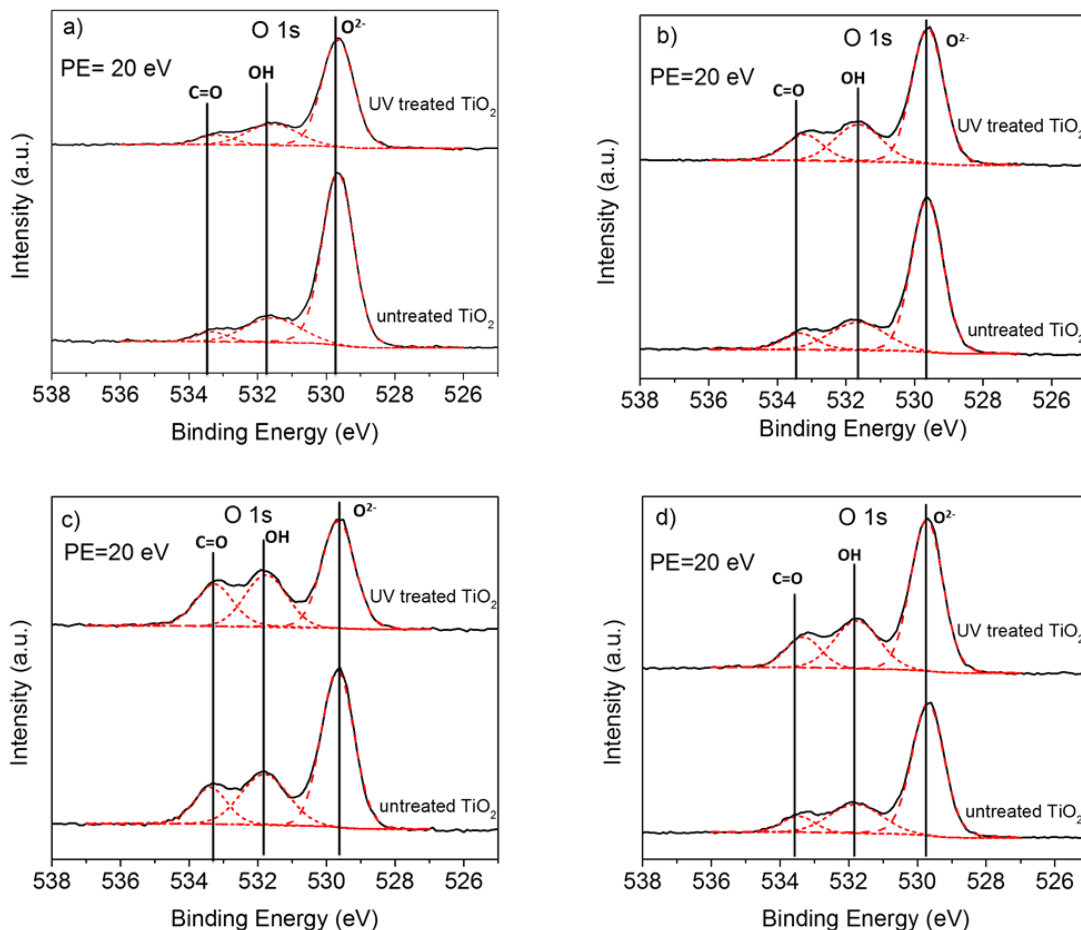


Figure 3.6. High resolution XPS spectra of O 1s for a) 110 °C dried TiO_2 (I); b) 450 °C calcined TiO_2 (I); c) 110 °C dried TiO_2 (II); d) 450 °C calcined TiO_2 (II).

As is shown in Figure 3.8, for the same TiO_2 sample, UV irradiation produced more additional OH and consumed more O^{2-} when the sample was treated at 110 °C than at 450 °C. From TGA results, TiO_2 samples treated at 110 °C contains more adsorbed H_2O than treated at

450 °C. The difference between the relative amount of OH before and after UV irradiation for the same TiO₂ sample under different temperature preparation is due to the relative amount of H₂O adsorbed on TiO₂ samples. Figure 8-9 also indicate that at the same preparation temperature, TiO₂ (I) sample produced more OH and consumed more O²⁻ by UV irradiation. Thus, for the same temperature

Table 3.2. Peak area fraction of different O species from deconvoluted XPS results

“In a high vacuum.”		TiO ₂ (I)		TiO ₂ (II)	
	Species	No UV	With UV	No UV	With UV
110 °C Dried	-OH	0.18	0.21	0.17	0.23
	O ²⁻	0.77	0.74	0.80	0.75
	C=O	0.05	0.02	0.03	0.02
450 °C Calcined	-OH	0.21	0.23	0.17	0.19
	O ²⁻	0.75	0.72	0.80	0.78
	C=O	0.04	0.05	0.03	0.03
“Ex-situ”		TiO ₂ (I)		TiO ₂ (II)	
	Species	No UV	With UV	No UV	With UV
110 °C Dried	-OH	0.17	0.24	0.18	0.22
	O ²⁻	0.80	0.73	0.77	0.75
	C=O	0.03	0.03	0.05	0.03
450 °C Calcined	-OH	0.16	0.21	0.16	0.19
	O ²⁻	0.80	0.76	0.81	0.78
	C=O	0.04	0.03	0.03	0.03

prepared TiO_2 samples, the additional OH generated by UV irradiation is related to the relative amount of adsorbed H_2O . Table 3 illustrates the relative number of OH and O^{2-} atoms per nm^2 before and after UV irradiation treatment for TiO_2 samples prepared at various temperatures. $N_{(\text{OH})}$ increased after UV treatment, whereas $n_{(\text{O}^{2-})}$ decreased. All the experimental results showed an almost identical ratio of $\Delta n_{(\text{OH})}$ over $\Delta n_{(\text{O}^{2-})}$ varied from -1.883 to -2.153. Accounting for

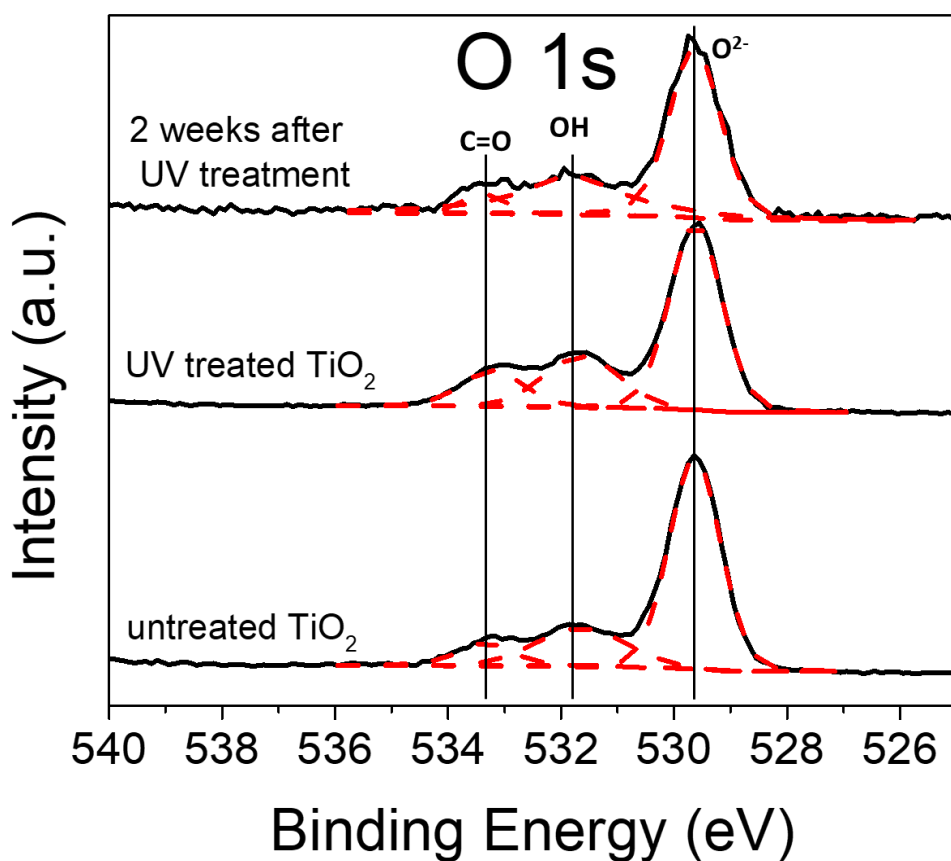


Figure 3.7. High-resolution XPS spectra of O 1s for 450 °C treated anatase TiO_2 (I) sample. potential error from the experiment and result in analysis, the actual value of this ratio is about 2.000. Based on this ratio, a reaction scheme was proposed based on an O^{2-} atom and an adsorbed H_2O molecule react and form two hydroxyl groups under UV irradiation. Table 2

illustrates that the higher quantity of H₂O adsorbed on TiO₂ sample leads the production of additional hydroxyl groups under the same UV irradiation condition.

3.4.4 XPS quantitative analysis and potential reaction mechanism

UV photo-assisted adsorptive desulfurization using anatase TiO₂ provided an advanced desulfurization capacity and efficiency over non-UV induced adsorptive method [28]. The mechanism study for the surface alteration by UV pretreatment determined from the results and

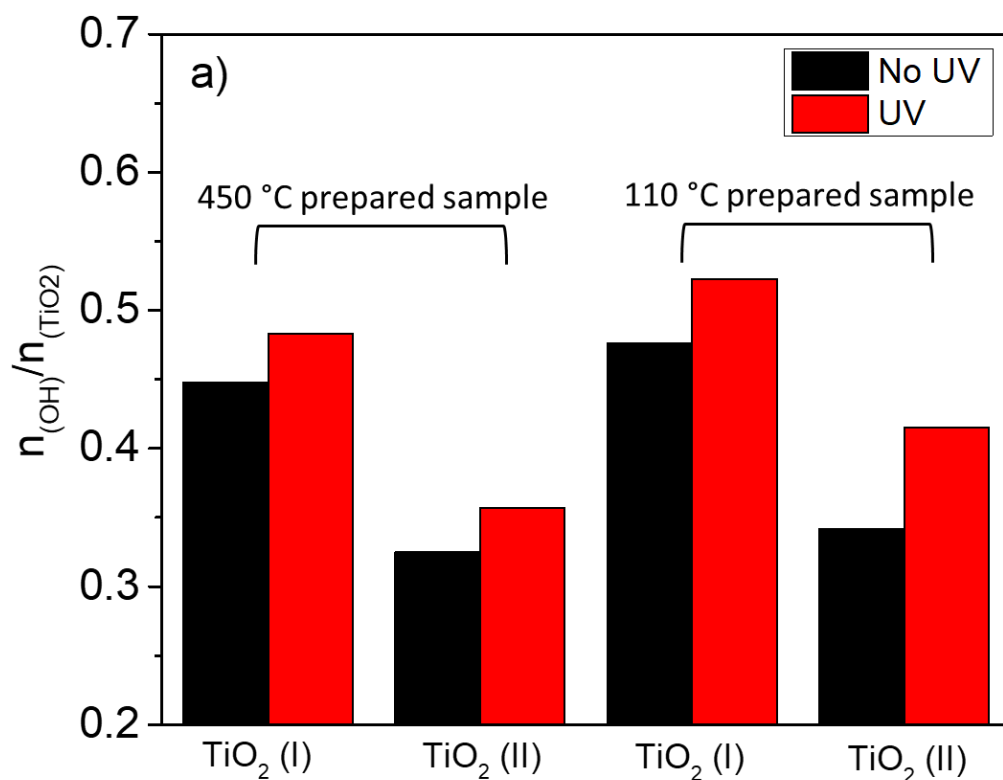


Figure 3.8. Atomic density ratio of $n(OH)/n(TiO_2)$ from “in high vacuum” UV pretreatment XPS spectra

analysis from “in high vacuum,” “ex-situ” XPS and Thermogravimetric Analysis (TGA) experiments on two different TiO₂ samples prepared at different temperatures. The differences

between two TiO₂ samples are the BET surface area and pore volume, which are related to the amount of adsorbed H₂O within a certain surface region. Based on the spectral and quantitative analysis, the enhancement of UV irradiation pretreatment on sulfur heterocycle removal capacity resulted from the photo-induced reaction between anatase TiO₂ and adsorbed H₂O.

Table 3.3. The relative concentration of OH and O²⁻ (atoms per nm²) under UV and dark conditions

		TiO ₂ (I)				TiO ₂ (II)			
“In a high vacuum.”		No	With	Δn	$\frac{\Delta n(-OH)}{\Delta n(O^{2-})}$	No	With	Δn	$\frac{\Delta n(-OH)}{\Delta n(O^{2-})}$
		UV	UV			UV	UV		
110 °C	n(-OH)	2.72	3.58	0.86		2.70	3.35	0.65	
Dried	n(O ²⁻)	12.34	11.91	-0.43	-2.00	12.45	12.13	-0.32	-2.03
450 °C	n(-OH)	2.48	3.25	0.77		2.45	2.89	0.44	
Calcined	n(O ²⁻)	12.26	11.86	-0.40	-1.92	12.30	12.06	-0.24	-1.83
		TiO ₂ (I)				TiO ₂ (II)			
“Ex-situ”		No	With	Δn	$\frac{\Delta n(-OH)}{\Delta n(O^{2-})}$	No	With	Δn	$\frac{\Delta n(-OH)}{\Delta n(O^{2-})}$
		UV	UV			UV	UV		
110 °C	n(-OH)	2.72	4.15	1.43		2.70	3.52	0.82	
Dried	n(O ²⁻)	12.34	11.58	-0.76	-1.88	12.45	12.05	-0.40	-2.05
450 °C	n(-OH)	2.48	3.75	1.27		2.45	3.11	0.66	
Calcined	n(O ²⁻)	12.26	11.67	-0.59	-2.15	12.30	11.97	-0.33	-2.00

A Ti 2p spectral change was absent. A peak intensity shift from O²⁻ to OH was observed from high-resolution O 1s spectra after UV irradiation. From the qualitative analysis, at the same

preparation temperature, TiO₂ (I) sample can produce more OH after UV treatment due to more H₂O adsorbed on TiO₂ (I). For the same sample prepared at different temperatures, UV irradiation on lower temperature prepared sample can produce more additional OH due to the loss of adsorbed H₂O by high-temperature treatment. For the same sample at same preparation

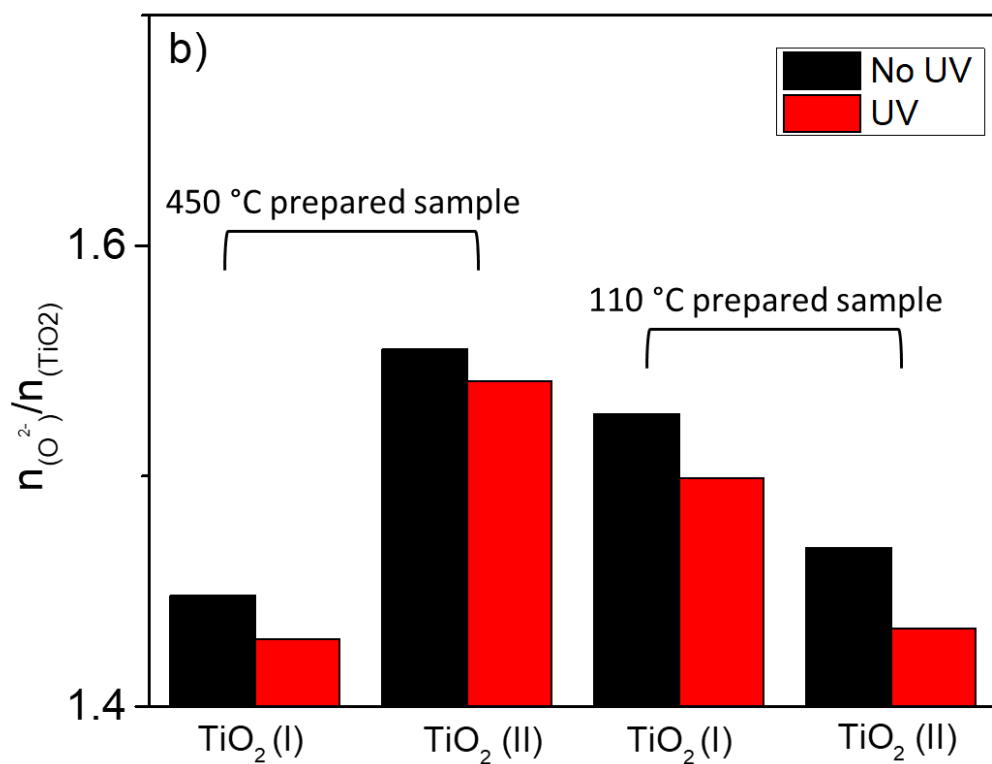


Figure 3.9. Atomic density ratio of $n(O^{2-})/n(TiO_2)$ from “in high vacuum” UV treatment XPS spectra

temperature, UV irradiation generated more OH in “ex-situ” experiment than “in high vacuum” experiment because there is more H₂O in atmospheric conditions than in high vacuum condition.

At the same time, the more OH produced, the more O^{2-} consumed. In other words, UV irradiation caused a photo-induced reaction between anatase TiO_2 and adsorbed H_2O to generate additional OH and consume O^{2-} . More adsorbed H_2O is responsible for higher hydroxyl group production and greater O^{2-} consumption rate. TGA analysis further confirms that higher surface area TiO_2 sample has more adsorbed H_2O since it loses more weight percentage at an identical temperature increase. From XPS quantitative analysis, all the experiments indicate that hydroxyl groups production level is twice the O^{2-} consumption level. Hydroxyl radicals could be an important intermediate for this UV induced chemical reaction [63-67], but due to the short lifetime of hydroxyl radicals (10^{-9} s in a cell), it is not discussed here since the current XPS measurement could not indicate the existence of hydroxyl radicals from our experiments. A detailed characterization of hydroxyl radicals along with related intermediate species formed will be included in future work.

Based on the experimental analysis, a mechanism for the reaction scheme shown below can be proposed as shown in Figure 3.10.

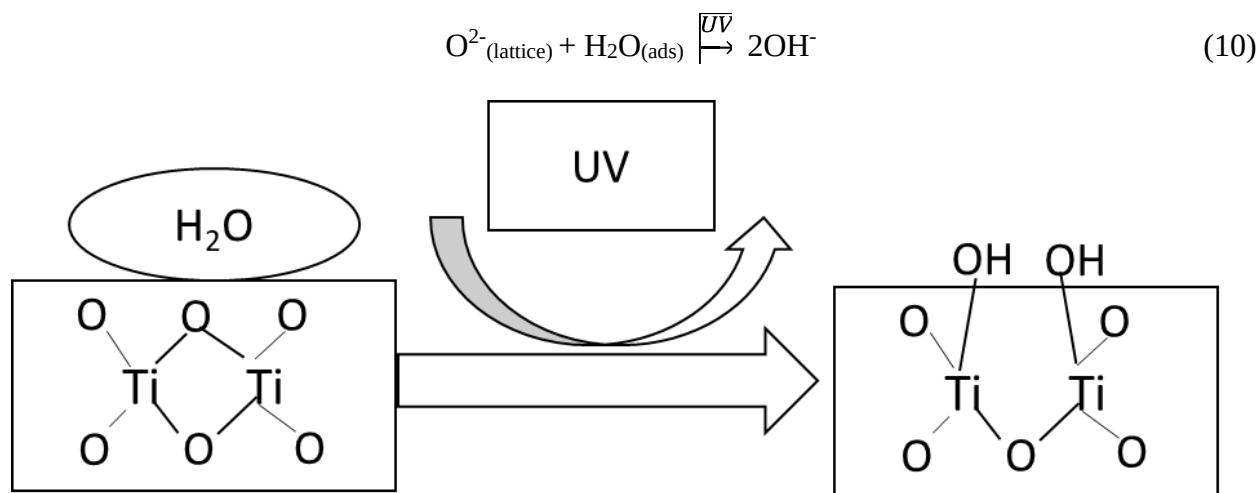


Figure 3.10. Schematic diagram of UV induced photo-catalytic reaction mechanism

3.5 Conclusion

This study provides qualitative and quantitative evidence to reveal the mechanism of anatase TiO₂ surface alteration by UV pretreatment and its impact on adsorptive desulfurization applications. “In high vacuum” and “ex-situ” XPS measurements were conducted on two different commercial anatase TiO₂ samples with different surface areas and pore volumes. Thermogravimetric Analysis (TGA) experiments conducted on the two TiO₂ samples revealed that higher surface area TiO₂ had more adsorbed H₂O. XPS and TGA results indicated that additional surface hydroxyl groups produced under UV irradiation are correlated to the relative amount of adsorbed H₂O. These additional hydroxyl groups produced by photo-induced reactions help improve the desulfurization capacity of the adsorbent for a prolonged period (2 weeks).

The current study provides an insight into the possible mechanism of the photo-induced pathway for UV pretreatment photo-assisted adsorptive desulfurization on anatase TiO₂ material.

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Chapter 4 XPS and FTIR investigations of the transient photocatalytic decomposition of surface carbon contaminants from anatase TiO₂ in UHV starved water/oxygen environments

4.1. Abstract

This paper explores the transient photocatalytic oxidation mechanism of carbon contaminants from a high surface area anatase TiO₂ pellet under starved water/oxygen reaction conditions created when specimens are irradiated via a 375 nm UV laser inside the UHV analysis chamber of an XPS spectrometer. Complementary results are also provided following similar UV irradiations and reaction procedures in an evacuated *in situ* reaction cell of a Fourier-transform infrared spectrometer (FTIR). An interactive and non-steady state transient photocatalytic reaction is observed between surface carbon species and strongly adsorbed H₂O brought to the exterior surface of the pellet via UV photodesorption from within the deeper lying pores of the pellet. The reaction stoichiometry and quantum efficiency of the reaction are reported at various irradiation intensities. *In situ* FTIR spectral features are also presented and discussed for a non-UV treated TiO₂ sample and a 2-hour UV-treated TiO₂ sample under evacuated conditions also showing the decomposition of carbon contaminants species and the consumption of adsorbed water/hydroxyls with the ensuing formation of carboxyl (HO-C=O) carbon species and isolated surface hydroxyls. The photocatalytic decomposition of carbon species and the concomitant consumption of oxygen containing species was also tracked by following the XPS spectral changes of a UV-irradiated area on the pellet surface compared to a dark reference spot on the same specimen. Eight different reaction cases at four different UV intensities, repeated twice each, were also investigated using separate pieces of the same TiO₂ media. The measured stoichiometry for the decomposition of carbon species and consumption of oxygen ranged from 0.53 during the first 10-20 minutes of irradiation and increased to 0.65 with

an average value of 0.59 and a standard deviation of 0.11. These data suggest that the reaction product and leaving group from the TiO₂ surface is primarily CO₂ during the first 10-20 minutes of initial reaction with perhaps a small fraction of CO toward the end of reaction. Heating the sample specimen to 100 °C for 2-hour inside the XPS-UHV analysis chamber prior to UV illumination was effective in eliminating photocatalytic oxidation and carbon removal from the surface thereby demonstrating that strongly adsorbed water (prior to heating in vacuum) was a critical and limiting reagent in the overall H₂O transport and reaction process.

Photon efficiencies for the reaction were calculated based on the number of carbon species removed from the XPS-observable surface versus the number of the UV photons adsorbed in the topmost 2 nm of the sample. The highest photon efficiency observed was 0.0186 after 5-10 minutes of UV exposure at 1.5 mW/cm². All reaction cases showed a significant efficiency drop after 30 minutes of UV irradiation due to the consumption of the adsorbed reactants, both carbon and water. From detailed deconvolution of the XPS C 1s spectra, UV irradiation showed a high selectivity towards hydrocarbon contaminant decomposition, which was 75%±5% of all carbon species removed.

Keywords: FTIR, XPS, Photocatalysis, UV, TiO₂, Hydrocarbon

4.2. Introduction

Titanium dioxide is a promising photocatalytic semiconductor that has been extensively studied since the discovery of photo-catalytic water splitting by Fujishima and Honda [1]. During the past several decades TiO₂ has also been examined for a number of other photocatalytic reaction mechanisms including: decomposition of hydrocarbons [2-5], water splitting [6-8], degradation of pollutants [9,10], energy storage [11], and adsorbent applications [12-14].

Hydrocarbon contaminants are inevitably present on the surface of catalyst materials during their preparation and can affect their overall catalytic efficiencies and mechanism [15,16]. Wang et al. [15] investigated photocatalyzed surface reaction mechanisms on nanoparticulate anatase TiO_2 films by visible-infrared sum frequency generation (SFG). A strongly adsorbed hydrocarbon layer was found on their freshly prepared TiO_2 films that could be removed by UV irradiation. X-ray photoelectron spectroscopy (XPS) results also show the presence of hydrocarbons on the surfaces of other freshly prepared catalyst materials [16,17], and researchers have been investigating methods to remove hydrocarbon contaminants [4,15,18]. Since the discovery of the photocatalytic removal of hydrocarbons from anatase TiO_2 , a variety of studies [4,19-21] have been reported regarding this phenomenon. Izumi et al. [19] proposed that the photogeneration of hydroxyl radicals ($\text{OH}\cdot$) was the key reactant for the photocatalytic oxidation of hydrocarbons from platinized TiO_2 powders. Einaga et al. [4] reported the photocatalytic oxidation of various hydrocarbons from a TiO_2 catalyst and the ensuing formation of CO_x .

Over the past decade, high surface area commercial anatase TiO_2 materials have been used in our laboratory as an adsorbent support, often times impregnated with 1 to 10 wt% Ag [12-14, 20,21]. Taking advantage of its inherent photochemical reactivity, both neat TiO_2 and Ag/TiO_2 have been studied. A significant enhancement in the sulfur heterocycle specificity and saturation capacity of TiO_2 adsorbents after UV irradiation pretreatment was found [12,13]. By tracking UV-induced chemical composition changes (as monitored by XPS and FTIR [13,14]), the adsorptive capacity enhancement was attributed to the conversion of adsorbed water and lattice oxygen into surface hydroxyls, which have a high selectivity and capacity to strongly bind sulfur heterocycles [21]. Furthermore, this effect was a persistent one that was retained after the first UV irradiation for numerous adsorption/desorption/calcination cycles and did not depend upon

or require subsequent UV irradiation. Other and perhaps related surface reactivity observations have also been reported by Kurtz et al. [22], Nakamura et al. [23], and Imanishi et al. [24].

X-ray photoelectron spectroscopy (XPS) has been widely used to study surface reaction mechanisms [14,25,26], surface reaction kinetics [27], and chemical adsorption-desorption mechanisms [29]. Kruse and Chenakin [25] studied X-ray irradiation effects on Au/TiO₂ via *in situ* time-dependent XPS, where a reduction of the initial Ti⁴⁺ oxidation state was observed in conjunction with a desorption of oxygen. Markus et al. [26] used *in situ* XPS and a UV laser to study the photochemical formation of nitrogenated organic species on TiO₂ (110). In the present study, systematic XPS experiments were carried out to elucidate the photocatalytic decomposition of surface carbon contaminants by coupling a UV laser diode module on a DUV window of the spectrometer's analytical chamber. Companion and comparison data were also generated following UV irradiation of identically prepared samples in an *in situ* FTIR cell. XPS characterization of 8 different reaction cases for UV induced photo-oxidative decomposition of hydrocarbons from anatase TiO₂ under ultra-high vacuum (UHV) conditions provided valuable qualitative and quantitative insight into the reaction mechanism and stoichiometry. Various elemental features were monitored to follow surface chemical composition as a function of UV intensity and fluence, initial hydrocarbon concentration, and initial or subsequent levels of adsorbed water/oxygen.

4.3. Experimental

4.3.1. Sample preparation

Sample preparation procedures have been reported elsewhere [14,21]. Commercial anatase TiO₂ (Saint Gobian Norpro, ST61120) was utilized. The measured BET surface area of this material was 163 m²/g. As received 3.2 mm pellets were crushed and sieved to 75-125 μm. The

resulting sample powder was dried at 110 °C for 24 hours in a convection oven and then calcined at 450 °C for 2 hours in flowing air followed by cooling in flowing air for an additional 2 hours. TiO₂ self-supporting films for suitable analyses (~400 µm thick) were prepared by a hydraulic press. While all samples were stored nearly immediately in capped bottles following their preparation, the initial level of surface hydrocarbons on the specimens was noted to depend on storage time as shown in Sections 4.3.4 and 4.3.5. In this way, the level of initial surface contamination on a specimen could be manipulated slightly by means of 0-to-10-day storage times or held constant by preparing all specimens near simultaneously and then transferring an entire set into the sample preparation/introduction/analytical chamber(s) of the spectrometer.

4.3.2. UV source and instrument setup

A UV laser diode module (model number Oxxius 375, manufactured by Oxxius) and operating at 375 nm was mounted on an adjustable holder adjacent to a DUV window on the XPS analysis chamber with a line-of-sight view to the sample analysis position. It was aligned with the X-ray irradiation spot by visually adjusting the irradiated spot on a fluorescent paper (Figure 4.1 and Figure 4.2). The UV laser diode was 20 cm from the XPS analysis position with an irradiation angle of 45° to the sample's surface normal. The UV irradiation intensity at the sample position inside the XPS analysis chamber (and through the DUV-UHV window on the vacuum system) was measured to be ca. 65% of the irradiation intensity of that indicated by a UV radiometer at the same distance outside the vacuum system (without the DUV window) and normal to the laser's axis. All photon fluxes and fluences are reported relative to those measured by the UV radiometer inside the analysis chamber at the appropriate incident angle. The UV irradiation spot size was slightly larger than the X-ray analysis spot. The XPS positioning control stage allowed switching the XPS analysis location between a UV illuminated area on the

a)

UV laser head

Adjustable frame

DUV window

Analyzer

X-ray

Temperature control unit

Sample holder

Valve

STC

Load Lock

N₂

WRG

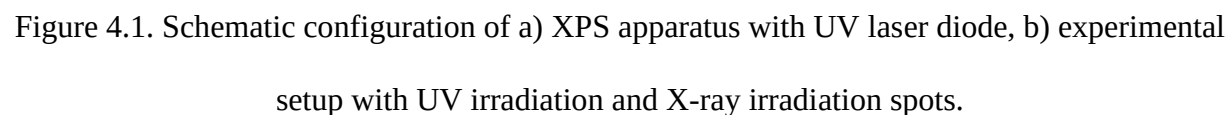
1

2

3

4

Pumping system



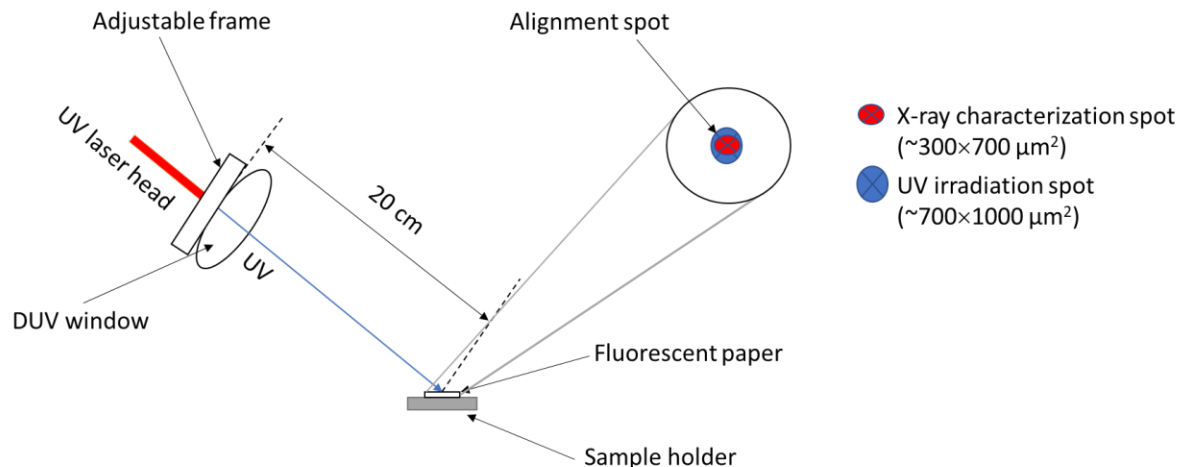


Figure 4.2. Schematic configuration of the UV laser alignment during the in-situ experiments.

4.3.3. Textural properties characterization

4.3.3.1. BET measurement

The BET surface area of the anatase TiO_2 sample was determined by N_2 adsorption at -196°C using a NOVA 220e surface area analyzer. The Barrett-Joyner-Halenda (BJH) desorption branch of the isotherm was also used to calculate the pore size distribution of the TiO_2 sample. Before analysis, the sample was degassed at 400°C for 5 hours under a flow of helium.

4.3.3.2. XRD measurement

An X-ray diffractometer (Bruker D-8) equipped with a $\text{CuK}\alpha$ X-ray source was used for XRD characterization. TiO_2 powder samples (75-125 μm) were utilized. The XRD scan was at 40 kV/40 mA from 20 to 90 degrees with a scan speed of 0.1 s/step (~ 5.85 degrees/min). XRD measurements were taken from sample powders before and after 2 hours of UV irradiation.

4.3.4. Thermogravimetric analysis

Thermogravimetric Analysis (TGA) was conducted with a TA Instrument TGA-Q500 to measure the level of adsorbed water on the TiO_2 specimen as a function of temperature. Thirty

milligrams of freshly prepared TiO₂ powder was heated from 25 °C to 700 °C at a rate of 20 °C/min followed by cooling from 700 °C to 100 °C at a rate of 25 °C/min in flowing N₂ at 40 cc/min.

4.3.5. UV-vis measurement

UV-vis measurements were conducted on a Shimadzu UV-3600 instrument in the transmission mode. TiO₂ powder (10 wt%) was mixed with 99.999% purity KBr powder (90 wt%) (International Crystal Laboratories) and then was dried at 110 °C in a convection oven for 24 hours. The powder mixture was finely ground in a high-frequency mechanical wiggler and pressed into a thin (~400 μm thick) pellet using a hydraulic press. UV-vis measurements were performed using the optically semi-transparent pellets of 10 wt% TiO₂ and 90 wt% KBr versus 100 wt% KBr as a reference.

4.3.6 FTIR measurements

TiO₂ pellets treated with and without UV irradiation were analyzed via *in-situ* Fourier-transform infrared spectroscopy (FTIR) coupled with a UV lamp (manufactured by UVP, 365 nm) as shown in Figure 4.3. The UV irradiation intensity on the sample surface was measured to be ca. 3.0 mW/cm² as indicated by a UV radiometer manufactured by UVP. For infrared measurements, 75-125 μm TiO₂ powders were pressed into a thin self-supporting film (~400 μm thick) by a hydraulic press. The TiO₂ pellet was then placed into a customized IR cell equipped with ZnSe windows. The IR cell was evacuated to 100 mtorr. *In situ* FTIR measurements were conducted for the non-UV treated sample and after 2 hours of UV irradiation. *In situ* FTIR experiments were conducted on a Thermo Scientific Nicolet IR100 spectrometer, with the analysis range between 1000 and 4000 cm⁻¹.

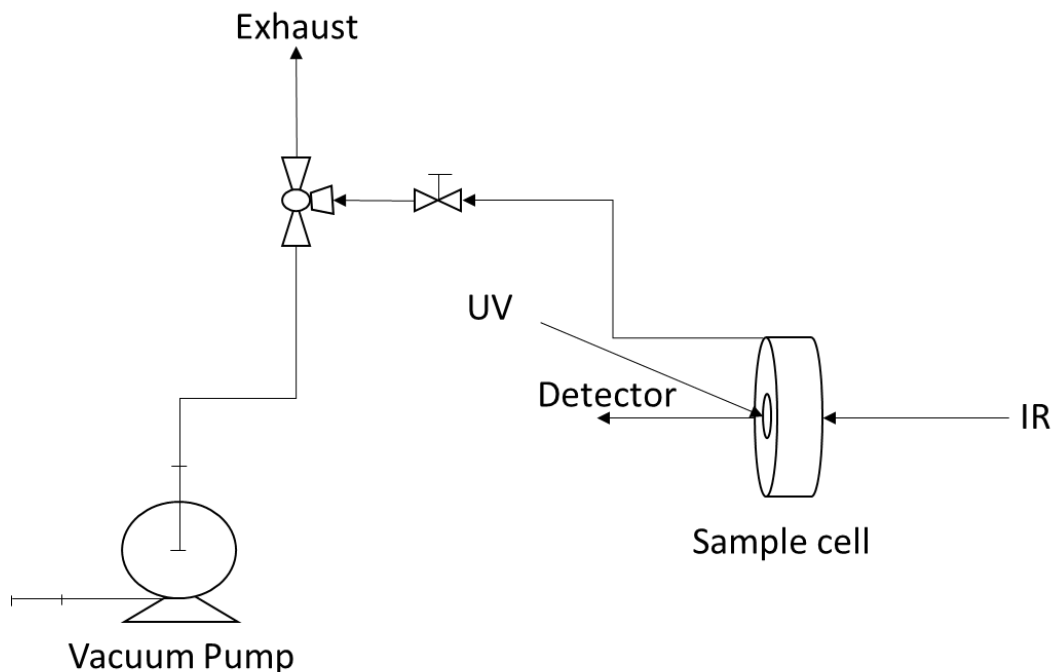


Figure 4.3. In situ FTIR experimental setup

4.3.7 XPS analysis

XPS analyses were carried out using a Kratos Analytical Ltd. AXIS Ultra delay line detector (DLD) X-ray photoelectron spectrometer (XPS). The entry station consisted of a fast entry load lock, sample treatment chamber and a sample analytical chamber as shown in Figure 1a). In the current study, a monochromatic Al K_{α} X-ray source was used at an operating power of 15 kV $\times$ 15 mA. The X-ray spot size was consistently set to be 300 $\times$ 700 μm^2 . The angle between the sample holder and the X-ray source was 35 degrees. Prior to analysis, samples were degassed for 80 hours in the sample treatment chamber at a base pressure of 3.2×10^{-10} torr. No Ar^+ sputtering or other surface cleaning treatments were used in the present experiments. A pass energy of 160 eV with a step size of 0.1 eV per point was used to obtain the survey scan of the TiO_2 sample. A pass energy of 20 eV with a step size of 0.1 eV per point was used to measure photoelectron core-level spectra for Ti 2p, O 1s, and C 1s. The overall resolution of the spectrometer was 0.65

eV measured as a full width half max (FWHM) for the Ag 3d_{5/2} line of a sputtered Ag foil. The spectrometer and work function of the instrument were calibrated by observing the binding energy of the Au 4f_{7/2} peak at 84.0 eV. A temperature control unit with a thermocouple located at the edge of the sample holder stage was used to maintain the overall specimen temperature at 25-26 °C. Temperature and background pressure profiles during all experiments were closely monitored. Background pressures increased during times when the X-ray source was turned on due to background heating or when UV photons were introduced (due to photo-desorption from the chamber walls or the sample itself) but these pressure excursions were not significant during the course of the runs given the high pumping speed of the system. No mass spectrometers were present in the analysis chamber and the characteristics of this experimental arrangement did not permit any type of quantitative photon stimulated or thermal desorption studies or analyses. XPS spectra were collected as a function of UV exposure time (0, 5, 10, 20, 30, 60, and 120 minutes) at different UV irradiation intensities. XPS spectra of the dark reference spot on the same specimen were also collected at roughly the same time intervals. The first set of spectra obtained were defined as “non-UV treated” with no UV exposure. The acquisition time of each spectrum was 40 seconds. After degassing at 3.2×10^{-10} torr in the sample treatment chamber for 80 hours, only strongly bound species prevailed on the sample surface prior to analysis.

The deconvolution of photoelectron spectra was performed using the public software package XPSPEAKS 4.1 using the same procedures as previously reported [28-30]. After subtraction of the Shirley-type background, the spectra were decomposed into their components at suggested binding energies with mixed Gaussian-Lorentzian lines by a non-linear least squares curve-fitting method. The binding energies and full width half max (FWHM) of the peaks were recorded by the fitting results. Surface chemical composition calculations were derived from the

deconvoluted peak areas, inelastic electron mean free paths and the atomic sensitivity factors (cross-sections) provided by the standard XPS handbook [14].

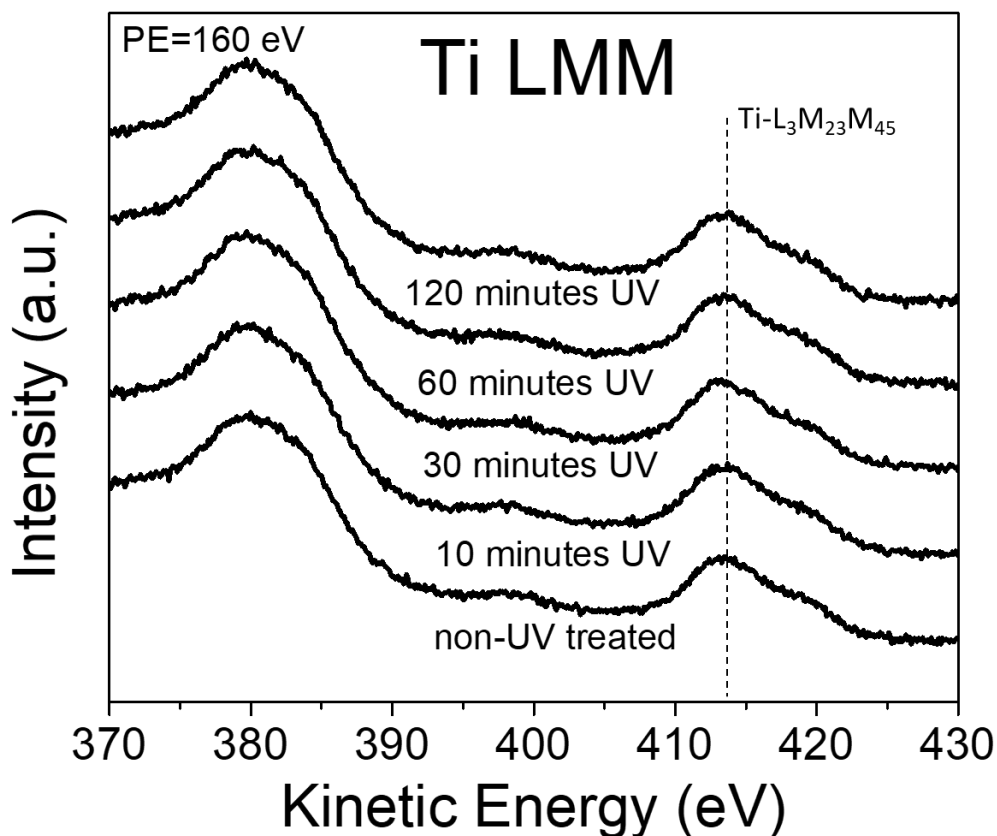


Figure 4.4. X-ray induced Ti LMM auger lines of TiO₂ non-UV treated and after UV treated at 3.0 mW/cm² UV irradiation.

Potential binding energy shifts caused by surface charging were corrected by aligning the C 1s line at 284.8 eV and appropriate Auger parameters were also used to examine potential charging effects as needed (Figure 4.4 and Table 4.1). Peak shape and FWHM values of various species and their variations were also used to indicate the presence of any spatial or differential charging, but such effects were not observed to be significant or affect the results of our analyses.

A specimen neutralizer was also used at times to ensure that uncompensated sample charging was not responsible for observed peak shifts or changes in apparent surface species.

Table 4.1. Auger parameter of TiO₂ sample non-UV treated and after UV treated at 3.0 mW/cm²

UV irradiation

UV irradiation time (mins)	Binding Energy of Ti 2p 3/2 (eV)	Kinetic energy of Ti-L ₃ M ₂₃ M ₄₅ (eV)	Auger parameter α' (Ti-L ₃ M ₂₃ M ₄₅ , Ti 2p 3/2) (eV)
0	458.52	413.48	872.00
10	458.51	413.50	872.01
30	458.50	413.50	872.00
60	458.49	413.52	872.01
120	458.50	413.51	872.01

XPS measurements as a function of UV fluence and irradiation intensity were conducted twice each at various conditions with all results providing uniform and reproducible trends and behavior.

4.4. Results and discussion

4.4.1. Physical properties characterization of TiO₂ sample

4.4.1.1. BET analysis

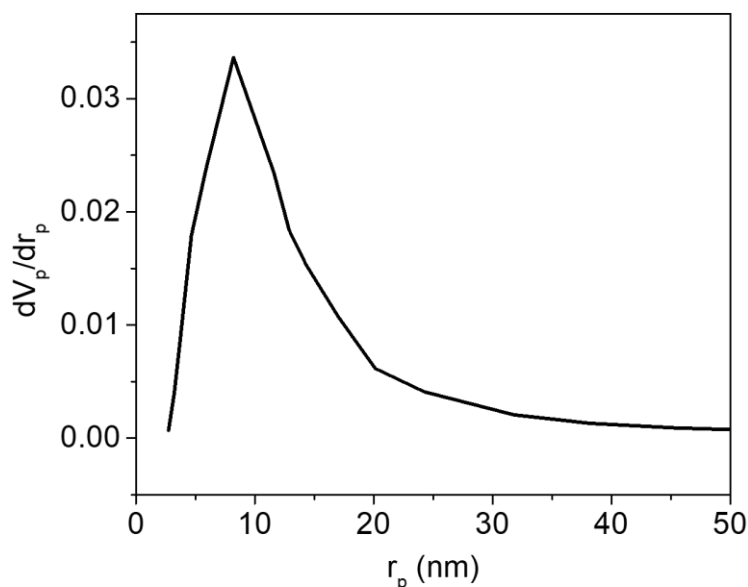


Figure 4.5. Pore size distribution of anatase TiO₂ sample.

The BET surface area of TiO₂ powder samples was determined to be 163 m²/g, with a pore volume of 0.47 cm³/g and an average pore radius of 10.9 nm. The pore size distribution of a representative TiO₂ sample is shown in Figure 4.5. Studies [28,29] have shown that porous high surface area materials like TiO₂ have a high capacity for adsorbing water and the average pore radius is suitable for water adsorption as discussed in section 4.2 and section 4.3.

4.4.1.2. TiO₂ phase identification

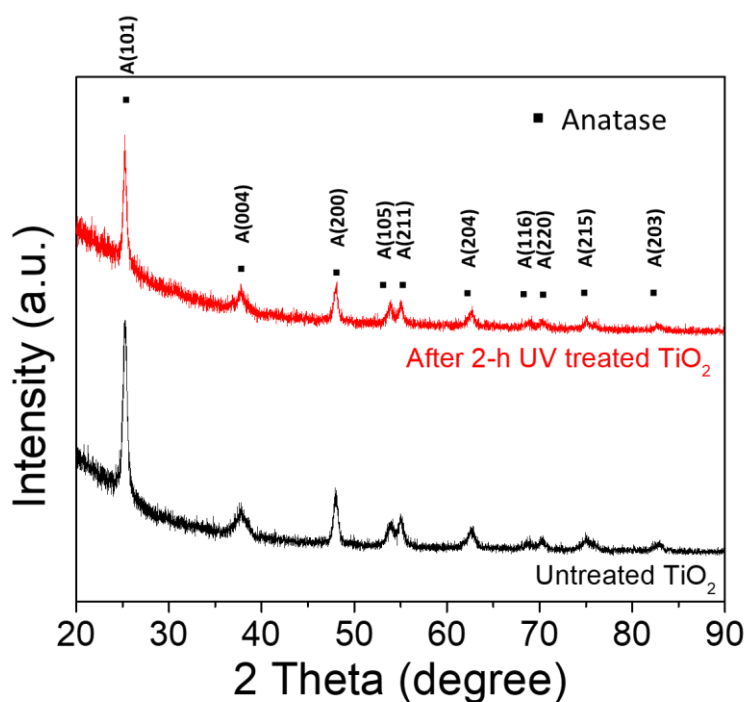


Figure 4.6. XRD patterns of 2-hour UV treated TiO_2 and untreated TiO_2

Figure 4.6 shows the XRD patterns of non-UV treated and 2-hour UV treated TiO_2 samples. UV irradiation did not cause any change in the XRD patterns. All peaks observed were consistent with anatase TiO_2 [30,31]. The band gap of anatase TiO_2 is 3.2 eV, 387 nm in wavelength, hence it is photo-active under 365 nm and 375 nm of UV irradiation.

4.4.2. Thermogravimetric analysis (TGA)

In order to verify the hypothesis made from BET results that the TiO_2 sample could have a high capacity for adsorbing water, TGA was conducted as explained in section 4.4. Figure 4.7 shows the weight change for a TiO_2 sample from 25 to 700 °C in flowing N_2 . From 25 to 100 °C, the sample showed a significant weight loss due to the desorption of water. From 100 to 450 °C, strongly adsorbed water was further removed as the weight of the TiO_2 sample decreased further.

From 450 to 700 °C, the weight loss was not significant, which means most of the adsorbed water could be driven off the specimen by heating below 450 °C.

Based on the above noted TGA results it appears that degassing near room temperature in UHV conditions will not remove all the adsorbed water [26,28,29]. TGA result estimated that our TiO₂ specimens held 3.5wt% adsorbed H₂O at room temperature, which corresponds to ca. 0.84 monolayers of adsorbed H₂O.

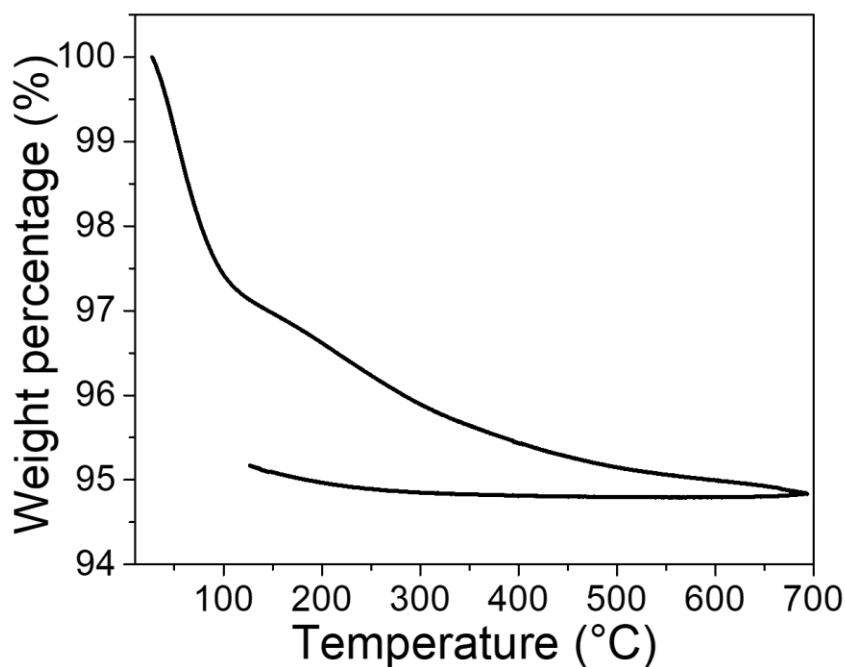


Figure 4.7 TGA result of TiO₂ sample from 25°C to 700 °C in flowing N₂ conditions

4.4.3. UV-vis spectrum result analysis

The diffuse reflectance UV-vis spectrum of an anatase TiO₂ sample is shown in Figure 4.8a. A bandgap of 3.2 eV was calculated by extrapolation of the absorption edge onto the energy axis [30,31]. These data were fitted for the indirect bandgap transition using $\alpha^{1/2}$ versus E_{phot} as shown in Figure 4.8b, where α is the absorption coefficient and E_{phot} is the photon energy. $E_{\text{phot}} = (1239/\lambda)$

eV and λ is the wavelength of the photon in nanometers. The bandgap E_g corresponds to the absorption energy as the value of E_{phot} extrapolated to $\alpha=0$. The indirect bandgap transition provided a good fit with the extrapolation yielding an E_g of 3.2 eV (Figure 4.8b). Commercial anatase TiO_2 samples are noted to provide indirect bandgap transitions, which is in good agreement with literature reports [32-34]. And the indirect transition of anatase TiO_2 leads to the lifetime of photogenerated electrons and holes longer than that of rutile phase TiO_2 [32].

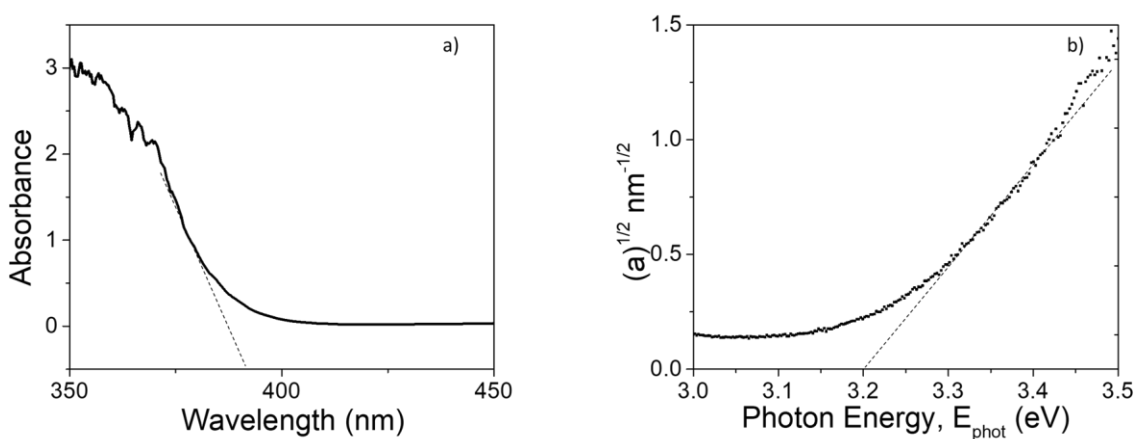


Figure 4.8. a) Diffused UV absorption spectra of commercial anatase TiO_2 ; b) Plot of $\alpha^{1/2}$ versus E_{phot} for indirect transition. Bandgap E_g is obtained by extrapolation to $\alpha=0$.

4.4.4. In situ FTIR analysis

The results of *in situ* FTIR analyses, as explained in section 4.2.6, are shown in Figure 4.9. Multiple sharp peaks were observed between 1000 and 2000 cm^{-1} . Sharp bands at 1160 cm^{-1} , 1560 cm^{-1} , and 1620 cm^{-1} of the non-UV treated TiO_2 sample correspond to the in plane bending vibrations of $(-\text{CH}_3)$, stretching vibrations of carbonyl groups ($\text{C}=\text{O}$), and bending vibrations of chemisorbed H_2O , respectively (see Table 4.2) [35-38]. After UV irradiation, the peak intensities at these three wavenumbers were significantly reduced, corresponding to the desorption, conversion and consumption of the adsorbed water and carbon containing species.

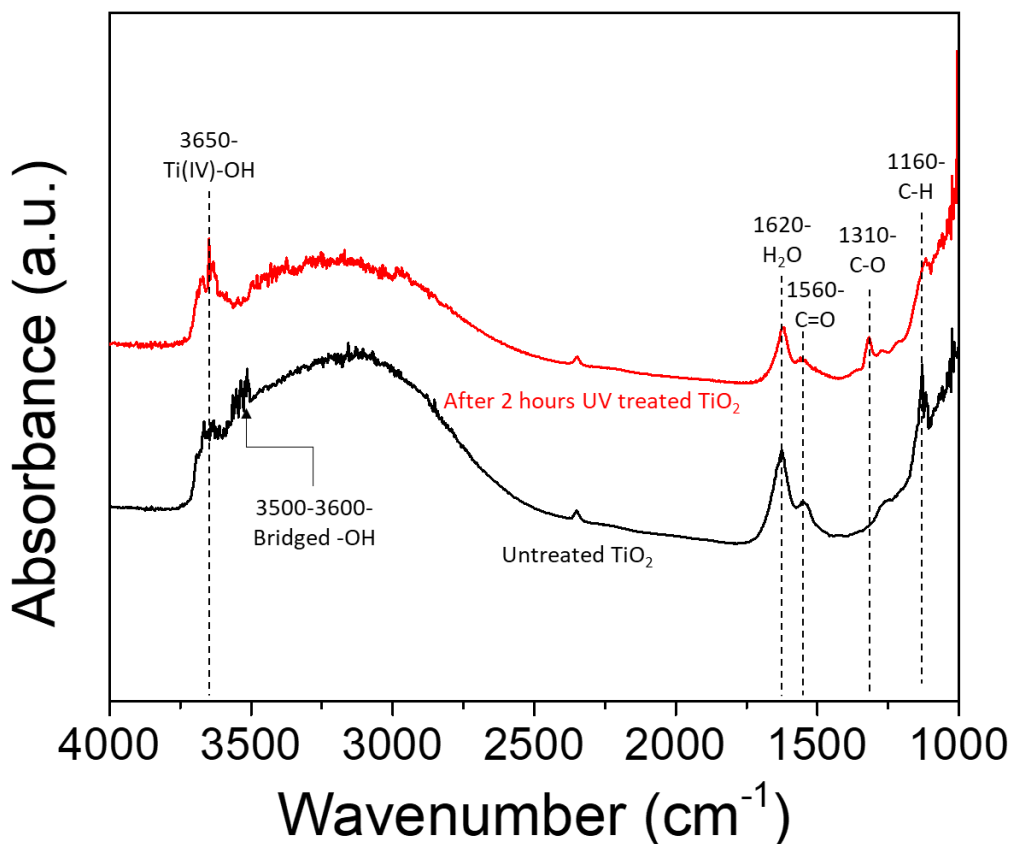


Figure 4.9. In situ FTIR spectra of untreated TiO₂ and after 2 hours UV treated TiO₂

The band at 1310 cm⁻¹ was enlarged after UV irradiation treatment, which indicates the formation of C-O containing species [35-38]. Meanwhile, in the 3000 to 4000 cm⁻¹ range, complex and sharp peaks were observed before and after UV treatment, indicating the stretching vibrations of surface hydroxyl groups and molecularly adsorbed water. The stretching vibrations of bridged hydroxyls (-OH) at 3500-3600 cm⁻¹ disappeared after UV irradiation while the stretching vibration of isolated surface hydroxyl groups (Ti(IV)-OH) at 3650 cm⁻¹ were present after UV irradiation [36,37,39,40]. The spectral change within the 3500 to 3700 cm⁻¹ range showed a significant conversion of bridged hydroxyls (-OH) to isolated hydroxyls (Ti(IV)-OH). Based on the above observations, a potential reaction mechanism can be proposed where UV

irradiation initiated a photocatalytic oxidation reaction between adsorbed water and bridged hydroxyl species with hydrocarbons to form C-O bonds containing surface species and isolated hydroxyl species. The summary of IR peaks and their assignments for anatase TiO₂ samples are listed in Table 4.2.

Table 4.2. IR peaks and their respected assignments for anatase TiO₂

Wavenumber (cm ⁻¹)	Assignments	Reference
1160	Bending vibration in-plane of C-H	[45], [47]
1310	Stretching vibration of C-O	[46], [47], [48]
1560	Stretching vibration of O=C-O	[45],[46]
1620	Bending vibration of chemisorbed H ₂ O	[45],[46],[47],[48]
3500-3600	Stretching vibration of bridged –OH	[46],[47],[49]
3650,	Stretching vibration of isolated Ti(IV)-OH	[46],[47],[49],[50]

4.4.5. XPS analyses

4.4.5.1. XPS analyses of decomposition of carbon contaminants

Survey spectra were collected as explained in section 4.2.7 on non-UV treated specimens and after 120-minutes of UV irradiation as shown in Figure 4.10a. The survey spectra show only titanium, oxygen, and carbon present on the surface, hydrogen is not directly visible. The origin of carbon is due to strong adsorption of a contaminant layer. According to the survey spectra, a significant decrease of C 1s and O 1s peak intensities was observed after UV exposure, indicating a decomposition of carbon species and consumption of oxygen species. A significant

drop in C 1s peak intensity and a relatively smaller decrease of the O 1s peak intensity was qualitatively observed.

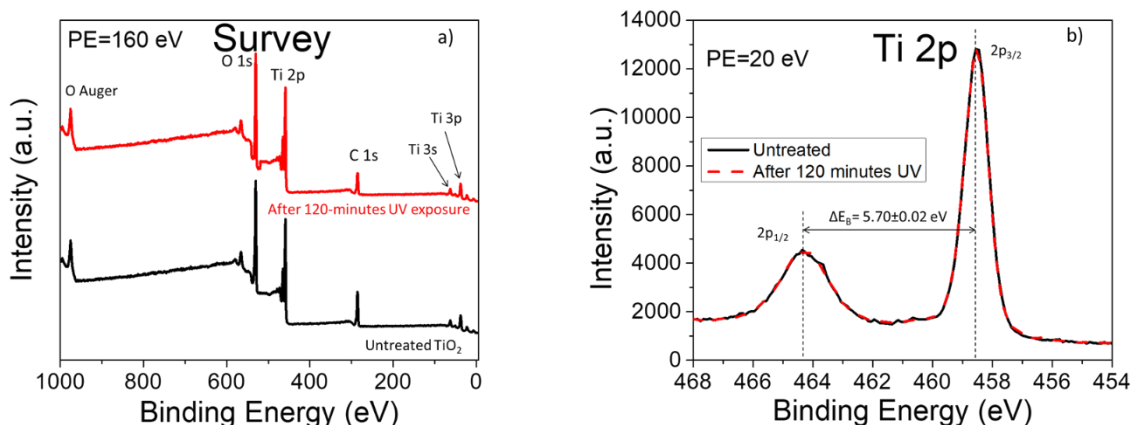


Figure 4.10 In situ photoelectron spectra of a) survey of untreated anatase TiO_2 and after 120-minutes UV irradiated TiO_2 ; b) Ti 2p of untreated anatase TiO_2 and after 120-minutes UV irradiated TiO_2

Care must be taken when looking at these raw decreases relative to the inelastic mean free paths of the corresponding photoelectrons while considering the large amount of oxygen that is resident in the sample at all depths and the preferential location of carbon nearer to the surface. Eight series of XPS measurements were performed and showed virtually no change in the Ti 2p spectra. For example, Figure 4.10b shows the Ti 2p spectra from one of the two experiments performed at 3.0 mW/cm^2 UV irradiation and there is no observable change between the non-UV treated TiO_2 sample and the 120-minute UV treated sample. The binding energies and FWHM of the Ti $2p_{3/2}$ peaks were measured after surface charging corrections to be at $458.48 \pm 0.02 \text{ eV}$ and $0.97 \pm 0.02 \text{ eV}$, respectively, and the corresponding binding energies and FWHM of the Ti $2p_{1/2}$ peaks were measured at $464.18 \pm 0.02 \text{ eV}$ and $1.91 \pm 0.03 \text{ eV}$, respectively. The binding energies,

FWHM, and the separation between the two peaks at 5.70 ± 0.02 eV was close to reported literature values [14,41,42]. No Ti^{3+} species or other spectral features were observed.

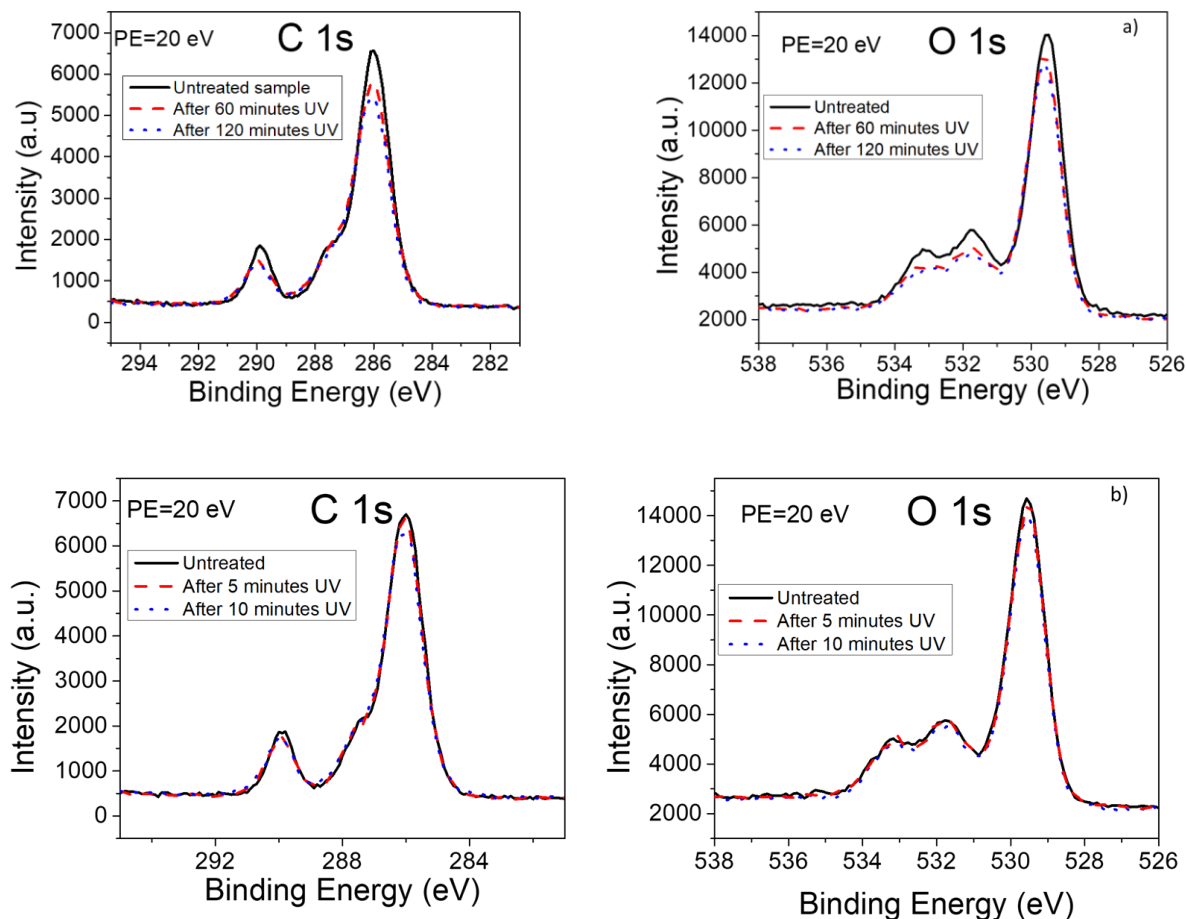


Figure 4.11. High resolution C 1s and O 1s XPS spectra of a) untreated TiO_2 , after 60-minutes, and after 120-minutes UV treated TiO_2 ; b) untreated TiO_2 , after 5-minutes, and after 10-minutes UV treated TiO_2 at UV intensity of 3.0 mW/cm^2 .

Figure 4.11a displays the high-resolution C 1s spectral comparison of the non-UV treated TiO_2 sample, and the same sample after 60-minutes and 120-minutes of UV irradiation at 3.0 mW/cm^2 . A significant intensity decrease of carbon species was observed in the UV treated samples. Likewise, Figure 4.11b shows the comparison of the corresponding C 1s spectra of the

non-UV treated TiO₂ sample and the same sample after only 5-minutes and 10-minutes of UV irradiation at 3.0 mW/cm². Even at short UV exposure times, the decrease in the C 1s peak was still observed.

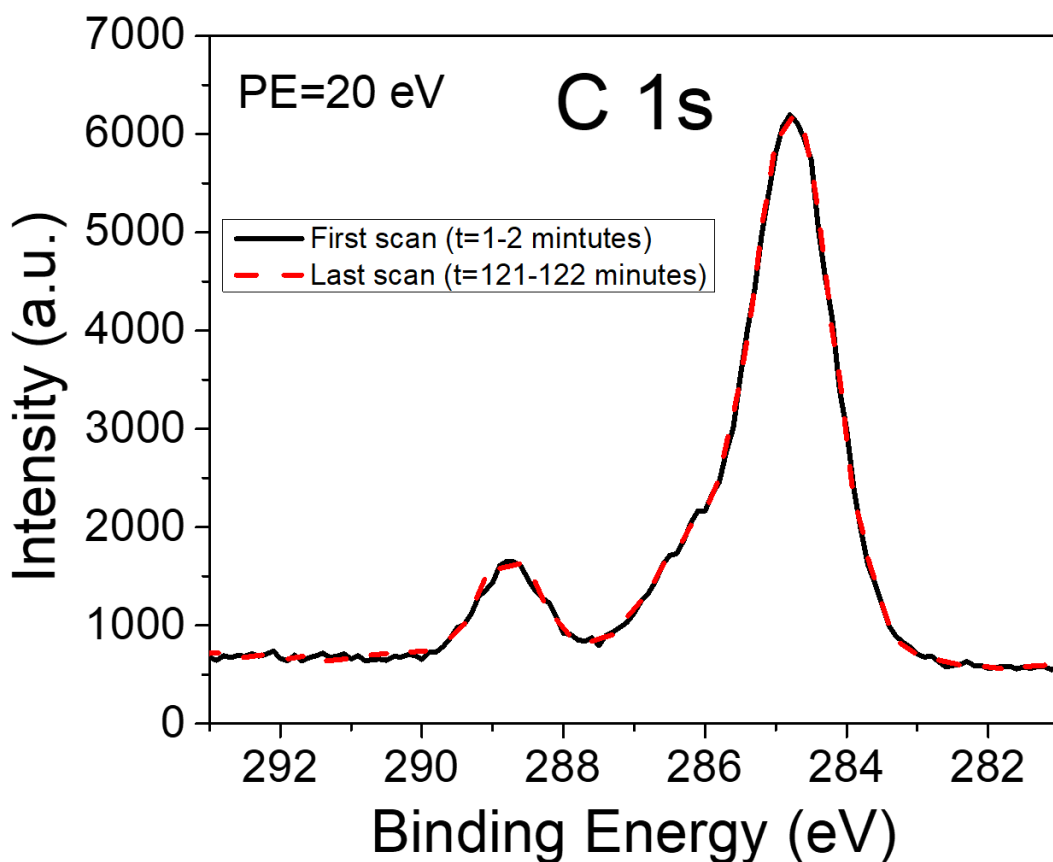


Figure 4.12. High-resolution C 1s XPS spectra of TiO₂ dark reference spot at the beginning and the end of the experiment.

Figure 4.11a displays the high-resolution C 1s spectral comparison of the non-UV treated TiO₂ sample, and the same sample after 60-minutes and 120-minutes of UV irradiation at 3.0 mW/cm². A significant intensity decrease of carbon species was observed in the UV treated samples. Likewise, Figure 4.11b shows the comparison of the corresponding C 1s spectra of the non-UV treated TiO₂ sample and the same sample after only 5-minutes and 10-minutes of UV

irradiation at 3.0 mW/cm^2 . Even at short UV exposure times, the decrease in the C 1s peak was still observed.

In order to analyze the composition changes, a comprehensive and detailed deconvolution of the photoelectron peaks was carried out. An example of the deconvoluted C 1s spectrum of a TiO_2 sample is shown in Figure 4.13a, where the hydrocarbon (C-C, C-H etc.) peak was constrained at 284.8 eV after surface charging correction, the FWHM of this peak for all the non-UV treated samples was held at $1.32 \pm 0.05 \text{ eV}$. The peaks at $288.75 \pm 0.02 \text{ eV}$ (with FWHM of $1.05 \pm 0.05 \text{ eV}$) and $286.30 \pm 0.02 \text{ eV}$ (with FWHM of $1.25 \pm 0.05 \text{ eV}$) were attributed to carboxyl (O=C-O etc.) and carbon-oxygen bond (C-O etc.) containing species, respectively. The peak binding energy positions and FWHM of the corresponding species agree with literature values [42-44]. As observed in Figure 4.11a and b, the peak intensity of C-O species did not change, which means UV irradiation has no effect on these species. But a significant intensity decreases of C-H and O=C-O containing species was observed for all the reaction cases. Since the initial hydrocarbon contamination level of the different specimens was slightly different, to better compare the change by UV irradiation at different intensities and exposure time, the ratios of the peak intensities of the different carbon species over the peak intensities of the corresponding titanium in the sample were calculated and the results are shown in Figure 4.15. The same normalization procedure was applied for the peak intensities of oxygen, shown in Figure 4.20. The variation of the ratios with respect to the UV irradiation levels is shown in Figure 4.16a. When compared with the deconvoluted spectral results of the dark reference spot, UV irradiation provided a higher decomposition rate for hydrocarbon and carboxylate species at higher UV irradiation intensities and exposure lengths. Figure 4.15 and Figure 4.16a clearly show that continuous exposure to UV irradiation generates a continuous loss of hydrocarbon and carboxylate species

on the TiO_2 surface, but at different rates depending upon intensity. It also reveals that the initial carbon contamination levels did not affect the overall decomposition rates of these species (Figure 4.14 and Figure 4.16). Figure 4.14b shows the same experiment conducted on 4 different specimens of the same TiO_2 material. These TiO_2 pellets were prepared at the same time and put into the XPS simultaneously to create near identical initial surface carbon levels. Figure 4.14b showed similar trends as the current experiment where the initial carbon concentrations of the TiO_2 pellets were different. At the same UV exposure time, higher irradiation intensities caused more loss of hydrocarbon and carboxylate species peak intensities. The loss of carbon and oxygen peak intensities suggests that UV catalyzed this reaction along with the desorption of carbon and oxygen containing species into the gas phase. After 30 to 60 minutes of UV exposure, the rates of decomposition slowed significantly, presumably due to the depletion of adsorbed water and to some degree surface carbon. For high surface area samples care must be exercised in appreciating that the movement of photo-desorbing water or reacting hydrocarbons from the sample can be occurring over a much larger depth into the specimen than that which is directly observable via XPS. UV illumination within a UHV system is known to create a reactive environment and has often been used during bakeouts to promote photodesorption of water from the walls of the chamber [45,46].

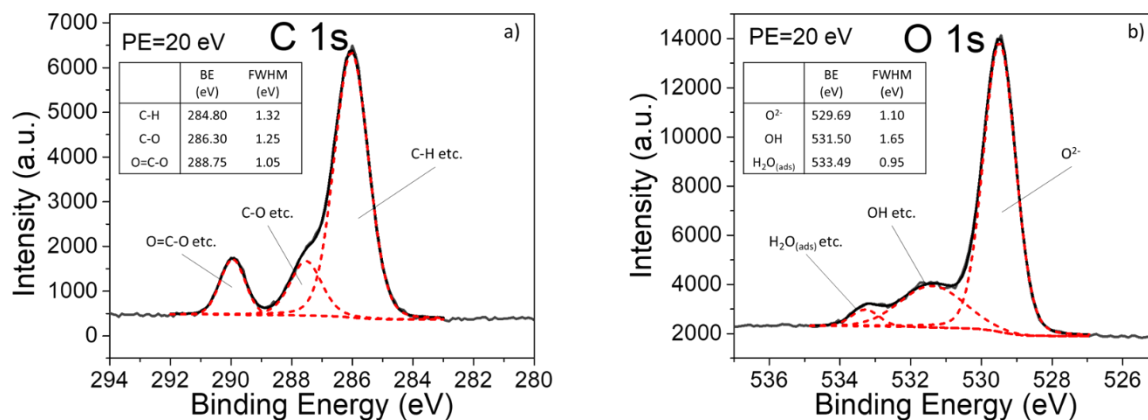


Figure 4.13. Deconvoluted as-measured a) C 1s and b) O 1s XPS spectra of TiO₂ sample.

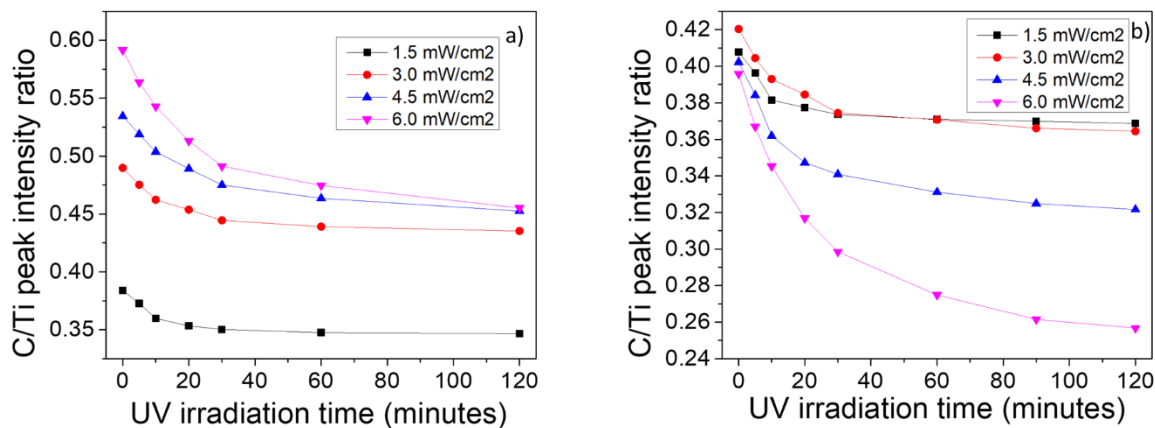


Figure 4.14. C/Ti peak intensity changes at different UV intensities for TiO₂ pellets with a) different initial carbon concentrations, b) close initial carbon concentrations.

When compared with the deconvoluted spectral results of the dark reference spot, UV irradiation provided a higher decomposition rate for hydrocarbon and carboxylate species at higher UV irradiation intensities and exposure lengths. Figure 4.11 and Figure 4.15a clearly show that continuous exposure to UV irradiation generates a continuous loss of hydrocarbon and carboxylate species on the TiO₂ surface, but at different rates depending upon intensity. It also reveals that the initial carbon contamination levels did not affect the overall decomposition rates

of these species (Figure 4.14 and Figure 4.16). Figure 4.14b shows the same experiment conducted on 4 different specimens of the same TiO₂ material. These TiO₂ pellets were prepared at the same time and put into the XPS simultaneously to create near identical initial surface carbon levels. Figure 4.16b showed similar trends as the current experiment where the initial carbon concentrations of the TiO₂ pellets were different. At the same UV exposure time, higher irradiation intensities caused more loss of hydrocarbon and carboxylate species peak intensities. The loss of carbon and oxygen peak intensities suggests that UV catalyzed this reaction along with the desorption of carbon and oxygen containing species into the gas phase. After 30 to 60 minutes of UV exposure, the rates of decomposition slowed significantly, presumably due to the depletion of adsorbed water and to some degree surface carbon. For high surface area samples care must be exercised in appreciating that the movement of photo-desorbing water or reacting hydrocarbons from the sample can be occurring over a much larger depth into the specimen than that which is directly observable via XPS. UV illumination within a UHV system is known to create a reactive environment and has often been used during bakeouts to promote photodesorption of water from the walls of the chamber [45,46].

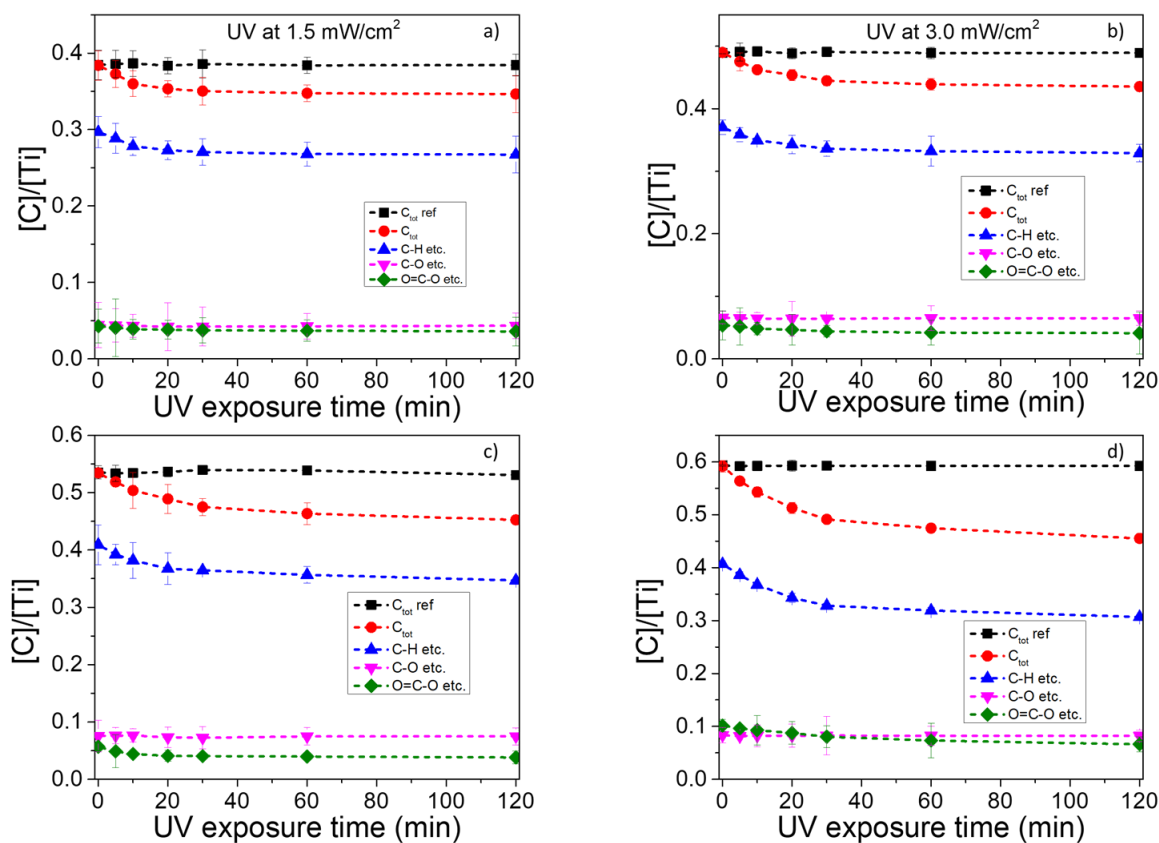


Figure 4.15. [C]/[Ti] peak intensity ratio changes in terms of UV exposure time a) at 1.5 mW/cm²; b) at 3.0 mW/cm²; c) at 4.5 mW/cm²; and d) at 6.0 mW/cm².

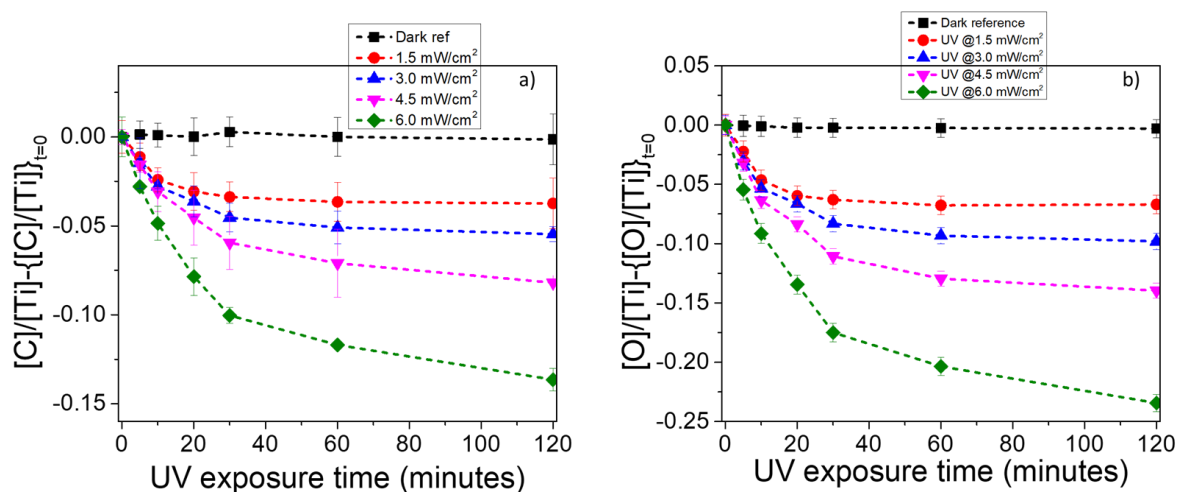


Figure 4.16. Peak intensity ratio changes caused by UV at different intensities in terms of UV exposure time: a) $[C]/[Ti] - \{[C]/[Ti]\}_{t=0}$; and b) $[O]/[Ti] - \{[O]/[Ti]\}_{t=0}$.

4.4.5.2. XPS analysis of Oxygen species

Figure 4.11a shows the corresponding high-resolution O 1s spectra of a non-UV treated TiO₂ sample, and the same sample after 60-minutes and 120-minutes of UV irradiation at 3.0 mW/cm². The O 1s spectra show a significant peak intensity decrease after UV irradiation when compared with the dark reference spot seen in Figure 4.17. Similar peak intensity decreases were also observed for shorter UV exposure times as shown in Figure 4.11b.

Figure 4.13b shows an example of the deconvoluted O 1s spectrum of a TiO₂ sample in terms of a three-component deconvolution. The O 1s peak at a binding energy of 529.69±0.02 eV (FWHM was 1.10±0.05 eV) was assigned to lattice oxygen (O²⁻) in TiO₂, the O 1s peak at a binding energy of 531.50±0.02 eV (FWHM of 1.65±0.05 eV) was identified as some combination of OH, C-O or O⁻, and finally the O 1s peak at a binding energy of 533.49±0.02 eV (FWHM was 0.95±0.05 eV) was assigned to adsorbed H₂O and/or C=O. These results and assignments appeared to be in good agreement with literature values [47-51].

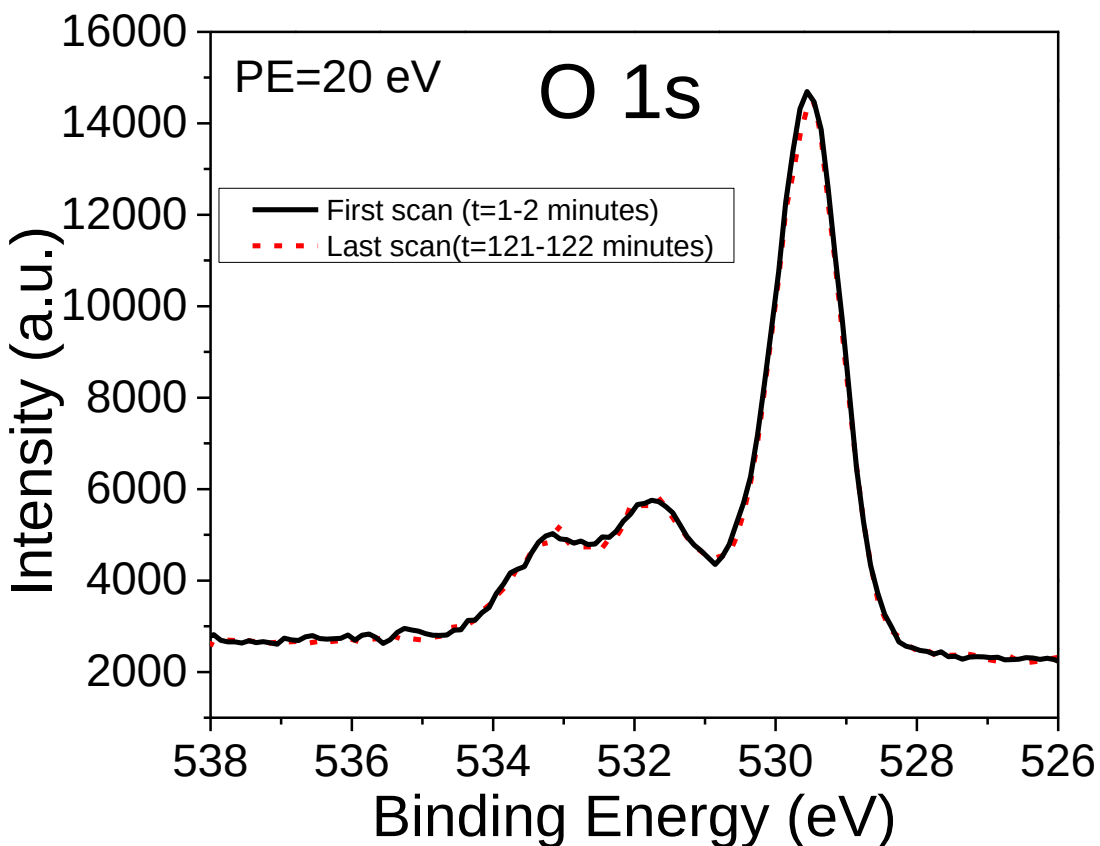


Figure 4.17. High-resolution O 1s XPS spectra of TiO₂ dark reference spot at the beginning and the end of the experiment.

In order to identify and quantify the amount of adsorbed oxygen species on anatase TiO₂, one non-UV treated TiO₂ specimen was heated from 25 °C to 100 °C and then 400 °C in UHV within the analytical chamber of the XPS. Figure 4.18a shows the O 1s spectrum of anatase TiO₂ at 25 °C and after heating to 100 °C, providing a significant peak intensity loss of adsorbed H₂O and adsorbed OH⁻. These results agree with those of FTIR (Figure 4.9) while the corresponding C 1s spectra (Figure 4.18b) do not display any significant change over this thermal annealing range.

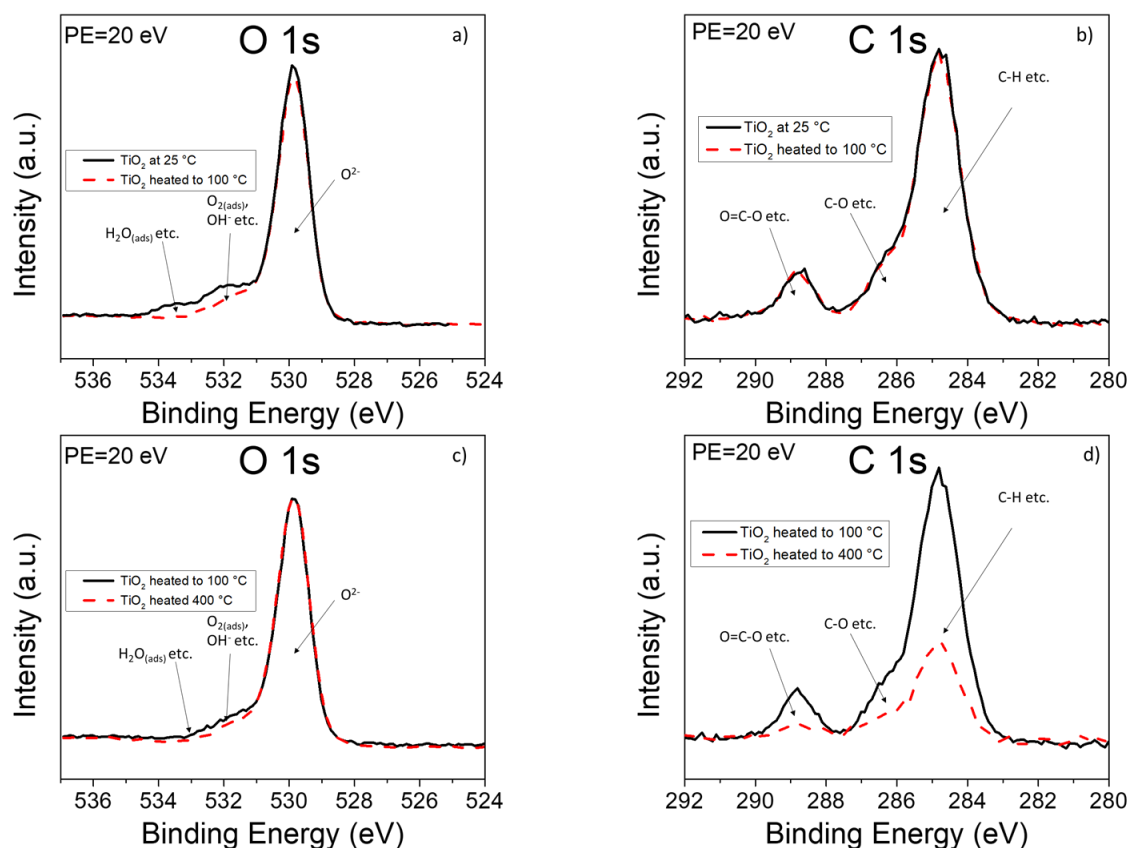


Figure 4.18. High-resolution XPS spectra of anatase TiO_2 sample a) O 1s at 25 °C and 100 °C, b) C 1s at 25 °C and 100 °C, c) O 1s at 100 °C and 400 °C, d) C 1s at 100 °C and 400 °C.

After the sample was heated to 100 °C for 2 hours, UV irradiation did not make any significant change on the resulting C 1s XPS spectra regardless of what fluence or UV intensity was applied (Figure 4.19). This result shows that adsorbed oxygen species (i.e., adsorbed $\text{H}_2\text{O}/\text{OH}^-$) were key reactants in the photocatalytic decomposition of carbon contaminants under these starved oxygen conditions. When the sample was further heated to 400 °C under UHV conditions, a significant intensity loss of carbon was also observed, as shown in Figure 4.19d. These results indicate a desorption/decomposition of carbon contaminants from the surface. The corresponding spectra change of O 1s displayed in Figure 4.19c show only a small decrease in

adsorbed H_2O and OH^- from 100 °C to 400 °C, indicating that most of the adsorbed oxygen species were already removed after annealing at 100 °C.

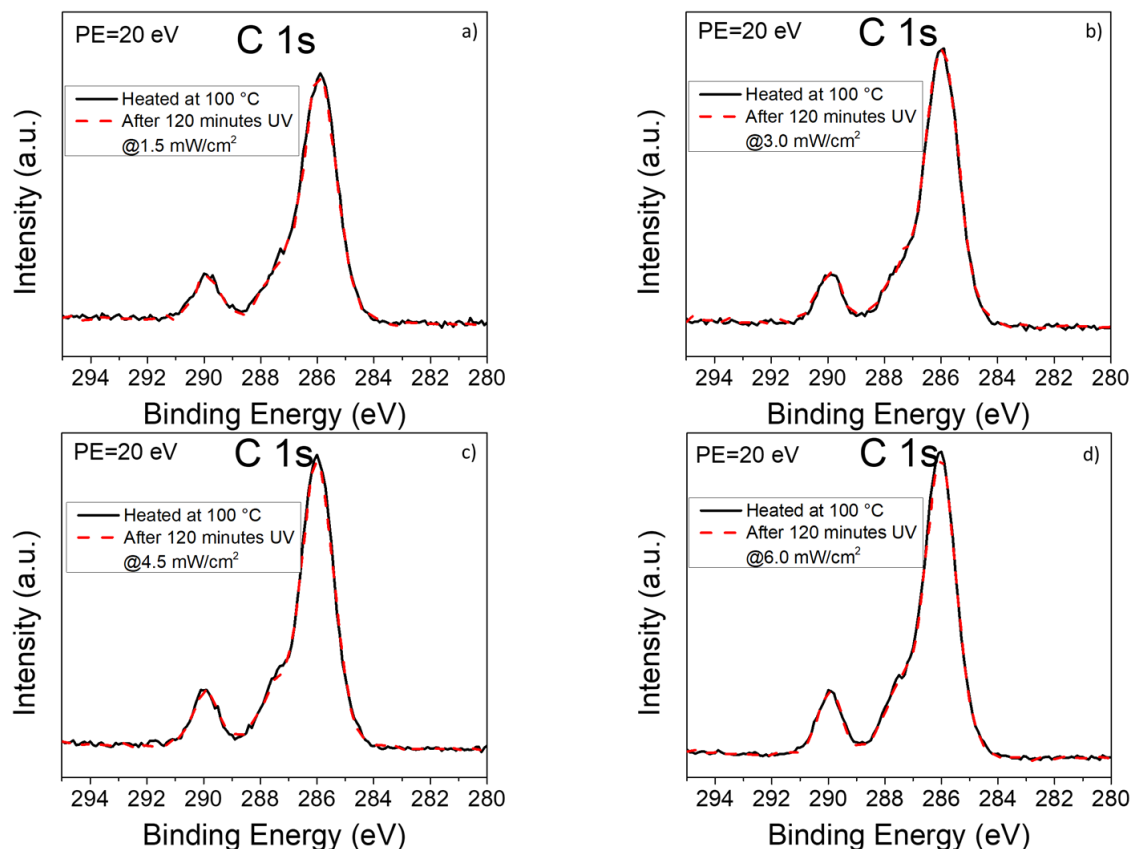


Figure 4.19. High-resolution C 1s XPS spectra of anatase TiO_2 sample after heated at 100 °C and after 120 minutes UV irradiation at a) 1.5 mW/cm^2 , b) 3.0 mW/cm^2 , c) 4.5 mW/cm^2 , d) 6.0 mW/cm^2 under UHV condition.

The ratios between the peak intensities of the oxygen species and the peak intensity of titanium in terms of UV exposure time and intensity are shown in Figure 4.20a-d. The total O 1s peak intensity and peak intensity of each component decrease with UV exposure time. However, the OH peak intensity showed a slight increase in the first 5-10 minutes of UV exposure, which indicates that OH species were generated at that stage of the experiment. Further UV irradiation depleted available reactants like OH radicals. The peak intensities of O^{2-} and $\text{H}_2\text{O}_{(\text{ads})}$ decreased throughout the experiments. Based on the above observations and in agreement with literature

[14,18-19], a potential reaction mechanism would consist of the photocatalytic reaction of one adsorbed water/oxygen species with one lattice oxygen to produce two surface hydroxyl species which would further interact with hydrocarbon and carboxylate species.

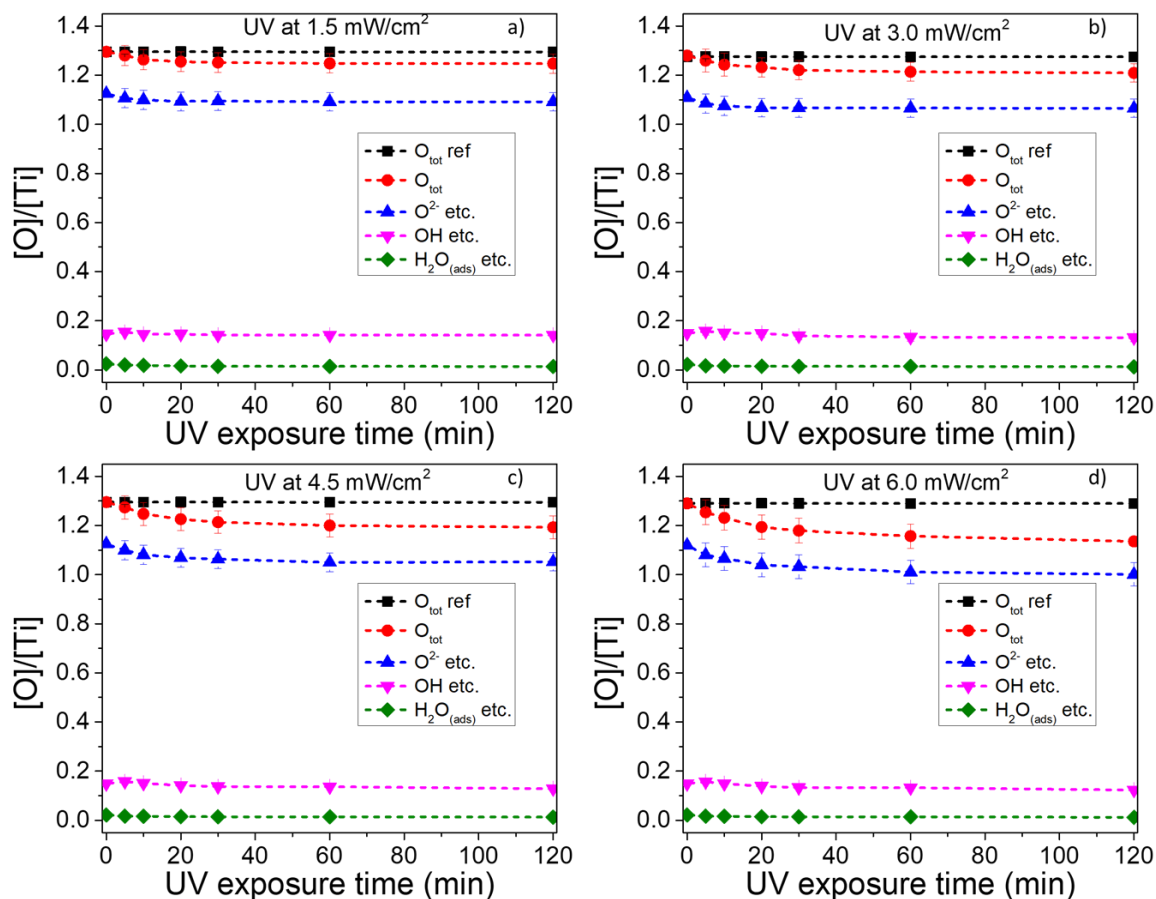


Figure 4.20. [O]/[Ti] peak intensity ratio changes in terms of UV exposure time a) at 1.5 mW/cm²; b) at 3.0 mW/cm²; c) at 4.5 mW/cm²; and d) at 6.0 mW/cm².

4.4.5.2 XPS quantitative analysis

The atomic ratios between carbon species and titanium can be derived from the first principles of photoelectron peak intensities [14,52]:

$$I = I_0 n \sigma \lambda(\varepsilon) D(\varepsilon) \int_0^t e^{-\frac{t}{\lambda}} dt \quad (1)$$

For oxygen and titanium species, the photoelectron peak intensity $I = I_0 n \sigma \lambda(\varepsilon) D(\varepsilon) \int_0^\infty e^{-\frac{t}{\lambda}} dt$, and for carbon species, the photoelectron peak intensity is $I = I_0 n \sigma \lambda(\varepsilon) D(\varepsilon) \int_0^d e^{-\frac{t}{\lambda}} dt$, where d is the diameter of one monolayer.

$$\frac{c(C)}{c(Ti)} = \frac{I(C) \sigma(C) \lambda(\varepsilon C) D(\varepsilon C) \int_0^d e^{-\frac{t}{\lambda}} dt}{I(Ti) \sigma(Ti) \lambda(\varepsilon Ti) D(\varepsilon Ti) \int_0^\infty e^{-\frac{t}{\lambda}} dt} \quad (2)$$

$$\frac{c(O)}{c(Ti)} = \frac{I(O) \sigma(O) \lambda(\varepsilon O) D(\varepsilon O) \int_0^\infty e^{-\frac{t}{\lambda}} dt}{I(Ti) \sigma(Ti) \lambda(\varepsilon Ti) D(\varepsilon Ti) \int_0^\infty e^{-\frac{t}{\lambda}} dt} \quad (3)$$

Where I_0 is X-ray flux, c is atomic concentration (atoms/nm²), σ is photoelectron cross-section, I_{Ti} is the XPS peak intensity (peak area), $\lambda(\varepsilon)$ is mean free path of energy(ε), $D(\varepsilon)$ is fraction of electrons detected by the analyzer, t is the sample depth from where electrons are ejected.

From equations (2) and (3), the ratios of atomic concentrations of carbon and oxygen containing species over Ti^{4+} are calculated for the non-UV treated sample in Table 4.3. In the current study, for the non-UV treated commercial anatase TiO_2 samples at 25 °C, the atomic ratios of O^{2-}/Ti^{4+} and O_{tot}/Ti_{tot} are equal to 2.09 ± 0.03 and 2.41 ± 0.02 , respectively, and these ratios are close to literature reported values [28,53]. After the sample was heated to 100 °C and 400 °C in UHV, the atomic ratios of O_{tot}/Ti_{tot} were 2.22 and 2.19, respectively. These decreases were attributed to the desorption of adsorbed H_2O and a loss of OH, both of which could be involved in the UV induced photocatalytic reaction. After annealing at 400 °C under UHV conditions, adsorbed H_2O and OH are diminished and the atomic ratios between adsorbed H_2O and OH and Ti_{tot} are 0.05 and 0.18, respectively (see Table 4.3). The atomic ratios of C_{tot}/Ti_{tot} were slightly different for the various specimens due to variations in specimen storage times and initial carbon contamination levels as noted earlier.

Table 4.3 Atomic ratio of carbon and oxygen species of untreated TiO₂ sample at different temperatures.

Temperature (°C)	Atomic ratio c(i)/c(Ti _{tot})							
	C-H	C-O	O=C-O	Total	O ²⁻	OH etc.	H ₂ O _(ads)	Total
	etc.	etc.	etc.	C			etc.	O
25	1.337	0.200	0.193	1.730	2.110	0.274	0.046	2.430
100	1.334	0.197	0.192	1.722	2.100	0.109	0.011	2.220
400	0.476	0.093	0.053	0.622	2.091	0.096	0.000	2.187
Desorbed from 25 °C to 400 °C	0.861	0.107	0.140	1.108	0.019	0.179	0.046	0.244

4.4.6 Quantum efficiency analysis and potential reaction mechanisms

Based on the nature of the anatase TiO₂ material, the number of Ti atoms per nm³ based on 1 g of TiO₂ can be determined by the following equation [14]:

$$N(\text{Ti}) = \frac{N_A \cdot n(\text{Ti})}{V(\text{TiO}_2)} \quad (4)$$

Where N(Ti) is the number of Ti atoms per nm³, N_A is the Avogadro constant (atoms/mol), n(Ti) is the mole of Ti (mol), and V(TiO₂) is the volume of 1g of anatase TiO₂ (nm³).

$$\text{The volume of 1 Ti atom} = \frac{1}{N(\text{Ti})}.$$

Assuming Ti atoms are spherical, the volume of 1 Ti atom = $\frac{4}{3} \times \pi \times r^3$. The radius of Ti atom can be calculated. The area of 1 Ti atom = $\pi \times r^2$.

The number of Ti atoms/nm² = $\frac{1}{\pi r^2}$.

Similarly, the number of species i atoms per nm² can also be determined from the ratio of species i peak area to the Ti peak area with equations (2) and (3).

Table 4.4 Relative concentration of carbon species (atoms per nm²) at different UV exposure time under different UV irradiation intensities.

UV exposure time (mins)	1.5 mW/cm ²				3.0 mW/cm ²				4.5 mW/cm ²				6.0 mW/cm ²			
	C-H etc.	C-O etc.	O=C etc.	Total	C-H etc.	C-O etc.	O=C etc.	Total	C-H etc.	C-O etc.	O=C etc.	Total	C-H etc.	C-O etc.	O=C etc.	Total
0	11.90	1.78	1.72	15.40	14.85	2.65	2.15	19.65	16.19	2.99	2.25	21.43	16.31	3.34	4.07	23.72
5	11.57	1.75	1.63	14.95	14.38	2.60	2.08	19.06	15.66	3.04	2.11	20.80	15.48	3.27	3.85	22.60
10	11.16	1.73	1.56	14.43	14.01	2.59	1.94	18.54	15.19	3.05	1.96	20.20	14.74	3.30	3.73	21.77
20	10.95	1.69	1.53	14.17	13.75	2.58	1.87	18.20	14.74	3.00	1.87	19.61	13.75	3.31	3.51	20.57
30	10.85	1.70	1.50	14.05	13.48	2.58	1.77	17.83	14.38	2.99	1.67	19.04	13.16	3.31	3.23	19.69
60	10.75	1.71	1.48	13.94	13.32	2.61	1.68	17.61	14.07	2.95	1.57	18.58	12.79	3.30	2.94	19.03
120	10.72	1.74	1.44	13.90	13.20	2.61	1.65	17.46	13.71	2.97	1.47	18.14	12.30	3.30	2.65	18.25

The number of the carbon and oxygen species per nm² at different UV irradiation intensities and exposure times are summarized in Table 4.4 and Table 4.5, respectively. In all the reaction cases, UV irradiation caused a loss of hydrocarbon and carboxylate species, adsorbed water, and hydroxyl species, and to a lesser extent lattice oxygen. The ratio of carbon decomposition with respect to oxygen consumption $\Delta N(C_{tot})/\Delta N(O_{tot})$ at the same operating conditions is given in Table 4.6. During the same UV exposure times, the experiments showed a similar value which varied from 0.53 to 0.65 with an average value of 0.59 and a standard deviation of 0.11. A lower carbon to oxygen reaction ratio was obtained during the first 10-20 minutes of UV irradiation, when there was a higher concentration of oxygen species on the surface, and the reaction product was most probably CO₂. After 20 minutes of UV irradiation, there was less oxygen on the

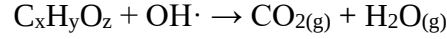
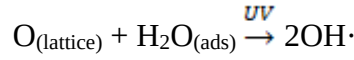
surface, and the reaction products could possibly be a mixture of CO₂ and CO [4]. These results generally show a high propensity toward hydrocarbon decomposition from the surface using UV.

Table 4.5. Relative concentration of oxygen species (atoms per nm²) at different UV exposure time under different UV irradiation intensities.

UV exposure time (mins)	1.5 mW/cm ²				3.0 mW/cm ²				4.5 mW/cm ²				6.0 mW/cm ²			
	O ²⁻	OH etc.	H ₂ O _(a) etc.	Total	O ²⁻	OH etc.	H ₂ O _(a) etc.	Total	O ²⁻	OH etc.	H ₂ O _(a) etc.	Total	O ²⁻	OH etc.	H ₂ O _(a) etc.	Total
0	18.78	2.44	0.41	21.63	18.51	2.49	0.37	21.37	18.78	2.49	0.36	21.63	18.69	2.49	0.36	21.54
5	18.47	2.58	0.34	21.38	18.12	2.63	0.28	21.03	18.36	2.63	0.28	21.27	18.04	2.62	0.28	20.94
10	18.36	2.43	0.31	21.1	17.96	2.52	0.27	20.75	18.05	2.51	0.27	20.83	17.80	2.49	0.27	20.56
20	18.26	2.44	0.27	20.96	17.83	2.49	0.25	20.57	17.85	2.37	0.25	20.47	17.37	2.32	0.24	19.93
30	18.28	2.37	0.25	20.9	17.82	2.32	0.24	20.38	17.75	2.29	0.23	20.27	17.24	2.22	0.23	19.69
60	18.23	2.37	0.24	20.84	17.80	2.23	0.24	20.27	17.53	2.28	0.23	20.04	16.88	2.21	0.23	19.32
120	18.23	2.36	0.23	20.82	17.79	2.19	0.21	20.19	17.57	2.14	0.21	19.92	16.71	2.05	0.20	18.96

UV induced photocatalytic decomposition of hydrocarbons on anatase TiO₂ has been widely investigated over a range of conditions, with the formation and reaction of hydroxyl radicals (OH·) on the TiO₂ surface providing the mechanism. This reaction also possesses a high selectivity toward gaseous products [14,18,19]. Previous efforts in our laboratory observed a formation of hydroxyl species on anatase TiO₂ following UV irradiation as observed by both by XPS and FTIR measurements [12-14]. In the current study under oxygen starved and evacuated conditions, there was a slight increase in hydroxyl species during the early stages of UV irradiation and the formation of isolated hydroxyl groups (Ti(IV)-OH). We suspect that the loss of oxygen is due to one lattice oxygen and/or adsorbed O₂ reacting with one adsorbed water to form two additional hydroxyl species, with the hydroxyl species subsequently reacting with surface hydrocarbons and/or carboxylate species. After 30-60 minutes of UV exposure, the

reaction rates reduced significantly due to the depletion of adsorbed reactant species. Based on the above stoichiometric analysis, the reaction mechanism could be proposed as the following:



A quantum efficiency analysis for the reaction was conducted based on the loss of various species of surface carbon per incident (adsorbed) photon. The calculation was performed according to the following equation:

$$\eta = \frac{\Delta n(C_{tot})}{Hp,o} ; \eta t = \frac{\Delta n(C_{tot})}{Hp,ot} \quad (5)$$

$$Hp,ot = Hp,o \times e^{(-At)} \quad (6)$$

$$SCH = \frac{\Delta n(CH)}{\Delta n(C_{tot})} \quad (7)$$

Where η is the photon efficiency, ηt is the photon efficiency accounting for the photon adsorbed at surface monolayers of the sample where XPS could monitor, S_{CH} is the selectivity factor toward reaction of surface hydrocarbons, $\Delta n(CH)$ is the number of hydrocarbon species decomposed by UV photons per nm^2 , $\Delta n(C_{tot})$ is the total number of carbon species decomposed by UV per nm^2 , Hp,o is the number of photons hitting the sample surface per nm^2 , Hp,ot is the number of photons adsorbed at the sample surface monolayers where XPS could monitor per nm^2 , A is absorbance, and t is the depth of surface monolayers where XPS could monitor.

The results are summarized in Table 4.7. The highest photon efficiency is 5.6×10^{-4} at 5-10 minutes of 1.5 mW/cm^2 UV irradiation intensity for the overall carbon contaminant species. The limited number of surface reactant species in our studies could be the reason of the low initial photon reaction efficiency which decreases during the course of UV exposure (see Table 4.7).

Table 4.6 Ratio of $\Delta N(C_{\text{tot}})/\Delta N(O_{\text{tot}})$ caused by UV at different intensities and UV exposure time.

UV exposure time (mins)	$\Delta N(C_{\text{tot}})/\Delta N(O_{\text{tot}})$			
	1.5 mW/cm ²	3.0 mW/cm ²	4.5 mW/cm ²	6.0 mW/cm ²
0	0	0	0	0
0-5	0.57±0.03	0.53±0.05	0.54±0.04	0.58±0.06
5-10	0.56±0.05	0.60±0.03	0.59±0.05	0.56±0.04
10-20	0.59±0.04	0.60±0.02	0.53±0.06	0.63±0.03
20-30	0.57±0.04	0.58±0.05	0.60±0.03	0.64±0.04
30-60	0.62±0.02	0.60±0.04	0.65±0.04	0.63±0.05
60-120	0.59±0.06	0.62±0.03	0.60±0.02	0.64±0.05

Another factor influencing this low efficiency is the fact that carbon is concentrated on the surface of the specimen whereas the UV photons have a far greater penetration depth and only a small fraction of these photons will be absorbed at the surface. Higher photon efficiencies and reaction rates would be expected should the reaction be carried out in an oxygen or water rich environment [14,18,19]. The reaction selectivity towards photodecomposition of surface hydrocarbons at 284.8 eV binding energy (as opposed to other surface carbonaceous species) is 75%±5% of all the carbon species removed.

Table 4.7 Photon efficiencies (η), average photon efficiencies (η_{ave}) and selectivity of hydrocarbons ($S_{\text{C-H}}$) at different UV irradiation intensities.

UV exposure time (mins)	1.5 mW/cm ²			3.0 mW/cm ²			4.5 mW/cm ²			6.0 mW/cm ²		
	$\eta \times 10^{-4}$	η_t	S_{CH}	$\eta \times 10^{-4}$	η_t	S_{CH}	$\eta \times 10^{-4}$	η_t	S_{CH}	$\eta \times 10^{-4}$	η_t	S_{CH}
0-5	4.921	0.0164	0.73	3.219	0.0107	0.80	2.290	0.0076	0.84	3.064	0.0102	0.74
5-10	5.602	0.0187	0.79	2.878	0.0096	0.71	2.197	0.0073	0.78	2.259	0.0075	0.89
10-20	1.455	0.0049	0.81	0.929	0.0031	0.76	1.083	0.0036	0.76	1.640	0.0055	0.83
20-30	0.681	0.0023	0.83	0.990	0.0033	0.73	1.021	0.0034	0.63	1.207	0.0040	0.67
30-60	0.217	0.0007	0.91	0.217	0.0007	0.73	0.279	0.0009	0.67	0.310	0.0010	0.56
60-120	0.031	0.0001	0.75	0.062	0.0002	0.80	0.124	0.0004	0.82	0.186	0.0006	0.63

4.5 Conclusion

In the present study we qualitatively and quantitatively investigated the transient UV induced photocatalytic removal of surface hydrocarbon contaminants on anatase TiO₂ by FTIR and XPS under starved H₂O/O₂ conditions. Four UV intensities as various fluences and initial carbon contamination levels were investigated. The reaction dynamics were not observably affected by slightly different initial carbon contamination levels of the specimens. Quantitative analysis showed a 1:2 carbon to oxygen loss from the surface following reaction. Both FTIR spectra and deconvolution details from XPS showed that hydroxyl radicals were produced by UV induced reaction between adsorbed water and lattice oxygen. The hydroxyl radicals, as intermediates, reacted with hydrocarbons and carboxylates to form gaseous products, i.e., CO₂ at early stages of the reaction sequence and perhaps a CO₂ and CO mixture as reactive surface oxygen was depleted. There was a significant drop in the reaction rate after 30-60 minutes of UV exposure (corresponding to 102,000 photons/nm²) due to the consumption and/or desorption of adsorbed carbon and water/oxygen containing surface species. Quantum efficiencies were

estimated for each reaction case, and due to the limitation of available adsorbed oxygen-containing reactant species which are leaving the system, 1.5 mW/cm² of radiation intensity showed a slightly higher efficiency. The photon efficiency and reaction rates would be significantly improved under oxygen/water rich environments.

The current study provides valuable insights into the fundamental and transient photocatalytic transport and reaction mechanism between surface carbon contaminants on anatase TiO₂ and adsorbed water/oxygen species. *In situ* XPS measurements during UV irradiation provided a unique understanding of this reaction behavior with care being required when interpreting these data due to the preferential location of carbon within the XPS-observable surface and yet a greater level of adsorbed water and oxygen species within the interior surface area of the specimen that is transported to the surface via photodesorption and readsorptive migration. Future efforts from our laboratory will report on the microkinetic modeling of the various fundamental steps that occur during this transient and oxygen-limited photocatalytic transport-reaction process. The current study provides a clear indication that the UV irradiation intensity not only affects the carbon removal reaction rate but also the extent of that reaction as well. The latter is not surprising since higher photon intensities promote greater water desorption/transport from the deeper lying photon penetration depths of the specimen, and water/oxygen is shown to be a limiting reagent in the carbon removal reaction mechanism.

4.7 Reference

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Chapter 5 Observation of a stabilized Titanium hole species from in situ time dependent XPS characterization of 4wt% Ag/TiO₂

5.1 Abstract

An anomalous and unique time dependent spectral change and a color change of 4wt% Ag/TiO₂ sample were observed during XPS characterization, and no similar result was observed from neat TiO₂ sample. Previous efforts from our laboratory indicated that Ag(I)OH was highly dispersed on the surface defective sites of the high surface area TiO₂ support in 4wt% Ag/TiO₂ sample. In this study, for the first time a time-dependent observation of a stabilized chemical species of titanium at 1.5 eV binding energy higher than Ti⁴⁺ in TiO₂ was observed, and it is assigned to be the TiO₂^{+(hole)} species generated by X-ray photon on 4wt% Ag/TiO₂ sample and it was stabilized by hydroxyls under ultrahigh vacuum (UHV) conditions. The TiO₂^{+(hole)} species were generated and then relaxed by X-ray irradiation due to photon stimulated desorption of hydroxyls. It has been verified by means of sample mounting method, sample particle size, neutralizer, and X-ray induced Auger spectra and Auger parameters that the time dependent spectral change observed from XPS was caused by chemical reactions. Thermogravimetric analysis (TGA) shows up to 1.14 monolayers of H₂O/OH were adsorbed on 4wt% Ag/TiO₂ sample surface. The deconvolution details of the photoelectron peaks demonstrate the potential reaction stoichiometry of the reaction, where one Ag(I)OH was able to capture one electron and providing one free OH to stabilize one titanium hole species. The X-ray photon quantum efficiency analysis illustrates that one X-ray photon was able to create at least 17 TiO₂^{+(hole)} species, which indicates the hole carriers were transferred to the sample surface from the bulk. This paper provides breakthrough evidence and a novel prospective on TiO₂ photocatalysis reaction mechanism to pave a huge potential progress on TiO₂ photocatalysis in the nearly future.

Keyword: In-situ time dependent XPS, Photocatalysis, Titanium dioxide, Silver, Hydroxyls, X-ray irradiation

5.2 Introduction

Titanium dioxide (TiO_2) material has been investigated by scientists and researchers since the discovery of photo-catalytic water splitting by Fujishima and Honda [1]. According to their studies, TiO_2 material has a brilliant potential in photocatalysis. Since then, photocatalysis on TiO_2 material has been applied to different purposes such as photocatalytic degradation of pollutant [2-5], photocatalytic energy renewal [6-8], and energy storage [9,10]. However, for the past several decades, the progress was not satisfying. One of the greatest challenges is the fundamental processes of photo-catalytic reactions on TiO_2 material have not been well illustrated. To efficiently separate the photoelectrons and photo-holes on TiO_2 , a variety of methods such as doping transition metal ions on TiO_2 have been applied to TiO_2 photocatalysis and several hypotheses have been proposed regarding the reaction mechanism of TiO_2 photocatalysis [11-13], but the direct and clear evidence is still lacking.

Silver is an exceptional transition metal because of its unique photochemical properties. Among the chemical states of silver, Ag(I) usually exhibits the highest catalytic activity for various chemical reaction applications [14-17]. The deposition of Ag(I) on the surface of TiO_2 highly improved the photocatalytic efficiency through Schottky barrier conduction band electron trapping [14]. Nanocomposite thin film of $\text{Ag-TiO}_2/\text{Ag/a-TiO}_2$ was applied to the study of photocatalytic antibacterial activities under visible and solar light irradiations [15], and the photocatalyst was proved to be one of the effective and long-lasting antibacterial nanocomposite materials. AHMS Hussain et, al. [16,17] investigated the adsorptive desulfurization of hydrocarbon fuels over TiO_2 and Ag(I)/TiO_2 . Ag(I)/TiO_2 showed a supreme desulfurization

capacity over neat TiO_2 and it was attributed to the formation of additional surface hydroxyls associated by the Ag(I) on TiO_2 surface.

A variety of research efforts have shown adsorbed H_2O played an important role in TiO_2 photocatalysis. Wang et, al. [18] performed an XPS and UPS study on a high surface area anatase TiO_2 material, and the results showed there were a lot of surface defective sites on the TiO_2 surface. Their study also indicated H_2O was mainly adsorbed on the surface defective sites of anatase TiO_2 , re-oxidizing Ti^{3+} defective sites into Ti^{4+} with formation of Ti(IV)-OH . And the more the defective sites on TiO_2 surface, the more H_2O could be adsorbed. Liu et, al. [19] reported that their Atomic Force Microscopy (AFM) study showed UV irradiation on TiO_2 film caused desorption and re-adsorption of H_2O from the bulk to the surface. A ~ 30 nm water layer was formed on the surface after 90 minutes UV illumination. This H_2O layer is physically absorbed H_2O and it can be wiped off by UHV. And UV irradiation converted Ti-O-Ti into Ti-OH . Tan et, al. [20] conducted a low temperature Scanning Tunneling Microscopy (STM) at 80 K, and the results showed UV irradiation initiated the dissociation of H_2O through oxidation by photo-holes to form additional terminal (free) hydroxyls OH_t . These OH_t could be diffused and even desorbed from the surface. Previous research efforts [16,17,21-23] by our group have shown UV irradiation on high surface area anatase TiO_2 with adsorbed H_2O caused formation of additional surface hydroxides with conversion of adsorbed H_2O and lattice O^{2-} by means of XPS study. Our previous FTIR and XPS study also showed UV irradiation on high surface area anatase TiO_2 converted adsorbed H_2O and bridged OH into isolated OH.

Hydroxyl groups are formed by the highly reactive hydroxyl radicals as intermediates for TiO_2 photocatalysis [24,25]. Hajnalka Czili and Attila Horvath [24] investigated the applicability of coumarin for detecting and measuring hydroxyl radicals generated by photoexcitation of TiO_2

nanoparticles. They used silver ion as electron acceptor and reported the luminescence intensity increased with irradiation time until the deposition of silver on the surface of TiO_2 was completed which indicated the silver ions were able to hold and separate the photoelectrons and holes by means of converting hydroxyl radicals into hydroxides. Rafik Addou et, al. [25] studied the agglomeration of transition metal atoms on TiO_2 by means of scanning tunneling microscopy experiments and density functional theory (DFT) calculations. They illustrated the hydroxylated surface promoted the dispersion of transition metal ions, and thus improved the photocatalytic activity of the transition metal ion doped TiO_2 catalyst. Besides, hydroxyl groups are also widely applied to the single atom catalysis [26-28] due to their unique electrochemical properties to stabilize highly active species.

X-ray photoelectron spectroscopy (XPS) is a perfect instrument to study the surface properties of semiconductors [29,30]. XPS has already been widely applied to study the mechanisms of adsorption, desorption, and surface chemical reactions [29-32]. With the booming development of XPS technique, “in-situ” XPS technique has been carried out and applied to some fundamental mechanism studies [33-35]. Although it is commonly believed that XPS is a non-destructive surface characterization technique, recent studies [36-38] showed X-ray damages were observed on various metal oxide materials such as Au/TiO_2 , CeO_2 , and CuO . Kruse et, al. [36] reported X-ray irradiation effects on Au/TiO_2 material that X-ray irradiation caused charge transfer from oxygen vacancies to Au particles. Paparazzo et, al. [37] investigated the X-ray irradiation effect on CeO_2 , and the results showed long term X-ray irradiation caused partially reduction of CeO_2 to Ce_2O_3 . Iijima et, al. [38] studied the reduction of CuO during XPS analysis and developed a method to prevent the reduction by applying a bias boltage of -250 V. Usually, low flux of high energy X-ray photon irradiation has negligible effect on sample surface.

However, in our case, an anomalous time dependent spectral change was observed associated with a color change of the X-ray illuminated spot on 4wt% Ag/TiO₂ sample surface, which indicated the X-ray irradiation caused significant surface alternation on the sample.

The current study takes advantage of the in-situ time dependent XPS characterization technique, by tracking the chemical properties change with continuous X-ray irradiation to provide valuable and direct evidence of the mechanism of photo-induced chemical reactions on 4wt% Ag/TiO₂. Surface charging effect were examined by means of sample mounting methods, neutralizer effect, sample particle size effect, and Auger parameters. The results excluded the possibility that the XPS spectral change on 4wt% Ag/TiO₂ sample was caused by surface charging effect. By qualitatively analyzing the chemical species change and quantitatively calculating the atomic fraction change of each species, the reaction mechanism was indicated. Sample color change was measured as an indicator of the chemical state of Ag.

5.3 Experimental

5.3.1 Sample preparation

The sample preparation procedures have been reported elsewhere [22]. Typically, the as-received 3.2 mm TiO₂ pellets were crushed and sieved to 75 to 125 μm followed by drying in a convection oven at 110 °C for 24 hours. Silver was introduced by incipient wetness using Ag(I)NO₃ solution followed by drying in a convection oven at 110 °C for another 24 hours. Then the sample was calcined in flowing air for 2 hours at 450 °C followed by in-situ cooling in flowing air for another 2 hours. As a contrast, 4wt% HNO₃/TiO₂ sample was prepared by incipient wetness using HNO₃ solution followed by the same calcination and in-situ cooling procedure as 4wt% Ag/TiO₂ sample. Neat TiO₂ sample was prepared using the same calcination

and in-situ cooling method. Then the samples were directly loaded into XPS system for XPS characterization.

5.3.2 Textural property characterizations

5.3.2.1 BET measurement

Brunauer-Emmett-Teller (BET) surface areas of the 4wt% Ag/TiO₂ sample, neat TiO₂, and 4wt% HNO₃/TiO₂ were determined by N₂ adsorption at −196 °C using a NOVA 2200e surface area analyzer. The BJH desorption branch of the isotherm was used to calculate the pore size distribution on 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ samples. Before analysis, all samples were degassed at 400 °C for 5 h under a flow of helium.

5.3.2.2 XRD characterization

XRD characterizations for 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ were carried out in a Bruker D-8 X-ray diffractometer equipped with a CuK α (40 KV/40 mA) source. The XRD scan range was 20-90 degrees, and the scan speed was 0.1 s/step (~5.85 degrees/min).

5.3.2.3 Thermogravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) experiments were carried out to measure the relative amount of adsorbed H₂O. TGA measurement was performed on a TA Instrument TGA-Q500 instrument. Typically, powder samples were pretreated at 110 °C in a convection oven for 24 hours. For TGA measurements, thirty mg of the samples were heated from 25 °C to 700 °C at a rate of 20 °C/min followed by cooling from 700 °C to 100 °C at a rate of 25 °C/min in flowing N₂ at 40 cm³/min.

5.3.3 XPS analysis

5.3.3.1 XPS measurement

A Kratos Analytical Ltd. AXIS Ultra DLD (delay lines detector) X-ray photoelectron spectrometer (XPS) with a monochromatic Al K α X-ray source (1486.6 eV) was used for the XPS experiment. The end station of the XPS instrument consists of a fast entry load lock, a sample treatment chamber and a sample analysis chamber. Samples were evacuated at a background pressure of 4.0×10^{-10} torr for at least 80 hours. The X-ray spot size was about $300 \times 700 \mu\text{m}^2$, and the angle between the sample holder and the X-ray source was 35 degrees. Pass energy of 160 eV was used for the survey scans. Time dependent XPS characterization was conducted using pass energy of 20 eV to measure the high-resolution spectra of Ti 2p, O 1s, and C 1s, and Ag 3d narrow scans every 30 minutes for neat TiO₂, 4wt% HNO₃/TiO₂, and 4wt% Ag/TiO₂ samples. The X-ray source was left on until the end of the experiment. The overall resolution of the spectrometer in the current setting mode was 0.65 eV measured as a full width half max (FWHM) of the Ag 3d_{5/2} line. The spectrometer was calibrated by constraining Binding Energy of Au 4f_{7/2} at 84.0 eV.

The deconvolution of the photoelectron spectra was conducted using the public software package XPSPEAKS 4.1 using the same procedure as reported by literature [36,39,40]. After subtraction of the Shirley-type background, the spectra were decomposed into their components at suggested binding energies with mixed Gaussian-Lorentzian lines by a non-linear least squares curve-fitting method. The binding energies and full width half max (FWHM) of the peaks were recorded by the fitting results. Surface chemical composition calculations were derived by the deconvoluted peak areas and the atomic sensitivity factors provided by the standard XPS handbook.

5.3.3.2 Atomic fraction calculation methodology from XPS results

From first principles, the intensity of the photoelectron peak (peak area) is described by [23]:

$$I = I_0 n \sigma \lambda(\varepsilon) D(\varepsilon) \int_0^t e^{-t/\lambda} dt \quad (1)$$

Where I_0 : X-ray flux; N : Density of atoms; σ : Photoelectron cross-section; I : XPS peak intensity (peak area); $\lambda(\varepsilon)$: Mean free path of energy(ε); $D(\varepsilon)$: Fraction of electrons detected by the analyzer; t : The sampling depth.

With the peak intensities of each species from deconvolution results, the mole fraction of each species can be calculated by:

$$C(i) = \frac{n(i)}{\sum n(i)} = \frac{I(i) \sigma(i) \lambda(\varepsilon i) D(\varepsilon i) \int_0^t e^{-t/\lambda} dt}{\sum I(i) \sigma(i) \lambda(\varepsilon i) D(\varepsilon i) \int_0^t e^{-t/\lambda} dt} \quad (2)$$

To better evaluate the results, the atomic fraction of total titanium is used as a reference, and the atomic fraction ratios of different species over total titanium could be calculated by:

$$\frac{c(i)}{c(Ti)} = \frac{I(i) \sigma(i) \lambda(\varepsilon i) D(\varepsilon i) \int_0^\infty e^{-t/\lambda} dt}{I(Ti) \sigma(Ti) \lambda(\varepsilon Ti) D(\varepsilon Ti) \int_0^\infty e^{-t/\lambda} dt} \quad (3)$$

Where $I(i)$: XPS peak intensity from the top monolayer of species i ; $\sigma(i)$: Photoelectron cross-section of species i ; $\lambda(\varepsilon i)$: Mean free path of energy(ε) for species i ; $D(\varepsilon i)$: Fraction of electrons detected by the analyzer for species i ; t : The sampling depth.

With the atomic fraction ratios calculated, the number of atoms per nm^2 on the sample surface could also be obtained. Based on the nature of the anatase TiO_2 material, the number of Ti atoms per nm^3 based on 1 g of TiO_2 can be determined by the following equation [23]:

$$N(\text{Ti}) = \frac{N_A \cdot n(\text{Ti})}{V(\text{TiO}_2)} \quad (4)$$

Where $N(\text{Ti})$ is the number of Ti atoms per m^3 , N_A is the Avogadro constant (atoms/mol), $n(\text{Ti})$ is the mole of Ti (mol), $V(\text{TiO}_2)$ is the volume of 1g of anatase TiO_2 (m^3).

The volume of 1 Ti atom = $\frac{1}{N(\text{Ti})}$.

Assuming Ti atoms are spherical, the volume of 1 Ti atom = $\frac{4}{3} \times \pi \times r^3$. The radius of Ti atom can be calculated. The area of 1 Ti atom = $\pi \times r^2$.

The number of Ti atoms/nm² = $\frac{1}{\pi \times r^2}$.

Similarly, the number of species i atoms per nm² can also be determined from the ratio of species i peak area to Ti peak area with equations (3).

5.3.3.3 Examination of charging effects

5.3.3.3.1 Sample mounting method

For XPS characterization of semi-conductive materials, various sample mounting methods were used to minimize the potential charging effects [41,42]. Here, we use both non-conductive double sized tapes and conductive specially designed copper microfiber foils to mount the samples. In both cases, neat TiO₂ and 4wt% Ag/TiO₂ samples form a thin layer of particles on the supports. XPS characterization of neat TiO₂ and 4wt% Ag/TiO₂ mounted on double sided tapes and copper microfiber foils were conducted using the same experimental settings. Continuous XPS characterization of Ti 2p narrow scans were measured every 2 minutes to compare the results using both mounting supports for neat TiO₂ and 4wt% Ag/TiO₂ sample.

5.3.3.3.2 Neutralizer

Neutralizer was turned on during time dependent XPS experiment for 4wt% Ag/TiO₂ sample. Another time dependent XPS experiment was conducted with neutralizer off on another 4wt% Ag/TiO₂ sample. The settings for neutralizer were as following: Filament current: 2.2 A, Charge balance: 3.6 V, Filament bias: 1.3 V.

5.3.3.3.3 Sample at different particle sizes

Neat TiO_2 and 4wt% Ag/TiO_2 samples were prepared following the same procedure described in section 2.1 but were crushed and sieved to 125-180, 180-250, 250-325, and 325-450 μm respectively to study the potential charging effects caused by uneven contact with the double sided tape support and poor conductivity of the sample.

5.3.3.3.4 X-ray induced Auger parameter analysis

To verify the possibility of any charging effects that could cause spectral changes on XPS narrow scans of neat TiO_2 and 4wt% Ag/TiO_2 samples, Auger parameter measurement was conducted. X-ray induced Auger Electron Spectroscopy (XAES) was measured using pass energy of 160 eV with energy step of 0.1 eV within the kinetic energy range of 380-430 eV and 485-530 eV. Time dependent Ti LMM and O KLL XAES spectra were measured every 30 minutes at the same time point of the time dependent Ti 2p and O 1s XPS spectra. Auger parameters were calculated as a sum of the binding energy of Ti 2p $3/2$ XPS lines and the kinetic energy of Ti $\text{L}_{3\text{M}_{23}\text{M}_{45}}$ Auger lines, and the binding energy of O 1s XPS lines and the kinetic energy of O $\text{KL}_{23}\text{L}_{23}$ Auger lines.

5.4 Results and discussion

5.4.1 Physical property characterizations

5.4.1.1 BET analysis

Table 5.1. BET surface area, pore volume, and average pore radius

Textural Properties	TiO ₂	4wt% Ag/TiO ₂	4wt% HNO ₃ /TiO ₂
Surface area (m ² /g)	163	173	162
Pore Volume (cm ³ /g)	0.47	0.43	0.45
Average Pore radius (nm)	10.93	9.2	10.1

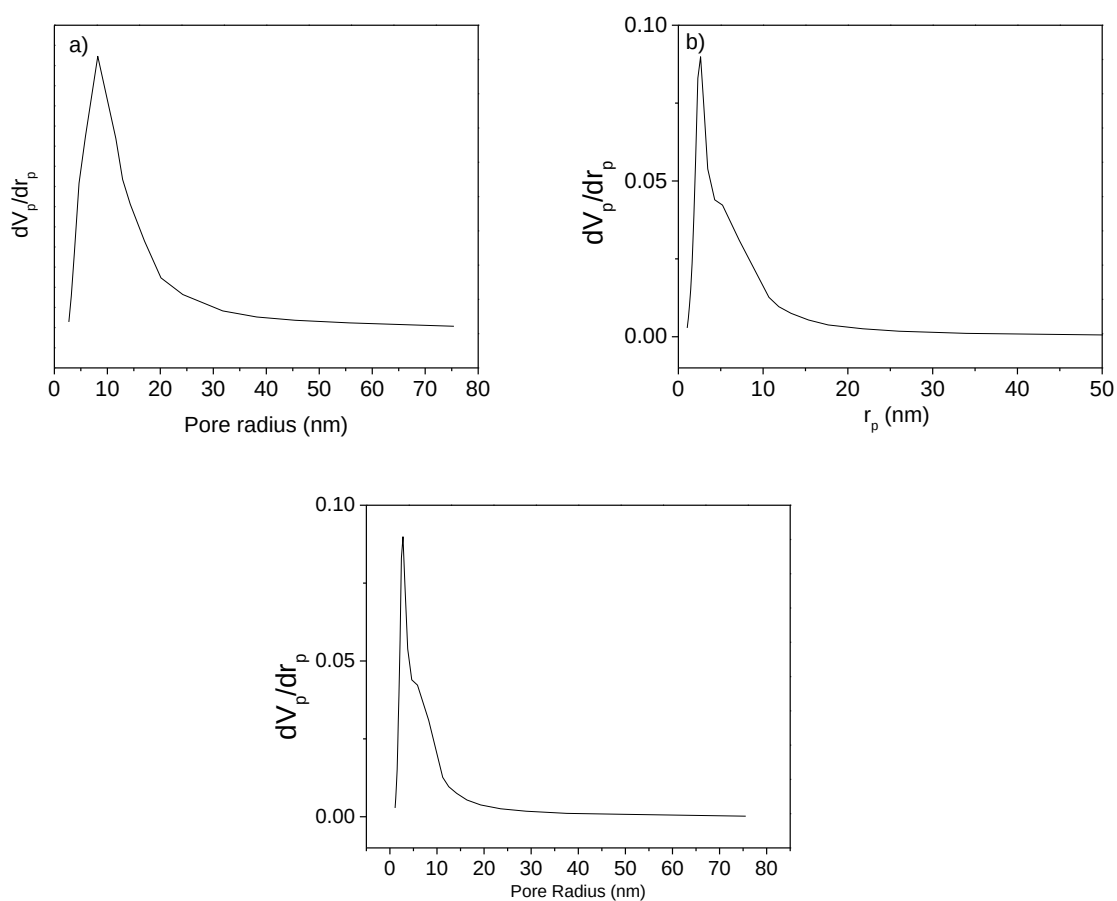


Figure 5.1. Pore radius distribution of a) 4wt% Ag/TiO₂, b) plain TiO₂, and c) 4wt% HNO₃/TiO₂

BET surface areas, pore volumes, and pore radius are summarized in Table 5.1. Slightly differences of the BET surface areas, pore volumes, and pore radius after doping 4wt% of Ag

onto TiO₂ were observed. The addition of Ag on TiO₂ slightly created more surface area. This result could indicate Ag atoms were highly dispersed on TiO₂ surface oxygen vacancy sites by the incipient wetness impregnation and 450 °C calcination procedure and the additional Ag atoms created additional surface area. The small reduction of pore volume and the average pore radius could be due to Ag atoms locate inside the pore structure of TiO₂ and occupy a little bit space inside the pores of TiO₂. The surface area, pore volume, and average pore radius of 4wt% HNO₃/TiO₂ sample are almost the same as neat TiO₂ sample, which illustrates the incipient wetness impregnation of HNO₃ and 450 °C calcination did not make significant difference for TiO₂. The high surface areas of 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ samples indicate there could be adsorbed H₂O on the sample surfaces.

Figure 5.1a) – c) illustrate the pore size distributions of 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ samples. The average pore diameters are 9.2 nm for 4wt% Ag/TiO₂, 10.9 nm for neat TiO₂, and 10.1 nm for 4wt% HNO₃/TiO₂. The average pore diameter for 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ samples are enough for H₂O adsorption [43,44].

5.4.1.2 XRD patterns

Figure 5.2 shows the XRD results of 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ samples. As it is shown in Figure 1, all the peaks indicate anatase phase of TiO₂. Peaks at 25, 38, 48, 54, 56, 63, 69, 71, 75, 83 degrees indicate (101), (004), (200), (105), (211), (204), (116), (220), (215), (303) anatase TiO₂ phases [45-47]. Since the bandgap of anatase TiO₂ is 3.2 eV (387 nm in wavelength) [48,49], any photon with energy higher than 3.2 eV is capable to excite the valence electron of TiO₂. There is no significant difference in XRD patterns for all the samples. No Silver XRD pattern is observed from 4wt% Ag/TiO₂ sample and it indicates silver

atoms are highly dispersed on TiO₂ surface and the particle size of silver is below the detection limit of XRD (<40 nm).

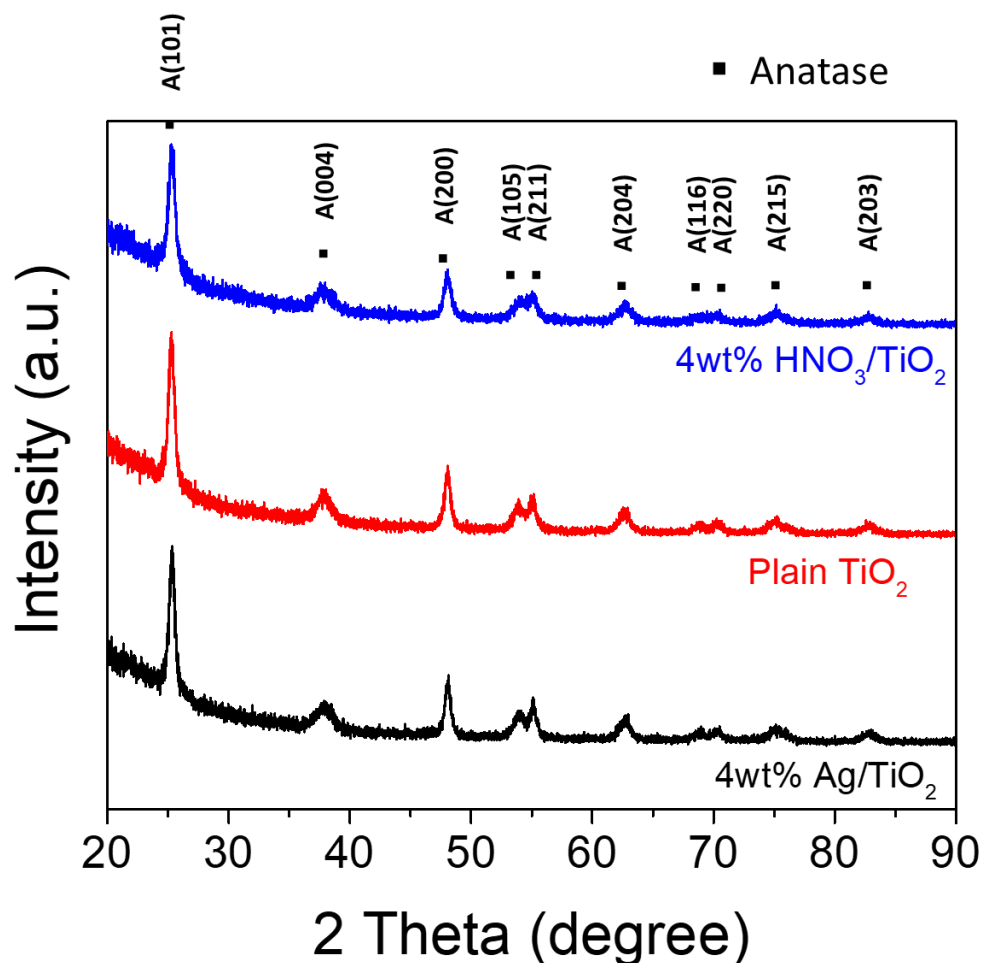


Figure 5.2. XRD patterns of 4wt% Ag/TiO₂, plain TiO₂, 4wt% HNO₃/TiO₂

5.3.3.2 Thermogravimetric analysis

To measure the relative amount of H₂O/OH adsorbed on 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ samples, Thermogravimetric Analysis (TGA) was conducted. Figure 5.3 shows the TGA results of these 3 samples from 25 °C to 700 °C under flowing N₂. When temperature was raised from 25 °C to 100 °C, all the samples showed a significant weight loss due to the desorption of moisture. The weight percentage drop of 4wt% Ag/TiO₂ is larger than

the other two samples, which shows 4wt% Ag/TiO₂ adsorbed more H₂O/OH than neat TiO₂ and 4wt% HNO₃/TiO₂ samples. Figure 5.3 also illustrates that from 100 °C to 700 °C region, there is only strongly adsorbed H₂O/OH on TiO₂ surfaces. At this temperature range, 4wt% Ag/TiO₂ sample dropped a higher weight percentage than neat TiO₂ and 4wt% HNO₃/TiO₂ samples. For the 4wt% Ag/TiO₂ sample, there was 5wt% of adsorbed H₂O/OH desorbed during TGA analysis, which is about 1.14 monolayers of H₂O/OH adsorbed on the surface of 4wt% Ag/TiO₂ sample.

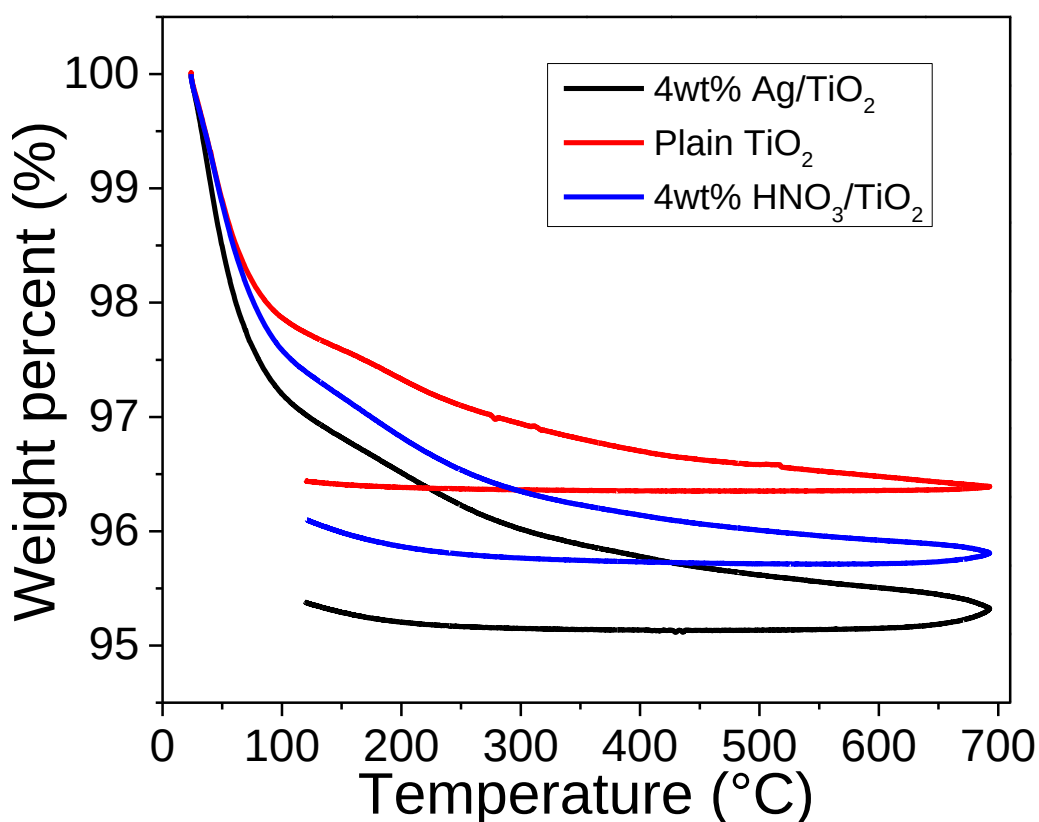


Figure 5.3. TGA results of 4wt% Ag/TiO₂, plain TiO₂, and 4wt% HNO₃/TiO₂

5.4.3 XPS qualitative analysis

The survey spectra of 4wt% Ag/TiO₂, neat TiO₂, and 4wt% HNO₃/TiO₂ are shown in Figure 5.4a) - c). No nitrogen peak (around binding energy of 400 eV) was observed in the survey

spectra of all the samples, which shows that 450 °C calcination in flowing air removes all nitrogen species from all the samples. The high-resolution XPS Ti 2p spectra of neat TiO_2 and 4wt% $\text{HNO}_3/\text{TiO}_2$

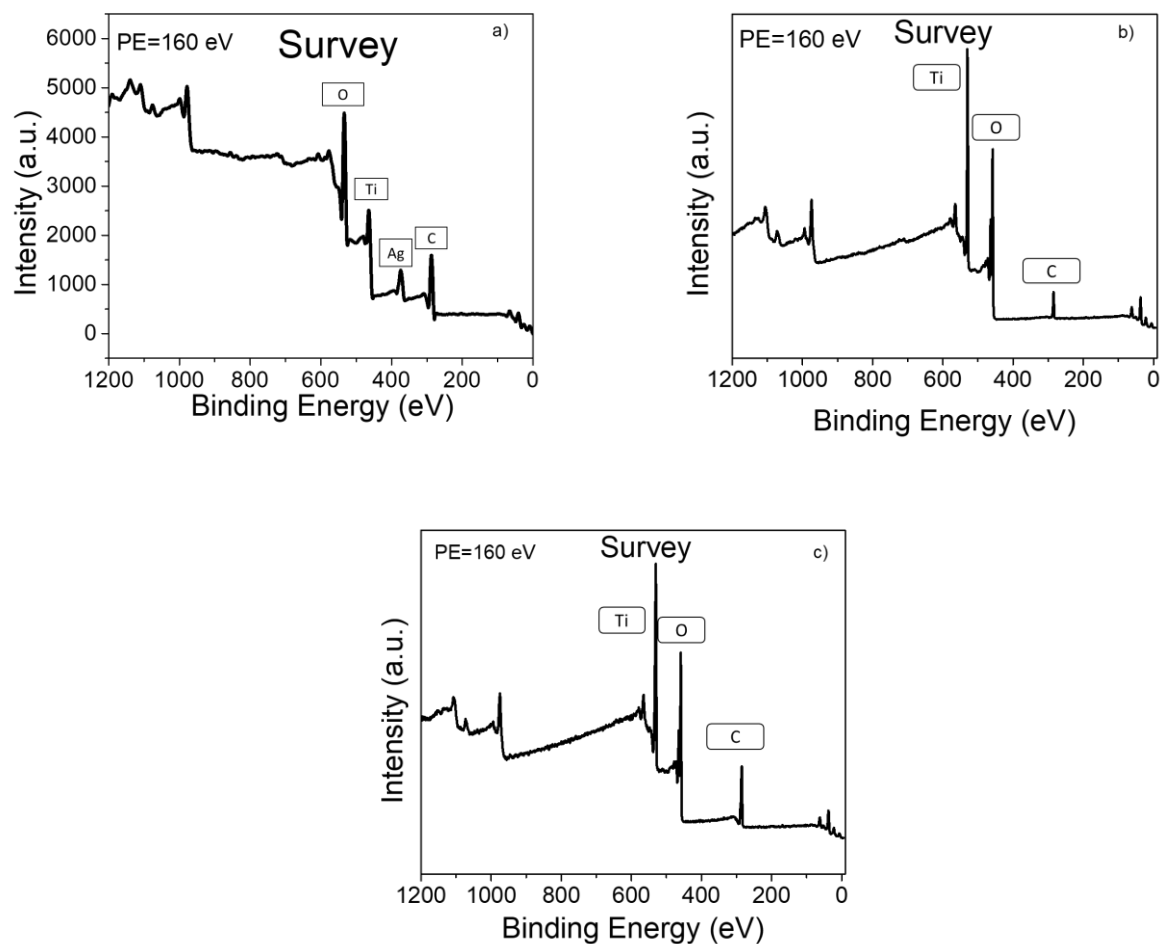


Figure 5.4 Survey spectra of a) 4wt% Ag/TiO₂, b) plain TiO₂, c) 4wt% HNO₃/TiO₂

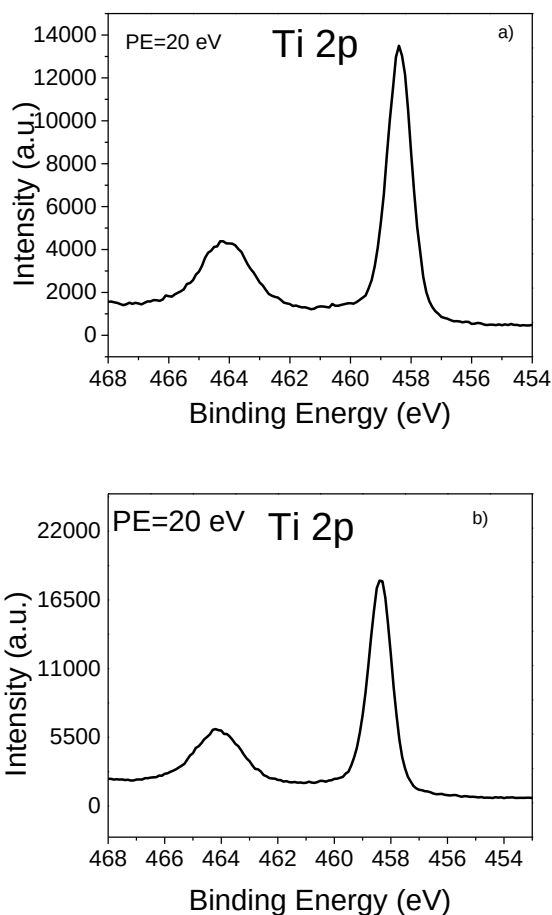
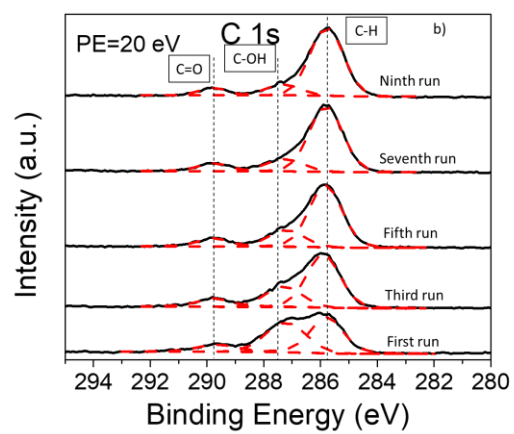
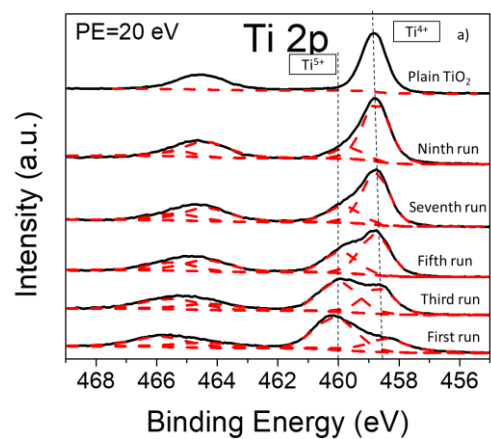


Figure 5.5 High-resolution XPS Ti 2p spectra of a) plain TiO_2 and b) 4wt% $\text{HNO}_3/\text{TiO}_2$ samples are shown in Figure 5.5a) and 5.5b). From Figure 5.5a) and Figure 5.5b), TiO_2 can be identified by $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$ peaks at binding energies of 464.2 eV and 458.5 eV respectively [29,50-52]. No time dependent spectral change was observed from the spectra and the addition of 4wt% HNO_3 did not make any difference on the Ti 2p spectra.



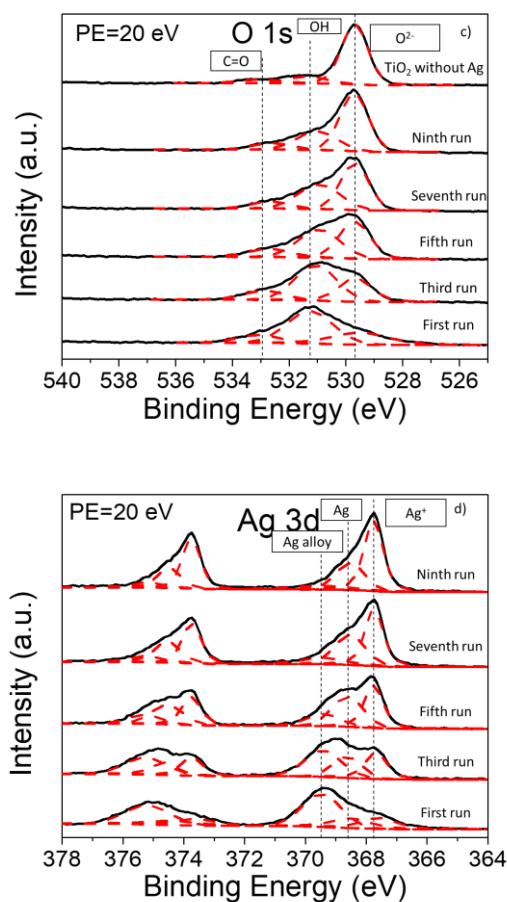


Figure 5.6 High-resolution time-resolved XPS spectra of 4wt% Ag/TiO₂: a) Ti 2p, b) C 1s, c) O 1s, and d) Ag 3d

As it is shown in Figure 5.6a)-d), time dependent spectral change was observed on Ti 2p, C 1s, O 1s, and Ag 3d spectra for 4wt% Ag/TiO₂ sample. The results indicate the addition of 4wt% Ag on TiO₂ significantly changed the properties of TiO₂. To verify and investigate the reason for such an anomalous spectral change of 4wt% Ag/TiO₂ sample, charging effect was examined first.

5.4.4 Examination of charging effects

5.4.4.1 Sample mounting method

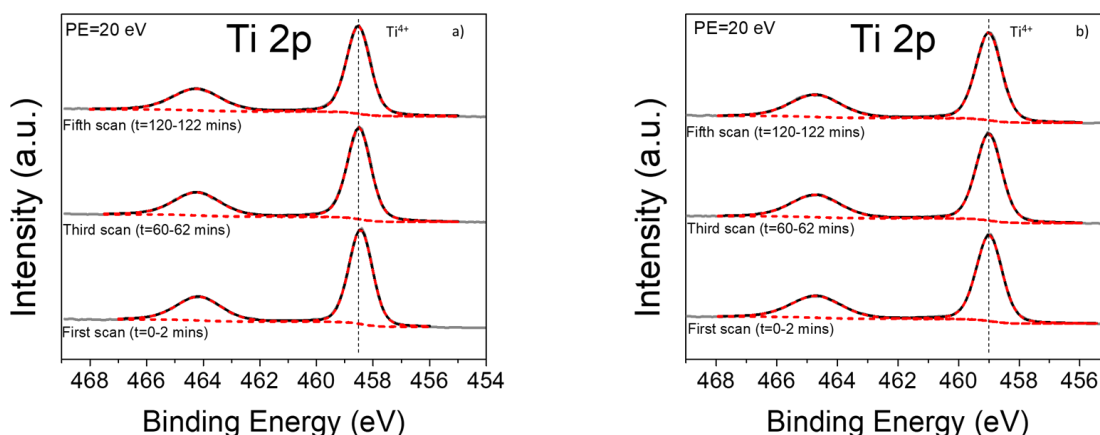


Figure 5.7. High-resolution time dependent XPS Ti 2p spectra of neat TiO₂ sample mounted on a) double sided tape, b) Cu microfiber foil

To verify the potential charging effect caused by sample mounting methods, both neat TiO₂ and 4wt% Ag/TiO₂ samples were mounted using both non-conductive double-sided tape and conductive copper microfiber foil. Figure 5.7a) and Figure 5.7b) show the time dependent high-resolution Ti 2p XPS spectra of neat TiO₂ sample using double sided tape and copper microfiber foil, respectively. As it is shown, TiO₂ is identified at Ti 2p 3/2 peak at binding energy of 458.5 eV and no TiO₂⁺_(hole) peak is observed. No time dependent spectral change was observed, and the results show the mounting methods did not make any difference on the XPS results for neat TiO₂ sample. Figure 5.8a) and Figure 5.8b) show the time dependent high resolution Ti 2p XPS spectra of 4wt% Ag/TiO₂ mounted by double-sided tape and copper microfiber foil. As it is shown in Figure 5.8a) and 5.8b), the peak binding energy positions of TiO₂⁺_(hole) and Ti⁴⁺ species remain at same levels and the spectral change looked very similar to each other. The time dependent peak

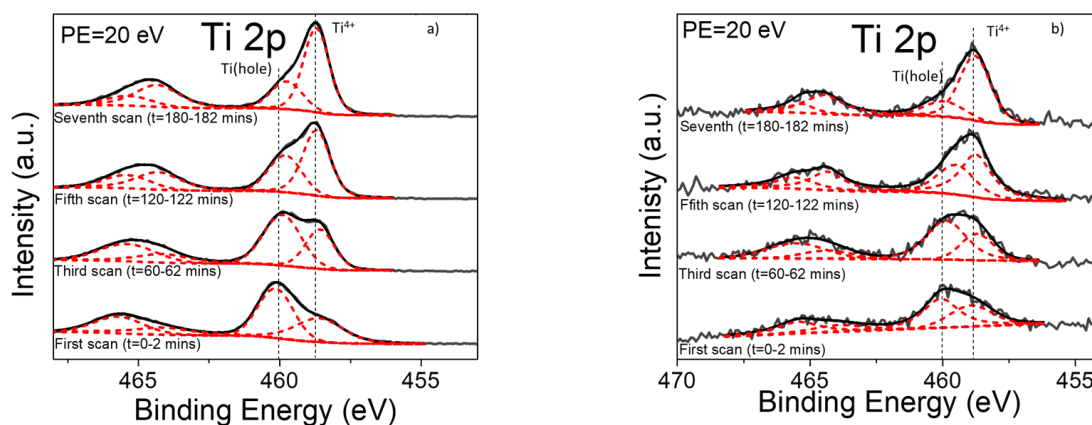


Figure 5.8. High-resolution time dependent XPS Ti 2p spectra of 4wt% Ag/TiO₂ sample mounted on a) double sided tape, b) Cu microfiber foil

intensity changes of TiO₂⁺_(hole) species of both the experiment cases are shown in Figure 5.8. The mounting method using non-conductive double-sided tape or conductive copper microfiber foil did not show significant difference to the time dependent observation of the TiO₂⁺_(hole) species and spectral change.

5.4.4.2 Neutralizer effect

Figure 5.9a) shows high-resolution time dependent Ti 2p XPS spectra result of 4wt% Ag/TiO₂ sample with neutralizer on and Figure 5.9b) shows the same experiment on another 4wt% Ag/TiO₂ sample with neutralizer off. As it is shown in Figure 5.9a) and 5.9b), the binding energy positions of TiO₂⁺_(hole) and Ti⁴⁺ remain at the same levels from the two experiments, and the overall spectral change trend seems not to be affected by the neutralizer.

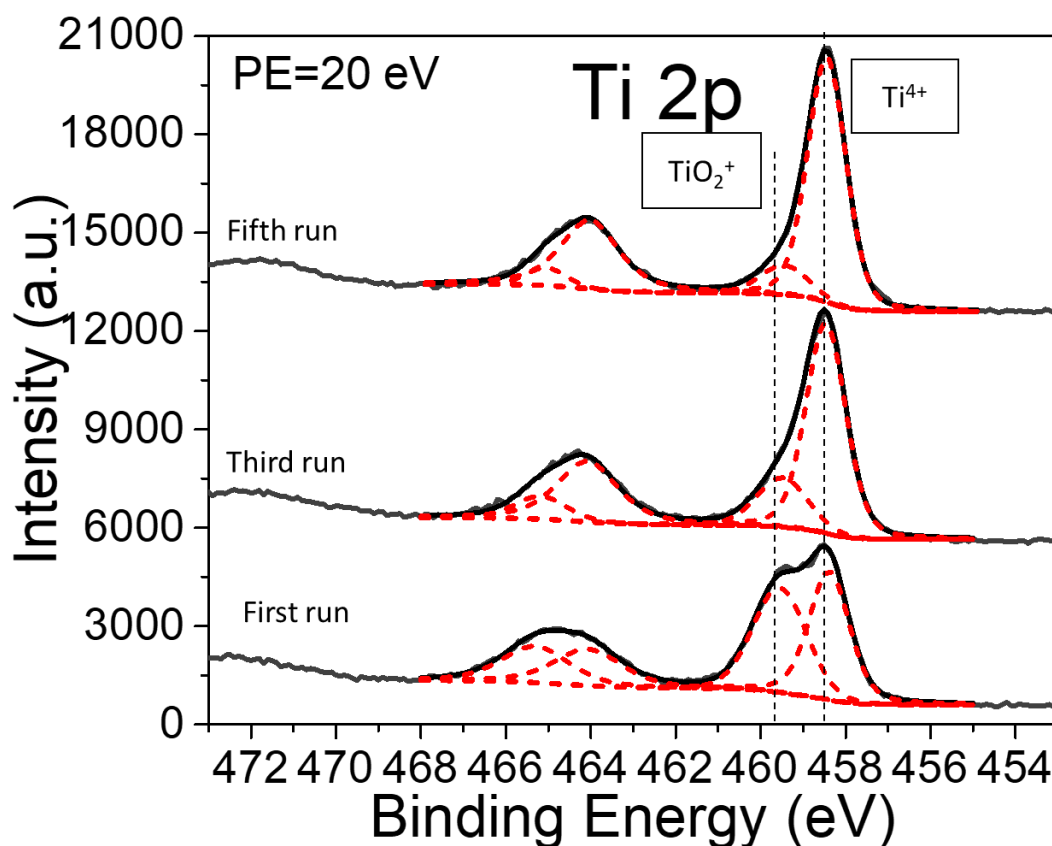


Figure 5.9 High-resolution time-resolved Ti 2p spectra of 4wt% Ag/TiO₂ with neutralizer

Figure 5.10 shows the relative peak intensities of TiO₂⁺_(hole) species during the time dependent XPS characterization with and without neutralizer. From Figure 5.10, neutralizer slightly reduced the peak intensity of TiO₂⁺_(hole) species. Since the neutralizer takes use of a low energy electron flood gun, the interaction between TiO₂⁺_(hole) species and low energy electrons from neutralizer would be expected. Thus, the neutralizer slightly affected on the TiO₂⁺_(hole) phenomenon and the spectral change was potentially caused by chemical reactions.

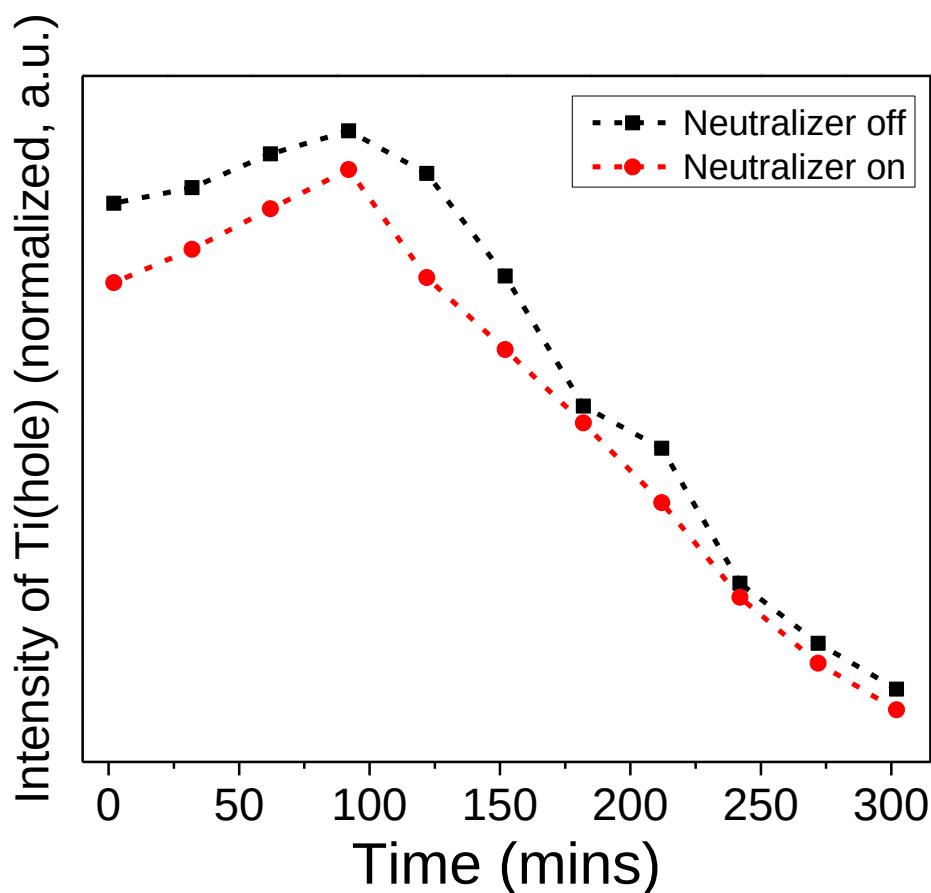


Figure 5.10. Time dependent $\text{TiO}_2^+_{(\text{hole})}$ peak intensity change with neutralizer on and off

5.4.4.3 Particle size effect on XPS results

Figure 5.11a) – e) show the images of neat TiO_2 samples at different particle sizes from the camera in sample analytical chamber. The spot marked on the monitor indicates the center of X-ray irradiation spot, and the parallel lines are the edges of the X-ray irradiation areas on the sample surface. High-resolution Ti 2p XPS spectra of neat TiO_2 samples at different particle sizes are shown in Figure 5.12a) – f). For neat TiO_2 samples at particle sizes less than $325\ \mu\text{m}$, the Ti 2p $1/2$ and Ti 2p $3/2$ peaks at binding energies of 464.2 eV and 458.5 eV are identified as

Ti⁴⁺. No spectral difference caused by charging effect was observed until particle sizes at 325-450 μm .

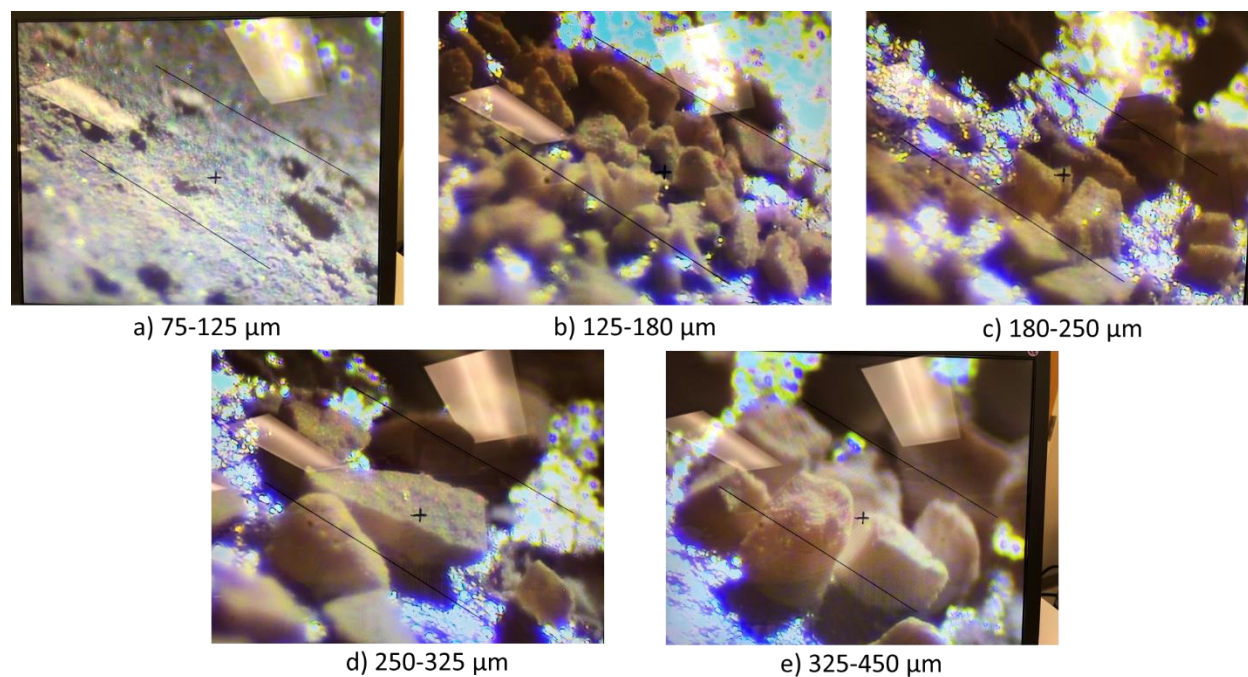


Figure 5.11 Images of plain TiO₂ samples at different particle sizes under the camera in SAC

Abnormal Ti 2p peaks were observed due to surface differential charging effect caused by poor conductivity of the sample due to the uneven contact of the particles with the support tape [51,52]. The abnormal Ti 2p peaks were not observed when neutralizer was turned on during the XPS characterization procedure (Figure 5.12f)). Similar results were observed for 4wt% Ag/TiO₂ samples (Figure 5.13a) – f)). The 4wt% Ag/TiO₂ samples at particle sizes less than 325 μm showed no abnormal peaks on Ti 2p spectra. But for sample particle size at 325-450 μm , abnormal Ti 2p peaks were observed and the abnormal peaks were eliminated by neutralizer. Thus, neat TiO₂ and 4wt% Ag/TiO₂ samples remain good conductivity on double sided sticky tapes until particle sizes larger than 325 μm . That is to say, the unique observation of TiO₂^{+(hole)}

species from XPS is not caused by differential charging effects due to poor conductivity caused by the poor contact between particles and the support tape.

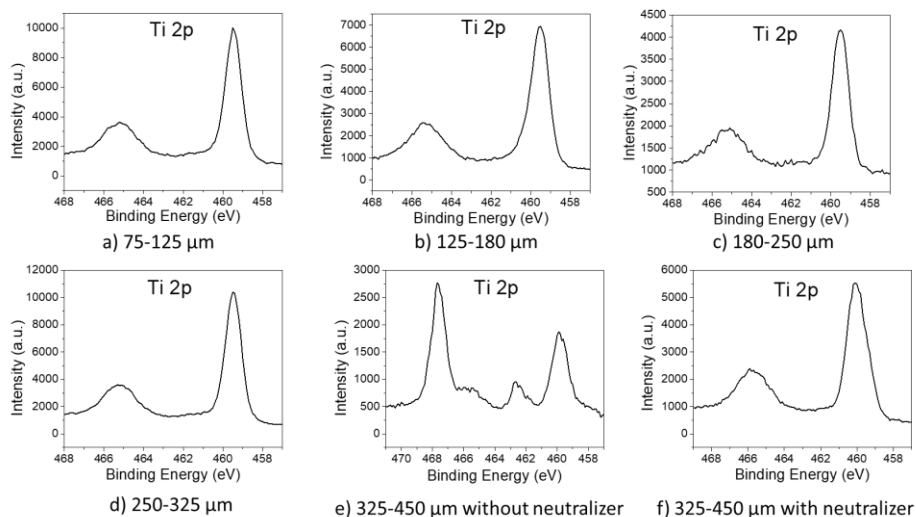


Figure 5.12 High-resolution Ti 2p spectra of TiO_2 at a) 75-125 μm , b) 125-180 μm , c) 180-250 μm , d) 250-325 μm , e) 325-450 μm without neutralizer, and f) 325-450 μm with neutralizer

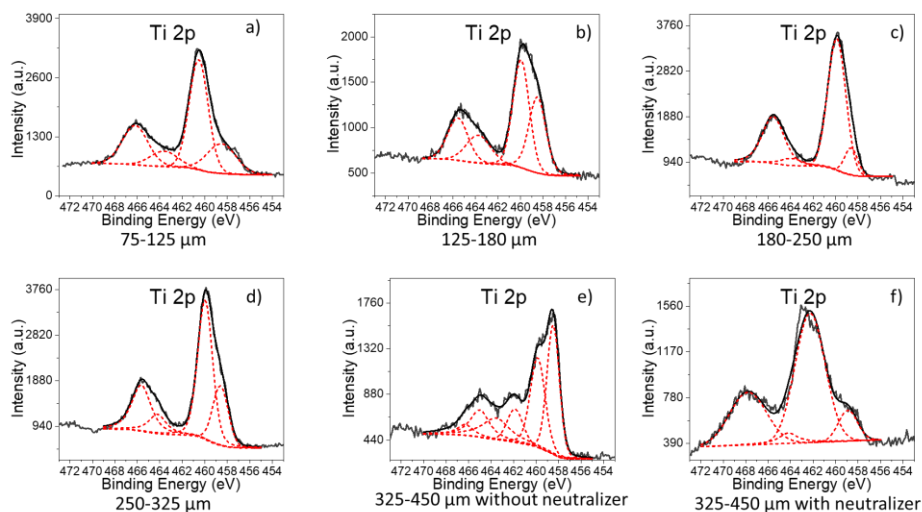


Figure 5.13 High-resolution Ti 2p spectra of 4wt% Ag/TiO_2 at a) 75-125 μm , b) 125-180 μm , c) 180-250 μm , d) 250-325 μm , e) 325-450 μm without neutralizer, f) 325-450 μm with neutralizer

5.4.4.4 Auger parameters of 4wt% Ag/TiO_2

Time dependent Ti 2p, O 1s XPS spectra and Ti LMM and O KLL Auger electron spectra of neat TiO₂ and 4wt% Ag/TiO₂ samples are shown in Figure 5.14 and 5.15. Figure 5.14 shows there is no spectral change of Ti 2p and O 1s XPS spectra as well as Ti LMM and O KLL Auger electron spectra of neat TiO₂ sample. The kinetic energies of Ti LMM and O KLL Auger peaks remained at the same level as well as the Auger parameters of the sample during the whole measurements.

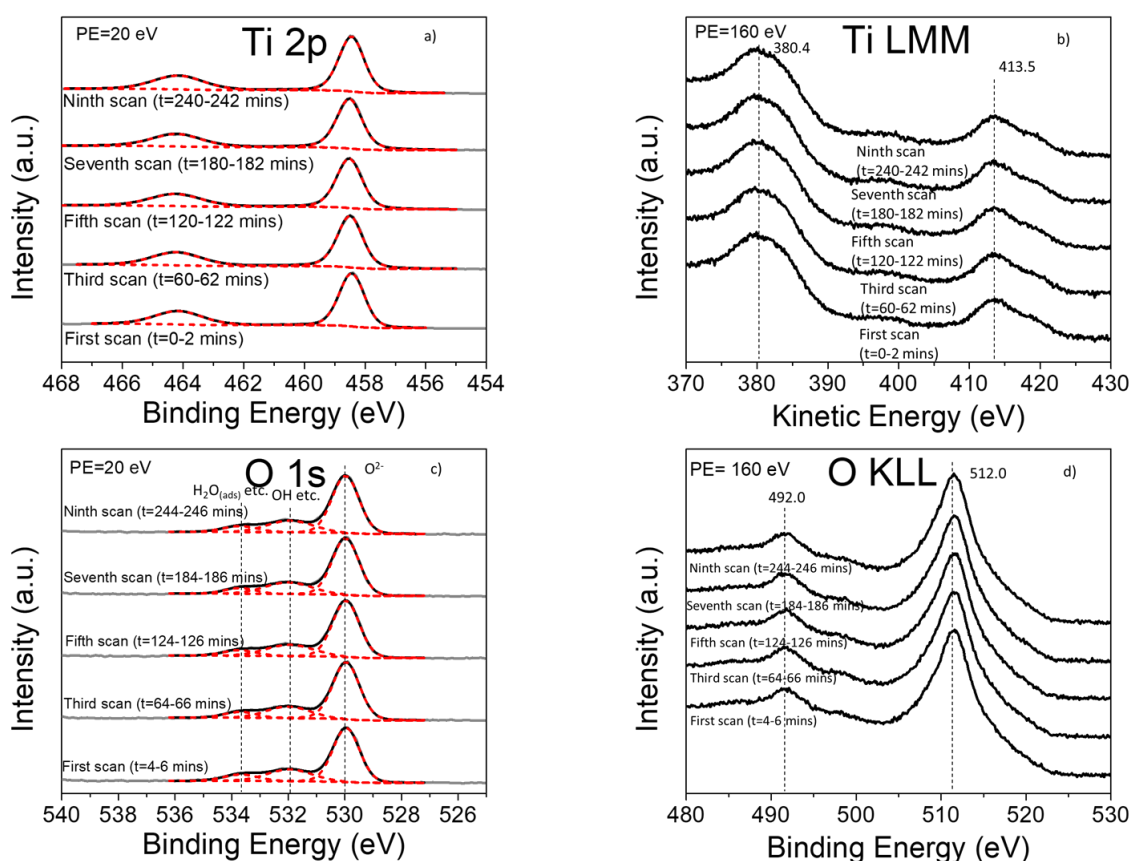


Figure 5.14. Time dependent a) Ti 2p, b) Ti LMM, c) O 1s, d) O KLL spectra of neat TiO₂ sample.

As it is shown in Figure 5.15a) and 5.15b), the Ti 2p XPS spectra and the Ti LMM Auger electron spectra both show time dependent change. Two Ti-L₃M₂₃M₄₅ peaks are observed from

the Ti LMM Auger spectra, one at 412.0 eV kinetic energy and the other at 413.5 eV kinetic energy. The Ti-L₃M₂₃M₄₅ peaks show peak intensity shift from 412.0 eV to 413.5 eV. And the kinetic energy difference between the two Ti-L₃M₂₃M₄₅ peaks is the same as the binding energy difference between TiO₂⁺_(hole) and Ti⁴⁺ peaks, which indicates chemical states change between TiO₂⁺_(hole) and Ti⁴⁺ species. Time dependent change of O 1s XPS spectra and O KLL Auger electron spectra is also observed as it is shown in Figure 5.15c) and 5.15d).

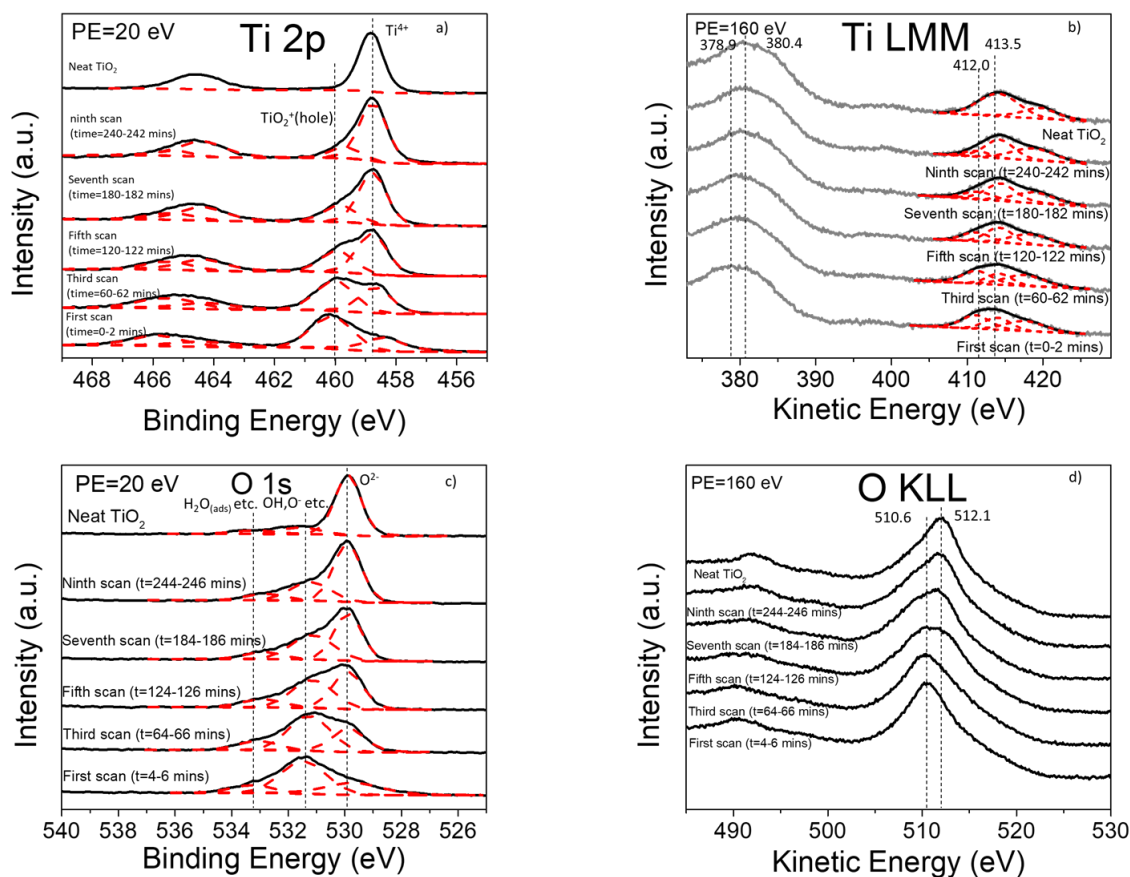


Figure 5.15. Time dependent a) Ti 2p, b) Ti LMM, c) O 1s, d) O KLL spectra of 4wt% Ag/TiO₂ sample.

Peak position and intensity shift are observed from 510.6 eV to 512.1 eV on O KLL Auger electron spectra, which indicates the conversion of O^-/OH to O^{2-} species. The Auger parameters of neat TiO_2 sample and 4wt% Ag/TiO_2 sample are summarized in Table 5.2 and Table 5.3. As it is shown in Table 5.2, the Auger parameters of $\alpha'(\text{O-KL}_{23}\text{L}_{23}, \text{O } 1s)$ and $\alpha'(\text{Ti-L}_3\text{M}_{23}\text{M}_{45}, \text{Ti } 2p \text{ } 3/2)$ are 1042.0 eV and 872.1 eV respectively. There is no change of the Auger parameters, so there is no charging effect for neat TiO_2 sample. Table 5.3 shows the peak positions and Auger parameters of 4wt% Ag/TiO_2 sample.

Table 5.2. Time dependent peak positions and Auger parameter of neat TiO_2 sample

Transition	Peak position (eV)			
	1 st scan	3 rd scan	5 th scan	7 th scan
O 1s (O^{2-})	529.9	529.9	529.9	529.9
O $\text{KL}_{23}\text{L}_{23}$	512.1	512.1	512.1	512.1
Ti 2p 3/2 (Ti^{4+})	458.5	458.5	458.5	458.5
Ti $\text{L}_3\text{M}_{23}\text{M}_{45}$	413.6	413.6	413.6	413.6

Auger parameter

$\alpha'(\text{O-KL}_{23}\text{L}_{23}, \text{O } 1s)$	1042.0	1042.0	1042.0	1042.0
$\alpha'(\text{Ti-L}_3\text{M}_{23}\text{M}_{45}, \text{Ti } 2p \ 3/2)$	872.1	872.1	872.1	872.1

Table 5.3. Time dependent peak positions and Auger parameter of 4wt% Ag/TiO₂ sample

Transition	Peak position (eV)				
	1 st	3 rd	5 th	7 th	9 th
	scan	scan	scan	scan	scan
O 1s (O ²⁻)	529.9	529.9	529.9	529.9	529.9
O-KL ₂₃ L ₂₃ (O ²⁻)	512.1	512.1	512.1	512.1	512.1
Ti 2p 3/2 Ti(hole)	460.0	460.0	460.0	460.0	460.0
Ti-L ₃ M ₂₃ M ₄₅	412.0	412.0	412.0	412.0	412.0
Ti(hole)					
Ti 2p 3/2 Ti ⁴⁺	458.5	458.5	458.5	458.5	458.5

Ti-L ₃ M ₂₃ M ₄₅ Ti ⁴⁺	413.5	413.5	413.5	413.5	413.5
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Auger parameter

α' (O-KL ₂₃ L ₂₃ , O 1s)	1042.0	1042.0	1042.0	1042.0	1042.0
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α' (Ti-L ₃ M ₂₃ M ₄₅ , Ti 2p) Ti(hole)	872.0	872.0	872.0	872.0	872.0
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α' (Ti-L ₃ M ₂₃ M ₄₅ , Ti 2p) Ti ⁴⁺	872.0	872.0	872.0	872.0	872.0
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Although time dependent spectra shape change and peak intensity shift is observed from both Ti 2p and Ti LMM, as well as O 1s and O KLL spectra, the Auger parameters do not show any change. Therefore, there is no charging effect for neat TiO₂ and 4wt% Ag/TiO₂ samples during time dependent XPS characterization [68,69]. That is to say, the observation of the anomalous Ti 2p peak at 1.5 eV higher binding energy than Ti⁴⁺ peak represents a higher valance state of titanium hole species (TiO₂⁺_(hole)).

5.4.5 Qualitative interpretation of XPS results

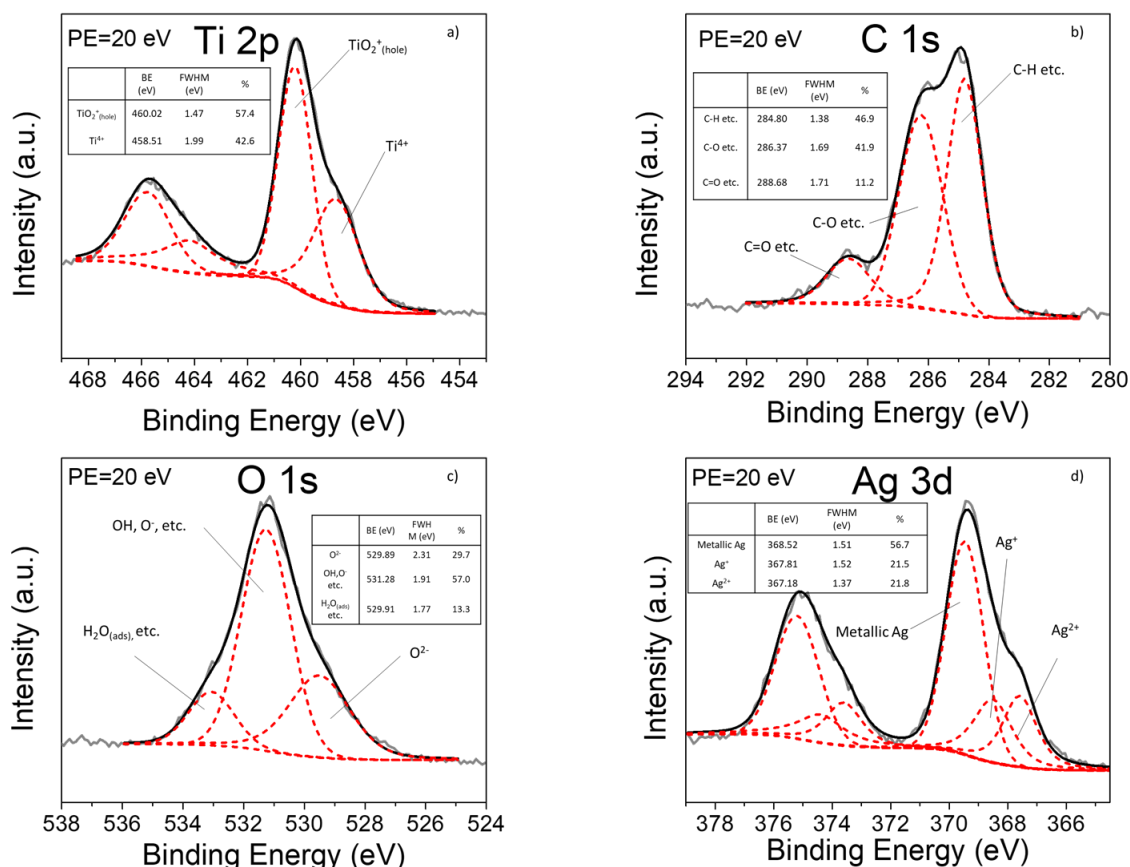


Figure 5.16. Example of deconvolution details of a) Ti 2p, b) C 1s, c) O 1s, and d) Ag 3d spectra of 4wt% Ag/TiO₂ sample.

Since the above analysis has excluded the possibility that the time dependent spectral change of 4wt% Ag/TiO₂ sample is caused by surface charging effect, a detailed qualitative interpretation of the XPS result is conducted based on the deconvolution details of the XPS spectra. Figure 5.16a)-d) show examples of the deconvolution results of Ti 2p, Ag 3d, O 1s, and C 1s spectra of the 4wt% Ag/TiO₂ sample. The high-resolution Ti 2p XPS spectra of 4wt% Ag/TiO₂ sample (Figure 5.6a)) shows there are two Ti 2p 3/2 peaks. The Ti 2p 3/2 peak at binding energy of 460.0 eV potentially shows a titanium species at a higher oxidation state than Ti⁴⁺ (binding energy of 458.5 eV). And Figure 5.6c) shows time dependent spectral change of O

1s, which indicates the chemical composition change of oxygen species. Peak intensity shift from OH/O⁻ to O²⁻ is observed with the peak intensity shift from TiO₂^{+(hole)} to Ti⁴⁺ from Ti 2p spectra. This result indicates the holes were entrapped within the titanium-oxygen centers, and the electron structure of both Ti⁴⁺ and O²⁻ were affected by the hole carriers. According to the corresponding spectral change behavior of oxygen peaks, we assume the hole species to be TiO₂^{+(hole)} species. With continuous XPS characterization, the time dependent Ti 2p XPS spectra shows peak intensity changes between Ti⁴⁺ and TiO₂^{+(hole)} peaks. At the beginning of the time dependent XPS characterization, the peak intensity of TiO₂^{+(hole)} species is much higher than Ti⁴⁺. With continuous XPS characterization, the peak intensity shifts from TiO₂^{+(hole)} species to Ti⁴⁺ species. The spectral change indicates that the TiO₂^{+(hole)} species were generated by X-ray irradiation and migrated to the sample surface, and then the TiO₂^{+(hole)} species were relaxed with further X-ray irradiation. After 11 consecutive XPS measurements, no more spectral change was observed and TiO₂^{+(hole)} species peak was no longer observable.

The time dependent high-resolution XPS C 1s spectra of 4wt% Ag/TiO₂ sample is shown in Figure 5.6b). The C=O, etc. species can be identified by C 1s peak at binding energy of 288.7 eV [53,54], no significant change of this peak was observed during the whole time dependent XPS characterization. The C-O, etc. and C-C, etc. species can be identified by C 1s peaks at binding energies of 286.4 eV and 284.8 eV [53-57]. The time dependent C 1s XPS spectra showed peak intensity shift between these two peaks, indicating the conversion between C-O and C-C species. Time dependent spectral change was also observed from O 1s XPS spectra as it is shown in Figure 3c). The O 1s peak at binding energy of 532.9 eV is identified as adsorbed H₂O, etc. species [55,56]. No significant change was observed of the adsorbed H₂O, etc. peak. The O 1s peak at binding energy of 531.3 eV is assigned as hydroxyls (OH[·] or OH⁻) and/or oxygen

holes carriers (O^- etc.) [58,59]. The O 1s peak at 529.9 eV is assigned as lattice oxide oxygen (O^{2-}) in TiO_2 [23,57-59]. The time dependent XPS spectra showed peak intensity shifts between OH/O^- , and O^{2-} with continuous X-ray exposure. With the relaxation of $TiO_2^{+ (hole)}$ species, OH/O^- etc. species were converted to O^{2-} , indicating the $TiO_2^{+ (hole)}$ species was stabilized by hydroxyls. Previous studies [21-23] have shown that the OH species could not be converted into lattice O^{2-} species, so the peak intensity shift was caused by conversion of O^- species to lattice O^{2-} species. Time dependent XPS spectral change was also obtained from high-resolution Ag 3d spectra for 4wt% Ag/ TiO_2 sample (Figure 5.6d)). The Ag 3d 5/2 peaks at binding energy of 367.2 eV, 367.8 eV, and 368.5 eV are identified as Ag^{2+} , Ag^+ and metallic Ag species respectively [60-65]. With continuous XPS characterization, the time dependent Ag 3d XPS spectral change shows peak intensity shifts between metallic Ag and Ag^{2+} . The spectral change indicates the chemical state conversion of Ag from Ag(I)OH to metallic Ag with the generation of $TiO_2^{+ (hole)}$ species, and during the relaxation of $TiO_2^{+ (hole)}$ species process, metallic Ag was oxidized to Ag^{2+} . The chemical state change of Ag was also confirmed by the color change of the sample (Figure 5.17). The as prepared 4wt% Ag/ TiO_2 sample shows a white color indicating that Ag is in Ag(I)OH form. And after the reaction process, the X-ray irradiated spot on the sample surface shows a dark brown color, which indicated Ag was oxidized into Ag^{+2} states.

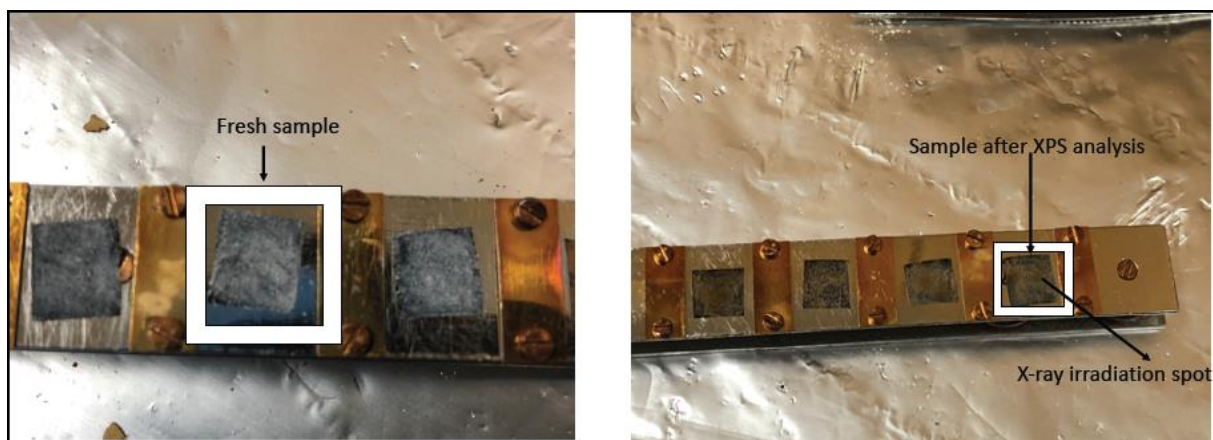


Figure 5.17. 4wt% Ag/TiO₂ color change caused by X-ray irradiation

The above observations show us a promising reaction mechanism scheme under UHV conditions that the X-ray irradiation initiated the generation of electrons and holes on TiO₂. The electrons were captured by Ag(I)OH on the surface defective sites of the high surface area TiO₂ sample, and Ag(I)OH was reduced to metallic Ag leaving free OH⁻ that could be diffused to the sample surface. The hole carriers were transferred to the surface titanium-oxygen center and formed TiO₂⁺_(hole) species, which were stabilized by the free OH⁻ provided during the electron induced reduction of Ag(I)OH under UHV conditions.

5.4.4.6 Quantitative analysis of XPS results

The time dependent XPS spectral change indicated continuous chemical reactions happened on 4wt% Ag/TiO₂ sample surface with continuous X-ray exposure. The atomic fractions of each species and element are calculated according to equation (2). To better evaluate the results, total titanium peak intensity is used as a reference and the atomic fraction ratio of different species over total titanium is calculated according to equation (3). Since the XPS sampling depth is two inelastic mean free path (IMFP) (~3.4 nm) and the X-ray photons can penetrate and cause reactions on deep layers and surfaces of the sample (~500-700 nm), but species underneath the top 3 nm depth could not be monitored by XPS, so adjustments have been applied to calculate the atomic fraction of carbon and silver species [71,72]. Carbon species are adsorbed on the top monolayer of the sample surface, the sampling depth for carbon species is the diameter of one monolayer carbon species (~0.4 nm). And due to the nature that silver is highly dispersed on every surfaces of TiO₂ surface defective sites but XPS could only monitor the top 3.4 nm surfaces, shadowing effect is applied for the calculation of silver species by assuming the initial

reaction happened in the same way on every surfaces of the sample and silver atoms are immobile during the reaction process.

The time dependent atomic fraction ratio $C(i)/C(Ti_{tot})$ is shown in Figure 5.18a-d). Figure 5.18a) shows the time dependent atomic fraction of titanium species. The atomic fraction of $C(TiO_2^{+}_{(hole)})/C(Ti_{tot})$ went up from 0.57 to 0.67 during the first 30-60 minutes of the experiment, which indicates the generation and accumulation of $TiO_2^{+}_{(hole)}$ species on the surface of the 4wt% Ag/ TiO_2 sample. Then the atomic fraction of $C(TiO_2^{+}_{(hole)})/C(Ti_{tot})$ species went down continuously, which implied the relaxation of $TiO_2^{+}_{(hole)}$ species to Ti^{4+} species. Simultaneously, Figure 9c) shows the time dependent atomic fraction ratio of oxygen species in terms of total titanium species. At the first 30-60 minutes of the experiment, the atomic fraction ratio of $C(OH/O^{-})/C(Ti_{tot})$ went up, which indicated the generation and accumulation of $TiO_2^{+}_{(hole)}$ species was accompanied with the formation of OH/O^{-} species. After 60 minutes of the experiment, when the $TiO_2^{+}_{(hole)}$ species began to relax, the atomic fraction ratio of $C(OH/O^{-})/C(Ti_{tot})$ went down correspondingly. At the same time, some of the O^{-} species were converted into O^{2-} . In other words, the generation, accumulation, stabilization, and relaxation of $TiO_2^{+}_{(hole)}$ species was closely related to the formation, diffusion, and conversion of OH/O^{-} species.

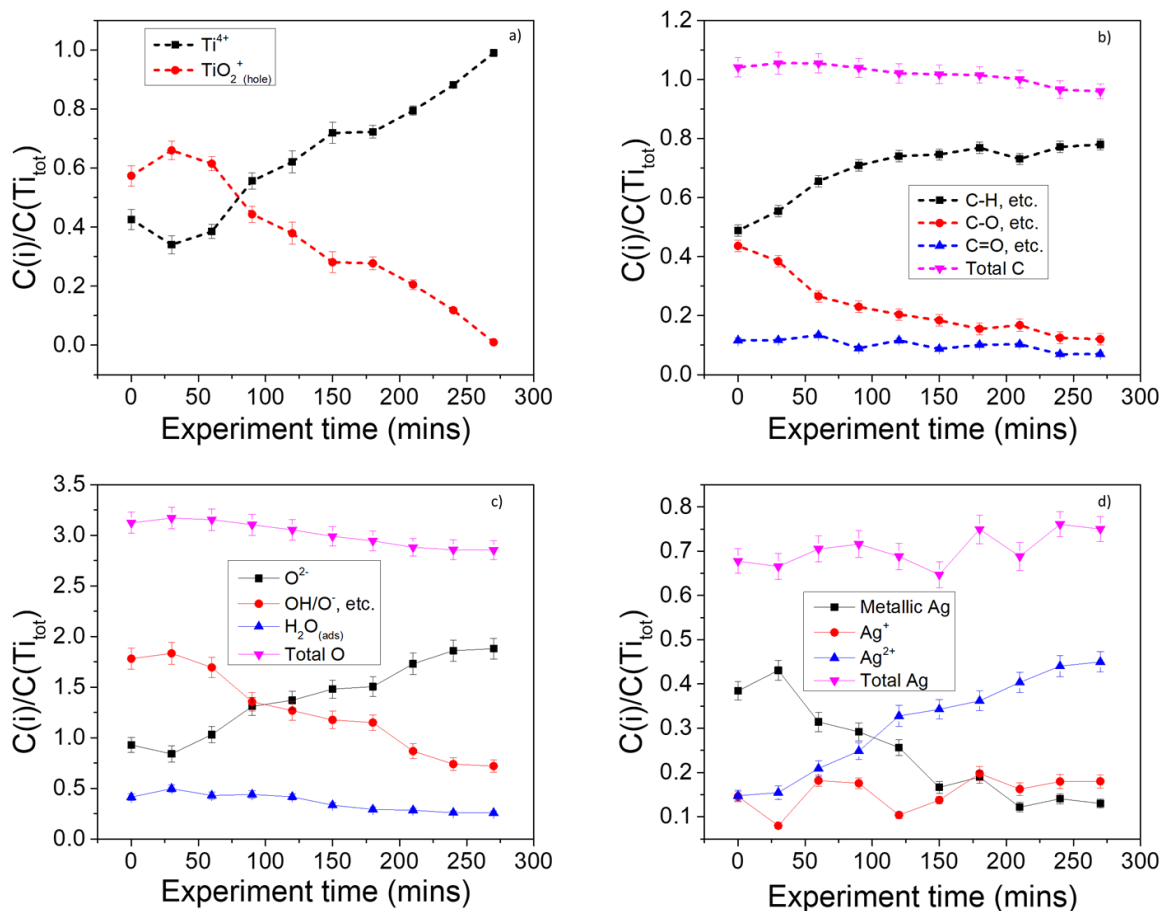


Figure 5.18. Atomic fraction ratio of $C(i)/C(Ti_{tot})$ in terms of experiment time

Figure 5.18c) also shows the atomic fraction ratio of $C(O_{tot})/C(Ti_{tot})$ went up from 3.12 to 3.17 during the first 30 minutes of experiment process, which potentially indicates the diffusion of oxygen species from the bulk to the surface with the generation and accumulation of $TiO_2^{+}(hole)$ species [73-75]. After 30 minutes of the experiment process, the atomic fraction ratio of $C(O_{tot})/C(Ti_{tot})$ decreased continuously with the relaxation of $TiO_2^{+}(hole)$ species. This result implies the desorption of oxygen species from the sample surface. As it is discussed earlier, the OH species was the key component to stabilize the $TiO_2^{+}(hole)$ species. X-ray photons could potentially cause desorption of adsorbed H_2O/OH and leave unstable $TiO_2^{+}(hole)$ species on the

sample surface to trigger the relaxation of $\text{TiO}_2^{+}(\text{hole})$ species. Additionally, Figure 5.18c) shows the atomic fraction of $\text{C}(\text{O}^{2-})/\text{C}(\text{Ti}_{\text{tot}})$ decreased and then increased during the experiment process. The atomic fraction ratio of $\text{C}(\text{O}^{2-})/\text{C}(\text{Ti}_{\text{tot}})$ was 0.92 and 0.83 from the result of the first two XPS scans, which was much lower than the value of 2.09 for neat TiO_2 . Thus, some of the lattice O^{2-} species were converted into hole species $\text{O}^{\cdot-}$ by the hole carriers (reversible) or were converted into OH species by photocatalytic reactions between anatase TiO_2 and adsorbed H_2O (irreversible) at the first 30 minutes of the experiment. After 30 minutes of the experiment, the atomic fraction ratio of $\text{C}(\text{O}^{2-})/\text{C}(\text{Ti}_{\text{tot}})$ increased continuously to 1.89 by the end of the experiment, which indicates the potential hole species $\text{O}^{\cdot-}$ were relaxed and converted back to lattice O^{2-} during the relaxation of $\text{TiO}_2^{+}(\text{hole})$ species process. The atomic fraction ratio of $\text{C}(\text{O}^{2-})/\text{C}(\text{Ti}_{\text{tot}})$ was 1.89 at the end of the experiment and it was still lower than the value of neat TiO_2 , so there were surface defective sites of the TiO_2 material and the surface defective sites was occupied by hydroxides or $\text{Ag}(\text{II})\text{O}$ at the end of the experiment. The atomic fraction ratio changes of oxygen species over Ti_{tot} , especially the change of O^{2-} demonstrated the relative amount of lattice O^{2-} that were 1:1 converted into hole species $\text{O}^{\cdot-}$. Due to the overlap of the binding energy of OH and $\text{O}^{\cdot-}$ peaks, the atomic fraction of OH could also be acquired by subtracting the total atomic fraction of the whole peak by the atomic fraction of $\text{O}^{\cdot-}$ species obtained by the change from O^{2-} species.

The atomic fraction ratio of carbon species over total titanium is shown in Figure 5.18b). The atomic fraction ratio of $\text{C}(\text{C}_{\text{tot}})/\text{C}(\text{Ti}_{\text{tot}})$ shows continuously decrease from 1.04 to 0.97, which indicates the desorption of carbon species during the reaction process. Besides, a continuous conversion from C-O to C-C species was also indicated by the atomic fraction ratio change of $\text{C}(\text{C-O})/\text{C}(\text{Ti}_{\text{tot}})$ and $\text{C}(\text{C-C})/\text{C}(\text{Ti}_{\text{tot}})$. The high atomic fraction ratio of $\text{C}(\text{C-O})/\text{C}(\text{Ti}_{\text{tot}})$

from the first two scans was potentially due to the interaction between C-C species and hydroxyls to form C-OH species. Then the atomic fraction ratio of $C(C-O)/C(Ti_{tot})$ decreased during the relaxation of $TiO_2^+_{(hole)}$ species, which implied the desorption OH from C-OH. There is almost a 1:1 ratio between the conversion of C-O species and formation of C-C species. The atomic fraction ratio of $C(O-C=O)/C(Ti_{tot})$ shows no significant change throughout the reaction process. Figure 5.18d) shows the change of atomic fraction ratio of silver species over total titanium. The results show that the Ag(I)OH was reduced to metallic Ag upon the irradiation of X-ray and the metallic Ag was re-oxidized to Ag^{2+} during the relaxation of $TiO_2^+_{(hole)}$ species. The atomic fraction ratio of $C(Ag^+)/C(Ti_{tot})$ shows random and insignificant change. Thus, the function of Ag(I)OH could be both reactant and catalyst.

The atomic fraction ratios of $C(O^{2-})/C(Ti^{4+})$, $C(O^-)/C(TiO_2^+_{(hole)})$, $C(OH)/C(TiO_2^+_{(hole)})$, and $C(O_{tot})/C(Ti_{tot})$ are summarized in Table 5.4. As it is shown in Table 5.4, at different time during the experiment process, the atomic ratios of $C(O^{2-})/C(Ti^{4+})$ and $C(O^-)/C(TiO_2^+_{(hole)})$ were slightly lower than 2:1. And the stoichiometry ratios indicated the existence of TiO_2 and the hole species is in form of $TiO_2^+_{(hole)}$. The atomic fraction ratios of $C(OH)/C(TiO_2^+_{(hole)})$ were always higher than 1.50, which means the positive charge of the hole center was neutralized by surface OH^- . The positive hole charge was entrapped by O^{2-} and shared by Ti^{4+} to form $TiO_2^+_{(hole)}$ species, which was stabilized by the OH^- species.

Table 5.4. Atomic fraction ratios between oxygen and titanium species

Time (mins)	$C(O^{2-})/C(Ti^{4+})$	$C(O^-)/C(TiO_2^+ \text{ (hole)})$	$C(OH)/C(TiO_2^+ \text{ (hole)})$	$C(O_{tot})/C(Ti_{tot})$
0	1.71	2.02	1.44	3.12
30	1.88	1.89	1.32	3.17
60	1.90	1.88	1.48	3.16
90	1.95	1.82	1.80	3.10
120	1.89	1.90	2.03	3.05
150	1.91	1.85	2.32	2.99
180	1.92	1.82	2.25	2.95
210	1.90	1.85	2.90	2.88
240	1.84	2.29	5.08	2.86

5.4.4.7 X-ray photon efficiency analysis

According to equation (4), the number of titanium atoms/nm² could be calculated. Since the TiO₂^{+(hole)} species was generated by X-ray photons, the X-ray photon efficiency could be obtained by the number of TiO₂^{+(hole)} species generated per X-ray photon absorbed at two IMFP depth. The monochromatic Al X-ray irradiation flux under the current experimental settings of the XPS system is provided by the manufacture (Kratos LLC.) of the XPS system, which is 1.20×10¹¹ photons/mm²/s. And the corresponding X-ray photon efficiency is summarized in Table 5.5.

Table 5.5. X-ray photon efficiency analysis

X-ray exposure time (mins)	X-ray Photons adsorbed /nm ²	Number of titanium holes /nm ²	Change by X- ray photons /nm ²	X-ray photon efficiency
2	0.36	5.11	5.11	14.19
32	5.76	5.87	0.76	0.14
62	11.16	5.47	-0.40	-0.07
122	21.96	3.95	-1.52	-0.14

182	32.76	2.50	-1.45	-0.13
242	43.56	1.05	-1.45	-0.13

From the results shown in Table 5.5, the first scan shows one X-ray photon could generate more than 14 $\text{TiO}_2^+(\text{hole})$ species. Previous photon efficiency studies [68-70] on photo excitation of TiO_2 material showed one high energy photon could produce as much as 8 electrons and holes on TiO_2 . Thus, the results obtained by the current XPS experiment indicate the migration of hole carriers from the bulk to the surface. According to some previous studies [2,12,71], the hole carriers could be transferred through O^- species. And the results from the current study show the holes are entrapped in both O^- and $\text{TiO}_2^+(\text{hole})$ species. After 60 minutes of X-ray exposure, when the relaxation of $\text{TiO}_2^+(\text{hole})$ species began, the X-ray photon efficiency remained at a relatively constant negative level, which hints the potential cause for the hole relaxation is the X-ray photon stimulated desorption of $\text{OH}/\text{H}_2\text{O}$.

5.4.5 Potential reaction mechanism

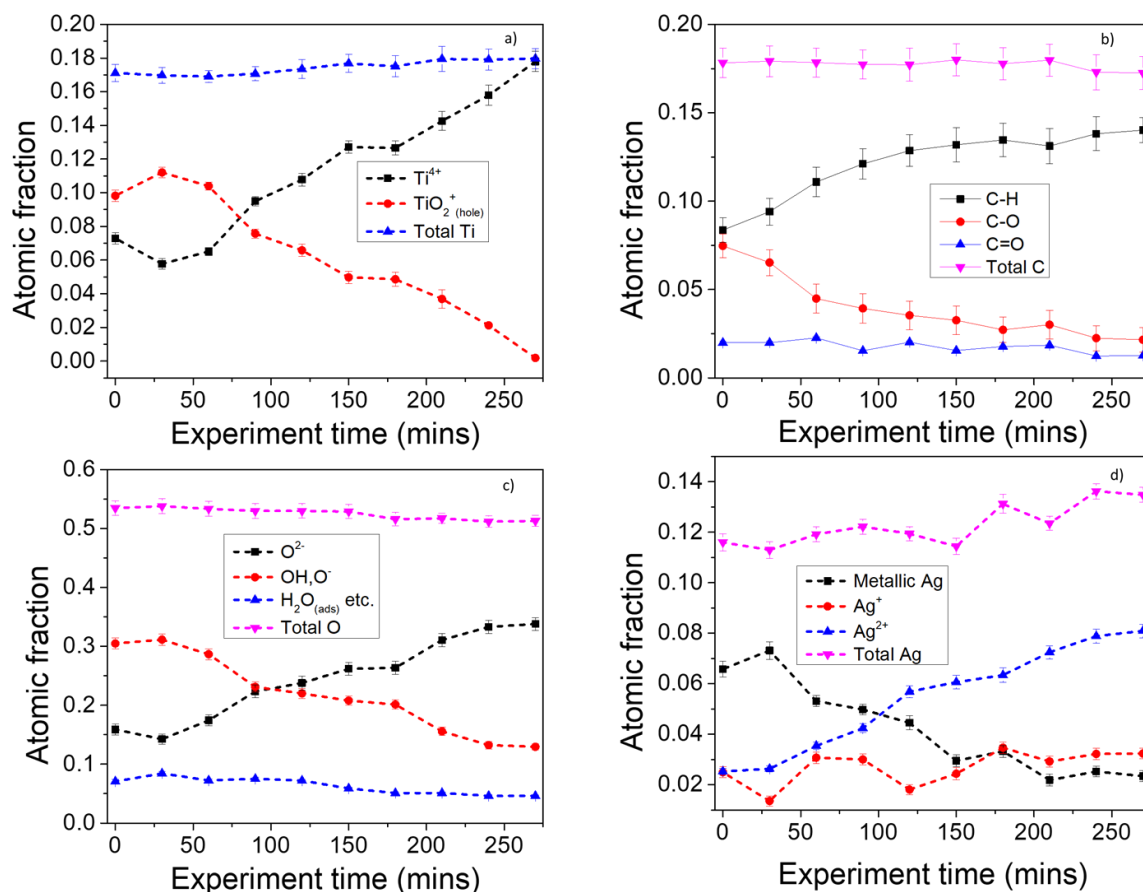


Figure 5.19. Atomic fraction change of each species with X-ray exposure time

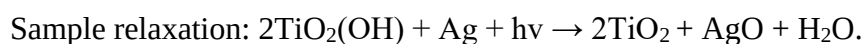
Based on equation (2), the atomic fraction of each species is summarized in Table 5.6 and the time dependent atomic fraction change is shown in Figure 5.19. The increase of atomic fraction of total titanium and silver provides direct evidence that some of the surface components desorbed and left during the reaction process. As it is shown earlier in Table 5.4, continuous drop of $C(O_{tot})/C(Ti_{tot})$ was observed. Since titanium atoms were immobile, the ratio drop could indicate desorption of oxygen species such as adsorbed H_2O and CO_2 as potential reaction products. The atomic ratio of $C(O_{tot})/C(Ti_{tot})$ was 3.12 from the first scan, which is much higher than the value of 2.42 for neat TiO_2 . This ratio indicates the diffusion of oxygen species to the surface. This ratio could also imply the $TiO_2^+_{(hole)}$ species need to be stabilized by additional

oxygen species such as hydroxyls [72-74]. The detailed analysis of the atomic fraction of oxygen species showed a much higher hydroxyl atomic fraction than neat TiO_2 , which implied the diffusion and transportation of hydroxyls from the bulk to the surface. The sampling depth of XPS is about two IMFP of photoelectrons in TiO_2 , which is about 3.4 nm. The overall atomic fraction of oxygen continuously decreased as it is shown in Figure 5.19c), which again confirms the desorption of oxygen species. This could be due to the X-ray photon stimulated desorption adsorbed $\text{H}_2\text{O}/\text{OH}$ from the sample surface. Besides, with Ag(I)OH getting reduced to metallic Ag , and the hydroxyl groups bonded with Ag^+ potentially became free hydroxyl groups and they were diffused to the surface. At the end of the time dependent experiment, the oxygen to titanium atomic fraction ratio was 2.85, which is still much higher than the one of neat TiO_2 at 2.42. The additional oxygen species was potentially attributed to the surface hydroxides as the reaction products of hydroxyl radicals and free hydroxyl groups. Besides, the atomic fraction of carbon showed a slightly decrease in terms of X-ray exposure time (Figure 5.19b)), which could be due to the oxidative decomposition of hydrocarbons by hydroxyl radicals and/or titanium hole species to form CO_2 as a gas phase product. The role of hydroxyl radicals and other reaction intermediates were not discussed in the current study due to their extreme short lifetime [19-21] during the photoexcitation on TiO_2 .

# of scans	C-H	C-O	C=O	Total C	O ²⁻	OH	H ₂ O (ads)	Total O	Ti ⁴⁺	TiO ₂ ⁺	Total Ti	Ag ²⁺	Ag ⁺	Ag	Total Ag	Sum
1	0.084	0.075	0.020	0.178	0.159	0.305	0.071	0.535	0.073	0.098	0.171	0.066	0.025	0.025	0.116	1.000
3	0.111	0.045	0.023	0.178	0.174	0.287	0.073	0.533	0.065	0.104	0.169	0.053	0.031	0.035	0.119	1.000
5	0.129	0.035	0.020	0.177	0.238	0.220	0.072	0.530	0.108	0.066	0.174	0.044	0.018	0.057	0.119	1.000
7	0.135	0.027	0.018	0.178	0.264	0.201	0.051	0.516	0.127	0.049	0.175	0.033	0.035	0.063	0.131	1.000
9	0.138	0.022	0.012	0.173	0.333	0.132	0.046	0.512	0.158	0.021	0.179	0.025	0.032	0.079	0.136	1.000

Table 5.6 Time dependent molecular fraction of each species from deconvolution of XPS spectra

By analyzing the atomic fraction change of different species during the reaction process, the molecular fraction change rates, and the stoichiometry of the reaction kinetics of different species are calculated according to Table 5.6 and Figure 5.19. And a reaction formula is proposed according to the following the stoichiometry, which is



5.5 Conclusion

This study provides valuable evidence for the observation of a stabilized high valence state of titanium hole species. An anomalous Ti 2p peak was observed and its peak intensity kept changing during the time dependent XPS characterization. The possibility of surface charging effect to cause this phenomenon was examined by means of sample mounting method, sample particle size, neutralizer, and the Auger parameters of the time dependent phenomenon on XPS

spectra. The results indicated the time dependent XPS spectral change was caused by chemical reactions.

Based on the above results and observations, a chemical reaction scheme was proposed with the time dependent XPS spectral quantitative analysis. Since the XPS characterization was conducted under UHV conditions (7.0×10^{-10} torr) in the XPS sample analytical chamber under dark condition, the only triggering source for the reaction is the X-ray irradiation. Under X-ray irradiation, continuous chemical reactions happened on the 4wt% Ag/TiO₂ sample surface. The high energy X-ray photons continuously created pairs of photo-generated electrons and holes; the electrons were captured by silver. Silver ions (Ag⁺) was reduced to form metallic silver during this procedure. The hydroxyl groups initially bonded to Ag⁺ became free hydroxyl groups and they were diffused to the surface. The hole carriers were entrapped by lattice O²⁻ to form O⁻ and the positive charge was further shared by surface Ti⁴⁺ and O⁻ to form TiO₂^{+(hole)} species. The photogenerated TiO₂^{+(hole)} species were stabilized by the surface hydroxyls under UHV conditions. With continuous XPS characterization and X-ray irradiation on the sample surface, X-ray photon stimulated desorption of OH triggered the relaxation of TiO₂^{+(hole)} species and the metallic Ag was re-oxidized to Ag²⁺ by the TiO₂^{+(hole)} species.

The current study provides an insight on a possible mechanism of X-ray induced chemical reactions on 4wt% Ag/TiO₂ material under UHV conditions, which could be the same or related to reaction mechanisms of TiO₂ photocatalysis under natural sunlight or UV irradiation. Recent studies showed the observation of stabilized titanium hole species is unique for Ag⁺ and Cu²⁺ doped on anatase TiO₂. Other transition metal ion doped on anatase TiO₂ did not show TiO₂^{+(hole)} species from the same XPS experiments. Other semiconductor materials (SiO₂ and Al₂O₃) were also investigated, and no similar phenomenon was observed as well. The reaction process is

irreversible, to regenerate the $\text{TiO}_2^{+}(\text{hole})$ species after the complete relaxation of $\text{TiO}_2^{+}(\text{hole})$ species, the sample needs to be recalcined in flowing air at 450 °C for 2 hours. It is also demonstrated that UV irradiation has similar effects on the generation and relaxation of $\text{TiO}_2^{+}(\text{hole})$ under UHV conditions and the reaction process is X-ray or UV photon fluence dependent. Different weight percentage loading of silver was also investigated and the generation of $\text{TiO}_2^{+}(\text{hole})$ species is highly dependent on the weight percentage loading of silver, and the detailed results will be included in future work.

5.6 References

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Chapter 6 X-ray irradiation and UV irradiation effects

6.1 Abstract

Previous chapters have shown that X-ray irradiation could cause generation of stabilized oxidation state of titanium hole species under ultrahigh vacuum conditions. The current study shows the variation of X-ray irradiation flux made a significant difference to the XPS spectral change rate (reaction rate). There is almost a linear relationship between the X-ray irradiation flux and the reaction rate in terms of X-ray exposure time from six experiments with three different X-ray irradiation intensities repeated twice each. By quantifying the amount of X-ray photons hit the sample surface, the reaction rate was found to be related to the X-ray photon fluence. The dependence of the reaction rate on the X-ray photon fluence is almost identical for all the reaction cases. Besides, UV irradiation was also investigated by coupling a 375 nm UV laser diode on the SAC chamber of the XPS. And the results showed UV irradiation prior to or during the time dependent XPS experiment made a significant difference to the XPS spectral changes. Different UV irradiation intensities and UV exposure time were also examined, and the results showed that the reaction rate (spectral change rate) was also linearly related to the UV irradiation fluence. But the UV irradiation could not relax all the titanium hole species, which is potentially because of the UV photons were not able to reach the deep layers of the Titania support due to its limited penetration depth when compared with X-rays.

The quantitative analysis showed UV and X-ray irradiation have significant difference in photon efficiencies. The results suggested X-ray has much higher efficiencies than UV and it was supposed UV irradiation partially reduced the surface-active Ag(I) species into metallic Ag so that the electrons could not be efficiently captured by silver atoms and as a result the electron and hole separation efficiency was limited.

6.2 Introduction

X-ray photoelectron spectroscopy (XPS) is generally thought to be an essentially non-destructive technique [1,2]. However, XPS studies on some of the metal salts, metal oxides, and organometallic compounds have already shown the X-ray induced decomposition and reduction damage to the materials [3-5]. Even at low X-ray doses, considerable damage may already be encountered. Recently, X-ray induced photocatalytic reactions on 4wt% Ag/TiO₂ was investigated, and the reaction kinetics was also examined for the relaxation of the hole species as indicated by earlier observations in chapter 5. TiO₂ as a promising photocatalyst shows its great potential in photocatalysis over the past several decades. Extensive research efforts have been paid to the development of TiO₂ based photocatalysts under ultraviolet (UV) and visible light irradiation [6-10]. Although various hypothesis and progress have been made by the application of nanocrystalline TiO₂ with different electron scavengers [11-13], the photocatalytic efficiency of a threshold 10% was still challenging [14,15]. According to one extensively cited study [16], the ultrafast recombination of photoelectrons and photo-holes happened within 10 ns, which made 60-80% of the electrons and holes recombine on a nanosecond time scale in TiO₂ colloid [17,18].

In the current study, UV was applied to the X-ray induced photocatalytic reactions on 4wt% Ag/TiO₂ to investigate the UV effects on this phenomenon and quantitatively estimate the UV and X-ray photon efficiencies based on their irradiation intensities and fluxes. Due to the difference in their irradiation wavelength and photon energy, UV irradiation is more intense, and it is mainly adsorbed on the surface layers of 4wt% Ag/TiO₂, which means the interaction between UV photons and the photocatalyst happened mainly near the surface. While the X-ray irradiation has a much higher penetration depth and most of the X-ray photons adsorbed at

deeper layers of the material so that the X-ray induced reaction between X-ray photons and TiO₂ material happened mainly in the bulk layers of the sample [19,20]. These differences make the photon efficiencies significantly different between UV and X-ray.

This study provides a comprehensive investigation of the X-ray and UV irradiation effects on the photocatalytic reactions of 4wt% Ag/TiO₂. By varying the X-ray irradiation power output and by coupling a UV laser diode on XPS, it allows the X-ray and UV irradiation flux varying within several magnitude and the associated reaction kinetics change was investigated by the XPS spectral results. The *in situ* point-to-point investigation also enables analysis of X-ray and UV irradiation effects separately. The X-ray and UV photon efficiencies were estimated by the relaxation of hole species per incident photon basis and the X-ray irradiation showed much higher efficiency than UV irradiation.

6.3 Experimental

6.3.1 Sample preparation

The 4wt% Ag/TiO₂ sample preparation procedure has been reported elsewhere [21]. The as-received 3.2 mm TiO₂ pellets (Saint Gobain Norpro ST6110) were crushed and sieved to 850-1400 µm followed by drying in a convection oven at 110 °C for 24 hours. Silver was introduced by incipient wetness using Ag(I)NO₃ solution followed by drying in a convection oven at 110 °C for 24 hours. The sample was further crushed and sieved to 75-125 µm and then was calcined in flowing air for 2 hours at 450 °C followed by *in-situ* cooling in flowing air for 2 hours.

6.3.2 XPS analysis

The XPS characterization was carried out using the same procedure as described in the earlier studies [21]. Typically, after degassing in the sample treatment chamber (STC) of the XPS instrument, the sample was transferred into the sample analytical chamber (SAC). Time

dependent XPS spectra were taken at the Ti 2p, Ag 3d, O 1s, and C 1s narrow regions to obtain the spectral change in terms of the X-ray irradiation time. For the current experiment, X-ray irradiation emission current was set to be 5 mA, 10 mA, and 15 mA with the high voltage was set to be 15 kV for all the reaction cases. X-ray irradiation flux is proportional to the operating power of the X-ray source [22]. By this setting, the X-ray irradiation photon flux was linearly related with the X-ray irradiation emission current so that the reaction kinetics (spectral change rate) was investigated in a linear manner with the X-ray flux. The current study investigates the X-ray irradiation effect by a magnitude of three of the X-ray irradiation flux due to the restriction of the maximum X-ray source operating power.

The XPS measurements were carried out with a Kratos Analytical Ltd. AXIS Ultra delay lines detector (DLD) X-ray photoelectron spectrometer (XPS). The end station consists of a fast entry load lock, sample treatment chamber (STC) and a sample analytical chamber (SAC) as shown in Figure 6.1. In the current study, a monochromatic Al K_{α} X-ray source was used at an operating power of 15 kV $\times$ 5 mA, 15 kV $\times$ 10 mA, and 15 kV $\times$ 15 mA. The X-ray spot size was consistently set to be 300 $\times$ 700 μm^2 , the angle between the sample and the X-ray source was 35 degrees. Prior to analysis in sample analytical chamber (SAC), the samples were degassed for 80 hours in the sample treatment chamber (STC) at a base pressure of 3.2×10^{-10} torr. No surface cleaning treatment was used in the present experiments. A pass energy of 20 eV with a step of 0.1 eV was used to measure photoelectron core-level spectra of Ti 2p, Ag 3d, O 1s, and C 1s. The overall resolution of the spectrometer in the current setting mode was 0.65 eV measured as a full width half max (FWHM) of the Ag 3d_{5/2} line from a piece of standard silver foil. The spectrometer was calibrated by constraining binding energy of Au 4f_{7/2} at 84.0 eV. Temperature control unit with a thermocouple at the edge of the stage was turned on to maintain the overall

experiment temperature at 25-26 °C. Spectra were measured as a function of X-ray exposure time at different X-ray irradiation intensities. The X-ray irradiation and XPS characterization was turned off at one hour since the beginning of the experiment and the sample was placed under dark and UHV conditions for 2 hours without any treatment. Then the XPS experiment was resumed with continuously X-ray exposure. By this special experiment design, the effect of X-ray irradiation was estimated and separated with possible self-reduction of the sample itself.

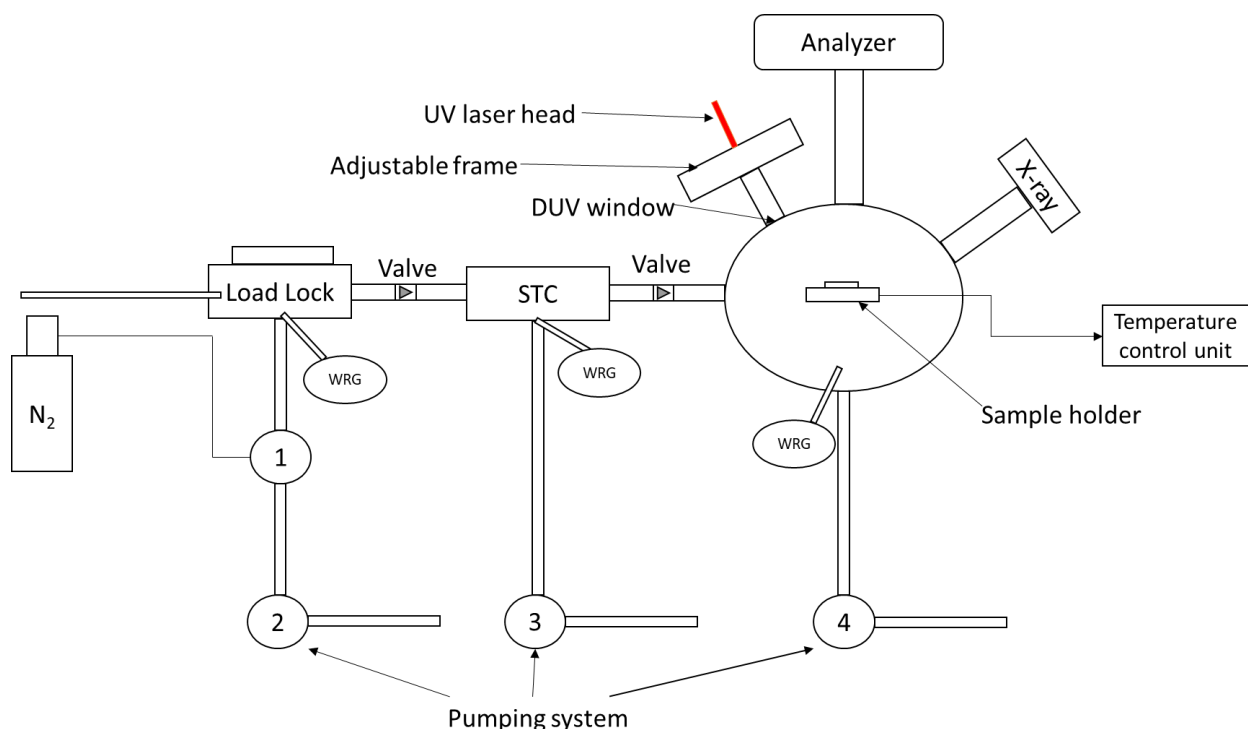


Figure 6.1 Schematic experimental setup for in situ XPS experiment

6.3.2 UV experiments

6.3.2.1 Ex-situ UV pretreatment effect

Ex situ UV pretreatment was carried out using a 365 UV lamp (manufactured by UVP) mounted on the load lock section of XPS. Two 4wt% Ag/TiO₂ specimens were treated by the UV lamp for 1 hour and 2 hours separately before the samples were transferred to the SAC. The base pressure of the load lock section was 1.1×10^{-7} torr. The UV irradiation intensity was

measured to be 1.2 ± 0.1 mW/cm² as indicated by a 365 nm UV radiometer (manufactured by UVP). After the samples were transferred into SAC, *in situ* time dependent XPS characterization of the sample was conducted immediately.

6.3.2.2 In-situ UV irradiation effect

The UV irradiation effect was investigated by means of measuring and interpreting the XPS spectra as a function of *in situ* UV exposure time (0, 5, 10, 20, 30, 60, and 120 minutes) at different UV irradiation intensities (2.9, 5.8, and 11.6 mW/cm²). To understand the UV irradiation effect on the relaxation of the titanium hole species, UV irradiation was conducted after one hour of continuous X-ray irradiation. When the X-ray source was turned off, the UV irradiation was turned on at different intensities and for different irradiation time. XPS spectra of dark reference spot on the same specimen were also measured at the same time (Figure 6.2). The first set of spectra obtained was defined as “untreated state” with no UV exposure. The acquisition time of each spectrum was 60 seconds. To better interpret the effect of UV irradiation on the XPS spectral change, a careful analysis of peak binding energy and peak intensity is the essential factor. Therefore, consistently setting the binding energy scale for the overall photoelectron peak deconvolution was the key procedure for the current study.

The deconvolution of the photoelectron spectra was conducted using the public software package XPSPEAKS 4.1 using same procedure as reported by literatures [3-5]. After subtraction of the Shirley-type background, the spectra were decomposed into their components at suggested binding energies with mixed Gaussian-Lorentzian lines by a non-linear least squares curve-fitting method. The binding energies and full width half max (FWHM) of the peaks were recorded by the fitting results. Surface chemical composition calculations were derived by the deconvoluted peak areas and the atomic sensitivity factors provided by the standard XPS

handbook [22]. The binding energy shifts caused by charging effect was corrected by constraining C 1s line at 284.8 eV.

The XPS spectral change as a function of UV irradiation intensity was conducted on the same sample two times on two different specimens of the same material at each intensity. The results showed reproducible spectral change.

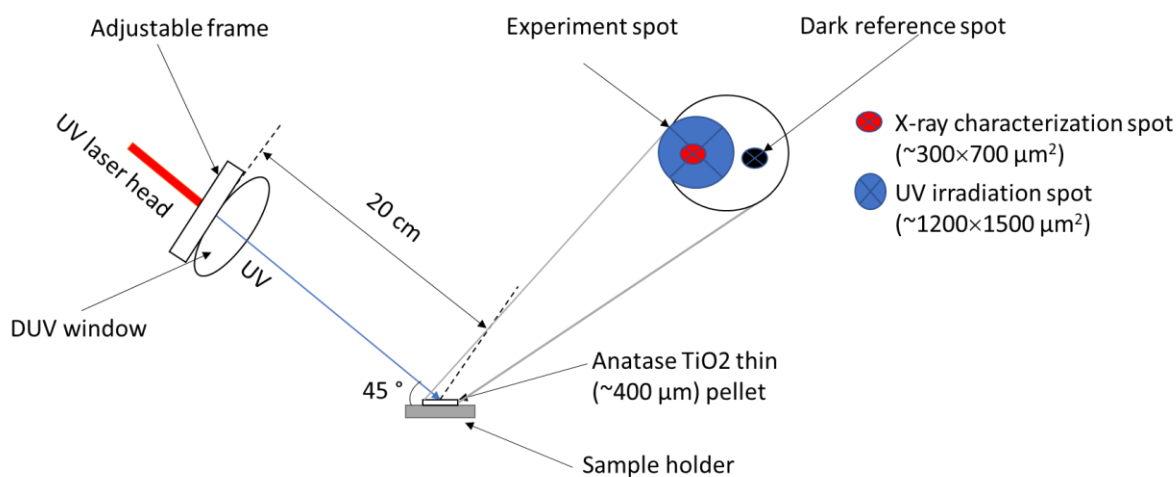


Figure 6.2 Schematic experimental setup for the in situ UV induced XPS experiments

6.4 Results and discussion

6.4.1 X-ray irradiation effects

The X-ray irradiation effect was estimated by the relative peak intensity change of titanium hole species as a function of X-ray exposure time. Figure 6.3 shows the titanium hole species peak intensity change in terms of X-ray exposure time at 5 mA and 15 kV operating power. The first several scans showed an increase of the hole species peak intensity, and it indicated a potential production and migration of holes from the bulk to the surface layers of the 4wt% Ag/TiO₂ sample [23-25].

Figure 6.3 also indicates the hole species was stable during the 2 hours under dark and UHV conditions as the peak intensity of the hole species did not show any significant change. This result confirms the earlier assertion that X-ray irradiation is the triggering source for the generation and relaxation of the electrons and holes on 4wt% Ag/TiO₂ sample.

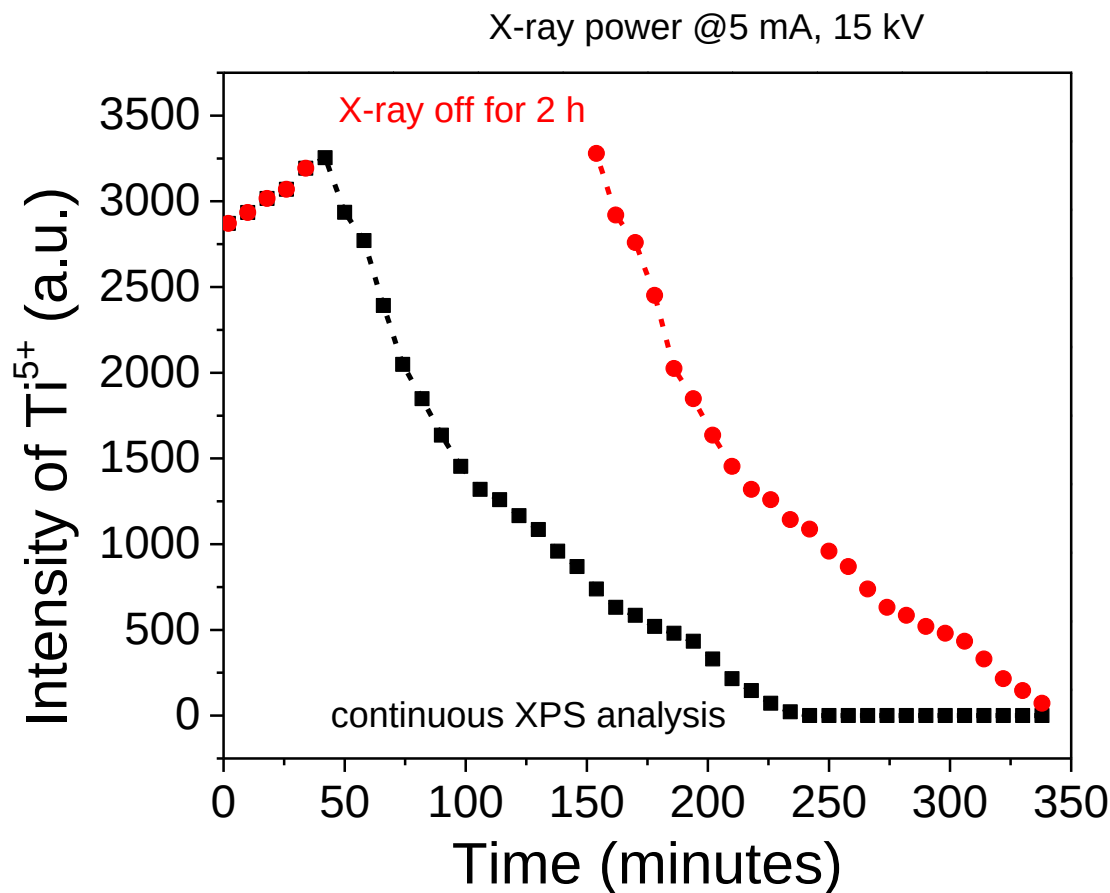


Figure 6.3 Titanium hole species peak intensity change at 5 mA and 15 kV operating power.

Figure 6.4 shows the results at the X-ray operating power at 10 mA×15 kV. No significant change was observed during the 2 hours when the sample was under dark and UHV conditions without any X-ray irradiation. Similar results were observed but the reduction rate of the titanium hole species was faster than that of X-ray operating power at 5 mA×15 kV.

Figure 6.5 shows the hole species peak intensity change in terms of X-ray exposure time at X-ray operating power at 15 mA×15 kV. Again the 2 hours under dark and UHV conditions did not make any significant change to the peak intensity of the hole species. But the overall reaction rate was even faster than the other two reaction cases.

As a result of the comparison among the three reaction cases, the hole species peak intensity change rate was directly related to the X-ray operating power. The higher the X-ray source operating power, the faster the hole species peak intensity change. To better compare the X-ray irradiation effect on the hole species, the results from the three experiments were plotted into one figure on the X-ray exposure time basis as it is shown in Figure 6.6. At 15 mA and 10 mA emission current, the spectral change was almost three and two times faster than at 5 mA emission current.

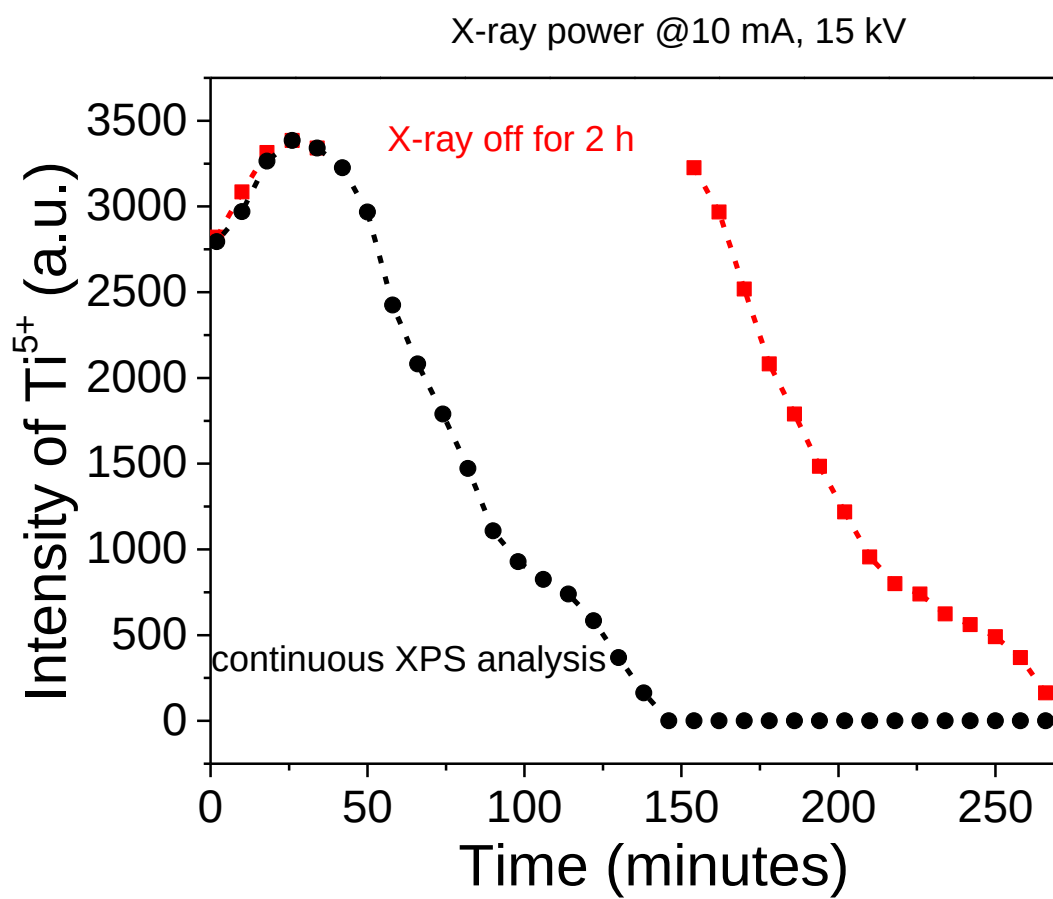


Figure 6.4 Titanium hole species peak intensity change with X-ray exposure time at 10 mA and 15 kV operating power.

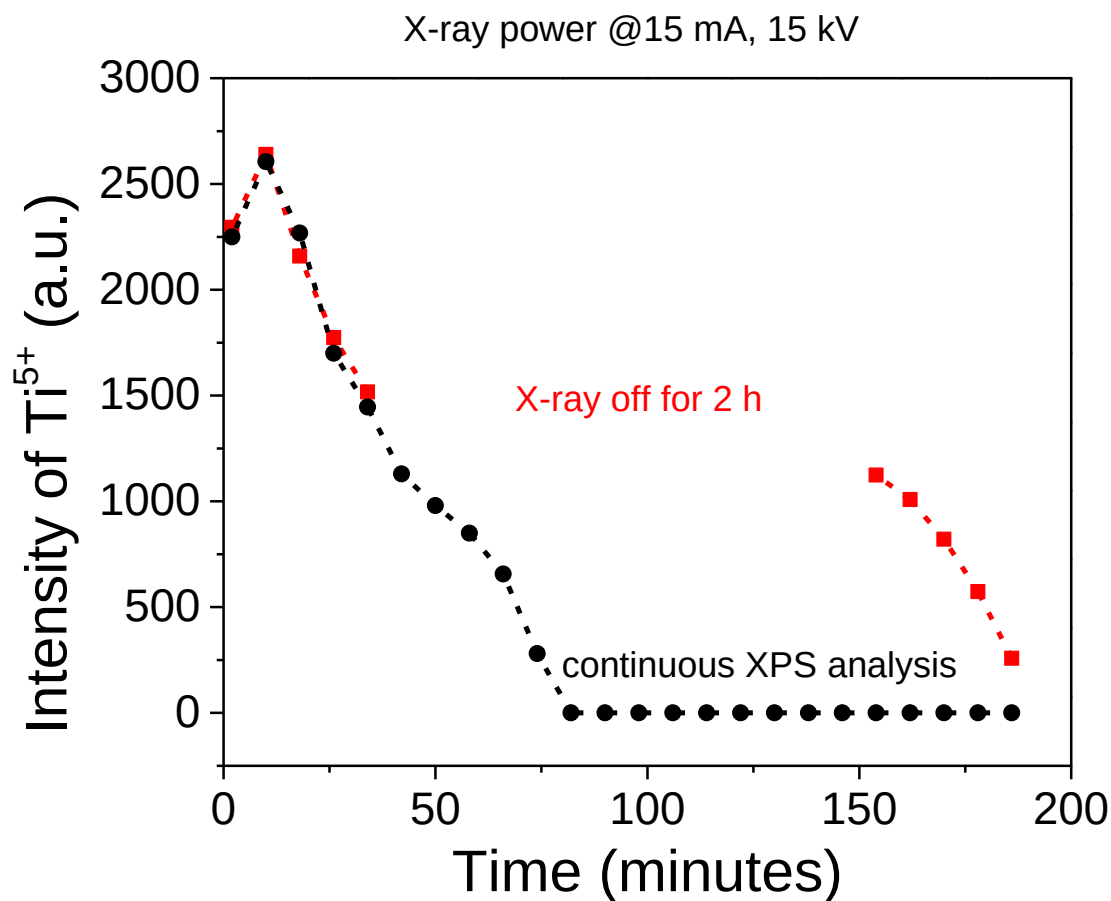


Figure 6.5 Titanium hole species peak intensity change with X-ray exposure time at 15 mA and 15 kV operating power.

To quantitatively analyze the relationship between X-ray operating power and the reaction rate, the XPS spectral change was related to the X-ray fluence based on the number of X-ray photons per mm^2 irradiated on the sample surface at the corresponding X-ray exposure time. Figure 6.7 illustrates the corresponding titanium hole species peak intensity change in terms of X-ray irradiation fluence. As it is shown in Figure 6.7, an almost identical peak intensity change for all the three reaction cases was observed.

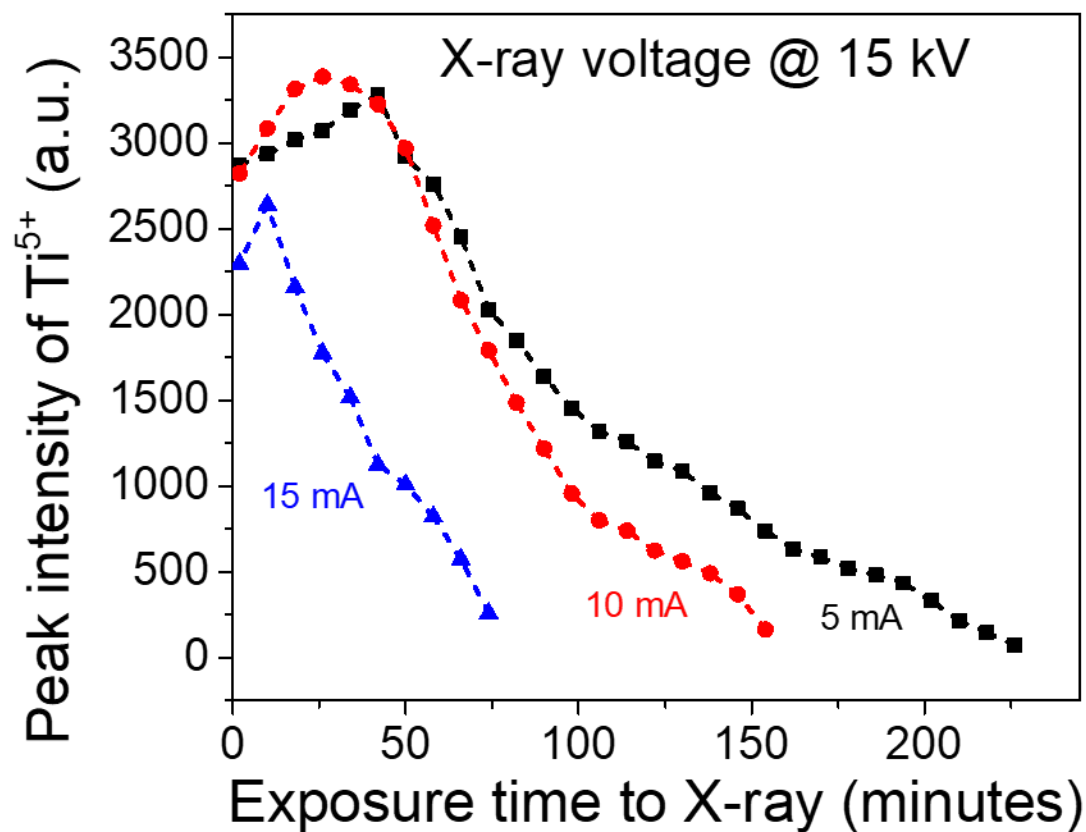


Figure 6.6 Titanium hole species peak intensity change with X-ray exposure time at 5, 10, and 15 mA and 15 kV operating power.

All the above observations and discussions indicate that the excitation and relaxation of the hole species on 4wt% Ag/TiO₂ showed a uniform X-ray photon triggered spectral change rate in terms of X-ray photon fluence, and there is no self-reduction of the hole species when the sample was left untreated under dark and UHV conditions.

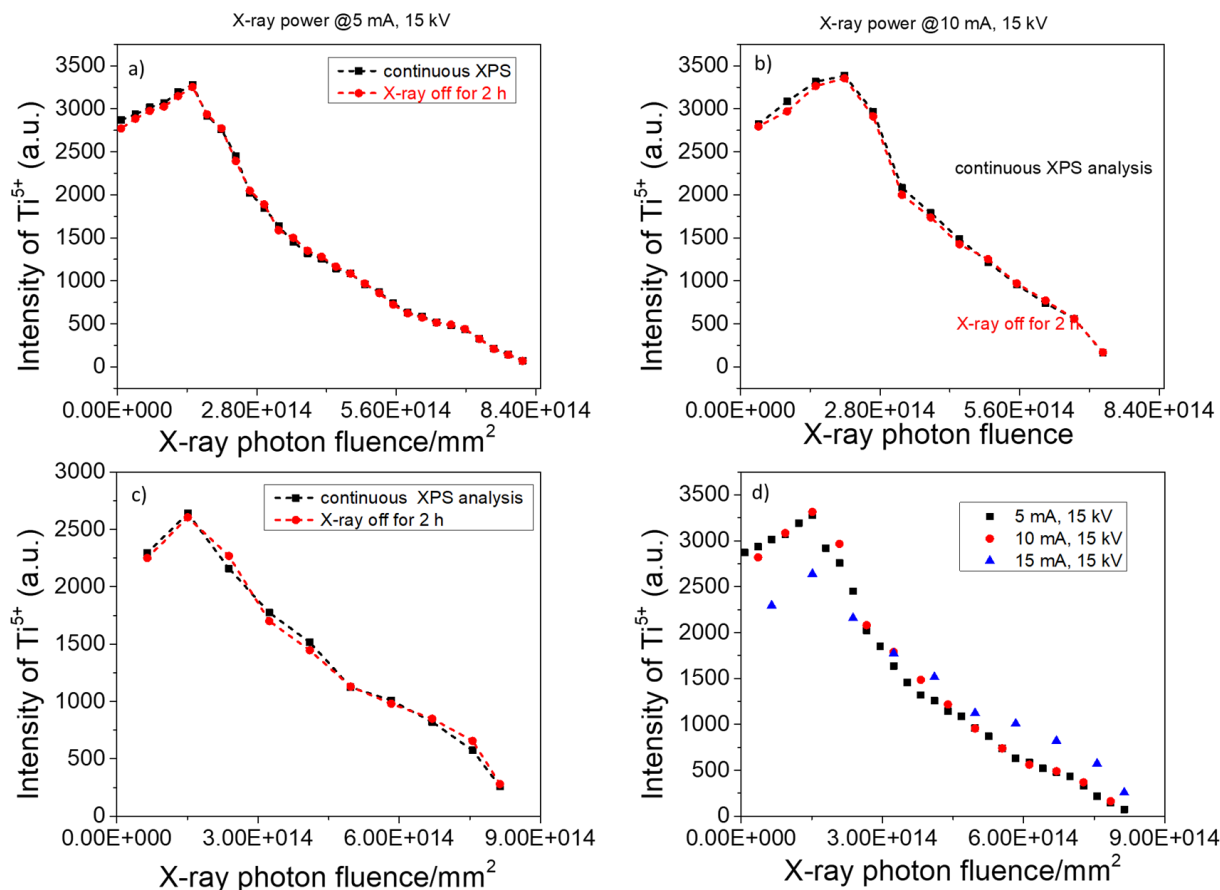


Figure 6.7 Titanium hole species peak intensity change with X-ray photon fluence/mm² at a) 5 mA×15 kV, b) 10 mA×15 kV, c) 15 mA×15 kV, and d) the above three operating power.

6.3.2 UV irradiation effect

6.3.2.1 Ex-situ UV irradiation effect

Figure 6.8a)-d) shows the spectral results of 4wt% Ag/TiO₂ sample pretreated by UV for 2 hours in the load lock section of the XPS. The Ti 2p spectral result (Figure 6.8a)) shows there is no Ti(hole) species and no time dependent spectral change caused by continuous X-ray exposure. From Figure 6.8a), Ti⁴⁺ in TiO₂ is identified by the Ti 2p 1/2 and Ti 2p 3/2 peaks at binding energy 464.5 eV and 458.8 eV with a binding energy difference $\Delta E_b=5.7$ eV. As it is shown in Figure 6.8b), metallic Ag is identified by the Ag 3d 3/2 and Ag 3d 5/2 peaks at binding energy 374.3 eV and 368.3 eV with binding energy difference $\Delta E_b=6.0$ eV. The results clearly illustrate

the ionic Ag^+ was reduced to metallic Ag by UV pretreatment in the load lock of XPS. Without ionic Ag^+ to capture electrons and separate electrons and holes, the photo-holes created by X-ray photons could not be stabilized as they recombined with photoelectrons immediately. The C 1s (Figure 6.8c)) spectra shows the C 1s peaks at binding energy 288.4 eV, 286.2 eV, and 284.8 eV indicating O=C-O etc., C-O etc., C-H etc. species as strongly adsorbed carbon contaminants on the sample surface. The O 1s spectra (Figure 6.8d)) shows O 1s peaks at binding energy 533.4 eV, 531.8 eV, and 529.5 eV indicating adsorbed H_2O etc., OH etc., and lattice O^{2-} species.

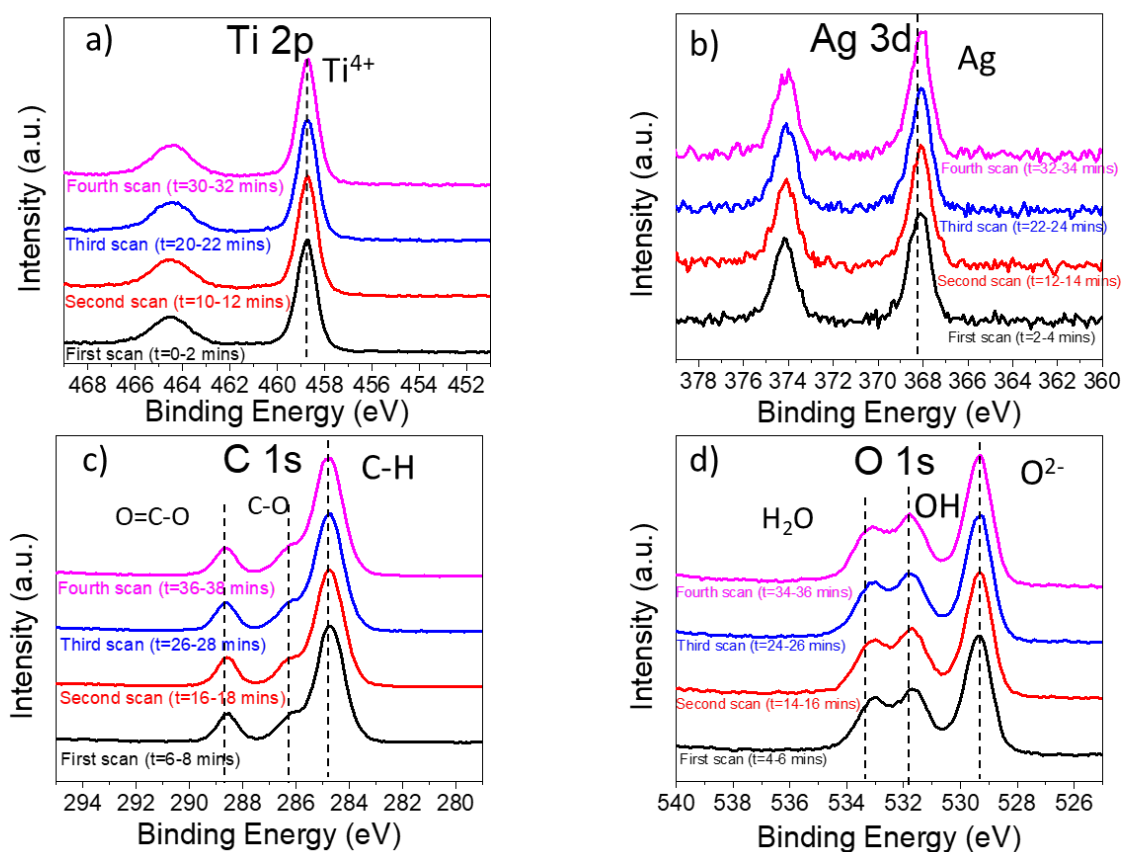


Figure 6.8 In situ time dependent high-resolution XPS spectra of a) Ti 2p, b) Ag 3d, c) C 1s, and d) O 1s of 4wt% Ag/TiO₂ sample pretreated by UV lamp for 2 h in load lock.

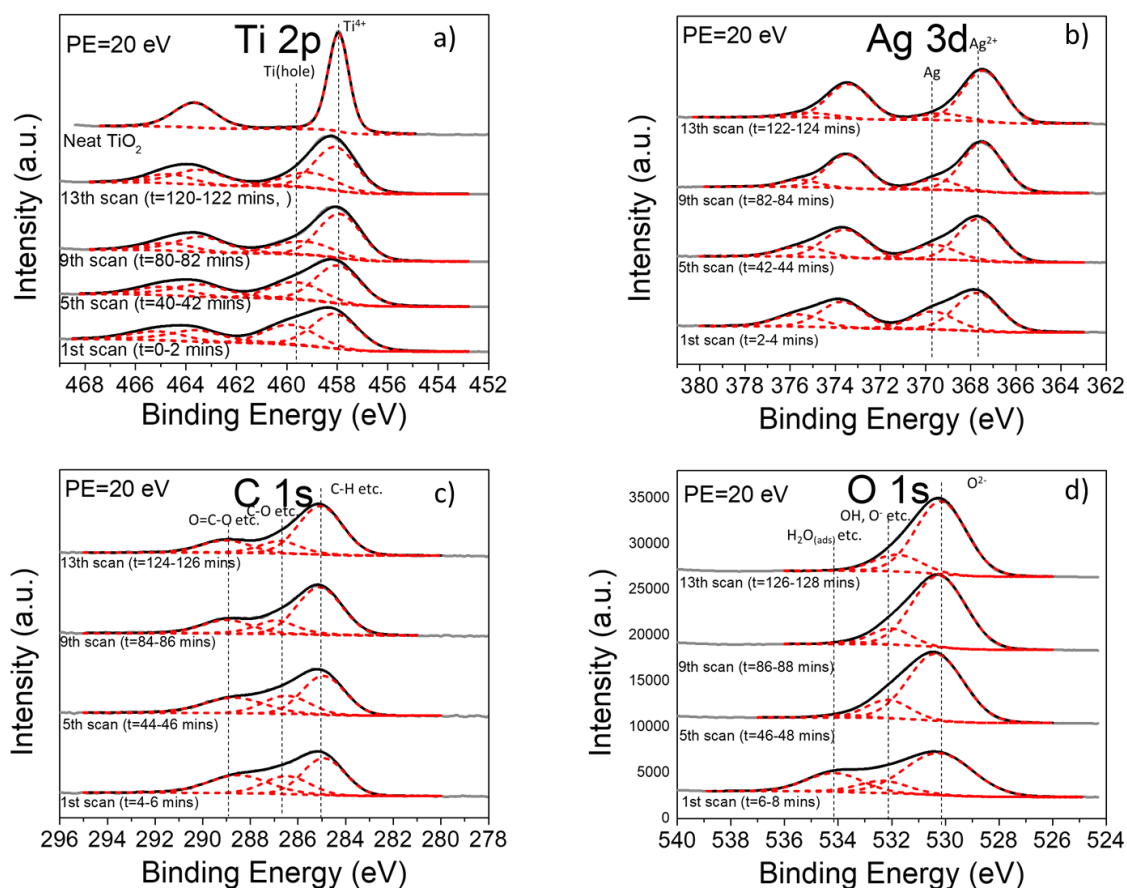


Figure 6.9 In situ time dependent high-resolution XPS spectra of a) Ti 2p, b) Ag 3d, c) C 1s, and d) O 1s of 4wt% Ag/TiO₂ sample pretreated by UV lamp for 1 hour in load lock.

Figure 6.9a)-d) shows the *in situ* time dependent high-resolution XPS spectra of 4wt% Ag/TiO₂ sample pretreated by UV lamp for 1 hour in the load lock of XPS. The results showed Ti(hole) species and time dependent spectral change. The Ti 2p spectra (Figure 6.9a)) shows two pairs of Ti 2p 1/2 and Ti 2p 3/2 peaks at binding energy 465.7 eV and 460.2 eV, 464.2 eV and 458.5 eV with binding energy difference $\Delta E_b = 5.7$ eV each, which indicates Ti(hole) and Ti⁴⁺ species. The time dependent spectral change lasted for 130 minutes with continuous X-ray exposure. All the Ti(hole) species was relaxed to Ti⁴⁺ by the end of the experiment. Correspondingly, the Ag 3d spectra (Figure 6.9b)) shows two pairs of Ag 3d 3/2 and Ag 3d 5/2

peaks at binding energy 375.3 eV and 369.3 eV and 373.3 eV and 367.3 eV indicating Ag metal and Ag^{2+} species. Time dependent spectral change indicated Ag metal was oxidized into Ag^{2+} with continuous X-ray irradiation. The C 1s spectra (Figure 6.9c)) shows C 1s peaks at binding energy 288.4 eV, 286.2 eV and 284.8 eV, which indicate O=C-O etc., C-O etc., C-H etc. species. Time dependent spectral change was observed from Figure 6.9c) that C-H peak intensity increased and the other two peak intensities decreased with continuous X-ray exposure, indicating the loss of C-O containing species and formation of C-H species.

The O 1s spectra (Figure 6.9d)) shows O 1s peaks at binding energy 533.5 eV, 531.7 eV, and 529.5 eV indicating adsorbed H_2O etc., OH etc., and lattice O^{2-} species, respectively. The time dependent O 1s spectral change showed consumption of adsorbed H_2O and production of OH and lattice O^{2-} . The relative large peak intensity of adsorbed H_2O from first scan potentially showed the 1 hour UV pretreatment produced a lot of adsorbed H_2O , but the adsorbed H_2O was desorped and/or was converted into hydroxyls upon X-ray irradiation.

The observations above provided us a potential reaction mechanism that UV irradiation caused photocatalytic reactions on 4wt% Ag/ TiO_2 with the reduction of Ag^+ into Ag and production of adsorbed H_2O .

6.3.2.2 In-situ UV irradiation effect

Besides X-ray irradiation and *ex situ* UV irradiation, *in situ* UV irradiation was also investigated by coupling a UV laser diode on one of the analytical chamber of the XPS instrument (Figure 6.1 and 6.2). The special design of the in situ point-by-point comparison of UV irradiated spot and the dark reference spot allows the analysis and understanding of UV irradiation and X-ray irradiation effects separately. The peak intensity change of titanium hole

species caused by UV irradiation at 2.9 mW/cm^2 in terms of UV irradiation exposure time is shown in Figure 6.10.

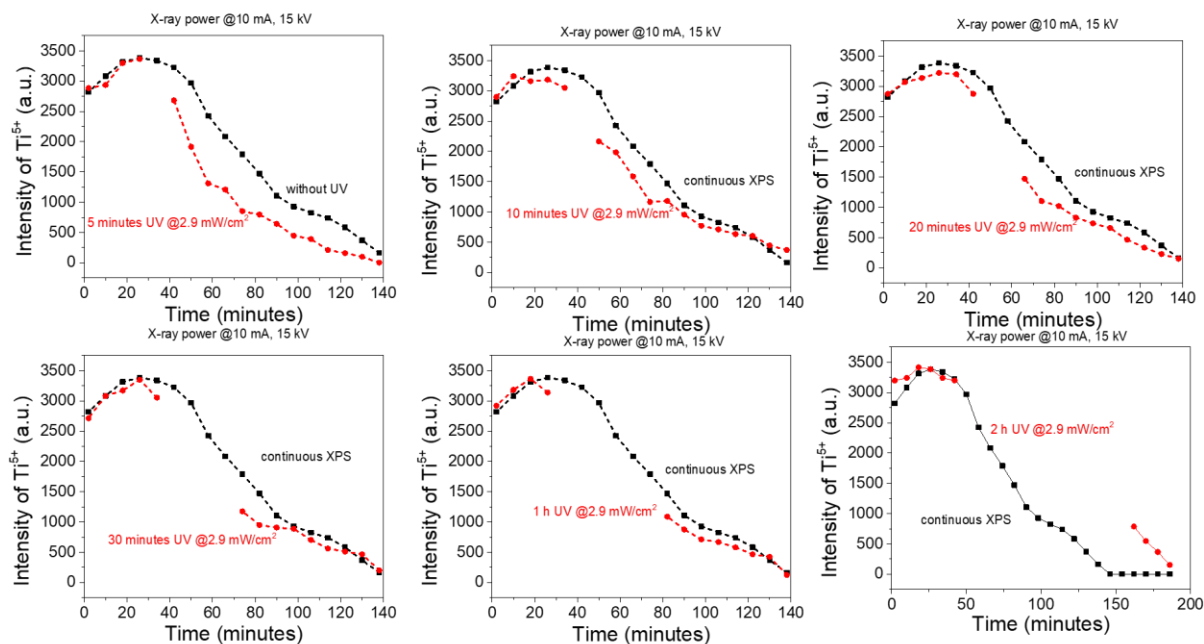


Figure 6.10 Titanium hole species peak intensity change caused by 2.9 mW/cm^2 UV irradiation (red curves) for various UV exposure time compared with dark reference spot (black curve).

The XPS spectral results from 6 different specimens (same material) indicated a similar trend that UV irradiation caused the relaxation of titanium hole species. At short UV exposure time, UV irradiation caused a faster spectral change (red curve) than the X-ray irradiated dark reference spot (black curve). But at longer UV exposure time (60 and 120 minutes), the red curves showed slower titanium hole species peak intensity decrease rate.

Similar results were also observed for UV irradiation at 5.8 mW/cm^2 and 11.6 mW/cm^2 as it is shown in Figure 6.11 and Figure 6.12. At higher UV irradiation intensities, the spectral change caused by short term UV exposure was even faster than at lower UV intensities. But at long term UV irradiation (60 and 120 minutes), the UV irradiation could not relax all the hole species and

the peak intensity of the hole species decreased slower when compared with X-ray irradiation or short term UV irradiation.

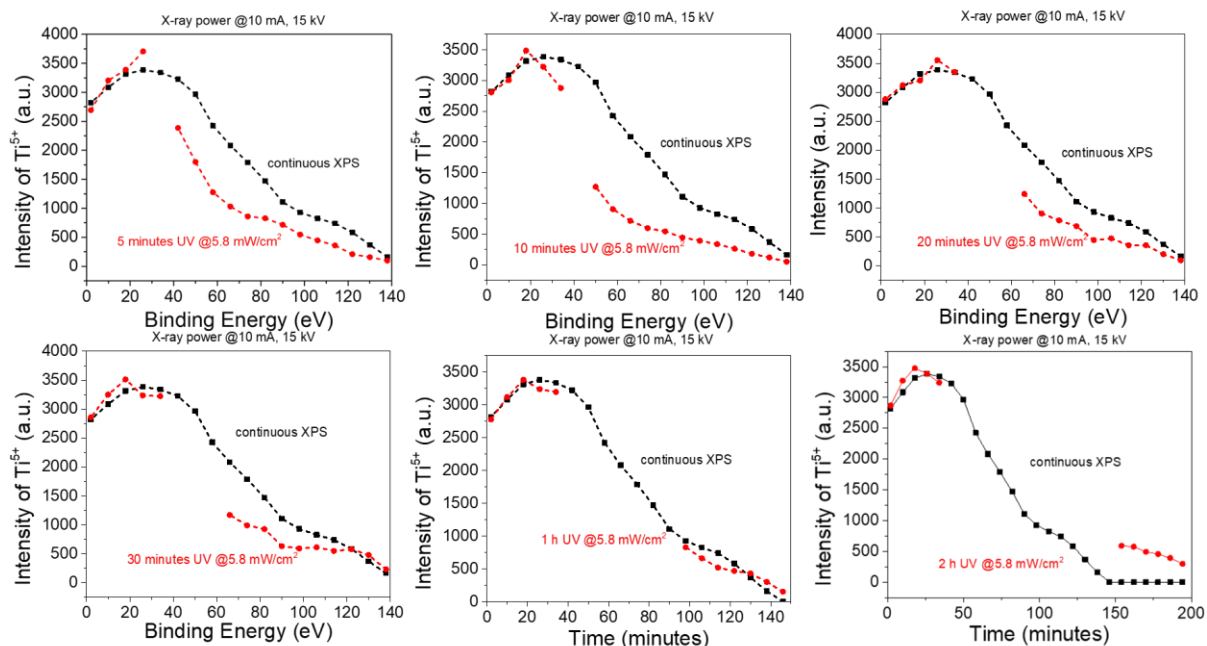


Figure 6.11 Titanium hole species peak intensity change caused by 5.8 mW/cm^2 UV irradiation (red curve) for different UV exposure time compared with dark reference spot (black curve).

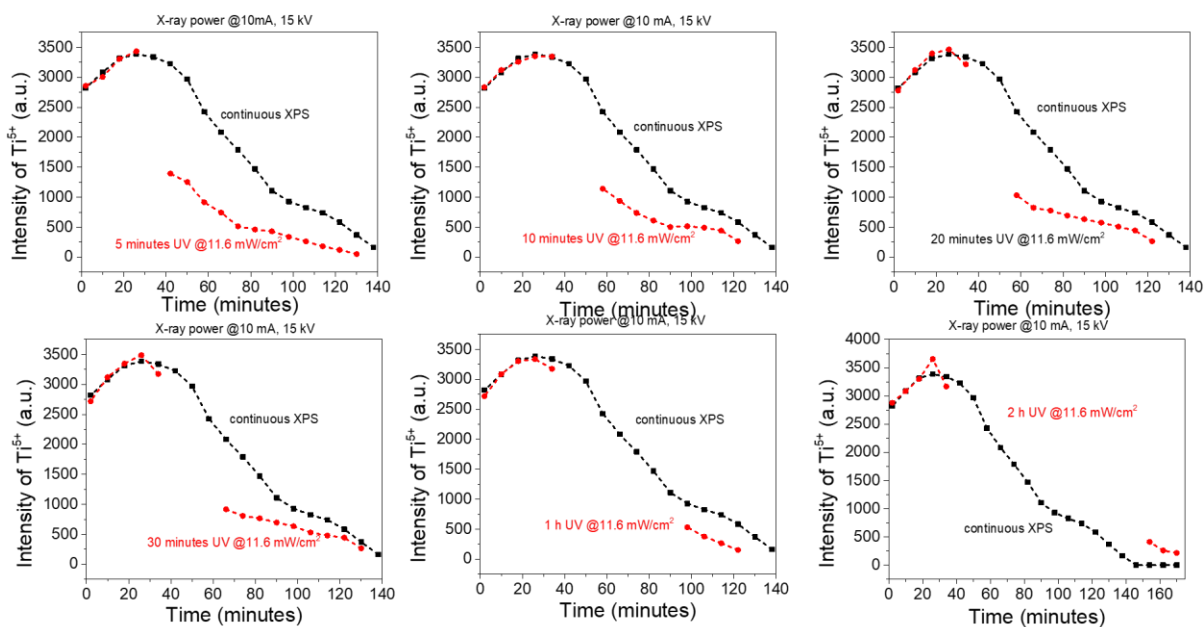


Figure 6.12 Titanium hole species peak intensity change caused by 11.6 mW/cm^2 UV irradiation (red curve) for different UV exposure time compared with dark reference spot (black curve).

From Figure 6.10-6.12, the higher the UV irradiation intensity and the longer the UV exposure time, the more of titanium hole species get relaxed by UV photons. The results are similar as the X-ray irradiation effect. To better investigate the UV irradiation effect on the titanium hole species, the titanium hole species peak intensity change in terms of UV photon fluence is shown in Figure 6.13. The titanium hole species peak intensity change was almost identical for all the three UV irradiation intensities at the same UV photon fluence.

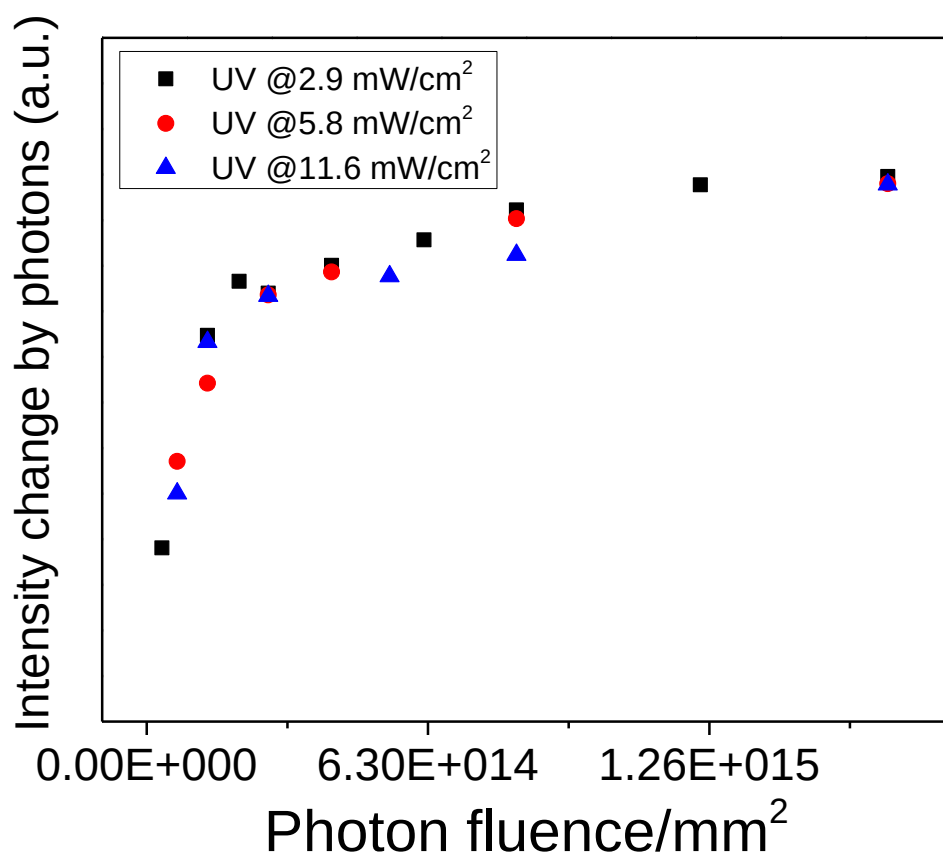


Figure 6.13 Titanium hole species peak intensity change in terms of UV photon fluence

Based on the above observations and analysis, both X-ray and UV photons were able to relax the titanium hole species. But due to the significant difference in photon energies and wavelengths, the X-ray and UV photon efficiencies are potentially different.

Further quantitative investigations of X-ray and UV photon efficiencies and reaction mechanisms need to be carried out to better understand the phenomenon and the potential applications of these novel observations.

6.4.3 Quantitative analysis photon efficiency and potential reaction mechanism

6.4.3.1 Photon efficiency analysis

The X-ray and UV photon efficiency is estimated based on the numbers of titanium hole species being generated and get relaxed per photon basis. The X-ray photon flux and fluence is estimated by the data provided by the XPS manufacture. And linear relationship between the X-ray irradiation flux and the X-ray operating power emission current at the same high voltage was assumed. The UV laser diode was 20 cm from the XPS analysis position with an irradiation angle of 45° to the sample's surface normal. The UV irradiation intensity at the sample position inside the XPS analysis chamber (and through the DUV-UHV window on the vacuum system) was measured to be ca. 65% of the irradiation intensity of that indicated by a UV radiometer at the same distance outside the vacuum system (without the DUV window) and normal to the laser's axis. All photon fluxes and fluences are reported relative to those measured by the UV radiometer inside the analysis chamber at the appropriate incident angle.

Based on the nature of anatase TiO₂ material, the number of Ti atoms per nm³ based on 1 g of TiO₂ can be determined by the following equation.

$$N(\text{Ti}) = \frac{N_A \cdot n(\text{Ti})}{V(\text{TiO}_2)} \quad (3)$$

Where $N(\text{Ti})$ is the number of Ti atoms per m^3 , N_A is the Avogadro constant (atoms/mol), $n(\text{Ti})$ is the mole of Ti (mol), $V(\text{TiO}_2)$ is the volume of 1g anatase TiO_2 (m^3).

The volume of 1 Ti atom = $\frac{1}{N(\text{Ti})}$. Assuming Ti atoms are spherical, the volume of 1 Ti atom = $\frac{4}{3}\pi r^3$. The radius of Ti atom can be calculated. The area of 1 Ti atom = πr^2 . The number of Ti atoms/ nm^2 = $\frac{1}{\pi r^2}$

Similarly, the number of species i atoms per nm^2 can also be determined from the ratio of species i peak area and Ti peak area.

$$I = I_0 n \sigma \lambda(\varepsilon) D(\varepsilon) \int_0^t e^{-t/\lambda} dt \quad (4)$$

$$\frac{n(i)}{n(\text{Ti})} = \frac{I(i) \sigma(\text{Ti}) \lambda(\varepsilon \text{Ti}) D(\varepsilon \text{Ti}) \int_0^t e^{-t/\lambda} dt}{I(\text{Ti}) \sigma(i) \lambda(\varepsilon i) D(\varepsilon i) \int_0^t e^{-t/\lambda} dt} \quad (5)$$

Where I_0 is X-ray flux, n is density of atoms, σ is photoelectron cross-section, I_i is the XPS peak intensity of species i (peak area), $\lambda(\varepsilon)$ is mean free path of energy(ε), $D(\varepsilon)$ is fraction of electrons detected by the analyzer, t is the sample depth from where electrons are ejected.

Table 6.1 X-ray photon efficiency at the photoexcitation stage

X-ray Fluence Photons/ nm^2	Number of titanium holes / nm^2	Change by X- ray photons / nm^2	X-ray photon efficiency
0.36	6.39	6.39	17.74
1.8	6.53	0.14	0.098
3.24	6.71	0.18	0.12
4.68	6.83	0.12	0.083

6.14	7.10	0.27	0.19
7.06	7.30	0.19	0.12

From Equation (5), the number of titanium hole species could be obtained. At the photoexcitation stage of the experiment, the hole species peak intensity showed an increase for all the experiment cases, which indicates the generation and migration of photo-holes from the bulk to the sample surface. After that, the peak intensity of hole species decreased. Thus, the photon efficiency analysis was divided into two stages, where the first stage is photoexcitation and the second one is photo relaxation. The results for the X-ray photoexcitation stage are summarized in Table 6.1. The first scan showed a 17.74 X-ray photon efficiency, which indicates one X-ray photon was able to create at least 17 pairs of electrons and holes. After the first scan and until the X-ray photon fluence reached 15.12 photons/nm², the number of titanium hole species increased slightly, but the photon efficiency was much lower, which potentially because of the recombination of electrons and holes or the accumulation of photo-holes underneath the surface (where XPS could not monitor). For the photo relaxation stage (after 18 photons/nm² X-ray fluence), the titanium hole species was gradually relaxed to Ti⁴⁺ and the X-ray photon showed a similar efficiency for the rest of the photo relaxation stage (Table 6.2).

Table 6.2 X-ray photon efficiency at the photo-relaxation stage

X-ray Fluence Photons/nm ²	Number of titanium holes /nm ²	Change by X-ray photons /nm ²	X-ray photon efficiency
18	7.497	0.799	0.277
35.28	3.23515	3.262	0.141
52.56	1.933525	1.302	0.070

69.84	0.963425	0.970	0.036
81.36	0.1602	0.803	0.057

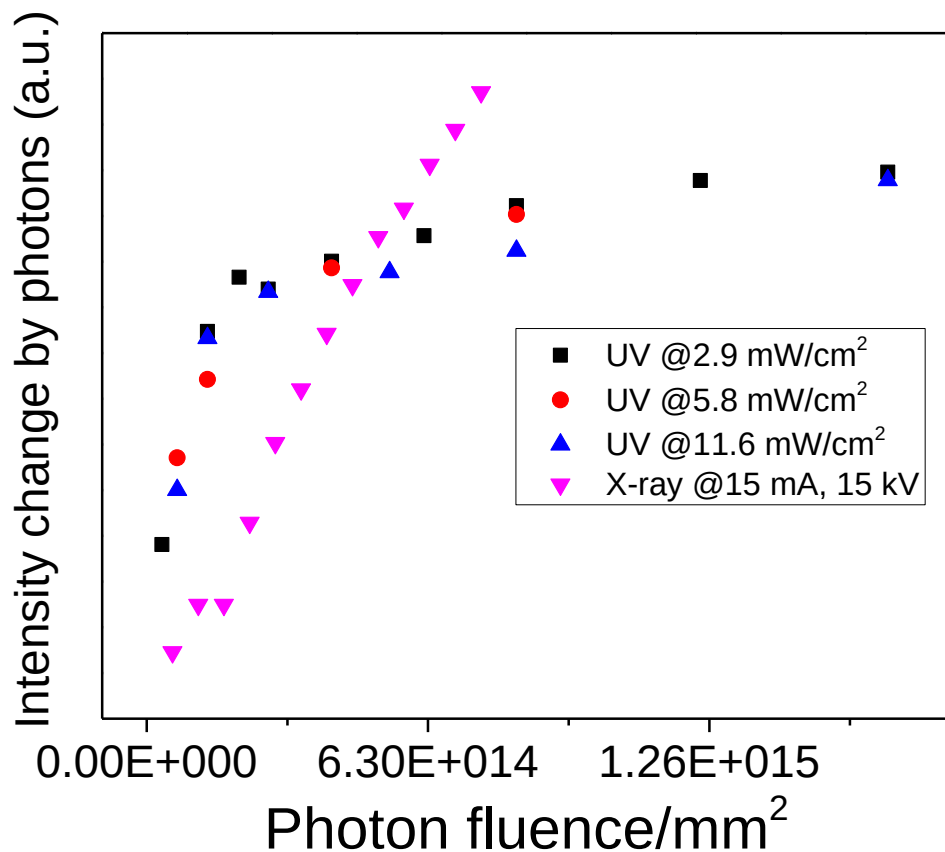


Figure 6.14 Titanium hole species peak intensity change caused by UV irradiation at 2.9, 5.8, and 11.6 mW/cm² in terms of UV photon fluence.

The UV photon efficiency was also investigated using similar methodology. UV irradiation prior to or during the X-ray induced photoexcitation and relaxation of titanium hole species was able to change the reaction dynamics as it is observed and discussed in the earlier sections. In the current study, only the UV induced photo-relaxation of hole species was investigated since the duration of photoexcitation stage was much shorter than the photo-relaxation stage. The UV irradiation was carried out at 18 X-ray photon fluence/nm² where the photo-relaxation initiated.

Short term UV exposure (from 5 minutes to 30 minutes) showed a faster relaxation dynamic than X-ray exposure. But the UV irradiation is more intense than X-ray and so that the UV photon efficiency was much lower than the X-ray photon. UV irradiation showed a decrease trend in photon efficiency at higher UV photon fluence as it is shown in Table 6.3, which potentially indicates the UV photons were only able to interact with the hole species that are close to the surface, but the hole species underneath the surface (beyond the penetration depth of UV photon) were not affected by UV photons.

Table 6.3 UV photon efficiency at the photo-relaxation stage

UV Fluence Photons/nm ²	Change by UV photons /nm ²	UV photon efficiency
0.51	1.56	0.031
2.04	4.16	0.020
3.12	4.82	0.016
4.08	4.67	0.011
6.9	5.01	0.008
9.3	5.32	0.006
12.42	5.69	0.005
18.6	5.99	0.003
24.9	6.10	0.002

6.4.3.2 Potential reaction mechanism

6.4.3.2.1 UV pretreatment

From quantitative analysis of deconvolution results of 4wt% Ag/TiO₂ sample pretreated by UV for 2 hours in load lock, the atomic fraction ratios of oxygen species over Ti⁴⁺ species is summarized in Table 6.4. When compared with neat TiO₂ sample, the atomic ratios of OH/Ti⁴⁺, H₂O/Ti⁴⁺ are much higher for 4wt% Ag/TiO₂ sample pretreated by UV for 2 hours in the load lock. The increased atomic concentrations of OH and H₂O potentially indicated H₂O and OH were the reaction products of the UV induced photocatalytic reactions on 4wt% Ag/TiO₂ sample.

Table 6.4. Atomic fraction ratios of oxygen species over Ti⁴⁺ species of 4wt% Ag/TiO₂ sample pretreated by UV for 2 hours in load lock (10⁻⁷ torr)

Atomic fraction ratio	4wt% Ag/TiO ₂ (After 2 hours UV)	TiO ₂ at 25 °C No UV	TiO ₂ at 25 °C After 2 hours UV	TiO ₂ at 400°C No UV
O ²⁻ /Ti ⁴⁺	2.11	2.07	1.98	2.05
OH/Ti ⁴⁺	1.85	0.49	0.58	0.29
H ₂ O/Ti ⁴⁺	0.97	0.062	0.052	0

Although Ti(hole) species and time dependent spectral change was still observable from 4wt% Ag/TiO₂ sample pretreated by UV for 1 hour in the load lock, an increased atomic concentration of H₂O was still captured by the first O 1s scan after the 1-hour UV exposure. To better analyze the reaction mechanism, atomic fractions between all the species over total titanium species were derived from quantitative analysis as it is shown in Figure 6.15 a)-d).

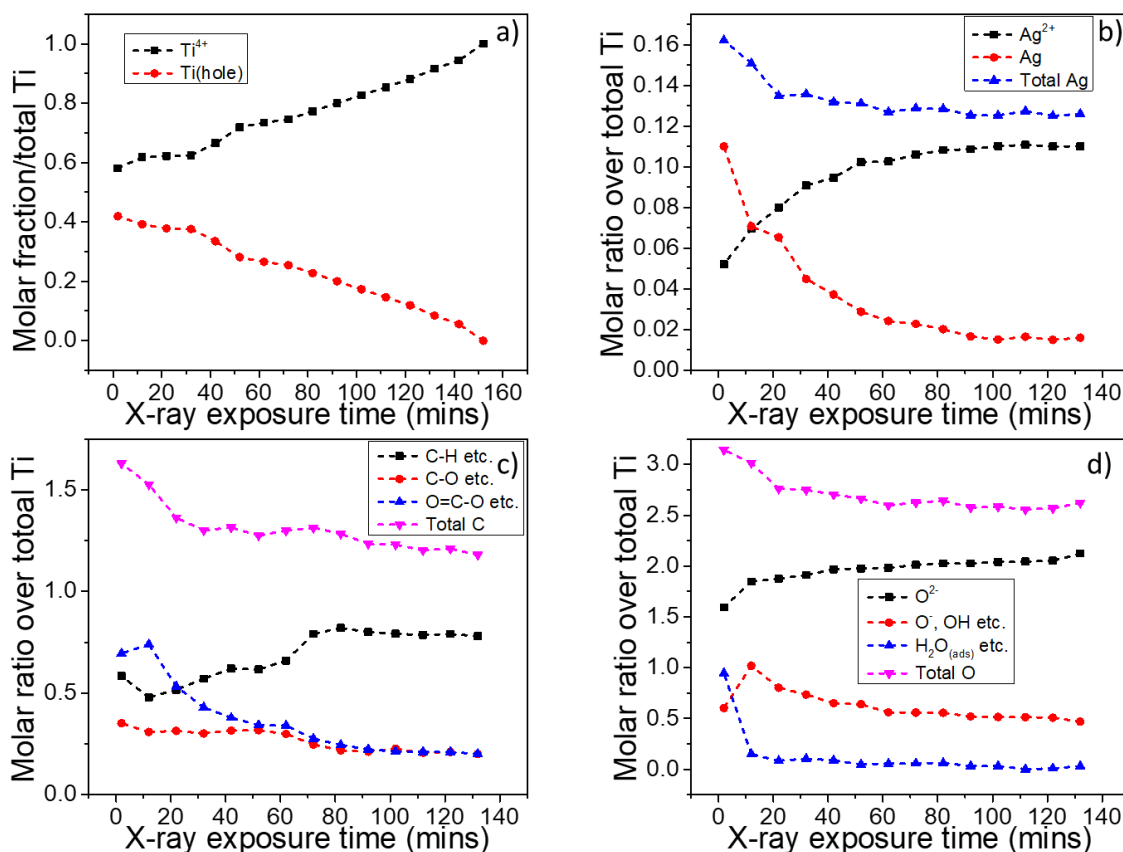


Figure 6.15 Atomic fraction ratios between a) Ti species over total titanium, b) Ag species over total titanium, c) C species over total titanium, d) O species over total titanium.

From first scan, Ti(hole) counts for 42% of total titanium species. Time dependent relaxation of Ti(hole) to Ti^{4+} was observed with continuous X-ray exposure for over 120 minutes. The total O/Ti atomic ratio was 3.14 at first scan with adsorbed H₂O counting for 0.95. Upon X-ray

irradiation, the adsorbed H₂O desorbed quickly as observed from the second scan 10 minutes later.

At the same time, OH/Ti ratio raised from 0.60 to 0.80, which indicated the diffusion and production of OH at the XPS observable surface. The total O/Ti ratios dropped from 3.14 to 2.60 by the end of the reaction process indicating the desorption of oxygen containing gaseous products. The C/Ti ratios also dropped from 1.58 to 1.25 indicating the desorption and decomposition of carbon species by X-ray irradiation.

6.4.4 Potential reaction mechanism

Since the sampling depth of XPS is 5-7 nm [26], the bulk composition at a depth larger than 7 nm was not able to be characterized by XPS. X-ray and UV irradiation have very different absorption cross-sections and transmission depths on TiO₂ as it is shown in Figure 6.16. For X-ray irradiation, the intensity change follows the Scofield absorption equation: $I/I_0 = e^{-(\mu/\rho)x}$, where μ/ρ is the X-ray mass attenuation coefficients, for TiO₂, $\mu/\rho = 2.4 \times 10^{-2}$, and $I/I_0 = e^{-(0.0024x)}$ [27]. For UV irradiation at 375 nm the intensity change follows $I/I_0 = e^{-(0.077x)}$ [28]. At the sampling depth of XPS, only c.a. 3% of UV photons were absorbed and only c.a. 1% of X-ray photons were absorbed. But most of the UV photons were absorbed at c.a. 50 nm transmission depth and the X-ray photons has a much higher transmission depth (c.a. 250 nm). Besides, X-ray photon has a much higher energy than UV photon, so we propose the initial photoexcitation by X-ray photons happened at both the surface layers and the deep layers of TiO₂. The photoelectrons and photo-holes were transferred with different rates to the surface [29-32]. Due to the much higher transfer rate of photoelectrons, photoelectrons reached the surface layers faster than the holes. Those high energy photoelectrons were trapped at surface defect sites of TiO₂. And silver captured most of the photoelectrons and got reduced to metallic silver as it is

indicated by the color change of the sample and the XPS spectral results. The black spot on the originally white sample surface indicates where the sample was exposed to X-ray irradiation and the color change indicates a reduction of ionic Ag(I) to metallic nanosized silver particles. Adsorbed water was another important feature for the photocatalytic reactions as it is indicated by TGA from the earlier studies. Electrons were captured and transferred to adsorbed water to form hydrogen and hydroxyls, and the latter was strongly bonded to the photo-holes to stabilize them [33-35].

After all the ionic Ag(I) was consumed, the photo-relaxation of the hole species initiated. The additional photoelectrons from deep bulk layers of the sample were transferred to the surface layers where XPS can monitor, and the photoelectrons caused photo desorption of hydroxyls in form of H₂O [33-35]. With insufficient hydroxyls to stabilize the holes, the relaxation of hole species occurred associated with a re-oxidation of metallic silver into Ag²⁺ as indicated by XPS Ag 3d spectral results. The anomalous spectral change and the X-ray induced photocatalytic reactions on 4wt% Ag/TiO₂ was observed only with silver as the dopant by incipient wetness impregnation and calcination at 450 °C on a nano porous Titania support. Based on a previous DFT study [36] of the bonding structure of 4wt% Ag/TiO₂ and several control experiments reported in earlier studies, we suppose the special bonding between TiO₂ and silver associated with adsorbed hydroxyls/water is the key for the stabilization of the photo-holes on TiO₂. Without such a special bonding structure, no similar result was observed.

For UV irradiation, the photocatalytic reaction mechanism is different because of its relative shorter transmission depth. In case of UV pretreatment of the sample before X-ray exposure, most of the UV irradiation interacted with silver other than TiO₂. UV induced photoreduction of ionic silver has been well studied and documented in the past. With UV interaction, the special

bonding between ionic silver and TiO_2 was broken and the ability and efficiency of ionic silver to separate electrons and holes was reduced. When UV irradiation was introduced to the sample during the photo-relaxation period, the XPS spectral results showed short term UV exposure accelerated the relaxation of hole species. This is potentially due to the UV induced photo desorption of hydroxyls in form of H_2O . The mechanism and reaction pathway are potentially the same as X-ray induced photo-relaxation of hole species, but UV irradiation is more intense than X-ray so that the overall reaction rate monitored by XPS was accelerated. After a certain period of UV exposure (60 mins), UV irradiation showed a much slower reaction rate for hole relaxation. This is potentially due to the penetration depth of UV is far less than X-ray so that those stabilized hole species at deep layers were not affected by UV irradiation. And during the following XPS characterizations, those hole species were transferred to the XPS observable depth so that the hole species were still observed by XPS.

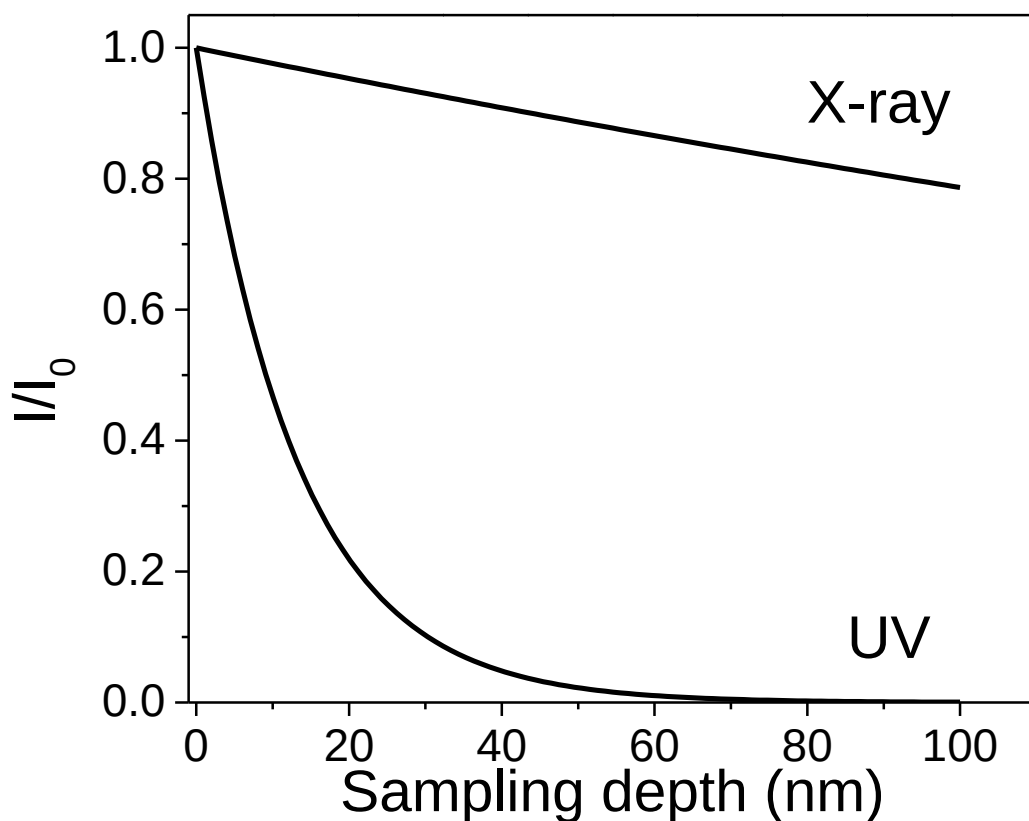


Figure 6.16 X-ray and UV intensity change with the transmission depth

6.5 Conclusion

In this chapter, the X-ray and UV irradiation effect on 4wt% Ag/TiO₂ and the time dependent photoexcitation and photo-relaxation of titanium hole species were investigated and discussed. So far, under UHV condition, only the X-ray and UV irradiation were able to produce and relax the titanium hole species. It seems to be no significant self-relaxation of the stabilized hole species under UHV without any treatment of the excited sample from the XPS study, which potentially means the photo-holes were stabilized under ultrahigh vacuum condition by hydroxyls. Different X-ray irradiation fluxes were examined, and the results showed a linear increase of the spectral change rate by X-ray irradiation flux. Further analysis of the reaction

rates showed a universal change rate with the X-ray irradiation fluence. Photoexcitation and accumulation of hole species on the surface layers persisted for about 1 h under X-ray operating power at 10 mA and 15 kV. After that, photo-relaxation of hole species initiated with further X-ray exposure.

UV irradiation prior to or during the X-ray induced photocatalytic reactions on 4wt% Ag/TiO₂ showed significant impact on the phenomenon. *In situ* point-by-point XPS investigation of UV irradiated spot and dark reference spot at different UV irradiation intensities and UV exposure time were examined. The UV irradiation analysis also showed a photon fluence dependence of the reaction dynamics.

Both X-ray and UV photon efficiency was estimated from the quantitative analysis of XPS results. The first XPS spectrum obtained under 60 seconds of X-ray exposure showed one X-ray photon was able to generate at least 17 pairs of electron and hole. Further XPS characterizations showed more photogeneration, migration and accumulation of hole species on the surface layers of the sample. During the photo-relaxation stage, X-ray photon efficiency dropped gradually. UV photon efficiency analysis also showed at higher photon fluence, the UV photon efficiency was lower.

The potential reaction mechanism of X-ray and UV irradiation is proposed according to the analysis and discussion from this study as well as earlier studies. Due to their significant difference in photon energies and transmission depth, the reaction mechanisms were supposed to be different for the photoexcitation stage. X-ray excitation happened both at the surface and in the deep bulk layers of the sample followed by transfer and migration of electrons and holes to the XPS observable surface. The special bonding between ionic silver and TiO₂ was the key for the separation of electrons and holes as well as the stabilization of the hole species on the surface.

UV irradiation pretreatment reduced the ionic silver atoms into metallic silver and destroyed the bonding between ionic silver and TiO_2 , resulting in decreased capability of 4wt% Ag/ TiO_2 to separate and stabilize holes. During the sample relaxation stage, both UV and X-ray irradiation caused photo desorption of hydroxyls. Short term (<60 mins) UV exposure has a higher hole relaxation rate than X-ray, which is potentially because UV irradiation is more intense than X-ray irradiation. But after 60 mins of UV exposure, UV irradiation has a slower hole relaxation rate than X-ray, which is potentially due to UV irradiation has a smaller penetration depth and could not reach and affect stabilized holes at the deep layers. Those holes could be transferred to the XPS observable surface during XPS characterization.

Recent studies also show this phenomenon is highly dependent on the weight percentage loading of Ag on TiO_2 . This phenomenon is also observed on Cu/ TiO_2 sample, but not on other transition metal (Ni, Pd, etc.) doped on TiO_2 support. Other high surface area and porous semiconductor support materials (SiO_2 , Al_2O_3 , etc.) were also examined, and no similar phenomenon was observed. The results and progress will be reported in future studies.

6.6 Reference

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Chapter 7 The effect of transition metal ions on the time dependent observation of stabilized hole species on TiO₂

7.1 Abstract

Our earlier studies have shown that ionic silver (Ag(I)) introduced by incipient wetness impregnation onto anatase TiO₂ support is the key factor for the time resolved X-ray induced photocatalytic excitation and relaxation of hole species on TiO₂. Previous research efforts from our laboratory have shown that there is a linear relationship observed at lower loadings of less than 0.03 mole fraction (<4 wt%) of silver, which suggests that silver is highly dispersed on the surface defective sites of the titanium dioxide support up to a certain critical value. In the current study, different weight percentage of silver loading onto anatase TiO₂ support were prepared and examined by XPS to reveal the impact of silver loadings on the stabilized hole species phenomenon. The results showed the titanium hole species concentration was determined by the dispersion of silver atoms on Titania support until a saturated dispersion of one monolayer of silver was reached (4wt%). From 1wt% to 4wt% loading of silver, the amount of titanium hole species generated by X-ray irradiation was proportional to the surface concentration of silver atom. After 4wt%, silver becomes to aggregate on TiO₂ surface, and so that the amount of titanium hole species generated by X-ray irradiation did not show any significant increase. The results potentially indicate only up to one monolayer of ionic Ag(I) was directly involved in the photocatalytic reactions due to their direct interaction with photoelectrons.

Besides silver, other transition metal ions and other semiconductor support materials were also investigated and similar spectral change was only observed for Cu/TiO₂ sample. Experiments on Ni/TiO₂ and Pd/TiO₂ did not show any evidence of the generation of stabilized hole species on TiO₂ from in situ time dependent XPS characterizations. Time dependent XPS

characterization of Pt/TiO₂ sample showed a small portion of stabilized hole species were generated by X-ray irradiation. The same XPS study on Ag/SiO₂ and Ag/Al₂O₃ samples did not show any time dependent spectral change nor the generation of hole species, which indicates the unique photoelectrical properties of the redox Ag(I) ion and the band structure of anatase TiO₂ with surface defective sites were the key factors for the stabilized hole species phenomenon. The current study potentially provides direct evidence to explore the capacity and efficiency of different transition metal ions to transfer and separate electrons and holes on anatase TiO₂.

7.2 Introduction

Silver ion (Ag⁺), due to its unique photoelectrical properties and sensitivity to photons, has been widely applied to the photography and X-ray photography for over a century [1-3]. Silver Halides (AgCl, AgBr, AgI, etc.) have been used as the key component of photographic film material. When an X-ray photon strikes a silver halide crystal, the supplementary electron of the large Halide ion will be kicked out. But the supplementary electron has too much energy to be captured by the silver ion, it will roam around the entire crystal. The electrons will be finally trapped by defective sites of the crystal and form a negative electric field that can attract the positive silver ions. Silver ions will be reduced to metallic silver atom when combined with an electron. The latent image is formed upon the gathering of metallic silver atoms. The defective sites of the crystal structure and the unique photoelectric properties of silver ion (Ag⁺) are the key factor for its anomalous sensitivity and reactivity with X-ray photons of the Silver Halides.

Incipient wetness impregnation methodology has been widely applied to the preparation of doped support materials as a surface modification technique [4-6]. Highly dispersed homogenous layers of dopant could be deposited onto the support material surface and the particle size of dopant species could be as small as several nanometers. Incipient wetness impregnation of silver

on TiO₂ has been widely used in our laboratory [7-9] for the past decades as an efficient surface modification method to improve the catalytic capacity of anatase TiO₂ support. Calcination at 450 °C in flowing air allowed silver ions to fill the surface defective sites on anatase TiO₂ support and created additional surface hydroxyls [10]. Most of the impurities on the Titania surface were also removed during the calcination procedure. Previous studies [7-9] on adsorptive removal of sulfur heterocycles in liquid model fuels have shown the addition of silver could improve the desulfurization capacity of anatase TiO₂ adsorbent by up to 80%. Previous FTIR and XPS studies [9,10] showed silver was bonded to TiO₂ as Ag(I)OH. A DFT study [8] also showed the existence of surface hydroxyls to modify the TiO₂ surface and enhance the desulfurization capacity of the sorbent. Zenda et, al. [9] performed a systematic study on the dispersion of silver on anatase TiO₂ with different weight percentage loading of silver by means of XPS characterization. They reported a linear relationship between the peak intensity ratio of Ag and Ti was observed at lower loadings of less than 0.03 mole fraction (<4 wt% Ag), which suggests that silver is highly dispersed on the titanium dioxide support up to a certain critical value.

Besides silver, doping with other transition metal ions on Titania support has been more and more popular for the photocatalytic applications of TiO₂ material. Tseng, I-Hsiang et, al. [12] investigated the photocatalysis of Cu/TiO₂ in CO₂ photoreduction and revealed that the primary Cu(I) served as the active site for the promoted photocatalytic performance for the photoreduction of CO₂. Ying Li et, al. [13] reported a significant enhancement in photocatalytic performance of photocatalytic reduction of CO₂ with H₂O on mesoporous silica supported Cu/TiO₂ catalysts. The addition of Cu(I) species increased the overall CO₂ conversion efficiency as well as the selectivity to the production of CH₄. Rossano Amadelli et, al. [14] modified commercial TiO₂ (Degussa, P-25) with incipient impregnation of cobalt acetate and the

performance of TiO₂ as a photocatalyst in the degradation of 4-chlorophenol and Bisphenol A was significantly enhanced. Besides, they also reported a more active efficiency for the reduction of O₂ in the dark by the addition of cobalt on TiO₂. Wan ting Chen et, al. [15] demonstrated a low-cost Ni/TiO₂ photocatalyst that can efficiently harvest solar energy and generate H₂ from ethanol-water mixtures under UV excitation. According to their study, 0.5 wt% Ni/TiO₂ catalyst displayed superior photocatalytic activity to a 2wt% Au/TiO₂ catalyst and Ni/TiO₂ is a promising alternative to M/TiO₂ (M=Pd, Pt or Au) photocatalysts. Bahruji et, al. [16] investigated photocatalytic evolution of hydrogen from a variety of alcohols over Pd/TiO₂ catalysts and explored the reaction mechanism by monitoring the reaction products by mass spectrometry. Bowker et, al. [17] performed an experimental and mathematical study on the photocatalytic degradation of methanol on Pd/TiO₂ catalyst under anaerobic conditions. According to their study, CO₂ and H₂ are the final products but the reaction was limited due to the blockage of the Pd by adsorbed intermediate CO. The role of light is to produce a reactive form of oxygen on the support, which cleans off CO from the Pd at the boundary. Yu, Jiaguo et, al. [18] investigated hydrogen production by photocatalytic water splitting over Pt/TiO₂ nanosheets with exposed (001) facets and found the addition of deposited Pt exhibited a much higher photocatalytic activity than Degussa P25 TiO₂ and pure TiO₂ nanoparticles prepared in pure water. Kumar, S. Girish and L. Gomathi Devi [19] reported in a review article on modified TiO₂ photocatalysis under UV/Visible light with selected results and related mechanisms on interfacial charge carrier transfer dynamics that the order of activity for metal ions in the modified Titania followed the sequence Fe³⁺>Cu²⁺>Ni²⁺>Cr³⁺ which was well in agreement with their reduction potentials.

In the current study, the effect of weight percentage loading of silver was investigated and *in situ* time dependent XPS characterization was also investigated for different transition metal ions

doped on Titania support. Same incipient wetness impregnation and 450 °C calcination in flowing air method was used to prepare the photocatalysts. The stabilized titanium hole species were only observed with Cu and Ag doped Titania, but Ni and Pd doped Titania showed no spectral results of hole species on XPS. Other semiconductor support materials were also investigated, and the results of Ag/Al₂O₃ and Ag/SiO₂ did not show hole species from XPS. The dispersion of silver atoms on TiO₂ surface and the relative photocatalytic activity of the transition metal ions on TiO₂ were supposed to be the reason for such observations.

7.3 Experimental

7.3.1 Sample preparation

The sample preparation steps are the same as it is described elsewhere [9]. Typically, the as received 3.2 mm TiO₂ pellets (Saint Gobian Norpro) were grounded and sieved to 850-1400 µm followed by drying in a convection oven at 110 °C for 24 hours. Then the transition metal ions were introduced by incipient wetness impregnation using the corresponding transition metal ion nitrate solutions followed by drying in a convection oven at 110 °C for another 24 hours. Then the sample was further grounded and sieved to 75-125 µm followed by calcination in flowing air at 450 °C for 2 hours. The sample was treated by in situ cooling using flowing air for another 2 hours.

Silver at 1wt%, 2wt%, 4wt%, 6wt%, 8wt%, and 10wt% on Titania samples and Cu/TiO₂, Ni/TiO₂, Pd/TiO₂, Pt/TiO₂, Ag/Al₂O₃, and Ag/SiO₂ samples that have the same atomic fraction of metal ions as that of Ag in 4wt% Ag/TiO₂ were prepared for the *in situ* time dependent XPS experiments.

7.3.2 In situ time dependent XPS characterization

Same XPS characterizations as reported in chapter 5 and chapter 6 were carried out for the as-prepared transition metal/TiO₂, Ag/SiO₂, and Ag/Al₂O₃ samples. Typically, after degassed in the sample treatment chamber (STC) of the XPS instrument at a background pressure of 3.2×10^{-10} torr, the sample was transferred into the sample analytical chamber (SAC) for the following XPS characterizations. High resolution time dependent XPS spectra were measured every 10 minutes at the Ti 2p, Ag 3d (Cu 2p, Ni 2p, Pd 3d, and Pt 4f), O 1s, and C 1s narrow scans to obtain the spectral change in terms of the X-ray irradiation time. For the current experiment, X-ray irradiation operating power was set to be 10 mA, 15 kV for all the experiment cases.

The XPS experiments were carried out with a Kratos Analytical Ltd. AXIS Ultra delay lines detector (DLD) X-ray photoelectron spectrometer (XPS). The end station consists of a fast entry load lock, a sample treatment chamber (STC) and a sample analytical chamber (SAC). In the current study, a monochromatic Al K α X-ray source was used at an operating power of 15 kV $\times$ 10 mA. The X-ray spot size was consistently set to be 300 $\times$ 700 μm^2 , the angle between the sample holder and the X-ray source was 35 degrees. Prior to analysis in sample analytical chamber (SAC), the samples were degassed for 80 hours in the sample treatment chamber (STC) at a base pressure of 3.2×10^{-10} torr. No surface cleaning treatment was used in the present experiments. A pass energy of 20 eV with a step of 0.1 eV was used to measure photoelectron core-level spectra. The overall resolution of the spectrometer in the current setting mode was 0.65 eV measured as a full width half max (FWHM) of the Ag 3d_{5/2} line. The spectrometer was calibrated by constraining binding energy of Au 4f 7/2 line at 84.0 eV. Temperature control unit with a thermocouple at the edge of the stage was turned on to maintain the overall experiment temperature at 25-26 °C. Spectra were measured as a function of X-ray exposure time.

7.4 Results and discussion

7.4.1 XPS analysis for different weight percentage loading of silver

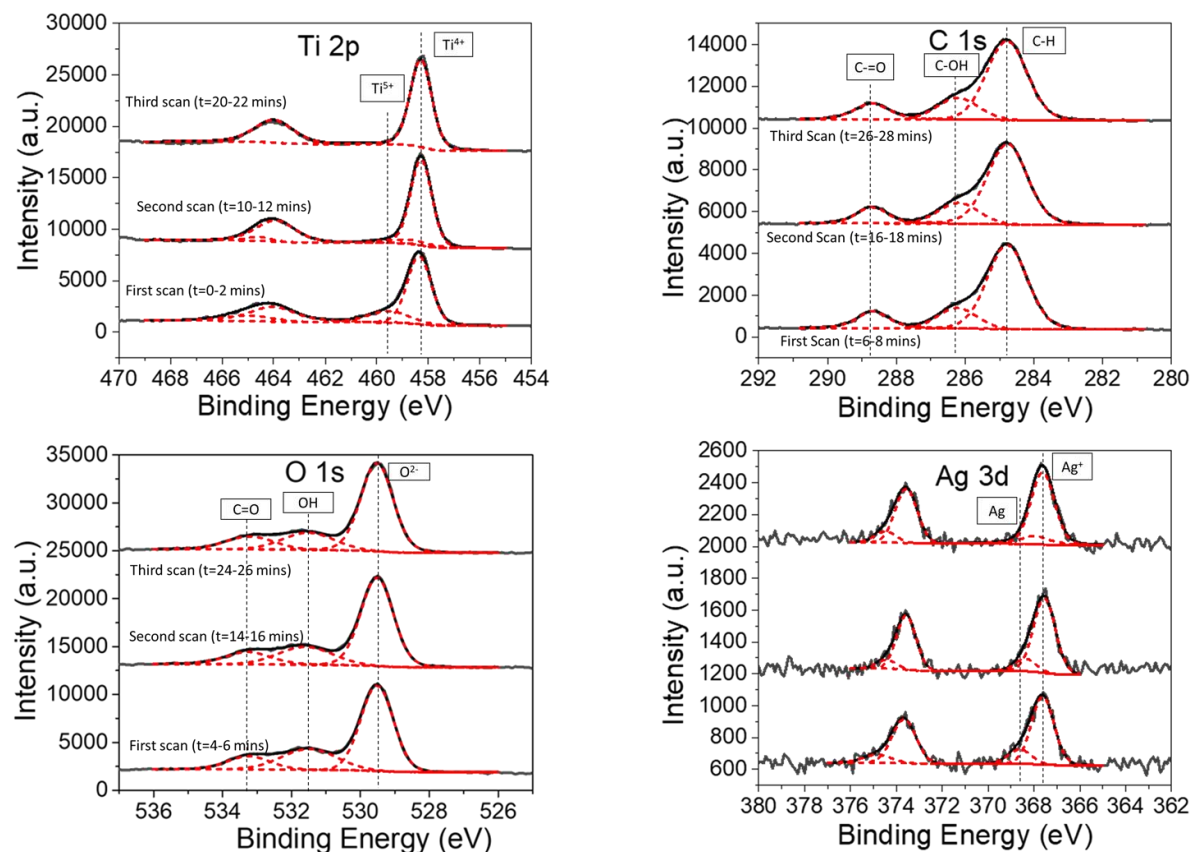


Figure 7.1 Time dependent high-resolution XPS region spectra of 1wt% Ag/TiO₂ sample

Photoelectron spectral results of 1wt% Ag/TiO₂ are shown in Figure 7.1. Due to the low loading of silver, the Ag 3d spectra was relatively noisy but the resolution of the spectra was still high (FWHM of Ag 3d 5/2 is 1.15 eV), which indicates that silver was highly dispersed on the porous Titania support surface. There are two Ag 3d 5/2 peaks at 367.7 eV and 368.4 eV binding energy, which are assigned as Ag⁺ and Ag metal species. The corresponding Ag 3d 3/2 peaks are located at 373.7 eV and 374.4 eV with a binding energy difference of 6.0 eV. The binding energy values are in good agreement with literature values [17-19]. From Ti 2p spectra, there are also two different Ti 2p 3/2 peaks at 458.5 eV and 459.8 eV indicating Ti⁴⁺ and Ti(hole) species. Their corresponding Ti 2p 1/2 peaks are at 464.3 eV and 465.6 eV with a binding energy

difference of 5.8 eV. The C 1s spectra shows three carbon species at 284.8 eV (C-H etc.), 286.3 eV (C-O etc.), and 288.8 eV (O=C-O etc.). The O 1s spectra also show three oxygen species at 529.5 eV (O^{2-}), 531.5 eV (OH^- etc.), and 533.3 eV ($H_2O_{(ads)}$ etc.). Time dependent spectral change that indicates the generation and relaxation of titanium hole species was observed. But the atomic concentration of hole species was smaller than 4wt% Ag/TiO₂ sample. And it took about 20 minutes of X-ray irradiation to relax all the generated hole species, which is much faster than the hole relaxation of 4wt% Ag/TiO₂ sample. No significant spectral change was observed for C 1s and O 1s spectra.

Figure 7.2 shows the time dependent high-resolution XPS spectra of 2wt% Ag/TiO₂ sample. The Ti 2p spectra for 2wt% Ag/TiO₂ sample shows two Ti 2p 3/2 peaks at 458.5 eV and 459.8 eV that are assigned as Ti⁴⁺ and Ti(hole) species. The corresponding Ti 2p 1/2 peaks are at 464.3 eV and 465.6 eV respectively. The Ag 3d spectra indicate the existence of Ag metal and Ag⁺ species at Ag 3d 5/2 of 367.7 eV and 368.4 eV and the corresponding Ag 3d 3/2 peaks at 373.7 eV and 374.4 eV respectively. The Ag 3d spectra show a better signal to background ratio than 1wt% Ag/TiO₂ sample, but the spectra were still a little bit noisy due to the low concentration of silver. The O 1s spectra were deconvoluted into three components at binding energy 529.5 eV (O^{2-}), 531.5 eV (OH^- etc.), and 533.3 eV ($H_2O_{(ads)}$ etc.). The C 1s spectra contain three components at binding energy 284.8 eV (C-H), 286.3 eV (C-O etc.), and 288.8 eV (O=C-O etc.). The binding energies and full width half max (FWHM) of the photoelectron peaks are in good agreement with 1wt% Ag/TiO₂ sample as well as the literature values [14-16].

From the time dependent XPS spectra of 2wt% Ag/TiO₂ sample (Figure 7.2), time dependent spectral change was observed in Ti 2p, Ag 3d, and O 1s spectra. The C 1s spectra did not show significant spectral change. The peak intensity of Ti(hole) species at the first XPS scan

was much larger than that of 1wt% Ag/TiO₂ sample. Time dependent relaxation of titanium hole species was observed with continuous X-ray exposure. For the first Ti 2p spectrum obtained, the peak intensity ratio between Ti⁴⁺ and Ti(hole) was almost 1:1. The Ag 3d spectra also show a time dependent spectral change in terms of X-ray exposure time. Peak intensity shift from Ag metal to Ag⁺ was observed. Time dependent peak intensity increase of O²⁻ species was also observed from O 1s spectra associated with peak intensity decrease of O⁻ etc. species, which potentially indicates the time dependent relaxation of O⁻ etc. species to O²⁻.

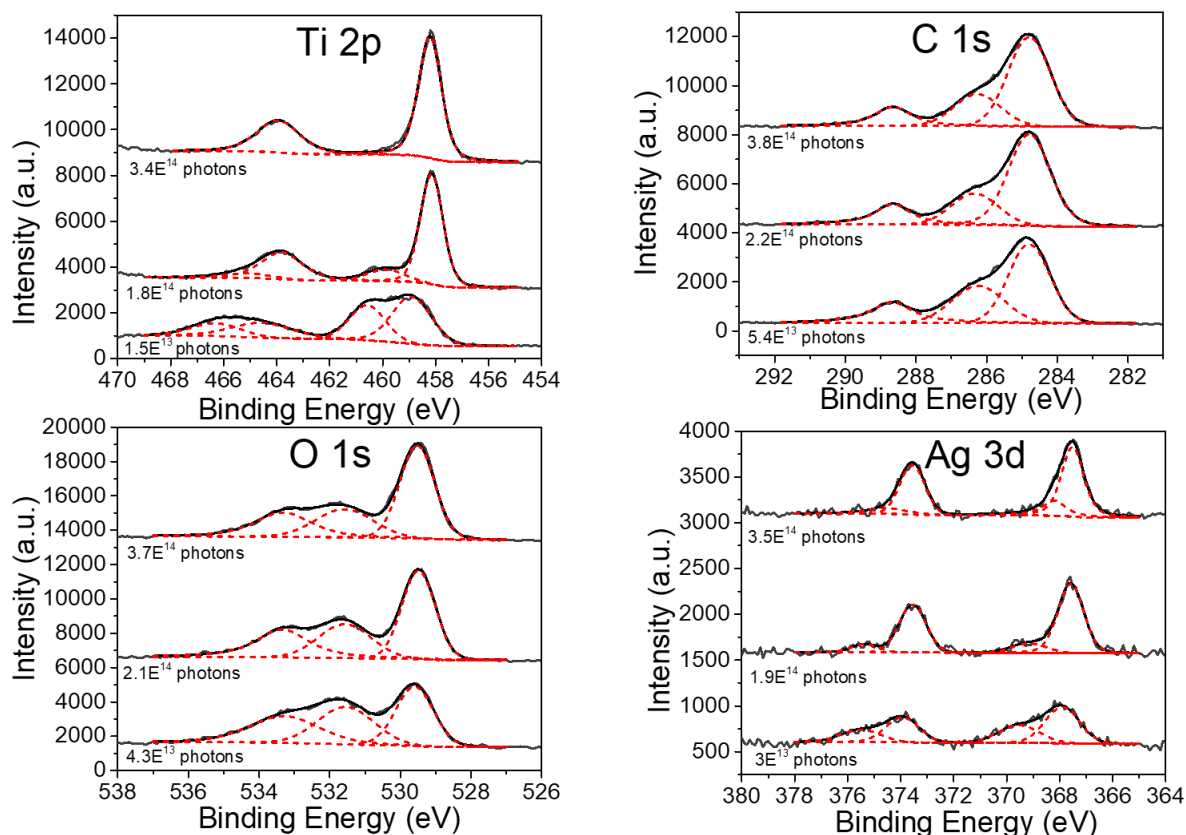


Figure 7.2 In situ time dependent high-resolution XPS spectra of 2wt% Ag/TiO₂ sample

Time dependent high-resolution XPS spectra of 4wt% Ag/TiO₂ sample is shown in Figure 7.3. From Ti 2p spectra, two Ti 2p 3/2 peaks are observed at binding energy 458.5 eV and 459.8

eV, indicating the Ti^{4+} and Ti(hole) species. The first spectrum shows the Ti(hole) species binding energy at 460.3 eV, which is 0.5 eV higher than the same peak of the rest spectra. This is possibly due to the photovoltaic effect [20,21] occurred with short term X-ray exposure.

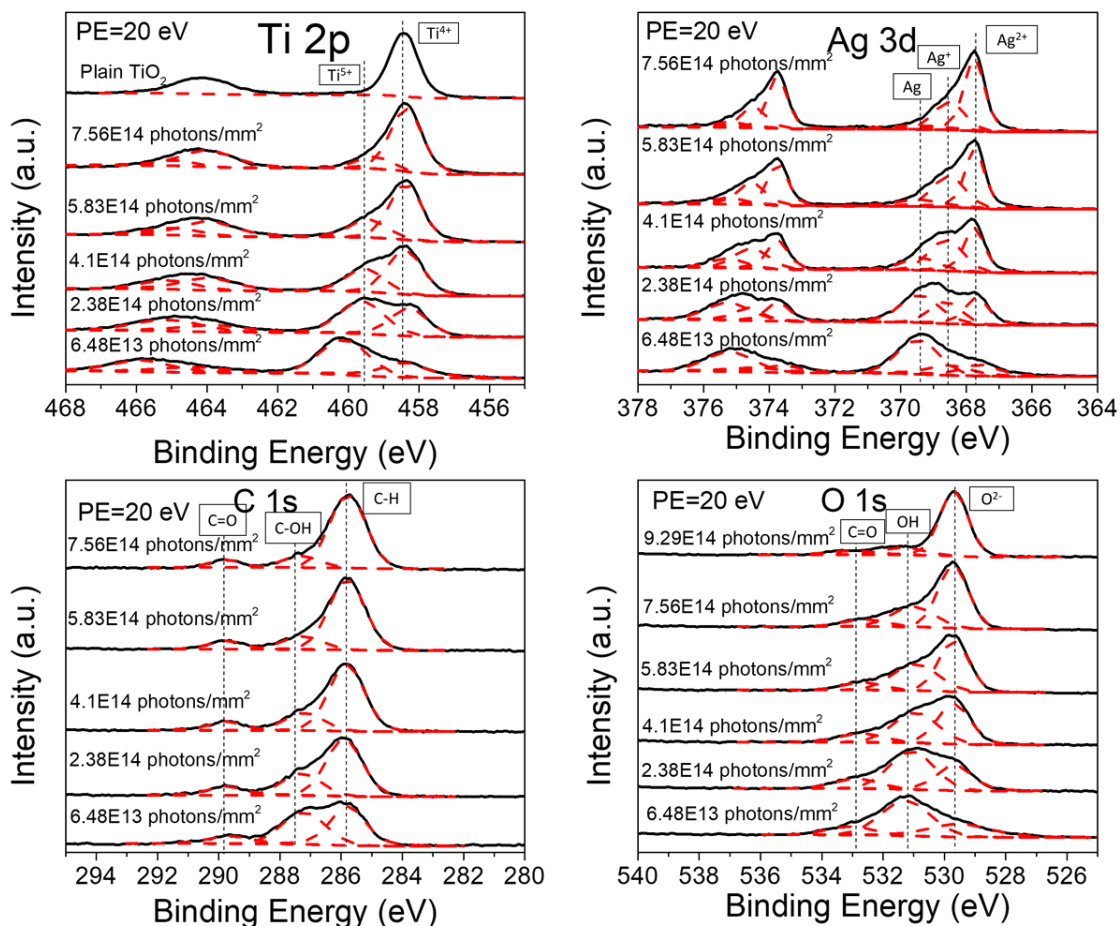


Figure 7.3 In situ time dependent high-resolution XPS spectra of 4wt% Ag/TiO₂ sample

Time dependent spectral change associated with peak intensity shift from Ti(hole) to Ti^{4+} species with continuous X-ray exposure was observed from Ti 2p spectra. The high-resolution Ag 3d spectra show three Ag 3d 5/2 peaks at binding energy 367.7 eV, 368.4 eV, and 369.2 eV which are assigned as metallic Ag, Ag^+ , and Ag^{2+} species. Peak intensity shift from metallic Ag to Ag^{2+} was observed in terms of X-ray exposure time. The Ag 3d spectra show a much better

photoelectron background baseline than lower loadings due to the relative higher concentration of Ag on the sample surface and the highly dispersion of silver on Titania support surfaces.

Color change of the X-ray irradiated spot on the sample surface was also observed. The as prepared 4wt% Ag/TiO₂ sample showed a white color, while the X-ray irradiated spot showed a brown color after X-ray exposure. The O 1s spectra also show time dependent spectral change with peak intensity shift from OH⁻, O⁻ etc. species (531.5 eV) to O²⁻ (529.5 eV) species. The X-ray induced photogenerated hydroxyl species was proposed to stabilize the hole species. Besides, C 1s spectra also show time dependent spectral change between C-O (286.3 eV) and C-H (284.8 eV) species. Peak intensity shift from C-O to C-H was observed. This change could potentially be due to the reaction intermediate OH was adsorbed and bonded with carbon species to form additional C-O species. Time dependent relaxation of C-O was observed due to the release of hydroxyls or O₂⁻ species from carbon. The O=C-O etc. species peak at binding energy 288.8 eV did not show any peak intensity and FWHM change throughout the experiment, which means there was no interaction of holes and electrons with O=C-O etc. species.

Figure 7.4 shows the high-resolution time dependent core level Ti 2p, Ag 3d, O 1s, and C 1s XPS spectra of 6wt% Ag/TiO₂ sample. Same Ti(hole) and Ti⁴⁺ species were observed at Ti 2p 3/2 binding energy 458.5 eV and 459.8 eV. Time dependent spectral change was observed with peak intensity shift from Ti(hole) species to Ti⁴⁺ species, which potentially indicates the X-ray induced excitation and relaxation of titanium hole species on the sample surface. The peak intensity of Ti(hole) from first Ti 2p spectrum and the overall peak intensity change with X-ray exposure time of 6wt% Ag/TiO₂ sample is very similar to the results of 4wt% Ag/TiO₂ sample. High resolution Ag 3d spectra show metallic Ag (369.4 eV) and Ag²⁺ (367.7 eV) species with time dependent spectral change and peak intensity shift from metallic Ag to Ag²⁺. At 6wt%

loading of silver, the Ag 3d spectra show even better resolution and photoelectron background baseline than that of 4wt% Ag/TiO₂ sample. Color change of the X-ray irradiated spot on the 6wt% Ag/TiO₂ sample surface was observed. The as prepared white sample turned into dark brown by X-ray exposure. The O 1s spectra show time dependent spectral change and peak intensity shift from O⁻, OH⁻ etc. (531.5 eV) to O²⁻ (529.5 eV), which indicates the generation and relaxation of X-ray induced photo-hole species. The C 1s spectra show similar change as 4wt% Ag/TiO₂ sample. The overall spectral change trend of 6wt% Ag/TiO₂ is close to 4wt% Ag/TiO₂ sample.

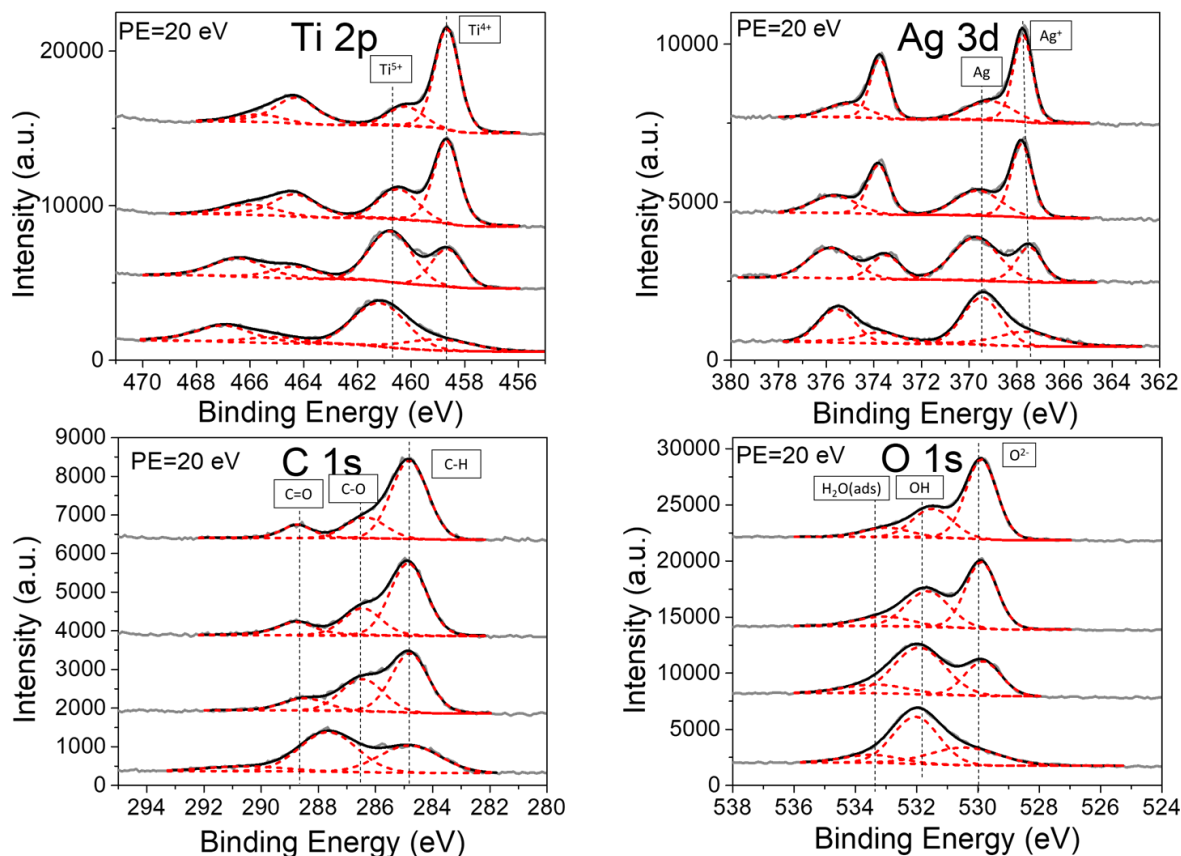


Figure 7.4 In situ time dependent high-resolution XPS spectra of 6wt% Ag/TiO₂ sample

In situ time dependent high resolution XPS spectra of 8wt% Ag/TiO₂ is shown in Figure 7.5.

The results are similar to 4wt% and 6wt% Ag/TiO₂ samples. The Ti 2p spectra show peak

intensity change from Ti(hole) at binding energy 459.8 eV to Ti^{4+} at binding energy 458.5 eV with continuous X-ray exposure. The X-ray induced photoexcitation and photo-relaxation of hole species was observed from Ti 2p spectra too.

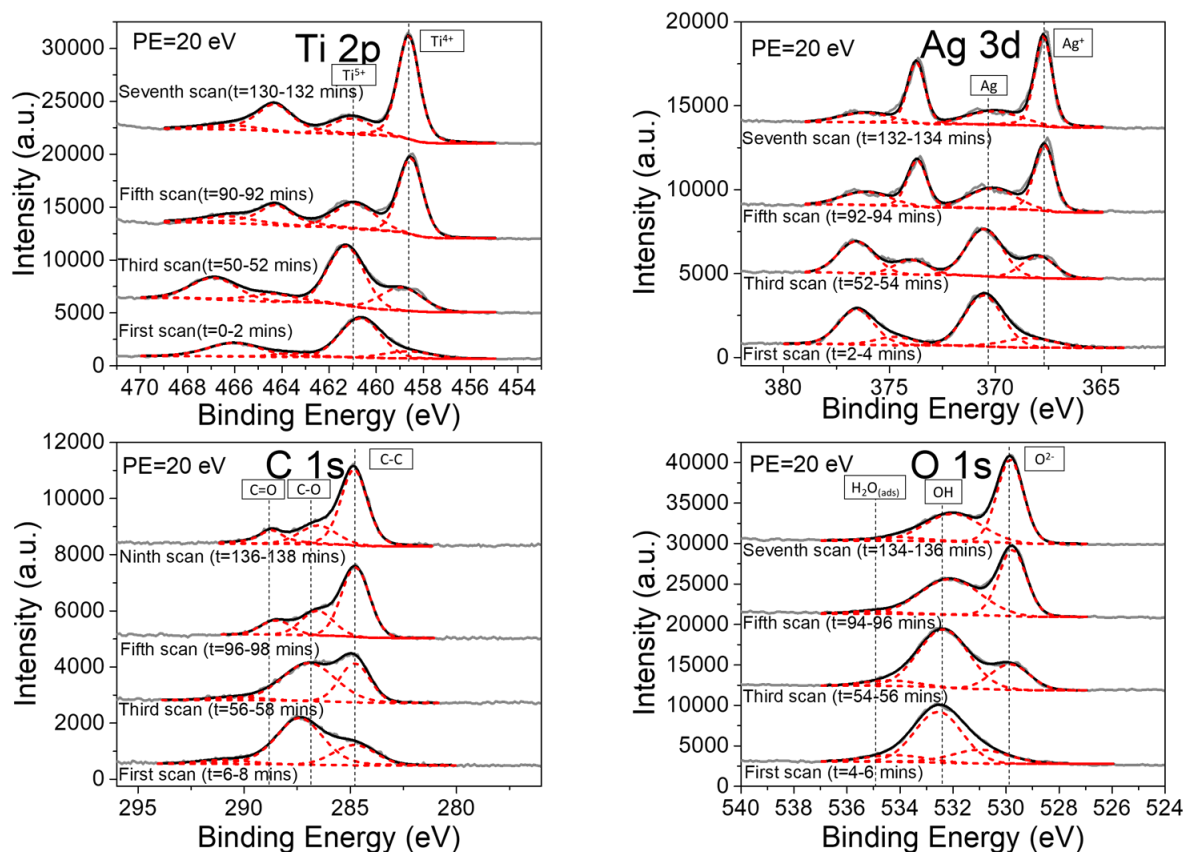


Figure 7.5 In situ time dependent high-resolution XPS spectra of 8wt% Ag/TiO₂ sample

Time dependent spectral change was observed from Ag 3d spectra with peak intensity shift from metallic Ag (367.7 eV) to Ag^{2+} (369.4 eV). The resolution of Ag 3d spectra are high and the background baseline of the photoelectron peaks are consistent, which is due to the relative high concentration of silver on the sample surface and the highly dispersion of silver atoms on the Titania surface. Color change of the X-ray irradiated spot on the sample surface was also observed. The as prepared white sample was turned into dark brown on the X-ray irradiated spot. Similar time dependent spectral change on O 1s and C 1s was also observed, and the spectral

change was similar as those observed from 4wt% and 6wt% Ag/TiO₂ samples. Time dependent peak intensity shift from O⁻, OH⁻ etc. species (531.5 eV) to O²⁻ species (529.5 eV) was observed, potentially indicating the X-ray induced generation of photogenerated holes such as O⁻ etc. species and stabilized by OH species, and the photo-relaxation of hole species into O²⁻. No significant change of adsorbed H₂O etc. peak (533.3 eV) was observed, which was potentially due to the photo stimulate desorption and re-adsorption of adsorbed H₂O.

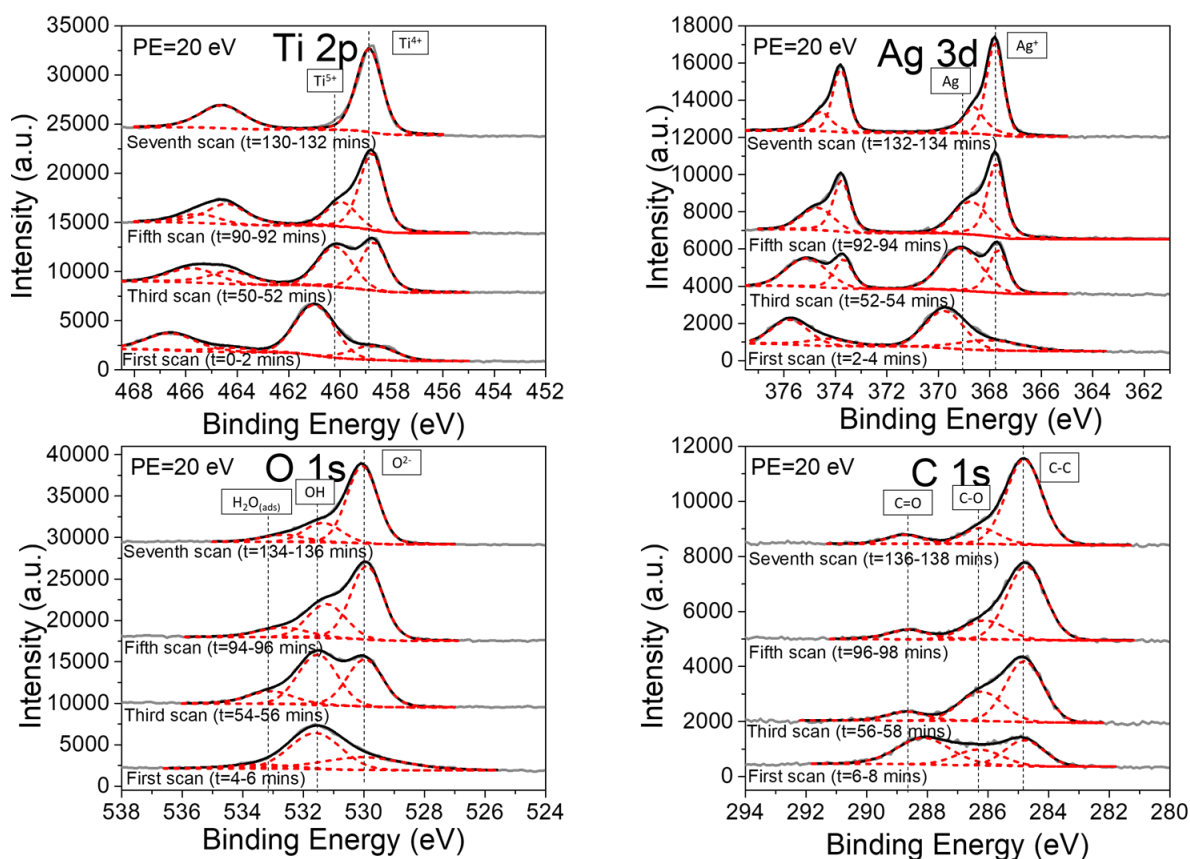


Figure 7.6 In situ time dependent high-resolution XPS spectra of 10wt% Ag/TiO₂ sample

Figure 7.6 shows the *in situ* time dependent high-resolution XPS spectra of 10wt% Ag/TiO₂ sample. As it is shown in Ti 2p spectra, Ti(hole) species at Ti 2p 3/2 binding energy 459.8 eV and Ti⁴⁺ species at 458.5 eV are observed. Time dependent spectral change indicates the photoexcitation and photogeneration of Ti(hole) species at the beginning of the X-ray exposure

followed by X-ray induced photo-relaxation of Ti(hole) species to form Ti^{4+} species. Photovoltaic effect was also observed in the first set of narrow scans of core level photoelectron peaks.

The Ag 3d spectra show even better resolution and background baseline of the photoelectron peaks than samples with lower weight percentage loadings of silver. Metallic Ag at Ag 3d 5/2 binding energy 367.7 eV was produced by the X-ray irradiation at the first scan, but it was re-oxidized into Ag^{2+} as the peak intensity of Ag^{2+} species (Ag 3d 5/2 at binding energy 369.4 eV) was enlarged with continuous X-ray exposure. Similar color was changed from as prepared white to dark brown on the X-ray irradiated spot. Time dependent spectral change was also observed from C 1s and O 1s spectra. The spectral change trend was close to those observed from 4wt%, 6wt%, and 8wt% Ag/TiO₂ samples.

Based on the time dependent XPS results on different weight percentage loading of Ag/TiO₂ samples, Ti(hole) species was observed for all the samples. Time dependent X-ray induced photoexcitation and relaxation of the hole species was observed by the time dependent spectral change from XPS results. With higher weight percentage loading of silver, the resolution and background baseline of Ag 3d spectra were significantly improved. The initial peak intensity of Ti(hole) species is highly related to the percentage loading of silver until 4wt%, which is due to the coverage of the dispersion of silver atoms on the surface of Titania support until a saturated monolayer of highly dispersed Ag was reached. The XPS results of 6wt%, 8wt%, and 10wt% Ag/TiO₂ samples showed similar spectral change as those of 4wt% Ag/TiO₂ sample. As it was reported in an earlier study by our laboratory [3], the incipient wetness impregnation of silver at higher than 4wt% loadings will cause the additional silver atoms to aggregate on the surface and only the surface silver atoms are active for surface reactions. The peak intensity ratios (Figure

7.7) between total Ag 3d peaks and total Ti 2p peaks are linear and close to theoretical values at lower loadings (<4wt%), which suggests the highly dispersion of silver atoms on Titania support. While at loadings at higher than 4wt%, the peak intensity ratios were smaller than the theoretical values due to the aggregation of silver atoms.

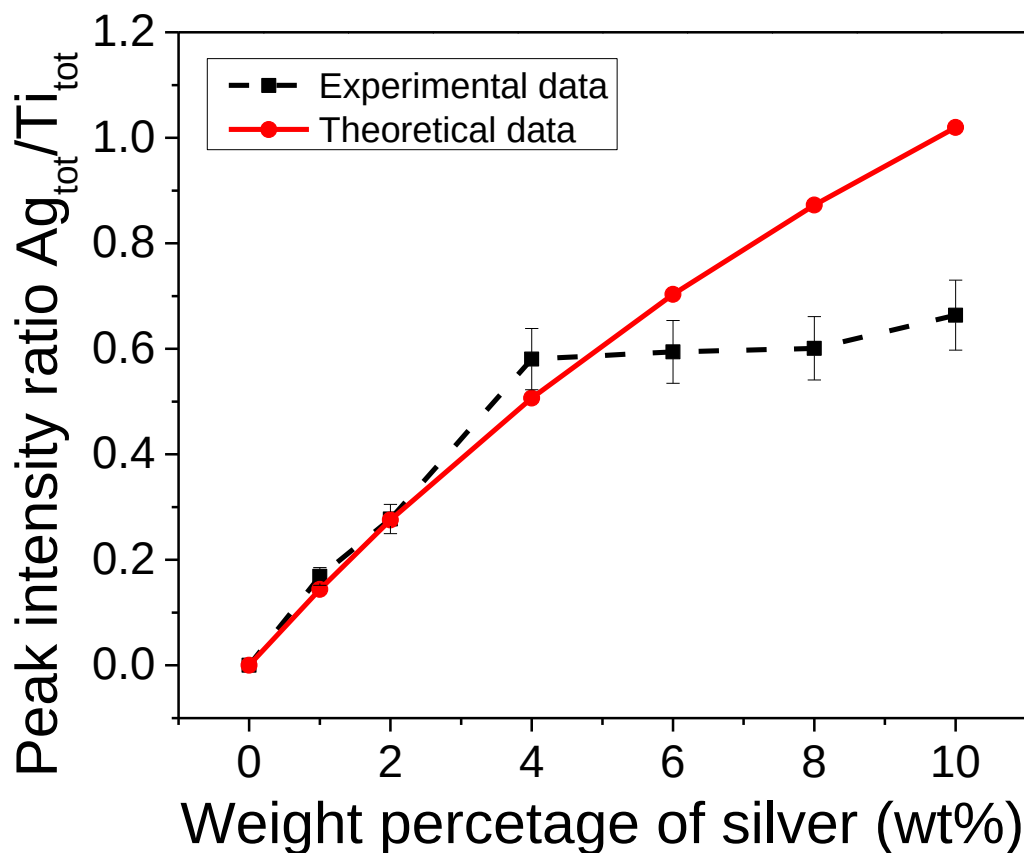


Figure 7.7 Measured peak intensity ratios between total Ag 3d peaks and Ti 2p peaks versus theoretical data.

7.4.2 XPS quantitative analysis of different weight percentage loading of silver

From first principles, the intensity of the photoelectron peak (peak area) is described by [22]:

$$I = I_0 n \sigma \lambda(\epsilon) D(\epsilon) \int_0^t e^{-t/\lambda} dt \quad (1)$$

Where I_0 : X-ray flux; N : Density of atoms; σ : Photoelectron cross-section; I : XPS peak intensity (peak area); $\lambda(\epsilon)$: Mean free path of energy(ϵ); $D(\epsilon)$: Fraction of electrons detected by the analyzer; t : The sampling depth.

The peak intensities of each species could be obtained from deconvolution results, the mole fraction of each species can be calculated by:

$$C(i) = \frac{n(i)}{\sum n(i)} = \frac{I(i)\sigma(i)\lambda(\epsilon i)D(\epsilon i)\int_0^t e^{-t/\lambda} dt}{\sum I(i)\sigma(i)\lambda(\epsilon i)D(\epsilon i)\int_0^t e^{-t/\lambda} dt} \quad (2)$$

Where $I(i)$: XPS peak intensity from the top monolayer of species i ; $\sigma(i)$: Photoelectron cross-section of species i ; $\lambda(\epsilon i)$: Mean free path of energy(ϵ) for species i ; $D(\epsilon i)$: Fraction of electrons detected by the analyzer for species i ; t : The sampling depth.

From Eq. (2), the time dependent atomic fraction change of 1wt% Ag/TiO₂ sample is shown in Figure 7.8.

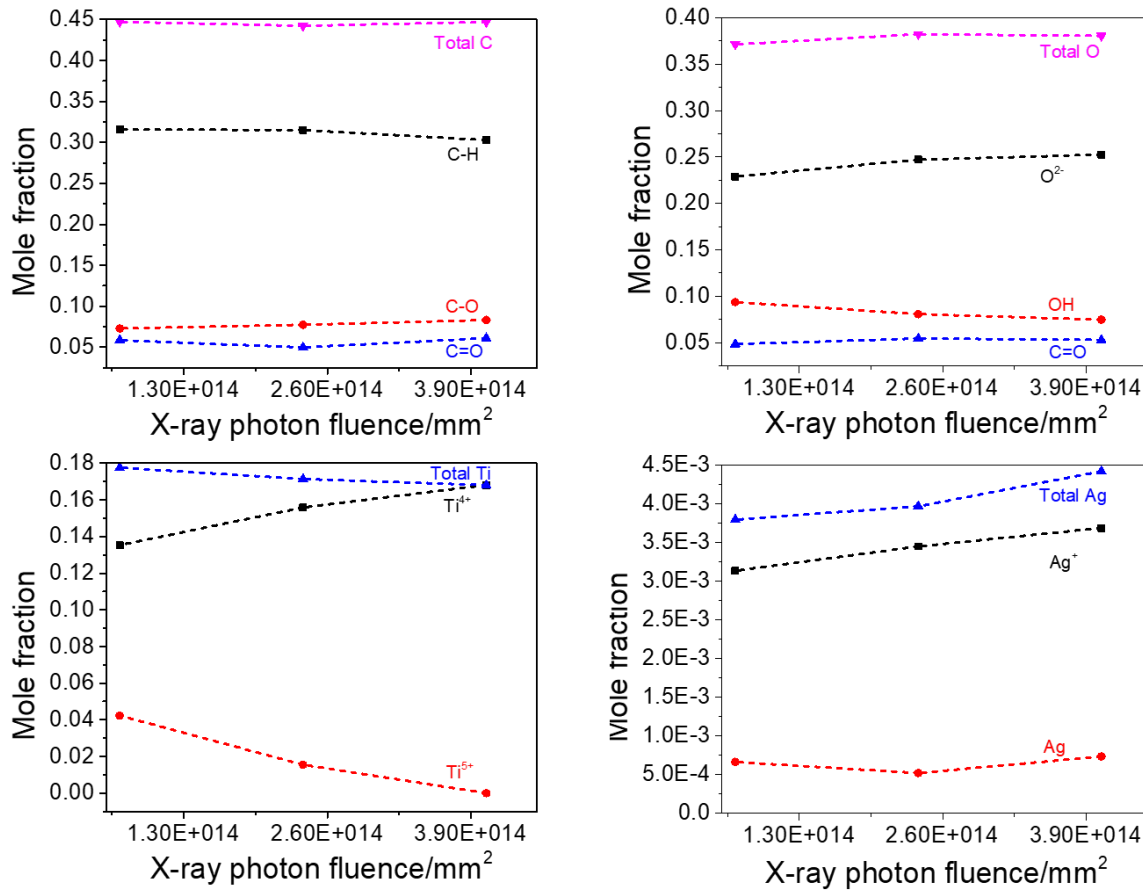


Figure 7.8 Time dependent atomic fraction change of C, O, Ti, and Ag species of 1wt% Ag/TiO₂ sample.

The atomic fraction change of 1wt% Ag/TiO₂ sample quantitatively shows there was 0.04 atomic percentage of Ti(hole) species generated by X-ray irradiation at first XPS scan. The hole species were relaxed to Ti⁴⁺ within 30 minutes of continuous X-ray exposure. X-ray irradiation reduced a small portion of silver oxide into metallic silver. Continuous X-ray exposure caused re-oxidation of silver. The atomic fraction change of carbon species was minimal. The atomic fraction change of oxygen species slightly shows X-ray induced conversion of O⁻, OH etc. species into O²⁻.

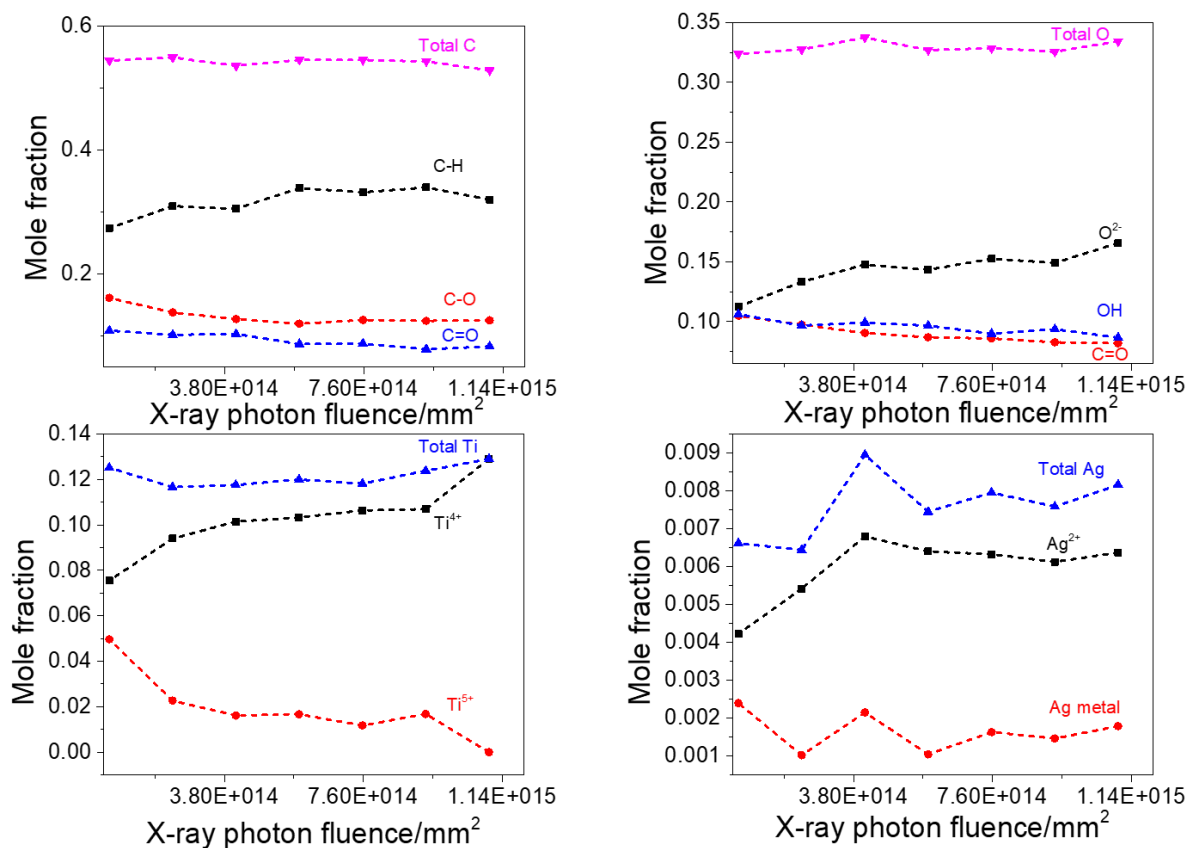


Figure 7.8 Time dependent atomic fraction change of C, O, Ti, and Ag species of 2wt% Ag/TiO₂ sample.

Figure 7.8 shows the time dependent atomic fraction change of 2wt% Ag/TiO₂ sample. The atomic fraction of Ti(hole) species was 40% of all the titanium species from the first XPS scan.

Continuous X-ray irradiation caused complete relaxation of the Ti(hole) species within 60 minutes. The interaction between hole species and carbon species was minimal as indicated by the slightly atomic fraction change of C-O and C-H species. Significant atomic fraction change of oxygen species was also observed. Continuous X-ray exposure converted 50% of the O⁻, OH etc. species into O²⁻, which potentially indicated the relaxation of hole species. The atomic ratio change of Ti(hole), Ti⁴⁺, O⁻ etc, and O²⁻ were evaluated and the atomic fraction change ratios among these species indicated a universal 1:1:1:1 stoichiometry, which implies a potential reaction mechanism:

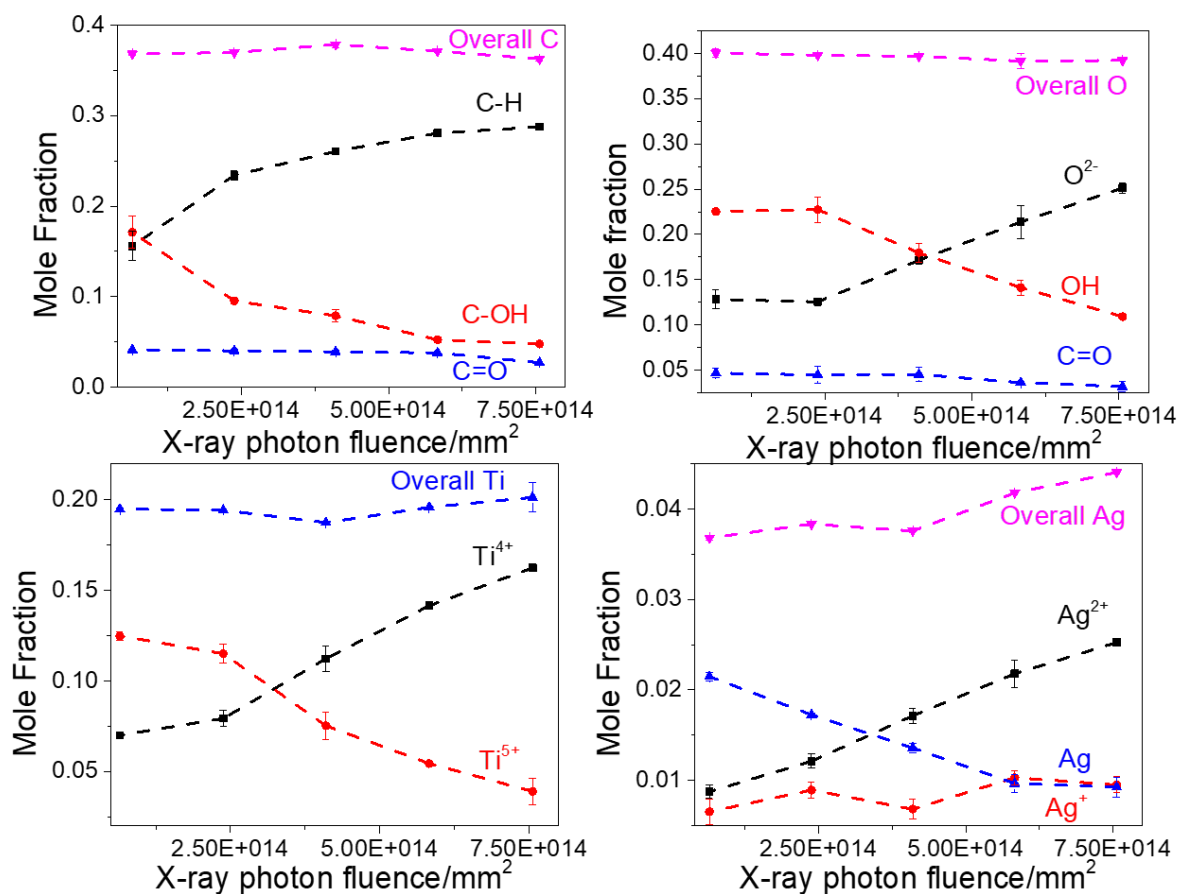
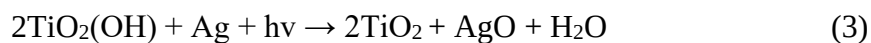


Figure 7.9 Time dependent atomic fraction change of C, O, Ti, and Ag species of 4wt% Ag/TiO₂ sample.

Time dependent atomic fraction change of 4wt% Ag/TiO₂ sample is shown in Figure 7.9. As it is analyzed and discussed in Chapter 5, the stoichiometry of the atomic fraction change of titanium species and oxygen species is also close to 1. The proposed reaction mechanism is same as that of 2wt% Ag/TiO₂ sample. The atomic fraction change of carbon species is significant, indicating the interaction between carbon species and hydroxyl/hole species. X-ray exposure caused conversion of C-H etc. species into C-O etc. species, which potentially indicated extensive hydroxyls and/or O⁻ etc. interacted with carbon species to form additional C-O species. The involvement of carbon species is possibly due to the interaction between reaction intermediates (hydroxyls and O⁻ etc.) and carbon species on sample surface [23-25].

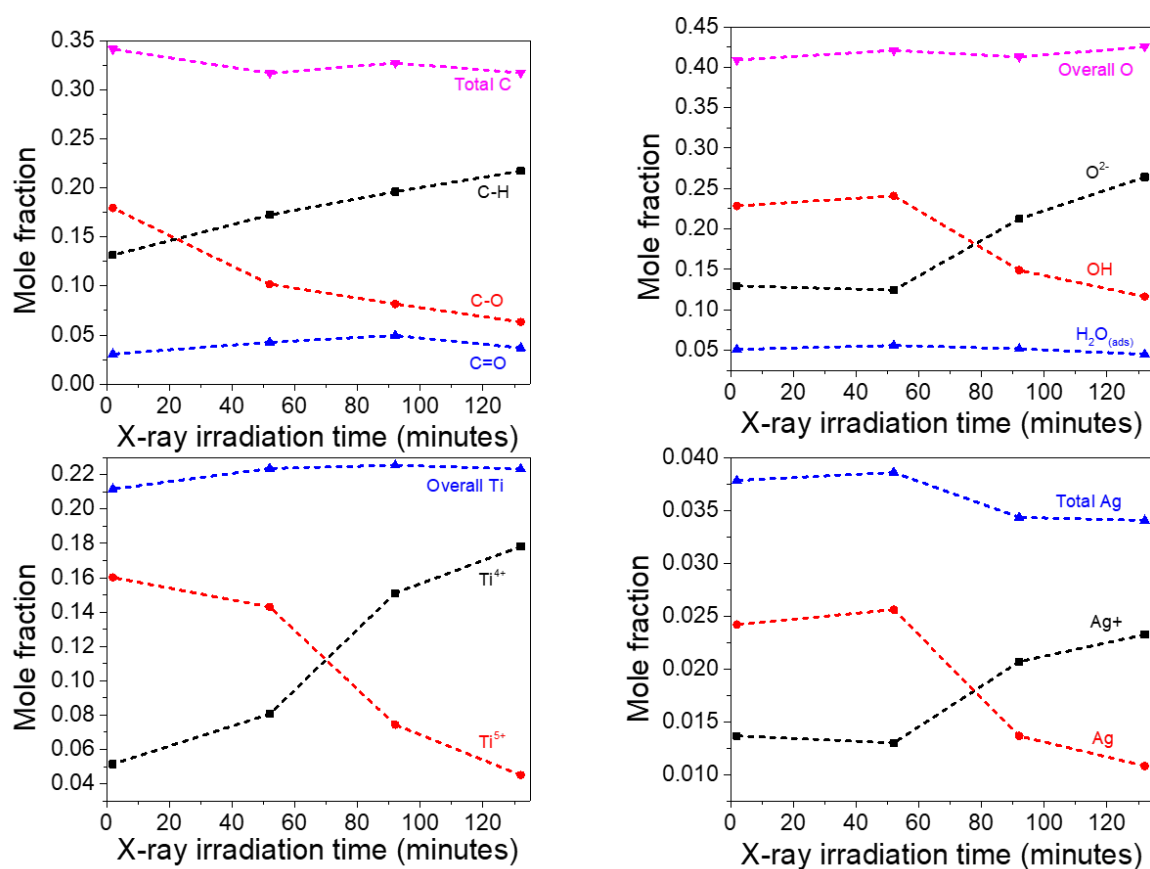


Figure 7.10 Time dependent atomic fraction change of C, O, Ti, and Ag species of 6wt% Ag/TiO₂ sample.

Figure 7.10 shows the time dependent atomic fraction change of 6wt% Ag/TiO₂ sample. The atomic fraction change of titanium species (Ti(hole) and Ti⁴⁺) and oxygen species (OH etc. and O²⁻) are similar to 4wt% Ag/TiO₂ sample. Atomic fraction change of carbon species (C-O etc. and C-H etc.) was also observed. The atomic fraction change ratio between titanium and oxygen species was also close to 1, which indicates the reaction mechanism is the same as 4wt% Ag/TiO₂ sample. The detailed reaction mechanism analysis is discussed in Chapter 5.

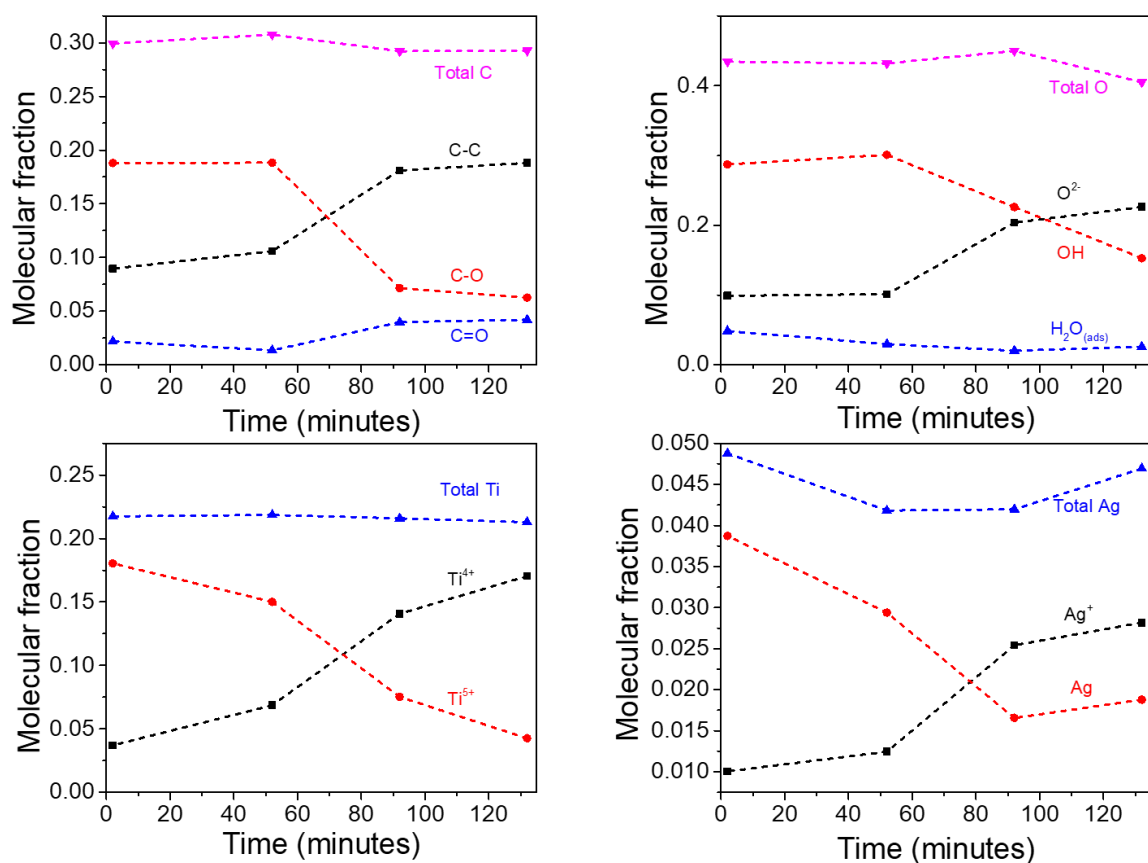


Figure 7.11 Time dependent atomic fraction change of C, O, Ti, and Ag species of 8wt% Ag/TiO₂ sample.

The atomic fraction change of 8wt% and 10 wt% Ag/TiO₂ samples are shown in Figure 7.11 and Figure 7.12. The atomic fraction change of Ti(hole), Ti⁴⁺, OH etc., O²⁻ species are similar to those of 4wt% and 6wt% Ag/TiO₂ samples. The atomic fraction change ratios of these species are also close to 1. The results show the additional loading of silver that exceed 4wt% did not change the reaction mechanism. Besides, the results also provide significant evidence in support of the previous assertion that silver (Ag⁺) atoms that are exceptionally bonded with titanium and hydroxyl are the active species for the X-ray induced photoexcitation and relaxation of the hole species. Time dependent atomic fraction change of carbon species was also observed.

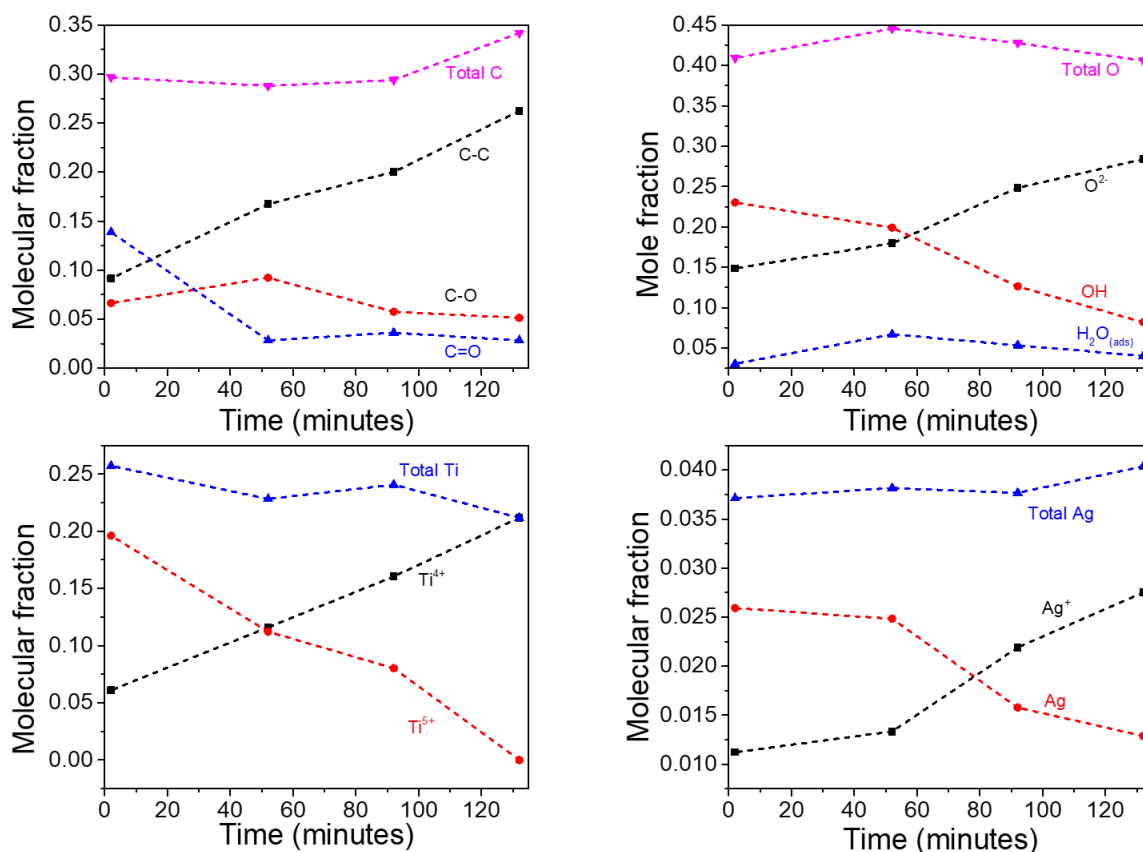


Figure 7.12 Time dependent atomic fraction change of C, O, Ti, and Ag species of 10wt% Ag/TiO₂ sample.

The atomic fraction change of silver was much smaller when compared with the changes of titanium and oxygen species. The atomic fraction change ratio between Ag^+ and Ti(hole) is 1:20 for all the reaction cases, which potentially indicates silver acts as the catalyst to capture and transfer electrons from TiO_2 to adsorbed $\text{H}_2\text{O}/\text{OH}$. Or it could be possibly due to the highly dispersion of silver on the porous surface of TiO_2 . The detection depth of XPS is only $\sim 5\text{-}7$ nm [26], silver atoms at deeper locations in the TiO_2 pores could not be detected by XPS. Considering the XPS spectrum of Ag 3d at the end of the time dependent experiment (usually after several hours of continuous X-ray exposure) showed most of the silver species was Ag^{2+} species and the dark brown color of the X-ray irradiated sample surface, we suppose a potential hole migration mechanism that the X-ray induced photo-holes are mobile and being transferred to the surface layers where XPS can detect, but the electrons are captured by silver atoms at deeper locations where XPS could not detect. The hole migrated to the surface and gradually re-oxidized the metallic silver atoms during the relaxation of the hole species, and so that the XPS results showed a relatively smaller atomic fraction change of silver when compared to titanium. But most of the silver atoms below the surface layers could not be detected by XPS and so that the atomic ratio of the hole species and silver species could be close to 1:1 since one electron was captured by one Ag^+ atom to form one metallic Ag and the hole was transferred to upper layers close to the surface. Due to the detection depth limit of XPS, more characterizations for the deeper depth from the surface layers need to be carried out and the progress will be included in future works.

7.4.3 XPS analysis of select transition metal oxides on TiO_2

Figure 7.12 shows the time dependent high-resolution core level Ti 2p, Cu 2p, O 1s, and C 1s XPS spectra of 2.4wt% (same atomic fraction as Ag of 4wt% Ag/ TiO_2) Cu/ TiO_2 sample.

Time dependent spectral change was also observed for 2.4wt% Cu/TiO₂ sample. Similar X-ray induced photoexcitation and relaxation of titanium hole species was observed from Ti 2p spectra. The Ti(hole) species at binding energy 459.8 eV was generated and relaxed by X-ray irradiation. Simultaneously, Cu 2p spectra showed time dependent oxidation state change of metallic Cu to Cu⁺ and Cu²⁺. The as prepared sample showed a light green color which indicates Cu was in form of Cu(OH)₂, and X-ray irradiation caused the sample surface color changed from light green to dark brown. The color change indicated the X-ray induced reduction of Cu²⁺ to metallic Cu. The peak intensity of signature satellite peak for Cu²⁺ species at binding energy 942.5 eV and 943.5 eV was significantly reduced indicating the reduction of Cu²⁺ species [27-32].

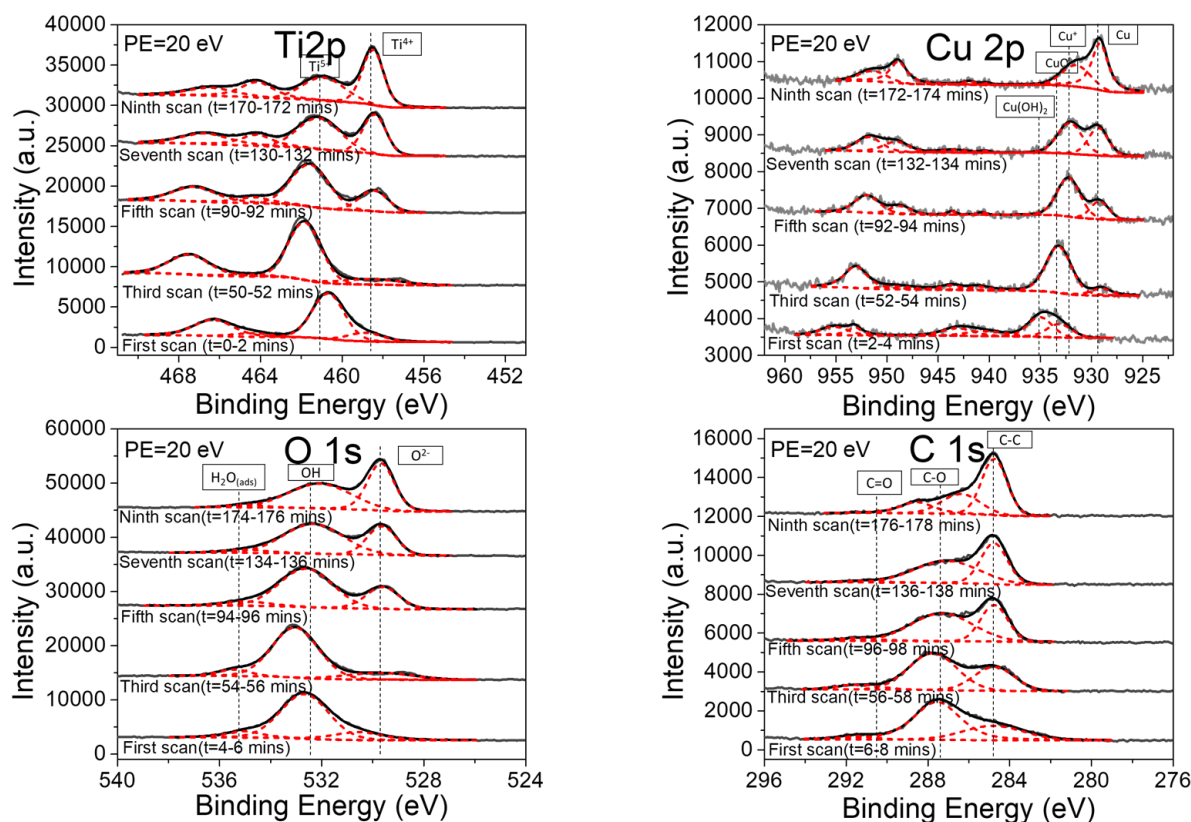


Figure 7.13 In situ time dependent high-resolution XPS spectra of 2.4wt% Cu/TiO₂ sample.

Both O 1s and C 1s spectra showed similar time dependent peak intensity change as the observation from 4wt% Ag/TiO₂ sample. The abundant OH etc. species were attributed to the stabilization of Ti(hole) species. And continuous X-ray exposure caused relaxation of Ti(hole) species and conversion of OH etc. species to O²⁻. The highly active intermediate hydroxyls and O⁻ species interacted with carbon species to form additional C-OH species, but time dependent X-ray irradiation caused desorption of OH from C-OH species to form C-H etc. species.

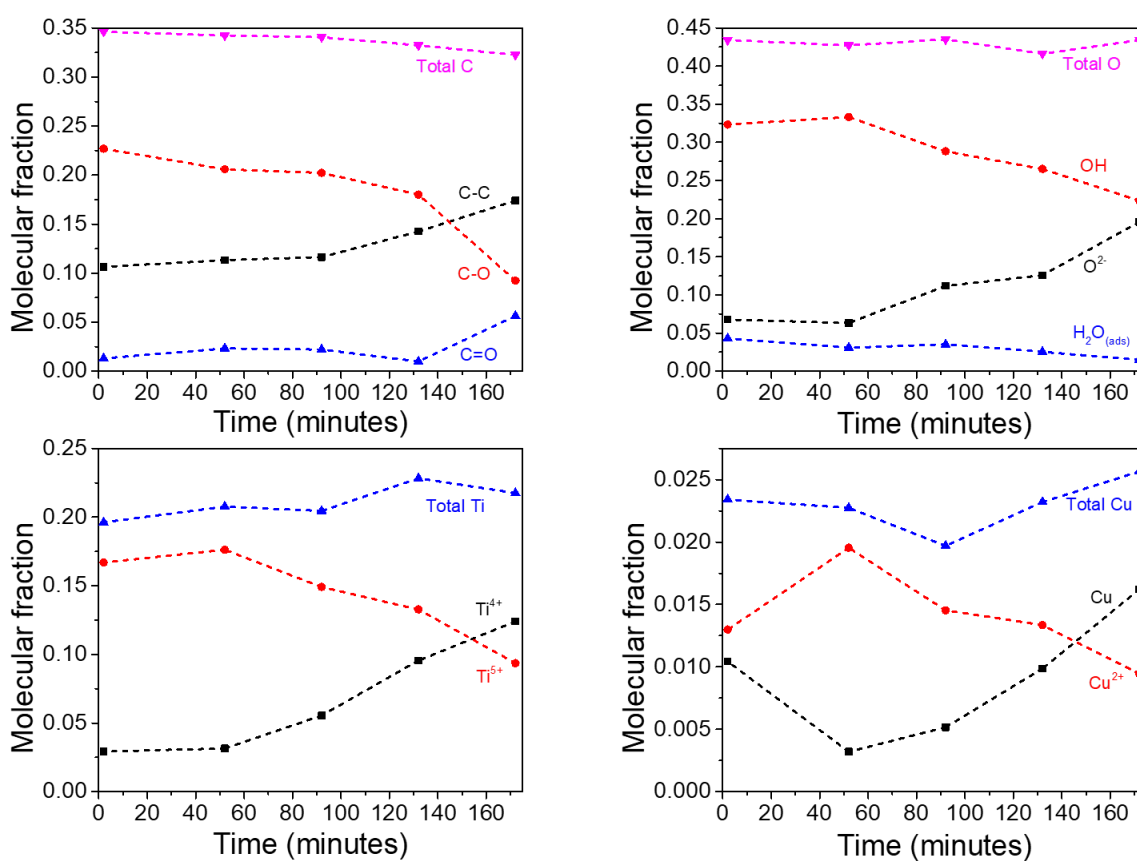


Figure 7.14 Time dependent atomic fraction change of C, O, Ti, and Cu species of 2.4wt% Cu/TiO₂ sample.

The atomic fraction analysis of 2.4wt% Cu/TiO₂ sample is shown in Figure 7.14. The reaction stoichiometry analysis based on the atomic fraction change of the reaction species showed a similar result as the 4wt% Ag/TiO₂ sample. The electrochemical properties of Cu and

Ag are close to each other due to their electronic structures are similar. The results indicate Cu has a similar function as Ag. They both capture electrons on TiO₂ surface and transfer electrons to adsorbed H₂O/OH to trigger the photoreduction reactions. Photo-holes were left on TiO₂ surface and stabilized by hydroxyls. Continuous X-ray irradiation potentially caused desorption of hydroxyls to free the holes so that the hole species reacted with metallic Cu species to get relaxed.

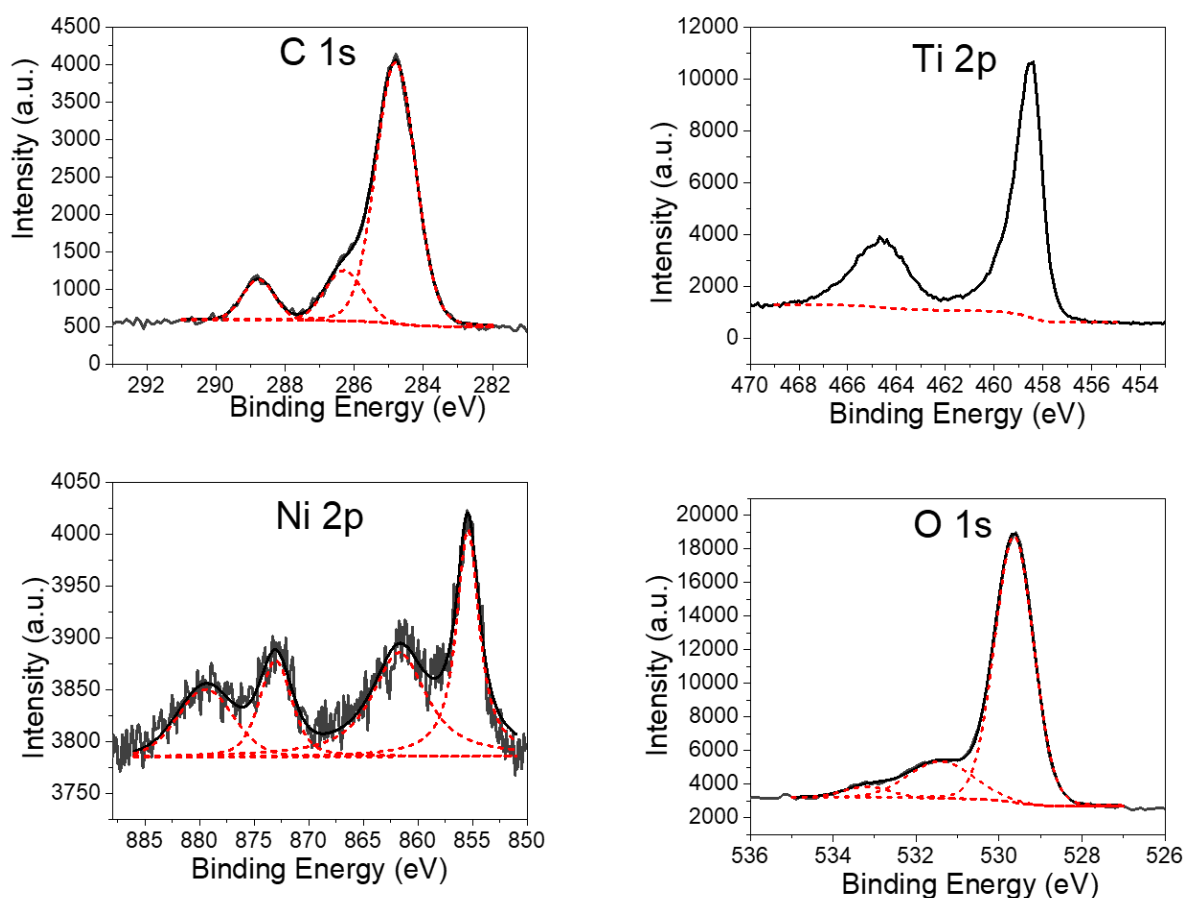


Figure 7.15 In situ time dependent high-resolution XPS spectra of 2.3wt% Ni/TiO₂ sample.

However, some other transition metal ions that exhibit high photocatalytic activities did not show similar effects when loaded onto Titania support. Figure 7.15 shows the time dependent high-resolution XPS spectra of 2.3 wt% Ni/TiO₂ (same atomic fraction of Ag of 4wt% Ag/TiO₂)

sample. The Ti 2p spectrum only shows one Ti 2p 3/2 peak at binding energy 458.5 eV, which indicates Ti^{4+} species, and no Ti(hole) species (at binding energy 459.8 eV) was observed. The Ni 2p spectrum shows the main Ni 2p 3/2 peak at 855.6 eV and the satellite Ni 2p 3/2 peak at 862.5 eV indicating Ni in form of $\text{Ni}(\text{OH})_2$ species [33-38]. The corresponding Ni 2p 1/2 and satellite Ni 2p 1/2 peaks at binding energy 872.9 eV and 879.9 eV show a 17.3 eV binding energy difference. Time dependent XPS characterization did not show any change of the Ni 2p spectra. The O 1s spectra were deconvoluted into 3 components, which are the O^{2-} species at binding energy 529.5 eV, OH etc. species at binding energy 531.5 eV, and $\text{H}_2\text{O}(\text{ads})$ etc. species at 533.3 eV. No time dependent spectral change was observed for the O 1s spectra. The C 1s spectra were also deconvoluted into 3 components, which are C-H etc. species at binding energy 284.8 eV, C-O etc. species at binding energy 286.3 eV, and O=C-O etc. species at binding energy 288.8 eV. There was no time dependent spectral change observed on 2.3wt% Ni/ TiO_2 sample, which indicates Ni/ TiO_2 sample does not have similar properties as Cu/ TiO_2 and Ag/ TiO_2 samples.

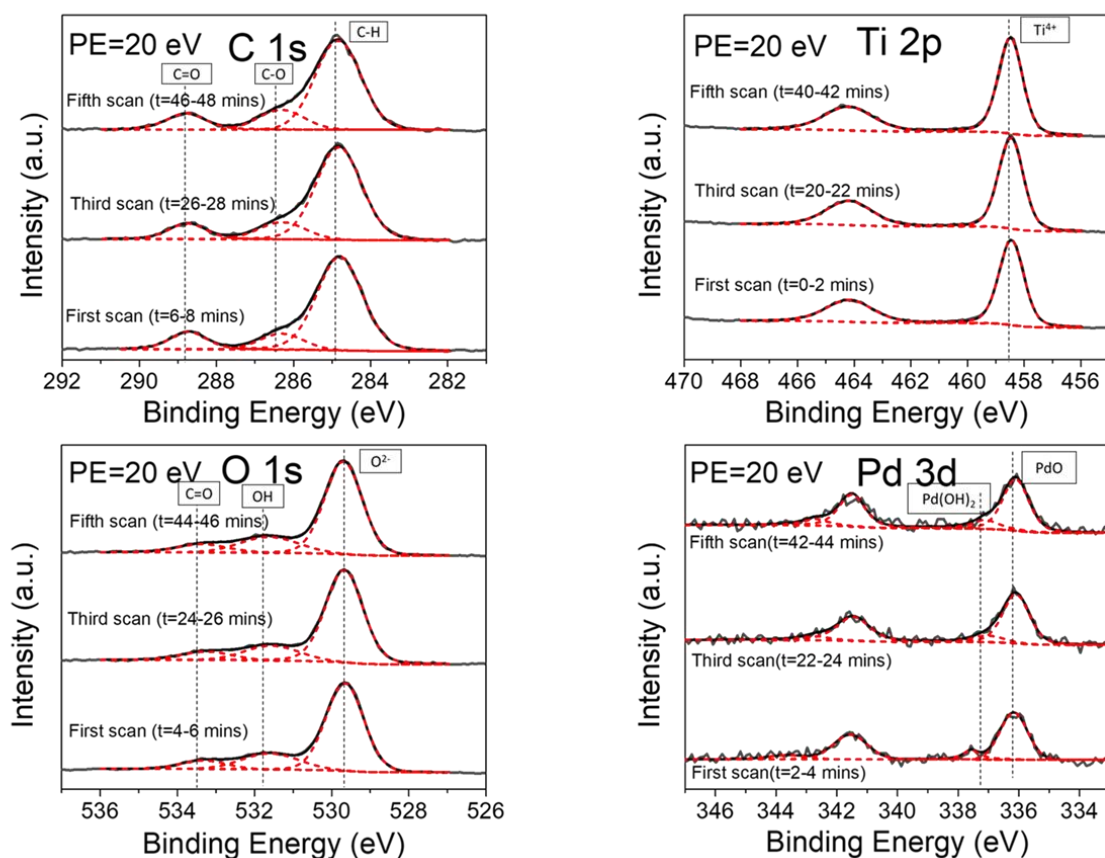


Figure 7.16 In situ time dependent high-resolution XPS spectra of 4wt% Pd/TiO₂ sample.

Besides, no time dependent spectral change was observed from 4wt% Pd/TiO₂ sample as it is shown in Figure 7.16. The Ti 2p spectra show universal Ti 2p 1/2 and Ti 2p 3/2 peaks at binding energy 464.2 eV and 458.5 eV, which indicate Ti⁴⁺ species and no time dependent spectral change was observed. The Pd 3d spectra shows Pd 3d 5/2 at binding energy 336.2 eV for PdO and at binding energy 338.2 eV for Pd(OH)₂ [39-43]. The corresponding Pd 3d 3/2 peaks at binding energy 341.5 eV and 343.5 eV shows a universal binding energy difference of 5.3 eV, which is in highly agreement with literature values. No time dependent spectral change was observed for Pd 3d spectra. The O 1s spectra were deconvoluted into 3 components at binding energy 529.5 eV (O²⁻), 531.5 eV (OH etc.), and 533.3 eV (H₂O_(ads) etc.). There is no change of these 3 peaks (both binding energy and intensity) observed from O 1s spectra. The C 1s spectra

were also deconvoluted into 3 components at binding energy 284.8 eV (C-H etc.), 286.3 eV (C-O etc.), and 288.8 eV (O=C-O etc.). The peak binding energy and intensity of these 3 components did not show any change by continuous X-ray exposure.

Besides, Pt/TiO₂ was also prepared and characterized by time dependent XPS. Figure 7.17 shows the time dependent XPS spectra of 7.2wt% Pt/TiO₂ (same atomic fraction of Pt as Ag of 4wt% Ag/TiO₂) sample. The Ti 2p spectra show two Ti 2p 3/2 peaks at binding energy 458.5 eV and 459.8 eV indicating Ti⁴⁺ and Ti(hole) species, respectively. Time dependent spectral change with peak intensity shift from Ti(hole) to Ti⁴⁺ was observed. The Ti 2p spectra show the photogeneration and relaxation of titanium hole species on TiO₂, but the Ti(hole) species peak intensity was only 20% of the overall Ti 2p 3/2 peak intensity from the first XPS scan. The phenomenon is similar to 1wt% Ag/TiO₂ sample, which we define it as “partially excited” state. The Pt 4f spectra show two Pt 4f 7/2 peaks at binding energy 72.0 eV and 74.0 eV indicating Pt²⁺ and Pt⁴⁺ species [44-48], respectively. Time dependent spectral change with peak intensity shift from Pt⁴⁺ to Pt²⁺ was observed simultaneously with the spectral change observed in Ti 2p spectra, which indicates the photoreduction of Pt⁴⁺ to Pt²⁺. Interestingly, minimal spectral change was observed in C 1s spectra, which demonstrates Ti(hole) and hydroxyl species did not interact with carbon species potentially be due to the low concentration of those reactive species. The O 1s spectra show insignificant spectral change with a small portion of OH etc. peak intensity shifted to O²⁻ peak. The X-ray induced spectral change ended at 30 minutes of X-ray exposure, and no more spectral change in any region scan was observed after 30 minutes X-ray irradiation.

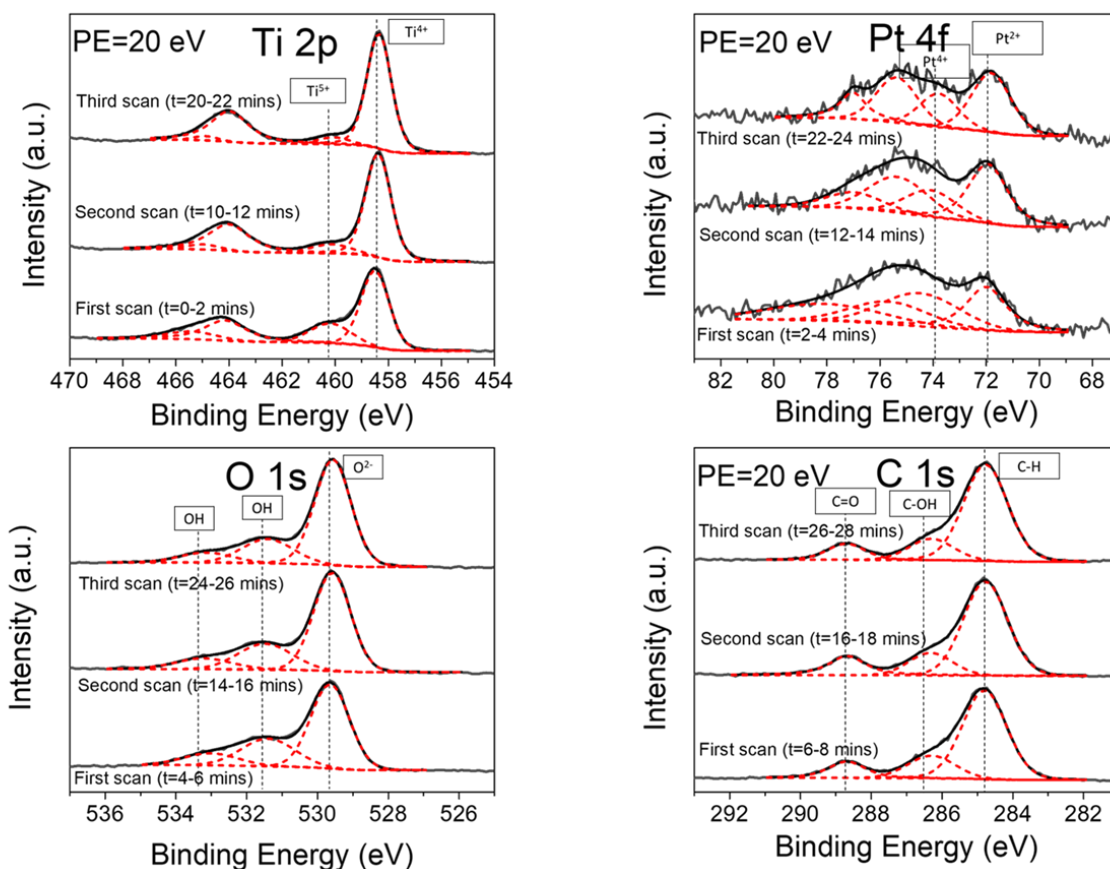


Figure 7.17 In situ time dependent high-resolution XPS spectra of 7.2 wt%Pt/TiO₂ sample.

The 7.2wt% Pt/TiO₂ sample is of interest as Pt has similar electrochemical properties as Ni and Pd, but the Ti(hole) species and the time dependent relaxation of Ti(hole) species was “partially” observed. A previous photocatalytic reactivity study illustrated the reaction activity of metal ions on Titania support is related to their reduction potentials. The standard reduction potentials of Ag⁺/Ag, Cu²⁺/Cu, Pt(OH)₂/Pt, Pd(OH)₂/Pd, and Ni²⁺/Ni are +0.800, +0.342, +0.140, +0.07, and -0.72 V, respectively. Accordingly, Ag⁺ served as a better electron acceptor owing to its higher positive reduction potential. We suppose that there is a critical reduction potential value, below which the photogenerated electrons and holes were not able to be separated by the dopant electron acceptor. Based on the experimental results from different transition metals doped on Titania support, the time dependent observation of Ti(hole) species is highly dependent

on the relative reduction potential of the metal ion dopant. The better the electron acceptor, the more hole species were observed. When the dopant metal ions were able to efficiently capture the electrons, the hole species were able to be stabilized by the reaction intermediates such as hydroxyl radicals. Due to the sampling depth of XPS is only $\sim 5\text{-}7\text{ nm}$, the chemical composition change below 5-7 nm depth needs to be characterized and analyzed in the future work.

7.4.4 XPS analysis of Ag/SiO₂ and Ag/Al₂O₃

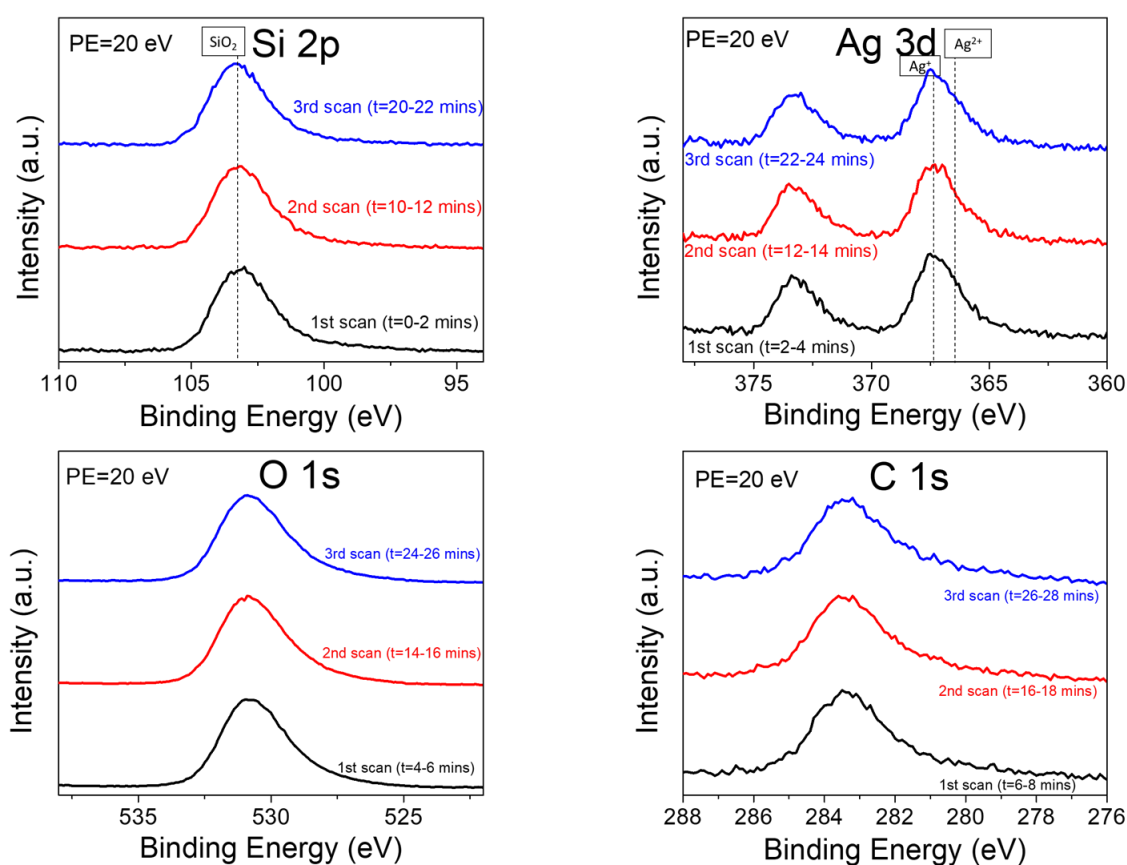


Figure 7.18 Time dependent XPS spectra of Si 2p, Ag 3d, O 1s, and C 1s of Ag/SiO₂ sample

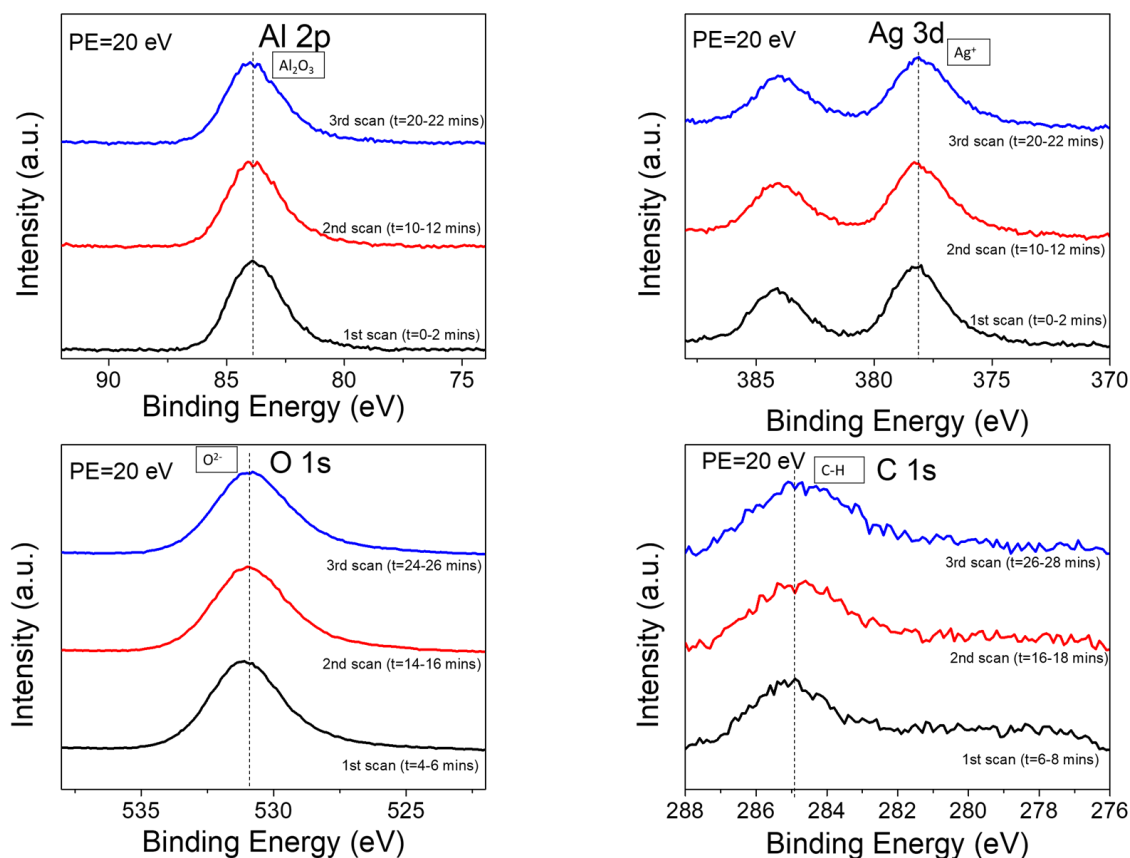


Figure 7.19 Time dependent XPS spectra of Al 2p, Ag 3d, O 1s, and C 1s of Ag/Al₂O₃ sample

Time dependent XPS spectra of Ag/SiO₂ and Ag/Al₂O₃ samples are shown in Figure 7.18 and Figure 7.19. There is no time dependent spectral change and Ti(hole) species observed from Figure 7.18 and Figure 7.19. From Figure 7.18, SiO₂ is identified by the Si 2p 1/2 peak at 103.3 eV in Si 2p spectra. And Ag⁺ and Ag²⁺ are identified by Ag 3d 3/2 peaks at 367.3 eV and 366.7 eV in Ag 3d spectra. The O 1s spectra were deconvoluted into 3 components, which are the O²⁻ species at binding energy 529.5 eV, OH etc. species at binding energy 531.5 eV, and H₂O(ads) etc. species at 533.3 eV. No time dependent spectral change was observed for the O 1s spectra. The C 1s spectra were also deconvoluted into 3 components, which are C-H etc. species at binding energy 284.8 eV, C-O etc. species at binding energy 286.3 eV, and O=C-O etc. species at binding energy 288.8 eV. There was no time dependent spectral change observed on Ag/SiO₂

sample, which indicates Ag/SiO₂ sample does not have similar properties as Ag/TiO₂ sample. Similar results are observed from Figure 7.19, which indicates Ag/Al₂O₃ sample also does not have similar properties as Ag/TiO₂ sample. The results from Figure 7.18 and Figure 7.19 potentially imply that the unique band structure of anatase TiO₂, the surface defect sites on anatase TiO₂, and the special bonding between Ag⁺ and anatase TiO₂ are the key factors for the Ti(hole) phenomenon.

7.5 Conclusion

In this chapter, the X-ray induced photocatalytic reactions on Ag/TiO₂ samples and other transition metal doped Titania samples were studied and a systemic XPS characterization of M/TiO₂ (M=Ag, Cu, Pt, Ni, and Pd) samples was conducted. The results indicate a potential reaction mechanism that the X-ray irradiation was capable to produce electrons and holes on the surface and in the bulk of TiO₂. And the dopant metal ions functioned as electron acceptors to capture the photogenerated electrons and to transfer those electrons to adsorbed H₂O or other reductive reactants. The photogenerated hole species were transferred to the surface and were stabilized by reaction intermediates such as hydroxyl radicals. The Ti(hole) phenomenon is highly related to the coverage of the dopant metal ions on Titania surface. With less than one monolayer of Ag ions, the peak intensity of Ti(hole) species from the first XPS scan was proportional to the coverage percentage of the Ag dopants on TiO₂ surface. When Ag becomes to aggregate on TiO₂ surface, the addition of silver did not show any significant impact on the Ti(hole) phenomenon.

The investigations on different transition metal ions doped on TiO₂ samples showed different results from in situ time dependent XPS experiments. Both Ag/TiO₂ and Cu/TiO₂ samples showed time dependent X-ray induced excitation and relaxation of Ti(hole) species, but

XPS study on Ni/TiO₂ and Pd/TiO₂ samples did not show any spectral change nor the observation of Ti(hole) species. The Pt/TiO₂ sample is of interest since it showed a “partial excitation” by X-ray irradiation, which means a small portion of Ti(hole) species was observed. The proposed mechanism of this phenomenon is highly related to the relative photocatalytic activity of the dopant metal ions on Titania support. The higher the reduction potential of the metal ions, the better it can separate electrons and holes so that the more Ti(hole) species was monitored by XPS. The results provide us a promise that there is a critical reduction potential value of the transition metal ions that below which no Ti(hole) species was able to be stabilized by the dopant metal ions.

Same XPS study on Ag/SiO₂ and Ag/Al₂O₃ samples did not show similar results as Ag/TiO₂ sample. The special band structure of semiconductor anatase TiO₂ and the surface defect sites on anatase TiO₂ and the unique bonding between Ag⁺ and anatase TiO₂ are proposed to be the key factors for the observation of the stabilized Ti(hole) phenomenon.

The X-ray irradiation has a much larger transmission depth compared to XPS sampling depth, which means the X-ray induced photocatalytic reactions could happen both on the surface and in the bulk layers of TiO₂. Because Ag atoms exist both on the surface and in the bulk of TiO₂, the X-ray induced reactions could potentially happen both on the surface and in the bulk. While electrons were captured by Ag⁺ atoms and Ag⁺ atoms were reduced to metallic Ag, the sample color turned from white to dark brown. The time dependent atomic fraction analysis shows a universal reaction stoichiometry between titanium and oxygenated species with an atomic fraction change ratio of 1:1 in terms of continuous X-ray exposure. But the ratios between Ag and Ti is way smaller than 1. It is potentially due to the Ag atoms are immobile in the sample, but the hole species could be transferred to the surface. So that the amount of Ag atoms

involved in the reactions were much larger than the calculational value obtained from XPS spectra.

The reaction mechanisms could be further explored by investigating the chemical composition change in the bulk layers by X-ray exposure using other surface characterization techniques with deeper sampling depth. The progress will be included in future work.

7.6 Reference

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8.1 Abstract

A stabilized titanium hole species was observed during in situ time dependent XPS characterization of 4wt% Ag/TiO₂ sample and previous studies by our laboratory showed the adsorbed H₂O and surface hydroxyls (OH) on TiO₂ surface defective sites played an important role to stabilize the X-ray induced hole species under ultra-high vacuum (UHV) conditions. The current study further explores the impact of oxygenated species on the titanium hole species phenomenon by means of temperature programmed X-ray Photoelectron Spectroscopy (XPS). Both neat TiO₂ and 4wt% Ag/TiO₂ were investigated at different hydration levels as determined by Thermogravimetric Analysis (TGA). 4wt% Ag/TiO₂ samples were prepared in flowing air and flowing oxygen environments and the as prepared 4wt% Ag/TiO₂ samples showed different colors. The 4wt% Ag/TiO₂ sample prepared in flowing oxygen showed black color and there was almost no adsorbed H₂O as well as no hole species observed by XPS. For the 4wt% Ag/TiO₂ sample prepared in air, time dependent spectral change associated with the generation and relaxation of titanium hole species was observed. Vacuum heating of this sample at 400 °C for 2 hours in the UHV chamber caused color change from white to black as well as significant desorption of adsorbed H₂O/OH. And the following in situ time dependent XPS characterization showed significantly reduced amount of titanium hole species, which indicates the adsorbed H₂O/OH was the essential component for the generation and stabilization of the hole species on 4wt% Ag/TiO₂ sample under UHV conditions. Further X-ray exposure caused desorption of hydroxyls in form of H₂O so that the relaxation of hole species was triggered as indicated by the XPS quantitative analysis results.

8.2 Introduction

As a promising photocatalyst and semiconductor material, TiO_2 has been widely used in photocatalytic removal of pollutants [1-5], renewable energy catalysis [6-10], and disinfection [11-13]. Due to its stability, high efficiency, and low cost, TiO_2 materials have drawn extensive interests by scientists and researchers. A variety of research efforts [14-20] have shown adsorbed H_2O plays an important role in TiO_2 photocatalysis. Wang et, al. [14] performed an XPS and UPS study on a high surface area anatase TiO_2 material, and the results showed there were a lot of surface defective sites on the TiO_2 surface. Their study also indicated H_2O was mainly adsorbed on the surface defective sites of anatase TiO_2 , re-oxidizing Ti^{3+} defective sites into Ti^{4+} with formation of Ti(IV)-OH . And the more the defective sites on TiO_2 surface, the more H_2O could be adsorbed. Liu et, al. [15] reported that their Atomic Force Microscopy (AFM) study showed UV irradiation on TiO_2 film caused desorption and re-adsorption of H_2O from the bulk to the surface. A ~ 30 nm water layer was formed on the surface after 90 minutes UV illumination. This H_2O layer was physically absorbed H_2O and it could be wiped off by UHV. And UV irradiation converted Ti-O-Ti into Ti-OH . Tan et, al. [16] conducted a low temperature Scanning Tunneling Microscopy (STM) at 80 K, and the results showed UV irradiation initiated the dissociation of H_2O through oxidation by photo-holes to form additional terminal (free) hydroxyls OH_t . These OH_t could be diffused and even desorbed from the surface.

Hydroxyl groups are formed by the highly reactive intermediates hydroxyl radicals for TiO_2 photocatalysis [21-25]. Hajnalka Czili and Attila Horvath [21] investigated the applicability of coumarin for detecting and measuring hydroxyl radicals generated by photoexcitation of TiO_2 nanoparticles. They used silver ion as electron acceptor and reported the luminescence intensity increased with irradiation time until the deposition of silver on the surface of TiO_2 was

completed which indicated the silver ions were able to hold and separate the photoelectrons and holes by means of converting hydroxyl radicals into hydroxides. Rafik Addou et, al. [22] studied the agglomeration of transition metal atoms on TiO_2 by means of Scanning Tunneling Microscopy (STM) experiments and Density Functional Theory (DFT) calculations. They illustrated the hydroxylated surface promoted the dispersion of transition metal ions, and thus improved the photocatalytic activity of the transition metal ion doped TiO_2 catalyst. Besides, hydroxyls are also widely applied to the single atom catalysis [26-28] due to their unique electrochemical properties to stabilize highly active species.

Our laboratory has been focused on TiO_2 adsorptive desulfurization of liquid fuels for decades and huge progress and improvements have been achieved [29-33]. Based on the unique photoelectrical properties of anatase TiO_2 , a novel photo-assisted adsorptive desulfurization method was introduced by one-time ex-situ UV treatment on the anatase TiO_2 adsorbent and the sulfur heterocycle removal saturation capacity was enhanced by 65% [29]. The enhancement was persistent over several adsorption and desorption cycles. The UV irradiation pretreatment has been proven to cause permanent surface alternation of the TiO_2 adsorbent. Both FTIR and XPS studies [30,31] demonstrated the UV irradiation caused photocatalytic reactions between adsorbed H_2O and lattice oxide oxygen on the surface defective sites of the TiO_2 sample to form additional isolated hydroxyl groups. The photocatalytic reaction is irreversible as the photogenerated isolated hydroxyls are stable under laboratory conditions for several weeks. The enhanced sulfur heterocycle removal saturation capacity was attributed to the formation of additional surface isolated hydroxyls.

By introducing 4wt% of Ag on anatase TiO_2 adsorbent, the adsorptive sulfur heterocycle removal saturation capacity of the adsorbent was also enhanced by 55% [31,32]. The unique

electrical and catalytic properties of Ag(I) ion promoted the density of surface hydroxyls on TiO₂ adsorbent surface. Both XPS, FTIR and Density Functional Theory (DFT) studies [31-33] showed the Ag(I) ions were highly dispersed on the surface defective sites of TiO₂ adsorbent and the positive charge of Ag(I) ion was neutralized by hydroxyls in form of AgOH so that it created more surface isolated hydroxyls on TiO₂ surface. Moreover, 4wt% Ag/TiO₂ sample exhibits unique photoelectrical properties and anomalous time dependent chemical reactions were observed by in-situ time dependent XPS characterization of 4wt% Ag/TiO₂ sample under ultrahigh vacuum (UHV) conditions [34]. A stabilized titanium hole species was observed by XPS and it was formed by the photo-holes created by X-ray photons on TiO₂. The photoelectrons were captured by AgOH to form metallic Ag and leave free hydroxyls on the sample surface. And the photo-holes were entrapped by Ti⁴⁺ and O²⁻ to form TiO₂^{+(hole)} species. The TiO₂^{+(hole)} species were proposed to be stabilized by surface hydroxyls.

The current study further investigates the effects of oxygenated species of neat TiO₂ and 4wt% Ag/TiO₂ samples by varying the initial hydration levels of the samples. By tracking the molecular composition change of oxygenated species from XPS characterizations, their influence on the time dependent observation of the stabilized titanium hole species was revealed and so that the relationship and impact of oxygenated species on the hole generation and stabilization by X-ray irradiation under UHV conditions was elucidated.

8.3 Experimental

8.3.1 Sample preparation

Neat TiO₂ sample was prepared by crushing and sieving the as-received 3.2 mm TiO₂ pellets to 75-125 μ m powders and then the powder sample was calcined at 450 °C in flowing air followed by in-situ cooling in flowing air for another 2 hours. Two methods were used to prepare

4wt% Ag/TiO₂ samples by varying the calcination environment. For both methods, the as-received 3.2 mm TiO₂ pellets were crushed and sieved to 800 to 1400 µm followed by drying in a convection oven at 110 °C for 24 hours. Silver was introduced by incipient wetness using Ag(I)NO₃ solution followed by drying in a convection oven at 110 °C for another 24 hours. Then the sample was further crushed and sieved to 75-125 µm. The sample was then calcined at 450 °C for 2 hours followed by in-situ cooling for another 2 hours in flowing air and flowing oxygen environment. To make it simple, the 4wt% Ag/TiO₂ samples are defined as 4wt% Ag/TiO₂ (I): was calcined and cooled in flowing air condition, 4wt% Ag/TiO₂ (II): was calcined and cooled in flowing oxygen condition. All the samples were directly loaded into XPS system for XPS characterization.

8.3.2 Brunauer-Emmett-Teller (BET) measurement

Brunauer-Emmett-Teller (BET) surface areas of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) samples were determined by N₂ adsorption at -196 °C using a NOVA 2200e surface area analyzer. The BJH desorption branch of the isotherm was used to calculate the pore size distribution of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) samples. Before analysis, all samples were degassed at 400 °C for 5 h under a flow of helium.

8.3.3 X-ray Diffraction (XRD) measurement

A Bruker D-8 X-ray diffractometer equipped with a CuKα (40 KV/40 mA) source was used for XRD characterizations of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) samples. The XRD scan range was 20-90 degrees, and the scan speed was 0.1 s/step (~5.85 degrees/min).

8.3.4 Thermogravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) were conducted to determine the hydration levels of the samples. A TGA-Q500 instrument (TA Instrument) was used for TGA experiments. TGA

experiments were conducted by using 30 mg of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) powder samples that were pretreated at 110 °C in a convection oven for 24 hours. The samples were heated from 25 °C to 700 °C at a rate of 20 °C/min followed by cooling from 700 °C to 100 °C at a rate of 25 °C/min in flowing N₂ at 40 cm³/min.

8.3.5 XPS characterization

The XPS characterizations were carried out using a Kratos Analytical Ltd. AXIS Ultra delay lines detector (DLD) X-ray Photoelectron Spectrometer equipped with a monochromatic Al K α X-ray source with irradiation photon energy of 1486.8 eV. The XPS end station contains a fast entry load lock, a sample treatment chamber, and a sample analytical chamber. All the powder samples were mounted on the sample holder bar by double-sided tapes or by specially designed copper microfiber foils. Prior to XPS characterization, all the samples were evacuated at a background pressure of 3.2×10^{-10} torr for at least 72 hours in the sample treatment chamber. Then the samples were transferred into the analytical chamber at background pressure of 7.9×10^{-10} torr for XPS characterizations. For the current XPS characterization settings, the X-ray irradiation power output was 10 mA and 15 kV for all the experiment cases. The X-ray irradiation spot size was about $300 \times 700 \mu\text{m}^2$ and the angle between the sample bar and the mono Al X-ray source was 35 degrees. No surface cleaning treatment was used in the present experiments. The overall resolution of the spectrometer in the current setting mode was 0.65 eV measured as a full width half max (FWHM) of the Ag 3d 5/2 line. The spectrometer was calibrated by constraining binding energy of Au 4f_{7/2} at 84.0 eV. A pass energy of 160 eV with a step of 0.5 eV was used to obtain the survey scan of the TiO₂ sample. A pass energy of 20 eV with a step of 0.1 eV was used to measure photoelectron core-level spectra of Ti 2p, O 1s, C 1s, and Ag 3d. The narrow scans were measured as a function of X-ray exposure time to the samples.

The deconvolution of the core level photoelectron peaks was conducted using the public software package XPSPEAKS 4.1 following the same procedure as reported by literature [35-37]. After subtraction of the Shirley-type background, the spectra were decomposed into their components at suggested binding energies with mixed Gaussian-Lorentzian lines by a non-linear least squares curve-fitting method. The binding energies and full width half max (FWHM) of the peaks were recorded by the fitting results. Surface chemical composition calculations were derived by the deconvoluted peak areas and the atomic sensitivity factors provided by the standard XPS handbook.

8.3.5.1 Atomic fraction calculation methodology from XPS results

From first principle, the intensity of the photoelectron peak (peak area) is described by [30,32]:

$$I = I_0 n \sigma \lambda(\epsilon) D(\epsilon) \int_0^t e^{-t/\lambda} dt \quad (1)$$

Where I_0 : X-ray flux; N : Density of atoms; σ : Photoelectron cross-section; I : XPS peak intensity (peak area); $\lambda(\epsilon)$: Mean free path of energy(ϵ); $D(\epsilon)$: Fraction of electrons detected by the analyzer; t : The sampling depth.

With the peak intensities of each species from deconvolution results, the mole fraction of each species can be calculated by:

$$C(i) = \frac{n(i)}{\sum n(i)} = \frac{I(i) \sigma(i) \lambda(\epsilon i) D(\epsilon i) \int_0^t e^{-t/\lambda} dt}{\sum I(i) \sigma(i) \lambda(\epsilon i) D(\epsilon i) \int_0^t e^{-t/\lambda} dt} \quad (2)$$

To better evaluate the results, the atomic fraction of total titanium $C(Ti_{tot})$ is used as a reference, and the atomic fraction ratios of different species over total titanium could be calculated by:

$$\frac{c(i)}{c(Titot)} = \frac{I(i)\sigma(i)\lambda(\epsilon i)D(\epsilon i)\int_0^{\infty} e^{-t/\lambda} dt}{I(Ti)\sigma(Ti)\lambda(\epsilon Ti)D(\epsilon Ti)\int_0^{\infty} e^{-t/\lambda} dt} \quad (3)$$

Where $I(i)$: XPS peak intensity from the top monolayer of species i ; $\sigma(i)$: Photoelectron cross-section of species i ; $\lambda(\epsilon i)$: Mean free path of energy(ϵ) for species i ; $D(\epsilon i)$: Fraction of electrons detected by the analyzer for species i ; t : The sampling depth.

8.3.6 Sample preheating in UHV

To verify the existence of adsorbed H_2O/OH and to investigate the contribution of adsorbed H_2O/OH to the time dependent observation of titanium hole species on 4wt% Ag/ TiO_2 sample, preheating of neat TiO_2 , 4wt% Ag/ TiO_2 (I), and 4wt% Ag/ TiO_2 (II) samples were conducted in the analytical chamber of XPS under UHV conditions.

8.3.6.1 Preheating of neat TiO_2 sample

The XPS characterization of neat TiO_2 sample mounted on a piece of copper microfiber foil was first conducted at room temperature (25 °C). Then the sample was heated to 100 °C and to 400 °C for 2 hours followed by XPS characterizations at each temperature. High-resolution Ti 2p, O 1s, and C 1s narrow scans were measured directly after the preheating procedures.

8.3.6.2 Preheating of 4wt% Ag/ TiO_2 (I) and 4wt% Ag/ TiO_2 (II)

Preheating of 4wt% Ag/ TiO_2 (I) and 4wt% Ag/ TiO_2 (II) samples were conducted by mounting the samples on copper microfiber foils. The samples were heated to 400 °C in the analytical chamber under UHV conditions (background pressure of 7.9×10^{-10} torr) for 2 hours. Time dependent XPS characterization of Ti 2p, Ag 3d, O 1s, and C 1s narrow scans were carried out every 30 minutes directly after the sample preheating process.

8.4 Results and discussion

8.4.1 BET analysis

Table 8.1. BET surface area, pore volume, and pore radius of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II).

Textual properties	Neat TiO ₂	4wt% Ag/TiO ₂ (I)	4wt% Ag/TiO ₂ (II)
Surface Area ² (m ² /g)	162.9	172.5	172.3
Pore Volume ³ (cm ³ /g)	0.47	0.43	0.43
Pore Radius (nm)	10.9	9.2	9.3

The BET surface areas, pore volumes, and average pore radius of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) samples are summarized in Table 8.1. There is no significant difference of BET results between 4wt% Ag/TiO₂ (I) and 4wt% Ag/TiO₂ (II) samples, which indicates the calcination and cooling in flowing air and flowing oxygen conditions did not make significant difference to the surface and pore structures of 4wt% Ag/TiO₂ samples. But the addition of 4wt% Ag on TiO₂ slightly created more surface area than neat TiO₂ sample. As it is reported in earlier studies [32,33], the Ag atoms are highly dispersed on TiO₂ surface defective sites so that additional surface area was created by the addition of Ag. And the small decrease of pore volume and average pore radius could be because Ag atoms locate inside the pore structure of TiO₂ and occupy a little bit space inside the pores of TiO₂. The high surface areas of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) samples indicate there could be adsorbed H₂O on the sample surfaces [38,39].

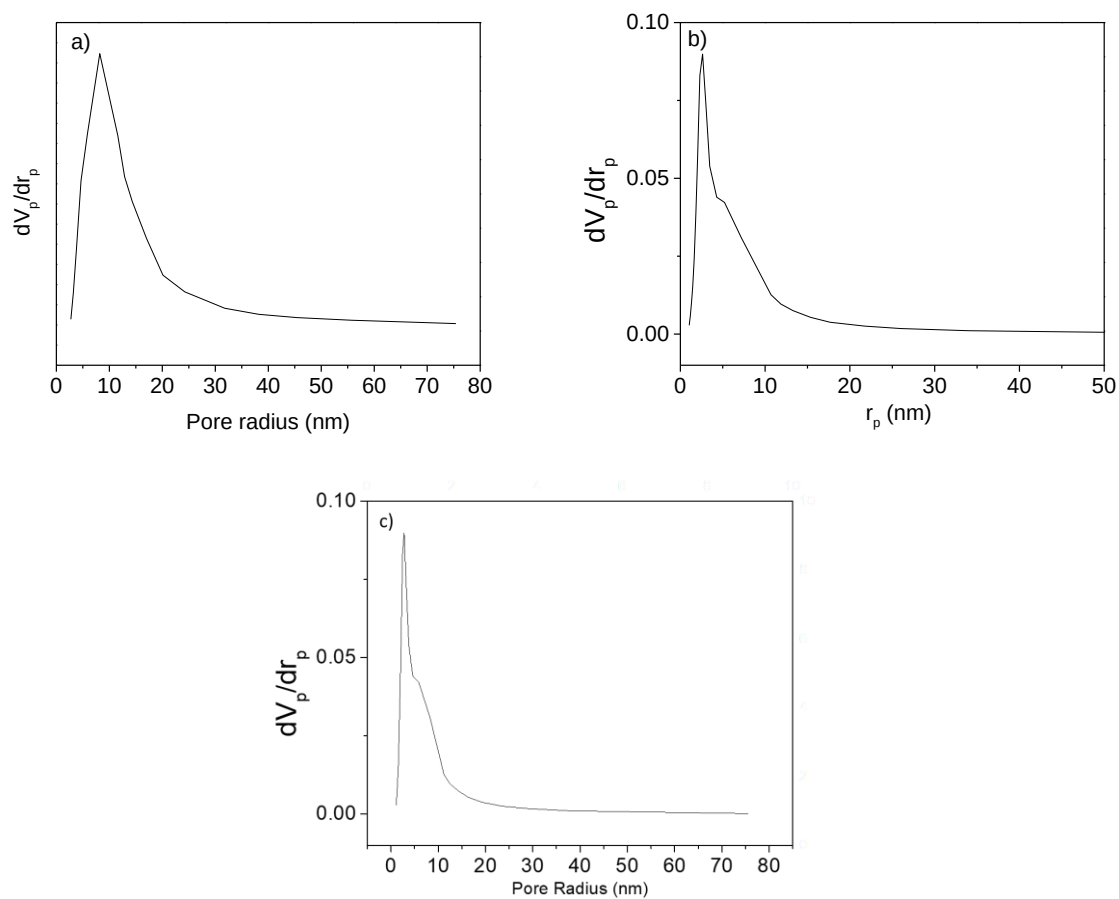


Figure 8.1. Pore radius distribution of a) neat TiO₂, b) 4wt% Ag/TiO₂ (I), and c) 4wt% Ag/TiO₂ (II).

Figure 8.1a) – c) illustrate the pore size distribution of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) samples. The average pore diameters are 10.9 nm for neat TiO₂ sample, 9.2 nm for 4wt% Ag/TiO₂ (I), and 9.3 nm for 4wt% Ag/TiO₂ (II). The average pore diameters of neat TiO₂, 4wt% Ag/TiO₂ (I), and 4wt% Ag/TiO₂ (II) samples are enough for H₂O adsorption [38,39].

8.4.2 XRD patterns

Figure 8.2 shows the XRD patterns of neat TiO_2 , 4wt% Ag/ TiO_2 (I), and 4wt% Ag/ TiO_2 (II) samples. As it is shown in Figure 3, all the peaks indicate anatase phase of TiO_2 . Peaks at 25, 38, 48, 54, 56, 63, 69, 71, 75, 83 degrees indicate (101), (004), (200), (105), (211), (204), (116), (220), (215), (303) anatase TiO_2 phases [40-42]. Since the bandgap of anatase TiO_2 is 3.2 eV (387 nm in wavelength) [43,44], any photon with energy higher than 3.2 eV is capable to excite the valence electron of TiO_2 . There is no difference in XRD patterns for all the samples. No Ag XRD pattern is observed from 4wt% Ag/ TiO_2 (I) and 4wt% Ag/ TiO_2 (II) samples. The results also indicate Ag atoms are highly dispersed on TiO_2 surface and the particle size of silver is below the detection limit of XRD (<40 nm) [32,33].

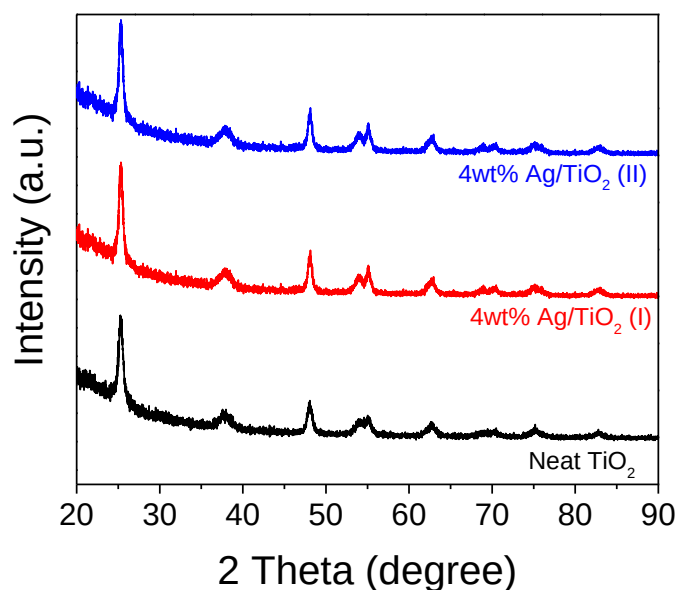


Figure 8.2. XRD patterns of neat TiO_2 , 4wt% Ag/ TiO_2 (I), and 4wt% Ag/ TiO_2 (II) samples.

8.4.3 Thermogravimetric analysis (TGA) of adsorbed H_2O

To measure the relative amount of $\text{H}_2\text{O}/\text{OH}$ adsorbed on neat TiO_2 , 4wt% Ag/ TiO_2 (I), and 4wt% Ag/ TiO_2 (II) samples, Thermogravimetric Analysis (TGA) experiments were conducted.

Figure 8.3 shows the TGA results of these 3 samples from 25 °C to 700 °C under flowing N₂. When temperature was raised from 25 °C to 100 °C, all the samples showed a significant weight loss due to the desorption of moisture. However, there is a significant difference between the TGA results of 4wt% Ag/TiO₂ (II) and 4wt% Ag/TiO₂ (I) samples. There is a minimal weight percentage loss of 4wt% Ag/TiO₂ (II) sample after 100 °C, which means the 4wt% Ag/TiO₂ (II) sample contains almost no adsorbed H₂O through the preparation procedure by calcinating and cooling in flowing oxygen condition. But the TGA result of 4wt% Ag/TiO₂ (I) shows continuous weight loss until up to 700 °C, which indicates the continuous desorption of adsorbed H₂O of the sample. The weight percentage loss was 3.5% till 700 °C for neat TiO₂ sample, 5.0% till 700 °C for 4wt% Ag/TiO₂ (I), and 1.9% till 700 °C for 4wt% Ag/TiO₂ (II). And most of the weight percentage drop of 4wt% Ag/TiO₂ (II) was attributed by the desorption of moisture before 100 °C, which potentially means the 4wt% Ag/TiO₂ (II) contains almost no adsorbed H₂O after degassing under UHV conditions.

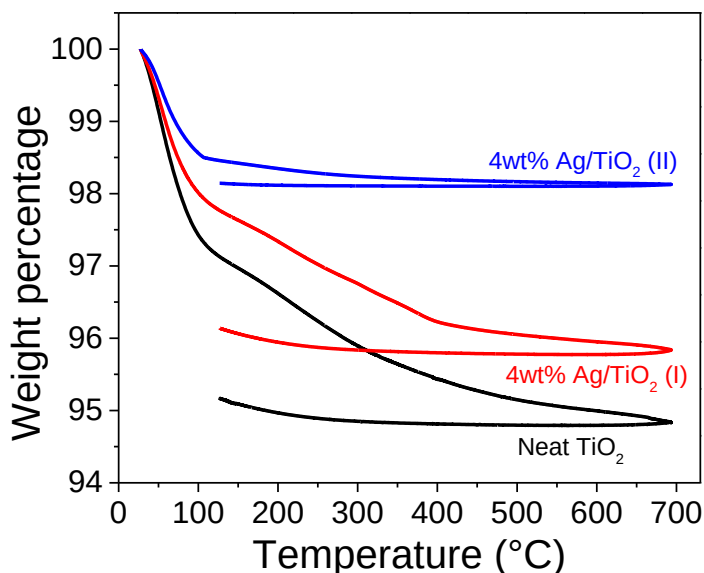


Figure 8.3. TGA results of Neat TiO_2 , 4wt% Ag/TiO_2 (I) and 4wt% Ag/TiO_2 (II) samples from 25°C to 700 °C in flowing N_2 conditions.

8.4.4 XPS results

8.4.4.1 XPS qualitative analysis

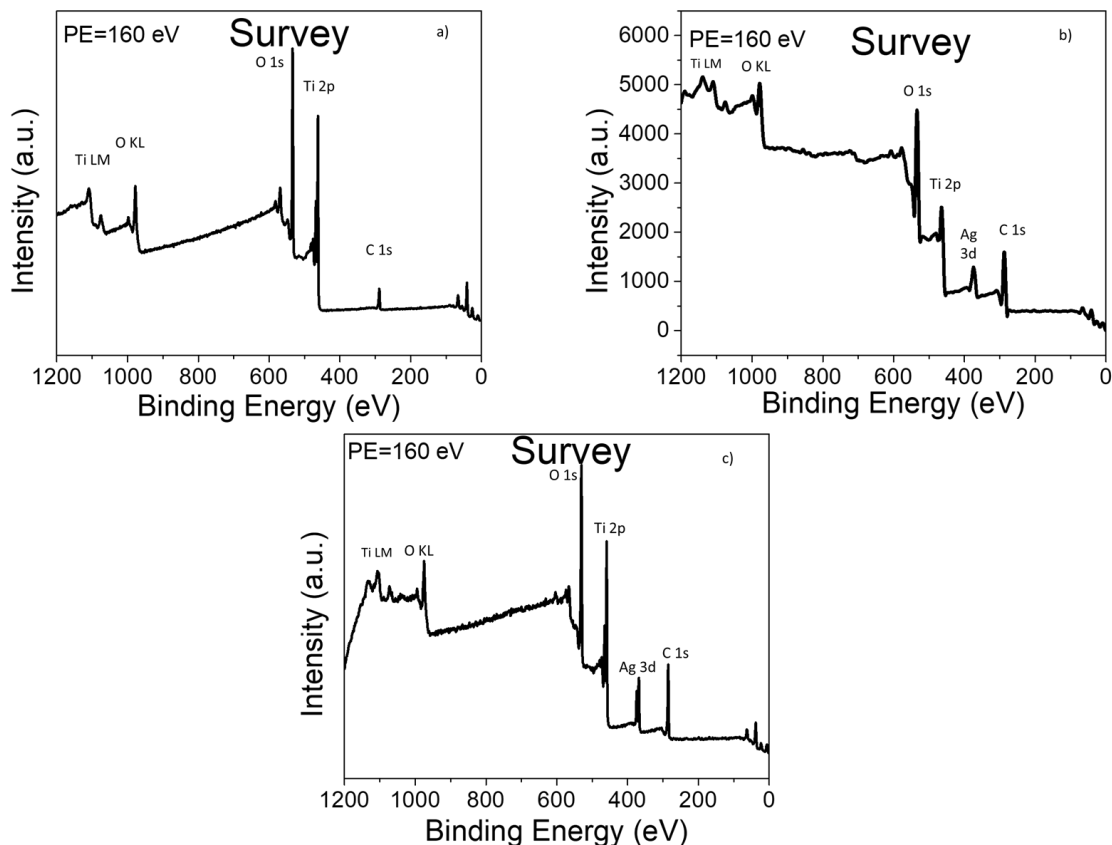


Figure 8.4. Survey spectra of a) neat TiO_2 , b) 4wt% Ag/TiO_2 (I), c) 4wt% Ag/TiO_2 (II) samples.

The survey spectra of neat TiO_2 , 4wt% Ag/TiO_2 (I), and 4wt% Ag/TiO_2 (II) samples are shown in Figure 8.4 a) – c). Figure 8.4a) shows there are only Ti, O, and C species on the survey scan of neat TiO_2 sample. Figure 8.4b) and Figure 8.4c) show there are Ti, Ag, O, and C species on 4wt% Ag/TiO_2 (I) and 4wt% Ag/TiO_2 (II) samples.

The high-resolution time dependent Ti 2p, C 1s, and O 1s spectra of neat TiO₂ sample is shown in Figure 8.5a) – c). Figure 8.5a) shows no time dependent Ti 2p spectral change and TiO₂ can be identified by Ti 2p 3/2 peak at binding energy of 458.5 eV. As it is shown in Figure 8.5b), no time dependent C 1s spectral change was observed, and the C-H etc., C-O etc., and C=O etc. species can be identified by C 1s peaks at binding energies of 284.8 eV, 286.4 eV and 288.7 eV. Figure 8.5c) shows no time dependent O 1s spectral change. The O 1s peak at binding energy of 529.8 eV is identified as lattice oxygen (O²⁻) in TiO₂, and the O 1s peak at binding energy of 531.5 eV is identified as OH species etc., and the O 1s peak at binding energy of 533.5 eV is identified as adsorbed H₂O species. The results agree with literature values [45-49].

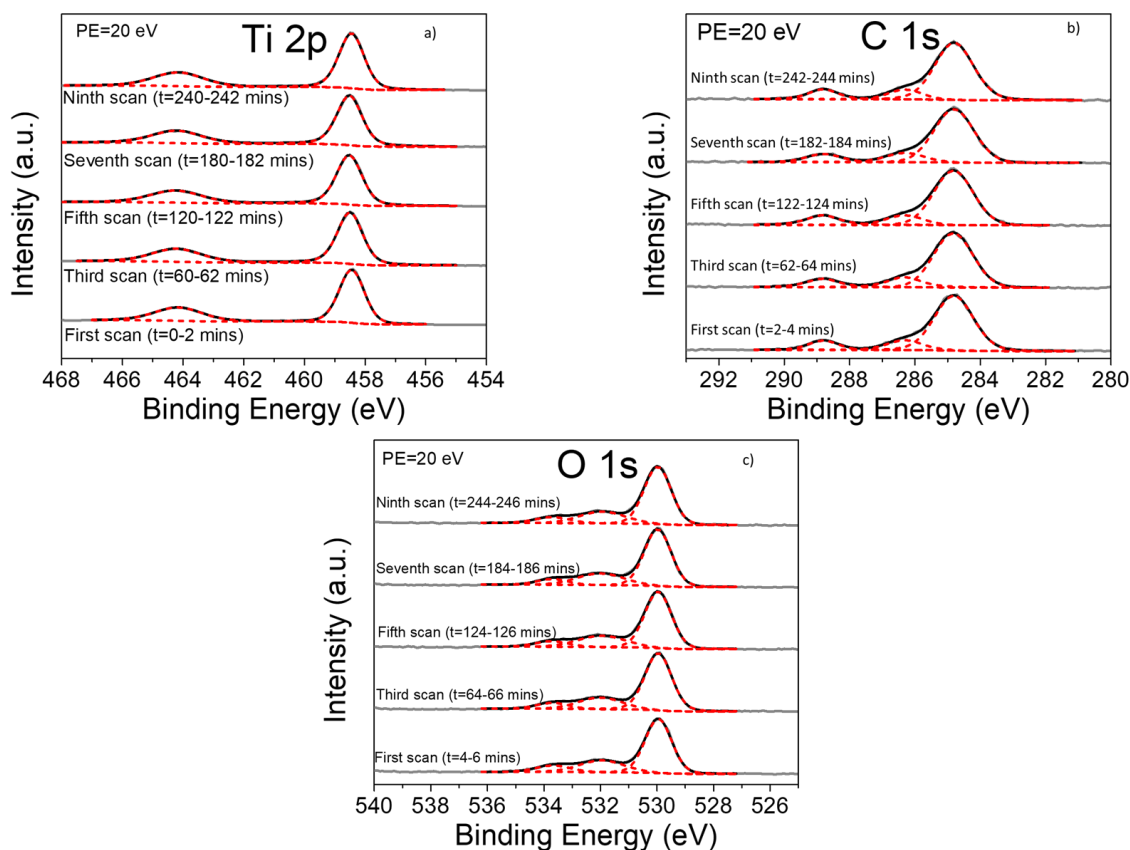
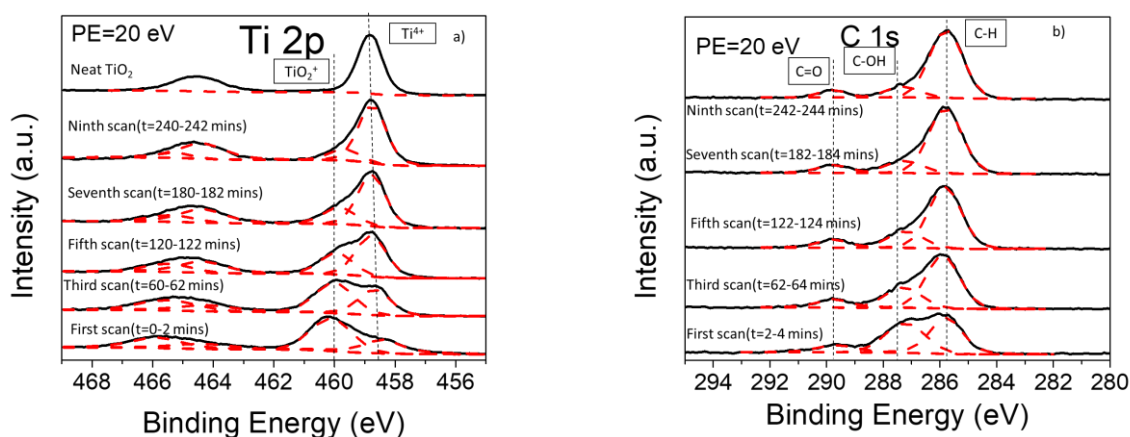


Figure 8.5. High-resolution time dependent Ti 2p, C 1s, and O 1s spectra of Neat TiO₂ sample.

Figure 8.6a-d) show the high-resolution time dependent Ti 2p, C 1s, O 1s, and Ag 3d XPS spectra of 4wt% Ag/TiO₂ (I) sample. The results have been reported earlier [35]. Figure 8.6a) shows two separate Ti 2p 3/2 peaks of TiO₂⁺_(hole) and Ti⁴⁺ at binding energies of 459.8 eV and 458.5 eV respectively. The time dependent spectral change of Ti 2p, C 1s, O 1s, and Ag 3d spectra indicate X-ray induced reactions on 4wt% Ag/TiO₂ (I) sample. The high energy X-ray photons continuously created pairs of photo-generated electrons and holes, and the electrons were captured by silver. Silver ions (Ag⁺) were reduced to form metallic silver during this process.



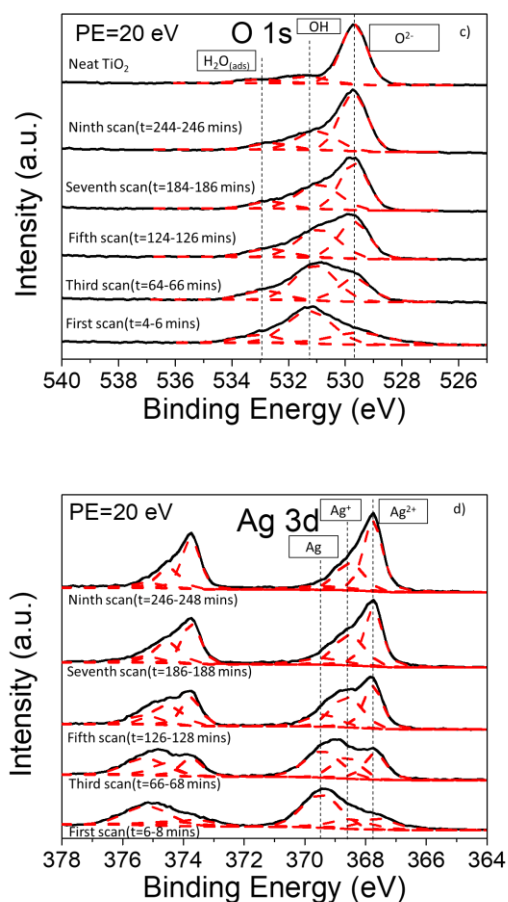


Figure 8.6. High-resolution time dependent XPS spectra of 4wt% Ag/TiO₂ (I): a) Ti 2p, b) C 1s, c) O 1s, and d) Ag 3d

The hydroxyl groups initially bonded to Ag⁺ became free hydroxyl groups and they were diffused to the surface. The hole carriers were entrapped by lattice O²⁻ to form O⁻ and the hole center was further shared by surface Ti⁴⁺ and O⁻ to form TiO₂^{+(hole)} species. The photogenerated TiO₂^{+(hole)} species were stabilized by the surface hydroxyls under UHV conditions. With continuous X-ray irradiation on the sample surface, X-ray photon stimulated desorption of OH potentially triggered the relaxation of TiO₂^{+(hole)} species. During the relaxation process of TiO₂^{+(hole)} species, metallic Ag was oxidized to Ag²⁺ by the TiO₂^{+(hole)} species.

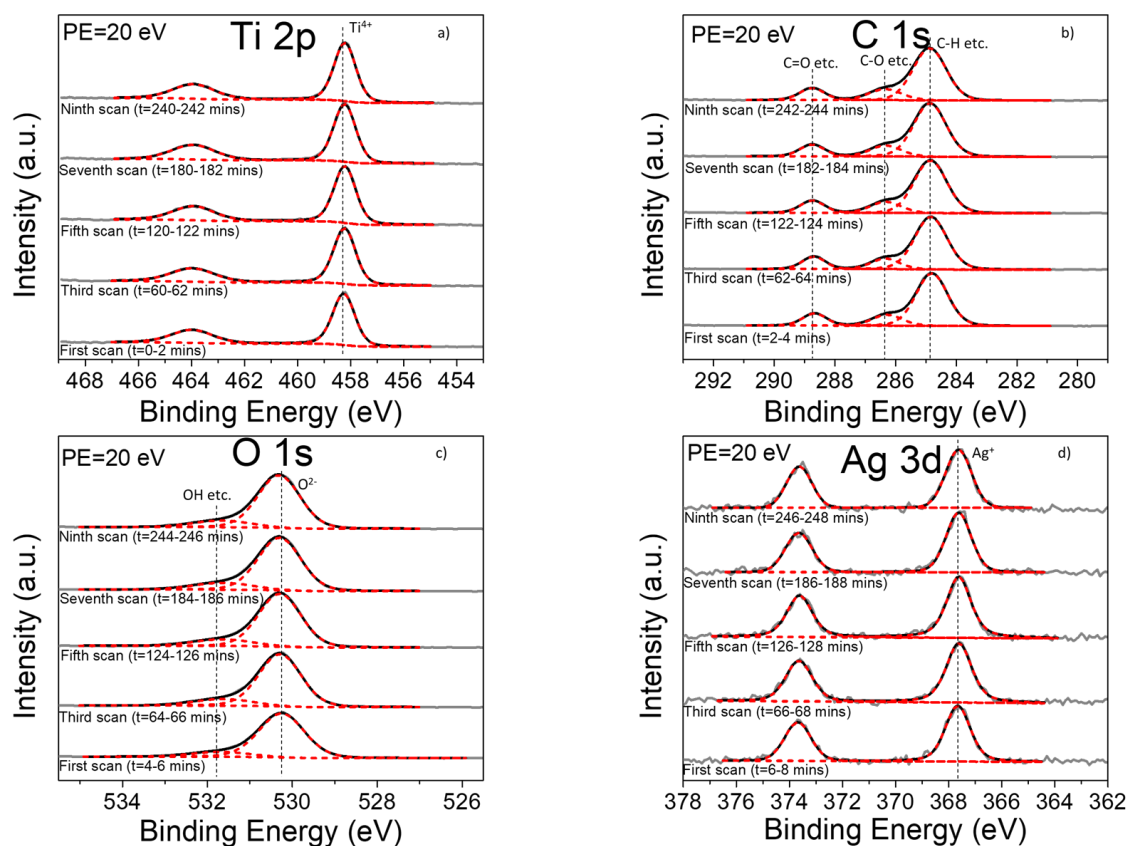


Figure 8.7. High-resolution time dependent XPS spectra of 4wt% Ag/TiO₂ (II): a) Ti 2p, b) C 1s, c) O 1s, and d) Ag 3d

However, Figure 8.7a-d) show different results for 4wt% Ag/TiO₂ (II) sample. No TiO₂⁺_(hole) species and no time dependent spectral change was observed. The difference between 4wt% Ag/TiO₂ (I) and 4wt% Ag/TiO₂ (II) sample is the initial hydration levels are different due to the calcination in flowing air and in flowing oxygen during the preparation process. And the TGA results confirm there was about 5% of adsorbed H₂O/OH on 4wt% Ag/TiO₂ (I) and only 1.9% of adsorbed H₂O/OH on 4wt% Ag/TiO₂ (II). And the 1.9% of adsorbed H₂O/OH was potentially wiped off by the evacuation pretreatment prior to the XPS characterizations [15,50]. The results potentially indicate the existence and availability of adsorbed H₂O/OH is the key factor for the

generation and stabilization of $\text{TiO}_2^{+}(\text{hole})$ species by X-ray irradiation on 4wt% Ag/TiO₂ sample under UHV conditions.

8.4.4.2 XPS analysis of preheated samples in UHV chamber

8.4.4.2.1 Preheating of neat TiO₂ sample

Table 8.2. Atomic ratios of oxygenated species with respect to Ti^{4+} of neat TiO₂ and 4wt% Ag/TiO₂ (II) sample at different temperatures.

Temperature (°C)	Atomic ratio $c(i)/c(\text{Ti}_{\text{tot}})$			
	O ²⁻	OH etc.	H ₂ O _(ads) etc.	Total O
25	2.110	0.274	0.046	2.430
100	2.100	0.109	0.011	2.220
400	2.091	0.096	0.000	2.187
Desorbed from 25 °C to 400 °C	0.019	0.179	0.046	0.244

In order to identify and calculate the amount of adsorbed oxygenated species on anatase TiO₂, neat TiO₂ sample was heated to 100 °C for 2 hours and was further heated to 400 °C for another 2 hours in UHV conditions in the analytical chamber of the XPS. Figure 8.8 shows the O 1s spectra of the neat TiO₂ sample at 25 °C, 100 °C, and 400 °C respectively. Significant peak intensity loss of adsorbed H₂O and OH was observed from Figure 8.8. The spectral results clearly indicate the existence of strongly adsorbed H₂O and OH species on TiO₂ surface even after 80 hours of degassing under UHV conditions. Table 8.2 shows the atomic ratios of oxygenated species over C(Ti_{tot}) of neat TiO₂ sample at different temperatures calculated by Equation (1), (2), and (3). The atomic ratios loss shows the desorption of adsorbed H₂O and hydroxyls by heating under UHV condition.

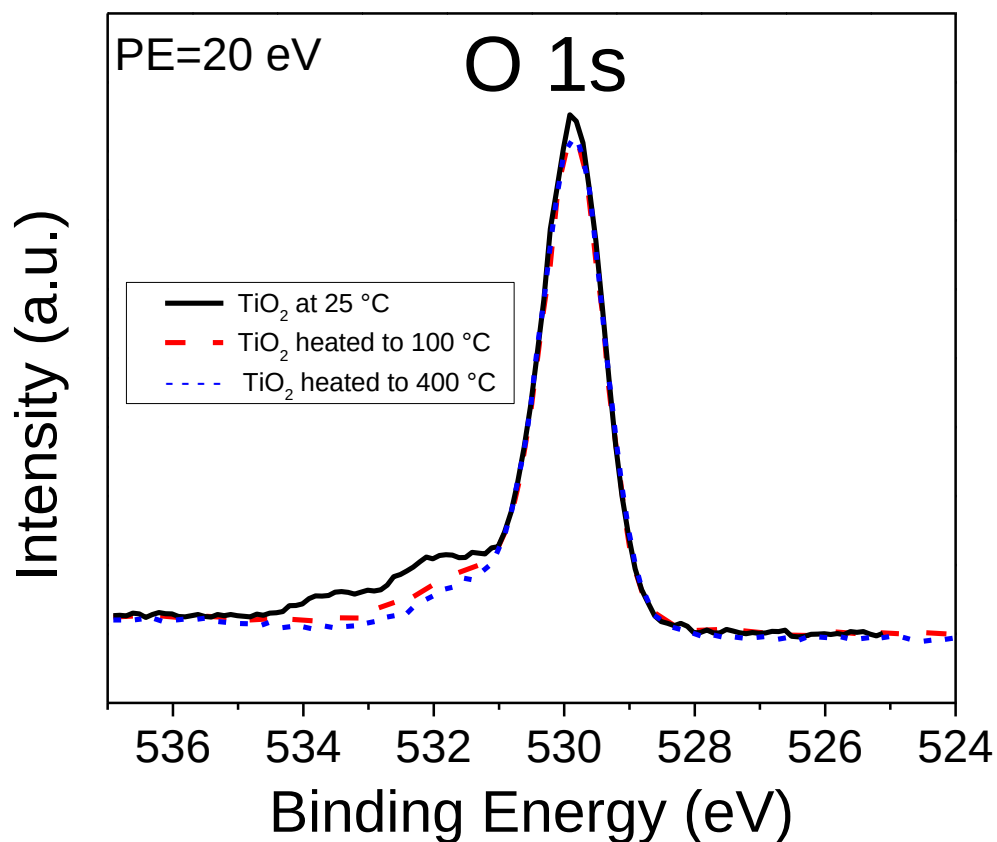


Figure 8.8. High-resolution O 1s spectra of neat TiO₂ sample at 25 °C, 100 °C, and 400 °C.

8.4.4.2.2 Preheating of 4wt% Ag/TiO₂ sample (I) and 4wt% Ag/TiO₂ sample (II)

To investigate the effect of adsorbed H₂O/OH on the time dependent observation of TiO₂⁺_(hole) species, 4wt% Ag/TiO₂ (I) and (II) (both mounted on copper microfiber tape) were heated to 400 °C under UHV conditions for 2 hours. The 2 hours heating under UHV conditions potentially caused desorption of most of the adsorbed H₂O/OH on 4wt% Ag/TiO₂ (I). And the sample showed a color change from white to black (Figure 8.10), which potentially indicates the chemical composition change of Ag from Ag(I)OH to Ag₂O. The following time dependent XPS results are shown in Figure 8.9a)-d). The first scan of Ti 2p shows a small shoulder peak at

binding energy of 459.8 eV, which is assigned as the $\text{TiO}_2^{+}(\text{hole})$ species. When compared with the first scan of non-heated 4wt% Ag/TiO₂ (I) (Figure 8.6a)), the peak intensity of $\text{TiO}_2^{+}(\text{hole})$ species was significantly reduced. Simultaneously, the OH/O⁻ species peak from O 1s spectra (Figure 8.9c)) was also significantly reduced when compared with non-heated 4wt% Ag/TiO₂ (I) (Figure 8.6c)). The corresponding spectral results on Ti 2p, Ag 3d, O 1s, and C 1s spectra are all significantly different when compared with non-heated 4wt% Ag/TiO₂ (I) (Figure 8.6).

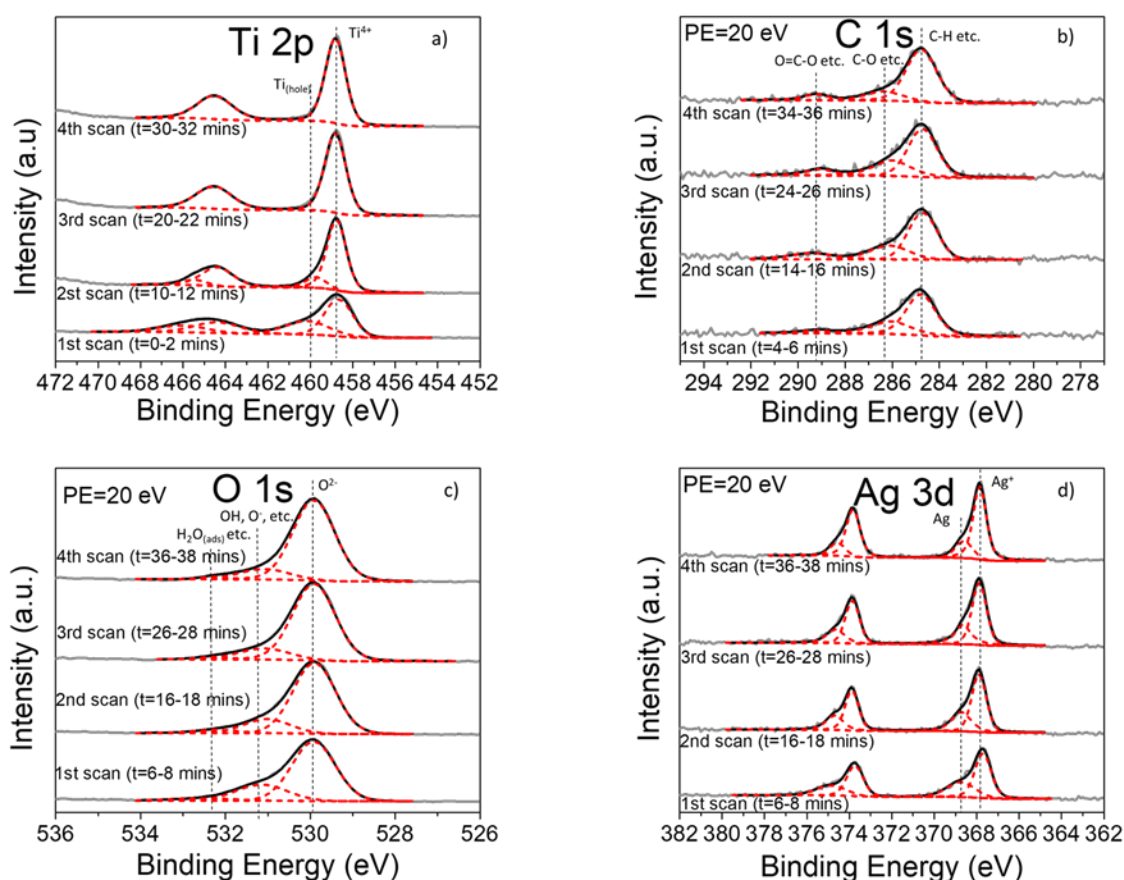


Figure 8.9. High-resolution time dependent XPS spectra of 4wt% Ag/TiO₂ (I) after heated at 400 °C under UHV for 2 h: a) Ti 2p, b) C 1s, c) O 1s, and d) Ag 3d

Table 8.3. Atomic ratios between oxygenated species and total titanium of 4wt% Ag/TiO₂ (I) after preheated at 400 °C for 2 hours under UHV conditions.

Time (mins)	$C(O^{2-})/C(Ti_{tot})$	$C(OH)/C(Ti_{tot})$	$C(H_2O)/C(Ti_{tot})$	$C(O_{tot})/C(Ti_{tot})$
0	2.05	0.40	0.05	2.50
10	2.08	0.32	0.04	2.44
20	2.10	0.28	0.03	2.41
30	2.10	0.25	0.03	2.38

Table 8.3 shows the atomic ratios of between oxygenated species and titanium species $C(i)/C(Ti_{tot})$ of 4wt% Ag/TiO₂ (I) after preheated at 400 °C for 2 hours in the XPS analytical chamber under UHV conditions. From Table 8.3, the atomic fraction ratio between total oxygen and total titanium $C(O_{tot})/C(Ti_{tot})$ was 2.50 for the first scan. This ratio is much smaller than the one of 3.12 for the non-heated 4wt% Ag/TiO₂ (I) sample. And it is due to the desorption of H₂O/OH during the heating process. Table 8.3 also shows the atomic fraction ratio $C(O_{tot})/C(Ti_{tot})$ decreased from 2.50 to 2.38 during the relaxation of TiO₂⁺_(hole) species, which indicates the continuous X-ray photo stimulated desorption of H₂O/OH from the sample during the relaxation of TiO₂⁺_(hole) species. But the ratio is still higher than the one of neat TiO₂ sample preheated at 400 °C (2.19), which means a small amount of adsorbed H₂O/OH was still on the sample surface. And this result is also confirmed by the TGA (Figure 8.3). With a small amount of adsorbed H₂O/OH still on the sample, a relatively smaller amount of TiO₂⁺_(hole) species were

stabilized by these hydroxyls as it was observable by XPS. Thus, the amount of the $\text{TiO}_2^{+}(\text{hole})$ species that could be stabilized in the XPS UHV chamber and be characterized by XPS is highly depended on the amount of adsorbed $\text{H}_2\text{O}/\text{OH}$ of the sample. Thus, the adsorbed $\text{H}_2\text{O}/\text{OH}$ was the key factor for the stabilization and observation of the X-ray photon generated $\text{TiO}_2^{+}(\text{hole})$ species on 4wt% Ag/ TiO_2 (I) under UHV conditions. And the X-ray induced relaxation of $\text{TiO}_2^{+}(\text{hole})$ species was potentially triggered by the X-ray photon stimulated desorption of OH in form of H_2O as the decrease of $\text{C}(\text{O}_{\text{tot}})/\text{C}(\text{Ti}_{\text{tot}})$ indicated continuously desorption of oxygenated species.

Table 8.4. Atomic ratios of oxygenated species and Ti^{4+} of 4wt% Ag/ TiO_2 (II) sample at different temperatures.

Temperature (°C)	Atomic ratio $c(i)/c(\text{Ti}_{\text{tot}})$			
	O^{2-}	OH etc.	$\text{H}_2\text{O}_{(\text{ads})}$ etc.	Total O
25	2.110	0.298	0.000	2.408
400	2.101	0.277	0.000	2.378
Desorbed from 25 °C to 400 °C	0.009	0.021	0.000	0.030

However, the 2 h heating at 400 °C of 4wt% Ag/ TiO_2 (II) under UHV conditions did not cause any significant change of the sample as it is shown from the XPS results. Table 8.4 shows the atomic fraction ratios of $\text{C}(\text{O}_{\text{tot}})/\text{C}(\text{Ti}_{\text{tot}})$ are 2.41 at 25 °C and 2.38 after the sample was preheated at 400 °C for 2 hours under UHV conditions. The results further confirm the observations from TGA that 4wt% Ag/ TiO_2 sample prepared by calcinating and cooling in flowing oxygen conditions makes the sample surface free of adsorbed $\text{H}_2\text{O}/\text{OH}$. Thus, X-ray

photo generated $\text{TiO}_2^{+}(\text{hole})$ species could not be stabilized under UHV conditions. And so that the XPS results did not show any $\text{TiO}_2^{+}(\text{hole})$ species or time dependent spectral change.

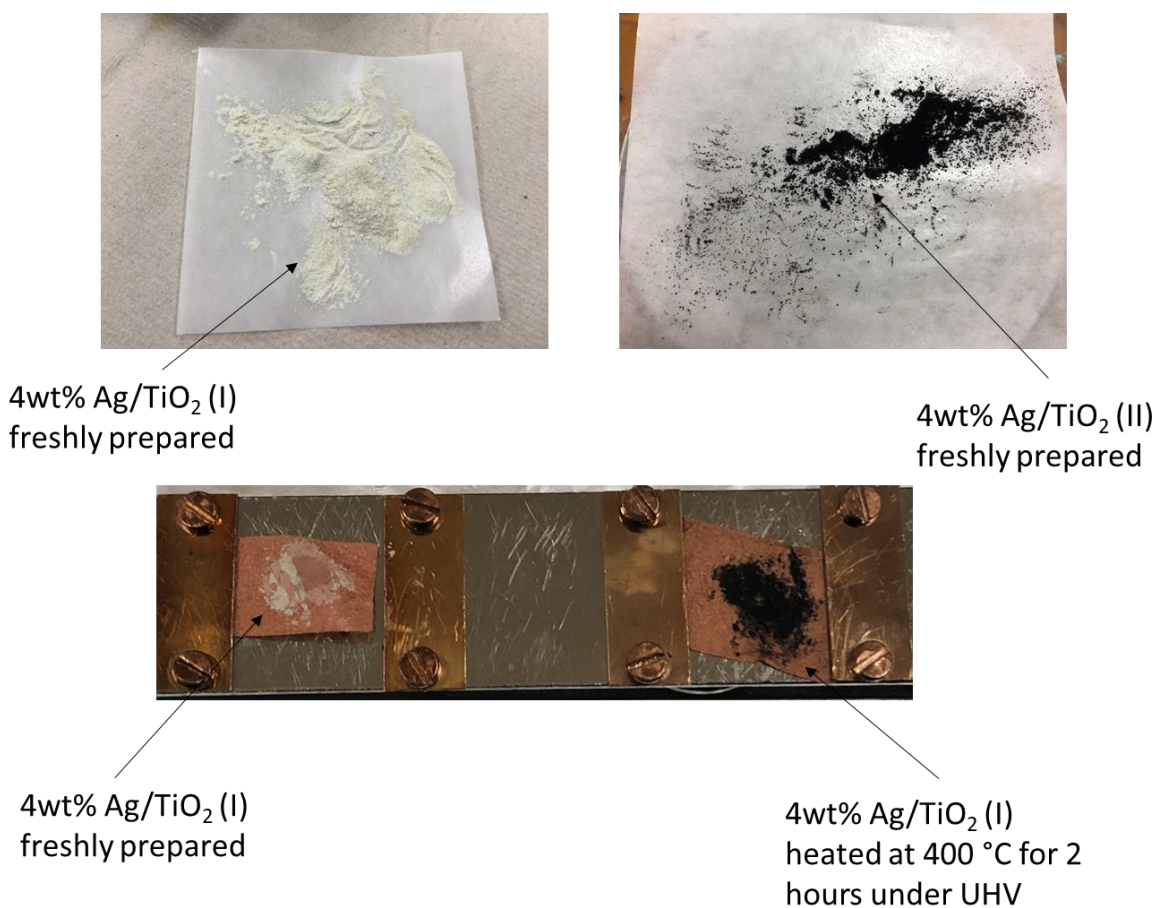


Figure 8.10. Sample color of as-prepared 4wt% Ag/TiO₂ (I), as-prepared 4wt% Ag/TiO₂ (II), and 4wt% Ag/TiO₂ (I) heated at 400 °C for 2 hours under UHV conditions.

8.5 Conclusion

This chapter further confirms the results of earlier observations of the stabilized high valence state of titanium hole species of 4wt% Ag/TiO₂ sample by temperature programmed XPS characterizations. This chapter also investigates the effects of oxygenated species on the observation of Ti(hole) phenomenon. By varying the initial hydration levels of 4wt% Ag/TiO₂ sample, the amount of stabilized titanium hole species that could be observed by XPS is

significantly different. By preparing the 4wt% Ag/TiO₂ sample in a water free environment, the sample surface was potentially free of adsorbed H₂O/OH as it is confirmed by TGA. And the sample showed a different color from the one prepared in humid environment. The in-situ time dependent XPS characterization of the adsorbed H₂O/OH free sample showed no titanium hole species and no time dependent spectral change, which indicates the importance and role of the adsorbed H₂O/OH for the stabilization and observation of Ti(hole) species by XPS.

By preheating the samples in UHV chamber, both neat TiO₂ sample and 4wt% Ag/TiO₂ sample (I) showed desorption of adsorbed H₂O/OH as monitored by XPS. Color change was also observed for the 4wt% Ag/TiO₂ (I) sample. The following XPS characterization showed a significantly reduced amount of TiO₂⁺_(hole) species on the sample, which is highly related to the amount of adsorbed H₂O/OH remained on the sample. The overall peak intensity (atomic concentration) of titanium was used as a reference for the quantitative analysis. Oxygenated species was diffused to the sample surface as it is confirmed by XPS quantitative analysis by analyzing the ratio of oxygenated species over titanium species. The relaxation of the stabilized TiO₂⁺_(hole) species was triggered by the desorption of oxygenated species as it was indicated by the atomic ratio drop of oxygenated species over titanium species. Thus, the relaxation of stabilized titanium hole species was potentially triggered by the X-ray photo stimulated desorption of oxygenated species so that the hole species was no longer stabilized and got relaxed thereafter.

The current study provides an insight of the function of oxygenated species on the stabilization and observation of Ti(hole) species under UHV conditions by XPS. Recent studies show the UV irradiation has similar effects on the stabilized high valence state of titanium hole species of 4wt% Ag/TiO₂ sample. The results will be included in future work.

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Chapter 9 Future work

The current study investigates the surface alternation mechanism by UV on anatase TiO_2 under atmospheric and UHV conditions as well as the photocatalytic behaviors of anatase TiO_2 and Ag/TiO_2 under UHV conditions. The results provide important fundamental understanding of the enhanced and permanent sulfur heterocycle removal capacity of TiO_2 sorbent by UV treatment. XPS study provides valuable information of the surface chemistry and reaction stoichiometry analysis. The future work will focus on ultrafast data acquisition and analysis of the *in situ* reaction mechanism on a microsecond time scale basis. By aligning and assembling a time to digital converter (TDC) with the UV laser coupled XPS, the system is able to stimulate the sample with a nanosecond UV laser pulse and collect the XPS spectrum within several microsecond. The challenge will lay on finding a suitable photocatalyst and reaction system that exhibit sample excitation and relaxation kinetics within microsecond time scale. The overall resolution of the resulting XPS spectra would be another subject due to the very short time photoelectron collection period. It is potentially achievable by adjusting the X-ray operation power output as well as the sample preparation and mounting method.

Another perspective of the future work is to explore the potential applications of the Ag/TiO_2 material, which is super active under X-ray and UV irradiation. It is a potential active ingredient for sunscreen products as well as the key component for the coatings of building materials such as glass to enhance the energy efficiency of the building or as a potential photo energy storage material. The progress will be reported in future works.