

CHAPTER V

SURFACE DEFECT (Ti^{3+}) CONTROLLING ON TiO_2 NANOCRYSTAL USING VARIOUS CALCINATION ATMOSPHERES AS THE FIRST STEP FOR SURFACE DEFECT CREATION

TiO_2 has been studied extensively in the field of surface science due to the wide range of its applications and the expectation that insight in to surface properties on the fundamental level will help to improve its properties [14]. The surface defect is one of the important topics in this field because the properties of the TiO_2 are often dependent on a nature and density of the surface defect sites [34]. In case of a nature of surface defect, however, Henrich and Kurtz have shown that the dominant defects on the TiO_2 surfaces are oxygen vacancies site (Ti^{3+}) [13]. To control a density of surface defect (Ti^{3+}), some common methods used for creation of surface defect (Ti^{3+}) on the TiO_2 are UV radiation, annealing under vacuum, ion sputtering, plasma-treating [17,18,19,34]. These methods are the second step creation which must prepare the crystalline TiO_2 in the first step prior, and then create the surface defect (Ti^{3+}) in the second step. Therefore, the surface defect (Ti^{3+}) creation in the first step coinciding with the preparation of crystalline TiO_2 (the so-called the first step creation technique) is the new class of defect creation and this is the goal of this work.

Based on the high photoactivity of TiO_2 in the anatase phase, Yamazaki et al. [2] and Park et al. [3] reported that an increase of surface defect (Ti^{3+}) can enhance its photoactivity by the photoelectron trapping. Further, to improve the hydrophilic property, Sakai et al. [30,31,32] reported that surface defect (Ti^{3+}) on anatase is an important parameter controlling this property. Also as a support with high surface area of anatase, Wallace et al. [33] reported that surface defect (Ti^{3+}) plays the significant roles enhancing the dispersion and stability of supported metal such as gold cluster and cobalt via the strong interaction (SMSI) between the defect site and metal cluster. Thus, it

demonstrates that the creation of surface defect (Ti^{3+}) on anatase is necessary for improving its properties for many applications. However, nearly all of the common techniques for surface defect (Ti^{3+}) creation (the so-called the second step creation technique) prefers the rutile and it is difficult to create surface defect on the anatase. This is because the surface must be cleaned at high temperature before creation [13,18,34,35,36,37]. In addition, some second step creation techniques were carried out under high temperature caused of phase transformation and significant surface area loss [18,34,37,38,39]. Moreover, for another reason, compared to rutile, the surface of anatase shows less tendency to form oxygen vacancies, because the removal of a bridging oxygen leads to the formation of a four-fold coordinated Ti site, which is less stable than a five-fold coordinated Ti site formed at oxygen vacancies on rutile [40,41].

In this chapter, however, we have been successful to create the surface defect (Ti^{3+}) on the anatase using the promising technique, the so-called “the first step creation”, by controlling the process parameter during sol-gel synthesis. The surface defect creation was performed in the first step coinciding with the preparation of anatase. The main mechanism involving the creation of surface defect through the first step creation was explained as being due to the removal of residual left after incomplete sol-gel reaction of alkoxide.

In principle of sol-gel synthesis, the precursor as an alkoxide will be hydrolyzed and condensed to form a metal oxide gel [58]. The relative rate between these reactions strongly influence the structure and properties of the final product as well as the amounts of inorganic and organic residuals left after synthesis. The controlling of these reaction rates can be performed by varying the processing parameter such as a water:alkoxide ratio, additive, and pH of reaction medium [58]. In this work, we decided to use the calcination atmosphere as a studied variable in order to create surface defect via the first step creation technique.

Here, the first step creation by controlling of calcination atmosphere was studied in order to create the surface defect (Ti^{3+}) on anatase. The amounts of surface defect (Ti^{3+}) were monitored by means of electron spin resonance (ESR) and CO_2 -temperature programmed desorption (TPD). Moreover, the resulting TiO_2 were also characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD) and single point BET surface area.

The nomenclature used for the catalyst samples in this study is the following:

- $TiO_2(X)$: the calcined TiO_2 with X% of O_2 in the feed during calcination.

5.1. Characteristics of TiO_2 samples

X-ray diffraction results were shown in Figure 5.1. XRD patterns of TiO_2 exhibited strong diffraction peaks at 26° , 37° , 48° , 55° , 56° , 62° , 69° , 71° and 75° indicating TiO_2 in the anatase phase [59]. It showed that all TiO_2 samples were in anatase phase. Based on Scherrer's equation, these samples had crystallite sizes in the range of 7-8 nm. From the XRD results, the TiO_2 samples had similar crystallinity shown by the same ordering in the structure of the TiO_2 particles with the same intensity of the XRD peaks. The measured BET surface areas of TiO_2 samples were in the range of 99-116 m^2/g . It was found that the surface area of TiO_2 decreased (as shown in Table 5.1) with increasing % O_2 in the feed during the oxidizing period whereas the crystallite size was apparently constant.

The typical SEM micrograph of a sample was shown in Figure 5.2. It indicated that the particles are spherical in nature. Based on SEM results (not shown for all samples), all titania samples exhibited the same morphologies and particle size. Moreover, the TEM micrograph of samples was also shown in Figure 5.3, which confirmed the nanoscale size of the samples. The crystallite size of these samples determined from the TEM micrographs were also listed in Table 5.1, which was similar to that obtained from XRD data.

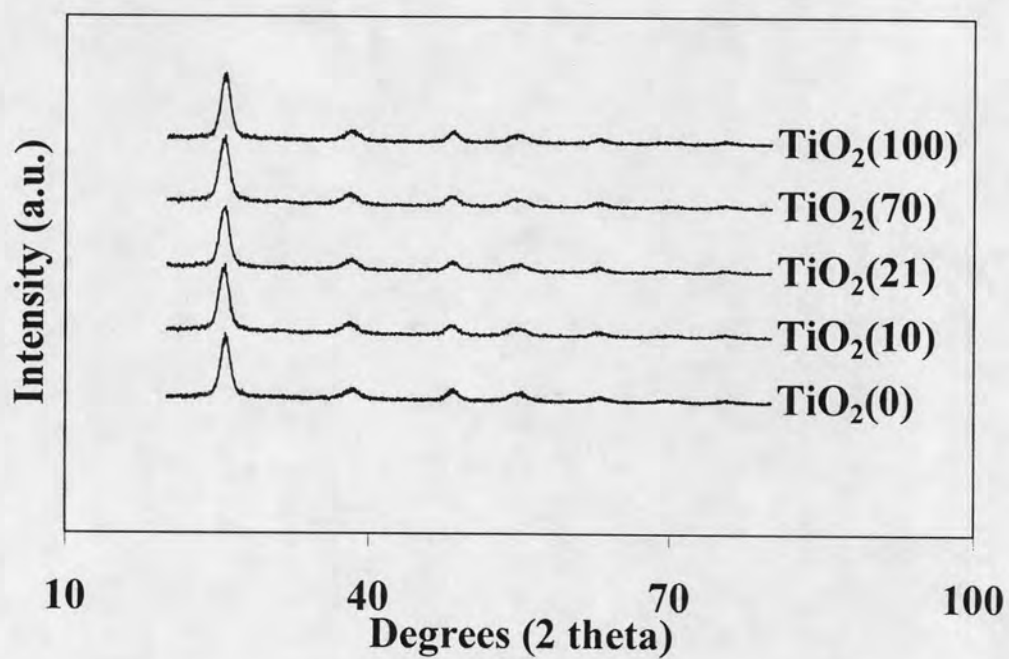


Figure 5.1: XRD patterns of TiO₂

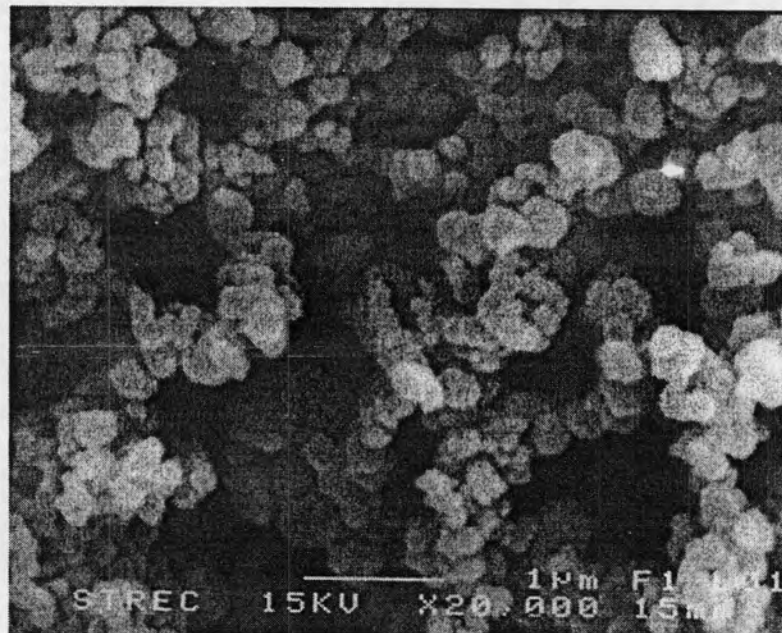


Figure 5.2: SEM micrograph of TiO₂(21)

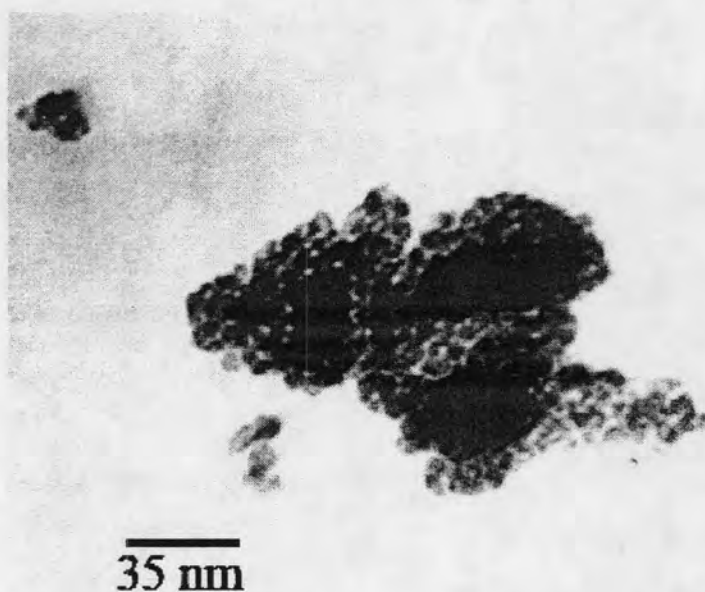


Figure 5.3: TEM micrograph of TiO₂(21)

5.2 CO₂-temperature program desorption (CO₂-TPD)

Thermal desorption spectra of CO₂ from a TiO₂ surface were shown in Figure 5.4. It revealed two desorption peaks at temperatures ca. 175 and 200 K. Thompson et al. [39] reported that the surface of TiO₂ incorporates regular fivefold-coordinated Ti⁴⁺ sites (surface perfect) and fourfold-coordinated Ti sites which are the surface defect (Ti³⁺) structure of TiO₂ formed after removal of O atoms. Based on their study, it was confirmed that the peak at ca. 170 K was attributed to CO₂ molecules bound to Ti⁴⁺ site. The second peak at ca. 200 K was considered to be the CO₂ molecules bound to a Ti³⁺ site. Thus, based on TPD results, it was observed that CO₂ desorption peak areas at ca. 200 K apparently increased with increasing %O₂ from 0% to 70% in the feed during calcination and then were constant when higher %O₂ was applied. Therefore, the surface Ti³⁺ increased with increasing %O₂ in N₂ of the feed. It should be mentioned that the formation of the surface Ti³⁺ in this study did not result from the reduction of Ti⁴⁺ due to low calcination temperature used with the absence of hydrogen [60,61,62].

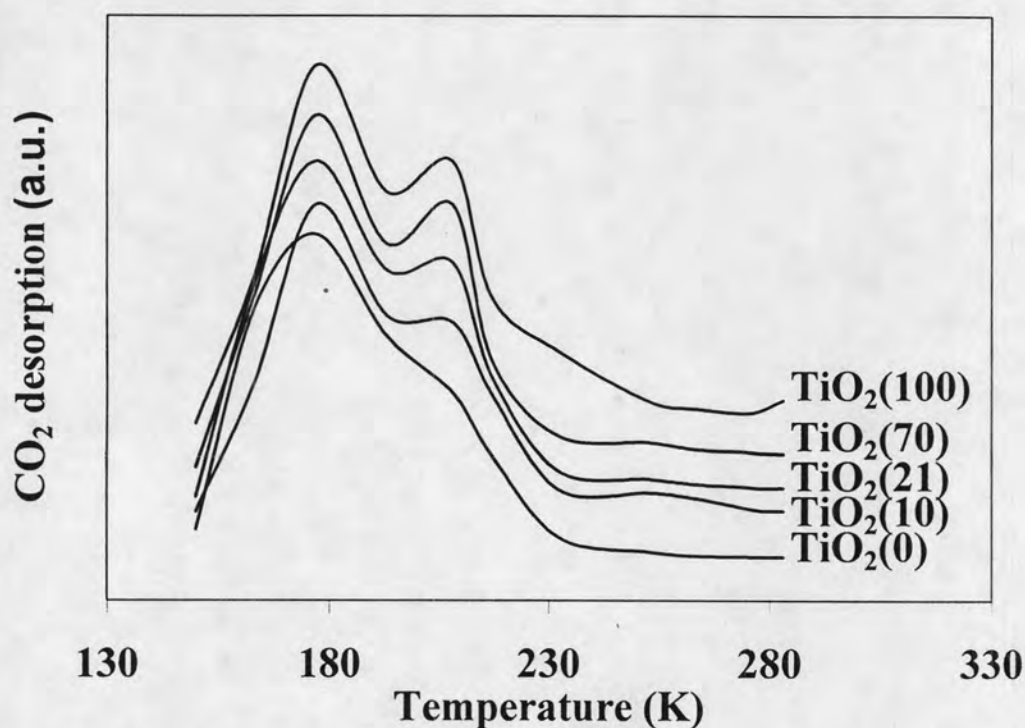
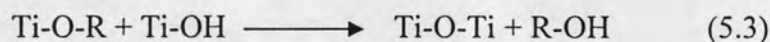
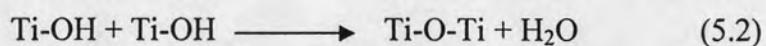
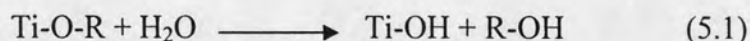


Figure 5.4: Thermal desorption spectra for CO₂ adsorbed on TiO₂ calcination at different atmospheres

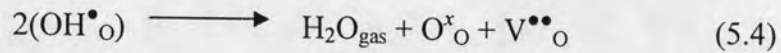
Based on sol-gel synthesis, the reactions of hydrolysis (equation 5.1) and polycondensation (equation 5.2 and 5.3) combine to form a TiO₂ gel as follows [9]:



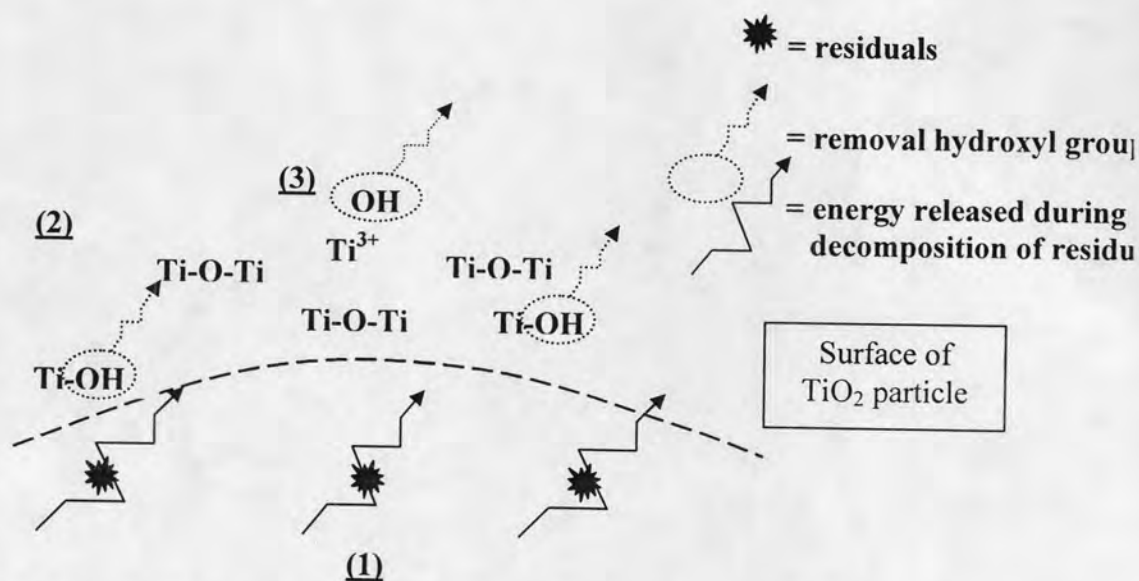
(where R = ligand)

During the sol-gel reaction, the alkoxide of titanium is hydrolyzed by water to form Ti-OH and alcohol as seen in equation 5.1 and then the Ti-OH condense to form Ti-O-Ti and water according to equation 5.2. Moreover, in equation 5.3, Ti-O-Ti and alcohol are formed by the reaction between Ti-O-R and Ti-OH. Therefore, based on these reactions, the resulting powder after sol-gel synthesis contains the organic and inorganic

residuals inside the powder such as alkoxide, alcohol, and Ti-OH and these residuals could be the main factor for surface defect (Ti^{3+}) creation in the first step. It is possible that during the calcination process, organic and inorganic residues were oxidized and then released energy after decomposition. This energy increased with increasing % O_2 during the calcination process. When this energy increased, surface hydroxyl could be removed easily and consequently increased oxygen vacancies (Ti^{3+}) were evident as seen from Scheme 5.1. The formation of oxygen vacant site due to the removal of hydroxyl group during calcination can be represented by the defect chemistry equation using the Kroger-Vink notation (is set of conventions used to describe electrical charge and lattice position for defect species in the crystals) as shown in equation 5.4.



According to this proposed equation, the removal of a hydroxyl groups which occupies on an oxygen lattice site (O) with singular positive charge (\bullet) leads to form the H_2O_{gas} releasing to atmosphere, oxygen atom [which occupies on an oxygen lattice site (O) with neutral charge (x)], and oxygen vacancy (V_O) with double positive charge ($\bullet\bullet$). This is similar to oxygen vacancy site creation on ZrO_2 . It was reported that the formation of oxygen vacancy sites may be associated with the removal of surface hydroxyl groups [62].



Scheme 5.1: The simplified scheme of the first step creation: (1) energy release during residuals decomposition at high concentration of oxidizing agent (O_2), (2) and then the removal of hydroxyl groups occur, (3) and form surface defect (Ti^{3+}) at the end

5.3 Electron spins resonance spectroscopy (ESR)

In this work, the ESR analysis was performed at 77 K and without illumination on samples. In addition, Nakamura et al. [19] and Serwicka et al. [63] reported two signals occurring on the surface of TiO_2 during ESR analysis without illumination indicating: (i) the surface Ti^{3+} and (ii) the bulk defect. In the previous section, we described that the TiO_2 in this work had bulk defects and surface Ti^{3+} sites. Based on the results of ESR analysis as shown in Figure 5.5, it can be observed that all TiO_2 samples exhibited one main signal at the g value of 1.996. According to the results as reported by Nakaoka et al. [16], this peak can be attributed to the Ti^{3+} on the surface.

In case of bulk defect, many researchers reported that TiO_2 has several types of bulk defect such as cationic defect and anionic defect. Based on thermodynamics, bulk TiO_2 has less inner Ti^{3+} when compared to surface Ti^{3+} . However, inner Ti^{3+} can only occur during heat treatment at high temperatures above 973 K. Therefore, in our work,



ESR spectra of TiO_2 did not show any signal of inner Ti^{3+} . This result agrees with the work of Howe et al. [64] and Lee et al. [65]. The intensity of the ESR spectra of all TiO_2 samples, which corresponded to the amounts of Ti^{3+} present on the TiO_2 surface was shown in Figure 5.5. It showed that the amount of surface defect (Ti^{3+}) increased with increasing $\% \text{O}_2$ fed during the calcination process.

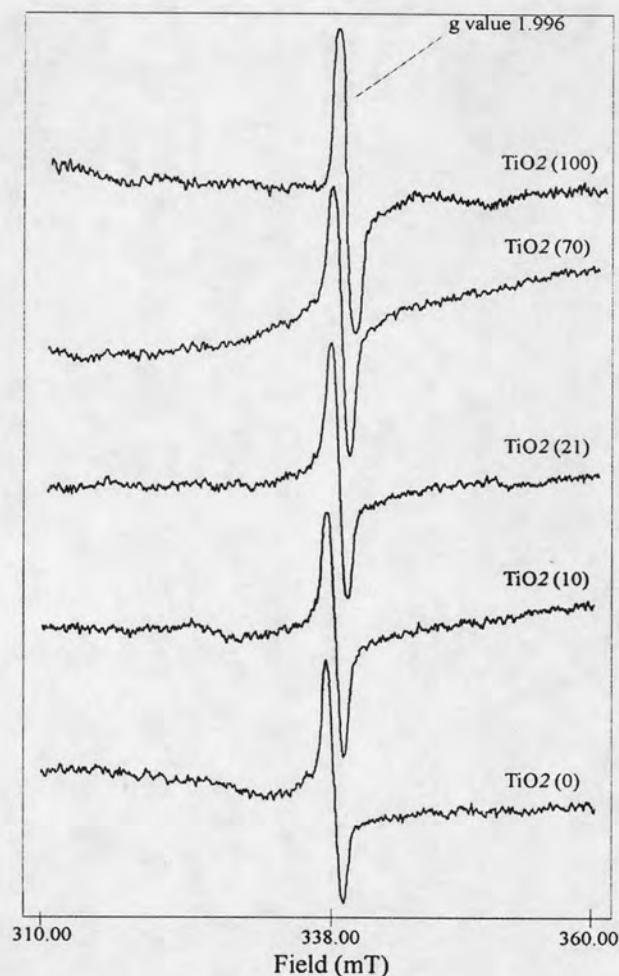
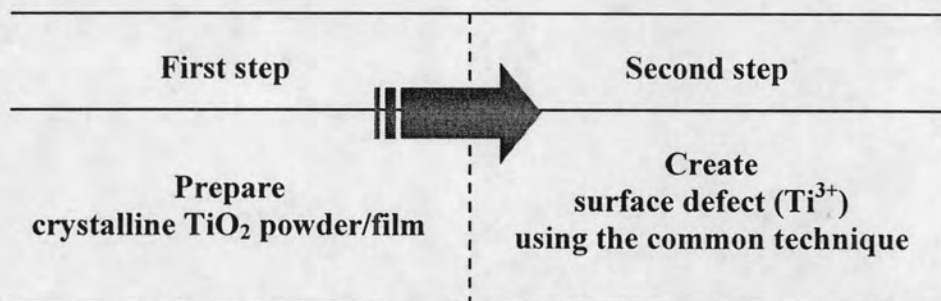


Figure 5.5: ESR spectra of TiO_2 obtained under vacuum at a 77 K without irradiation

Observing the presence of Ti^{3+} on TiO_2 from CO_2 -TPD and ESR revealed that the first step creation of surface defect on TiO_2 can be performed by controlling the calcination atmosphere. When the first step creation was compared to the common methods used to create defect sites in the second step such as UV radiation [17],

annealing in vacuum [18], ion sputtering [18], and plasma-treating [19], it was seen that the second step creation consumed more energy and time. The simplified scheme of second step creation was shown in Scheme 5.2. The TiO₂ powder/film was prepared in the first step, and then the surface defect (Ti³⁺) was created in the second step using the common technique. Some details concerning the second step creation were shown in Table 5.1 [17-19, 38]. The procedure of UV irradiation to create surface defect (Ti³⁺) on 1st TiO₂ (the TiO₂ which was prepared in the first step) was described in this table. The 1st TiO₂ surface was irradiated using 500W high pressure mercury lamps. Rutile phase is preferred for this method because the TiO₂ surface must be cleaned by annealing at 900 K (we have observed that phase transformation of TiO₂ from anatase to rutile occurs at approximately 800 K). Based on surface defect determination by STM, they reported that the creation potential of UV irradiation is very low. According to the work of Pan et al. [18], they reported that a medium and high density of surface defect creation can be created using annealing in vacuum and Ar⁺ sputtering, respectively. The details of the plasma-treating method were also shown in this table. This method can create surface defect on anatase phase because the procedure was performed at a lower temperature without phase transformation. The common techniques of ultrahigh vacuum, ion sputtering, and plasma for second step creation consumes comparatively more energy, time, and special knowledge. However, in first step creation, surface defect was formed coinciding with the 1st TiO₂ preparation, and the preparation consumes less energy and time than the former. Moreover, it is easier to perform and understand. Many researchers reported that anatase has the highest photoactivity when compared to rutile and brookite [66,67]. Yamazaki et al. [2] and Park et al. [3] reported that surface defect (Ti³⁺) can enhance the photocatalytic activity of TiO₂. However, almost all second step creation techniques prefer the rutile phase and it is difficult to create surface defect on the anatase phase. This is because the surface must be cleaned at high temperature before creation. In addition, some second step creation techniques were performed at high temperature. Moreover, another reason is presumably because the oxygen vacancy site as a fourfold coordinated Ti site on anatase phase is less stable than a fivefold coordinated Ti site formed at oxygen vacancies on rutile phase [41]. In this work, the first step creation was performed coinciding with TiO₂ preparation at mild temperature. Preparation at lower

temperature is better for anatase phase, and prevents significant surface area loss and phase transformation. The yield of first step creation is difficult to quantify because there is not a standard measurement of the amount of surface defect (Ti^{3+}) available for comparison. However, the technique is a promising new method for the creation of surface defect at mild temperature on anatase phase. In particular, it can save time and energy when compare to the other conventional methods.



Scheme 5.2: The simplified scheme of the second step creation

Table 5.2: Characteristics of prepared titania samples.

Sample	Surface area (m^2/g)	Crystallite size (nm)	
		XRD ^a	TEM ^b
$\text{TiO}_2(0)$	116	7	~7
$\text{TiO}_2(10)$	113	7	~6
$\text{TiO}_2(21)$	101	7	~7
$\text{TiO}_2(70)$	99	7	~6
$\text{TiO}_2(100)$	99	7	~7

^a Calculated from Sherrer's equation.

^b Calculated from 50 particles of titania.

Table 5.1: Common methods for surface defect creation in the second step

No.	Method	Procedure in second step	Available TiO ₂ phase ^a	Note
1.	UV radiation [19]	Irradiate TiO ₂ ^b with 500 W high pressure mercury UV lamp	Rutile ^f	Low amount of surface defect created, monitored by STM ^d
2.	Annealing in Vacuum [20, 39]	Heating TiO ₂ ^b at 1000 K In UHV ^e (2x10 ⁻¹⁰ Torr)	Rutile ^f	Medium amount of surface defect created, monitored by XPS ^g
3.	Ar ⁺ Sputtering [20]	Sputter TiO ₂ ^b with 500 eV Ar ⁺	Not identified	High amount of surface defect created, monitored by XPS ^g
4.	Plasma-treating [21]	Treat 1 st TiO ₂ ^b using radio-frequency discharge (500W) under 2 Torr H ₂ At 673 K	Anatase /Rutile ^f	Not identify

^a Available TiO₂ phase for each creation method determined base on the temperature during surface cleaning before creation and temperature during creation.

^b The meaning of 1st TiO₂ is the TiO₂ powder/film was prepared in the first step before surface defect creation.

^c The cleaning surface was cleaned before surface defect creation by annealing at 900 K. Therefore, it was available for rutile phase.

^d This note based on the report in [19].

^e Ultrahigh vacuum.

^f This method was performed at 1000 K. Therefore, it was available for rutile phase.

^{g,h} This note based on the report in [20].

ⁱ This method was performed at a lower temperature of 673 K. Therefore, it was available for both anatase and rutile phase.