CHAPTER VI

SURFACE DEFECT (Ti^{3+}) CONTROLLING ON TiO_2 NANOCRYSTAL USING VARIOUS WATER:ALKOXIDE MOLAR RATIOS USED DURING SOL-GEL SYNTHESIS AS THE FIRST STEP FOR SURFACE DEFECT CREATION

In previous chapter, 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 calcination atmosphere. 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 water:alkoxide ratio as a studied variable in order to create surface defect via the first step creation technique. The preparation of TiO_2 via sol-gel technique has followed the work of Wang et al. [9], However, the decreasing of a water:alkoxide ratio can affect the crystallite size which is the main cause of the significant surface area loss. To solve this problem, in this work, ultrasonic technique was employed to remain the narrow crystallite size distribution of the final product following the works of Yu et al. [68] and Awati et al. [69]. It demonstrated that the synthesis of crystalline TiO_2 via sol-gel technique, which was reacted under ultrasonic irradiation, can increase the surface area and decrease the crystallite size of the final product.

Here, the first step creation by controlling of a water:alkoxide ratio was studied in order to create the surface defect (Ti^{3+}) on anatase without significant surface area loss. 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 thermal gravimetric analysis (TGA), transmission electron microscopy (TEM), selected area electron diffraction (SAED), powder X-ray diffraction (XRD) and single point BET surface area.

6.1 Characteristics of Crystalline TiO_2.

The XRD analysis was employed to determine the crystallite phase and crystallinity of the resulting TiO_2. Variances of TiO_2 were synthesized by sol-gel technique combined with ultrasonic vibration at room temperature and then calcined at 723 K. The water:alkoxide molar ratio was varied (R=165, 80, 40, 16, 4) in order to affect the amounts of organic and inorganic residual left on the TiO_2 gel. The nomenclatures used for representing the resulting TiO_2 have been listed in the Table 6.1.

Table 6.1: Characteristics of TiO_2 samples

Sample	Water:Alkoxide	Crystallite size[a] (nm)	Surface Area (m^2/g)
TiO_2-R165	165	6.9	101
TiO_2-R80	80	7.0	99
TiO_2-R40	40	8.5	97
TiO_2-R16	16	8.9	97
TiO_2-R4	4	9.1	96

[a] Estimated from XRD at anatase (101) peak

After calcination at 723 K, as seen in the Figure 6.1, all XRD patterns match the known pattern for anatase (JCPDS 21 – 1272) [70]. No brookite and rutile were observed on these samples. Based on Scherrer's equation (Table 6.1), the resulting TiO_2 had the crystallite size within the range of 6 – 9 nm. The crystallite size slightly increased with decreasing a water:alkoxide ratio used during sol-gel synthesis cooperating with ultrasonic vibration. Intensity of XRD also increase with decreasing the water:alkoxide molar ratio showing that the crystal structure of the resulting TiO_2 obtained from the sol-gel synthesis in the present of lower water:alkoxide ratio exhibited higher crystallinity [71].
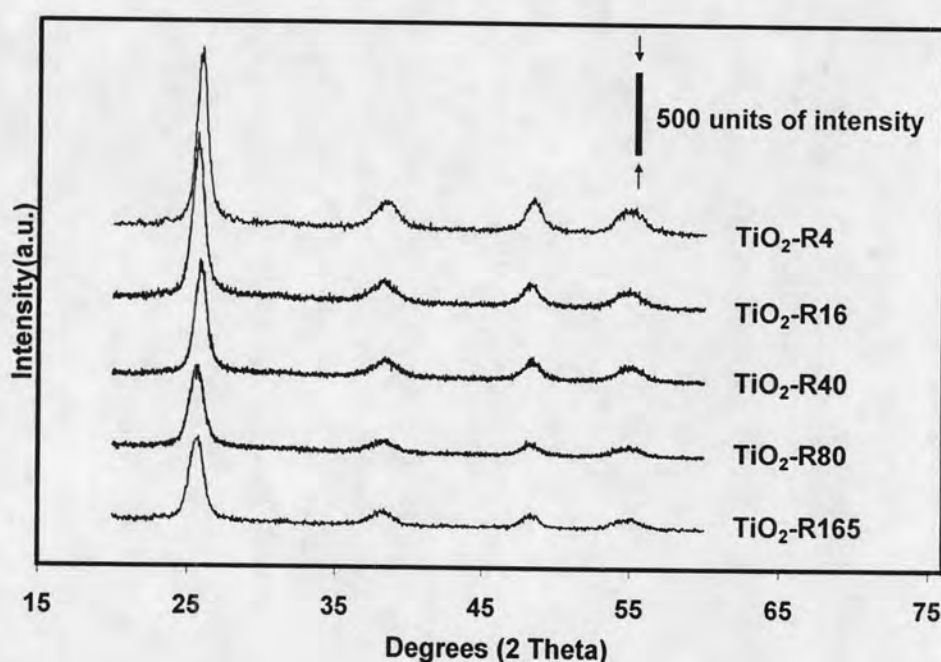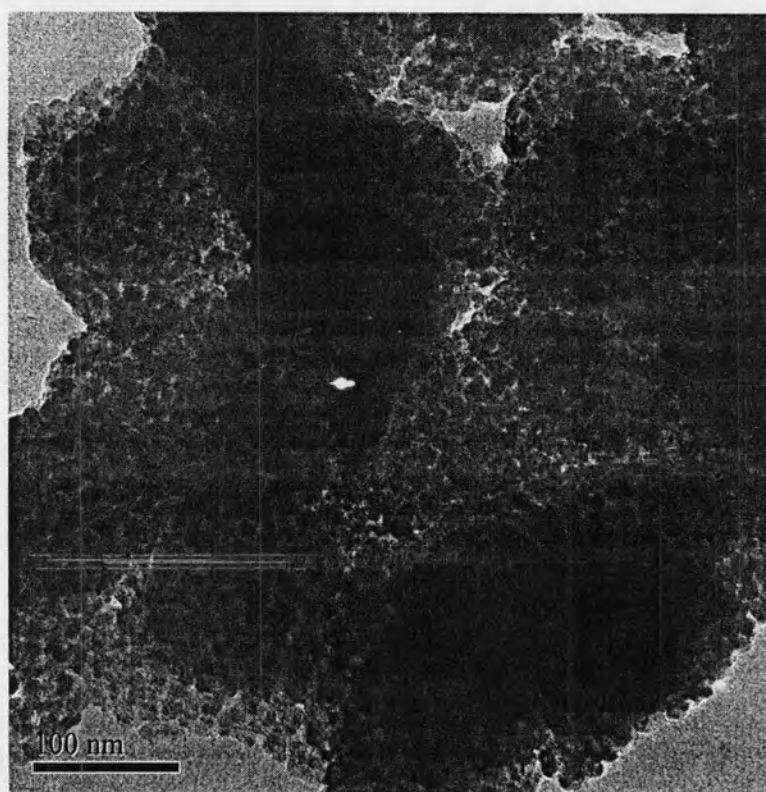

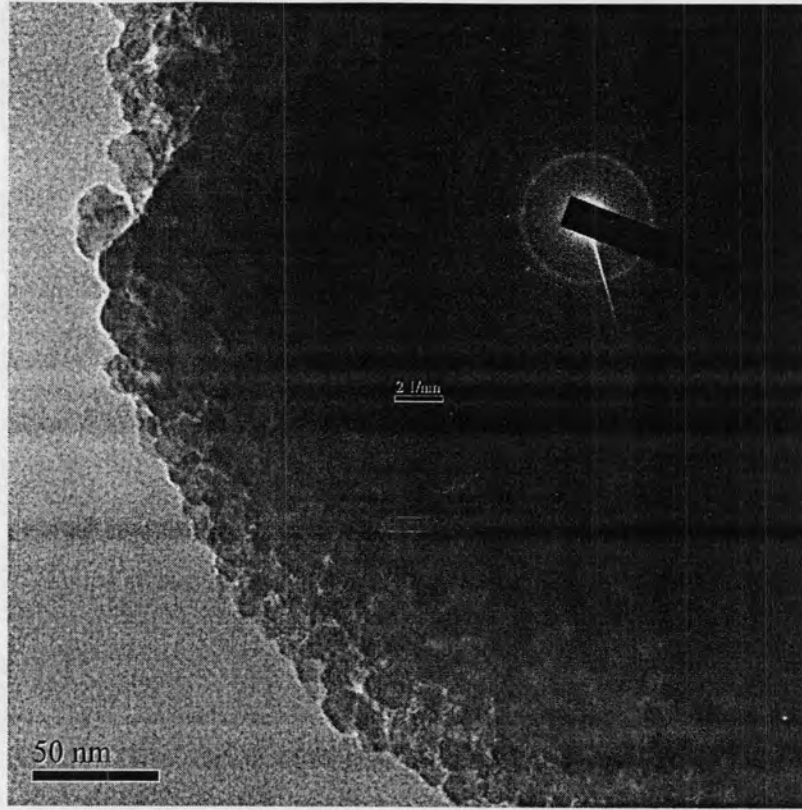**Figure 6.1:** XRD patterns of resulting TiO_2 after first step creation

Transmission electron microscope (TEM) images of TiO_2-R165 (with low and high magnification), TiO_2-R40, and TiO_2-R4 are shown in the Figure 6.2a – 6.2d, respectively. At low magnification [Figure 6.2(a)], the aggregated primary particles were observed showing that these primary particles were spherical by nature. At higher magnification (Figure 6.2b – 6.2c), it shows that the TiO_2-R165, TiO_2-R40, and TiO_2-R4 had the average particle size of 8, 10, and 11 nm, consequently. These sizes are in close

agreement with those obtained from the XRD peak broadening. No change in particle shape was observed as the result of a lower water:alkoxide ratio. The selected area electron diffraction patterns (SAED) of TiO_2-R165, TiO_2-R40, and TiO_2-R4 are also shown as inserts in the Figure 6.2(b – c), respectively, indicating that these samples were in a polycrystalline structure. These patterns also show the slightly increase of crystallinity when the lower water:alkoxide ratio was used corresponding with the XRD results.
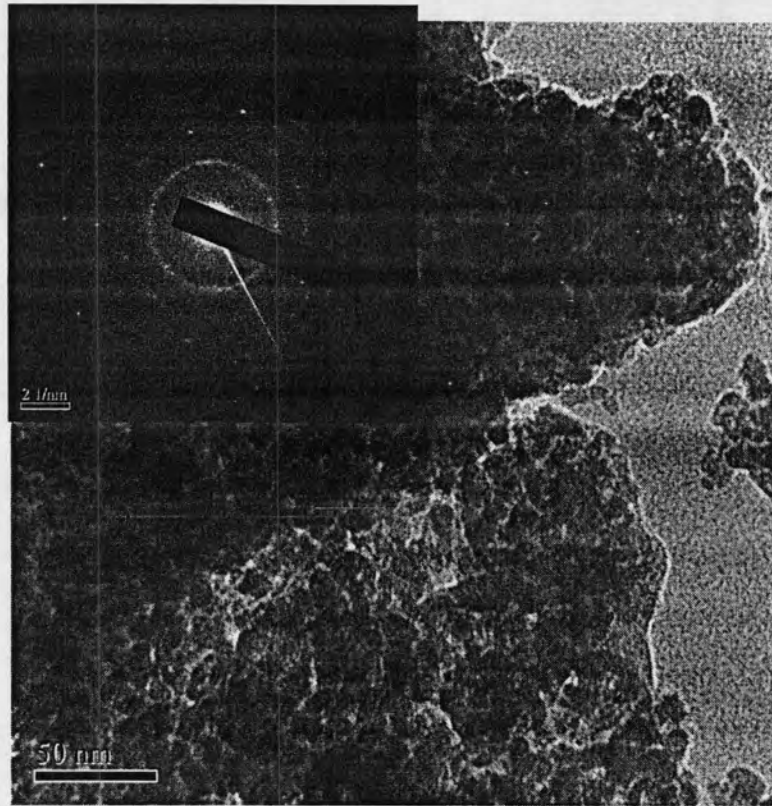
The surface areas of the resulting TiO_2 are listed in Table 6.1. No significant surface area loss was found among these samples. In summary, the preparation of the crystalline TiO_2 via sol-gel technique under the ultrasonic vibration can inhibit the loss of surface area on the sample obtained from the sol-gel synthesis at low water:alkoxide ratio.
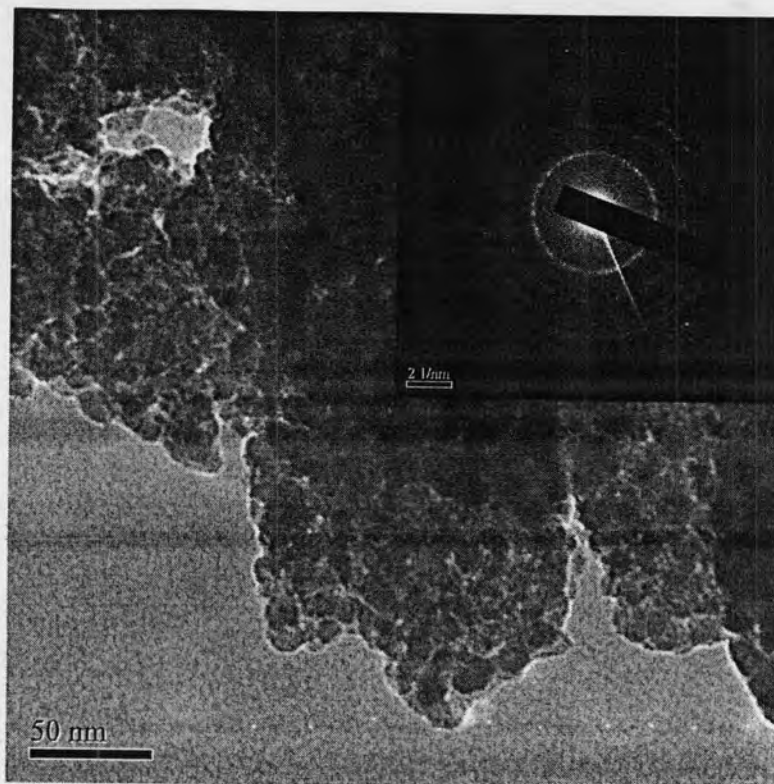

(a)

100 nm

(b)

(c)

(d)

Figure 6.2: TEM images and SAED patterns of resulting TiO_2 after first step creation: (a) low magnification of TiO_2-R165, and high magnification of (b) TiO_2-R165, (c) TiO_2-R40, and (d) TiO_2-R4

6.2 Thermal Analysis.

Thermal gravimetric analysis (TGA) was adopted to evaluate the weight loss of all as-synthesized TiO_2 samples before calcination (did not show all). The TGA curves of TiO_2-R4, TiO_2-R40, and TiO_2-R165 are shown in the Figure 6.3 (a, b, and c, respectively). Based on literatures, these curves can be classified to be mainly two regions including (i) the losses of ethanol and water residuals after synthesis (273 – 473 K), and (ii) the losses of unreacted alkoxide, terminal i-Opr (formed from the partial unreacted alkoxide), and terminal hydroxyl group (473 – 700 K) [72,73,74]. The total weight loss in the whole temperature range between 298 to 1073 K is approximately 16 % for TiO_2-R4 and TiO_2-R40, and 19 % for TiO_2-R165. In the first region, TiO_2-R165 had the highest weight loss at 15 % and then TiO_2-R40 and TiO_2-R4 at 10 and 5 %,

respectively. This matter is consistent with the increase of water:alkoxide ratio used during the sol-gel synthesis ensuring a complete hydrolysis of alkoxide. Based on this complete reaction, the less amounts of unreacted alkoxide and terminal i-Opr on TiO_2-R165 were observed in the second region characterized by a lower weight loss (3 %) than other those of TiO_2-R40 and TiO_2-R4 (5 and 10 %, consequently). The approximately 1 % left on the TGA curves of all samples (at temperature 700 to 1073 K) can be accounted for the loss of carbon remained in the structure of TiO_2 [72]. In summary, the as synthesized TiO_2 preparing by using higher water:alkoxide ratio exhibited lower amounts of unreacted alkoxide and terminal i-Opr when compared to those of the other samples.
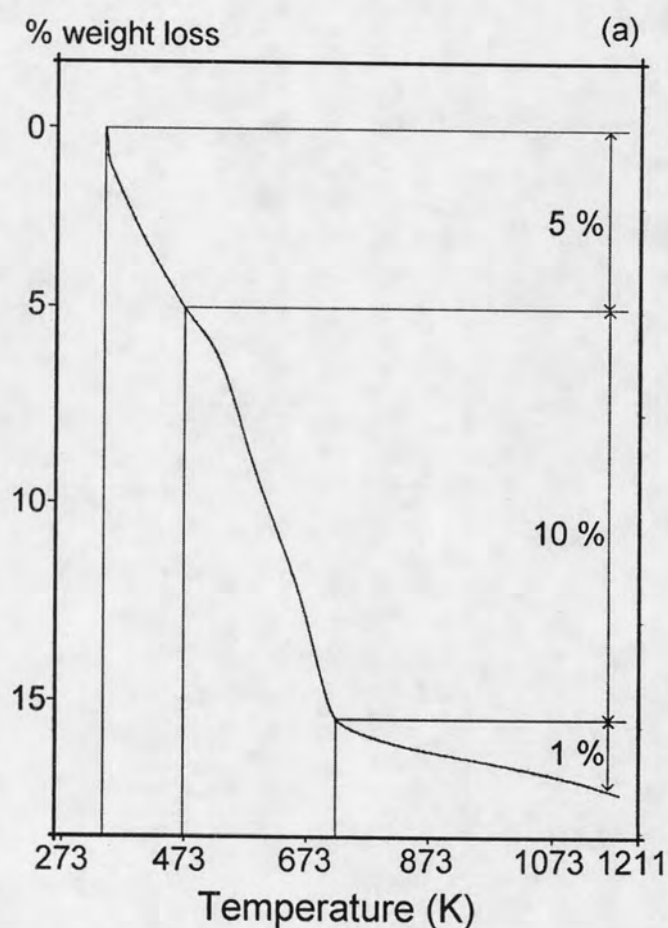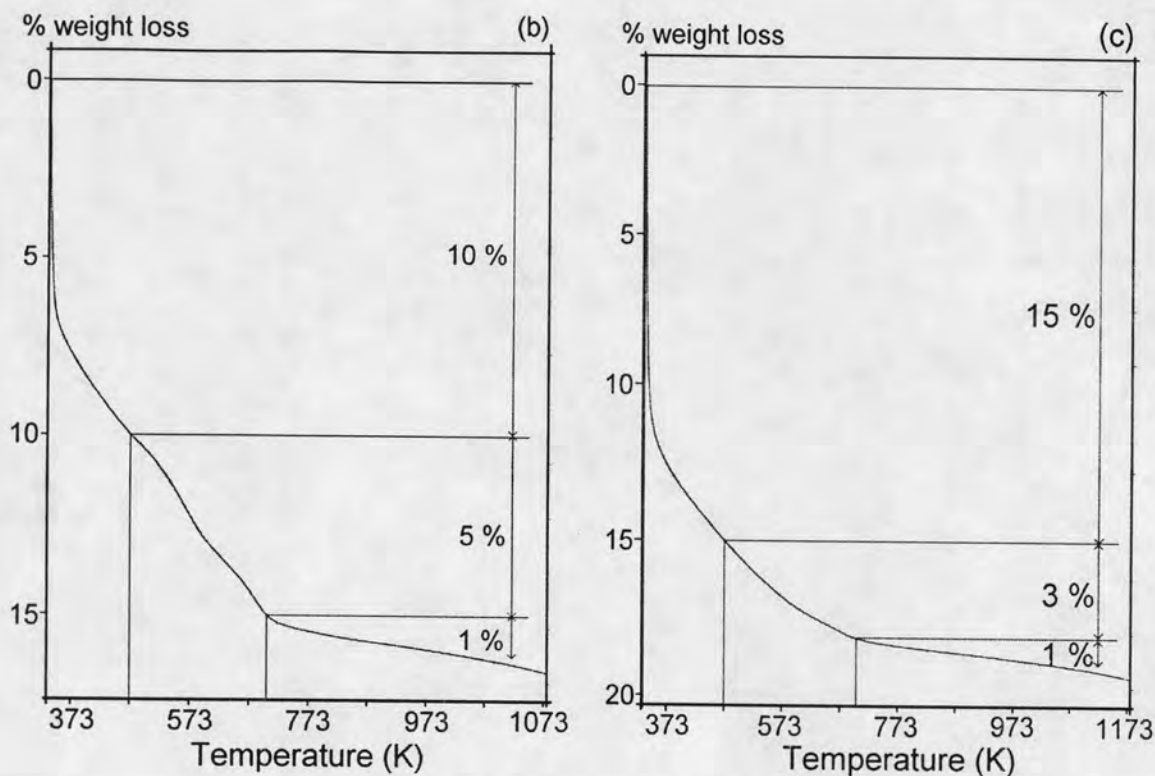
Figure 6.3: TGA curves of as-synthesized TiO_2: (a) TiO_2-R4, (b) TiO_2-R40, and (c) TiO_2-R165

6.3 The Evidence of Surface Defect (Ti^{3+}): Monitored by TPD and ESR.

Figure 6.4 shows thermal desorption spectra of CO_2 from the surface of resulting TiO_2. It reveals two desorption peaks at temperature ca. 177 and 200 K. Followed work of Thomson et al. [39], which is the original work investigating this technique, they reported that the surface of TiO_2 incorporates regular Ti^{4+} sites and oxygen vacancy site (Ti^{3+}). Based on their work, it can be concluded that the thermal desorption peak at ca. 177 K is attributed to CO_2 molecules bonded to Ti^{4+} site. Further, the thermal desorption peak at ca. 200 K is considered to be the CO_2 molecules bonded to Ti^{3+} site. Similar TPD spectra have also been found on the desorption of CO from surface of reduced TiO_2, based on the strong interaction between CO and surface defect (Ti^{3+}) sites, Gan et al. [50] reported that the CO molecules desorped at higher temperature (170 K) when compared to desorption of CO from the stoichiometric TiO_2 (140 K). In this work, it can be clearly

seen that the intensity of desorption peak at temperature ca. 200 K representing the surface defect (Ti^{3+}) increases when the lower water:alkoxide molar ratio was used during sol-gel synthesis. Thus, it demonstrates that the formation of surface defect (Ti^{3+}) can be favored by decreasing water:alkoxide molar ratio during synthesis.
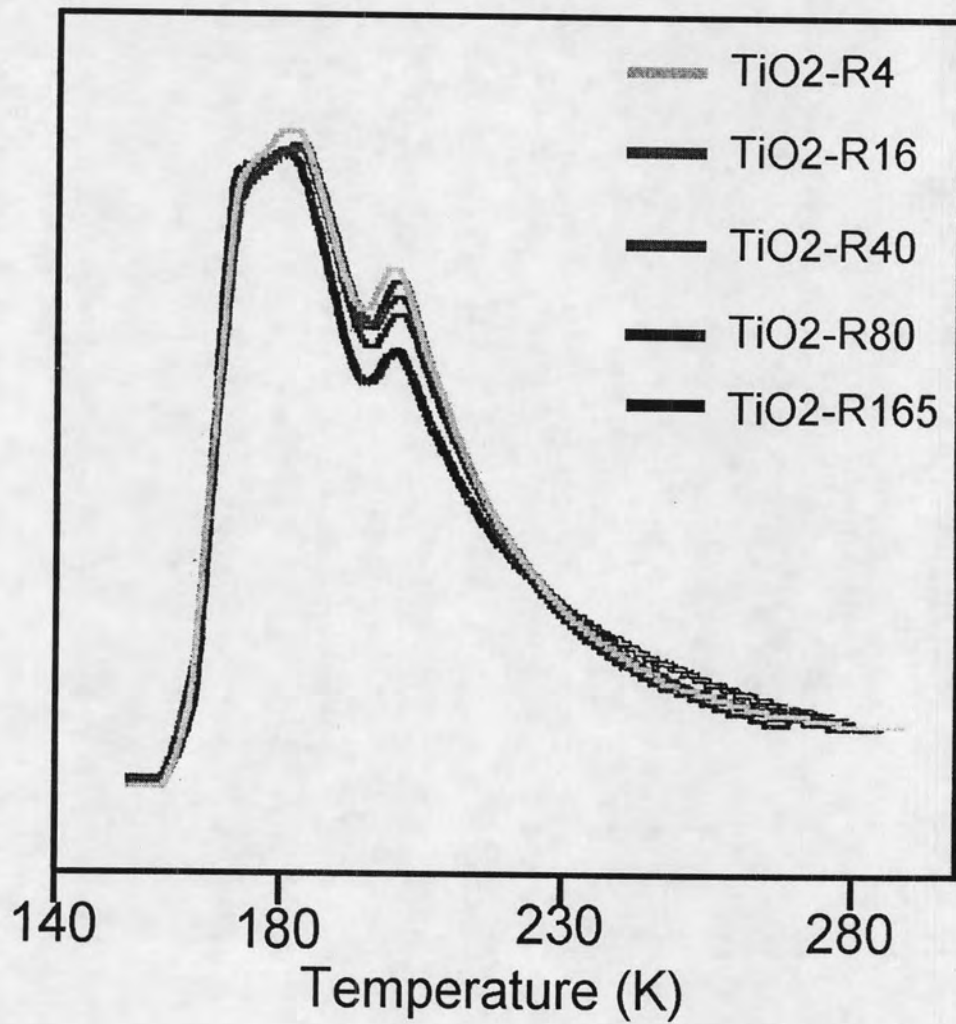
CO2-Desorption (a.u.)

Figure 6.4: Thermal desorption spectra for CO_2 adsorped on resulting TiO_2 after first step creation

The Ti^{3+} ($3d^1$) was also monitored by mean of ESR which is the simplest of all forms of spectroscopy to detect a free radical with one unpaired electron. ESR analysis was recorded at 77 K without illumination on samples. Based on the ESR spectrum of TiO_2-R165, the sharp signal at g = 1.975, the big broad signal at g = 2.033, and the small signal at g = 2.198 are observed as seen in the Figure 6.5. The sharp signal at g = 1.975 is assigned to be a surface defect (Ti^{3+}) occurring on TiO_2 [75,76,77,78]. This signal locates in the big broad signal at g = 2.033 which is considered to be a bulk defect in TiO_2 [16,75]. This corresponds to the works of Nakamura et al. and Serwicka reporting two signals occurring on TiO_2 during ESR analysis without illumination indicating: (i) the surface defect (Ti^{3+}) and (ii) the bulk defect [16,75]. The small signal at g = 2.198, it can not be ascribed completely, however, it seems to be a signal of H radical occurring after calcination [3]. As seen in the Figure 6.5, the evidence of sharp signal at g = 1.975 becomes stronger as the result of lower water:alkoxide molar ratio corresponding with the CO_2-TPD result. In contrast, the intensity of a big broad signal at g = 2.033 becomes lower and disappears on the sample prepared at the water:alkoxide molar ratios of 16 and 4. The TiO_2-R4 exhibited closer perfect crystal (lower bulk defect) with the higher surface defect (Ti^{3+}) than the other one.

As known that bulk defect inside TiO_2 is one of the main parameters controlling crystallinity of TiO_2 [68.79]. The decrease of bulk defect is consistent with the increase in intensity of XRD and also SAED pattern which reveals that the crystallinity of the TiO_2-R165 sample was the lowest (XRD) containing the highest amount of the bulk defect (ESR). Conversely, the crystallinity was the highest (XRD) for the sample having the lowest amount of bulk defect (ESR) (TiO_2-R4).
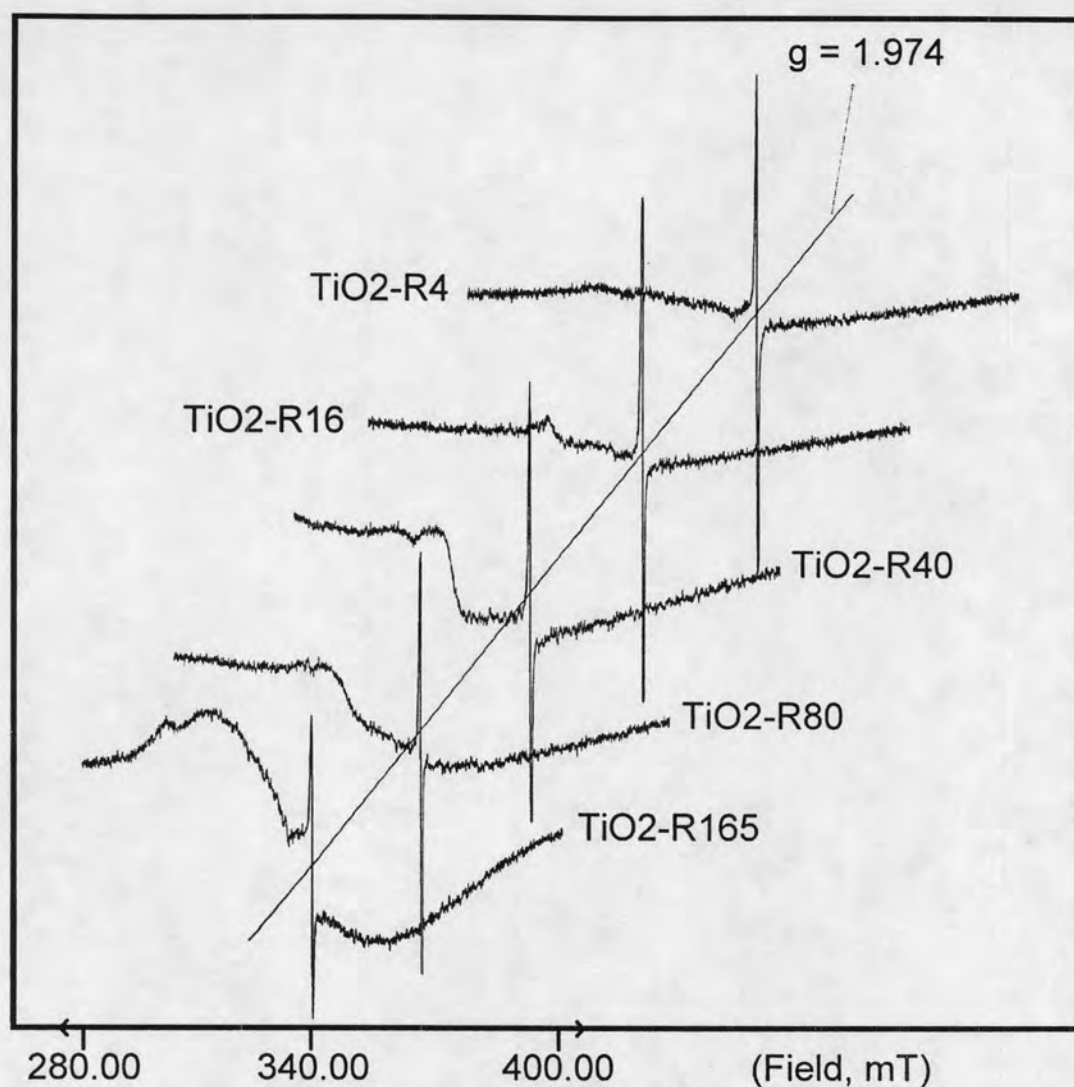
Figure 6.5: ESR spectra of resulting TiO_2 after first step creation

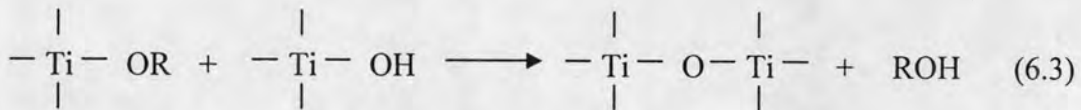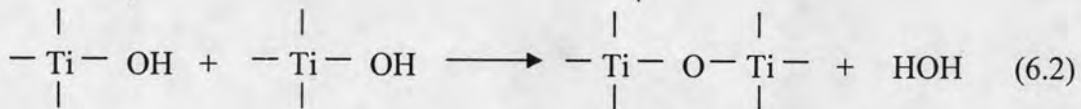## 6.4 Creation of Surface Defect (Ti^{3+}) on Anatase.

The data reported here demonstrate that the surface defect (Ti^{3+}) has been successfully created on the anatase when the lower ratio of water:alkoxide was used for synthesizing the TiO_2 gel via sol-gel synthesis. As known that nearly all of the study regarding the creation of surface defect (Ti^{3+}) has been investigated on rutile phase, in general, the formation of this defect on the surface of the rutile has been explained as the result of removing a lattice oxygen atom and one electron, with one electron being left in the d orbital of the neighboring surface Ti site, so that Ti^{4+} is reduced to Ti^{3+}

[37,39,80,81]. However, this mechanism is impossible to be the main mechanism for the surface defect creation on anatase in this work. This is because (i) the removal of a lattice oxygen atom can occur when crystalline TiO_2 is treated at high temperature in the presence of reduced gas (H_2, CO, or vacuum) but the surface defect creation in this work was done at mild temperature in the presence of oxidized gas (air) and (ii) a lattice oxygen atom on anatase is more difficult to remove than that of rutile, so that the removal of lattice oxygen atom on anatase should occur at higher temperature (with the presence of reduced gas) than that of rultile phase. Therefore, we infer that the surface defect creation in the first step is not attributed to the removal of lattice oxygen atom.

The water:alkoxide ratio has direct effect on the amounts of organic and inorganic residuals left after synthesis [9,58]. Therefore, at present, we infer that the amounts of these residuals would be the main cause accounting the surface defect creation in the first step which will be discussed latter. As stated in the introduction part, the method for synthesizing the crystalline TiO_2 by sol-gel has been followed work of Wang et al [9]. They also investigated the effect of a water:alkoxide molar ratio on the characteristics of anatase. In their work, a significant increase of crystallite size was found in the range of 20, 57, and 82 nm on the anatase prepared from sol-gel method (without ultrasonic technique) using a water:alkoxide molar ratio as a 165, 10, and 3.3, consequently. In contrast, using the ultrasonic technique, the anatase samples had the smaller crystallite sizes (Table 6.1) than those in the work of Wang et al [9]. The crystallite size of anatase was still in the narrow range between 6 and 9 nm corresponding with the observation of no significant surface area loss (Table 6.1). This is because the ultrasonic technique can increase the hydrolysis rate during sol-gel reaction [68,69]. In summary, the first step creation combining with the ultrasonic technique can be successfully used for creating the surface defect (Ti^{3+}) without significant surface area loss and phase transformation.

6.5 Bulk Evolution.

We started with the sol-gel reaction of alkoxide as a Ti(i-Opr)$_4$ [9,82]. The alkoxide is hydrolyzed by water to form Ti-OH and alcohol (Equation 6.1). Then, the groups of Ti-OH condense and rearrange to form a network of Ti-O-Ti with another product as water (Equation 6.2). Moreover, alkoxide can also react with Ti-OH to form a Ti-O-Ti network and alcohol (Equation 6.3).

$$-\overset{|}{\underset{|}{Ti}}-OR \; + \; HOH \; \longrightarrow \; -\overset{|}{\underset{|}{Ti}}-OH \; + \; ROH \quad (6.1)$$

$$-\overset{|}{\underset{|}{Ti}}-OH \; + \; -\overset{|}{\underset{|}{Ti}}-OH \; \longrightarrow \; -\overset{|}{\underset{|}{Ti}}-O-\overset{|}{\underset{|}{Ti}}- \; + \; HOH \quad (6.2)$$

$$-\overset{|}{\underset{|}{Ti}}-OR \; + \; -\overset{|}{\underset{|}{Ti}}-OH \; \longrightarrow \; -\overset{|}{\underset{|}{Ti}}-O-\overset{|}{\underset{|}{Ti}}- \; + \; ROH \quad (6.3)$$
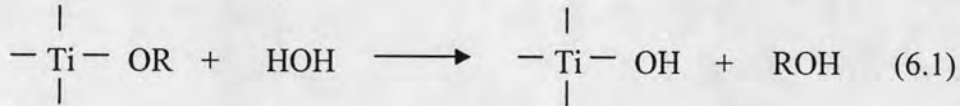
Where R = ligand (-Pr)

In the presence of excess water with alkoxide (in case TiO$_2$-R165), as seen in Eq. (6.1), high amounts of Ti-OH and alcohol were obtained as the result of complete reaction. At this point, the high condensation rate in the both Eq. (6.2) and (6.3) were obtained leading to a rapid rearrangement to form a Ti-O-Ti network [9,58,82]. In finally, the rich products as a water and alcohol and the lower amount of reactant (alkoxide) were obtained confirming by the higher weight loss in the first region and the lower weight loss in the second region of TGA curve (Figure 6.3c), respectively. In contrast, in the presence of deficient water with alkoxide (in case TiO$_2$-R4), the lower rate of three reactions were determined resulting in a slow rearrangement of Ti-O-Ti network [9]. The presence of deficient water caused in an incomplete reaction of alkoxide confirming by higher weight loss in the second region of TGA curve (Figure 6.3a).

After sol-gel synthesis, the resulting TiO_2 was amorphous. As known that the anatase will be formed from Ti-O-Ti network during calcination process coinciding with the removals of inorganic and organic residuals [25,28-33]. In this work, in the temperature below 473 K, only the removal of water and alcohol was found (Figure 6.3) without the formation of anatase. At higher temperature, the unreacted alkoxide was removed (Figure 6.3) coinciding with the beginning of crystallization to be an anatase upon temperature 523 K characterized by the observing of small XRD peak at this temperature (Figure 6.6). This initial anatase preparing by using the deficient water (TiO_2-R4) exhibited the highest crystallinity consequently with those of TiO_2-R40 and TiO_2-R165 (Figure 6.6). This is attributed to the slow rearrangement to form the Ti-O-Ti network during sol-gel synthesis of TiO_2-R4 [9,82]. At this temperature, although, the TiO_2-R4 had the highest amount of unreacted alkoxide remained in this sample (Figure 6.3a), this sample still exhibited highest crystallinity. Therefore, we infer that the unreacted alkoxide should not locate inside the bulk structure, but it should be around the surface.

At higher temperature, unreacted alkoxide still moved out until approximately 700 K, the removal rate became too slow (Figure 6.3a). Finally, at the desired temperature (723 K), the TiO_2-R4 exhibited closer perfect bulk structure (Figure 6.1 and 6.2) with the lower bulk defect (Figure 6.5) than those of TiO_2-R16, TiO_2-R40, TiO_2-R80, and TiO_2-R165, respectively. This apparently causes by the slow rearrangement to form Ti-O-Ti network during the sol-gel synthesis.

The improving of bulk properties after the creation of surface defect (Ti^{3+}) on the anatase is a valuable for many applications of TiO_2. As well known that to improve the photocatalytic activity, SMSI, and hydrophilic properties, besides the surface defect (Ti^{3+}), an increase of crystallinity can also enhance these properties [83,84,85].
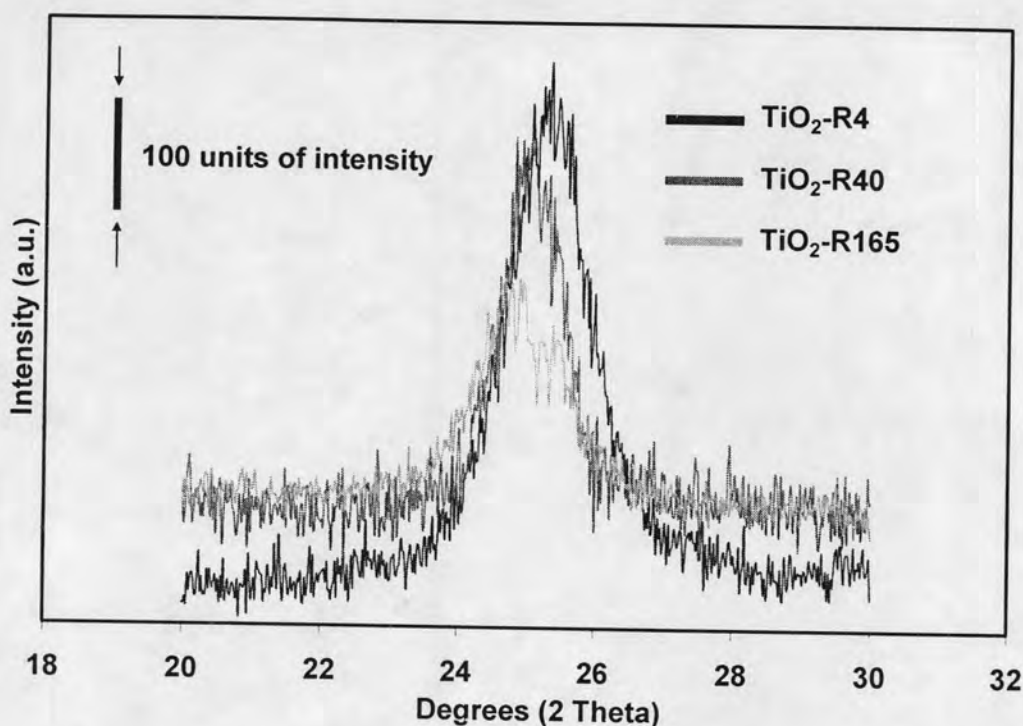
Figure 6.6: XRD patterns in the main peak ca. 25° of resulting TiO_2 after calcination at
523 K

6.6 Surface Evolution.

It was found that the number of unreacted alkoxide that had been removed (the highest on TiO_2-R4 sample) is consistent with the number of surface defect that had been created on the anatase surface (also highest on TiO_2-R4). As mentioned above, these unreacted alkoxide should be around the surface of anatase. Therefore, we infer that the first step creation of surface defect (Ti^{3+}) was determined by the removal of unreacted alkoxide from the surface during calcination process.

The proposed mechanism to create surface defect (Ti^{3+}) on the TiO_2-R4 has been drawn in Scheme 6.1. As mentioned previously, before calcination, in the presence of deficient water with alkoxide, the unreacted alkoxide (Ti^{4+}-OR) and the structural unreacted alkoxide remained on the surface of anatase. The structural unreacted alkoxide (OR-Ti^{4+}-O-Ti^{4+}-OR) came from the partial reaction between alkoxide and water or Ti-

OH [82]. As illustrated in Scheme 6.1(a), at higher 473 K, the both of unreacted alkoxide and terminal i-Opr (which bonds to $-Ti^{4+}-O-Ti^{4+}-$, represented by $-OR$ in the model) will be removed. In this step, the amorphous Ti-O-Ti network begins to be crystallized upon temperature 523 K until 723 K. As seen in the Scheme 6.1(b), the surface defect site (Ti^{3+}) will be created by the removal of terminal i-Opr (represented by $-OR$) coinciding with the presence of higher amount of crystal structure in anatase phase.

The first step creation by removal of terminal i-Opr during calcination can be represented by the defect chemistry equation using the Kroger-Vink notation as shown in the proposed Eq. (6.4).

$$2(i\text{-Opr}_O^{\bullet}) \longrightarrow 2(i\text{-Opr})_{gas} + V_O^{\bullet\bullet} \qquad (6.4)$$
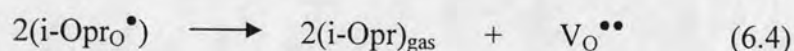
The removal of i-Opr [which occupies on an oxygen lattice site ($_O$) with singular positive charge ($^{\bullet}$)] to atmosphere leads to form the surface defect (Ti^{3+}) as an oxygen vacancy site (V_O) with double positive charge ($^{\bullet\bullet}$).

As mentioned above that the first step creation is not attributed to the removal of lattice oxygen atom because it is difficult to remove this oxygen atom from the surface of anatase at mild temperature without the presence of reduced gas. However, this work shows that the removal of oxygen atom with alkyl group as an i-Opr from the Ti^{4+} site during the crystallization from amorphous to anatase is the possible way to use for creating the surface defect (Ti^{3+}) on anatase at mild temperature without reduced gas. We postulate that during crystallization process, the surface of TiO_2 (which consists of amorphous and initial anatase) is not stable enough to protect the removal of the oxygen atom from Ti^{4+} atom.
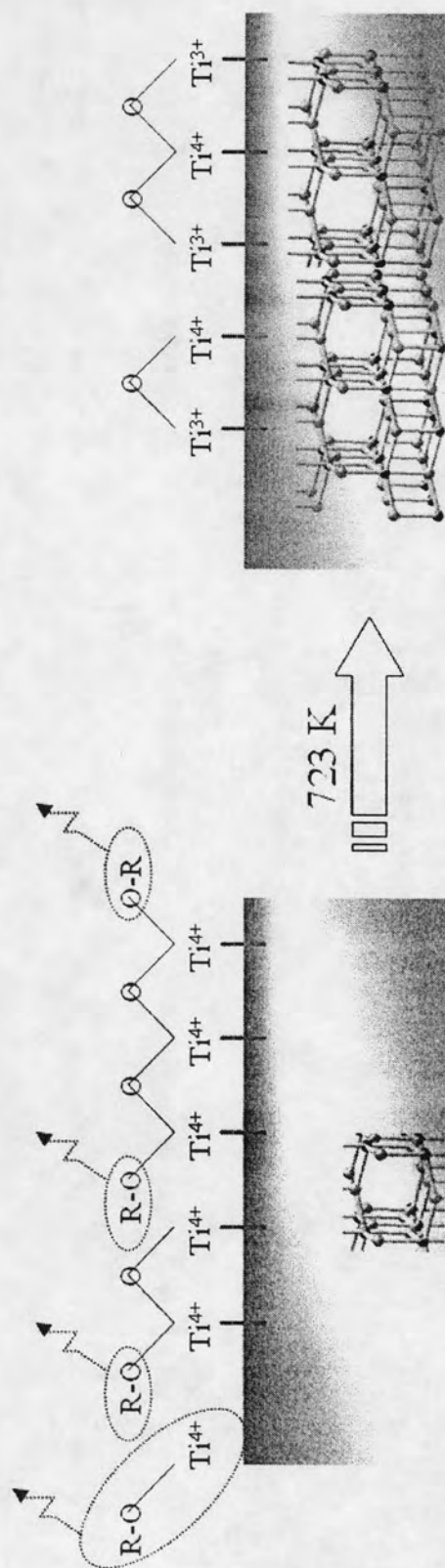
Scheme 6.1: The simplified scheme of the first step creation: (a) the removal of unreacted alkoxide and the terminal i-Opr group at temperature higher 473 K, (b) the forming of surface defect (Ti^{3+}) after removal of terminal i-Opr group after calcinations at 723 K

6.7 First vs. Second Step Creation.

The details regarding the common techniques for surface defect (Ti^{3+}) creation on the 1st TiO_2 (the TiO_2 which was prepared in the first step) have been summarized in the Table 6.2. The details of vacuum annealing technique are described in this table [37]. This technique prefers rutile because the creation must be done under high temperature (1000 or 1100 K). The details for creating the surface defect by the ion bombardment and UV irradiation are also summarized in this table [35,17]. It shows that these techniques also prefer the rutile because the surface must be cleaned at high temperature (900 or 1100 K) prior to create surface defect in the second step. Many researchers also reported that the surface defect creation in the second step must be done by either cleaning and or creating under high temperature resulting unavailable for anatase and causes of significant surface area loss [45,17,37,43,38,39]. However, using the plasma technology, Nakamura et al. reported that this method can create surface defect on both anatase and rutile due to it was operated at mild temperature [19].

The common second step creation consumes comparatively more energy, time, and special knowledge. In contrast, the first step creation consumes less energy and time than the former. The yield of first step creation is difficult to quantify because there is not a standard measurement of the amount of surface defect available for comparison. However, this technique shows a promising new method for the creation of surface defect (Ti^{3+}) on anatase at mild temperature in the absence of reduced gas.

Table 6.2. The common techniques for surface defect creation in the second step.

Technique	Cleaning Procedure	Procedure in second step	Avialable phase[a]	Note
Anealling in vaccum	Sputtering and annealing in UHV	Heat the 1st TiO_2[b] in UHV at 1000[18] or 1100[6] K	Rutile	Medium efficiency[c]
Ion bombarded	Ar^+ sputtering and annealing in UHV at 1100 K	Bombard the 1st TiO_2[b] with 500 Ev Ar ion	Rutile	Not identified
UV irradiation	Ar^+ sputtering and annealing in UHV at 900 K	Irradiate the 1st TiO_2[b] with 500 W high pressure mercury UV lamp	Rutile	Low efficiency[d]
Plasma-treating	Not identified	Treat the 1st TiO_2[b] with radio-frequency discharge (500W) at 673 K	Anatase/rutile	Not identified

[a] Determined based on that we have found the phase transformation to rutile occurred approximately 600 K.
[b] It means the TiO_2 was prepared from the first step prior to surface defect creation in the second step.
[c] Based on the report in the Ref. (18).
[d] Based on the report in the Ref. (17).