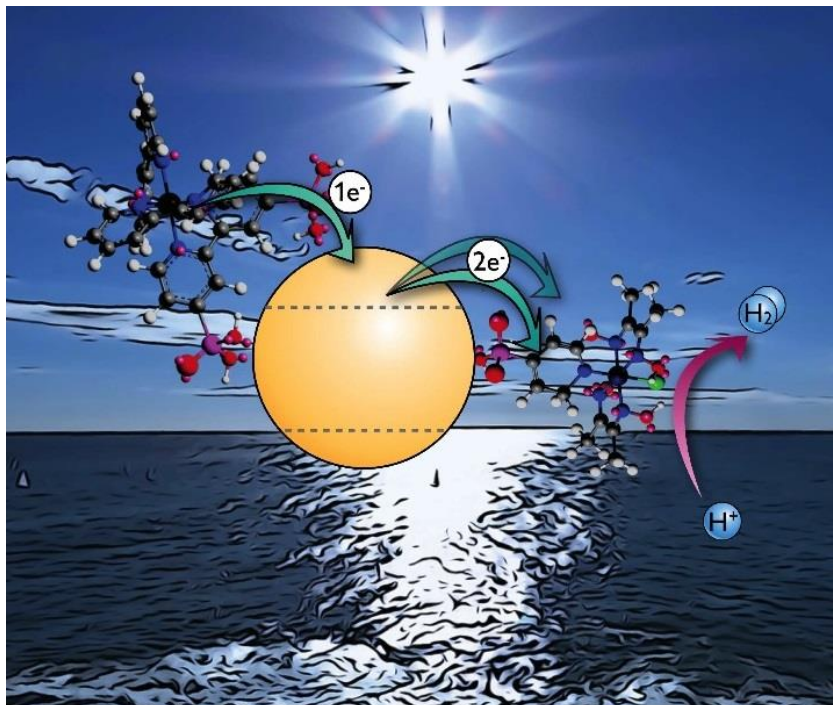


Photocatalytic Enhancement of SiO₂ coated Degussa P25 TiO₂ Powder by Scalable Atomic Layer Deposition

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Master Thesis

Photocatalytic Enhancement of SiO₂ coated Degussa P25 TiO₂ Nanoparticles by Scalable Atmospheric Pressure Atomic Layer Deposition

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Abstract

This work investigates the enhancement of photocatalytic activity of titanium dioxide (TiO_2) commercial particles by ultrathin silicon dioxide (SiO_2) films deposited *via* atmospheric pressure atomic layer deposition (ALD) carried out in fluidized bed reactor (FBR). The ALD process enabled precise control for the growth of ultrathin film at sub-nanometer level. At an operating temperature which can be lowered to room temperature ($\sim 27^\circ\text{C}$), the growth per cycle (GPC) smaller than 1 angstrom ($\sim 0.8 \text{ \AA}$) allowed us to study on the relationship between the thickness of SiO_2 thin film and photocatalytic activities of SiO_2 coated TiO_2 nanoparticles (NPs). Importantly, a considerable enhancement of photocatalytic activity was found which resulted from the formation of crosslinking of Si-O-Ti bonds in the interface between SiO_2 and P25 TiO_2 nanoparticles as indicated by XPS and FT-IR. The band gap of this interfacial layer can be tuned from 3.10 to 3.23 eV slightly narrower than P25 TiO_2 by varying the number of ALD cycles and the ALD processes at different temperature corresponding to the thickness of SiO_2 thin film. Such band gap led to a red-shift of the absorption spectra which means the better absorption of visible light and enhanced the charge transfer from TiO_2 to the interface, thereby prevented the rapid recombination of generated carriers. As for the precursors SiCl_4 and deionized water vapor, the saturating state of dosing at the first stage of ALD process related to self-limiting reaction can be got after 5 seconds. In addition, annealing could also enable the enhancement of photocatalytic activity *via* modifying the morphology of interface. Practically speaking, our approach provided a scalable, energy effective and precise method to tune the photocatalytic properties of SiO_2 coated Degussa P25 TiO_2 nanoparticles. When it goes to applications, the enhancement of photocatalytic activity can be used for photocatalyst.

Keywords: atomic layer deposition, Si-O-Ti interface, self-limiting reaction, TiO_2 photocatalysis, ultrathin SiO_2 film, atmospheric pressure.

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Chapter I

1. Introduction

As an excellent photocatalyst, the catalytic activity of TiO_2 was discovered by Fujishima [1] in 1972. Since then, this kind of materials are used in many industrial fields such as purification of water and air pollution, hydrogen evolution and photoelectrochemical conversion due to its nontoxicity, excellent structural and chemical stability and abundant supply [2]. However, because of the relatively wide band gap, TiO_2 is not capable for harvesting efficiently sunlight in the visible and infrared range to generate sufficient photon flux [3]. In the field of photocatalyst, doping and surface modification are addressed to enhance harvesting efficiency and prevent rapid recombination of charge carriers (*e.g.*, holes and electrons). Doping in some cases can tune the electronic properties as create mid-band gap which is easier to excite electrons or holes due to the lower demand of energy resulting in a red-shift of optical absorption [4]. Additionally, doping accompanying with defects can trap the excited carriers to prevent rapid recombination [5]. Surface modification such as ultrathin films and nanoclusters made by metals or metal oxides serves as another approach to enhance the photocatalytic activities by reducing the charge combination [5]. Growth of Pt islands on the surface of TiO_2 is a good example to achieve enhancement and it is explained that Pt nanoparticles (NPs) act as the conduction band electron sink due to its lower Fermi level [6]. Previously, silicon dioxide (SiO_2) was used for suppressing the photocatalytic activities of TiO_2 due to its large band gap (~ 9 eV) which will block the charge transfer from TiO_2 to surface. Nevertheless, it is reported that the TiO_2 - SiO_2 binary system could enhance the photocatalytic activity which is attributed to the presence of silica promote the absorption of dye materials and the active oxygen species could react in the vicinity of the interface between two different materials. Moreover, the presence of Si-O-Ti interfacial layer gives a narrower band gap which could alter the absorption of light and charge recombination [7,8]. However, it is not that easy to coat ultrathin SiO_2 films (< 1 nm) on nanoparticles. Such ultrathin film consists of pure SiO_2 layer and the the Si-O-Ti interfacial layer and it will make the pure SiO_2 layer as thin as possible and the Si-O-Ti interfacial layer relatively thick to boost the charge transfer and avoid fast electron-hole recombination which further could enhance the photocatalytic activity. ALD is able to control the growth of thin film precisely compared with chemical vapor deposition (CVD) and sol-gel process.

1.1 Atomic Layer Deposition

1.1.1 General ALD

In the past decades, liquid-phase epitaxy played an important role of synthesis in the field of Nano-materials owing to the simplicity. However, the restrictions of liquid-phase deposition method like limited morphology (crystal orientation) control, rough surface and poor dimensional control make gas-phase deposition more attractive. Atomic layer deposition (ALD) is a gas-phase deposition based technique to meet the requirement of atomic control and conformal deposition which could fabricate inorganic ultrathin layers by chemisorption between monolayers. In this way, the much better adhesion than CVD due to chemisorption could avoid exfoliation of layers. Based on the sequential self-limiting reactions, one characteristic ALD cycle consists of the following steps as shown in Fig. 1.1.

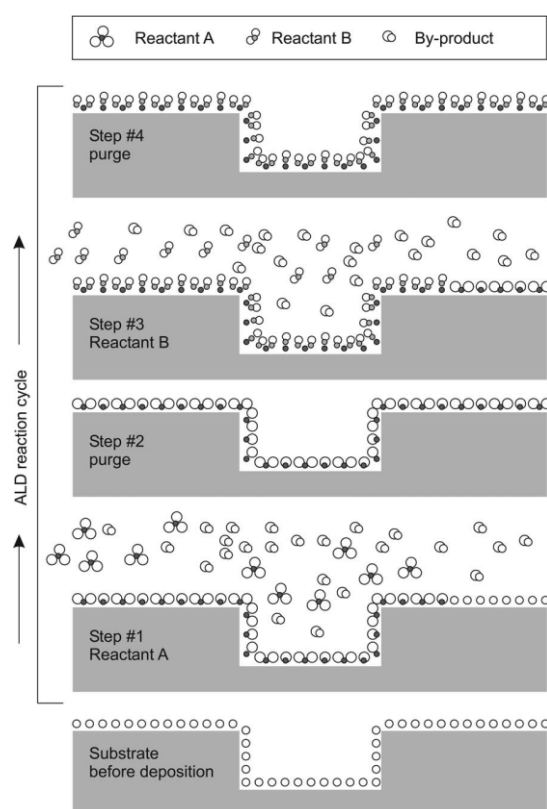


Figure 1.1 Schematic illustration of one ALD reaction cycle [9].

Self-limiting reaction occurs in step 1 that the reactant A contact the surface of substrate in finite sites for a short time. In order to remove the by-products and non-reacted reactants, the first purge is applied followed by the second self-limiting reaction of the second reactants or surface treatment to activate the surface sites again like oxidization. After a relatively long purge with the same function of the first purge, one ALD cycle is finished. In addition, for some inert substrate materials, surface treatments or heat treatments are required before the

beginning of the ALD process. The growth of the thin film by means of ALD is identified as growth per cycle (GPC).

The surface chemistry of ALD is mainly about the self-limiting reaction where the adsorption counts. If the surface area adsorbs enough reactant to react and cover the whole surface, the reaction will not proceed anymore. Adsorption could be divided into two interactions physisorption and chemisorption. The former one is caused by landing of molecules or atoms on the substrate which is weak interaction in this case and it is always reversible. The latter one is dominant which is determined by three main classes: ligand exchange, dissociation and association. As shown in Fig. 1.2a, the first step is ligand exchange. The reactant molecule is split on the surface and then the ligand combines with surface groups to form a volatile compound that is released as a gaseous by-product and the remaining part of the molecule chemisorbs to the surface. The next step is dissociation (see Fig. 1.2b). The split molecule forms new ligands with the active sites on the surface without releasing gaseous by-products. In Fig. 1.2c, the last step association occurs. The molecule forms a coordinative bond with one active site and does not dissociate the ligand [9].

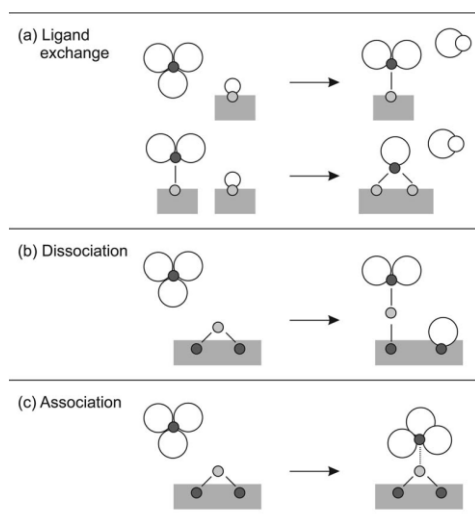


Figure 1.2 Chemisorption mechanisms identified for ALD: (a) ligand exchange, (b) dissociation, and (c) association [9].

One advantage of ALD is the precise thickness control at monoatomic scale due to the self-limiting reaction to grow one monolayer per cycle. Moreover, the ultrathin film fabricated by ALD is very smooth and conformal to the substrate, therefore, there are rare active sites left on the surface after fabrication. Owing to this reason, annealing could be a very attractive method to enhance the photocatalytic activity *via* changing roughness of interface. Last but not least, the growth of thin film is independent of substrate geometry because the gaseous precursor will fill the whole space in the chamber or column which means the thin film will cover the surface area of the substrate with the same thickness.

1.1.2 ALD in Fluidized Bed Reactor

For ALD of coating on nanoparticles, normally, the advantages of using fluidized bed reactor can be concluded as the good solid mixing, good heat transfer and ease of process control. Moreover, absence of solvent reduces the waste generated in ALD process. Fluidization is a method of suspending particles in moving fluid causing them to behave in a liquid-like state [10]. Gas-solid fluidization offers high contacting efficiency due to its high rates of physical mixing and bed turnover frequency. This prevents localized temperature hot spots that can lead to detrimental changes in operating conditions. In addition to high heat transfer coefficients, high mass transfer rates exist in fluidized bed reactors (FBRs). Low operating pressures assist in proper vapor phase adsorption of ALD precursors on solid particle surfaces. Reduced pressure fluidization is used industrially for various drying, coating and particle synthesis processes. The technology exists to carry out nanoscale ALD reactions in scalable fluidized beds for enhanced particle coating technologies. The gas-phase surface adsorption of ALD precursors is a very rapid process, with the self-limiting step being determined by the probability of a precursor molecule finding a vacant surface nucleation site and reacting. This process will take longer for powders with a higher degree of soft agglomeration or cohesiveness due to increased tortuosity of the gas diffusion pathway. The high particulate circulation frequency of a well-fluidized bed promotes a significant number of surface collisions before unreacted precursor molecules can escape from the bed. This work presents a ALD-FBR process of depositing SiO_2 on P25 TiO_2 nanoparticles for the use of photocatalyst. For most catalytic applications, it is crucial to deposit the catalytic material on a particulate support material. An example of ALD in fluidized bed reactor about depositing platinum clusters on titania nanoparticles at atmospheric pressure is as follows.

Deposition of Pt on TiO_2 Nanoparticles *via* ALD-FBR

Deposition of platinum clusters on TiO_2 nanoparticles is one representative example of ALD-FBR in the field of catalyst. Using MeCpPtMe_3 and ozone as reactants, this process was at a relatively low temperature, 250 °C and atmospheric pressure. Goulas *et al.* [11] found Pt islands formed at the substrate while dispersed uniformly in fluidized bed reactor. But at atmospheric pressure, mixing was much worse especially in a large-scale system [12]. In this ALD process, ozone worked as the oxidizers that could solve this problem mostly at atmospheric pressure. Fig. 1.3a shows the TiO_2 support particles after 1 ALD cycle. A uniform distribution of the active phase Pt particles can be seen. Fig. 1.3b shows the substrate after 5 ALD cycles. The average particle size clearly increased for an increase in the Pt content from 1.6 to 5.8 w.t.% (see Fig. 1.4).

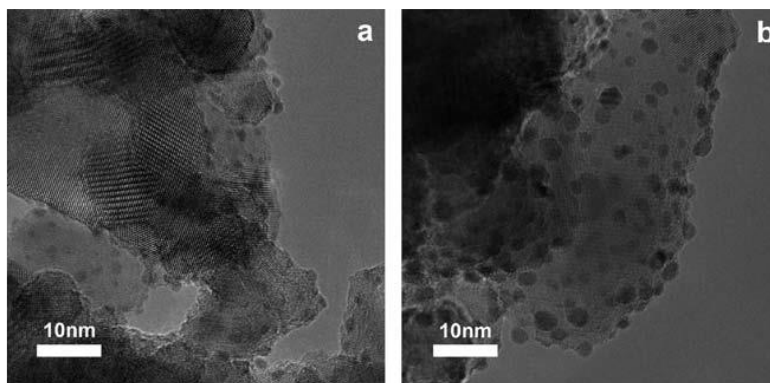


Figure 1.3 TEM image of Pt nanoclusters deposited onto the TiO_2 support after 1 ALD cycle (a) and 5 ALD cycles (b) [11].

Fig. 1.4 shows that about 95% of the precursor provided was converted into Pt clusters, which could reduce the loss of precursors. When processing larger amounts of powder, it would be possible to reduce even further these losses [12]. Fig. 1.4 also shows that with the increasing of the number of cycles from 1 to 4, a monotonic increase in the Pt loading was observed.

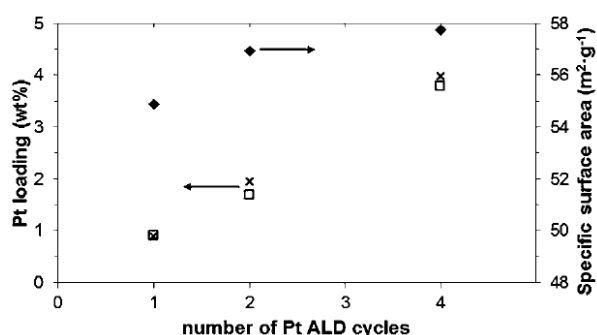


Figure 1.4 Pt loading measured by ICP (□) and predicted for ideal ALD (x) along with changes in specific surface area (◆) as a function of ALD cycles (Pt content values corrected for changes in specific surface area) [11].

Varying dosing time and number of ALD cycles allowed the precise control to get homogeneously distributed and highly dispersed Pt nanoclusters with small size of particles. In this case, the synthesis of catalyst with excellent performance is achieved [13].

1.2 Comparison of Different SiO_2 Thin Film Deposition Methods

For silica thin film deposition, there are three methods which are widely used such as wet chemical method (*e.g.*, sol-gel), CVD and ALD. It is helpful to weigh the pros and cons among different methods in order to fulfill the requirements of the applications especially for photocatalysis.

1.2.1 Wet-chemical Deposition of SiO₂

Sol-gel is the most widely used method for deposition of thin film due to the simple route and low cost. Marage *et al.* [14] reported commonly used method of depositing silica thin film which were fabricated by the sol-gel technique using tetraethylorthosilicate (TEOS) as a precursor. The introduction of glacial acetic acid at the molar ratio TEOS:acetic acid 1:15 causes acetate modification, resulting in an exothermic reaction and the solution is modified by a small amount of water later on. Acetylacetone acts as a stabilizer, hence it is added in the molar ratio TEOS: acetylacetone 1:1. Different molar content of TEOS enables the deposition of SiO₂ layers with different thickness [15]. Such wet chemical deposition has the following pros: 1. Cost effective; 2. No need of vacuum equipment; 3. Roughly control of coverage and thickness.

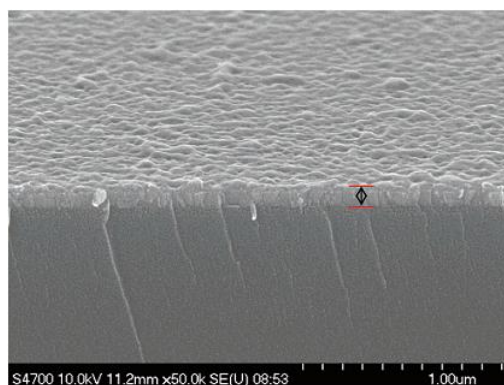


Figure 1.5 SEM of SiO₂ film [16].

Generally, the thickness of silica thin film fabricated by sol-gel is about 100 nm which could be seen in Fig. 1.5. However, the quality of silica film is quite poor owing to the porosity which will result in the poor electronic properties and stability. As for the morphology, it is characterized by AFM according to the variation of the volume ratio of EtOH:TEOS as shown in Fig. 1.6 [17].

In order to avoid porosity, another similar method is used as sol electrophoretic deposition (EPD) which requires a reactor to allow the colloidal particles suspended in a liquid medium migrate under the influence of an electric field, process called electrophoresis and are deposited onto an electrode. But the surface of substrate must be electrically conductive. The precise control of growth compared with normal sol-gel enables low operating temperature and ultrathin film (~5 nm) that leads to better quality of thin films [18]. From Fig. 1.6, on the one hand, it is obvious that the pores become larger and number of pores decreases if the volume ratio of EtOH and TEOS decreases. Finally, the pores almost disappear when the ratio decreased to 2:1. On the other hand, after heat treatment, the film surface becomes much flatter and smoother than that without heat treatment.

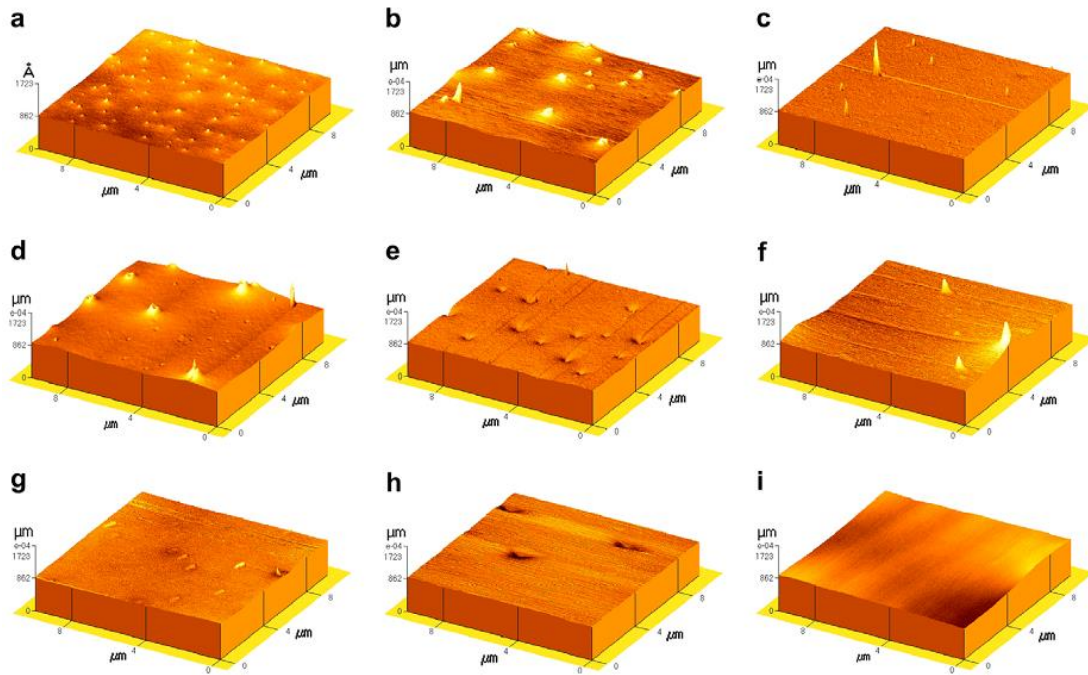


Figure 1.6 The surface morphology of the sol-gel and the EPD SiO_2 films. The films were processed using the following conditions, EtOH:TEOS volume ratio: (a) 10:1, without annealing, (b) 10:1, annealing for 1 h at 100°C , (c) 10:1, EPD for 72 h with annealing for 1 h at 100°C , (d) 5:1, without annealing, (e) 5:1, with annealing for 1 h at 100°C , (f) 5:1, EPD for 72 h with annealing for 1 h at 100°C , (g) 2:1, without annealing, (h) 2:1, with annealing for 1 h at 100°C and (i) 2:1, EPD for 72 h with annealing for 1 h at 100°C [17].

1.2.2 CVD of SiO_2

Chemical vapor deposition (CVD) which is used to fabricate various insulator films is paramount in semiconductor industries. In general, CVD of insulator thin film is proceeded under very high temperature ($700\text{--}1200^\circ\text{C}$) and relatively high pressure. The film is much more uniform than that deposited by sol-gel process, however, for a film coated on high radius of curvature substrate like nanoparticle, the quality of thin film is not that good as the thin film deposited on flat substrate as shown in Fig. 1.7 [19]. Owing to feeding precursors simultaneously, general CVD cannot control the growth of thin film very precisely which is very important for the enhancement of photocatalytic activity of SiO_2 coated TiO_2 nanoparticles.

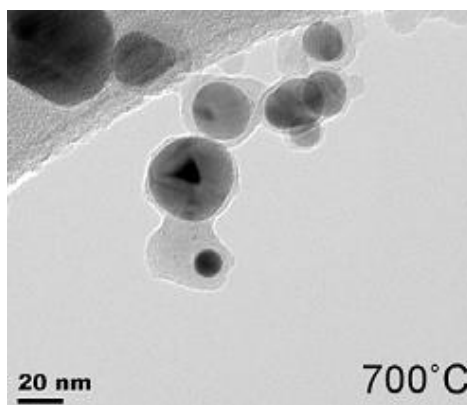
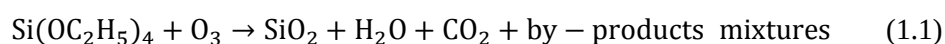


Figure 1.7 TEM of SiO₂ coated silver nanoparticle [19].

Recently, Maeda *et al.* [20] proposed mixing precursor TEOS with ozone in the presence of relatively high temperatures under atmospheric pressure. In this case, the growth of uniform silica film at 400 °C with growth rates of 0.1 µm/min or more could be achieved. The process could be described as the reaction below [20].



Water as an undesirable residue is quite hard to be removed unless heated to 500 °C while the moisture consisting of oxides which are reflowed or densified at relatively high temperature could be eliminated. The advantage of CVD provided by this process are the excellent step coverage and in-situ flow owing to the surface mobility prior to formation of silica. However, for CVD, the ability of controlling the growth of thin film is much better than sol-gel process but worse than ALD.

1.2.3 ALD of SiO₂

As a precise controlling deposition technique, ALD exhibits saturation growth behavior and the thickness of SiO₂ thin film could be lowered to several angstroms based on self-limiting and sequential surface reactions while the GPC is about 1 Å. Previously, volatile silanes with halogen, alkyl and alkoxy ligands are used as the silicon sources [21,22].

Table 1.1 Parameters of commonly used combination of precursors for ALD-SiO₂.

1 st Precursor	Oxidizer	Temperature (°C)	Pressure (×10 ⁻³ MPa)	Ref.
Tetramethyl orthosilicate [Si(OCH ₃) ₄]	H ₂ O	150	133-267	23
Tetrakis(ethylamino)silane [Si(NHC ₂ H ₅) ₄]	O ₃	325-514	0.3-1.3	24
Tris-dimethylaminosilane [SiH(N(CH ₃) ₂) ₃]	H ₂ O ₂	100-250	0.3-0.4	25
Silicon tetrachloride [SiCl ₄]	H ₂ O	320-420	0.1-1.7	26
H ₂ Si[N(C ₂ H ₅) ₂] ₂	O ₂ plasma	50-400	20	27

Nowadays, due to the wide range of structural variations, rigid safety requirement and higher chemical reactivity, new combination of precursors are used. Some commonly used experimental conditions and chemicals are shown in Table 1.1.

As shown in Table 1.1, some of the precursors need vacuum equipment such as tetramethyl orthosilicate and others need high operating pressures saying tetrakis (ethylamino) silane and tris-dimethylaminosilane. For the precursors of silicon tetrachloride and water vapor, the ALD process is at low temperature and low pressure (atmospheric pressure) and the ultrathin film based on these two precursors can be varied from 0.7 nm to several nanometers [26]. Morphology of SiO₂ ultrathin film fabricated by ALD can be quite flat as shown in Fig. 1.8. Precursors are very important for the synthesis process because the selection of specific precursors is related to the selection of experimental conditions (*e.g.*, operating temperature and pressure). Moreover, operating temperature and pressure will influence the coverage and quality of thin films to a great degree. A low deposition temperature below a certain level (so called ALD window) may limit the growth of thin film because it cannot reach the activation energy of chemisorption or the growth will be faster due to the condensation [9]. If the deposition temperature is too high, the sufficient thermal energy will result in a situation that more precursor molecules covered on the surface increases the Si-O bond while most of the hydroxyl bonded water is lost and hydroxyl condensation will occur [28]. High density and low surface roughness of SiO₂ film *via* ALD can be observed at high temperature. In ALD process, operating pressure and partial pressure of precursors influences the reaction path and partial pressures of carrier gas and by-products are very sensitive to the growth of thin films. In principle, high pressure can stabilize adsorbates thermodynamically, otherwise it will desorb at low pressure [9].

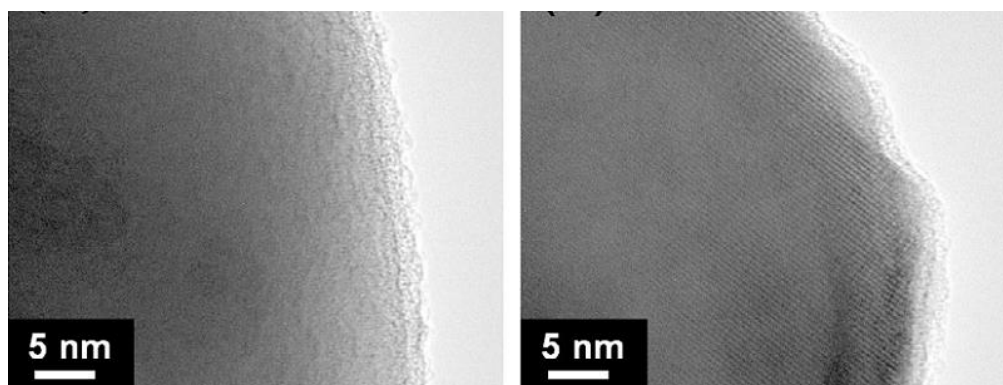


Figure 1.8 HRTEM images of Conformal SiO₂ ALD films on (left) anatase and (right) rutile TiO₂ substrates [26].

TiO₂ has propensity to photodegrade organic-based substance in the vicinity of the surface as a commonly used photocatalyst because of the free radical and superoxide ion generation under UV irradiation. Some achieved the enhancement of photocatalytic properties in the TiO₂/SiO₂ binary system. For instance, multi-layer of SiO₂/TiO₂, porous nanostructure and

mixture of $\text{TiO}_2/\text{SiO}_2$ are reported that can enhance the photocatalytic activity of pure TiO_2 [8,37,38]. Weighing all the pros and cons of different synthesis methods including wet chemical process (*e.g.*, sol-gel method) and gas phase-based process (*e.g.*, CVD and ALD-FBR), liquid based process is not that good due to the impurities inside the thin film and the bad stability *etc.* Compared with different gas phase-based methods, CVD is the most widely used method. All the precursors are sent into the reactor simultaneously which further will make the growth of film uncontrollable. Furthermore, it is tough to control the tortuosity of pores for pinhole-laden SiO_2 thin films and the growth of thin films (< 1 nm) by CVD. During photocatalyst batches, neither sol-gel method nor CVD process can handle the growth of thin film precisely. In a nutshell, ALD process can overcome these shortcomings and achieve ultrathin films (< 1 nm) on the surface of substrate as well as the precise control of growth of thin films which enables the study on the relationship between thickness of thin films and photocatalytic activities especially the enhancement in this work.

1.3 Self-Limiting Reactions of Depositing SiO_2 on TiO_2 in ALD Process

During the ALD process using SiCl_4 and deionized water vapor, the sequential self-limiting gas-solid reactions take place directly on the surface *via* substitution reactions of surfaces groups (*i.e.*, $-\text{Cl}$ and $-\text{OH}$ groups). The presence and amount of initial surface concentration of $-\text{OH}$ groups of TiO_2 can be got by TGA. The second step of self-limiting reaction will produce $-\text{OH}$ groups for the next ALD cycle. Roger *et al.* [29] worked on the surface composition of titania particles by TGA as shown in Fig. 1.9.

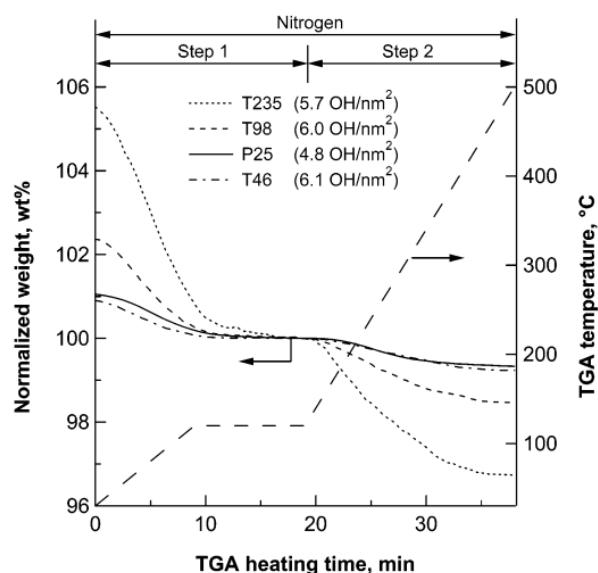
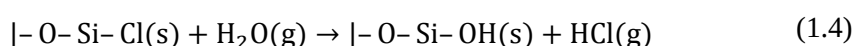
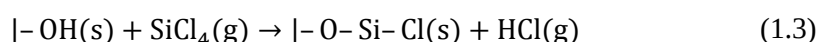


Figure 1.9 TGA graph of pure fumed titania (T235, T98 and T46) which indicate the surface areas of 235, 98 and 46 $\text{m}^2 \text{g}^{-1}$, respectively, and commercial fumed titania P25 [29].

The physically absorbed water and chemically bonded water (always –OH group in principle) could be distinguished in Step 1 and Step 2 respectively *via* these three dash lines of pure titania particle. The first plateau means the temporary stable state except the physically absorbed water while the last plateau tells the final stable state at high temperature, 500°C, where the chemically bound water is evaporated [30]. The reaction of depositing silica on titania can be divided into two containing the two pulsing processes of different precursors (SiCl₄ and water). Total reaction is described as [30]:



For ALD process, the first and second part of self-limiting reaction are as follows [30].



where $|-\text{OH}(\text{s})$ and $|-\text{Si}-\text{Cl}(\text{s})$ represent the surface hydroxyl and chlorosilicon groups, respectively [30].

In this work, as for the first cycle, the hydroxyl groups on the surface of P25 TiO₂ nanoparticles will react with SiCl₄ to produce the functional groups $|-\text{O}-\text{Cl}$ and HCl in the first pulsing step as shown in equation (1.3). After the first pulsing, it takes 3 minutes to purge the reactor to make sure the by-products and residual precursors are removed completely. Hereafter, the generated HCl will be absorbed by the gas washer containing NaOH solution connected to the outlet. In the second pulsing, $|-\text{O}-\text{Cl}$ is oxidized by water vapor to form $|-\text{O}-\text{Si}-\text{OH}$ and HCl as shown in equation (1.4) and the purging after the second pulsing needs 8 minutes. In order to avoid the water vapor that may come back into the reactor from outlet, a gas washer containing silicon oil is connected to the outlet in front of the one containing NaOH solution. The second ALD cycles will start with the –OH groups generated from the first cycle and so on.

1.4 Photocatalysis of P25 TiO₂ Particles

Based on the high chemical stability and photocatalytic activity, TiO₂ is widely used as the photocatalyst and TiO₂ has three crystalline structures: anatase, rutile and brookite, where anatase exhibits the best photocatalytic properties. The phase transformation from anatase to rutile occurs in air at ~600 °C [31]. However, the reported transition temperatures vary in the range 400-1200 °C owing to the raw materials (*e.g.*, particle size, particle shape (aspect ratio) and surface area) and processing methods [32,33]. Hence, it is necessary to lower the processing temperature to avoid phase transformation for the use of photocatalyst. As for the applications of TiO₂ related to its good photocatalytic activity, it can be used for self-cleaning, decomposition of gas pollution and *etc.*

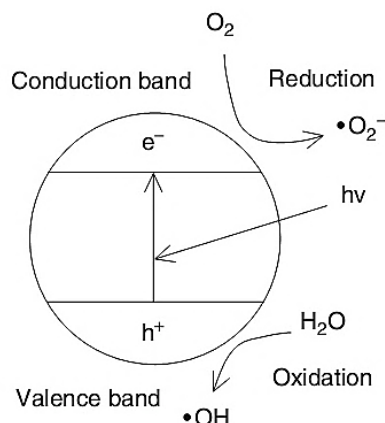
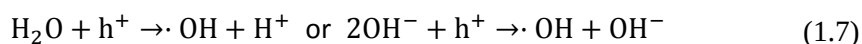


Figure 1.10 Schematic of TiO₂ Oxidation-Reduction reactions under illumination.

For uncoated TiO₂, under illumination, the induced separation of carriers occurs by photons to generate electrons (e⁻) from conduction band to valence band, leaving holes (h⁺) behind in the valence band. The minimum required energy equals to energy difference of band gap (E_g) and E_g of P25 TiO₂ is 3.26 eV, which corresponds to the photons with a wavelength of 380 nm. As shown in Fig 1.10, the generated electrons are able to reduce acceptor molecule A which could be described as the equation below.



Meantime the donor molecule B will be oxidized by photo-generated holes and such holes are accepted by hydroxyl group or water molecule which depends on the pH value to produce hydroxyl radical ($\cdot OH$) afterwards and prevent electron-holes recombination to yield high reaction rate which further correlates with high photocatalytic activity:



Oxygen in water or air acting as electron acceptor can be reduced by generated electrons to form superoxide ion ($\cdot O_2^-$) which is very reactive for oxidation of organic molecules.



The generated oxygen superoxide ions act as the active species to degrade dye materials.

1.5 Photocatalytic Enhancement in SiO₂/TiO₂ Binary System

1.5.1 Photodegradation Process of Rhodamine B Solution by SiO₂/TiO₂

Dye used for photocatalytic test in this work is Rhodamine B (RhB). Feng *et al.* [34] studied the degradation processes of TiO₂ and TiO₂/SiO₂ in RhB solution with pH~4.3. The different

mechanism at different irradiations are as follows. (i) Under visible irradiation, RhB can absorb photons and then the excited RhB molecules transfer the lowest unoccupied molecular orbital (LUMO) electrons from RhB molecules to the conduction band of TiO_2 which react with preadsorbed oxygen to produce active oxygen species. (ii) Under UV irradiation, photon absorption of TiO_2 plays a major role which further reacts with H_2O , O_2 and $-\text{OH}$ groups to produce active oxygen species. Furthermore, in the second case, the sites to produce the active oxygen species are no longer restricted beside the adsorption site of RhB, which means that the attack of active oxygen species are less selectivity and the deethylation process are not so obvious as that under the visible irradiation. It must be noted that there is a fast dynamic adsorption/desorption equilibrium of RhB and its deethylated species between the solution bulk and the TiO_2 particle surface during the photocatalytic deethylation stepwise process of RhB (as shown in Fig 1.11).

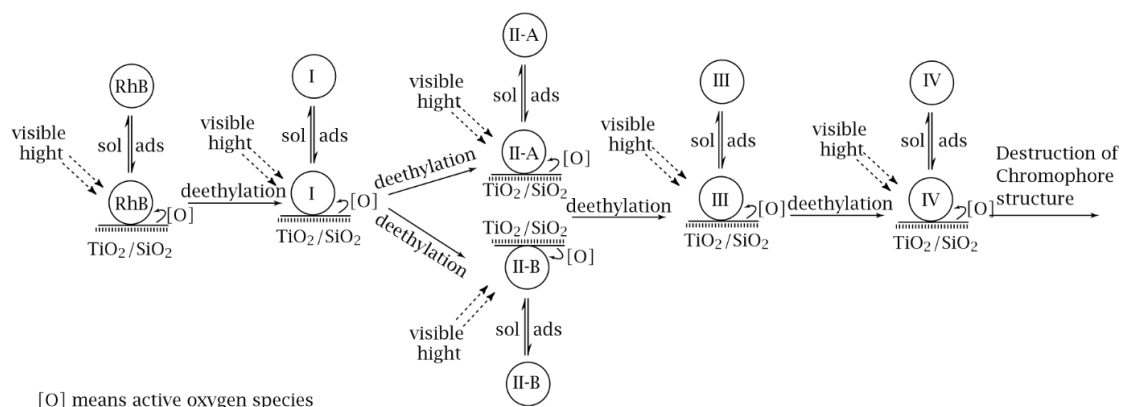


Figure 1.11 Schematic of stepwise deethylation process, dynamic equilibrium and deethylation intermediates species of RhB between the surface of $\text{TiO}_2/\text{SiO}_2$ and bulk solution in the photocatalytic oxidation of RhB [34].

In the second case, the adsorption of dye materials is the minor factor for photodegradation process. Thus, for the diethylamino group adsorption, RhB would prefer to be deethylated by the active oxygen species under visible light irradiation [34,35].

1.5.2 Mechanisms of Photocatalytic Enhancements

Enhancement of photocatalytic activity about $\text{TiO}_2/\text{SiO}_2$ binary system can be concluded as three main mechanisms from literature, which are (i) better adsorption of dye molecules on the surface of the nanoparticles with TiO_2 sites due to the presence of SiO_2 [8,36], (ii) larger specific surface area owing to the porous structure than bare TiO_2 [37,38] and (iii) the charge imbalance of Si-O-Ti crosslinking inducing more hydroxyl radicals [39]. There are two models built by Tanabe *et al.* [40] to explain the enhancement of photocatalytic activity based on charge imbalance.

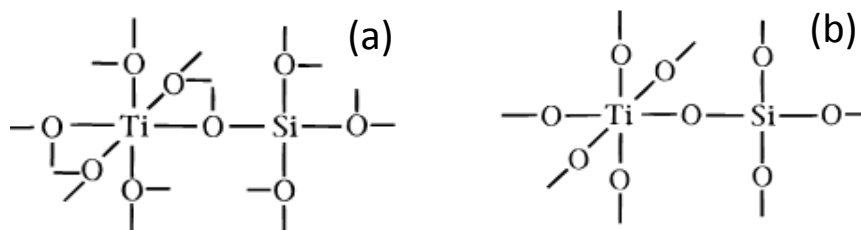


Figure 1.12 Illustration of Si-O-Ti linkage (a) Lewis sites and (b) Bronsted sites [39].

TiO₂ is octahedrally coordinated with oxygen which is bonded to 2 Si atoms and Ti ion enters the lattice of SiO₂ with the same coordination number. And the Ti ions are still bonded to the same number of oxygens with different coordination number. In this case, the charge negative imbalance is created. As shown in Fig. 1.12a, Lewis sites match the lattice of interface if the charge is positive while the imbalance is calculated by integration of contribution of every individual bond. Extra protons can be found in Bronsted sites (see Fig. 1.12b) when the charge imbalance is negative (-1/3). More surface hydroxyl groups are expected since the negative imbalance attracts more protons around the oxygen atoms. The different physical crosslinking model of lattice substitution is based on the different Si/Ti content ratio. Doolin *et al.* [39] reported Bronsted sites are preferential with less content of silica and vice versa. Besides the Si-O-Ti bonds charge effect, it also reduces the mobility of electrons in TiO₂ phase and polarizability of oxygen atoms which prevents the rapid recombination of carriers at the interface [40]. However, given that the SiO₂ coating layers in our work are uniform and conformal, which prevent the contact between the TiO₂ surface and the dye molecules. Hence, these mechanisms may not fully explain our observations.

Here, we demonstrate that ultrathin SiO₂ films on TiO₂ nanoparticles can be achieved by ALD using SiCl₄ and H₂O as the precursors. The SiO₂ ALD is carried out in a fluidized bed reactor operating at atmospheric pressure. Remarkably, we found that the operating conditions at atmospheric pressure enables ALD of SiO₂ at temperatures as low as room temperature (~27 °C), which is significantly lower than the typical temperature range (*i.e.*, above 300 °C) used for the SiCl₄/SiO₂ thermal ALD carried out in low pressure range [26]. With a GPC of approximately 0.8 Å, the thickness of the coating layer can be controlled at sub-nanometer level, which enables the study on the influence of the coating thickness and the Si-O-Ti interfacial layer on the photocatalytic activity of TiO₂ nanoparticles. importantly, we demonstrate that by varying the thickness of the coating layer from a few angstroms to several nanometers, the photocatalytic activity of the TiO₂ can be tuned from enhancement to suppression. XPS, FTIR and UV-VIS analyses indicate the presence of an Si-O-Ti interfacial layer, which enhances the optical absorption to visible light region and plays the key role in the photocatalytic activity enhancement. Based on our observation, a simple model describing the photocatalytic enhancement of the TiO₂/SiO₂ core/shell nanoparticles is proposed.

Chapter II

2. Experimental Section

2.1 Experimental Set-up

Experiments are carried out in a fluidized bed reactor are described by David *et al.* [42], which is composed by a vertical glass column of 26 mm internal diameter and 500 mm height, placed on a single motor Paja PTL 40/40-24 vertical vibration table to assist the fluidization. The vibration table is operated at 35 Hz, and provides a vibration amplitude of 2 mm to the column.

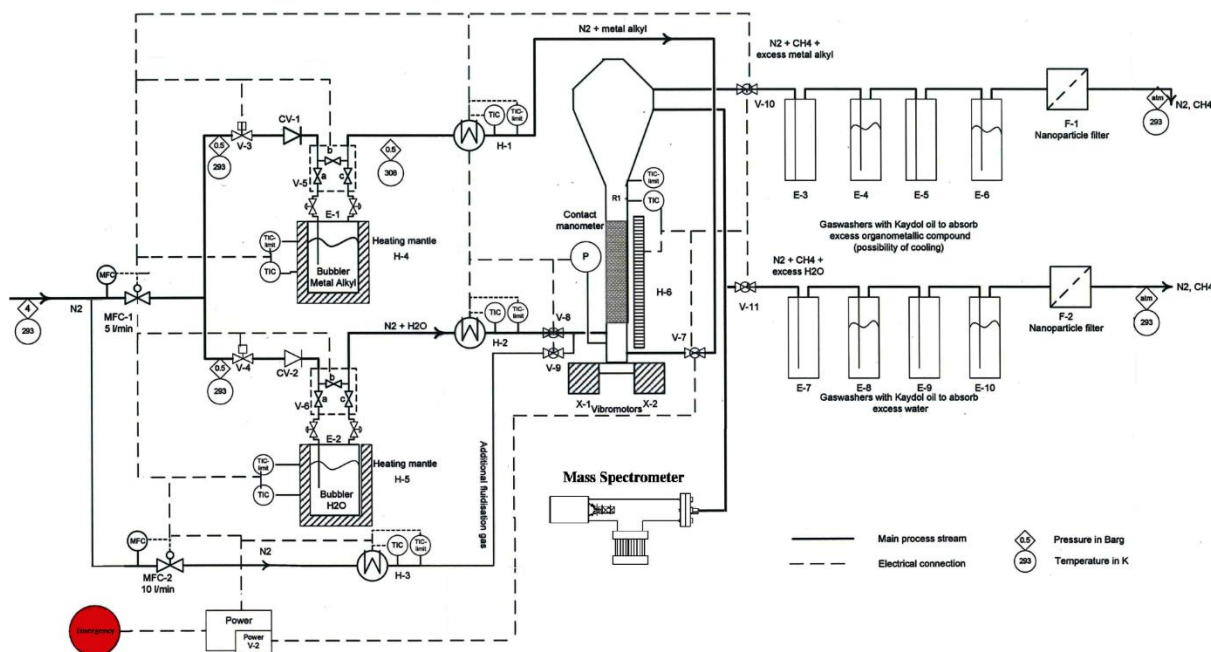


Figure 2.1 Set-up of Atomic Layer Deposition in Fluidized Bed Reactor (The detailed parts can be found in Table 1 of Appendix A).

An infrared lamp placed parallel to the column, and a type-K thermocouple inserted in the column, are used to control the bed temperature with a fluctuation about ± 5 °C. The gas is introduced to the column through a stainless-steel SIKA-R 20 AX distributor plate of sintered particles with a pore size of 37 μ m, to achieve a homogenous flow of gas through

the full cross-section of the column. An identical distributor plate is placed on top of the column twined around cylindrical surface by Teflon tape to prevent nanoparticles from leaving the column. Although the pore size of the distributor plates is several orders of magnitude larger than the particle size, the risk of losing particles is small since they do not fluidize as individual particles, but as agglomerates of 200-300 μm . These agglomerates, which have a void fraction of 98%-99%, demonstrate a dynamic behavior during fluidization [43]. This means that the agglomerates break and recombine constantly as a consequence of the collisions between solids. The dynamic behavior and large porosity of the agglomerates ensure that the precursor molecules reach the whole surface area of the individual particles, even though they exist as agglomerates.

Degussa P25 TiO_2 with the mean diameter about 21 nm and specific surface area of approximately $54\text{m}^2/\text{g}$ measured by BET method (Brunauer-Emmett-Teller) were supplied by Evonik Industries (Hanau, Germany). Silicon tetrachloride (SiCl_4) was provided by Akzo Nobel HPMP (Amersfoort, the Netherlands) and the second precursor was deionized water vapor. Both of these two precursors were kept in stainless steel bubbler while the former is 500ml and the latter is 150 ml. Pressurized nitrogen (99.99 vol.%) was used as the carrier gas. A flow of nitrogen which is 0.5L/min is applied to fluidize the powder and carry precursors.

2.2 Design of the Experiment

To calculate the precursor dosing times, we estimated the total amount of active sites in the bed of particles, *e.g.*, hydroxyl groups. This amount is calculated using the surface area of the Degussa TiO_2 ($54\text{ m}^2/\text{g}$), the mass of powder placed inside the column (1.5 g), and the surface concentration of hydroxyl groups ($3.3\text{ OH}/\text{nm}^2$) [44]. Furthermore, it can be got that the initial amount of $-\text{OH}$ groups is $4.44 \times 10^{-4}\text{ mol}$. SiCl_4 is easy to be evaporated hence we didn't heat the bubbler containing SiCl_4 which means kept it at room temperature ($\sim 27^\circ\text{C}$). According to the ideal gas law, the amount of evaporated SiCl_4 can be calculated *via* the equation below as $13.95\text{ mol}/\text{m}^3$.

$$C = \frac{n}{V} = \frac{P}{RT} \quad (2.1)$$

where P is the vapor pressure, R is the ideal gas constant as $8.314\text{ Pa}/(\text{m}^3 \cdot \text{mol} \cdot \text{K})$ and T is the operating temperature of bubbler. Vapor pressure of SiCl_4 at 27°C calculated by August equation is 3.48 kPa. The nitrogen flow rate we used is 0.5 L min^{-1} and assuming all of the sent SiCl_4 are reacted with the active sites of P25 TiO_2 nanoparticles. Estimation about dosing saturated time of SiCl_4 can be given by amount of $-\text{OH}$ groups divided by the amount of evaporated SiCl_4 times nitrogen flow. The saturating dosing time of first precursor is about 3.82 seconds but the assumption is quite ideal and not all of the molecule of SiO_4 will react

with –OH groups. Therefore, the dosing time of SiCl_4 we used varied from 5 s to 1 min (5 s, 10 s, 20 s, 40 s and 1 min). Moreover, the purging time after pulsing of SiCl_4 is 3 min while it is 8 min after second pulsing of deionized water vapor and the dosing time of oxidizer is 3 min. Briefly, the pulsing sequence is 1 min /3 min /3 min /8 min. Operating temperature is varied from room temperature ($\sim 27^\circ\text{C}$) to 250°C (RT, 100°C , 200°C and 250°C). The substrate temperature must be high enough to prevent condensation of any reactants. If condensation occurs during an ALD cycle, undesirable or uncontrollable reactions might happen, resulting in the formation of porous and impure films. However, an undesirable decomposition of a reactant will happen if the temperature is too high. Furthermore, CVD reactions will start to occur, which leads to an uncontrolled deposition of the film. Moreover, different number of cycles influences the thickness of SiO_2 thin film directly with 2, 5, 8, 10, 12, 20, 30 and 40 cycles. In addition, the effects of annealing for SiO_2 coated TiO_2 nanoparticles on photocatalytic activity is also studied.

2.3 Characterization of Nanoparticles

As-coated $\text{SiO}_2/\text{TiO}_2$ powders were suspended in ethanol and transferred to regular transmission electron microscopy (TEM) grids (3.05 mm in diameter). TEM images were taken at several locations on the grids using a JEOL JEM 1400 transmission electron microscope operating at a voltage of 120 kV and a current density of 50 pA/cm^2 .

X-ray photoelectron (XPS) characterizations were carried out using a ThermoFisher K-Alpha system using Al $\text{K}\alpha$ radiation with photon energy of 1486.7 eV. A sufficient amount of powders was immobilized on carbon tape before loading into the XPS chamber. Survey scans were acquired using a $200\text{ }\mu\text{m}$ spot size, 55 eV pass energy and 0.1 eV/step with charge neutralization. The peaks positions were calibrated according to the C 1s peak at 284.8 eV. The specific surface area (SSA) of the powders was determined by performing N_2 physisorption on a Micromeritics Tristar II at 77 K. For each measurement, 160 mg of the powders was used. All the samples were annealed in N_2 at 150°C for 16 hours prior to the measurements. Data analysis was performed using Microactive software V3.02. The BET SSA was determined by fitting of data points in the $P/P_0 = 0.05\text{--}0.225$ region. The microporous volume and external surface area were determined by the t-method, obtaining a linear fit in the De Boer thickness of more than 15 data points [45].

A Mettler Toledo TGA/SDTA 851e thermogravimetric analyzer was used for studying the thermal behavior of the synthesized powders. An amount of approximately 10 mg of powders was used for each TGA measurement. The TGA curves were recorded while (1) heating up the powders from 25 to 120°C with a ramping rate of 10°C/min in a N_2 flow of 100 mL/min ; (2)

maintaining at 120 °C for 10 min; (3) ramping up to 550 °C with a ramping rate of 20 °C/min; and (4) finally maintaining at this temperature for 10 min. Steps (1) and (3) are commonly used to determine the density of physisorbed water and chemisorbed hydroxyl groups on the surface, respectively [46].

Optical absorption measurements were performed using a PerkinElmer-Lambda 900 spectrometer equipped with an integrated sphere device. The powder was suspended in ethanol, which was transferred onto a quartz substrate and dried in atmosphere. The spectra were acquired in the wavelength range of 600-200 nm, with fine steps of 1 nm.

The atomic concentration of the deposited SiO₂ was determined using instrumental neutron activation analysis (INAA), which was carried out at Reactor Institute of Delft (Delft University of Technology). The powders (about 100 mg for each sample) were loaded into high purity polyethylene capsules. The samples and a standard sample (reference) were then packaged and irradiated in a suitable reactor at a constant neutron flux. All reactors used for neutron activation employed uranium fission, which provides a neutron flux in the order of 10¹² cm⁻². These neutrons have low kinetic energy, typically less than 0.5 eV. Upon irradiation, a neutron can be absorbed by the target nucleus (*e.g.*, Si), forming a radioactive nucleus, which carries its own half-life characteristics. The nuclear decay of the radioactive nuclei produces gamma-rays, which are detected by the NAA detectors, from which the Si loading was determined. For SiO₂/TiO₂ samples, the waiting time of 5 days was applied during the decay of radioactive nuclei. For Si, the NAA used in this work allows to detect at the level in the range of 10⁻¹-10⁻² nanograms.

The photocatalytic activity of the SiO₂/TiO₂ powders was evaluated by the photodegradation of RhB solution. For each test, 30 mg of the powders were added to 30 mL RhB solution (concentration of 8 mg/L) and continuously stirred in the dark for 30 min to obtain a uniform suspension. Thereafter, the suspension was exposed to UV radiation generated by a mercury lamp with an irradiance of 45 W m⁻² for different exposure times. The set-up allowed to carry out up to 10 samples simultaneously, which ensured that all samples were irradiated under the same conditions, such as light intensity, exposure time, and temperature. The suspension was then centrifuged to separate the powders from the solution. Finally, the solution was analysed by UV-visible spectrophotometry to determine the residual concentration of the RhB in solution with the wavelength from 300 nm to 800 nm where the characteristic wavelength used is 554 nm, which was used to evaluate the photocatalytic activity of the SiO₂ thin films about enhancement.

Chapter III

3. Results and Discussion

3.1 Film Thickness and Si Concentration Characterized by TEM and INAA

The self-limiting reaction of $\text{SiCl}_4/\text{H}_2\text{O}$ in ALD process demands a relatively high temperature as the driving force of ligand exchange among functional groups in the surface such as hydroxyl groups and the typical range is about 300 °C to 400 °C which could be lowered by adding catalyst such as NH_3 [26,47]. However, silicon tetrachloride is a potential material to enable the ALD process at relatively low temperature and atmospheric pressure which is attributed to its low vapor pressure of SiCl_4 at room temperature and low vapor temperature of it in atmosphere. On the one hand, for industrial applications and scaling up, due to the energy-saving, safe operating conditions and stable working state, room temperature is competitive. On the other hand, room temperature avoids fluctuation of operating temperatures in the reactor. In the first case, Jing *et al.* [28] demonstrated an approach to run the $\text{SiCl}_4/\text{H}_2\text{O}$ system at room temperature without catalyst accompanied with high operating pressure and H_2O partial pressure. At these kind of experimental conditions, high total and H_2O partial pressure is dominant for silica nucleation and growth of silica thin films [48]. Here, we propose an atmospheric pressure ALD method in fluidized bed reactor at low temperatures to grow conformal silica thin film on P25 TiO_2 nanoparticles using silicon tetrachloride and deionized water vapor. The saturation state of dosing SiCl_4 is studied with different pulsing time which was already calculated above at the nearly ideal circumstances from 5 s to 1 min. TEM was implemented to characterize the thickness of SiO_2 ultrathin film while silicon concentration was measured by INAA as shown in Fig. 3.1. As for the silicon concentration with different SiCl_4 dosing time indicated in Fig. 3.1g, the same amount of silicon products was found for 5 s and 1 min both at 100 °C and 200 °C which are approximately 2.1 at. % and 2.5 at. % respectively which means 5 seconds is enough for dosing the precursor SiCl_4 to get saturation for self-limiting reaction. For 12 cycles, the tendency of Si concentration at different temperatures is in agreement with the thickness of SiO_2 thin film. Here it has to be noted that the thicknesses of SiO_2 thin film at different temperatures are almost the same except at room temperature as well as the Si concentration. In other words, in such range of

operating temperature (100 °C to 250 °C), the GPC is independent of temperature while at room temperature, condensation will occur due to the vapor temperature of water which is higher than operating temperature in Fig. 3.1h. At 100 °C, the Si concentration as well as the coating thickness increased almost linearly with the number of cycles as shown in Fig. 3.1h (right). And the slope of linear estimation represents a small GPC (~ 0.8 Å) using the pulsing sequence $\text{SiCl}_4/\text{N}_2/\text{H}_2\text{O}/\text{N}_2$ with the corresponding exposure times of 1 min/3 min/3 min/8 min at 100 °C.

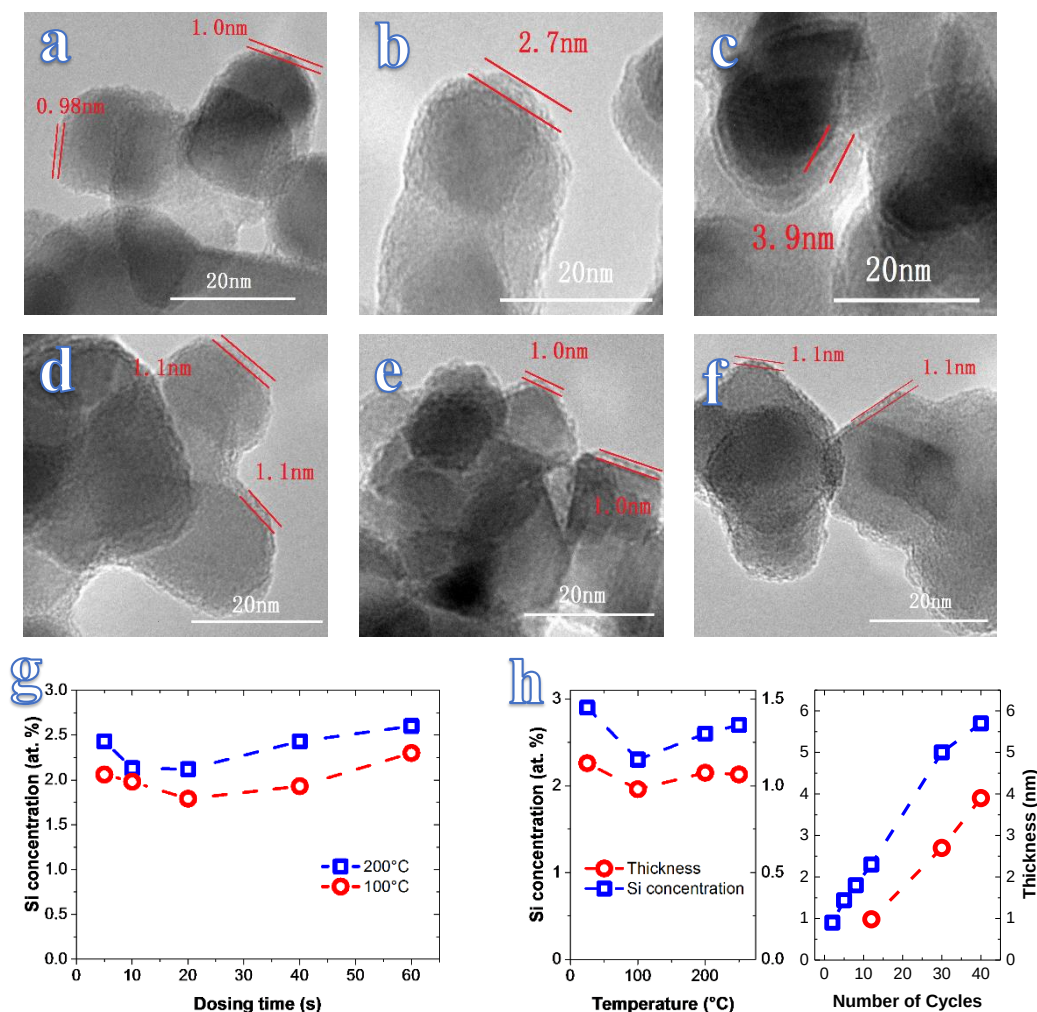


Figure 3.1 Representative TEM images of the TiO₂ NPs coated with SiO₂ grown for (a) 12 cycles, (b) 30 cycles, and (c) 40 cycles at 100 °C, and for 12 cycles at (d) room temperature, (e) 200 °C and (f) 250 °C. The plot of Si concentration as vs dosing time of SiCl₄ at 100 °C and 200 °C is shown in (g). The left of (h) shows the plot of temperature vs Si concentration and thickness for 12 cycles and right of (h) indicates the function of number of cycles vs Si concentration and thickness at 100 °C).

Here, the specific surface area (SSA) of P25 TiO₂ nanopowders we used for the calculation of dosing time in the *Experimental Section* was determined by N₂ physisorption isotherm as well as the pore volume of the coating layer. For uncoated P25 TiO₂ nanoparticles, the SSA is 54.5

m²/g. The plot demonstrates a trend that the volume of micropores and SSA would increase with the increasing of number of cycles although a slight fluctuation of total SSA was found as shown in Fig. 3.2 which means the external SSA was reduced. The thickness can be calculated with the approximation of SSA as a function of average diameter of particles as follows.

$$SSA = \frac{6}{\rho D} \quad (3.1)$$

where ρ is the density of nanopowders and D is the particle diameter. The initial particle diameter is 21 nm and density of Degussa P25 TiO₂ nanopowders is 4.26 g/mL. The increasing of thickness when increased the number of cycles in ALD process are almost in consistent with the growth of SiO₂ thin films and the agglomeration is the minor factor in this kind of ALD process.

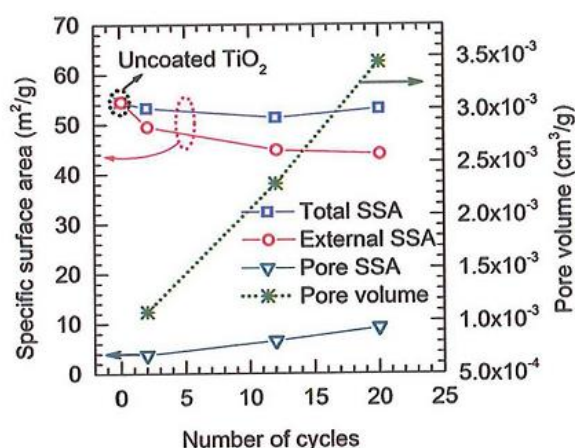


Figure 3.2 Total and external specific surface area of the uncoated TiO₂ and the TiO₂ coated with SiO₂ at 100 °C for different number of cycles.

3.2 Characterization of Composition and Interface of SiO₂ Coated TiO₂

The composition of uncoated TiO₂ and SiO₂ coated TiO₂ at room temperature (~27 °C), 100 °C and 200 °C are characterized by XPS which can be seen in Fig. 3.3. The binding energies (BE) of the elements were calibrated by referencing the C-C peak of C 1s to 284.8 eV (Fig. 3.3 a-d) [28]. In the region of Si 2p and O 1s, the Si 2p peak at 103 eV (Fig. 3.3 e-h) in conjunction with the O 1s peak at 532.5-532.7 eV which was designated as O_{-Si} afterwards in Fig. 3.3 i-l correspond to the Si-O coordination [49]. For stoichiometric SiO₂, a BE difference (ΔBE) between O_{-Si} and Si 2p of 429.3-429.4 eV is expected [49]. In this work, ΔBE was found to be in the range of 429.5-429.7 eV that slightly differed in deposition temperature. The higher ΔBE indicates the formation of nonstoichiometric SiO_x films ($x < 2$), which can be expected for ultrathin coating layers with a thickness of about 1 nm as measured by TEM in Fig. 3.1 a, d, e and f. For instance, $\Delta BE = 429.5$ eV represents a nonstoichiometric SiO_x with $x = 1.6$ [48]. The intense peak around 530 eV of the O 1s spectra which was designated as O_{-Ti} afterwards in

Fig. 3.3 i-l and the peak around 458.8 eV of the Ti 2p spectra (Fig. 3.3 m-p) stand for the fingerprints of Ti-O bonds of the P25 TiO₂ support [50]. Noticeably, there was one remarkable shift towards higher binding energy of both the O-Ti of the O 1s and the Ti 2p peaks of the SiO₂ coated TiO₂ compared with uncoated TiO₂, which is evidence of the formation of Si-O-Ti crosslinkage (e.g., interfacial layers) [26, 50]. Furthermore, for the O-Ti peak, a shift of 0.3 eV, 1.5 eV and 1.6 eV was observed for the SiO₂/TiO₂ deposited at room temperature, 100 °C and 200 °C, respectively, whereas for the Ti 2p peak, the corresponding shift is 0.3 eV, 0.4 eV and 0.6 eV. Accordingly, the shift is caused by the difference in electronegativity between Si (~1.8) and Ti (~1.5) [51, 52]. The formation of Si-O-Ti bonds attracts more electrons around Si atoms owing to the larger electronegativity which induced drop of the electron density around the Ti atom.

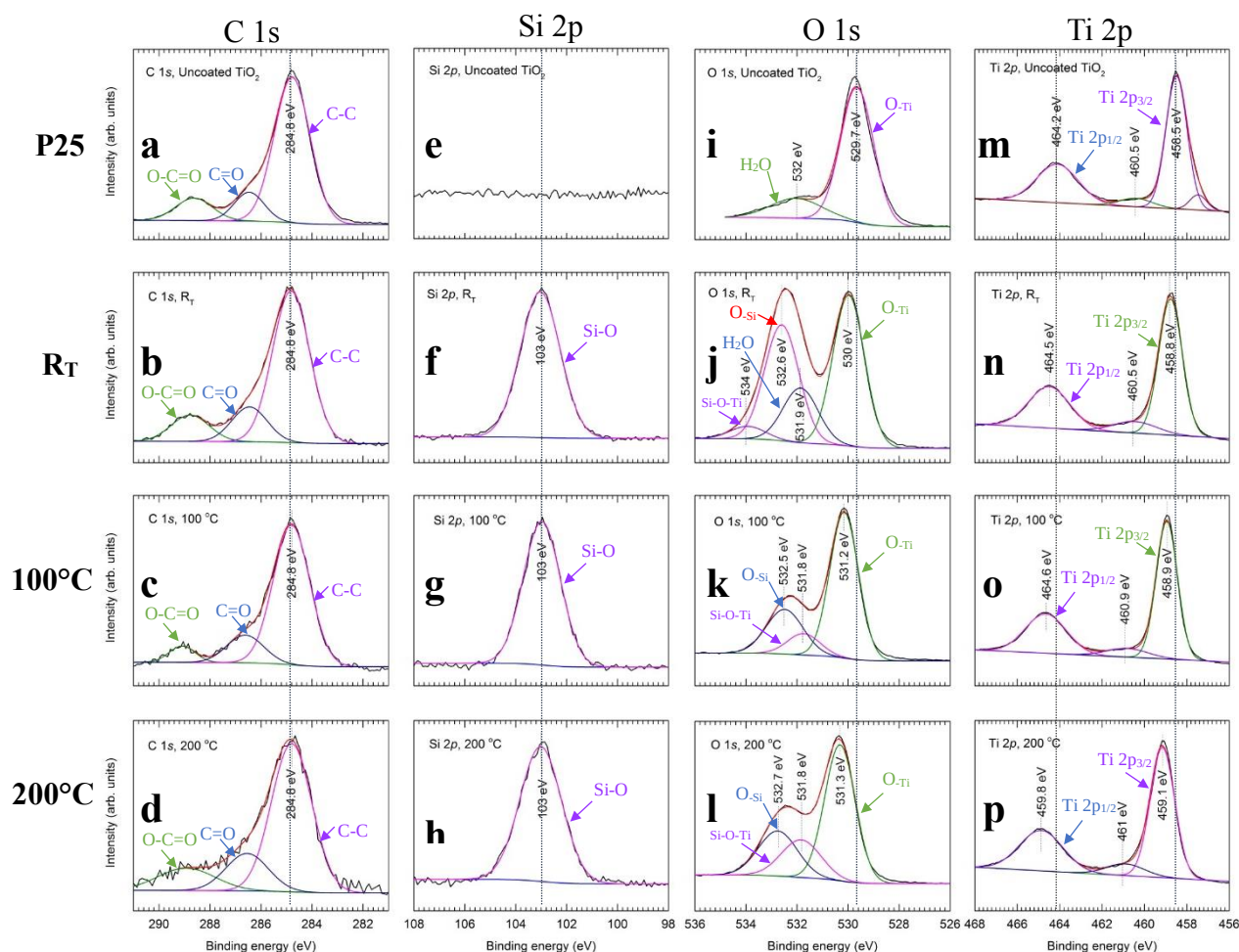


Figure 3.3 XPS spectra of bare TiO₂ and the TiO₂ coated with SiO₂ at room temperature, 100 °C and 200 °C. The binding energies are calibrated by referencing the C 1s peak to BE=284.8 eV (a-d). From left to right: C 1s, Si 2p, O 1s and Ti 2p; from top to bottom: Uncoated TiO₂, SiO₂ coated TiO₂ at room temperature, 100 °C and 200 °C for 12 cycles.

This consequently increases the effective positive charge on the Ti atom, and therefore the binding energies of both O-Ti and Ti 2p [26,50,53]. In addition to the shift of binding energy, the presence of the Si-O-Ti interfaces was also observed from the deconvolution of XPS spectra, indicated by the peaks at 531.8-531.9 eV of the O 1s (Fig. 3.3 i-l) and 460.5-461 eV (Fig. 3.3 m-p) in Ti 2p regions [28].

The presence of SiO₂ and the formation of Si-O-Ti interfaces are additionally evidenced by the FT-IR spectra shown in Fig. 3.4 a. In these spectra, the features of the TiO₂ NPs are represented by the absorption band in the low wavenumber range, *i.e.*, 400-800 cm⁻¹, whereas the broad absorption band with a peak at around 3500 cm⁻¹ corresponds to the hydroxyl groups [54]. The signatures of SiO₂ are featured by the two peaks in the wavenumber range of 1000-1250 cm⁻¹ [54]. The Si-O-Ti interface is represented by the absorption band in the wavenumber

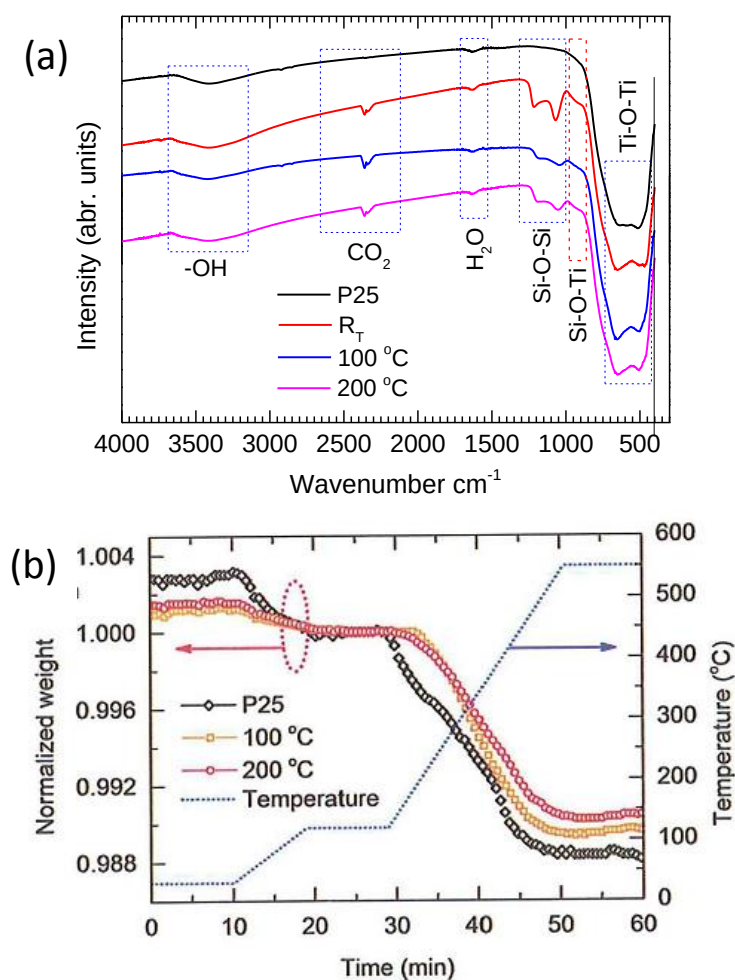


Figure 3.4 (a) FT-IR and (b) TGA diagrams of uncoated TiO₂ and the TiO₂ coated with SiO₂ layers grown for 12 cycles at room temperature, 100 °C and 200 °C.

range of 920-930 cm⁻¹ [54]. This absorption band arises from the stretching vibration of Si-O-

Ti bonds, which is not present in the spectrum of the uncoated TiO₂. In addition, the FT-IR spectra of the SiO₂ coated TiO₂ show a pronounced absorption band of CO₂ at 2356 cm⁻¹, suggesting that the SiO₂ layers are favourable for the adsorption of CO₂. This is in consistent with the observation reported by Yuan *et al.* [50], which demonstrated that a thin SiO₂ layer coated on TiO₂ nanoparticles could significantly enhance the CO₂ adsorption capacity compared to bare TiO₂. The hydroxyl groups are better demonstrated in TGA diagram as shown in Fig. 3.4b. As for the TGA diagram, samples lost free water at 66 °C and hydroxyl bonded water at 90 °C which showed a slightly slow process than that of free water. At the last stage, hydroxyl condensation occurred which showed the chemical dehydration of the inner molecule at 130 °C for bare TiO₂ and the sample fabricated at 200 °C when the one made at 100 °C is at about 200 °C. At the end, one thing should be noted that all of these three samples have less hydroxyl groups than the bared TiO₂ nanoparticles. As shown in Fig. 3.4b, the TGA diagrams demonstrate that the -OH density on the SiO₂ coated TiO₂ is slightly lower than that on the uncoated TiO₂ surface. This is an indication of the complete removal of H₂O and -OH groups in the SiO₂ ALD, which is a common challenge in ALD at low temperature using H₂O as the reactant.

3.3 Optical Absorption Spectra and Band Gap of SiO₂ Coated TiO₂

Silica thin film has a large band gap (~9 eV) which will hinder the charge transfer or block the active sites for photocatalysis as mentioned above. Due to its large band gap, SiO₂ film commonly has negligible effects on the optical properties of TiO₂ NPs. These makes SiO₂ an excellent material for suppressing the TiO₂ photocatalytic activity in pigmentary and optical applications [28]. However, in this work, the ultrathin SiO₂ film caused red-shift in the absorption spectra Fig. 3.5a and shift goes to 24 nm with rising of number of cycles in ALD process for 12 cycles and then being constant. Such red-shift of absorption spectra resulted in a reduction of band gap. The band gaps can be calculated *via* UV-VIS spectroscopy using Tauc Plots. The translation of the absorption spectra into the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) plots, where α is the absorption coefficient, which is proportional to the absorbance, enabled the determination of the band gap of the material as shown in Fig. 3.5b. The value of intersection between the linear fitting line and x axis represents the band gap of samples. Furthermore, the band gap of uncoated TiO₂ is 3.26 eV as the initial state while after two cycles' coating, the value was slightly reduced to 3.22 eV which is followed by 3.16 eV after 5 cycles. Finally, saturation state was reached after 12 cycles with the band gap as 3.10 eV (see the inset of Fig. 3.5b). A significant difference of band gap energy between Si-O-Ti interface and TiO₂ will lead to a considerable promotion of charge transfer and excellent prevention of rapid recombination which is vital for enhancement photocatalytic activity.

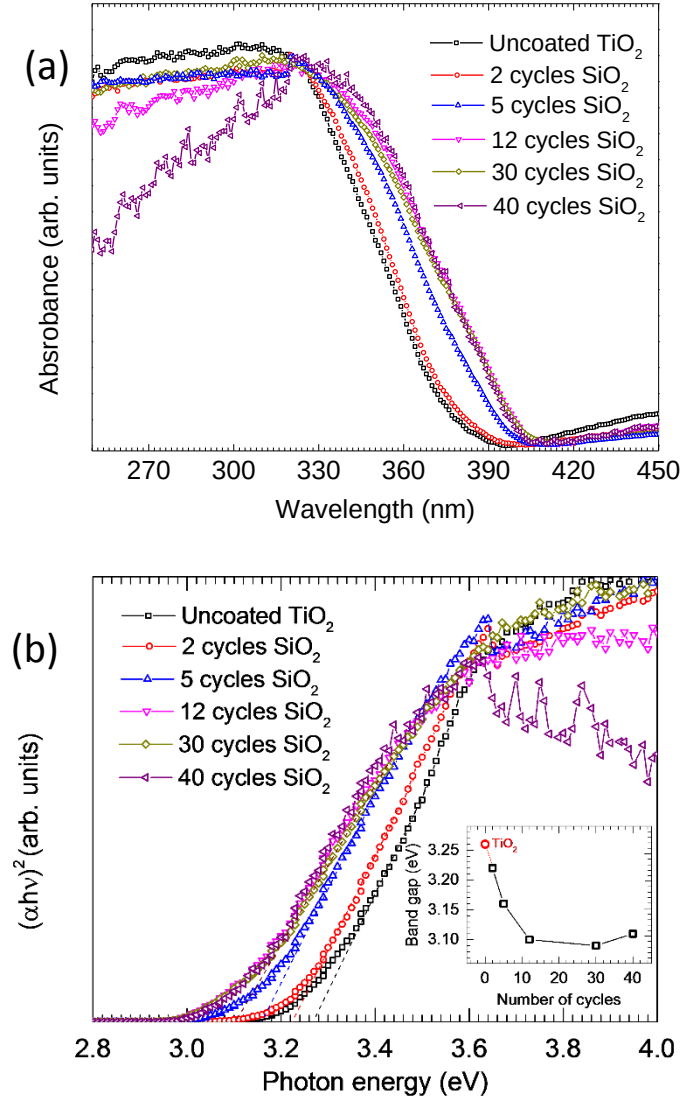


Figure 3.5 (a) Optical absorption spectra of the initial P25 TiO₂ and the TiO₂ coated with SiO₂ layers grown for different numbers of cycles and (b) the corresponding plots $(\alpha h\nu)^2$ vs photon energy $h\nu$, from which the band gap of the material was determined. The inset of (b) shows the band gap values as a function of the number of cycles. All of the depositions were carried out at 100 °C with the pulse sequence of 1 min /3 min /3 min /8 min.

3.4 Photocatalytic Activity of SiO₂ Coated TiO₂

The photocatalytic properties here emphasize more on the activity which is characterized by UV-VIS spectrometry after sunlight irradiation by a solar simulator with different intervals to get the whole photodegradation curve of RhB. In this work, the photocatalytic activities of the SiO₂ coated TiO₂ powders were investigated from the photodegradation of RhB dyes. Importantly, the low GPC of 0.8 Å enabled the ability to control the coating thickness at sub-nanometer level, which allowed us to study the influence of the SiO₂ thickness on the catalytic performance of TiO₂, as demonstrated in Fig. 3.6a. In Fig. 3.7, the samples fabricated at

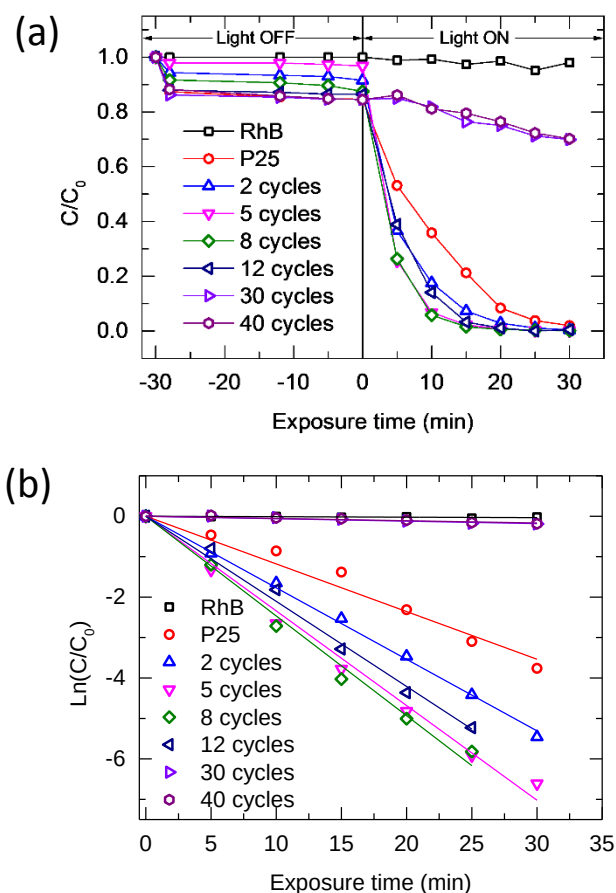


Figure 3.6 Photocatalytic activity of TiO₂ powders with or without the SiO₂ coating layers deposited at 100 °C: (a) normalized concentration as a function of exposure time and (b) kinetic plots varying the number of cycles in ALD process.

different temperatures have the same trend of photodegradation corresponding to the thickness of silica thin films and those samples with different number of cycles in ALD process are shown in Fig. 3.6. The threshold before UV irradiation, the solution was continuously stirred in the dark labelled as light-off stage in both of Fig. 3.7 and 3.8 for 30 min to obtain adsorption/desorption equilibrium of RhB and uniform suspensions. When the irradiation begins, the critical points of every samples need to be collected every 5 minutes in order to determine the concentration of residual dye materials. In the first stage of experiment (dark environment), the RhB concentration of the blank sample (pure RhB) remained while others exhibited a small drop at the beginning due to the adsorption of RhB molecules on the surface of TiO₂ nanopowders with or without silica and then get stable very quickly. In the second stage (solar irradiation) after 40 minutes, the blank sample stayed at the same level without any TiO₂. After 40 min of irradiation, the RhB was entirely decomposed. The samples with different ALD cycles in Fig. 3.6 and operating temperatures in Fig. 3.7 corresponding to

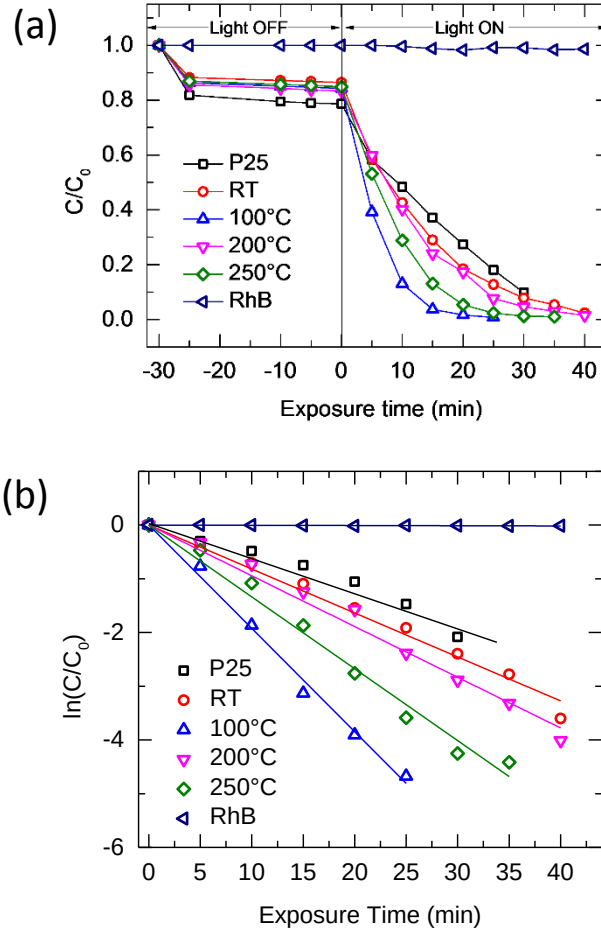


Figure 3.7 Photocatalytic activity of TiO₂ powders with or without the SiO₂ coating layers for 12 cycles: (a) normalized concentration as a function of exposure time and (b) kinetic plots varying the operating temperature in ALD process.

different thickness of silica thin films have a strong relationship between thickness and photocatalytic activities. Remarkably, instead of suppressing the photocatalytic activity, which is commonly observed for SiO₂ coated TiO₂ [28], the coating of ultrathin SiO₂ films resulted in enhancement of the TiO₂ photocatalytic activity, which showed a strong dependence on the coating thickness. Generally speaking, the thickness-dependence can be quantitatively estimated by the kinetics of photodegradation reaction, which is described by the kinetic equation below [55].

$$\ln\left(\frac{C_0}{C}\right) = k_{app} \cdot t, \text{ or } C = C_0 \cdot \exp(-k_{app} \cdot t) \quad (3.2)$$

where k_{app} is the apparent first-order kinetic constant that represents the reaction rate. C_0 is the initial concentration of the dye solution and C is the concentration of the dye molecule at different exposure times. t is the exposure time. The extracted plots according to the kinetic equation above are shown in Fig. 3.6b, 3.7b, 3.8b and 3.9b with the linear estimated trendlines.

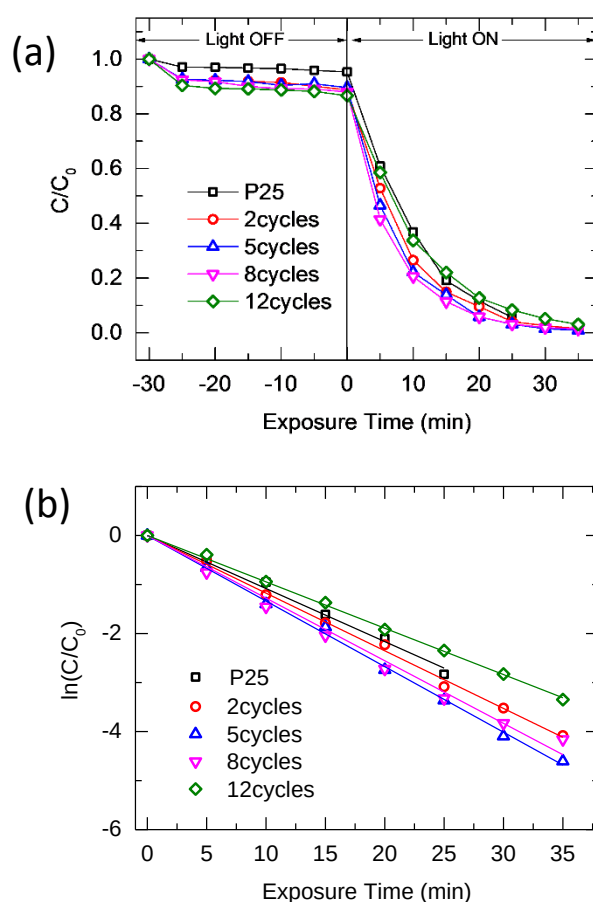


Figure 3.8 Photocatalytic activity of bare P25 TiO₂ nanopowders and TiO₂ powders with SiO₂ coating layers deposited at room temperature: (a) normalized concentration as a function of exposure time and (b) kinetic plots varying the number of cycles in ALD process.

Table 3.1 Apparent first-order rate constant k_{app} of SiO₂ coated P25 TiO₂ nanopowders under different experimental conditions.

Sample	$K_{app} (\times 10^{-3} \text{ min}^{-1})$	Samples	$K_{app} (\times 10^{-3} \text{ min}^{-1})$
Bare TiO ₂	117.9	Annealed 2cycles 100°C	240.3
2 cycles at 100 °C	176.9	Annealed 5cycles 100°C	285.4
5 cycles at 100 °C	234.1	Annealed 8cycles 100°C	316.9
8 cycles at 100 °C	246.6	Annealed 12cycles 100°C	247.1
12 cycles at 100 °C	210.5	2 cycles at 27 °C	117.6
30 cycles at 100 °C	6.1	5 cycles at 27 °C	133.8
40 cycles at 100 °C	5.6	8 cycles at 27 °C	127.8
12 cycles at 200 °C	192.8	12 cycles at 27 °C	64.6
12 cycles at 250 °C	197.8	RhB	0.3

All the data of k_{app} can be seen in Table 3.1. A k_{app} of $117.9 \times 10^{-3} \text{ min}^{-1}$ was obtained for the uncoated titania. In Fig. 3.6, coating SiO_2 on TiO_2 initially resulted in a sharp increase of k_{app} with increasing the number of cycles, which reached the maximum value of $246.6 \times 10^{-3} \text{ min}^{-1}$ at 8 cycles. Hereafter, k_{app} gradually decreased and finally flattened out from 30 cycles, which corresponds to a film thickness of about 2.8 nm as measured by TEM. In this stage, the degradation of RhB caused by the SiO_2 coated TiO_2 is slightly faster than the self- degradation

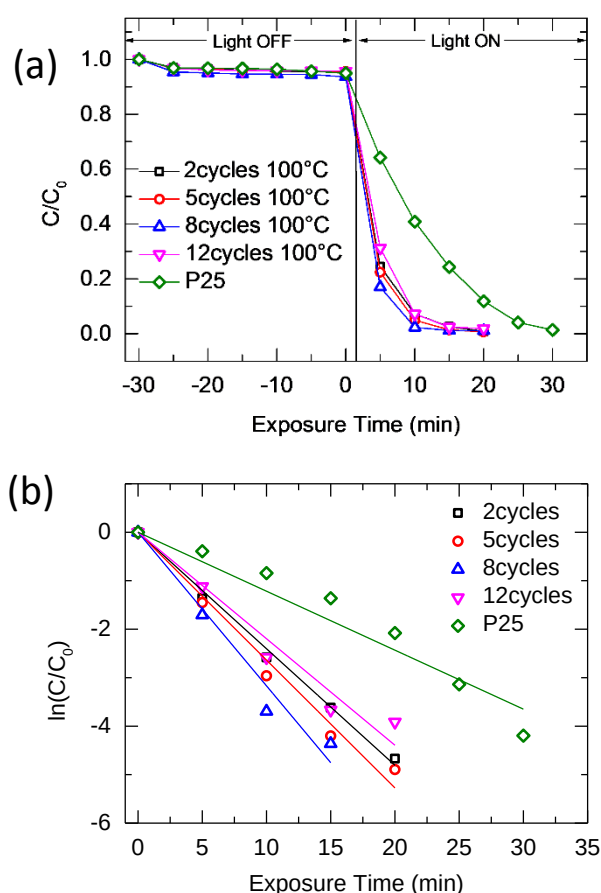


Figure 3.9 Photocatalytic activity of Bare P25 TiO_2 nanopowders and annealed TiO_2 powders with SiO_2 coating layers deposited at 100 °C: (a) normalized concentration as a function of exposure time and (b) kinetic plots varying the number of cycles in ALD process.

of RhB, indicating that the coating layer efficiently suppressed the photocatalytic activity of the TiO_2 . Annealing will result in the induced stress at the interface owing to different thermal expansion coefficient between TiO_2 substrate and SiO_2 ultrathin film which further change the roughness of the Si-O-Ti interface for better adsorption and provide more active sites by enlarging the specific surface area [56]. Therefore, as shown in Fig. 3.9 and Table 3.1, the photodegradation rate of the annealed sample is much faster than the sample without annealing. From Fig. 3.10, it could be concluded that the sample coated at 100 °C after annealing has the best photocatalytic performance as well as other annealed samples due to the induced stress at the interface compared with the samples without annealing. The

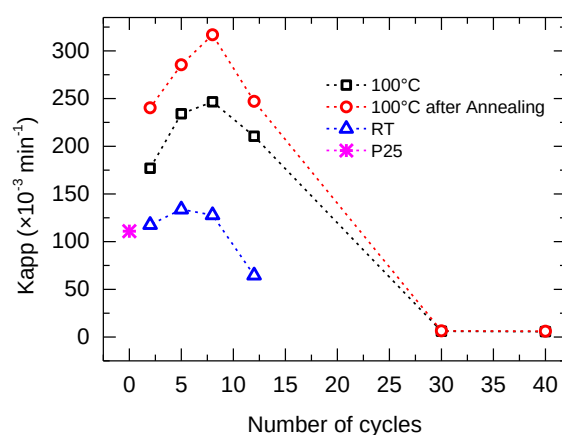


Figure 3.10 Kinetic constant k_{app} as a function of number of cycles deposited at room temperature and 100 °C as well as the annealed samples deposited at 100 °C.

annealing was carried out in air at 450 °C for 12 hours. For the samples at 100 °C with different ALD cycles indicated that the thin film which is 7 Å thick supports the photocatalytic enhancement best as explained above. At room temperature, the photocatalytic enhancement is weakened to a certain extent and turns to suppression for 12 cycles as shown in Fig. 3.9 even though the thickness is about 7 Å. When the temperature goes above 100 °C, there is a lower number of hydrogen bonded groups and an increased level of Si-O-Ti bond cleavage characterized by FT-IR with H₂O vapor addition which means the thickness of the Si-O-Ti interfacial layer cannot reach the level of other operating temperatures [57]. The growth of SiO₂ thin film on TiO₂ begins from the initial growth of Si-O-Ti interfacial layer and then followed by the growth of SiO₂ layer which is studied by Gallas *et al.* [53]. For the samples deposited at room temperature, the intensity of Si-O-Si as indicated in FT-IR spectra (see Fig. 3.4a) and the intensity of O-Si bond as indicated in XPS (see Fig. 3.3) are much stronger than 100 °C and 200 °C. Meanwhile, the intensity of Si-O-Ti bond is much lower than 100 °C and 200 °C as shown in Fig. 3.3. In other words, the thickness of interfacial layer is thinner and SiO₂ layer is thicker than 100 °C and 200 °C resulting in the not good enhancement. Hence, at room temperature in this work, the growth of Si-O-Ti interfacial layer is more difficult than 100 °C and 200 °C. Nevertheless, depositing at room temperature is still attractive due to the advantages mentioned above. In order to overcome such shortcoming, the catalyst NH₃ can be used in ALD process to support the formation of Si-O-Ti bond cleavage [58]. In addition, another possible reason is the quality of silica thin film due to the condensation of water vapor at room temperature which is indicated in XPS (see Fig. 3.3j) resulting in a porous nature which may hinder the formation of Si-O-Ti interfacial layer. As for other samples deposited at 100 °C, 200 °C and 250 °C, they all showed maximum enhancement of photocatalytic activities with a 7 Å thick thin film and the photocatalytic activities dropped with the increasing of ALD cycles since the relatively thick silica layer with a large band gap blocked the charge transfer from Si-O-Ti interfacial layer and TiO₂.

3.5 Mechanism of Photocatalytic Enhancement

As discussed above, when the thickness of SiO₂ thin film on P25 TiO₂ nanopowders is lower than 1 nm, an excellent enhancement of photocatalytic performance will be realized. The presence of silica thin film promotes the adsorption of dye materials, *e.g.*, RhB, on the surface of the nanoparticles and in the vicinity of TiO₂ sites which is proposed by Andreas *et al.* [8, 59] of the mixed SiO₂/TiO₂ system. But what they did is about mixing these two compounds while some of the TiO₂ are still contact with the environment, *e.g.*, air or solution, just like the partially coated TiO₂ by SiO₂. According to the presence of Si-O-Ti interfacial layer characterized by XPS and FT-IR and red-shift measured by optical absorption analysis, we come up with another mechanism to provide better explanation based on the role of Si-O-Ti interfacial layer. Gallas *et al.* [53] reported the Si-O-Ti interfacial layer can be several angstroms to one nanometer thick which is dependent to the surface morphology. And small amount of silicon atoms act as dopants entering the TiO₂ lattice and create sub energy level in favour of lowering band gap [60] and this is proved by optical absorption test in this work. In the photocatalytic process, after irradiation, the photons from sunlight will generate electron from conduction band to valence band both in the Si-O-Ti interfacial layer and TiO₂ due to the comparable band gap while silica can be omitted since the band gap is quite large which means it is almost transparent to sunlight. However, the Fermi level in SiO₂ coated TiO₂ remains unknown which means there are two models to explain the mechanisms of photocatalytic enhancement as shown in Fig. 3.11.

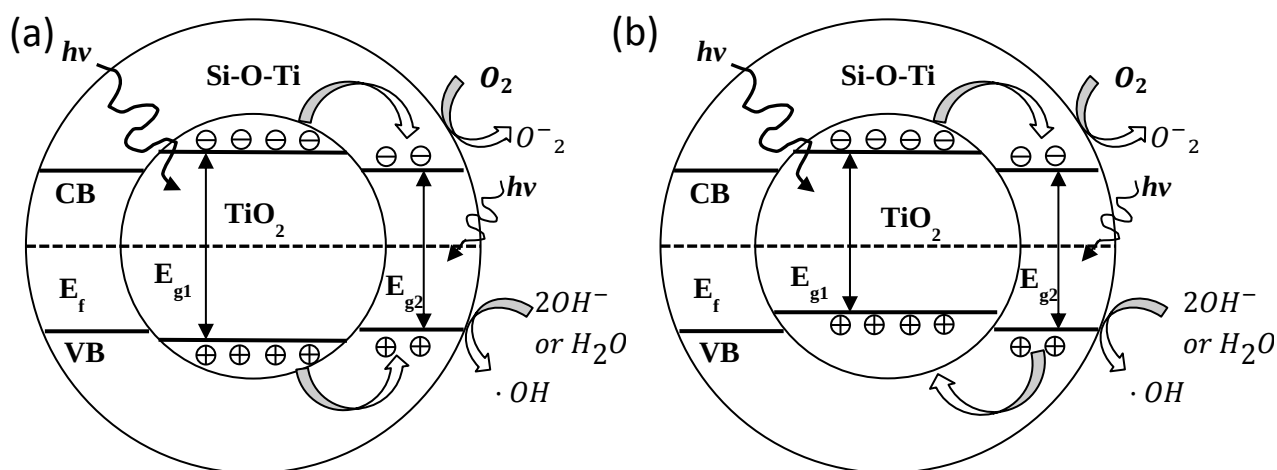


Figure 3.11 Schematics of enhancement of photocatalytic properties in SiO₂ coated TiO₂ nanoparticles. During the photocatalytic process, the left figure (a) represents the electronic structure when the Fermi levels of these two materials are almost the same and the right figure (b) represents the electronic structure when Fermi levels of these two are significantly different. Both of these two diagrams include the photon absorption process in the Si-O-Ti interfacial layer and TiO₂ cores, charge transfer, recombination of carriers, production of oxygen superoxide ion and the formation of hydroxyl radical.

In the first case, Fermi level of Si-O-Ti interfacial layer and TiO_2 are almost the same before contact which means the valence band maximum (VBM) of TiO_2 is lower than that of interfacial layer and conduction band minimum (CBM) is opposite. Because of the lower energy level in the interfacial layer, the excited electrons in conduction band and holes in valence band of TiO_2 will migrate to the interfacial layer and this charge transfer supply sufficient generated carriers, *e.g.*, electrons and holes, to produce oxygen superoxide ion at the conduction band and hydroxyl radicals at the valence band in the interfacial layer. The formation of oxygen superoxide ion and hydroxyl radicals enables the degradation of dye materials-Rhodamine B which is demonstrated in Fig. 1.11. Such charge transfer avoids the rapid recombination of carriers in TiO_2 in turn owing to the relatively low concentration. In the second case, Fermi level of Si-O-Ti interfacial layer and TiO_2 before contact are significantly different as both of the VBM and CBM of Si-O-Ti interfacial layer are lower or higher than those of TiO_2 . The former is shown in Fig. 3.8b, the excited electrons in TiO_2 will move to the interfacial layer which is driving by the lower energy of CBM of the interfacial layer and the generated holes in the interfacial layer will migrate to TiO_2 in which leading to the fast hole trapping and then excited electrons have time to reduct oxygen to superoxide ion, meanwhile, the charge separation occurs that prevent the rapid recombination at both sides. In this way, the efficiency of photocatalysis can be improved. For the latter, in the same manner, it induces the fast electron trapping and generated holes have time to oxidize $-\text{OH}$ groups or H_2O to form hydroxyl radicals which could enhance the photodegradation while the electron-hole recombination is avoided. Finally, the efficiency is improved. If the thickness of thin film increased to a critical value, the enhancement will become weaker and finally converted to suppression because the inert and insulating nature of silica would block the active sites at the surface around the interfacial layer and weaken the charge transfer. After 8 cycles at 100°C or the thickness of thin film is lower than 0.7 nm , the enhancement becomes weaker and weaker and finally transferred to suppression for 30 cycles.

4. Conclusions and Recommendations

4.1 Conclusions

Atmospheric pressure atomic layer deposition in fluidized bed reactor using silicon tetrachloride and deionized water vapor can be used to deposit SiO_2 ultrathin film on Degussa P25 TiO_2 nanoparticles at the temperature which can be lowered to room temperature ($\sim 27^\circ\text{C}$). The growth of thin films is almost independent of operating temperature in the range from 100°C to 250°C while at room temperature the condensation of water vapor caused a highest GPC in the comparison with others. The saturating state of feeding SiCl_4 is achieved for 5 seconds of pulsing that is evidenced by TEM and INAA to measure the thickness of thin film and Si concentration. The relatively low GPC ($\sim 0.8 \text{ \AA}$) enables the precise control of growing SiO_2 thin film which further is able to investigate the dependence of thickness and photocatalytic activity. Another study of the deposition operating at room temperature which is very attractive in the field of industrial application and scaling up fits the trend at other temperatures with the largest GPC. Moreover, annealing is such a method that could enhance the photocatalytic properties based on the induced stress at the interface by changing the roughness. The peak value of photocatalytic activity is about 0.7 nm thick thin film and then the k_{app} value decreases to suppression eventually. The formation of Si-O-Ti interfacial layer plays the most important role in enhancing photocatalytic performances which is characterized by XPS and FT-IR. The narrower band gap of the Si-O-Ti interfacial layer is able to tune the electronic structure, thereby inducing the charge transfer, charge separation and avoiding rapid electron-hole recombination while such enhancement will be weakened if the growth of interfacial layer gets saturation, meanwhile, the growth of SiO_2 layer starts. In addition, the red-shift in optical absorption spectra indicates a better absorption of light with a wider range of wavelengths. Last but not least, depositing SiO_2 on TiO_2 at room temperature is very promising not only about the easily controlled operation but the relatively high content of hydroxyl groups compared with other operating temperatures which is vital for the decomposition of RhB under solar irradiation in the field of photocatalyst.

4.2 Recommendations

In this work, the growth of Si-O-Ti interfacial layer at room temperature using water vapor is hindered as indicated by XPS resulting in the much thinner interfacial layer and thicker pure SiO₂ layer than 100 °C as the total thickness of thin film is the same. This shortcoming may be overcome by adding catalyst such as NH₃ etc. Meanwhile, the selection of precursors also matters for the growth of thin film because of its effect on ALD processes such as operating temperature and pressure.

The enhancement of photocatalytic performance depends on several criteria including the amount of hydroxyl groups, the growth of interfacial layer, the growth of SiO₂ layer, band gap of interface and quality of coating. In the field of photocatalyst, the relatively thick Si-O-Ti interfacial layer while SiO₂ layer negligible is highly required which means the band gap of the interfacial layer is relatively narrow and the negligible SiO₂ layer cannot block the surface for the contact between the interfacial layer and environment (*e.g.*, air or solution). The operating temperature should be as low as possible unless it will cause condensation in ALD process like room temperature in this work to obtain more hydroxyl groups which support better enhancement of photocatalytic activities. In addition, annealing is a good method to promote the photocatalytic activity *via* modifying the roughness of interface. The coating on P25 TiO₂ nanoparticles in this work consists of the Si-O-Ti interfacial layer and pure SiO₂ layer. For the use of enhancement in photocatalyst in this work, the relatively thick interfacial layer and thin pure silica layer support it quite well *via* tuning the absorption of light and charge recombination.

Last but not least, the precise control for the growth of silica thin film is required for the enhancement of photocatalytic activity.

Appendix A

ALD Set-up

Table A.1 Parts in ALD Set-up corresponding to Fig. 2.1.

Code	Part
E1 to E2	Bubbler containing precursor (E1: SiCl_4 , E2: H_2O)
E3 to E10	Gaswashers (E4/E8 contains silicon oil, E6/E10 contains NaOH)
F1 to F2	HEPA filter for Nanoparticles in effluent
H1 to H3	Heating tape for tubing
H4 to H5	Heating mantle for bubbler E1 and E2
H6	Infrared lamp for heating reactor R1
MFC-1	Mass Flow Controller for controlling flow rate of N_2 carrier and purge gas
MFC-2	Mass Flow Controller for controlling flow rate of additional N_2 fluidization gas
R1	Glass Reactor
MS	Mass Spectrometer
V3 to V4	Ball valve electronically actuated for N_2 supply through the precursor line
V5 to V6	3-way manifold valve, pneumatic, for switching between bubbling through and by-passing E1&E2
V7 to V9	Bellows sealed valve, pneumatic, for windbox feed stream (to prevent back flow into other precursor line)
V10 to V11	Bellows sealed valve, pneumatic, for exhaust stream into gas washers (to preventing mixing of SiCl_4 and H_2O)
CV1 to CV2	Check valve for protecting MFC-1 from back-flowing precursor
X1 to X2	Vibromotors for fluidization assistance

Appendix B

TEM Images

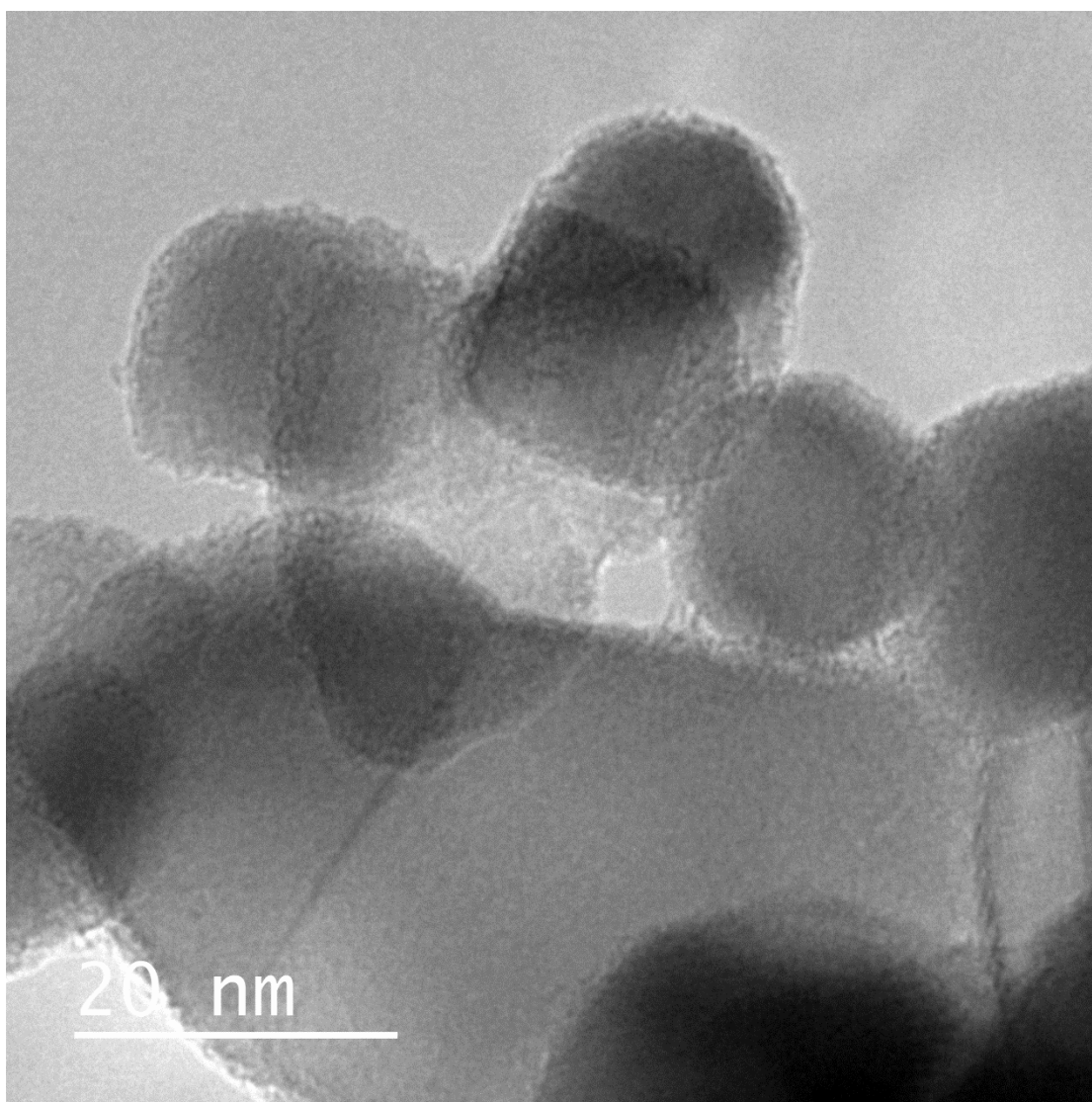


Figure B.1 TEM Image of SiO₂ coated TiO₂ nanopowders fabricated at 100 °C for 12 cycles.

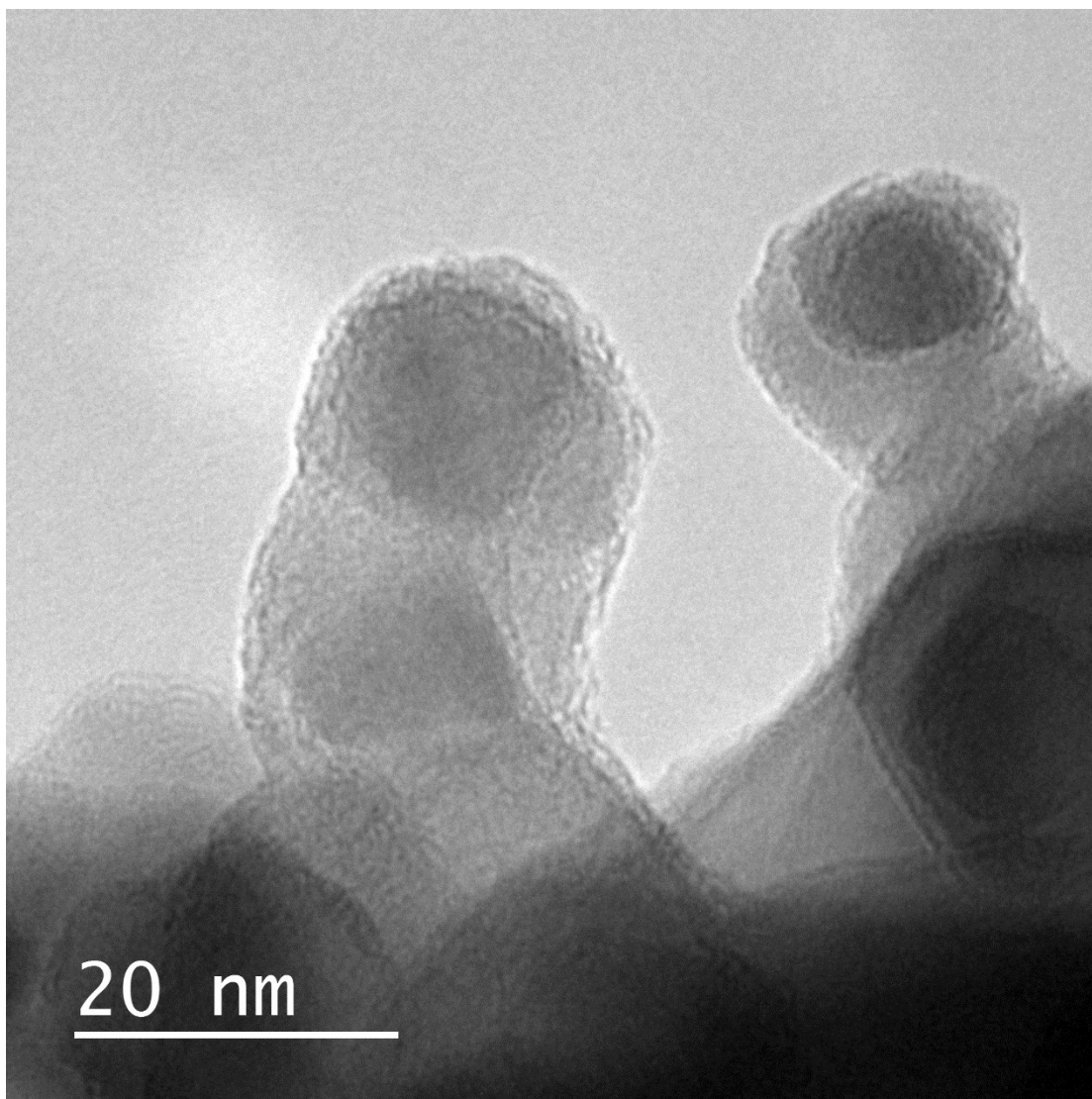


Figure B.2 TEM Image of SiO₂ coated TiO₂ nanopowders fabricated at 100 °C for 30 cycles.

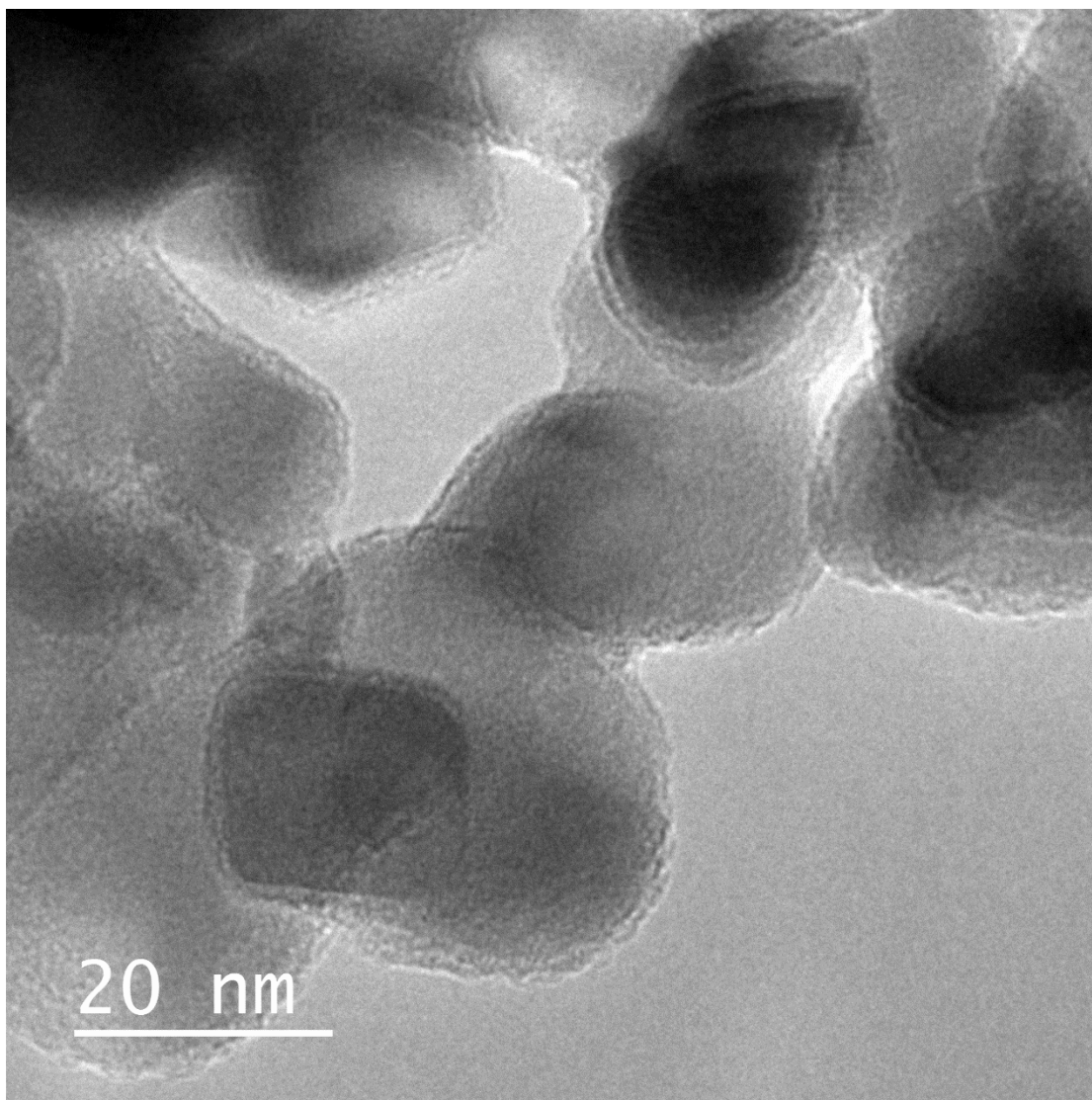


Figure B.3 TEM Image of SiO₂ coated TiO₂ nanopowders fabricated at 100 °C for 40 cycles.

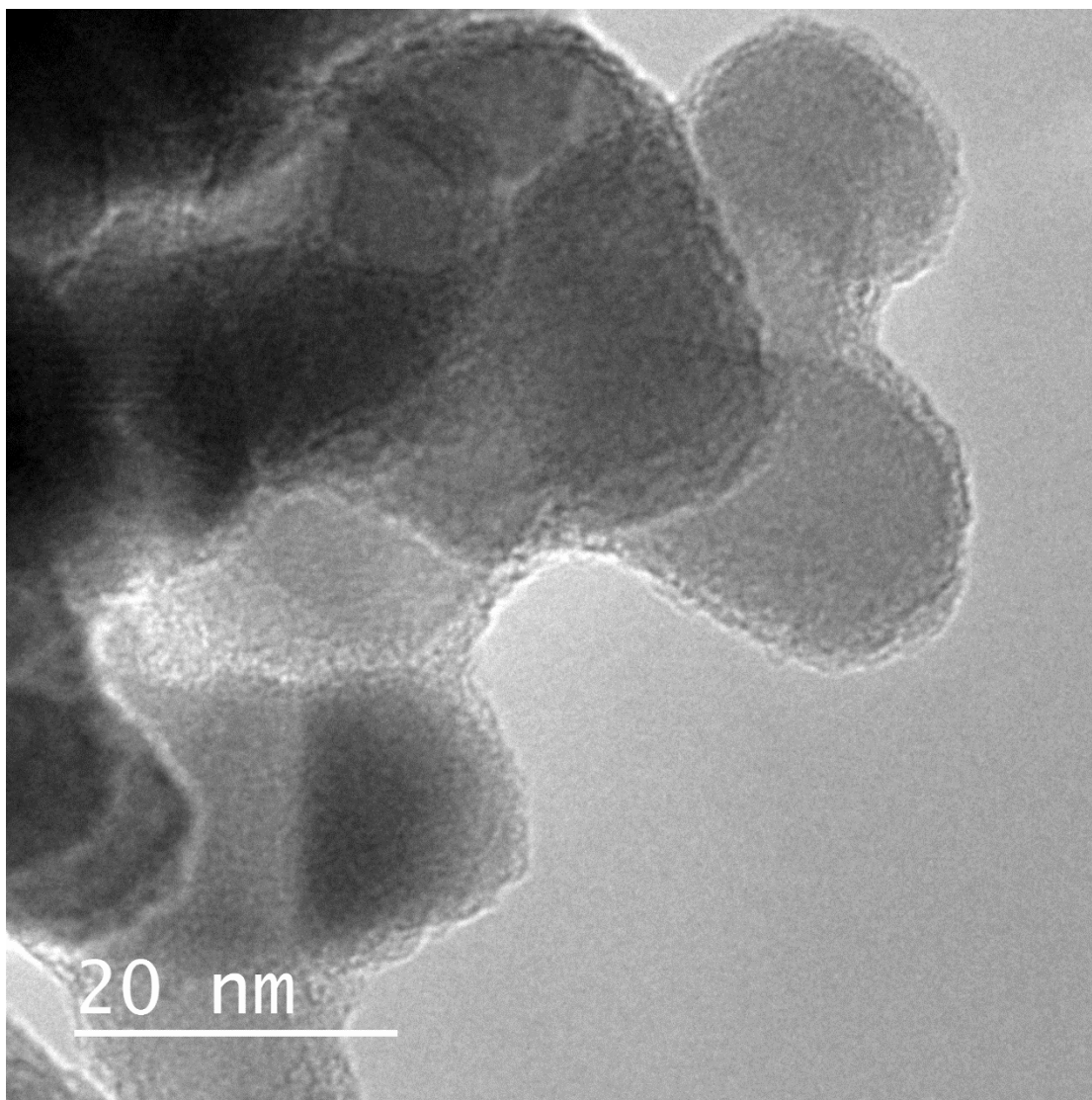


Figure B.4 TEM Image of SiO₂ coated TiO₂ nanopowders fabricated at 200 °C for 12 cycles.

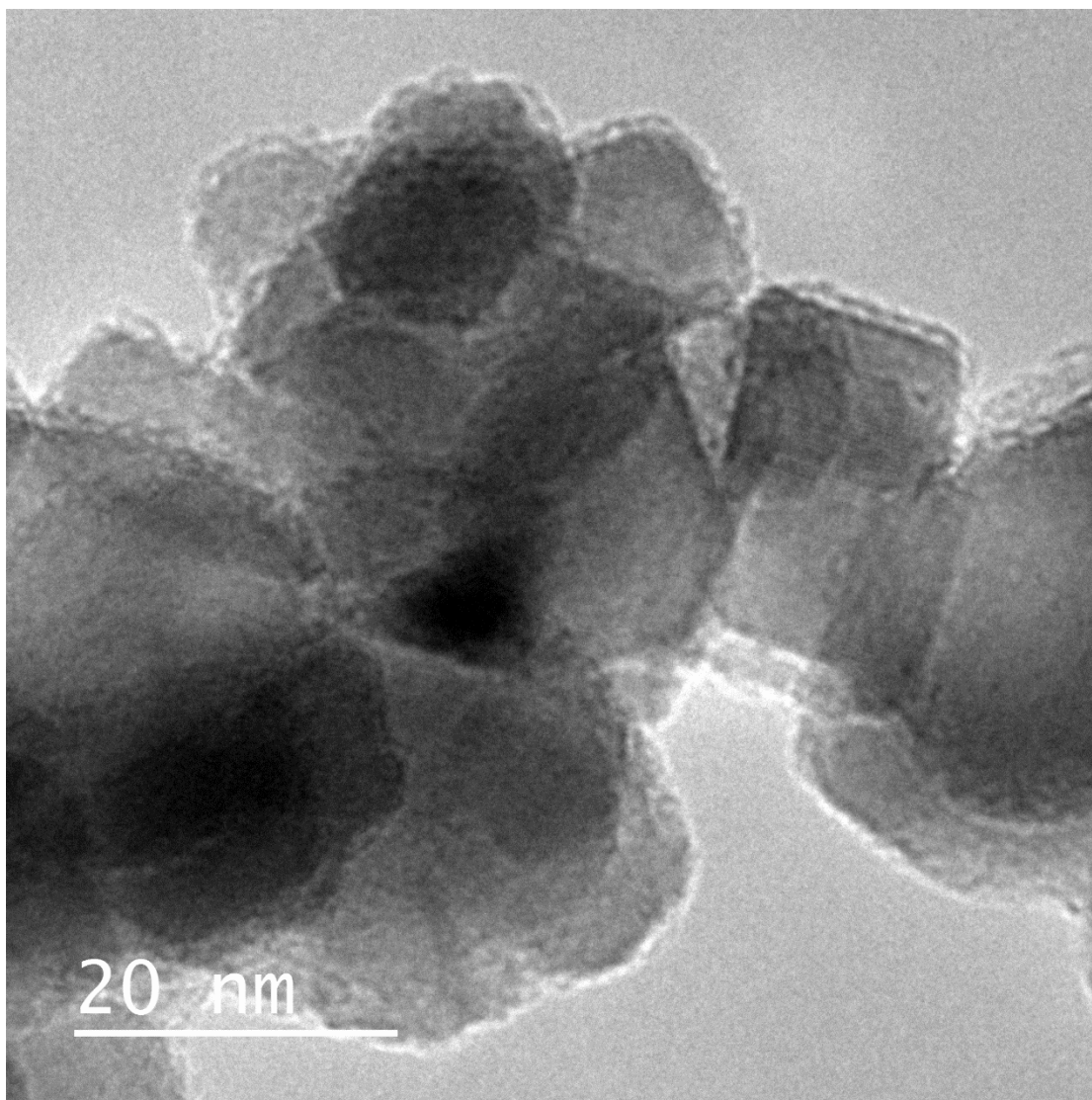


Figure B.5 TEM Image of SiO_2 coated TiO_2 nanopowders fabricated at 250 °C for 12 cycles.

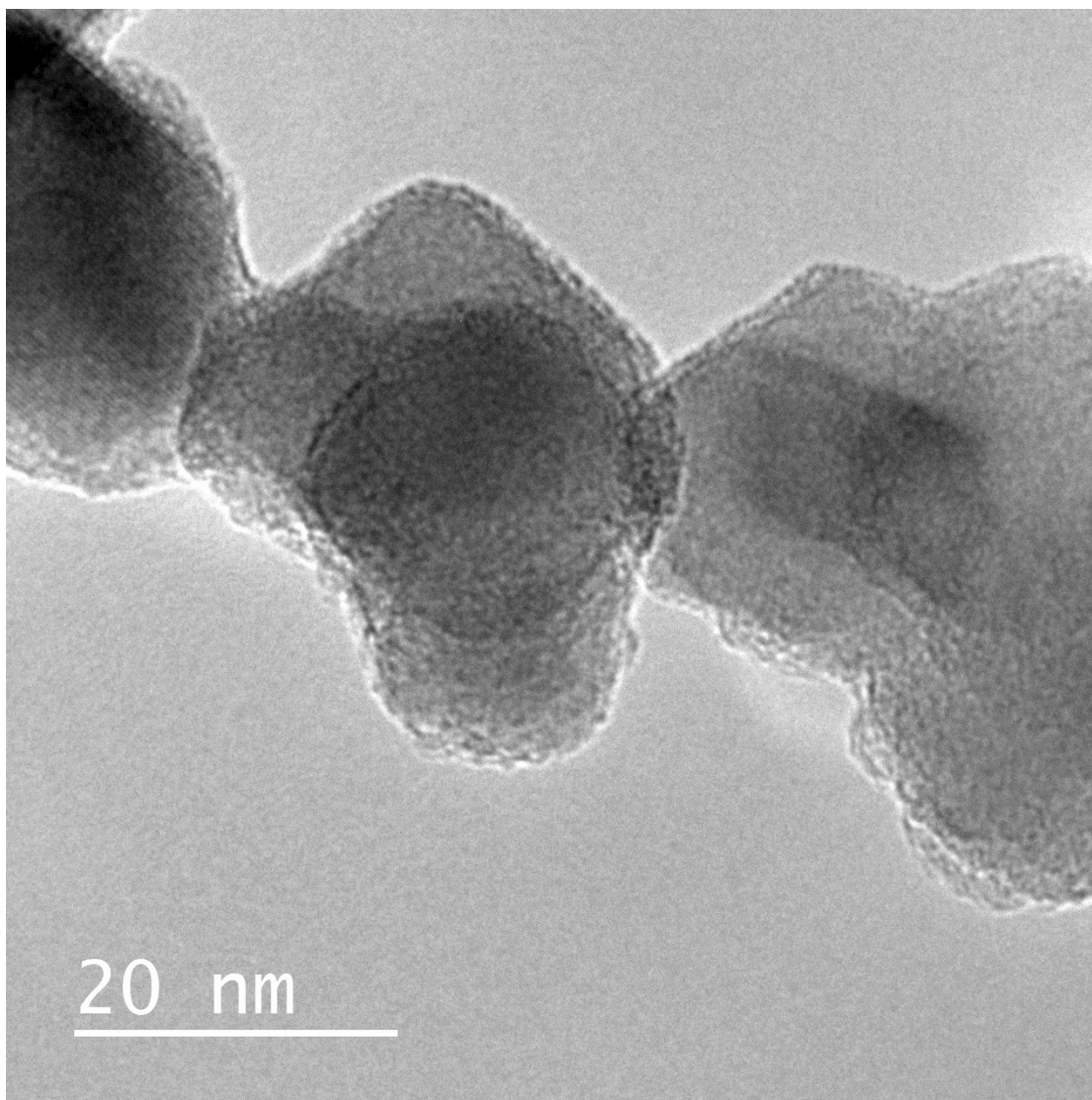


Figure B.6 TEM Image of SiO₂ coated TiO₂ nanopowders fabricated at room temperature for 12 cycles.

Appendix C

Results of INAA

Table C.1 Si Concentration of different samples

Number	Reactor Temperature (°C)	cycles	Time Sequence (seconds)	Si Concentration (w.t.%)
1	100	5	60/180/180/480	1.44
2	100	12	10/180/180/480	1.98
3	100	8	60/180/180/480	1.80
4	200	12	20/180/180/480	2.12
5	100	12	5/180/180/480	2.06
6	100	20	60/180/180/480	2.50
7	200	12	5/180/180/480	2.43
8	100	12	20/180/180/480	1.79
9	250	12	20/180/180/480	2.10
10	200	12	40/180/180/480	2.43
11	100	12	40/180/180/480	1.93
12	100	2	60/180/180/480	0.90
13	200	12	10/180/180/480	2.13
14	100	8	60/180/180/480	1.97
15	25	12	60/180/180/480	2.90
16	100	12	60/180/180/480	2.30
17	200	12	60/180/180/480	2.60
18	250	12	60/180/180/480	2.70

Results of Photocatalytic Test

Table C.2 Photocatalytic Test of the samples varying number of cycles at 100 °C after annealing.

Exposure Time (min)	2 cycles 100°C	5 cycles 100°C	8 cycles 100°C	12 cycles 100°C	P25
-30	1.00000	1.00000	1.00000	1.00000	1.00000
-25	0.96949	0.96628	0.95449	0.96747	0.96845
-20	0.96585	0.96303	0.95048	0.96150	0.96776
-15	0.96055	0.96057	0.94652	0.95955	0.96706
-10	0.95659	0.95838	0.94555	0.95857	0.96372
-5	0.95562	0.95762	0.94458	0.95864	0.95680
0	0.95465	0.95644	0.93616	0.95764	0.94988
5	0.24523	0.22434	0.17005	0.31265	0.64200
10	0.07220	0.04952	0.02327	0.07220	0.40871
15	0.02566	0.01432	0.01193	0.02446	0.24344
20	0.00895	0.00716	0.01134	0.01909	0.11874
25	-	-	-	-	0.04117
30	-	-	-	-	0.01432

Table C.3 Photocatalytic Test of the samples varying number of cycles at 100 °C.

Exposure Time (min)	RhB	P25	2 cycles	5 cycles	8 cycles	12 cycles	30 cycles	40 cycles
-30	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
-28	1.00000	0.81839	0.94361	0.97875	0.91672	0.87905	0.86227	0.88252
-12	1.00000	0.79526	0.93361	0.97875	0.90672	0.87153	0.85359	0.85822
-5	1.00000	0.78962	0.92952	0.97343	0.89590	0.86516	0.84664	0.84838
0	1.00000	0.78680	0.91542	0.96812	0.87508	0.86400	0.84606	0.84491
5	0.98843	0.58319	0.36565	0.25634	0.26350	0.38889	0.84954	0.86169
10	0.99248	0.48393	0.17567	0.06831	0.05791	0.14063	0.81829	0.81134
15	0.97338	0.37169	0.07287	0.02212	0.01561	0.03241	0.76389	0.79514
20	0.98553	0.27411	0.02863	0.00781	0.00586	0.01100	0.75058	0.76447
25	0.95197	0.18105	0.01106	0.00260	0.00260	0.00000	0.71238	0.72280
30	0.98032	0.09814	0.00390	0.00130	0.00130	0.00463	0.69907	0.70197
45	0.95023	-	-	-	-	-	0.53472	0.59664
105	0.87500	-	-	-	-	-	0.09780	0.23958

Table C.4 Photocatalytic Test of the samples varying number of cycles at room temperature.

Exposure Time (min)	P25	2 cycles	5 cycles	8 cycles	12 cycles
-30	1.00000	1.00000	1.00000	1.00000	1.00000
-25	0.97089	0.92585	0.92659	0.92420	0.90391
-20	0.96968	0.92212	0.92239	0.91737	0.89284
-15	0.96748	0.9184	0.91819	0.90055	0.89129
-10	0.96527	0.91468	0.90399	0.89137	0.88737
-5	0.95907	0.90095	0.90979	0.89090	0.88186
0	0.95286	0.88723	0.89558	0.88007	0.86635
5	0.60859	0.52804	0.46539	0.41408	0.58532
10	0.36814	0.26492	0.22136	0.20525	0.33771
15	0.19033	0.14916	0.13842	0.11396	0.22017
20	0.11635	0.09547	0.05788	0.05788	0.12709
25	0.05609	0.04057	0.03103	0.03162	0.08294
30	-	0.02625	0.01492	0.01909	0.05131
35	-	0.01498	0.00895	0.01372	0.03043

Table C.5 Photocatalytic Test of the samples varying operating temperatures for 12 cycles.

Exposure Time (min)	P25	RT	100°C	200°C	250°C	RhB
-30	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
-25	0.81839	0.88278	0.86405	0.85619	0.86949	1.00000
-10	0.79526	0.8719	0.85136	0.84278	0.85752	1.00000
-5	0.78962	0.86828	0.84713	0.83831	0.85353	1.00000
0	0.78680	0.86465	0.8429	0.83384	0.84955	1.00000
5	0.58319	0.58429	0.39154	0.59879	0.53172	1.00000
10	0.48393	0.42659	0.13051	0.40242	0.28822	0.99637
15	0.37169	0.29003	0.03686	0.24109	0.13112	0.98852
20	0.27411	0.18489	0.01692	0.17341	0.05378	0.98308
25	0.18105	0.12749	0.00785	0.07674	0.02356	0.99215
30	0.09814	0.07855	-	0.04653	0.01208	0.99154
35	-	0.05378	-	0.03021	0.01027	0.98429
40	-	0.02356	-	0.01511	-	0.9861

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List of Acronyms

ALD Atomic Layer Deposition

FBR Fluidized Bed Reactor

AFM Atomic Force Microscopy

TEM Transmission Electron Microscopy

FTIR Fourier Transform Infrared Spectroscopy

GPC Growth Per Cycle

TGA Thermogravimetric Analysis

UV-VIS Ultraviolet Visible spectroscopy

BET Brunauer-Emmett-Teller Method

TEOS Tetraethylorthosilicate

INAA Instrumental Neutron Activation Analysis

XPS X-ray Photoelectron Spectroscopy

EPD Sol Electrophoretic Deposition