Nitrogen-doped titanium dioxide supported on activated carbon for synergistic removal of aqueous organic pollutants

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NANYANG
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**NITROGEN-DOPED TITANIUM DIOXIDE SUPPORTED
ON ACTIVATED CARBON FOR SYNERGISTIC
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YAP POW SENG

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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SUMMARY

In recent years, increasing global water scarcity has resulted in intense research to improve the quantity and quality of drinking water. Adsorption via activated carbon (AC) is a proven technology for water treatment and reclamation, while heterogeneous photocatalysis using titanium dioxide (TiO_2) is highly energy-efficient in degrading and mineralizing various recalcitrant organic pollutants. Thus, the coupled adsorption-solar photocatalysis processes potentially present an environmentally-friendly and cost-effective treatment technology for water reclamation and reuse. This study therefore focused on developing a novel bifunctional adsorptive-photocatalytic material which was photoexcitable under solar light irradiation.

In this study, various types of nitrogen-doped TiO_2 supported on powdered AC (N- TiO_2/AC) composites were synthesized via the modified sol-gel techniques. These include the composites prepared via single-stage calcination, two-stage calcination, and also facile techniques incorporating commercial titania P25 (N-P25- TiO_2/AC). The composites were characterized using X-ray diffraction (XRD), porosimetry, UV-Vis spectrophotometry, electrophoretic mobility measurement, Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy coupled with energy-dispersive X-ray (SEM/EDX), and transmission electron microscopy (TEM). Three aqueous recalcitrant organic pollutants of varying molecular properties, namely bisphenol-A (BPA), sulfamethazine (SMZ), and clofibric acid (CFA), were chosen as the model pollutants in this study.

The first phase of this study was the investigation of BPA removal efficiencies, as exhibited by the N- TiO_2/AC composites produced from single-stage and two-stage calcinations. The N- TiO_2/AC composites produced from the two-stage calcination technique were superior to that of the N- TiO_2/AC composite produced from the single-stage calcination. The best performing composite was the N- TiO_2/AC (400M-700T) composite, produced from two-stage calcination (400°C for 2 h in air atmosphere with subsequent 700°C for 2 h in NH_3/N_2 atmosphere). This composite comprised anatase-rutile phase and exhibited significant photocatalytic degradation (PCD) efficiency for

degrading BPA under the irradiation of simulated solar light, UV (280-400 nm), and visible-light (420-630 nm), with initial pseudo first-order rate constant (k_{app}) of 0.67 h^{-1} , 0.44 h^{-1} and 0.29 h^{-1} , respectively. The N-TiO₂/AC (400M-700T) composite exhibited greater solar photocatalytic activity for BPA degradation as compared to that of the N-TiO₂ or binary mixture of TiO₂ and AC. It also exhibited satisfactory BPA removal performances over several cycles of reuse, and it was photostable even under high-intensity UV irradiation.

The effects of co-existing aqueous species viz. prevalent inorganic anions (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , H_2PO_4^- and silica), organic anion ($\text{C}_2\text{O}_4^{2-}$), photocatalysis inhibitor (CH_3OH), and oxidant (H_2O_2) on BPA degradation were also studied using N-TiO₂/AC (400M-700T). Introduction of H_2PO_4^- (0.01 to 0.1 mM) led to a slight enhancement in the PCD efficiency for BPA removal. Provision of AC support for N-TiO₂ abated the inhibitory effect induced by SO_4^{2-} at high concentrations up to 100 mM. A decreased BPA degradation was observed with increasing concentration of $\text{C}_2\text{O}_4^{2-}$, suggesting that direct hole oxidation occurred. Variation of pH (from 4 to 10) in the presence of 0.1 mM of silica induced little effect on BPA degradation.

The second phase of this study was the examination of solar photocatalytic regeneration (SPR) of the pollutant-loaded N-TiO₂/AC (400M-700T) of varying N-TiO₂ loadings. BPA, SMZ and CFA were the model adsorbates. The adsorption of BPA and SMZ by the N-TiO₂/AC was significantly higher than that of CFA. The performance of solar photocatalytic regeneration (SPR) of the spent N-TiO₂/AC composite generally increased with light intensity, N-TiO₂ loading and temperature. The regeneration efficiency (RE) for the CFA-loaded spent composite was the highest compared to the other pollutant-loaded spent composites, achieving 77% within 8 h of solar irradiation (765 W m^{-2}). The rate-limiting process was pollutant desorption from the interior AC adsorption sites. A simplified kinetic model was developed to predict the transient concentration of the adsorbate remaining in the spent composite during SPR. Comparison studies using the solvent extraction technique indicated a different order of RE for the three pollutants, attributable to their varying solubilities in the aqueous and organic solvents.

In consideration of the need of scale-up production, it is desirable to develop a facile and cost-effective sol-gel synthesis technique for the bifunctional composite. Thus, the last phase of this study was the development of a novel bimodal nitrogen-doped P25-TiO₂ coated on AC (N-P25-TiO₂/AC) composite via facile modified sol-gel techniques. Besides adding urea as the nitrogen source, the N-doping could also be induced through extended calcination under a mixed NH₃/N₂ atmosphere. The bimodal composite exhibited good physical stability under ultrasonic disruption treatment. The bifunctional characteristics of this bimodal composite were evaluated using SMZ as the model pollutant. The best performing bimodal composite was N-P25-TiO₂ (25+10)/AC, which comprised 25% of N-P25 and 10% N-TiO₂ (sol) by weight content (wt%). The maximum adsorption capacities of the N-P25-TiO₂ (25+10)/AC for SMZ adsorption at pH 3.0, 6.0 and 10.0 were 183 ± 3 , 194 ± 3 , and 103 ± 2 mg g⁻¹, respectively. The N-P25-TiO₂ (25+10)/AC composite exhibited significantly enhanced PCD efficiencies as compared to the other types of bimodal composites, under the irradiation of the simulated solar light, UV (280-400 nm) and visible-light (420-630 nm), with k_{app} of 0.48 h⁻¹, 0.35 h⁻¹ and 0.13 h⁻¹, respectively. This was because the higher N-P25 content led to a greater photocatalytic activity, as induced by the synergism of its mixed anatase-rutile phase.

Overall, the major contribution arising from this study is four-fold, namely efficient removal of various recalcitrant aqueous organic pollutants, minimization of chemical consumption, reduction of energy consumption/carbon footprint, and production of zero-waste stream. It is worth noting that the N-TiO₂/AC composite has the potential for further practical application in water and wastewater reclamation. Specifically, N-TiO₂/AC can be integrated into other wastewater treatment processes, such as membrane technology, biological treatment, or ultrasonication to treat the real wastewaters. For these applications, real sunlight can serve as the light source to irradiate the N-TiO₂/AC composite. Thus, the coupling of N-TiO₂/AC into the aforementioned treatment systems is expected to present a cost-effective and sustainable water treatment technology.

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ABBREVIATIONS

AC	Activated carbon
ACF	Activated carbon fiber
AOPs	Advanced oxidation processes
BE	Binding energy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BPA	Bisphenol-A
CFA	Clofibric acid
CVD	Chemical vapor deposition
DRS	Diffuse reflectance spectra
DTG	Differential thermogravimetry
E _a	Activation energy
EDCs	Endocrine disrupting chemicals
EDX	Energy dispersive X-ray
ESR	Electron spin resonance
E _g	Bandgap energy
FESEM	Field-emission scanning electron microscopy
FTIR	Fourier transform infrared
FWHM	Full width half maxima
GAC	Granular activated carbon
HPLC	High performance liquid chromatography
HRTEM	High-resolution transmission electron microscopy
IC	Ion chromatography
IEP	Isoelectric point
K _{ads}	Langmuir adsorption constant
k _{app}	Pseudo first-order rate constant
MB	Methylene blue
NOM	Natural organic matter
N-P25-TiO ₂ /AC	Bimodal nitrogen-doped titania supported on activated carbon

N-TiO ₂	Nitrogen-doped titanium dioxide
N-TiO ₂ /AC	Nitrogen-doped titanium dioxide supported on activated carbon
NTU	Nephelometric turbidity unit
PAC	Powdered activated carbon
PCD	Photocatalytic degradation
PPCPs	Pharmaceutical and personal care products
RE	Regeneration efficiency
SEM	Scanning electron microscopy
S _{max}	Maximum adsorption capacity
SMZ	Sulfamethazine
SPR	Solar photocatalytic regeneration
TBOT	Titanium butoxide
TEM	Transmission electron microscopy
TG	Thermogravimetry
TiO ₂ /AC	Titanium dioxide supported on activated carbon
TOC	Total organic carbon
TTIP	Titanium tetraisopropoxide
UPW	Ultrapure water
UVA	Ultraviolet-A
VOCs	Volatile organic compounds
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF PUBLICATIONS

Parts of the findings presented in this thesis have been published in the following journal papers:

Yap, P.S., Lim, T.T., Lim, M., Srinivasan, M., 2010. Synthesis and characterization of nitrogen-doped TiO₂/AC composite for the adsorption-photocatalytic degradation of aqueous bisphenol-A using solar light. *Catalysis Today*. 151(1-2), 8-13.

Yap, P.S., Lim, T.T., Srinivasan, M., 2011. Nitrogen-doped TiO₂/AC bi-functional composite prepared by two-stage calcination for enhanced synergistic removal of hydrophobic pollutant using solar irradiation. *Catalysis Today*. 161(1), 46-52.

Yap, P.S., Lim, T.T., 2011. Effect of aqueous matrix species on synergistic removal of bisphenol-A under solar irradiation using nitrogen-doped TiO₂/AC composite. *Applied Catalysis B: Environmental*. 101(3-4), 709-717.

Lim, T.T., Yap, P.S., Srinivasan, M., Fane, A.G., 2011. TiO₂/AC composites for synergistic adsorption-photocatalysis processes: present challenges and further developments for water treatment and reclamation. *Critical Reviews in Environmental Science and Technology*. 41(13), 1173-1230.

Yap, P.S., Lim, T.T., 2012. Solar regeneration of powdered activated carbon impregnated with visible-light responsive photocatalyst: factors affecting performances and predictive model. *Water Research*. 46(9), 3054-3064.

Yap, P.S., Cheah, Y.L., Srinivasan, M., Lim, T.T., 2012. Bimodal N-doped P25-TiO₂/AC composite: preparation, characterization, physical stability, and synergistic adsorptive-solar photocatalytic removal of sulfamethazine. *Applied Catalysis A: General*. 427-428, 125-136.

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Lim, T.T., Yap, P.S., Lim, M., Srinivasan, M., 2010. Nitrogen-doped TiO₂/AC composite for the removal of aqueous bisphenol-A under solar irradiation, Proceedings of the 6th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA6), 13-16 June, 2010, Prague, Czech Republic. Paper OP4.6, pp 407-408.

Yap, P.S., Lim, T.T., Lim, M., Srinivasan, M., 2010. Bi-functional TiO₂/AC composite for adsorption and photocatalytic degradation of recalcitrant organics under solar light: insights and outlook. Proceedings of the 1st IWA Malaysia Young Water Professionals Conference, 02-04 March, 2010, Kuala Lumpur, Malaysia, ISBN 983-9805-86-4, Paper ID: 110.

Patents or intellectual properties filed for the invention of N-TiO₂/AC:

Composite photocatalyst for adsorptive-photocatalytic oxidation-reduction of organic substances. US Provisional Patent filed on 22 June 2009 (Application Number 61/219,066). Inventors: Lim, T.T., Yap, P.S., Srinivasan, M., Fane, A.G.

Doped catalytic carbonaceous composite materials and uses thereof. PCT Patent filed on 22 June 2010 (Int. Pub. No. : WO 2010/151231 A1). Inventors: Lim, T.T., Yap, P.S., Srinivasan, M., Fane, A.G.

Publication as co-authors in others' work:

Gao, B., Yap, P.S., Lim, T.M., Lim, T.T., 2011. Adsorption-photocatalytic degradation of Acid Red 88 by supported TiO₂: effect of activated carbon support and aqueous anions. Chemical Engineering Journal. 171(3), 1098-1107.

Wang, P., Yap, P.S., Lim, T.T., 2011. C–N–S tridoped TiO₂ for photocatalytic degradation of tetracycline under visible-light irradiation. Applied Catalysis A: General. 399(1-2), 252-261.

Chapter 1 Introduction

1.1 Background

In recent years, as a consequence of rapid urbanization, rising human population, deteriorating water quality, and climate change, the global water scarcity has become more critical than ever. Thus, an attractive and sustainable solution to the above-mentioned problem is to focus on water reclamation and reuse. The reclaimed water can then be employed for various applications such as industrial processes, agricultural irrigations, recreation, cooling, or indirect drinking purposes.

However, due to the elevated amount of recalcitrant chemicals being introduced into the natural and engineered water systems, the task of treating water and wastewater is becoming increasingly challenging nowadays. For example, pharmaceuticals and their metabolites are often found in sewage effluents due to their recalcitrant characteristics (Ternes, 1998; Kolpin et al., 2002; Vieno et al., 2005; Shon et al., 2006; Peng et al., 2008c; Loos et al., 2009; Oulton et al., 2010; Fatta-Kassinos et al., 2011). This indicates that the conventional treatment technologies are rather inefficient in removing many of the pharmaceutical and personal care products (PPCPs). In general, the removal efficiency for most of the PPCPs was less than 30% (Suárez et al., 2008; Onesios et al., 2009; Oulton et al., 2010; Behera et al., 2011; Reif et al., 2011; Yang et al., 2011; Bueno et al., 2012).

It is worth noting that the concentrations of PPCPs detected in wastewater effluents and receiving waters (e.g. surface waters or groundwaters) around the world are in the range of ng L^{-1} to $\mu\text{g L}^{-1}$ levels (Suárez et al., 2008; Yang et al., 2011; Bueno et al., 2012; Onesios and Bouwer, 2012). Despite the trace concentrations of the PPCPs in the aquatic environment, a number of these compounds pose significant environmental and public health concern because they are known or suspected carcinogens and endocrine disrupting chemicals (EDCs). For example, several toxicological studies have shown that the mixture of some of these pollutants in water may potentially

induce detrimental effects on living beings and plants (Cleuvers, 2003; Pomati et al., 2008; Parrott and Bennie, 2009).

In order to efficiently remove the recalcitrant emerging organic contaminants (including PPCPs) and other dissolved organic compounds, several suitable water treatment technologies such as carbon adsorption, advanced oxidation processes (AOPs), and membrane separation such as nanofiltration or reverse osmosis can be employed (Suárez et al., 2008; Yang et al., 2011). Activated carbon (AC) has high affinity for hydrophobic and non-polar compounds. It has been reported to be an excellent adsorbent for pesticides (Hu et al., 1998; Cougnaud et al., 2005; Chang and Lee, 2012), hepato-, neuro- and phyto-toxins (Newcombe and Nicholson, 2002; Hilal et al., 2004; Hille and Ouden, 2005; Wang et al., 2009a; Ho et al., 2011), dyes (Demirbas, 2009; Chan et al., 2012; Vargas et al., 2012), taste- and odor-causing compounds (Cook et al., 2001; Ridal et al., 2001; Kim and Bae, 2007; Matsui et al., 2009; Zhang et al., 2011a; Zoschke et al., 2011) and many other synthetic organic compounds which are classified as emerging contaminants and EDCs (USEPA, 2001; Westerhoff et al., 2005; von Gunten et al., 2006; Snyder et al., 2007; Yu et al., 2009; Grover et al., 2011). In addition, AC can be used to remove polar and ionogenic organics (Hu et al., 1998; Rivera-Utrilla et al., 2011), natural organic matter (NOM) (Jacangelo et al., 1995; Chaudhary et al., 2002; Shon et al., 2006; Gur-Reznik et al., 2008; Iriarte-Velasco et al., 2008; Ando et al., 2010; Velten et al., 2011), and certain perfluorinated chemicals (Ochoa-Herrera and Sierra-Alvarez, 2008; Qu et al., 2009; Takagi et al., 2011).

Among the AOPs, heterogeneous photocatalysis or semiconductor photocatalysis is attractive because it offers the following salient advantages: (i) it avoids the use of toxic or hazardous chemicals such as ozone or hydrogen peroxide, (ii) it is more energy efficient as compared to photolysis or sonolysis, and (iii) it allows solar-powered applications, either through utilizing the UV spectral range of the solar light irradiation (Malato et al., 2002; Malato et al., 2007; Blanco et al., 2009), or through tapping the visible-light spectral range of the solar irradiation by doping the photocatalyst to induce visible-light photoresponsive properties (Asahi et al., 2001). Moreover, Klavarioti et al. (2009) examined the efficiency of various AOPs for degradation of pharmaceuticals and found that heterogeneous photocatalysis was the

most efficient (32%), followed by other processes namely ozonation (30%), Fenton/photo-Fenton (13%), UV/H₂O₂ (12%), electrolysis (8%), sonolysis (4%), and wet air oxidation (1%). Among the various types of semiconductors, titanium dioxide or titania (TiO₂) has emerged as the leading candidate for application in water treatment and reclamation because it is commercially available, of low toxicity, chemically and biologically stable, inexpensive, and exhibits remarkable photocatalytic activity upon excited by UV irradiation ($\lambda \leq 387.5$ nm) (Hoffmann et al., 1995). It is worth noting that TiO₂-based photocatalysts using UV irradiation can degrade almost all types of organic pollutants except certain groups of perfluorinated chemicals (Lim et al., 2011).

Recently, several programs which are mostly involving solar-driven processes, such as SOLARDETOX, FITOSOL, SOLWATER and AQUACAT projects (Malato et al., 2007; Navntoft et al., 2007; Blanco et al., 2009), have been carried out in order to demonstrate the technical feasibility of heterogenous photocatalysis for water and wastewater treatment at field-scale applications. Indeed, the potential of harnessing the abundant, clean and free solar light serves as a great impetus to employ heterogeneous photocatalysis for water reclamation and reuse.

1.2 Motivation and knowledge gap

The practical applications of bare TiO₂ powders in water treatment are faced with two major limitations. The first challenge is the poor separation of TiO₂ nanoparticles from the treated water. To overcome this limitation, many researchers have developed supported TiO₂ systems, using either organic materials (Wang et al., 2007b; Zhu and Zou, 2009) or inorganic materials (Alinsafi et al., 2007; Menesi et al., 2008). Since heterogeneous photocatalysis is a surface-mediated reaction, TiO₂ supports which can reduce mass transfer limitation are desirable. As there are various organic pollutants omnipresent in contaminated waters, carbonaceous supports for TiO₂ are favorable because they have high affinity for organic compounds. Among the carbonaceous supports, AC is the most promising candidate because: (a) it possesses excellent affinity for a myriad of organic pollutants, especially the hydrophobic and non-polar contaminants, (b) it can also adsorb most of the intermediates and byproducts to allow

further degradation on the TiO_2 surface, (c) it is available commercially, (d) it is suitable for water treatment applications, and (e) it has been reported to enhance photonic efficiency for the supported TiO_2 by increasing the time-scale of charge separation (Cordero et al., 2007b). The synergistic effect of adsorption-photocatalysis processes for efficient pollutant removal, as exhibited by the TiO_2 supported on AC (TiO_2/AC) composite, is shown in Figure 1.1. Upon absorbing photon energy greater than the bandgap energy (E_g) of TiO_2 , hydroxyl radicals ($\cdot\text{OH}$) are produced and these highly reactive species can degrade the concentrated pollutants in proximity.

Figure 1.1 Schematic illustrating the synergistic effect of adsorption-PCD processes for TiO_2/AC (Lim et al., 2011).

The second drawback associated with the bare TiO_2 nanoparticles is their weak visible-light photoresponsiveness, thus limiting their opportunity to harness solar light as the excitation source. Since solar photocatalysis is a green technology which has a great potential for practical applications in water treatment (Malato et al., 2002), it is desirable to modify the bare TiO_2 powders to exhibit enhanced photoresponsiveness under visible-light irradiation. Recent studies revealed that TiO_2 could demonstrate increased photocatalytic activity under visible-light irradiation when it was doped with metal (Choi et al., 1994; Lam et al., 2007) or non-metal (Ohno et al., 2004; Di Valentin et al., 2007; Zaleska et al., 2008) dopants. However, metal dopants have several disadvantages such as exorbitant material costs and possible secondary water contamination (if the metals are toxic). Therefore, the more attractive option is to focus on non-metal dopants. Nitrogen is a promising non-metal dopant as numerous studies have shown that nitrogen-doped TiO_2 (N-TiO_2) manifested pronounced visible-light photoresponsiveness (Asahi et al., 2001; Di Valentin et al., 2007). Thus, the

motivation of this study is to develop a novel bifunctional nitrogen-doped titanium dioxide supported on powdered activated carbon (N-TiO₂/AC) composite which can be employed for water reclamation and reuse.

It is worth noting that the real water contains various dissolved aqueous matrix species. Although there have been some early studies on the effects of various interfering aqueous species on the photocatalytic activity of TiO₂ (Abdullah et al., 1990; Burns et al., 1999; Cho et al., 2002; Hu et al., 2003; Özkan et al., 2004; Achilleos et al., 2010), the study on this research area is still inadequate. In addition, there appears to be only a few investigations on the effects of solution matrix species on the pollutant removal efficiencies as exhibited by the TiO₂/AC system, and those studies (Sun et al., 2006; Sun et al., 2009) focused solely on UV photocatalysis. It is anticipated that the presence of interfering species in the water may have various influences on the bifunctionality characteristics of the N-TiO₂/AC composite. Thus, it is imperative to examine the influences of aqueous matrix species on the synergistic adsorptive-solar photocatalytic removal of recalcitrant organic pollutants to understand the mechanism involved and process efficiency.

Although AC is a competent adsorbent for a myriad of organic contaminants, it will eventually become a spent AC after it is loaded with adsorbates. The spent AC is usually considered as a hazardous waste and thus its disposal is not environmentally-friendly on a long-term basis. Therefore, it is appealing to regenerate the spent AC for reuse. To date, several regeneration techniques have been attempted for regenerating the spent AC. These include thermal regeneration (Sheintuch and Matatov-Meytal, 1999), chemical regeneration (Leng and Pinto, 1996; Guo et al., 2011), microbial regeneration (Coelho et al., 2006), ultrasound regeneration (Lim and Okada, 2005), electrochemical regeneration (Ania and Béguin, 2008), microwave regeneration (Foo and Hameed, 2009), Fenton-based regeneration (Kan and Huling, 2009), and photocatalytic regeneration (Crittenden et al., 1997; Liu et al., 2004; Tao et al., 2006; Park et al., 2010). It is worth noting that the majority of the photocatalytic regeneration studies of spent AC were about granular AC and the excitation source employed was usually UV irradiation. To the best knowledge of the author, there appears to be no well-documented articles reporting the solar regeneration of the spent powdered AC as induced by a visible-light photoresponsive photocatalyst. Solar photocatalytic

regeneration (SPR) technique is a greener and relatively cost-effective technique as compared to all other types of regeneration techniques since it does not entail carbon footprint and chemical consumption during the spent AC regeneration. Thus, it is appealing to investigate solar regeneration of the pollutant-loaded N-TiO₂/AC as like a spent AC.

Although there have been many investigations on TiO₂/AC composites pertaining to the fundamental and application aspects (Lim et al., 2011), there appears to be little work carried out on the preparation of TiO₂/AC composites through the incorporation of commercial TiO₂. This is because the coating of commercial TiO₂ powder on AC is somewhat challenging. In general, the commercial TiO₂ such as Degussa P25, Hombikat TiO₂, Ishihara TiO₂ and Millenium TiO₂ exhibit good photocatalytic activity under UV irradiation in degrading and mineralizing various recalcitrant organic pollutants. Among the commercial TiO₂, Degussa P25 stands out as the most widely investigated photocatalyst because of its excellent photocatalytic activity under UV irradiation. The integration of P25 and titania (sol) to produce nanotitania composite has been attempted and the findings revealed enhanced photocatalytic or photoelectrochemical efficiencies (Chen and Dionysiou, 2008; Chen et al., 2009). To improve the photocatalytic activity of P25 under solar light irradiation, N-doping is crucial. Thus, it is appealing to develop facile synthesis techniques for preparing bimodal N-P25-TiO₂/AC composites which are physically stable and subsequently examine their performance for the synergistic removal of aqueous recalcitrant organic pollutants.

1.3 Objectives

The objectives of this study were as follows:

- i. To develop a synthesis technique which could produce a bifunctional composite that exhibits adsorption-photocatalysis processes in synergism, possesses good photostability, photochemical stability, and physical stability,

as well as photoexcitable under the irradiation of solar light, UV, and visible-light;

- ii. To investigate the removal efficiencies of selected recalcitrant organic pollutants of varying hydrophobicities;
- iii. To develop a green technique for regenerating the spent powdered AC in the form of N-TiO₂/AC via the SPR technique;
- iv. To develop a facile synthesis technique which is more amenable for the scale-up production of the bifunctional composite.

1.4 Scopes of work

The scopes of work for this study were as follows:

- i. To provide a critical review on the research area of TiO₂/AC composites and N-TiO₂ photocatalysts, respectively;
- ii. To synthesize and characterize the N-TiO₂/AC composites as prepared via single-stage and two-stage calcinations, and examine their adsorptive-solar photocatalytic performances using bisphenol-A (BPA) as the model pollutant, by specifically evaluating the effects of calcination condition, light wavelength spectrum, composite dosage, cycles of reuse, and solution matrix species such as inorganic anions (Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, H₂PO₄⁻ and silica), organic anion (C₂O₄²⁻), photocatalysis inhibitor (CH₃OH), and oxidant (H₂O₂);
- iii. To evaluate the efficiency of SPR technique by using BPA, sulfamethazine (SMZ), and clofibric acid (CFA) as the model adsorbates, by investigating the effects of light intensity, N-TiO₂ loading, areal loading, and temperature, as well as establishing a kinetic model for predicting the regeneration process;
- iv. To synthesize and characterize the bimodal N-P25-TiO₂/AC composites as prepared via facile sol-gel synthesis techniques, and investigate their adsorptive-solar photocatalytic characteristics for the synergistic removal of SMZ as influenced by the total loading of N-doped titania, synthesis technique, weight distribution between N-P25 and N-TiO₂ (sol), composite dosage, light wavelength spectrum, and solution pH.

1.5 The organization of thesis

This thesis comprises seven chapters. Chapter 1 presents the background perspective, motivation and knowledge gap, objectives of this study, scopes of work and the organization of this thesis. Chapter 2 provides a review of the fundamentals of heterogeneous photocatalysis, and discusses the recent findings in the research area of TiO₂/AC composites and N-TiO₂ photocatalysts. Chapter 3 describes the materials and methods used in this study, including the experimental procedures adopted. Chapter 4 presents the synthesis and characterization of various N-TiO₂/AC composites as prepared via single-stage and two-stage calcinations, and evaluation of their bifunctional characteristics for removing BPA. Chapter 5 presents the studies on the solar regeneration of the spent N-TiO₂/AC composites loaded with BPA, SMZ or CFA, respectively. Chapter 6 elucidates the facile preparations of the bimodal N-P25-TiO₂/AC composites and their characteristics, physical stabilities, and efficiencies of SMZ removal in water. Chapter 7 presents a summary of important conclusions derived from this study and also several recommendations for the future work.

Chapter 2 Literature Review

2.1 Fundamentals of heterogeneous photocatalysis

The fundamentals of heterogeneous photocatalysis have been widely discussed elsewhere (Hoffmann et al., 1995; Linsebigler et al., 1995; Carp et al., 2004; Herrmann, 2005; Fujishima and Zhang, 2006). In water, photocatalytic degradation (PCD) of a pollutant involves five sequential steps (Herrmann, 2005): (1) transfer of the pollutant from the bulk solution to the photocatalyst surface, (2) adsorption of the pollutant by the photocatalyst, (3) photocatalytic reaction in the adsorbed phase that oxidizes (sometimes reduces) the pollutant, (4) desorption of the products from the photocatalyst surface, and (5) removal of the products from the interface region to the bulk solution. Among the various single metal oxides/chalcogenides (e.g. TiO_2 , Fe_2O_3 , SnO_2 , WO_3 , V_2O_5 , ZnO , ZrO_2 , CdS , MoS_2 and ZnS), TiO_2 is the most intensively examined heterogeneous photocatalyst (Mills and Le Hunte, 1997; Bhatkhande et al., 2002). This is because TiO_2 is inexpensive and commercially available, of low toxicity, and has high chemical and biological stability (Hoffmann et al., 1995). Importantly, its bandgap energy for anatase and rutile (as shown in Table 2.1) permits remarkable PCD efficiency under UV irradiation for the degradation and mineralization of various organic contaminants in the aqueous phase.

Table 2.1 Bandgap energy of various heterogeneous photocatalysts (Rajeshwar, 1995; Bhatkhande et al., 2002).

Photocatalyst	Bandgap energy (eV)
ZnS	3.7
SnO_2	3.5
SrTiO_3	3.4
TiO_2 (anatase)	3.2
ZnO	3.2
$\alpha\text{-Fe}_2\text{O}_3$	3.1
TiO_2 (rutile)	3.0
WO_3	2.7
CdS	2.4
Fe_2O_3	2.2
WSe	1.2

The working mechanism of PCD with TiO_2 is shown in Figure 2.1. Briefly, when the TiO_2 is irradiated with photon energy that is greater than its intrinsic bandgap energy, photogenerated electrons (e^-) are transferred from its valence band into its conduction band, hence leaving photogenerated holes (h^+) in its valence band. The e^- and h^+ may recombine in the bulk or migrate to the surface and participate in photocatalytic redox reactions with the pollutants adsorbed on the surface of the photocatalyst. The reaction between h^+ and electron donors such as adsorbed water or OH^- produces $\bullet\text{OH}$. Simultaneously, the reaction between e^- with electron acceptors such as dissolved O_2 produces superoxide radical ($\bullet\text{O}_2^-$), which may further undergo successive one-electron reduction to produce $\bullet\text{OH}$.

Figure 2.1 Schematic diagram of PCD mechanism: (a) reduction involving photogenerated electrons, (b) oxidation involving photogenerated holes, (c) recombination of charge carriers in the bulk of TiO_2 , and (d) recombination of charge carriers at the surface of TiO_2 (modified from Linsebigler et al. (1995)).

The photocatalytic redox reactions are delineated as follows:

The production of $\bullet\text{OH}$ is desirable because it is a non-selective and extremely reactive oxidant. Its standard redox potential of +2.8 V vs NHE (normal hydrogen electrode) makes it the second most powerful oxidizing species, preceded only by that of fluorine (+3.03 V vs NHE) (Egerton and Christensen, 2004). If the charge carriers (e^-/h^+) are not timely scavenged on the TiO_2 surface by the water molecules, electron acceptors, or trapped within the photocatalyst defect sites, they may recombine and thus compromise the $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ production or photonic efficiency. A summary of the main processes involving the charge carriers and their associated characteristic timescales are given in Table 2.2. Since the recombination timescale of e^- and h^+ is in the order of nanoseconds (Rothenberger et al., 1985), it is therefore critical to provide adequate scavengers for these charge carriers in the aqueous phase.

Table 2.2 Characteristic times for charge carrier trapping and recombination dynamics in photo-excited TiO_2 (Hoffmann et al., 1995; Mills and Le Hunte, 1997)

Major processes*	Characteristic time
Charge carrier generation $\text{TiO}_2 + h\nu \rightarrow h^+ + e^-$	fs (very fast)
Charge carrier trapping $h^+ + >\text{Ti}^{\text{IV}}\text{OH} \rightarrow [>\text{Ti}^{\text{IV}}\text{OH}^{*+}]$ $e^- + >\text{Ti}^{\text{IV}}\text{OH} \leftrightarrow [>\text{Ti}^{\text{III}}\text{OH}]$ $e^- + >\text{Ti}^{\text{IV}} \rightarrow >\text{Ti}^{\text{III}}$	10 ns (fast) 100 ps 10 ns (deep trap)
Charge-carrier recombination $e^- + [>\text{Ti}^{\text{IV}}\text{OH}^{*+}] \rightarrow >\text{Ti}^{\text{IV}}\text{OH}$ $h^+ + >\text{Ti}^{\text{III}}\text{OH} \rightarrow >\text{Ti}^{\text{IV}}\text{OH}$	100 ns (slow) 10 ns (fast)
Interfacial charge transfer $[>\text{Ti}^{\text{IV}}\text{OH}^{*+}] + \text{organic pollutant} \rightarrow \text{Ti}^{\text{IV}}\text{OH} + \text{oxidized pollutant}$ $[>\text{Ti}^{\text{III}}\text{OH}] + \text{O}_2 \rightarrow >\text{Ti}^{\text{IV}}\text{OH} + \bullet\text{O}_2^-$	100 ns (slow) ms (very slow)

* In the general mechanism, it is assumed that organic pollutant does not undergo oxidation via direct h^+ transfer, but takes place through a surface-bound hydroxyl radical $[>\text{Ti}^{\text{IV}}\text{OH}^{*+}]$

The PCD mechanism requires the pollutant to be adsorbed on the photocatalyst surface as a prerequisite step. In general, the Langmuir adsorption isotherm is widely accepted for modeling the equilibrium adsorption. The reaction rate (r) based on the associated Langmuir–Hinshelwood (L-H) model is delineated as follows:

$$r = k\theta = k \left[\frac{K_{\text{ads}} C_{\text{eq}}}{1 + K_{\text{ads}} C_{\text{eq}}} \right] \quad (2.6)$$

where θ = fractional surface coverage by pollutant, k = reaction rate constant, K_{ads} = Langmuir adsorption constant of pollutant, and C_{eq} = equilibrium concentration of pollutant after adsorption in the dark.

Thus, the efficiency of photocatalysis can be enhanced because the concentrated pollutants around the surface of the photocatalyst can readily react with the short-lived $\bullet\text{OH}$ and to serve as scavengers for e^- and h^+ . The discussions on the effects of various governing factors (e.g. light intensity, TiO_2 photocatalyst dosage, solution pH, and aqueous matrix species) on the photocatalytic degradation efficiency of various organic pollutants, as exhibited by TiO_2 , are available elsewhere (Bhatkhande et al., 2002; Konstantinou and Albanis, 2004; Gaya and Abdullah, 2008; Sin et al., 2012).

2.1.1 Structure and properties of TiO_2

TiO_2 exists in four polymorphs crystal phases, namely anatase, rutile, brookite and TiO_2 (B) (Carp et al., 2004). Anatase and rutile exist as tetragonal crystal structures, while brookite and TiO_2 (B) are formed from orthorhombic and monoclinic unit cells, respectively. These different phases are distinguished by the distinct distortion and arrangement of their intrinsic octahedral (TiO_2^{6-}) systems, as shown in Figure 2.2.

Figure 2.2 The crystal structures of (a) anatase, (b) rutile, (c), brookite (Carp et al., 2004).

Thermodynamically, rutile is the most stable TiO_2 phase. It is able to withstand high temperatures and ca. 60 kbar of pressure (Navrotsky et al., 1967; Jamieson and Olinger, 1969). However, there is only a small difference in the Gibbs free energy (4 - 20 kJ mol^{-1}) between the metastable polymorphs (i.e. anatase and brookite) and rutile under normal temperature and pressure (Navrotsky et al., 1967; Jamieson and Olinger, 1969). Among these crystal phases, anatase is generally regarded as the most photocatalytically active type of TiO_2 . TiO_2 possesses amphoteric characteristic, whereby its surface charge is known to be pH-dependent. Since the isoelectric point (IEP) for TiO_2 is in the range of pH 5-7, its surface functional groups will be rendered positive ($\equiv \text{Ti}-\text{OH}_2^+$) and negative ($\equiv \text{Ti}-\text{OH}^-$) when subjected to acidic ($\text{pH} \leq 5$) and alkaline ($\text{pH} \geq 7$) conditions, respectively (Choi, 2006).

2.2 Syntheses of TiO_2/AC

Various synthesis techniques have been adopted by previous researchers to produce TiO_2/AC . The techniques may be divided into two main groups, namely: (i) chemical methods such as sol-gel, chemical vapor deposition (CVD), hydrothermal, binders and molecular adsorption-deposition; and (ii) physical methods such as ionized cluster beam. Table 2.3 summarizes the literature reporting syntheses of various TiO_2/AC composites and evaluation of their PCD performances. Various types of powdered activated carbon (PAC), granular activated carbon (GAC), and activated carbon fiber (ACF), have been used as TiO_2 supports. The details of each synthesis technique, its conditions and the reported findings are summarized in Table 2.4. The chemical synthesis methods require a calcination step to produce TiO_2 crystal phase (e.g. anatase, rutile or brookite). The calcination temperature has a profound effect on the TiO_2 photocatalytic activity as well as the thermal stability of AC. Another important factor affecting the photocatalytic properties of TiO_2/AC is the type of Ti precursors and the resulting amount of TiO_2 loading on AC. Many researchers also emphasized the need to modify the surface of AC in order to facilitate deposition of TiO_2 onto AC. Most TiO_2/AC preparation methods showed that the pore structures of AC could be satisfactorily preserved. This was largely because the coating of TiO_2 (either as clustered particles or thin films) was limited to the external surface of AC.

Table 2.3 Summary of literature on TiO₂/AC syntheses along with the photocatalytic degradation experiments and findings

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Ao et al. (2008a)	Sol-gel (0.67 wt%)	PAC (Shanghai AC Ltd, coconut shells, 120 µm)	UV: 20 W FL, 365 nm; (phenol: 100 mg L ⁻¹ , solution volume: 400 mL, composite dosage: 1.5 g L ⁻¹); [6 cycles]	TiO ₂ /AC yielded higher apparent rate constant and quantum yield than that of the TiO ₂ , at 5 and 2.5 times, respectively.
Ao et al. (2008b)	Sol-gel	PAC (Shanghai AC Ltd, coconut shells, 120 µm)	UV: 20 W FL 365 nm; (phenol: 100 mg L ⁻¹ , solution volume: 500 mL, composite dosage: 1.5 g L ⁻¹); [6 cycles]	(TiO ₂ with γ-Fe ₂ O ₃)/AC mass ratio of 1:7 exhibited ca. 2 times the efficiency of P25.
Ao et al. (2009)	Sol-gel	PAC (Shanghai AC Ltd, coconut shells, 120 µm)	UV: 200 W lamp, Visible light: 500 W halogen lamp with < 400 nm cut-off filter; (reactive brilliant red: 50 mg L ⁻¹ , solution volume: 200 mL, composite dosage: 1 g L ⁻¹); [6 cycles]	Magnetic TiO ₂ /AC exhibited 83% and 81% PCD efficiency after 6 cycles under UV and visible-light irradiation, respectively.
Aruldoss et al. (2011)	Impregnation technique	AC	UV: 254 nm, 25 W, 5 nos; (phenolic syntan: 100 mL, composite dosage: 10 g L ⁻¹)	Acidic pH was favorable for phenolic syntan degradation, whereby the maximum COD removal of 87% was achieved at pH 2.5.
Cao et al. (2010)	Dip-coating	GAC (Japan EnviroChemicals Ltd, Osaka, Japan), 1-2 mm.	UV: 6 W blacklight blue FL; (2,4- dinitrophenol: 250 mg L ⁻¹ , solution volume: 500 mL); [6 cycles]	The PCD efficiency of TiO ₂ -AC PET film was greater than that of TiO ₂ -PET film by a factor of 2.9.
Cao and Shiraishi (2010)	Dip-coating	GAC (Japan EnviroChemicals, 1-2 mm)	UV: 6 W blacklight blue FL, 300-400 nm; (2,4-dinitrophenol, solution volume: 500 mL)	A mathematical model was proposed to describe the mechanism of pollutant removal using the TiO ₂ /AC-PET film.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Ding et al. (2001)	CVD	GAC (Norit Row 0.8 Supra)	UV: 8 W FL, 356 nm (phenol: 400 mg L ⁻¹ , solution volume: 150 mL)	Usage of TiO ₂ /AC resulted in higher concentration of phenol in the bulk solution, possibly due to the release of adsorbed phenol.
El-Sheikh et al. (2007)	CVD (20 - 77 wt%)	GAC (Jordanian olive stones) (< 1mm)	UV: 100 W Hg lamp, 365 nm, 7 mW cm ⁻² (3-chlorophenol: 40 mg L ⁻¹ , solution volume: 250 mL, O ₂ bubbling: 50 mL min ⁻¹)	1 g of TiO ₂ /AC (23.5 wt% TiO ₂) yielded 40% mineralization of 3- CP in 5 h, as opposed to 58% as yielded by 0.5 g of TiO ₂ .
Fu et al. (2004)	Molecular adsorption deposition (16.0 - 29.5 wt%)	ACF (Sichuan, China), viscous rayon in felt form	UV: 24 W LP Hg lamp, 254 nm; (methylene blue: 799 mg L ⁻¹ , solution volume: 400 mL, air blowing: 90 mL min ⁻¹); [3 cycles]	TiO ₂ was coated on ACF with size of approximately 100 nm film thickness.
Gao et al. (2011)	Sol-gel	PAC (Darco G-60 and Norit SA UF)	UV: 365 nm, 9 W black light blue lamp; (acid red 88, solution volume: 300 mL, composite dosage: 0.5 g L ⁻¹); [3 cycles]	The TiO ₂ /AC-D was superior than TiO ₂ /AC-N in degrading Acid Red 88 due to the effect of the TiO ₂ dispersion onto the AC support.
Geng and Cui (2010)	Spin-coating technique	GAC (Nantong Tongsen Active Carbon Co. Ltd., China, ca. 400 mesh)	UV: $\lambda_{\max}$ = 253.7 nm, 25 W; (reactive brilliant red K-2BP, bubbling rate: 0.4 L min ⁻¹)	The maximum photocatalytic activity was achieved when the solution pH was ca. 5.7.
Hou et al. (2009)	Liquid phase deposition (ca. 5 wt%)	ACF (felt form) (Xuesheng Technology Co. Ltd., Shandong, China)	UV: 15 W germicidal lamp, 253.7 nm; (acid orange II: 200 mg L ⁻¹ , electrical bias of 0.5 V)	TiO ₂ /AC electrode achieved 91% of PCD efficiency in 3 h for an initial concentration of 200 mg L ⁻¹ .
Huang et al. (2011)	Low temperature impregnation method or sol-gel	GAC (Prepared from bamboo leaves, Qingpu district, Shanghai, China)	UV: Halogen lamp; (methylene blue: 1 x 10 ⁻³ mol L ⁻¹ , solution volume: 100 mL)	The TOC removal as exhibited by the composites was higher than that of the bare TiO ₂ .

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Keane et al. (2011)	Low temperature impregnation method	PAC (Aquasorb 2000, Jacobi Carbons)	UV: 366 nm, 125 W, MP Hg lamp; (famotidine, composite dosage: 1.5 g L ⁻¹)	The highest rate constant for famotidine removal (0.237 mg L ⁻¹ min ⁻¹) was exhibited by composite with 10 wt% TiO ₂ .
Lee et al. (2004a)	Sol-gel	GAC (coconut shell, 1 mm)	UV: 4 W black light FL, 370 nm, 0.6 mW cm ⁻² (microcystin-LR: 200 mg L ⁻¹ , composite dosage: 1.0 g L ⁻¹); Fluidized bed reactor: 4 black light UV lamp (microcystin- LR: 50 mg L ⁻¹)	The continuous flow in a fluidized bed reactor employing the TiO ₂ /AC composite maintained over 95% removal efficiency.
Lee et al. (2004b)	Sol-gel (0.6 - 1.9 wt%, with 0.6 wt% as optimum)	GAC (coconut shell, 1 mm)	UV: 4 W black light FL, 370 nm, 0.6 mW cm ⁻² (microcystin-LR: 200 mg L ⁻¹ , solution volume: 1 L, composite dosage: 1.0 g L ⁻¹)	Almost complete removal of microcystin-R was achieved in 20 minutes.
Li et al. (2005b)	Sol-gel (2.63 wt%)	GAC	UV: 40 W FL, 365 nm; (methyl orange, solution volume: 250 mL, air sparging: 56 mL s ⁻¹ , composite dosage: 2 g L ⁻¹); [20 cycles]	Optimum operating condition for maximum PCD efficiency was initial concentration of 12 x 10 ⁻³ M, pH 6 and light power 40 W.
Li et al. (2005a)	Sol-gel (1.78 - 2.11 wt%)	GAC	UV: 40 W FL, 365 nm; (rhodamine B: 2395 mg L ⁻¹ , solution volume: 250 mL, air sparging : 56 mL s ⁻¹ , composite dosage: 2 g L ⁻¹); [20 cycles]	TiO ₂ /AC achieved complete rhodamine B degradation in 200 min as opposed to 80% and 70% removal efficiencies for TiO ₂ and mixture of TiO ₂ -AC, respectively.
Li et al. (2006b)	Sol-gel (5 - 63 wt%, with 47 wt% as optimum)	GAC (JSY X33, Tianjin, coconut shell of grain size 0.12 cm)	UV: 40 W FL, 365 nm; (1.0 x 10 ⁻³ to 10.0 x 10 ⁻³ mol L ⁻¹ methyl orange, solution volume: 200 mL, composite dosage: 2 g L ⁻¹)	TiO ₂ /AC (47 wt% TiO ₂) exhibited the best removal performance, with the adsorption constant and rate constant of 0.1116 L mmol ⁻¹ and 0.1872 mmol ⁻¹ min ⁻¹ , respectively.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Li et al. (2007)	Sol-gel	GAC (JSY X33, Tianjin, coconut shell of grain size 0.12 cm)	UV: 40 W FL, 365 nm; (methylene blue, solution volume: 250 mL, air sparging: 56 mL s ⁻¹ , composite dosage: 2 g L ⁻¹)	Within 200 min of irradiation time, TiO ₂ /AC could completely degrade MB while TiO ₂ only achieved 60% removal.
Li et al. (2008)	Sol-gel	GAC (Porous carbon, PC, Hainan, China).	UV: 40 W FL, 365 nm; (methylene blue, solution volume: 250 mL, air sparging: 56 mL s ⁻¹ , composite dosage: 2 g L ⁻¹)	Optimum operating condition for maximum removal of MB was 20 mg L ⁻¹ of MB initial concentration, pH 6 and 2.5 g L ⁻¹ loading of TiO ₂ /AC.
Liu and Chen (2007)	Sol-gel (95 wt%)	PAC (Tianda Chemical Factory, China)	UV: 8 W FL, 365 nm. Visible light: 380 W Xe lamp, 500 nm, UV cut off film; (phenol: 50 mg L ⁻¹ , solution volume: 250 mL, composite dosage: 1 g L ⁻¹); [5 cycles]	The composite calcined at 500°C for 4 h, could remove phenol in 40 and 70 min, under the irradiation of visible-light and UV, respectively.
Liu et al. (2006a)	Sol-gel	ACF (viscous rayon)	UV: 500 W HP Hg lamp, 380 nm; (methylene blue: 20 mg L ⁻¹ , solution volume: 100 mL)	TiO ₂ /AC achieved almost 100% MB removal in 1 h as opposed to 25% removal in 3 h for bare TiO ₂ .
Liu et al. (2007a)	Hydrothermal (80 - 98 wt%, with 95% as optimum)	PAC (Tianda Chemical Factory, China)	UV: 8 W FL, 365 nm; (methyl orange or phenol, solution volume: 250 mL, composite dosage: 1 g L ⁻¹); [8 cycles]	The optimum AC content for yielding the highest PCD activity was 5 wt%.
Liu et al. (2007b)	Sol-gel (7.98 wt%)	GAC (coconut shell, 0.355-0.900 mm, < 1% ash)	UV: 254, 297, 313, 366 nm. Visible light: 406, 436, 547, 579 nm; electrodeless discharge lamp, (phenol: 10 mg L ⁻¹ , solution volume: 50 mL, composite dosage: 2 g L ⁻¹).	TiO ₂ /AC demonstrated 2 times higher PCD efficiency than P25.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Mahmoodi et al. (2011)	Binder (polymer) (98 wt%)	GAC (<i>Canola</i> hull, Iran)	UVC: 200-280 nm, 15 W, 2 nos.; (basic red 18: 0.128 mM, basic red 46: 0.120 mM, solution volume: 5 L)	Degradation and mineralization of dyes were observed through formation of intermediates (carboxylic acids) and byproducts (inorganic anions).
Shi (2009)	Sol-gel	ACF	UV: 500 W HP Hg lamp, 365 nm; (methyl orange: 120 mg L ⁻¹ , air bubbling); [4 cycles]	Fe(III) and Ho(III) co-doped TiO ₂ /AC maintained > 99% of PCD efficiency after 4 cycles of reuse.
Shih and Chang (2006)	Sol-gel	GAC (Norit, 1.5 mm)	Continuous downflow fixed-bed reactor, stainless steel tube with inner diameter of 2.1 cm and volume of 94.0 mL (methanol)	Pt/TiO ₂ -AC exhibited greater PCD efficiency the Pt/AC as the former could remove 45% of methanol in 170 min, while that of the latter was only < 10%.
Subramani et al. (2007a)	Hydrothermal (0.09 - 0.33 wt%)	PAC (M/S Ranbaxy, India)	UV: 8 W FL (indigo carmine dye: 5 x 10 ⁻⁵ mol L ⁻¹ , solution volume: 50 mL, composite dosage: 0.6 g L ⁻¹)	COD removal efficiencies were 91.06% and 48% via PCD and adsorption in the dark, respectively.
Subramani et al. (2007b)	Hydrothermal (0.09 - 0.33 wt%)	PAC (M/S Loma Chemie)	N.A.	0.17 wt% of TiO ₂ in TiO ₂ /AC was the threshold for the TiO ₂ impregnation.
Sun et al. (2006)	Sol-gel	GAC (0.45-0.9 mm)	UV: 300 W, 365 nm (orange G, solution volume: 2500 mL, air flow rate: 0.2 m ³ h ⁻¹)	Optimum Sn(IV) content in the composite was 2.5 at%.
Sun et al. (2009)	Sol-gel + Dip coating	GAC (0.45-0.9 mm)	UV: 500 W, 365 nm (congo red dye, solution volume: 2000 mL, air flow rate: 0.2 m ³ h ⁻¹)	The degradation efficiencies as exhibited by WO ₃ -TiO ₂ /AC and TiO ₂ /AC within 2 h were 95% and 80%, respectively.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Torimoto et al. (1996)	Sol-gel (70 wt%)	PAC (Wako Pure Chemicals)	UV: 400 W Xe lamp, UV cutoff filter of 300 nm, 135 mW cm ⁻² ; (propyzamide: 7.8 mg L ⁻¹ , solution volume: 10 mL)	TiO ₂ /AC was superior to TiO ₂ as the former further adsorbed the toxic intermediates produced.
Torimoto et al. (1997)	Sol-gel (30, 65, 80, 90, 100 wt%)	PAC (Wako Pure Chemicals)	UV: 10 W FL, 352 nm, 1.8 mW cm ⁻² (dichloromethane, solution volume: 10 mL)	TiO ₂ /AC achieved higher apparent rate constant than that of the mixed suspension of 80 wt% TiO ₂ and 20 wt% AC.
Toyoda et al. (2003)	Hydrothermal without calcination (3.1 - 24.4 wt%)	PAC (coconut shells)	UV: 10 W black light FL; (methylene blue and iminocadine triacetate); [4 cycles]	Initial hydrothermal treatment resulted in TiO ₂ deposition near the vicinity of AC pore entrance, while subsequent repetitions led to more uniform TiO ₂ coverage.
Tryba et al. (2003a)	Sol-gel (46, 50, 55 wt%)	PAC (Gryfskand Co. Poland, charcoal)	UV: 6 FL of 20 W; (phenol: 50 mg L ⁻¹ , solution volume: 500 mL, composite dosage: 0.6 g L ⁻¹)	TiO ₂ /AC calcined at 900°C was predominantly rutile phase and demonstrated the maximum PCD efficiency of 88% removal of phenol within 6 h.
Tryba et al. (2003b)	Sol-gel (96.7 - 99.1 wt%)	PVB (Polyvinyl butyral)	UV: 6 FL of 20 W; (phenol: 50 mg L ⁻¹ , solution volume: 500 mL, composite dosage: 0.6 g L ⁻¹)	TiO ₂ /AC (2.5 wt% carbon, calcined at 700°C) achieved almost complete removal of phenol under 12 h of UV irradiation.
Wang et al. (2007c)	Sol-gel	PAC (Darco G-60, 100 mesh, Aldrich, peat)	UV: 3 W LP Hg lamp, 253.7 nm; (chromotrope 2R dye)	Calcination temperature of 450°C produced composite with good synergistic interaction between TiO ₂ and AC.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Wang et al. (2009b)	Hydrothermal (8 wt%)	GAC (0.15-0.25 mm)	UV: 365 nm; (methyl orange: 50 mg L ⁻¹ , solution volume: 250 mL, airflow: 0.6 L min ⁻¹ , composite dosage: 2 g L ⁻¹); [5 cycles]	TiO ₂ /AC calcined at 600°C exhibited the highest PCD efficiency, and superior to that of P25-AC and TiO ₂ -AC mixtures.
Wang et al. (2009c)	Hydrothermal	GAC (Shanghai Zhenghai Active Carbon Co. Ltd., China, coconut shell)	UV: 365 nm, 300 W; (methyl orange: 50 mg L ⁻¹ , solution volume: 250 mL, air flow rate: 0.6 L min ⁻¹ , composite dosage: 2 g L ⁻¹)	Kinetics of PCD activity using TiO ₂ /AC2 and TiO ₂ /AC3 were higher than that of the mixture of TiO ₂ -AC.
Wang and Zhou (2010)	Sol-gel with dip-coating	PAC (Zhejiang Quzhou Minxin Carbon Industry Co. Ltd), mesh size: 300 µm	UV: 365 nm; (methyl orange: 20 mg L ⁻¹ , solution volume: 250 mL, air flow rate of 0.6 L min ⁻¹ , composite dosage: 0.4 g L ⁻¹); [5 cycles]	The PCD efficiency of the magnetically separable photocatalytic composite (TFAC) was superior than that of P25 and bare TiO ₂ , and the composite could be separated from solution using magnetic field.
Xu et al. (2008a)	Sol-gel	AC cloth (PAN based)	UV: 365 nm; (methylene blue: 9.4 mg L ⁻¹ , solution volume: 100 mL)	CT22-N700 was the best sample due to the high efficiency achieved for adsorption and PCD.
Xu et al. (2008c)	Sol-gel	PAC	Visible light: 250 W halogen lamp, cut-off filter of 400 nm, 11.3 mW cm ⁻² (phenol: 25 mg L ⁻¹ , solution volume: 200 mL, composite dosage: 1 g L ⁻¹)	F-TiO ₂ /AC demonstrated ca. 60% removal of phenol as opposed to less than 10% and ca. 10% for P25 and TiO ₂ /AC, respectively.
Xu et al. (2010)	Sol-gel	PAC (Shanghai Activated Carbon Co. Ltd).	Visible-light: 250 W Hg lamp (cut-off filter of 400 nm); (reactive brilliant red, X-3B: 50 mg L ⁻¹ , solution volume: 10 mL)	The PCD efficiency of the vanadium-doped TiO ₂ /AC film was superior to that of the vanadium-doped TiO ₂ , TiO ₂ and P25, respectively.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Xue et al. (2011)	Sol-gel with dip-coating (ca. 8 - 28 wt%)	GAC (Shanghai, China, 70- 100 mesh, nut kernels)	UV: 500 W Hg lamp, 365 nm, 12.5 mW cm ⁻² ; (humic acid: 15 mg L ⁻¹ , solution volume: 500 mL, composite dosage: 2 g L ⁻¹)	A remarkable 99.5% of degradation efficiency for humic acid removal was achieved within 3 h of UV irradiation.
Yamashita et al. (2000)	Ionized cluster beam (3 wt%)	ACF (Toho Rayon, FX-300)	UV: HP Hg lamp, $\lambda > 280$ nm (1,2- dichloromethane: 2.6×10^{-3} mol L ⁻¹ , solution volume: 25 mL)	The photocatalytic activity of TiO ₂ /ACF was more than two times higher than that of the efficiency of bare TiO ₂ .
Yang and Fu (2008)	Binder (~9 to 35 wt%)	ACF (Sichuan Carbon Fibers Co. Ltd., China)	UV: 24 W LP Hg lamp, 254 nm; (methylene blue, solution volume: 1.2 L, air flowrate: 120 mL min ⁻¹); [12 cycles]	Composite with 31.3 wt% TiO ₂ exhibited the highest PCD efficiency; 90% efficiency was retained after 12 cycles of reuse.
Yao et al. (2010)	Sol-gel	ACF (Zichuan Carbon Fiber Co. Ltd., China)	UV: 300 W Hg lamp, 365 nm; (phenol: 80 mg L ⁻¹ and methyl orange: 120 mg L ⁻¹ , composite dosage: 1-3 g L ⁻¹ ; [4 cycles]	The highest PCD efficiency for pollutant removal was exhibited by the composite calcined at 500°C in argon atmosphere.
Yoneyama and Torimoto (2000)	Sol-gel (70 wt%)	PAC (Wako Pure Chemicals)	UV: 400 W Xe lamp (propylamide: 30.5 μ mol L ⁻¹ , solution volume: 10 mL, air- bubbling, composite dosage: 1.0 g L ⁻¹)	A significant contrast of 91.5% versus 1.4% of PCD efficiency was exhibited by TiO ₂ /AC and bare TiO ₂ , respectively.
Yuan et al. (2005a)	Binders (43.9 wt%)	ACF (rayon)	UV: 500 W HP Hg lamp, 365 nm; (methylene blue: 85 mg L ⁻¹ , air bubbling); [6 cycles]	Mineralization for MB was confirmed with the evolution of ammonium ions.
Yuan et al. (2005b)	Binders (43.9 wt%)	ACF (rayon)	UV: 500 W HP Hg lamp, 365 nm, 12.5 mW cm ⁻² ; (β -cyclodextrin: 200 mg L ⁻¹ , air bubbling); [4 cycles]	The increase in pore size of AC resulted in concomitant increase in the PCD efficiency.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Yuan et al. (2005c)	Binders (43.9 wt%)	ACF (rayon)	UV: 500 W HP Hg lamp, 365 nm; (methylene blue: 85 mg L ⁻¹ , air bubbling); [7 cycles]	TiO ₂ /ACF calcined under 460°C in N ₂ exhibited the highest MB removal, greater than that of the P25.
Yuan et al. (2006)	Binders (43.9 wt%)	ACF (rayon)	UV: 500 W HP Hg lamp, 365 nm; (methylene blue: 85 mg L ⁻¹ , air bubbling); [6 cycles]	Hydrophilicity of TiO ₂ /AC was attributed to the increased of hydroxyl and C-O groups.
Yuan et al. (2007)	Binders (43.9 wt%)	ACF (rayon)	UV: 500 W HP Hg lamp, 365 nm; (COD from paper mills effluent: 215 mg L ⁻¹); [3 cycles]	The best TiO ₂ /ACF exhibited almost 10% higher PCD efficiency as compared to P25.
Zhang et al. (2004)	CVD (4.3 - 21.8 wt%)	PAC (40-60 mesh)	N.A.	Highest deposition rate of 8.2 mg g ⁻¹ h ⁻¹ was obtained through optimizing the N ₂ flowrate, source temperature and deposition temperature.
Zhang et al. (2005d)	CVD	PAC (Zhejiang Xingda, 50-80 mesh)	UV: 356 nm; (methyl orange: 100 mg L ⁻¹)	HNO ₃ oxidation could increase more oxygen functional groups on AC than H ₂ O ₂ oxidation and (N ₂ + O ₂) oxidation (v/v: 95:5).
Zhang et al. (2005c)	CVD (ca. 12 wt%)	PAC (Zhejiang Xingda, 50- 80 mesh)	UV: 356 nm, 1.2 mW cm ⁻² ; (methyl orange: 200 mg L ⁻¹); [5 cycles]	The optimum Ag/Ti ratio for maximum PCD activity was 0.0595.
Zhang et al. (2005b)	CVD (4 - 25 wt%, with 12 wt% as optimum)	PAC (Zhejiang Xingda, 50-80 mesh)	UV: 356 nm, 1.2 mW cm ⁻² ; (methyl orange: 100 mg L ⁻¹ , solution volume: 1 L, composite dosage: 2.0 g L ⁻¹); [10 cycles]	After 10 cycles of reuse, TiO ₂ /AC and the mixture of AC- P25 exhibited ca. 80% and 20% of PCD efficiency, respectively.

References	Synthesis technique (bulk TiO ₂ wt%)	AC type	Irradiation source; (aqueous organic pollutant & experimental conditions); [cycle of reuse]	Findings
Zhang et al. (2006)	CVD (4.26 - 4.41 wt%, with 4.41 wt% as optimum)	PAC (Zhejiang Xingda, 50-80 mesh)	UV: 356 nm, 1.2 mW cm ⁻² ; (100 mg L ⁻¹)	Modification of AC with 6 M HNO ₃ enhanced the TiO ₂ deposition rate by 4.5 times.
Zhang et al. (2011c)	Self-assembly technique or sol-gel	PAC (PS1300 Activated Carbon Technologies Pty Ltd).	Visible-light: 420-630 nm, 100 W Xe lamp; (humic acid: 11.2 mg L ⁻¹ , solution volume: 100 mL); [5 cycles]	The PCD efficiency for humic acid removal, as influenced by solution pH, decreased in the order: pH 3 > pH 7 > pH 11.
Zhang et al. (2011b)	Hydrothermal (5 - 67 wt%)	GAC (AC, Nanjing, Chian)	UV: 50, 100, 150, and 200 W; (rhodamine B: 5 x 10 ⁻³ mol L ⁻¹ , air flow: 0.6 L min ⁻¹ , composite dosage: 2.5 g L ⁻¹)	A kinetic model for rhodamine B degradation was established based on the light intensity, TiO ₂ content and initial concentration of pollutant.
Zhang and Lei (2008)	Sol-gel (3.9 - 13.6 wt%, with 13.6 wt% as optimum)	PAC (Zhejiang Xingda, 50-80 mesh)	UV: 300 W HP Hg lamp, 365 nm; (methyl orange: 100 mg L ⁻¹ , air bubbling: 1.2 m ³ h ⁻¹); [5 cycles]	The maximum PCD efficiencies as exhibited by the composites produced via sol-gel (13.6 wt% TiO ₂) and CVD (12 wt% TiO ₂) were 80% and 90%, respectively.
Zhang and Lei (2008)	CVD (3 - 12 wt%, with 12 wt% as optimum)	PAC (Zhejiang Xingda, 50-80 mesh)	UV: 300 W HP Hg lamp, 365 nm; (methyl orange: 100 mg L ⁻¹ , air bubbling: 1.2 m ³ h ⁻¹); [5 cycles]	Hybrid interfacial film (ca. 3 µm) formed in TiO ₂ /AC and the composite could mineralize intermediates compounds.
Zhu and Zou (2009)	Sol-gel (1.3, 1.4, 1.5, 1.7 wt%)	GAC & extruded AC pellets	UVC (6 nos 18 W NEC Germicides lamp), UVA (6 nos. 18 W NEC Blacklight lamp); (non-chlorinated effluent from Melbourne's sewage treatment plant, MW: 400-10,000 Da, photocatalytic regeneration for 16 h)	Photocatalytic regeneration of the spent composite using UVC or UVA was feasible and the regenerated composite could be reused for color removal.

Note: N.A. = Not applicable; FL = fluorescent lamp; LP = low pressure; HP = high pressure; PCD = photocatalytic degradation.

Table 2.4 Summary of various TiO₂/AC synthesis techniques

Synthesis technique	Precursors attempted	Synthesis conditions	Remarks
<i>Chemical</i>			
Sol-gel	Ti precursor: Organic: titanium (IV) ethoxide, TTIP, TBOT; Inorganic: TiCl ₄ Solvent: Isopropanol, absolute ethanol Catalysts: Strong acid (HCl, HNO ₃ , H ₂ SO ₄), Strong base (NH ₄ OH, TBAOH), weak base (diethanolamine)	T (°C): 300 to 900 D (h): 1 to 10 A: Air, N ₂ , Air + N ₂ , CO ₂	In general, anti-calcination effect occurs, whereby the TiO ₂ coated onto TiO ₂ /AC is observed to be smaller as compared to that of the bare TiO ₂ , hence resulting in enhanced PCD efficiency due to increased surface area.
CVD	Ti precursor: Organic: TTIP, TBOT; Inorganic: TiCl ₄	T (°C): 200 to 600 D (h): 4 to 24 A: N ₂	An interfacial film is formed between the deposition of TiO ₂ on AC.
Hydrothermal	Ti precursor: Inorganic: TiOSO ₄ , TiCl ₄ , peroxotitanate; P25 Mineralizer: HNO ₃ , NaOH	T (°C): 150 to 800 (low T are without calcination) D (h): 2 to 15 A: N ₂	Generally involves mild temperature synthesis ($\leq 200^{\circ}\text{C}$), although subsequent calcination at higher temperature (300°C-800°C) has also been reported.
Binder	Ti precursor: P25	T (°C): 400 to 580 D (h): 2 A: N ₂	TiO ₂ is observed to form large clusters deposition on ACF, hence the surface area of TiO ₂ may not be optimized.
Molecular adsorption-deposition	Ti precursor: Inorganic: TiCl ₄	T (°C): N.R. D (h): 1.5 A: Ar	Ti precursor having low boiling point is preferable for ease of vaporization.
<i>Physical</i>			
Ionized cluster beam	Ti precursor: Ti metal (99.9% purity)	Acceleration voltage (0.25 kV), substrate temperature (523K), oxygen gas pressure (10 ⁻⁵ to 10 ⁻⁴ torr)	TiO ₂ may only be deposited in the form of clusters, and not thin films owing to the limitation in ion beam transportation.

Note: T = Temperature of calcination, D = Duration of calcination, A = Atmosphere, N.R. = Not reported, TTIP = titanium tetraisopropoxide, TBOT = titanium butoxide

Due to its versatility, the sol-gel technique is the most commonly used chemical method for TiO₂/AC preparation. Sol-gel synthesis has several distinct advantages. First, the morphology of TiO₂ on AC may be properly controlled, e.g. resulting in formation of thin TiO₂ film on AC (Liu et al., 2007b). Second, various synthesis routes can be attempted and this provides versatility. For example, Tryba et al. (2003b) adopted a novel synthesis route to prepare TiO₂/AC directly from organic precursors such as polyvinylbutyral. Third, sol-gel technique may be conveniently employed to introduce various desirable functionalities into TiO₂/AC. Examples of the modified TiO₂/AC which are of practical interest include: (i) visible-light responsive TiO₂/AC, e.g. N-TiO₂/AC (Liu and Chen, 2007; Yap et al., 2010; Yap and Lim, 2011; Yap et al., 2011; Yap et al., 2012; Yap and Lim, 2012), F-TiO₂/AC (Xu et al., 2008c), and V-TiO₂/AC (Xu et al., 2010); and (ii) TiO₂ coated on Fe₃O₄-loaded AC which allows separation using a magnet (Ao et al., 2009). Various Ti-precursors, organic solvents, and acid/base catalysts may be attempted for sol-gel synthesis technique. It has been elucidated that the formation of Ti-O-Ti chains is most pronounced under the conditions of low hydrolysis rates, low water content and excess of Ti-alkoxide (Chen and Mao, 2007).

Several techniques to enhance the coating of TiO₂ on the external surface area of AC have been suggested. These include: (i) AC pre-treatment with HNO₃ (Sun et al., 2006) and HCl (Liu et al., 2007b); (ii) viscosity-controlled immersion method (Li et al., 2005a; 2005b); (iii) UV-assisted irradiation (Liu et al., 2006a); (iv) Ti sol formed during hydrolysis serving as binder between AC and anatase TiO₂ (Kubo et al., 2007); (v) pH manipulation (Zhang and Lei, 2008); and (vi) repeated coating (Carpio et al., 2005). The pre-treatment of AC with HCl may facilitate the dislodgement of metal impurities attached on the surface of AC (Matsumura et al., 1985), exposing more sites for TiO₂ anchorage. The UVA irradiation ($\lambda = 320\text{--}400\text{ nm}$) of the suspension mixture of TiO₂ sol and AC may enhance grafting of TiO₂ sol onto AC. It has been reported that under extremely acidic pH conditions, 3-10 nm of TiO₂ nanoparticles are formed in a stable transparent colloidal solution (Weng et al., 2000). Besides having a larger surface area with smaller particle size, the transparent solution may be thought of as promoting the establishment of chemical bonding between TiO₂ and AC.

In the CVD process, various deposition techniques can be used to deposit a single or multi component volatile precursor on the substrate (Li Puma et al., 2008). The volatile precursors will either react or decompose onto the surface of the substrate, forming a deposited thin-film material. The synthesis of TiO₂/AC via CVD technique involves the deposition of the vaporized Ti alkoxide precursors (e.g. TTIP or TBOT), TiCl₄ or tetranitratotitanium on the AC support. The identified benefits of CVD technique are that it (Ding et al., 2000; Aksoylu et al., 2003; Zhang et al., 2005b): (i) reduces several conventional handling steps since the synthesis steps are in a continuous process; (ii) preserves the integrity of the AC pore structures; and (iii) allows for the control of suitable chemical precursors for deposition. Several important considerations for ensuring an efficient CVD operation include: (i) carrier gas to be inert, high-purity and completely dry, (ii) gas line to be sufficiently heated to avoid condensation of Ti precursors, and (iii) AC filters and carrier gas flow under vacuum to be provided in order to minimize AC losses. Zhang et al. (2004) examined the effect of carrier gas flow rate, source temperature, and deposition temperature on CVD deposition rate. They reported that a maximum TiO₂ deposition rate of 8.2 mg g⁻¹ h⁻¹ on AC was achieved under the optimized condition of the above-mentioned three operating parameters.

TiO₂ nanoparticles can be obtained by hydrothermal treatment of peptized precipitates of a Ti precursor in water, or hydrothermal reaction of titanium alkoxide in an acidic ethanol-water solution, under autogenous pressure (Chen and Mao, 2007). The sizes of the resulting TiO₂ particles can be controlled by adjusting the concentration of Ti precursor and the composition of the solvent system, while the peptizers and their concentrations can influence the morphology of the TiO₂ particles. The hydrothermal method has been adopted to synthesize TiO₂/AC with different precursors, such as TiOSO₄ (Toyoda et al., 2003), TiCl₄ (Liu et al., 2007a), peroxotitanate (Wang et al., 2009b) and commercial TiO₂ (Subramani et al., 2007a; Subramani et al., 2007b).

TiO₂/AC synthesis using binders was adopted by Guan and co-workers (Yuan et al., 2006; Yuan et al., 2007). They utilized diglycidyl ether of bisphenol-A epoxy resin as the chemical to bind P25 and ACF. Though this technique seems feasible to mount TiO₂ onto the ACF, it is possible that trace amounts of binders may still exist after calcination that may cause water contamination with the residue. If excessively large

binder molecules block the AC pores, various adsorption sites may be rendered inaccessible to target pollutants and the adsorption capacity of the composite may be considerably compromised.

Molecular adsorption-deposition method is another chemical method to produce TiO_2 coating on AC. In this method, a Ti precursor of small molecular size, such as TiCl_4 , is to be adsorbed into the micropores of AC in vapor phase. After hydrolysis of the Ti precursor, pyrolysis proceeds at a relatively low temperature to produce TiO_2 anatase. By changing the vapor pressure of the Ti precursor during adsorption, the molecular adsorption-deposition method can be used to control the final thickness of the TiO_2 layer formed. This method has been attempted to coat a thin TiO_2 layer of about 100 nm in thickness on ACF using TiCl_4 as Ti precursor (Fu et al., 2004). However, this method may result in a significant amount of TiO_2 embedded into the AC internal pores, thus losing its functionality and reduce the AC adsorption capacity.

The ionized cluster beam technique has been applied to produce high quality thin films at high deposition rates by utilizing the effects of ion bombardment and the influence of the charge of ionized particles (Takagi, 1988). To deposit TiO_2 onto a substrate, Ti is used as the source material and oxygen gas pressure (10^{-5} to 10^{-4} Torr) is introduced in the deposition chamber, while the crystal phase of the deposited TiO_2 can be controlled by the content of ionized clusters and the acceleration voltage. One of the advantages of this synthesis technique is that it does not require calcination of the product formed, thus avoiding AC gasification. This technique has been attempted by Yamashita et al. (2002) to load TiO_2 onto ACF. TiO_2 particles are formed on the supports mainly as an anatase phase.

Mixing of TiO_2 and AC in aqueous suspension is another physical method to prepare TiO_2 -AC, as demonstrated by Matos and co-workers (Matos et al., 2001; Cordero et al., 2007a; Cordero et al., 2007b; Matos et al., 2007), and Araña et al. (Araña et al., 2002; 2003a; 2003b). Physical agitation of the TiO_2 and AC particles in aqueous suspension promotes their collisions and attachment to form a pseudo- TiO_2 /AC composite. In view of practical application, production of TiO_2 /AC that involves less chemical consumption and minimizes environmental pollution is desirable. In this context, simply mixing commercial TiO_2 and AC powder together appears to be the

favorable option. However, in such physical mixing, the physical bonding or straining of TiO₂ on the surface of AC is likely to be weak. This may result in appreciable amount of TiO₂ particles that can be dislodged from the AC in solution, and thus, subsequent separation of the TiO₂ nanoparticles from the treated water can be challenging.

Adsorption-photocatalysis synergism has been also found to depend on the surface chemistry of AC. The quantification of the synergistic and inhibitive effects may be determined by the R factor, which is defined as follows (Matos et al., 1999):

$$R = \frac{k_{app}(TiO_2 + AC)}{k_{app}(TiO_2)} \quad (2.7)$$

where $k_{app}(TiO_2 + AC)$ = apparent rate constant for the composite of TiO₂ and AC, and $k_{app}(TiO_2)$ = apparent rate constant for the bare TiO₂.

Synergy factor and inhibition factor are assigned when $R > 1$ and $R < 1$, respectively. The studies based on binary mixture of AC (H-type and L-type AC were used) and TiO₂ by Matos and his co-workers (Matos et al., 2001; Cordero et al., 2007a; Cordero et al., 2007b; Matos et al., 2007) observed both synergistic and antagonistic effects on the removal of phenol, 4-chlorophenol, and 2,4-dichlorophenoxyacetic acid. In general, the AC type and its activation process affect its surface functional groups, pI_{IEP} and topological properties. These properties affect the creation of the TiO₂-AC interface which has direct impact on interfacial electron transfer rate and thus PCD efficiency of the TiO₂-AC mixture. For example, Cordero et al. (2007b) demonstrated that L-type AC pre-treated with low chemical concentration such as ZnCl₂ (5%) and H₃PO₄ (5%) yielded a synergy factor of $R = 2.22$ and 1.66 , respectively. They ascribed this synergism to the formation of carboxylic acid groups on the AC surface, which were found to promote e⁻ transfer between AC and TiO₂ via the common contact interface, and thus improving the efficiency of photocatalysis. They also found that H-type AC to be superior to L-type AC in dispersing TiO₂ on AC surface. The former also has a higher pI_{IEP} which can increase the interfacial e⁻ transfer.

Other factors requiring consideration are listed below:

- Particle size of AC: Although both GAC and PAC have been used by the previous researchers (Table 2.3), there are several advantages to use the smallest particle size available for AC, such as: (i) to ensure that the resulting TiO_2/AC has good dispersibility even with simple air bubbling, (ii) to ensure superior adsorption kinetics for the target pollutants by reducing intraparticle diffusion path, (iii) to reduce the migration path for the short-lived $\bullet\text{OH}$ radical to the pollutants adsorbed at internal pore sites of AC, and (iv) to facilitate regeneration of the spent AC, whereby the desorbed pollutants in the interior of AC would take a shorter diffusion path to the surface for PCD.
- Type of AC activation/pre-treatment: It has been reported that the thermally-activated AC has a lower adsorption irreversibility (hysteresis), which is a crucial factor affecting AC regeneration, as compared to the chemically-activated AC (Aktas and Çeçen, 2006). In addition, AC pre-treatment with acid/base may create different surface functional groups, hence result in the varying affinities for different organic pollutants.
- Types of AC raw materials: Different raw materials result in different degrees of thermal resistance and auto-ignition (ashing) temperatures of AC. Because the synthesis of TiO_2/AC most often involves a calcination step at elevated temperatures (as shown in Table 2.4), the AC used should remain thermally stable at the calcination temperature.
- Type of AC porosity: Porosity influences total pore volume and specific surface area of the AC. Most recently, it has been demonstrated that the AC porosity affected the sorption capacity, amount of surface TiO_2 deposition and the performance of PCD (Wang et al., 2009c).

2.3 Characterization of TiO₂/AC

Various characterization techniques have been used to examine the physical, mineralogical, photochemical and crystallochemical properties of TiO₂/AC. The widely employed characterization techniques include: X-Ray diffraction (XRD), porosimetry analysis, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, thermogravimetric (TG) analysis, UV-Vis diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Table 2.5 summarizes the characterization techniques for TiO₂/AC and the reported characteristics.

XRD provides structural and mineralogical information for TiO₂/AC, through examination of the crystal phases (e.g. anatase, rutile, or brookite). XRD has also been used to verify the phenomenon of anti-calcination effect induced by AC, i.e., the suppression of anatase to rutile at higher calcination temperatures (Tryba et al., 2003b; Li et al., 2005a; Li et al., 2007). The presence of AC support may also baffle the TiO₂ crystal growth, as evidenced by the corresponding lower intensity of TiO₂ peaks for TiO₂/AC composite as compared to the case of bare TiO₂ (Li et al., 2007). To determine the polycrystalline compositions of the TiO₂, Rietveld analysis may be carried out. TiO₂ crystallite size is often estimated using Scherrer's equation (Debye and Scherrer, 1917), as shown below:

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (2.8)$$

where d = crystallite size (nm), k = Scherrer's constant (0.9), λ = wavelength of X-ray radiation (nm), β = full width half maxima (FWHM) (radian), θ = X-ray diffraction angle (°).

Table 2.5 Characterization techniques for TiO₂/AC

Technique/Instrument	Characteristics studied	Findings or characteristic peaks
Powder XRD with Rietveld analysis	Qualitative and quantitative crystal phase analysis	Anatase: 25.3° (101), 37.8° (004), 48.0° (200), 53.8° (105), 54.9° (211) and 62.5° (204); rutile: 27.4° (110), 36.1° (101), 41.2° (111) and 54.3° (211) (Zhang et al., 2005b). Brookite: 31.1° (Ao et al., 2008a). AC: 24° (002) and 44° (101) (Liu et al., 2006a)
Porosimeter, gas adsorption/desorption	Specific surface area, pore size distribution	The extent of AC pore blockage by TiO ₂ nanoparticles is insignificant as generally the pore structures of AC are well preserved (Yuan et al., 2007)
SEM/ EDX/ elemental mapping	Surface morphology and elemental compositions	TiO ₂ deposited as particles (range of 5-100 nm) (Zhang et al., 2005b) and thin films (ca. 100 nm) (Fu et al., 2004) onto AC.
TEM	Crystal shape and perfection; sizes of TiO ₂ particles	Anchorage of TiO ₂ onto AC is observed through the distinctive regions of crystalline and amorphous phase (El-Sheikh et al., 2004).
XPS	Elemental surface chemistry of TiO ₂	Ti : Ti ⁴⁺ is verified by Ti 2p _{3/2} and Ti 2p _{1/2} at ca. 458.6 and 464.4 eV (Zhang et al., 2005b).
FTIR	Analysis of organic and inorganic deposits on TiO ₂ /AC	Formation of Ti-O-C bonds at 1062 cm ⁻¹ for TiO ₂ /AC produced from CVD method (Zhang and Lei, 2008).
Raman	Structural composite of TiO ₂ /AC	Anatase: 152.86, 195.82 and 424.45 cm ⁻¹ ; rutile: 611.15 cm ⁻¹ (Li et al., 2005a). Graphite: 1335.3 cm ⁻¹ and 1590.5 cm ⁻¹ (Wang et al., 2009b).
UV-Vis DRS	Photoactivity of TiO ₂	Absorbance onset for TiO ₂ /AC is found at ca. 360 nm. (Liu et al., 2007b)
TGA	Decomposition points of materials and residues, and water absorption	Weight loss of the composite is found to be reasonable (Wang et al., 2007c)
Settling and turbidity analysis	Decantability	Gravity settling at selected time intervals indicates the separation efficiency of TiO ₂ /AC (Liu et al., 2007a).

In addition, the amount of rutile in the anatase-rutile mixture can be estimated using the Spurr and Myers equation (Spurr and Myers, 1957), as follows:

$$F_R = \frac{1}{1 + 0.8 \left[\frac{I_A(101)}{I_R(110)} \right]} \quad (2.9)$$

where F_R = mass fraction of rutile in the anatase-rutile mixture, and $I_A(101)$ and $I_R(110)$ are the main peak intensities of anatase (at $2\theta = 25.4^\circ$) and rutile (at $2\theta = 27.4^\circ$), respectively.

The BET surface area (S_{BET}) and porosity of TiO_2/AC have been commonly determined through gas adsorption-desorption isotherms and porosimeters. Some contradictory findings are observed for the S_{BET} of TiO_2/AC , whereby both marginal increases and significant decreases in S_{BET} , have been reported following TiO_2 coating onto AC. For the former phenomenon, Li et al. (2005a) reasoned that the increase in S_{BET} was attributed to the non-deposition of TiO_2 on the micropores of AC. A significant decrease in S_{BET} from $1150 \text{ m}^2 \text{ g}^{-1}$ to a range of $89.59 - 94.88 \text{ m}^2 \text{ g}^{-1}$ (for ca. 95 wt% N- TiO_2 loading) was reported by Liu and Chen (2007).

To gain insights into the surface morphology, mass distribution and crystallinity of the TiO_2 supported on AC in the composite, SEM and TEM may be employed. TEM may be employed to observe the particle sizes of TiO_2 and the interface between TiO_2 and AC. From SEM micrographs, the particle sizes of TiO_2 in TiO_2/AC were found to be smaller than those of bare (bulk) TiO_2 synthesized with a similar method (Li et al., 2007). This is because AC may inhibit the agglomeration of TiO_2 on TiO_2/AC , thus allowing the homogeneous dispersion of TiO_2 over the entire surface of AC. A residual super thin film layer was observed to remain on the surface of ACF after the elimination of TiO_2 film of ca. 100 nm thickness (Fu et al., 2006). Liu et al. (2007b) described that slight cracks were detected at relatively thicker regions of the thin film, attributable to the drying-induced contraction stress developed in the thicker films. In a recent finding, Shi (2009) found that cracks in TiO_2 thin films supported on AC could be minimized by co-doping of Fe(III) and Ho(III). The distribution of TiO_2 on the

surface of AC may be determined using energy-dispersive X-ray (EDX) analysis combined with elemental mapping.

The surface chemistry of TiO_2/AC may be studied using XPS, FTIR and Raman spectroscopy. XPS is useful for the determination of the chemical states of the elements present on the surface of TiO_2/AC . The chemical state of Ti is Ti^{4+} if the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ are with ca. 458.6 and 464.4 eV of binding energies, respectively, while other Ti chemical states (and the corresponding Ti $2p_{3/2}$ binding energies) are Ti^0 (453.1 eV), Ti^{2+} (455 eV) and Ti^{3+} (456.7 eV). FTIR and Raman spectra provide specific information on the types of molecular chemical bonding for both organic and inorganic deposits on the surface of TiO_2/AC . The bulk titania skeletal typically shows the region of weak and broad peaks from 400 to 800 cm^{-1} in its FTIR spectrum (Kumar et al., 2000). At around 1630 cm^{-1} , the bending vibration band of the surface -OH groups (corresponding to chemisorbed water) is observed (Jensen et al., 2005; Liu et al., 2007b). A broad band at 3400 cm^{-1} is the characteristic of associated hydroxyl groups of weakly chemisorbed water (Kumar et al., 2000). Impregnation of TiO_2 onto AC has been found to cause decreases in the following characteristic peak intensities of surface groups on AC: (i) C-H groups at both 804 cm^{-1} and 876 cm^{-1} ; (ii) C-O groups at 1094 cm^{-1} ; (iii) C=C groups at 1416 cm^{-1} ; and (iv) C=O groups at 1568 cm^{-1} (Zhang and Lei, 2008). Besides FTIR, other available methods include Boehm titration methods, thermal desorption spectroscopy and electrokinetic studies (Boehm, 2002).

UV-Vis DRS (diffuse reflectance spectroscopy) is a powerful tool to determine the photoactivity of a photocatalyst under UV and visible-light. In the context of TiO_2/AC , the UV-Vis spectra may be influenced by the surface coverage of TiO_2 on AC. A higher TiO_2 surface coverage on AC leads to a relatively smaller visible light absorption and more distinctive UV absorption edge in the UV-Vis DRS. Liu et al. (2007b) observed blue-shift in the absorption edge of TiO_2/AC (with an absorption edge onset ca. 360 nm instead of ca. 400 nm as for the bulk anatase), which may be attributed to the quantum size effects manifested in photocatalysts with decreasing particle size. However, a contradictory finding has earlier been documented, whereby the possibilities of quantum size effect and blue shift have been ruled out (Fu et al., 2004).

TG analysis may be conducted to examine the effect of AC thermal stability. Wang et al. (2007c) performed TG analysis for their TiO₂/AC in a flow of air (25 °C to 800 °C) with a heating rate of 5°C min⁻¹. For the TiO₂/AC, a sharp and a mild decrease in mass losses occurred at ca. 80°C and 250°C, respectively. The former was due to the loss of solvent and the latter was ascribed to the incipient crystallization of TiO₂. Slightly more than 10% composite mass losses occurred in a temperature range of 400°C - 500°C, and negligible further mass loss at 600°C-800°C. This indicated that the TiO₂/AC had a reasonable thermal stability. Indeed, the raw materials used for AC production is an important factor governing the thermal stability of TiO₂/AC produced.

Decantability of TiO₂/AC can be determined using simple sedimentation technique whereby the elevations of settled particles in a stagnant suspension are monitored at discrete times (Liu et al., 2007a). An alternative technique is to monitor changes in turbidity of a stagnant suspension over time (Araña et al., 2003).

There are several methods available for determining the TiO₂ wt% (bulk) in TiO₂/AC. These include gravimetry (ashing analysis) (Tryba et al., 2003a), X-ray fluorescence (XRF) (El-Sheikh et al., 2004), acid dissolution with subsequent analysis of Ti concentration (Lee et al., 2004b; El-Sheikh and Sweileh, 2007), and colorimetry (Torimoto et al., 1997). The TiO₂ wt% on the surface of TiO₂/AC composite has been analyzed using EDX (Carpio et al., 2005) and XPS (Zhang et al., 2005c). The TiO₂ wt% is critical because this parameter is likely to have a significant effect on the composite's bifunctionality as adsorbent and photocatalyst. In general, TiO₂/AC synthesized from sol-gel method can produce a wide range of TiO₂ wt%.

In addition to the above-mentioned techniques, complementary information can be also provided by the following characterization techniques: (i) differential thermogravimetry (DTG) analysis (Li et al., 2007), (ii) mercury intrusion porosimetry (El-Sheikh et al., 2004); (iii) temperature programmable desorption (Zhang et al., 2005d); (iv) positron lifetime spectrometry (Subramani et al., 2007b); (v) diffuse reflectance infrared Fourier transform (Yuan et al., 2005a; Cordero et al., 2007a); and (vi) extended X-ray absorption fine structure (Shih and Chang, 2006).

2.4 Performance of TiO₂/AC for pollutants removal

To date, the performances of TiO₂/AC have been investigated at the bench scale. The reported performances of various TiO₂/AC composites in PCD of pollutants are shown in Table 2.3. In general, TiO₂/AC composites have been found to be more versatile and providing more reliable pollutant removal compared to the systems with bare TiO₂ and mixtures of TiO₂-AC, because of its bifunctionality and the synergistically enhanced PCD. Ao et al. (2008a; 2008b; 2009) fabricated magnetic TiO₂/AC and found that their composite yielded a greater rate constant than that of the bare TiO₂. Li et al. (2005a) revealed that the synergistic effect afforded by TiO₂/AC led to the total removal of rhodamine B as compared to its 80% and 70% removal with bare TiO₂ and a mixture of TiO₂-AC, respectively. Liu et al. (2006a) observed 100% of methylene blue removal through PCD in 1 h with TiO₂/AC as opposed to only 25% removal with bare TiO₂ in 3 h.

The TiO₂/AC may be less prone to be deactivated compared to the bare TiO₂. For example, Liu et al. (2007a) reported that at the 8th cycle of reuse, their TiO₂/AC showed ca. 10% decrease while the bare TiO₂ suffered > 70% drop in their PCD efficiencies compared to their respective efficiencies at the 1st cycle, for phenol degradation. Mineralization of pollutants has also been demonstrated (Torimoto et al., 1997), whereby TiO₂/AC resulted in greater CO₂ evolution than that with a TiO₂-AC mixture. Other examples which demonstrated the synergistic effect provided by TiO₂/AC are also reported (Yamashita et al., 2000; Wang et al., 2009b).

In addition, the micron-size TiO₂/AC composites are desirable due to their ease of recovery for reuse compared to the commercial TiO₂ such as Degussa P25, Hombikat UV1000, ST01, PC500, etc. Several experiments shown in Table 2.3 (column 4) were conducted for a number of cycles. Depending on the types of pollutants and conditions of the PCD experiments, the percentages of photocatalytic activity remaining after numerous cycles of reuse varied, but were generally encouraging. Fu et al. (2006) found that even after 15 cycles of reuse, the removal efficiency for methylene blue was still greater than 92%. Zhang et al. (2005b) reported that even after 10 cycles of reuse, TiO₂/AC could still offer ca. 80% of its initial PCD efficiency as opposed to only 20%

exhibited by the mixed P25-AC. Interestingly, Yuan et al. (2005c) elucidated that the PCD efficiencies exhibited by their TiO_2/ACF at the second and subsequent cycles were higher than that achieved in the first cycle. They attributed this phenomenon to the residual epoxy resins (used in the synthesis) which had shielded some catalytic sites of TiO_2/AC .

While the PCD performance is the most interesting and critical, it is essential to evaluate the adsorption performance for TiO_2/AC . Unfortunately, such investigation appears to be often not reported in the TiO_2/AC literature. It was only reported in a few articles of TiO_2/AC or TiO_2 -AC mixtures (Torimoto et al., 1997; Cordero et al., 2007a; Matos et al., 2007; Yuan et al., 2007). Understandably, the adsorption capacity of TiO_2/AC could be reduced somewhat compared to that of virgin AC due to pores blocking. Quantifying changes in BET surface area after the TiO_2 deposition could perhaps indicate the possible extent of reduction in adsorption capacity. Varying degrees of reductions in BET surface areas for TiO_2/AC compared to the virgin AC have been reported. This reduction could be minimal (ca. 10%) (Zhu and Zou, 2009), moderate (ca. 30%) (Carpio et al., 2005) or significant ($> 65\%$) (Ao et al., 2009). Increased BET surface areas for TiO_2/AC as compared to AC were also reported (Li et al., 2005a).

Given that AC is a superior adsorbent, in conducting experiments to evaluate the performance of TiO_2/AC composite for contaminant removal, a few methods can be employed to distinguish the effects of adsorption and PCD. The most commonly adopted method is to perform batch PCD experiment after achieving contaminant adsorption equilibrium in the dark, and observe for continual decrease of the contaminant concentration under UV irradiation. The batch experiment with multiple spikings of the target contaminant along with determinations of its removals over several cycles and mass balances can also indicate the extent of PCD effect. Another approach is to run a continuous flow-through experiment with TiO_2/AC confined within a photoreactor (e.g., with a suitable membrane) and monitor its contaminant removal efficiency at the steady state condition. Direct evidence of contaminant removal through PCD can be revealed through detection of its intermediates or byproducts.

The present state of the research on TiO_2/AC composites still needs to be further advanced to evaluate its potential for practical applications. Thus far, the majority of photocatalysis experiments were conducted under ideal laboratory conditions, e.g., in batch reactor systems, or in closed-loop re-circulation system (Sun et al., 2006; Sun et al., 2009), using ultrapure/distilled water and at natural pH of the aqueous system. A continuous flow system was investigated briefly by Lee et al. (2004a). Most studies on TiO_2/AC investigated typical classes of model compounds, particularly organic dyes and simple phenolic compounds. Indeed, there is evidence that both UV/ TiO_2 and AC are able to remove various hydrophobic and hydrophilic pollutants as mentioned in the above-mentioned discussions. Future endeavors should therefore evaluate TiO_2/AC for hybrid adsorption-PCD treatment of a much larger variety of pollutants and in real water matrix.

2.5 Fundamentals of N- TiO_2

On the basis of spin-restricted local density approximation calculations performed by Asahi et al. (2001), nitrogen has appeared to be a promising anion to induce visible-light photoresponsiveness for TiO_2 . Based on this computation method, Asahi et al. (2001) hypothesized that N-doping of TiO_2 crystals was the most effective because the N 2p states contributed to band-gap narrowing by mixing with O 2p states in the valence band. Furthermore, they discovered that sulfur (S^{2-}) was too large to be incorporated into TiO_2 as compared to N. Moreover, they found that the states introduced by C^{4-} and P^{3-} were too deep in the gap to overlap sufficiently with the band states of TiO_2 .

Di Valentin et al. (2005) suggested that two possibilities for N-doping exist, namely substitutional (N_s) and interstitial (N_i), as shown in Figure 2.3. Di Valentin et al. (2004) provided a detailed analysis on the possible reasons which lead to the photocatalytic activity in the anatase and rutile N- TiO_2 . They developed a model whereby 1, 2, 3 oxygen atoms and 1 or 2 oxygen atoms were substituted with nitrogen in the 96 atom anatase and 72 atom rutile supercells, respectively. An illustration of this anion replacement is depicted in Figure 2.4. They proposed that N- TiO_2 might be

stoichiometrically represented by $\text{TiO}_{2-x}\text{N}_x$, whereby the N concentration (x) was found to be $0.031 < x < 0.094$ and $0.042 < x < 0.084$, corresponding to anatase and rutile, respectively. They also highlighted that N_s had insignificant electronic changes since there were no noticeable changes in the structural aspect (i.e. bond length) of N-TiO₂ in anatase. To date, three possible mechanisms have been proposed for the visible light photocatalytic activity as exhibited by the N-TiO₂ (Beranek et al., 2007; Di Valentin et al., 2007), namely: (1) band gap narrowing, (2) production of N-dopant localized states slightly above the valance band maximum of the N-TiO₂, and (3) formation of oxygen vacancies. Furthermore, the debate on with XPS peaks (i.e. 396 eV or 400 eV) has yet to reach a consensus. Thus, it is important that future studies may aim to eventually resolve the above-mentioned ambiguities.

Figure 2.3 Schematic representation of N-TiO₂: (a) N_s, and (b) N_i (Di Valentin et al., 2005).

Figure 2.4 Schematic of N-TiO₂ crystal structure: (a) anatase, and (b) rutile (Di Valentin et al., 2004).

2.6 Syntheses of N-TiO₂

A comprehensive summary on the synthesis techniques of N-TiO₂, highlighting important details such as the physical characteristics of N-TiO₂, irradiation source, aqueous organic contaminants, experimental conditions and important findings is presented in Table 2.6. In general, synthesis of N-TiO₂ may be divided into two main groups, i.e. chemical methods and physical methods. Chemical methods include sol-gel, hydrothermal, solvothermal and CVD, while physical methods encompass direct current/radio frequency magnetron sputtering, ion beam assisted deposition, ion implantation and plasma surface modification.

Sol-gel method is the most commonly used chemical synthesis as it offers greatest flexibility to control the morphology of N-TiO₂, i.e. particles or films (dip-coating). Both Ti-organic and Ti-inorganic precursors may be used; the former involves TTIP and TBOT, while the latter involves TiCl₄ and Ti(SO₄)₂. Kisch et al. (2007) have attempted using Ti(OH)₄ because they postulated that the higher density of -OH groups may have better chemical interaction with N precursors and thus facilitate the N-doping process. The N precursor may be from N organic (e.g. TMAH, urea, thiourea, amines-groups and guanidine groups) and also N inorganic (e.g. NH₄OH, NH₄Cl, NH₄, (NH₄)₂CO₃, (NH₄)(HCO₃), NH₄NH₃). A range of calcination atmosphere has been used, namely air, N₂, mixture of N₂-NH₃ as well as mixture of NH₃-Ar. Several measures to aid in the sol-gel synthesis of N-TiO₂ include the provision of oxalic acid when urea is used (Gandhe et al., 2005), utilization of supercritical CO₂ (Horikawa et al., 2008), pH manipulation (Gole et al., 2004), and incorporation of surfactants that serve as pore templating material (Choi et al., 2007; Pelaez et al., 2009). Interestingly, while normal sol-gel method requires the calcination step, this procedure was not undertaken by Burda et al. (2003). Instead, they reported low temperature synthesis (at room temperature) where the N-TiO₂ was produced by vacuum drying at 5×10^{-2} Torr.

Table 2.6 Synthesis techniques of N-TiO₂ along with the PCD conditions and findings

References	Synthesis technique	Physical characteristics (crystal phase, N%)	Irradiation source; (aqueous organic pollutant & experimental conditions)	Findings
Abazović et al. (2008)	(i) Sol-gel: TTIP, ammonia solution, calcined at 400°C in air, (ii) Solid state chemistry: Ti(OH) ₄ (from TTIP), urea calcined at 400°C for 1 h.	Powder (anatase)	N.A.	Bandgap energy was lowered from 3.20 to 2.20 eV and the particle size of N-TiO ₂ nanoparticles ranged from 6-20 nm.
Ananpattarachai et al. (2009)	Sol-gel: TTIP, diethanolamine, triethylamine, and urea	Powder (anatase or anatase-rutile), (0.64-5.01 at%)	Visible-light (> 420 nm): 150 W Hg lamp (Sylvania), filtered through 1 M of sodium nitrate; (2-chlorophenol: 25 mg L ⁻¹ , photocatalyst dosage: 1 g L ⁻¹)	The highest PCD efficiency was achieved using N-TiO ₂ prepared using diethanolamine as N-dopant, with rate constant of 2.34 x 10 ⁻² min ⁻¹ .
Asahi et al. (2001)	Sputtering: TiO ₂ sputtered with gas mixture of N ₂ (40%)/Ar, calcined at 550°C, 4 h in N ₂ gas	Film (anatase, rutile)	Fluorescent lamp, 2.45 x 10 ⁻⁹ Einsteins ⁻¹ cm ⁻² , between 350-520 nm; (methylene blue)	N-TiO ₂ films exhibited increased hydrophilicity and photocatalytic activity under visible-light irradiation (< 500 nm).
Batzill et al. (2007)	Sputtering: N ₂ ⁺ low-energy ion implantation (600 eV - 1 keV), ca. 10 ¹⁵ ions cm ⁻²	(Powder) Single crystals rutile and anatase, respectively.	N.A.	N anion in the photocatalyst was found to be in -3 chemical state and occupied ca. 5% of the O-anions.
Beranek et al. (2007)	Solid-state chemistry: Ti(OH) ₄ and urea, calcined in air at 400°C for 0.5, 1, and 2 h.	Powder (anatase), 0.5, 1.0 and 11.7 wt%.	N.A.	Weak surface photovoltage under the visible-light irradiation occurred when air and hole scavenger was present and absent, respectively.
Burda et al. (2003)	Sol-gel: TTIP, triethylamine	Powder (anatase)	Femtosecond laser system (800 fs, 1 kHz, 120 fs laser pulse train); (methylene blue, solution volume: 2 mL, photocatalyst dosage: 5 g L ⁻¹)	Up to 8 at% of N was doped, and this led to the absorption of almost 600 nm in the visible-light spectrum.
Chi et al. (2007)	Solvothermal: TBOT, urea, heated in teflon-lined autoclave at 130°C for 6 h.	Spheres (anatase)	500 W xenon lamp with filters: visible light, $\lambda > 420$ nm, UV source: 250 < λ < 390 nm; (methylene blue: 8 mg L ⁻¹ , solution volume: 50 mL, photocatalyst dosage: 0.8 g L ⁻¹)	Urea played two major roles, namely as N-precursor and refining the mesoporosity properties of the N-TiO ₂ spheres.

References	Synthesis technique	Physical characteristics (crystal phase, N%)	Irradiation source; (aqueous organic pollutant & experimental conditions)	Findings
Choi et al. (2007)	Sol-gel (utilizing nitrogen-containing surfactant, i.e. the dodecylammonium chloride as the pore templating material and also nitrogen source)	Powder (anatase)	Visible-light: 2 nos. of 15 W fluorescent lamps, equipped with a UV block filter to ensure light irradiation with $\lambda > 420$ nm. UV: 2 nos of 15 W low-pressure mercury UV tubes ($\lambda_{\text{max}} = 365$ nm); (microcystin-LR: 5 mg L ⁻¹ , titania loading = 0.5 g L ⁻¹ , solution volume: 10 mL, temperature: 25 $\pm$ 3°C)	The mesoporous as-synthesized N-TiO ₂ which was calcined for 5 h could completely degrade microcystin-LR within 2 h. The N-TiO ₂ also exhibited good photocatalytic performance in removing microcystin-LR under UV irradiation.
Clouser et al. (2008)	Sol-gel with coating (added dropwise)	Thin film (anatase), 7.9 at% (as coated)	Visible-light: 130 W Xe lamp with UV filter; (stearic acid: 0.02 M, polyethylene glycol: 0.02 M)	The N-TiO ₂ thin film exhibited higher degradation rate for polyethylene glycol than that of stearic acid.
Cong et al. (2007)	Microemulsion-hydrothermal: TBOT, triethylamine, urea, thiourea, and hydrazine hydrate, heated in autoclaves at 120°C for 13 h.	Powder (anatase)	1000 W halogen lamp, glass cut-off filter of 420 nm; (rhodamine B: 20 mg L ⁻¹ , 2,4-dichlorophenol: 100 mg L ⁻¹)	Optimal N concentration (molar ratio of N/Ti: 2:1) resulted in the highest PCD efficiency.
Di Valentin et al. (2007)	Sol-gel: TTIP, NH ₄ Cl, NH ₃ , N ₂ H ₄ , NH ₄ NO ₃ , calcined at 500°C in air for 1h.	Powder (anatase)	N.A.	The N in the N-TiO ₂ (anatase) could either exist as neutral paramagnetic bulk N centers or as charged diamagnetic bulk N centers.
Diwald et al. (2004)	Sputtering: 80%/20% (N ₂ :Ar) gas (accelerating voltage of 3 kV, total fluence of 10 ¹⁷ ions cm ⁻²), annealing at 627°C in 3-5 h under ultrahigh vacuum condition.	Powder (rutile single crystals)	N.A.	N concentration in the first 200 Å at the surface of N-TiO ₂ was found to be 10 ²⁰ cm ⁻³ .
Duminica et al. (2007)	CVD: TTIP, N ₂ H ₄	Film (anatase, rutile)	52 W (2 units of fluorescent lamps), UV-cutoff filter at 400 nm, 3 mW cm ⁻² over 450-550 nm. UV: 125 W, 365 nm; (orange G)	Mixture of anatase-rutile crystalline phase was obtained at calcination temperature of 450-550°C.

References	Synthesis technique	Physical characteristics (crystal phase, N%)	Irradiation source; (aqueous organic pollutant & experimental conditions)	Findings
Dunnill and Parkin (2009)	Atmospheric pressure CVD: TiCl_4 , t-butylamine	Thin film (anatase), 0.3 at%	Visible-light: Full spectrum white light; (stearic acid: 0.01 M)	The N-TiO ₂ thin film exhibited greater hydrophilicity and visible-light photocatalytic activity as compared to TiO ₂ thin film.
Gandhe et al. (2005)	Sol-gel: TiCl_3 (15%), urea	Powder (anatase, rutile)	Solar light; (methylene blue: 10^{-4} M, solution volume: 100 mL, photocatalyst dosage: 5 g L ⁻¹ , pH 7.5)	Oxalic acid was found to govern the N content, crystal phase and porosity in the N-TiO ₂ .
Gole et al. (2004)	Sol-gel: TTIP, alkylammonium salts	Powder (anatase)	Laser excitation: 390 nm and 540 nm; (methylene blue)	The incorporation of trace Pd in chloride/nitrate salts increased the N uptake, resulting in red-shift.
Horikawa et al. (2008)	Sol-gel: TTIP, urea solution, calcined at N ₂ /NH ₃ for 2h.	Powder (anatase and brookite)	N.A.	Supercritical CO ₂ -assisted method yielded relatively high specific surface area (116 m ² g ⁻¹) and a total pore volume of 0.33 cm ³ g ⁻¹ .
Hu et al. (2010)	Sol-gel: TTIP, urea	Powder (anatase), 0.46 or 1.20 at%	Visible-light: 160 W Hg lamp, using 1 M NaNO ₂ solution as UV-filter; (methyl orange: 100 mg L ⁻¹ , photocatalyst dosage: 1 g L ⁻¹)	The best performing N-TiO ₂ was prepared from incorporating urea (0.15 mol L ⁻¹) into the Ti sol and the N-TiO ₂ exhibited ca. 50% removal of methyl orange in 4 h of irradiation time.
Huang et al. (2008)	Modified hydrothermal: TBOT, triethylamine, urea	Powder (anatase, rutile)	150 W tungsten Hg lamp, filter to include only 400-500 nm; (rhodamine B: 5.0 mg L ⁻¹ , solution volume: 100 mL, photocatalyst dosage: 1 g L ⁻¹)	Highest PCD effect observed for N-TiO ₂ (anatase : rutile = 4:1) was postulated to be due to the synergistic effect of its bicrystalline state.
Kisch et al. (2007)	Solid-state chemistry: $\text{Ti}(\text{OH})_4$ (from TiOSO_4), urea, calcined at 400°C for 1h.	Powder (anatase, brookite)	150 W Xenon arc lamp, 420 nm cut-off filter; (4-chlorophenol, hydroquinone, formic acid, solution volume: 15 mL)	N-doping resulted in the Fermi level of the electrons to shift in the range of 0.07-0.16 eV.
Kosowska et al. (2005)	Annealing: Amorphous TiO ₂ heated in NH ₃ gas for 4h in the range of 200-800°C.	Powder (anatase, rutile)	Visible light: 100 W lamp, 385 W m ⁻² ; (phenol: 100 mg L ⁻¹ , reactive red 198: 5 mg L ⁻¹ , solution volume: 500 mL, photocatalyst dosage: 0.2 g L ⁻¹)	Highest PCD performances for the phenol and dye were 6.55% and ca. 40-45%, respectively.

References	Synthesis technique	Physical characteristics (crystal phase, N%)	Irradiation source; (aqueous organic pollutant & experimental conditions)	Findings
Liu et al. (2009)	Solvothermal: TiCl_3 and hexamethylene tetramine, autoclave, heated to 90°C and temperature maintained for 1 h, and then heated to 190°C and temperature maintained for 2 h.	Powder (anatase or rutile anatase-rutile or anatase-brookite) (1.83-2.88 at%)	Visible-light ($> 420\text{ nm}$): 500 W Xe lamp with cut-off filter; (methyl orange: $1.0 \times 10^{-4}\text{ M}$, solution volume: 100 mL, photocatalyst dosage: 0.5 g L^{-1})	N- TiO_2 with anatase-brookite mixture exhibited the highest visible-light photocatalytic activity as compared to that of other samples and P25 for degradation of methyl orange.
Mwabara et al. (2004)	Sputtering: Direct current magnetron sputtering, pre-sputter with Ar for 5 min, followed by subsequent sputtering with Ar, N_2 , O_2 (N_2 flow was kept constant)	Thin film (anatase, rutile)	N.A.	Nitrogen gas flowrate ratio in the sputtering was varied from 0-0.025, and resulted in the nitrogen concentration to vary from 0-0.022.
Parida and Naik (2009)	Template free homogeneous co-precipitation: titanium oxysulfate sulfuric acid complex hydrate, urea.	Sphere (anatase) (0.56-0.91 at%)	Visible-light ($> 420\text{ nm}$), or UV ($> 380\text{ nm}$), in which the light source for both visible-light and UV was a 450 W Xe lamp; (methylene blue: 100 mg L^{-1} , methyl orange: 100 mg L^{-1} , photocatalyst dosage: 1 g L^{-1})	The N- TiO_2 spheres demonstrated higher degradation efficiency for dyes removal as compared to that of the bare TiO_2 and Degussa P25.
Pelaez et al. (2009)	Sol-gel (utilizing fluorosurfactant as pore template material which served as fluorine source and ethylenediamine as nitrogen source)	Powder (anatase)	Visible-light: 2 nos. of 15 W fluorescent lamps equipped with UV block filter to ensure $\lambda > 420\text{ nm}$; (microcystin-LR: 1 mg L^{-1} , 10 mL)	The performance of the N- TiO_2 for degradation of microcystin-LR under visible-light could be significantly improved through the co-doping of fluorine.
Peng et al. (2008a)	Hydrothermal: P25, triethanol amine, heated at 140°C for 24 h, followed by cooling, washing, and centrifuging and finally dried at 200°C in air for 10 h.	Powder (anatase, rutile)	1000 W, 1 M sodium nitrite as 400 nm cut-off filter; (methyl orange: 20 mg L^{-1} , solution volume: 200 mL, oxygen bubbling: 100 mL min^{-1} photocatalyst dosage: 0.1 g L^{-1})	The highest N concentration in the N- TiO_2 was 21% (molar ratio) and the XPS indicated Ti-N-O bonding (397.4 eV) and Ti-O-N bonding (400.3 eV and 402.5 eV).
Peng et al. (2008b)	Hydrothermal: P25, urea, heated at 1000 W, 2450 MHz for 10-30 min and heated at temperature above 135°C .	Powder (anatase, rutile)	1000 W, 1 M sodium nitrite as 400 nm cut-off filter; (methyl orange: 20 mg L^{-1} , phenol: 100 mg L^{-1} , solution volume: 200 mL, photocatalyst dosage: 0.2 g L^{-1})	Higher PCD performance under visible-light irradiation was obtained from interstitial N-doping as opposed to substitutional N-doping.

References	Synthesis technique	Physical characteristics (crystal phase, N%)	Irradiation source; (aqueous organic pollutant & experimental conditions)	Findings
Sakthivel and Kisch (2003)	Sol-gel: TiCl_4 , ammonia, ammonium carbonate, ammonium bicarbonate (400°C in air)	Powder (anatase)	150 W xenon arc lamp; (4-chlorophenol: $2.5 \times 10^{-4} \text{ mol L}^{-1}$)	The PCD efficiency of N-TiO ₂ and TiO ₂ was ca. 50% and less than 1%, respectively, under 6 h of visible-light irradiation.
Sathish et al. (2005)	Sol-gel: TiCl_3 , NH_3 , calcined at 400, 500, 600°C for 4 h in air.	Spherical (anatase)	400 W Hg lamp with 365, 405, 436, and 546 nm cut-off filters; (methylene blue: 110 mg L^{-1} , solution volume: 25 mL, photocatalyst dosage: 1 g L^{-1})	The absorbance edge was shifted from 380 nm to 550 nm following successful N-doping into TiO ₂ .
Subagio et al. (2010)	Sol-gel using TTIP and polystyrene spheres, NH_4OH (25%), calcined at 500°C for 2 h in air.	Hollow sphere (anatase)	Blue light LED ($\lambda_{\text{max}} = 465 \text{ nm}$), green light LED ($\lambda_{\text{max}} = 523 \text{ nm}$), and yellow light LED ($\lambda_{\text{max}} = 589 \text{ nm}$) (bisphenol-A: 5 mg L^{-1} , solution volume: 400 mL, photocatalyst dosage: 0.5 g L^{-1})	The N-doped hollow sphere titania could achieve 90% degradation efficiency for BPA removal in 2 h under blue light irradiation.
Wang et al. (2005)	Sol-gel with subsequent hydrothermal: TBOT, ammonia solution (25%), subsequent heating in autoclave at 400, 500, 600, 700, 800°C for 1 h.	Powder (anatase, rutile)	1000 W Xe lamp, 400 nm glass filter; (phenol: 20 mg L^{-1} , solution volume: 1000 mL, photocatalyst dosage: 0.5 g L^{-1})	N-TiO ₂ exhibited higher PCD activity as compared to P25 under visible-light irradiation, while the converse was true under solar light irradiation.
Wang et al. (2006)	Solvothermal: TiCl_3 , diethylamine, triethylamine, ethylenediamine, heated at 140°C for 96 h	Powder (anatase, rutile)	100 W, high pressure Hg lamp, cut-off filter 420 nm; (phenol: 40 mg L^{-1} , solution volume: 220 mL, photocatalyst dosage: 1 g L^{-1})	97.88% of phenol was removed under 6 h of visible-light irradiation using N-TiO ₂ with ethylenediamine as N-precursor.
Wang et al. (2007a)	Sol-gel: TTIP, NH_4OH , calcined at 250, 350, 450, 550, and 650°C for 2h	Powder (anatase)	40 W tungsten bulb, 400-2500 nm; (methylene blue: 30 mg L^{-1} , solution volume: 200 mL, photocatalyst dosage: 0.9 g L^{-1})	Bandgap energy was increased from 1.55 to 2.95 eV because N content decreased when calcination temperature was increased.
Wang et al. (2007d)	Sol-gel: TBOT, NH_4OH (25%), nitric acid, ethanol	Powder (anatase)	125 Xe lamp; (benzoic acid: 25 mg L^{-1} , solution volume: 1250 mL, photocatalyst dosage: 0.1 g L^{-1} , air bubbling)	The absorbance onset for N-TiO ₂ was shifted to ca. 459 nm and the N 1s peak was detected at both 396.6 eV and 400.9 eV.

References	Synthesis technique	Physical characteristics (crystal phase, N%)	Irradiation source; (aqueous organic pollutant & experimental conditions)	Findings
Wang et al. (2010)	Liquid phase deposition: $(\text{NH}_4)_2\text{TiF}_6$, urea, using anodic alumina membrane as template	Nanotube array film (Anatase)	Visible-light: HP Hg lamp, with UV filter (< 410 nm), UV: HP Hg lamp, with UV filter (< 290 nm); (methylene blue: 50 mg L^{-1} , solution volume: 100 mL)	The photocatalytic activity of N-TiO ₂ nanotube array film under visible-light and UV irradiation was greater than that of TiO ₂ nanotube array film by ca. 3 and 1.5 times, respectively.
Wu et al. (2005)	Ion-beam assisted deposition: TiO ₂ evaporation rate ca. 0.1 nm s^{-1} , ion accelerating voltage 300 V , ion-beam voltage 500 V , working pressure ca. $5.0 \times 10^{-5} - 3.0 \times 10^{-4}$	Film (anatase)	N.A.	An extremely high N concentration in the N-TiO ₂ was obtained, i.e. ca 30 at%.
Xu et al. (2008b)	Template-free hydrolysis technique	Microtubes (Anatase), 2.9 at%	Visible-light: 420 nm (8 nos), UV: 254 or 365 nm (8 nos, respectively) ; (phenol: 60 mg L^{-1} , methyl orange: 20 mg L^{-1} , solution volume: 50 mL , dosage: 1 g L^{-1} , air bubbling)	The PCD efficiency as exhibited by N-TiO ₂ microtubes under visible-light irradiation was higher than that of P25 for both the degradation of phenol and methyl orange.
Yamada et al. (2006)	Plasma surface modification: TiO ₂ ST01, rotation 20 rpm , discharge power of $100\text{--}400 \text{ W}$, discharge time of $2\text{--}20 \text{ min}$, treated with Ar and N ₂ plasma in series.	Film (anatase)	500 Xe lamp, with cut-off filters of 420 nm and 750 nm ; (methylene blue)	The duration of plasma irradiation governed the concentration of N doped into the film, and the visible-light photocatalytic activity was due to the Ti-N bonding in N-TiO ₂ .
Yang and Gao (2008)	Solvothermal: TiCl ₄ , TBOT, heated in 180°C and 220°C for 24 h .	Powder (rutile)	300 W , cut-off filters at 400 nm ; (methylene blue: 20 mg L^{-1} , solution volume: 400 mL , photocatalyst dosage: 0.04 g L^{-1} , oxygen bubbling)	Visible-light photocatalytic activity was dependent on the concentration of doped nitrogen, morphology and also the crystallinity of the N-TiO ₂ .
Yang et al. (2004)	Ion assisted electron beam: TiO ₂ (99.99%), base pressure $< 8.0 \times 10^{-4} \text{ Pa}$, O ₂ atmosphere of $6.7 \times 10^{-3} \text{ Pa}$, substrate temperature 300°C , N ₂ gas, ion gun voltage -1000 V , beam current 10 mA , deposition rate of 0.2 nm s^{-1}	Thin film (rutile)	Fluorescent lamp, power density of 4.12 mW cm^{-2} , 550 nm ; (methylene blue)	The highest PCD efficiency at rate constant, $k = 0.293 \text{ h}^{-1}$ was obtained from using the N-TiO ₂ (1.8 at% N), which was synthesized under N ₂ partial pressure of $3.1 \times 10^{-2} \text{ Pa}$.

Note: N.A. = Not applicable

Hydrothermal (Peng et al., 2008a) and solvothermal (Chi et al., 2007; Liu et al., 2009) techniques have also been conducted. Although Ti-organic (TBOT) and Ti-inorganic (TiCl_3 , TiCl_4 , TiSO_4) are usually used, direct employment of P25 has also been attempted. This raises the question of whether N-doping may encounter any form of resistance since it is expected that nitrogen would be more difficult to be doped into the lattice of TiO_2 once its complete crystal structure has formed. In addition, a separate procedure of N-doping following post- TiO_2 synthesis was performed by Yang and Gao (2008). Recently, modifications of hydrothermal and solvothermal methods have been attempted, such as the microemulsion-hydrothermal (Cong et al., 2007), hydrothermal coupled with sol-gel (Huang et al., 2008) and homogeneous precipitation-solvothermal process (Yin et al., 2005). CVD appears to be the least attempted chemical method, most possibly due to the difficulty in providing the suitable nitrogen precursors and the bulky experimental rigs required. Nevertheless, Duminica et al. (2007) had reported CVD method for N- TiO_2 synthesis using TTIP and hydrazine (N_2H_4). Physical methods involving direct current/radio frequency magnetron sputtering, ion beam assisted deposition, ion implantation, plasma surface modification are superior in terms of producing accurate thickness of N- TiO_2 thin films. However, these techniques usually require highly advanced equipments which are expensive and non-compact. High energy consumption associated with the production of highly energetic N ions may be a drawback for production at industrial scales. Recently, it is reported that N- TiO_2 has been made available commercially (TPS 201, Sumitomo Chemicals, Japan) (Zhang et al., 2009).

2.7 Characterization of N- TiO_2

N- TiO_2 may be characterized from various aspects by using specific characterization equipments. These include structural and mineralogy (XRD), physical properties (BET/BJH analysis, TG-DTG analysis), surface chemistry (XPS, FTIR, Raman spectroscopy, secondary ion mass spectrometry, UV photoelectron spectroscopy, scanning tunneling microscopy, atomic force microscopy and goniometry), photoactivity or optical properties (UV-Vis DRS, photoluminescence), morphology (SEM/elemental mapping/EDX, FESEM, TEM/HRTEM), and photoelectrochemical

properties (electron spin resonance, surface photovoltage spectroscopy and current-voltage measurements). It has been reported that the doping of nitrogen into TiO₂ may not induce noticeable changes in the XRD pattern (Peng et al., 2008b). This result is consistent with the reported works of other researchers (Sathish et al., 2005; Li et al., 2006a). The presence of N-doping is also difficult to be detected using SEM, EDX, elemental mapping and TEM.

Thus, the N-doping should be verified using XPS, UV-Vis DRS and FTIR analyses. For XPS analysis, two types of N-doping have been reported, namely substitutional or interstitial. The former and latter are also known as atomic N or β -N (N 1s binding energy ca. 396 eV) and molecularly-chemisorbed N or γ -N₂ (N 1s binding energy at ca. 400 eV), respectively. The peak of 396 eV is associated with Ti-N (Saha and Tompkins, 1992). Some researchers reported that there were no Ti-N peaks observed in the XRD pattern for their as-synthesized N-TiO₂ nanoparticles (Wang et al., 2005; Huang et al., 2008), hence they postulated that O-Ti-N linkages were formed instead. Although Di Valentin (2007) argued that the N-TiO₂ nanoparticles prepared via sol-gel synthesis technique might not exhibit N 1s peak at 396 eV, several works by other researchers suggested otherwise (Miyauchi et al., 2004; Gandhe et al., 2005; Nosaka et al., 2005; Wang et al., 2007a; Li and Shang, 2008). On the other hand, some of the N 1s peaks at 396 eV as reported by some researchers (Irie et al., 2003; Wang et al., 2005) were not very eminent as they appeared to be affected by the background noise. Intriguingly, both substitutional and interstitial N-doping were found to induce enhanced PCD efficiency under visible-light irradiation (Peng et al., 2008b).

UV-Vis DRS is a superior characterization technique whereby the phenomenon of red-shift is observed through absorbance vs. wavelength (nm) plot, or alternatively the Kubelka-Munk plot, i.e. $[F(R_{\infty})E]^{1/2}$ vs. photon energy (eV). It is generally agreed that the eminent second absorption edge onset arising between 400-550 nm serve as the evidence of N-doping. This is a typical feature which confirms the phenomenon of increased visible-light photoresponsiveness. Many researchers employed the following equation to determine the bandgap energy following successful N-doping (Horikawa et al., 2008):

$$E_g = \frac{1240}{\lambda} \quad (2.10)$$

where E_g = bandgap energy (eV), and λ = absorption wavelength (nm)

However, it appears that there is no standard technique to determine the extrapolation of the absorbance onset to the horizontal axis of E_g . This has caused the quantitative comparisons of various E_g to be difficult. Another related aspect which merit attention is the amount of nitrogen for the optimum visible-light photocatalytic activity. Irie et al. (2003) reported that there was an optimum amount of nitrogen, whereby excess nitrogen content would lead to a decrease in PCD efficiency since the N-doping sites could become charge carriers recombination sites. In contrast, Liu et al. (2006b) attributed high PCD performance to the high nitrogen content (21.38 at%) in the photocatalyst.

From FTIR examinations, in addition to the usual bands at 1630 cm^{-1} , 3500 cm^{-1} (attributed to the bending and stretching of $-\text{OH}$, respectively) and below 500 cm^{-1} (ascribed to TiO_2 characteristic peaks), some new peaks related to N-doping have been observed. These include the presence of hyponitrite ions $(\text{N}_2\text{O}_2)^{2-}$, at ca. 1060 , 1104 , 1387 cm^{-1} (Sakthivel et al., 2004; Peng et al., 2008b) as well as nitrite peaks at 1160 , 1261 and 1450 cm^{-1} (Sakthivel et al., 2004). Interestingly, Li et al. (2006a) attributed 1386 cm^{-1} peak to the surface adsorbed NH_3 . It appears that thus far no agreement has been reached regarding the origin of peak position at ca. 1386 cm^{-1} . Nevertheless, it is generally agreed that the hyponitrite ions are responsible for the $\gamma\text{-N}_2$ (N_{1s} at 400 eV).

2.8 Photocatalytic activity of N-TiO₂

Due to the enhancement of photoresponsiveness under visible-light (generally in the wavelength region of $400\text{-}550\text{ nm}$), the N-TiO₂ nanoparticles have been found to exhibit greater photocatalytic activity under visible-light irradiation as compared to the bare TiO₂. In general, the extent of photocatalysis of an organic pollutant may be evidenced through the degradation of the pollutant, the degree of mineralization based on TOC analysis, or formation of intermediates or byproducts.

For example, Subagio et al. (2010) revealed that at pH 6.0, the BPA degradation efficiencies as exhibited by the N-doped TiO₂ hollow sphere, bare TiO₂ hollow sphere and Hombikat TiO₂ under 6-h of blue light irradiation (using light emitting diode (LED) strips) were 99%, 90% and 80%, respectively. It is worth noting that the N-doped TiO₂ hollow sphere could achieve 90% of BPA degradation efficiency within 2 h of blue light irradiation. In addition, the TOC removal efficiencies as achieved by N-doped TiO₂ hollow sphere, bare TiO₂ hollow sphere and Hombikat TiO₂ after 6 h of blue light irradiation were 66%, 49%, and 52%, respectively. Several intermediate compounds were detected in the solution (i.e. isopropanolphenol, 4-hydroxyacetophenone, 4-isopropylphenol and 4-isopropenylphenol), thus further confirming the mineralization effect as induced by the visible-light photocatalysis.

Huang et al. (2008) reported that their as-synthesized N-TiO₂ powder (anatase : rutile = 4:1) could achieve 41.4% of mineralization for rhodamine B after 8-h irradiation of visible-light. In contrast, there was no TOC removal under the same irradiation period in the case of bare TiO₂. Chi et al. (2007) reported that their N-TiO₂ sphere (prepared using molar ratio of urea to TBOT = 3:1) could achieve ca. 57.5% removal of methylene blue within 6 h of irradiation time. In comparison, the bare TiO₂ and Degussa P25 could only achieve degradation efficiencies of ca. 20% and 18%, respectively. Wang et al. (2005) revealed that the extent of mineralization for phenol as exhibited by their as-synthesized N-TiO₂ (calcined at 400°C) was 35.6% within 2 h of visible-light (> 400 nm) irradiation, while that of P25 was insignificant (< 2.5%). The concentrations of intermediates such as lactic acid, acetic acid, formic acid, and hydroquinone generally increased during the initial hours of irradiation period, but consequently decreased. This indicated that a complete treatment could potentially be achieved since the intermediates were also removed from the solution. Sakthivel and Kisch (2003) reported that PCD efficiencies for 4-chlorophenol degradation, as exhibited by the N-TiO₂ and TiO₂, were ca. 50% and < 1%, respectively.

Choi et al. (2007) had reported the efficient degradation of microcystin-LR using their mesoporous N-TiO₂ prepared via sol-gel surfactant-assisted synthesis technique. Their as-synthesized N-TiO₂ exhibited remarkable PCD efficiency in removing microcystin-LR. In particular, one of their N-TiO₂ sample (which was prepared through calcination at 350°C for 5 h) could achieve almost complete degradation of microcystin-LR within

2 h under visible-light irradiation. In comparison, both the Degussa P25 and bare TiO_2 only exhibited ca. 10% of microcystin-LR degradation in 2 h under visible-light irradiation. Based on their derived apparent reaction rate constants, the photocatalytic removal of microcystin-LR at pH 3.5 was ca. 2.5 times greater than that of the removal at pH 5.7. This is because at acidic conditions, electrostatic attractions occurred between the positively-charged N- TiO_2 and the negatively-charged microcystin-LR species, thus facilitating the adsorption of microcystin-LR onto the surface of N- TiO_2 for degradation. Interestingly, their N- TiO_2 powders also performed better than that of the bare TiO_2 powders under UV irradiation. They ascribed these results to the enhanced structural properties of the former as compared to the latter. A more recent study by Pelaez et al. (2009) revealed that their N-F co-doped TiO_2 exhibited higher degradation efficiency of microcystin-LR under visible-light irradiation as compared to N- TiO_2 . The reason was due to the synergistic effect of the nitrogen- and fluorine-doping. This suggests potential improvement of N- TiO_2 through incorporation of other suitable dopants.

Notwithstanding the proven visible-light photocatalytic activity of N- TiO_2 nanoparticles, there remains several pertinent aspects which merit discussion. First, there is a variation in the amount of nitrogen doped into TiO_2 (as reported in the literature) which led to the good visible-light photocatalytic activity. For example, Yang et al. (2004) reported that the best PCD efficiency was achieved using the rutile N- TiO_2 (nitrogen amount of 1.8 at%) for the removal of methylene blue, but Burda et al. (2003) revealed that their N- TiO_2 (nitrogen amount of 8 at%) was efficient for degradation of methylene blue. Meanwhile, Cong et al. (2007) reported that an optimum N:Ti molar ratio of 2:1 in their as-synthesized N- TiO_2 would result in the highest photocatalytic degradation for rhodamine B and 2,4-dichlorophenol. Understandably, there would be no consensus on the suitable amount of nitrogen to be doped into TiO_2 , since the N- TiO_2 nanoparticles were synthesized using different synthesis techniques. However, it is likely that for a same synthesis technique of producing N- TiO_2 , there exists an optimum amount of nitrogen in the TiO_2 which would yield the maximum PCD efficiency for pollutant removal.

Second, most of the highly-efficient N- TiO_2 nanoparticles exhibit various unique morphologies/characteristics as induced from their varying synthesis techniques. For

example, hollow sphere N-TiO₂ (Subagio et al., 2010), nanoarray tube film (Wang et al., 2010), microtubes (Xu et al., 2008b), mesoporous microsphere N-TiO₂ (Cong et al., 2007) or powder N-TiO₂ with anatase-rutile mixture (Huang et al., 2008). It appears that further tailoring on the morphology or crystal phase of the N-TiO₂ may potentially result in enhanced PCD efficiency for pollutant removal. Apparently, the PCD efficiency is highly dependent on the type of synthesis technique employed.

Third, it is important that an appropriate model pollutant to be chosen for examining the visible-light photocatalytic activity of N-TiO₂ in the future. It can be observed from the literature that the majority of researchers who conducted N-TiO₂ studies attempted dye-based pollutants such as methylene blue (Burda et al., 2003; Gole et al., 2004; Yang et al., 2004; Gandhe et al., 2005; Sathish et al., 2005; Yamada et al., 2006; Chi et al., 2007; Wang et al., 2007a; Yang et al., 2008a; Wang et al., 2010), rhodamine B (Cong et al., 2007; Huang et al., 2008), orange G (Duminica et al., 2007), reactive red (Kosowska et al., 2005), and methyl orange (Peng et al., 2008a; Hu et al., 2010). Though, phenolic compounds such as phenols (Kosowska et al., 2005; Wang et al., 2005) or chlorophenols (Sakthivel and Kisch, 2003; Cong et al., 2007; Kisch et al., 2007; Ananpattarachai et al., 2009) and acids such as stearic acid (Dunnill and Parkin, 2009), formic acid (Kisch et al., 2007) or benzoic acid (Wang et al., 2007d) were also investigated. It is worth noting that there are some issues highlighted pertaining to the usage of methylene blue as the model pollutant, especially for evaluating the PCD efficiency under visible-light irradiation (Yan et al., 2006). This is because methylene blue (and possibly other dyes) may exhibit photosensitization effect. Thus, this may cause some possible ambiguities in the interpretation of the visible-light photocatalytic activity of the as-synthesized N-TiO₂. On the basis of the above-mentioned reason, it is imperative that future researchers working on the N-TiO₂ photocatalysis area to consider selecting colorless pollutants as their model pollutants.

Chapter 3 Materials and Methods

3.1 Materials and synthesis techniques

3.1.1 Chemicals and materials

All chemicals employed in this study were analytical grade. Titanium tetraisopropoxide (TTIP) (Assay (ex Ti) 100.5%), absolute ethanol (Assay 99.9%), urea (Assay 99.8%), hydrochloric acid (HCl, Assay 37-38%) and phosphoric acid (H_3PO_4 , Assay 85%) were procured from Merck. Sodium hydroxide (NaOH, Assay 97%) was purchased from Scientific Resources. Powdered AC (Norit SA UF) was purchased from Behn Meyer (Singapore) and was pre-treated in 1.0 M NaOH overnight and vacuum-dried prior to usage. Its d_{50} , which denotes the 50% of the cumulative AC particle size distribution, was 5 μm .

The aqueous solutions of target pollutants, namely BPA, SMZ and CFA were prepared using BPA (Merck, Assay 97%), SMZ (Sigma Aldrich, Assay 99%) and CFA (Sigma Aldrich, Assay 97%). Solutions of inorganic anions such as chloride, nitrate, sulfate, bicarbonate, phosphate and silica were prepared from NaCl (Merck, Assay 99%), NaNO_3 (Merck, Assay 99.5%), Na_2SO_4 (BDH, Assay 99%), NaHCO_3 (Merck, Assay 99.5%), $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma Aldrich, Assay 99%), and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich, Assay 98%). Oxalate solution was prepared from $\text{Na}_2\text{C}_2\text{O}_4$ (Sigma Aldrich, Assay 99%). Acetonitrile (Assay 99.9%) and ethyl acetate (Assay 99.9%) were obtained from Fisher. Hydrogen peroxide (H_2O_2) (Assay 30%) was procured from Sigma Aldrich. Degussa P25 was provided by Jebsen & Jessen Chemicals (S) Pte Ltd. Milli-Q ultrapure water (UPW) (18.2 M Ω .cm) was used for all the experiments. Hombikat TiO_2 was purchased from Sigma Aldrich.

3.1.2 N-TiO₂/AC prepared via single-stage calcination

The N-TiO₂/AC composite was prepared using the modified sol-gel technique. 4 mL of TTIP was dissolved in 60 mL of absolute ethanol and this solution was denoted as solution A. Another solution was prepared by mixing 40 mL of absolute ethanol with 3 mL HCl and this solution was denoted as solution B. Solution B was added dropwise to solution A. 400 mL of UPW was added dropwise and the resulting solution was left to mix. The virgin AC (as received) was first rinsed with UPW and subsequently pre-treated in NaOH (1.0 M) solution for at least overnight. The pre-treated powdered AC was immersed into the solution, left to homogenize and the resulting solution was gradually heated to form gel-coated precipitates. After the resulting solution was cooled to the room temperature, 26.4 mL of urea solution (2.0 M) was added. The gel-coated precipitates were centrifuged and vacuum-dried. Two repeating coatings were conducted to ensure a greater coverage of N-TiO₂ nanoparticles on AC surface. Finally, the vacuum-dried precipitates were calcined in single stage calcination. The as-synthesized composite is denoted as (aM), where a denotes the calcination temperature, and M denotes the 2 h calcination under air atmosphere in a muffle furnace.

3.1.3 N-TiO₂/AC prepared via two-stage calcination

The synthesis technique is the same as that of described in Section 3.1.2, except that an additional calcination step in a different atmosphere was further introduced. The as-synthesized composites are denoted by (aM-bT), where both a and b denote the calcination temperature, while M denotes the 2 h calcination under air atmosphere using muffle furnace and T denotes 2 h calcination under NH₃/N₂ atmosphere in a tube furnace.

3.1.4 Bimodal N-P25-TiO₂/AC prepared via facile synthesis technique

The bimodal N-P25-TiO₂/AC composite was synthesized via the modified sol-gel technique. In general, the current synthesis technique was a modification of the technique as described in Section 3.1.3, i.e. with the following modifications: without urea, with addition of P25 powders, single-coating process instead of three coatings, and single-stage calcination instead of two-stage calcination in different atmospheres. Thus, the advantage of the current synthesis method is that it is a facile method, involving lesser preparation steps and less chemicals leading to an overall cost-saving even with the addition of P25. In this synthesis technique, different amounts of P25 and AC were added into the titania sol to yield different loadings of bimodal titania on AC. All the N-P25-TiO₂/AC composites were directly calcined under mixed NH₃/N₂ atmosphere at 700°C for 4 h in a tube furnace. The as-synthesized bimodal N-P25-TiO₂/AC composite is denoted as N-P25-TiO₂ (x+y)/AC whereby x denotes the weight percentage (wt%) of the N-doped P25 and y denotes the wt% of N-doped TiO₂ (sol) as produced from the titania sol. The total loading of N-P25-TiO₂ (wt%) in the resulting composite could be determined via gravimetry method, i.e. calcining the sample at 700°C for 2 h under air atmosphere in a muffle furnace to decompose the AC into ash (ca. 3 wt%). The values of x and y were stoichiometrically determined. For comparison, two additional types of N-P25-TiO₂/AC samples were prepared. The first sample was prepared with the addition of urea (during sol-gel synthesis stage) and this sample is denoted as N-P25-TiO₂ (x+y)/AC-U. The second sample was synthesized via the similar technique except that the P25 was only added into the aqueous solution to mix with the pre-coated composite (i.e. coated with titania sol only and dried), and this composite is denoted as N-P25-TiO₂ (x+y)/AC-Pseudo.

3.2 Characterization techniques and analytical methods

3.2.1 Characterization

The X-ray diffraction (XRD) patterns were obtained at a scanning rate of $0.8^{\circ} \text{ min}^{-1}$ from $2\theta = 5^{\circ}$ to $2\theta = 80^{\circ}$ with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) using a Bruker AXS (D8 advance) X-ray diffractometer operated at 40 kV voltage and 40 mA current. The nitrogen adsorption-desorption experiments for porosimetry were conducted at 77 K using QuantaChrome Autosorb-1 Analyzer. Prior to the measurements, all samples were outgassed at 200°C under nitrogen gas flow for at least overnight to ensure that the samples are thoroughly dried. The specific surface area was determined from the adsorption isotherm using Brunauer-Emmett-Teller (BET) method, while the pore volume and pore size distribution were determined from the desorption isotherm using Barrett-Joyner-Halenda (BJH) method. The absorbance spectra of solid samples were obtained using UV-Vis spectrophotometer (Perkin Elmer, Lambda 35) equipped with an integrating sphere accessory.

The X-ray photoelectron spectroscopy (XPS) spectra were determined using a KratosAXIS Ultra spectrometer, operating with Al-K α X-ray (1486.71 eV). All binding energies for elements of interest were calibrated with reference to the adventitious carbon (C 1s = 284.8 eV). All XPS peaks were fitted using Shirley background together with Gaussian-Lorentzian function. The Fourier transform infrared spectroscopy (FTIR) analysis was obtained using a FTIR spectrometer (Perkin Elmer 2000). Briefly, 0.0020 g of sample was mixed with 0.275 g of potassium bromide. In order to produce the pellet for analysis, the mixture was initially subjected to a hydraulic pressure of 1 ton for 1 min, and then the pressure was subsequently increased to 10 ton pressure for another 1 min. FTIR spectra were analyzed from wavenumber 4000 to 400 cm^{-1} . For the electrophoretic mobility measurement, Zetasizer (Malvern Nano ZS) was used to determine the pH_{IEP} of samples. The sample dosage used was 0.25 g L^{-1} , and the pH of the suspension was adjusted with dilute HCl or NaOH solutions. Particle size analyzer (Malvern 2000) equipped with sample dispersion unit (Hydro 2000S) was used to determine the particle size distribution from 0.02 to $2000 \text{ }\mu\text{m}$.

Scanning electron microscopy (SEM) images combined with elemental mapping/energy dispersive X-ray (EDX) spectra were obtained using a JSM-6360 microscope equipped with JED-2300 X-ray analyzer (with tungsten electrode source) and the operating voltage was in the range of 0.5-30 kV. Prior to the analysis, the samples were coated with gold using sputter coater to reduce the effect of surface charging. Transmission electron microscopy (TEM) images were obtained using JEOL JEM-2100F microscope, operating at an acceleration voltage of 200 kV. To investigate the degree of crystallinity of the samples, selected area electron diffraction (SAED) was also performed. Prior to the TEM analysis, the samples were ultrasonicated in ethanol for about 10 min and then the samples were transferred to a copper grid with carbon film.

The thermal stability of the pre-treated AC was examined using thermogravimetry analyzer (Perkin-Elmer). The bulk N-TiO₂ (wt%) in AC was quantified using the gravimetric method, i.e. ashing the composite under air atmosphere in a muffle furnace at 700°C for 2 h.

3.2.2 Analysis of BPA, SMZ and CFA

The concentrations of aqueous BPA, SMZ and CFA were analyzed using a high performance liquid chromatography (HPLC) (Perkin Elmer), in which a C18 column (Inertsil ODS-3, 4.6 mm i.d. x 150 mm length, 5 μ m) was used. A UV-Vis detector was employed and 225 nm, 270 nm, and 228 nm were set as the detection wavelength for BPA, SMZ and CFA, respectively. For analysis of BPA, the mobile phase was UPW/acetonitrile (20:80, v/v). For analysis of SMZ, the mobile phase was UPW (pH adjusted with H₃PO₄ to pH 2.5)/acetonitrile (75:25, v/v). For analysis of CFA, the mobile phase was UPW (pH adjusted with H₃PO₄ to pH 2.5)/acetonitrile (50:50, v/v). The flowrate used for the analysis of these pollutants was 1 mL min⁻¹. All calibrations were conducted using five known standards which sufficiently covered the range of sample concentrations. The coefficients of determination (R²) obtained from the all calibration curves were at least 0.999. Prior to analysis, all samples were filtered through 0.45 μ m cellulose acetate membrane syringe filter.

3.2.3 Analysis of chloride, sulfate, nitrate, acetate, formate and oxalate

The concentrations of chloride, sulfate, nitrate, acetate, formate, and oxalate were determined using ion chromatograph (IC, Dionex ICS-1000). The Dionex equipment system was equipped with an autosampler, a 4-mm IonPac AS15 analytical column, a 4-mm IonPac AG15 guard column, and a 4-mm ASRS-ULTRA II suppressor. The eluent used was potassium hydroxide.

3.3 Experimental procedures

3.3.1 Adsorption experiments

All the batch adsorption isotherm and kinetic studies for the model pollutant was carried out in the dark in order to eliminate the effect of photocatalysis. Solution pH was adjusted as necessary using diluted HCl or NaOH solutions. The conditions for adsorption studies, such as sample dosage, solution pH, equilibrium time, and temperature are provided in the associated figures shown in the Chapter 4, 5 and 6. The sampled aliquots were filtered through 0.45 μm cellulose acetate membrane syringe filters. The extent of pollutant adsorption by the samples at equilibrium, S (mg g^{-1}), was calculated using the following equation:

$$S = \frac{(C_i - C_e)V}{W} \quad (3.1)$$

where C_i = initial concentration of the model pollutant (mg L^{-1}), C_e = equilibrium concentration of the model pollutant after adsorption in the dark (mg L^{-1}), V = solution volume (L), and W = the mass of the sample used (g).

In order to obtain S_{max} and K_{ads} values, the experimental data from the adsorption isotherm experiments was fitted into the linearized form of the Langmuir adsorption isotherm model.

3.3.2 Desorption experiments

The temperature-dependent desorption of various model pollutants was investigated in the dark using an incubator shaker. The conditions for desorption studies, such as sample dosage, equilibrium time, and temperature are provided in the associated figures shown in the Chapter 5. All sampled aliquots were filtered using 0.45 μm cellulose acetate membrane syringe filters.

3.3.3 Photocatalytic degradation experiments

All photocatalytic testings were carried out after the adsorption equilibrium in the dark had been reached. PCD studies were conducted using a solar simulator (Newport, USA) equipped with a 150 W Xe arc lamp (Figure 3.1).

Figure 3.1 Photo of the Newport solar simulator used in this study.

The light intensity of the simulated solar spectrum was ca. 1000 W m^{-2} (as measured using digital power meter, EDTM). Dichroic mirrors were used to control light wavelengths in specific ranges of UV irradiation (280-400 nm) and visible-light irradiation (420-630 nm). For visible-light (420-630 nm) experiments, an additional polycarbonate filter was used to further minimize UV intensity. The UV and visible-light intensities were ca. 65 W m^{-2} and 400 W m^{-2} , respectively. In Chapter 4, the initial concentration of BPA used was 36 mg L^{-1} . In Chapter 6, the initial

concentration of SMZ used was 30 mg L^{-1} . All other experimental conditions such as solution volume, solution pH, composite dosage were provided in the associated figures in the respective chapters. The solution pH was adjusted as necessary using diluted HCl or NaOH solutions. During the PCD experiments, aeration by air bubbling was not provided and a quartz cover was provided on top of the borosilicate glass photoreactor to minimize evaporation. Aliquots were sampled at pre-determined time intervals. Mineralization measurements were carried out using total organic carbon (TOC) analyzer (Shimadzu, ASI-V). Turbidity of solutions was measured using a turbidimeter (HACH, 2100N).

3.3.4 Solar photocatalytic regeneration experiments

The experimental protocol for SPR involved three major steps, namely, adsorbate loading to the composite, regeneration of the spent composite, and evaluation of subsequent adsorption capacity of the regenerated composite. Briefly, the N-TiO₂/AC composite was loaded with the BPA, SMZ or CFA (single pollutant system) in the dark following the same method as described in Section 3.3.1.

The composite was loaded with the model pollutant to its maximum loading possible. The adsorption equilibrium period was 12 h to ensure that the pollutant had migrated into the internal AC sorption sites and achieved a uniform saturation of the AC throughout. The dosage of the composite during the adsorbate loading was the same as that used for establishing the adsorption isotherm. The spent N-TiO₂/AC composite was then filtered using 0.45 μm cellulose acetate filter paper, recovered, oven-dried at 80°C overnight and used in the SPR experiment.

The light source used for all the SPR experiments was a solar simulator (Suntest CPS+, Atlas) equipped with a 1500 W Xe lamp and a temperature control system (as shown in Figure 3.2). The solar simulator can generate solar light intensity in the range of 250 W m^{-2} (e.g. overcast day) to 765 W m^{-2} (e.g. bright sunny day).

Figure 3.2 Photo of the Suntest CPS+ solar simulator used in this study.

The setup and the custom-made glass-covered test cells for SPR, along with the derivation of the areal loading are shown in Figure 3.3. In a typical SPR experiment, the spent composites were added into 10 mL of UPW in each of the test cells. The UPW served as the pollutant carrier, source of $\bullet\text{OH}$ radicals, and also allowed for aliquots sampling for subsequent analysis of the pollutant concentration. Prior to light on, the composite would be allowed to settle down to the bottom of the test cells evenly. Since only the top layer of the composite would be exposed to the incident solar light, intermittent mixing (at appropriate time intervals) was provided to ensure that the whole spent composite in each test cell was uniformly regenerated at the end of the regeneration period. The dosage of the spent composite used in the SPR experiments was investigated as areal loading, whereby the areal loading is defined as the mass of spent composite per unit area of the bottom of the test cell (i.e. area irradiated with the simulated solar light).

Figure 3.3 SPR experimental set-up: (a) arrangement of glass test cells inside the CPS+ solar simulator, and (b) the spent N-TiO₂/AC composite as spread out on the bottom of a glass test cell (areal loading of 0.035 kg m⁻²) (note: the internal diameter of the bottom of glass test cell is 4.2 cm, thus the corresponding surface area is 13.85 cm². The areal loadings of 0.007, 0.018 and 0.035 kg m⁻² were calculated from the corresponding masses of the spent composite (i.e. 0.010, 0.025 and 0.050 g, respectively) per unit area of the bottom of test cell).

The SPR experiments were carried out for different durations of up to 24 h, and thereafter the regenerated composites were filtered using 0.45 µm cellulose acetate filter paper, rinsed with ultrapure water, recovered and oven-dried at 80°C overnight. The regenerated composites were then re-loaded with respective pollutants, in which the dosage of the regenerated composite remained quite unchanged because the regenerated composite could be fully recovered from the test cell. The regeneration efficiency (RE) for the spent N-TiO₂/AC composite is defined as follows:

$$RE = \frac{S_n}{S_0} \times 100\% \quad ; \quad n = 1, 2, 3 \quad (3.2)$$

where S_0 = adsorption capacity of the fresh N-TiO₂/AC composite [-], and

S_n = adsorption capacity of the regenerated N-TiO₂/AC composite at n cycle of SPR [-]

3.3.5 Thermal stability experiments

To investigate the thermal stability of the pre-treated AC, TG analysis was conducted using a thermogravimetry analyzer. The program used was as follows: ramping rate: 10°C min⁻¹ from 30°C to 900°C, gas used: purified air, and gas flow rate: 20 mL min⁻¹.

3.3.6 Photostability experiments

In this experiment, the freshly-prepared N-TiO₂/AC (400M-700T) composite and the virgin AC were respectively added into 250 mL of UPW at the dosage of 0.25 g L⁻¹. A 35-W (output power) UVA lamp (Labino), with maximum wavelength (λ_{max}) of 365 nm, was employed as the excitation source. UVA intensity at the surface of the solution was determined to be ca. 14.5 mW cm⁻² (measured using AccuMAX XRP-3000 radiometer). After irradiation by UVA at pre-determined time intervals, the solution samples were filtered through 0.45 μm cellulose acetate membrane syringe filter and the filtrate was analyzed using TOC analyzer. A similar experiment was also conducted using the virgin AC for comparison.

3.3.7 Photochemical stability experiments

The virgin AC (of comparable AC loading for the composite) was first mixed in 250 mL of UPW overnight to leach out organic impurities. The contaminated water was discarded. The recovered AC was washed thoroughly, and immersed in 250 mL solutions of 0.1, 1, 10 and 100 mM H₂O₂, respectively (prepared using UPW). The solution pH was adjusted to circumneutral pH (6.0 ± 0.4), and the slurry suspensions were irradiated for 3 h under simulated solar light (using the Newport solar simulator). A quartz cover was placed on top of the glass photoreactor to minimize evaporation. At the end of the experiments, the slurry solutions were filtered and the filtrates were analyzed using the TOC analyzer.

3.3.8 Physical stability experiments

Ultrasonication can produce high-energy acoustic cavitation in water, which leads to nucleation, growth and implosive collapse of bubbles (Suslick, 1990; Ince et al., 2001). It has been used in several industrial and environmental applications, e.g. for disintegrating the wastewater sludge (Khanal et al., 2007), surface cleaning of silica and mineral sands (Farmer et al., 2000; Zhao et al., 2007) and enhancing the leaching or extraction of inorganic and organic species from environmental samples (Luque-

García and Luque de Castro, 2003; Pumure et al., 2009). In this study, a new technique was developed to investigate the physical stability of the bimodal composite by introducing cavitation effect through ultrasonication. The principle behind this technique is based on the changes observed in the particle size distribution of the samples after the ultrasonication treatment.

The ultrasonicator used was Kudos (Model SK7210HP). The ultrasonication frequency was 53 kHz and the corresponding ultrasonic power was 350 W. The control experiment was the examination of particle size distribution of the virgin AC (as-received). A baseline was first determined by dispersing 0.10 g of N-P25-TiO₂ (20+15)/AC composite (without ultrasonication) in the sample dispersion unit (with 150 mL of UPW as dispersant) and analyzed for its particle size distribution. The suspension was then recovered and ultrasonicated using 40% of the ultrasonic power (i.e. 140 W) for 3, 6, 9 and 12 min, incrementally in stages, each followed by determination of the particle size distribution. As comparison, N-P25-TiO₂ (20+15)/AC-Pseudo was also analyzed by using the same experimental procedure.

Chapter 4 Nitrogen-doped TiO₂/AC Composite: Examination of Bifunctional Characteristics and Effect of Aqueous Matrix Species on the Removal of Bisphenol-A

4.1 Introduction

In this study, a bifunctional N-TiO₂/AC composite was developed. This unique composite potentially offers four-fold benefits for water and wastewater reclamation and reuse, namely (1) minimizes chemical consumption, (2) lowers carbon footprint, (3) removes various recalcitrant organic pollutants with diverse characteristics, and (4) produces zero-waste stream. BPA, which is both a plasticizer and an EDC, was chosen as a model pollutant for this study. BPA is used for the production of polycarbonate plastics, epoxy resins, flame retardants, baby bottles, adhesives, paints, coatings, lenses, and insulators for electrical or electronic items (Staples et al., 1998). BPA is a non-volatile hydrophobic pollutant with log K_{ow} of 3.40 (Leverkusen, 1989), Henry's constant of $1.0 \times 10^{-10} \text{ atm}\cdot\text{m}^3 \text{ mol}^{-1}$ (Howard, 1989), and high affinity for AC adsorption. It has been found ubiquitous in many water systems, and has been reported to be a potential toxicological threat to living organisms (Tsai, 2006; Kang et al., 2007).

For practical applications in water treatment, it is important that the as-synthesized N-TiO₂/AC composites continuously exhibit bifunctionality of adsorption-photocatalysis processes and also maintain satisfactory efficiencies under prolonged usage. It is worth noting that in real waters, the complexity of aqueous phase composition may greatly influence the removal efficiency of various pollutants. Cho et al. (2002) reported that the photocatalytic degradation of landfill leachates (at pH 4) was inhibited at high concentrations of Cl⁻, and Achilleos et al. (2010) found that the mineralization of diclofenac via photocatalysis was significantly reduced in municipal wastewater and groundwater as compared to the case of deionized water. Apparently, the co-existing aqueous species in real waters are likely to induce deleterious effects on photocatalysis. Thus, to evaluate practical application of photocatalysis in water

treatment, it is essential to assess the potential interferences induced by the presence of various aqueous species. Though there are some early studies on these aspects (Abdullah et al., 1990; Burns et al., 1999; Cho et al., 2002; Hu et al., 2003; Özkan et al., 2004; Achilleos et al., 2010), the effect of aqueous inorganic species on the photocatalytic activity of TiO_2 has not been adequately examined. Literature reporting the impacts of matrix species on the TiO_2/AC system is especially scarce, lacking in details and dealing with only UV photocatalysis (Sun et al., 2006; Sun et al., 2009). In addition, although silica is omnipresent in the aqueous systems, the effect of silica as a solution matrix species on photocatalysis of organic pollutants has not been sufficiently studied or understood. Given the bifunctionality of $\text{N-TiO}_2/\text{AC}$, it is envisaged that this composite would be less susceptible to the detrimental effects of the co-existing matrix constituents. The desirable application of $\text{N-TiO}_2/\text{AC}$ in water treatment serves as an impetus to examine the adsorptive-solar photocatalytic characteristics of this composite in the presence of various potentially interfering matrix species.

This chapter reveals the characteristics of $\text{N-TiO}_2/\text{AC}$ composites prepared via the sol-gel synthesis technique incorporating single-stage and two-stage calcination procedures (as mentioned in Chapter 3), and their bifunctional properties for the synergistic removal of BPA. The results showed that the $\text{N-TiO}_2/\text{AC}$ prepared via the single-stage calcination was inferior to that of the composite prepared via the two-stage calcination. Various pertinent aspects such as effect of light wavelength, influence of composite dosage, performance under repeated use and composite photostability were investigated in this study. Furthermore, the effects of common inorganic anions (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , H_2PO_4^- and silica), organic anion ($\text{C}_2\text{O}_4^{2-}$), photocatalysis inhibitor (CH_3OH), and oxidant (H_2O_2) on BPA degradation, as exhibited by the bifunctional $\text{N-TiO}_2/\text{AC}$, were discussed. Specifically, the effect of AC support on the synergistic removal of BPA in the presence of the above-mentioned interfering species was elucidated.

4.2 Experimental section

The chemicals, materials and methods used in this part of study have been described in Chapter 3. The composites used in this study were the N-TiO₂/AC prepared via the two-stage calcination technique (Section 3.1.3), while the composite prepared from the single-stage calcination (Section 3.1.2) was used as a comparison. The composites were characterized using XRD, porosimetry, UV-Vis spectrophotometry, electrophoretic mobility, XPS, SEM/EDX and TEM. In the first part of this study, photostability experiments using high-intensity UV irradiation were performed. In the second part, the adsorption and PCD performances of the composite for the synergistic removal of BPA were systematically evaluated using UPW as the aqueous phase. As comparison, N-TiO₂ nanoparticles were prepared using the same procedure but without addition of the AC. Bare TiO₂ powders were prepared using the same procedure but without addition of the urea and AC, and calcined under pure N₂ atmosphere (denoted as T-N₂). The virgin AC which was directly calcined at 700°C under NH₃/N₂ atmosphere for 2 h was denoted as AC (700T). In the third part, the influences of various aqueous matrix species (at various concentrations and different pH values) on BPA degradation were comprehensively studied.

Prior to synthesizing the N-TiO₂/AC composites, the pre-treated powdered AC was checked for its thermal stability under high temperature calcination in air. The TG/DTG analysis results revealed that the pre-treated AC exhibited good thermal stability at 400°C in air atmosphere (Figure 4.1). From the DTG analysis, it appeared that the temperature of ca. 450°C would be the incipient temperature for the gasification of pre-treated AC. It is worth noting that when the titania sol was coated onto the AC surface, this would further increase the thermal stability of the N-TiO₂/AC composite under calcination in air atmosphere at 400°C. This is because some portion of the calcination energy would be used to change the amorphous TiO₂ to crystalline state. Thus, the composite would indeed be able to withstand the thermal condition of the first-stage calcination in air. The second-stage of calcination was conducted in a non-oxidizing atmosphere (i.e. mixture of NH₃/N₂ gas), thus it would not result in the gasification of the AC support. For this reason, the two-stage calcination procedure was applicable for this study.

Figure 4.1 The investigation of thermal stability of the pre-treated powdered AC using TG/DTG analysis.

4.3 Results and discussion

4.3.1 Characteristics of N-TiO₂/AC composites

The physico-chemical properties of the various N-TiO₂/AC composites, as-synthesized TiO₂, N-TiO₂ as well as the commercial titania are shown in Table 4.1. As shown in Table 4.1, increasing the calcination temperature in the second-stage calcination led to only slight increment (< 10%) in the bulk N-TiO₂ content and minor reduction in the S_{BET} for N-TiO₂/AC composites. This was due to the insignificant AC mass loss resulting from high temperature calcination under the non-oxidizing atmosphere. The amount of nitrogen (Table 4.1) was largely dependent on the type of calcination condition. It can be observed that with the provision of NH₃/N₂ atmosphere, nitrogen content being doped into the N-TiO₂/AC (400M-700T) composite was enhanced by at least a factor of 2.0, when comparing to that of the N-TiO₂/AC (400M) composite.

Table 4.1 Physico-chemical characteristics of selected materials

Sample	Structural and mineralogy	Surface chemistry		Physical property		
	Crystallite size ^a (nm)	N ^b (at%)	pH _{IEP} ^c	N-TiO ₂ ^d (wt%)	S _{BET} ^e (m ² g ⁻¹)	V ^f (cm ³ g ⁻¹)
P25	25.0	-	-	-	57.8	0.14
Hombikat (Sigma-Aldrich)	22.8	-	-	-	57.9	-
TiO ₂ (400M-700T-N ₂)	24.8	-	5.6	-	1.15	0.007
N-TiO ₂ (400M-700T)	25.1	0.35	5.7	-	2.76	0.014
N-TiO ₂ /AC (400M)	7.3	0.63	-	29	591	0.31
N-TiO ₂ /AC (400M-500T)	10.6	1.29	-	31	556	0.27
N-TiO ₂ /AC (400M-600T)	19.5	1.37	-	33	548	0.25
N-TiO ₂ /AC (400M-700T)	24.4	1.43	6.7	37	536	0.25
Virgin AC (as received)	-	-	4.7	-	799	0.39
AC (700T)	-	1.84	-	-	810	0.35

(-) Data not available or not determined

^a Anatase crystallite size, estimated using Scherrer's equation (Debye and Scherrer, 1917)^b Determined using XPS^c Determined using Zetasizer^d Bulk composition of N-TiO₂ in composite, as determined via gravimetric method^e BET specific surface area^f BJH total pore volume

Figure 4.2 depicts the XRD patterns for various types of the as-synthesized N-TiO₂/AC composites and titania. At a moderate calcination temperature of 400°C, the N-TiO₂/AC composite as produced from first-stage calcination exhibited smaller N-TiO₂ crystallite size and the predominant crystal phase was anatase, though brookite was also observed. The growth of N-TiO₂ nanocrystals was found to be enhanced by a factor of ca. 3.3 when the second-stage calcination temperature was increased from 400°C to 700°C (Table 4.1). The brookite phase in the composite was observed when the N-TiO₂/AC was calcined from 400°C to 600°C, but it was completely disappeared at 700°C. Although the rutile phase could be observed to emerge gradually at 600°C and 700°C, the anatase phase was still predominant (Figure 4.2a). The rutile contents in N-TiO₂/AC (400M-600T) and N-TiO₂/AC (400M-700T) (determined using the Spurr and Myers equation (Spurr and Myers, 1957)) were estimated to be ca. 15% and 40%, respectively. Thus, the photocatalytically active anatase phase was predominant over rutile phase even at high calcination temperature of 700°C. This suggests that AC might have contributed to the suppression of rutile phase transformation.

As shown in Figure 4.2b, the bare titania without nitrogen-doping and AC support underwent complete transformation to rutile phase at 700°C. Nitrogen-doping, on the other hand, slightly abated the phase transformation from anatase to rutile, and this is in agreement with article published elsewhere (Wang et al., 2007a). Evidently, AC played a significant role in retaining the anatase phase in the N-TiO₂/AC composite. The creation of interfacial energy between the surface of AC and N-TiO₂, besides resulted in anti-calcination effect (Li et al., 2007), might have also significantly restrained the growth of rutile phase.

Figure 4.2 XRD pattern for (a) various as-synthesized N-TiO₂/AC composites, and (b) TiO₂ (400M-700T-N₂) and N-TiO₂ (400M-700T) nanoparticles.

According to the IUPAC classification, the nitrogen adsorption-desorption isotherm for N-TiO₂/AC (400M-700T) composite (Figure 4.3) was of Type IV (Sing et al., 1985), due to the observed prominent hysteresis loops. The type of hysteresis loop appeared to be of Type H4 loop, indicating the presence of narrow slit-like pores which were likely to be contributed by the AC pores in the composite. The BJH pore size for all types of N-TiO₂/AC was found to be ca. 3.8 nm, indicating that these composites were mainly mesoporous (Sing et al., 1985). For example, the corresponding pore size distribution of the N-TiO₂/AC (400M-700T) is shown as inset of Figure 4.3.

Figure 4.3 Nitrogen adsorption-desorption isotherm analysis for N-TiO₂/AC (400M-700T) (inset: the corresponding pore size distribution of the composite).

Based on the electrophoretic mobility measurement, the variations of zeta potential as a function of solution pH for various selected samples were obtained and the results are shown in Figure 4.4. The pI_{IEP} of TiO₂ (400M-700T-N₂), N-TiO₂ (400M-700T), N-TiO₂/AC (400M-700T) and virgin AC (as received) was determined to be ca. 5.6, 5.7, 6.7, and 4.7, respectively. Apparently, the higher pI_{IEP} of N-TiO₂/AC (400M-700T) as compared to that of virgin AC was likely to be caused by the deposition of N-TiO₂ onto the AC support. The N-TiO₂/AC (400M-700T) composite would exhibit a net positive charge below pH 6.7, and vice versa.

Figure 4.4 The variations of zeta potential as influenced by solution pH for various selected samples.

Figure 4.5 shows the UV-Vis absorption spectra for the N-TiO₂/AC (400M-700T) composite, selected photocatalysts, and virgin AC. P25 and TiO₂ (400M-700T-N₂) exhibited only one absorption band edge, while N-TiO₂ (400M-700T) displayed two absorption band edges. The first bandgap energy for P25, TiO₂ (400M-700T-N₂), and N-TiO₂ (400M-700T) was determined to be 3.01, 2.81 and 2.73 eV, respectively. The emergence of the second band edge for both N-TiO₂ (400M) and N-TiO₂ (400M-700T) indicates that N-doping had occurred. Particularly, the N-TiO₂ (400M-700T) exhibited significant visible-light photoresponsiveness. As confirmed by XPS analysis (Table 4.1), additional amount of nitrogen was doped into the TiO₂ through the provision of NH₃/N₂ gas. As expected, N-TiO₂/AC (400M-700T) and the virgin AC exhibited huge absorption spectra for UV and visible-light spectra because these materials are black in color. N-TiO₂/AC (400M-700T), however, exhibited a relatively lesser absorbance of the UV-Vis spectra as compared to that of virgin AC, due to the surface deposition of N-TiO₂.

Figure 4.5 UV-Vis absorption spectra for P25, TiO_2 (400M-700T- N_2), N-TiO_2 (400M-700T), $\text{N-TiO}_2/\text{AC}$ (400M-700T), and virgin AC.

The deconvoluted XPS spectra for the $\text{N-TiO}_2/\text{AC}$ (400M-700T) composite are presented in Figure 4.6. From Figure 4.6a, the difference in binding energy (BE) between $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ was ca. 5.7 eV, thus verifying that Ti element existed as Ti^{4+} (TiO_2) (Fu et al., 2004). No peaks were present at BE 455 eV (assigned to Ti^{2+}) and 456.7 eV (assigned to Ti^{3+}) and these results are consistent with the findings reported elsewhere (Zhang et al., 2006). From Figure 4.6b, the main O 1s peak was observed at 530.5 eV, thus confirming the existence of Ti-O-Ti linkages (Zhao et al., 2008). O 1s peak at 532.4 eV is associated with the oxygen atoms in hydroxyl and ethers (in AC), while O 1s peak at 533.8 eV corresponds to the adsorbed H_2O or CO (Boyano et al., 2008). From Figure 4.6c, interstitial N-doping was evidenced with the detection of N 1s peaks at 398.2 eV and 400.1 eV, respectively (Asahi et al., 2001; Di Valentin et al., 2007). From Figure 4.6d, no C 1s peak was observed at ca. 281.8 eV, indicating undetectable Ti-C bond (Zhang and Koka, 1998) or negligible incidental C-doping into the TiO_2 lattice.

Figure 4.6 Deconvoluted XPS spectra of (a) Ti 2p, (b) O 1s, (c) N 1s, and (d) C 1s for N-TiO₂/AC (400M-700T).

The EDX spectra along with the SEM micrograph and the associated elemental mapping for N-TiO₂/AC (400M-700T) are shown in Figure 4.7. C element was observed on the elemental mapping (Figure 4.7b), suggesting that the surface of AC was not entirely covered up by N-TiO₂ nanoparticles, thus preserving carbon adsorption sites on the surface of the composite. Ti was found to cover a large fraction of the AC surface (Figure 4.7c), indicating somewhat well-dispersed N-TiO₂ nanoparticles over the AC surface as a result of repeated coating during the synthesis. It is worth noting that EDX/elemental mapping is a micro-analytical technique for surface characterization of materials. Thus, it may not be suitable for the detection of low concentrations of nitrogen. In this study, though nitrogen was undetectable using EDX/elemental mapping, the presence of nitrogen was indeed confirmed by XPS analysis (as shown in the Figure 4.6c).

Figure 4.7 EDX spectra for N-TiO₂/AC (400M-700T) composite, with insets (a), (b) and (c) depicting the SEM micrograph of the composite, C element distribution, and Ti element distribution, respectively.

The TEM image in Figure 4.8a depicts the anchorage of N-TiO₂ on AC for N-TiO₂/AC (400M-700T) composite and the corresponding crystallite size (inset) of the N-TiO₂ nanoparticles. It can be seen that the N-TiO₂ particles adhered onto the surface of AC. The size of N-TiO₂ nanocrystals were in the range of ca. 23-25 nm, and this is in agreement with the estimated average crystallite sizes from Scherrer's equation (Debye and Scherrer, 1917). To gain insights into the intensity profile of Ti and C elements as a function of distance, EDX analysis was conducted across a selected location on the surface of the N-TiO₂/AC composite. The results (as shown in Figure 4.8b) revealed that Ti element became more predominant near the interface of N-TiO₂ and AC. The greater amount of Ti at the interface could likely serve as a seed layer for subsequent deposition of N-TiO₂ nanoparticles. Meanwhile, the slight increase of C element for distance 90-150 (Figure 4.8c) could be ascribed to some residual AC particles located underneath the N-TiO₂ crystals. The successful deposition of N-TiO₂

onto the AC surface could be due to the strong anchorage of the N-TiO₂ sol on the pre-treated AC during the sol-gel synthesis technique (Section 3.1.3).

Figure 4.8 TEM image for N-TiO₂/AC (400M-700T): (a) anchorage of N-TiO₂ nanoparticles on the AC surface (inset: the corresponding crystallite sizes of N-TiO₂), (b) Ti intensity-distance profile, and (c) C intensity-distance profile.

As shown in the FTIR results in Figure 4.9, the amount of phenolic groups of the pre-treated AC was particularly eminent from 3200-3000 cm^{-1} as compared to that of the virgin AC (as received). Apparently, the pre-treatment of AC was essential and the increased surface hydroxyl groups would improve the coating of N-TiO₂ sol onto the pre-treated AC during the sol-gel synthesis.

Figure 4.9 Comparison of the phenolic functional groups of pre-treated AC and virgin AC.

4.3.2 Photostability

Figure 4.10 shows the amount of TOC being leached out from N-TiO₂/AC (400M-700T) and the virgin AC in UPW upon irradiation with high-intensity UVA. As the baseline study, leachings in the dark were conducted for both samples to determine the amount of inherent organic impurities which are readily released into water. The obtained trend seems to suggest that TOC concentration would approach a steady-state condition. The results show that both N-TiO₂/AC (400M-700T) and the virgin AC were photostable after 6 h of UVA irradiation, with the amount of TOC leached to be less than ca. 0.1% and 0.05%, respectively.

In the case of N-TiO₂/AC (400M-700T), although the amount of carbon in contact with UV was reduced due to the deposition of N-TiO₂ nanoparticles, increased production of •OH in the N-TiO₂/AC (400M-700T) composite system apparently

resulted in relatively more amount of leached TOC. To investigate the role of $\bullet\text{OH}$ in the aqueous system, an additional study was carried out to subject the N-TiO₂/AC (400M-700T) under 4 h of UV irradiation, with addition of 100 mg L⁻¹ H₂O₂. The results indicated ca. 1.4 fold increment in TOC leaching as compared to the case without H₂O₂ addition, thus confirming the oxidizing effect of $\bullet\text{OH}$ radical. However, since UV intensity in the solar spectrum is lesser than the UV intensity employed in this photostability experiment, it can be inferred that the structural integrity of N-TiO₂/AC composites will be even less affected under irradiation of the solar light. Thus, this assures the good performance of the N-TiO₂/AC (400M-700T) composite under prolonged solar irradiation.

Figure 4.10 Time-dependent profile for the amount of leached TOC from samples.

4.3.3 Adsorption performances

The results of adsorption kinetics study revealed that 1.5 h of contact time was sufficient for the N-TiO₂/AC composites, AC and AC (700T) to reach BPA adsorption equilibrium (Figure 4.11).

Figure 4.11 Adsorption kinetics of virgin AC, AC (700T) and various as-synthesized N-TiO₂/AC composites.

4.3.3.1 Adsorption isotherms in ultrapure water

The adsorption isotherms for the various types of N-TiO₂/AC composites, AC and AC (700T) are presented in Figure 4.12. The maximum adsorption capacity ($S_{\max}$) and Langmuir adsorption constant (K_{ads}) are compared in Table 4.2. Due to the deposition of N-TiO₂ on AC surface, adsorption capacity for N-TiO₂/AC composites was expected to be reduced considerably. Interestingly, for composites calcined under the NH₃/N₂ atmosphere, an increasing trend of adsorption capacities for BPA with respect to calcination temperature was observed. The elevated adsorption capacity may be ascribed to the surface functionalization of AC, as a result of its interaction with ammonia gas, since nitrogen is an inert gas. Moreover, it can be seen that AC (700T) exhibited a significant increase of BPA adsorption as opposed to virgin AC. This is in agreement with some previous studies (Dimotakis et al., 1995; Cheng et al., 2005;

Quinlivan et al., 2005; Przepiórski, 2006), whereby ACs being treated under ammonia gas were found to possess improved adsorption capacities for several types of organic pollutants. It was postulated that a significant amount of nitrogen species would be found attached onto the surface of AC (700T). Thus, XPS analysis was carried out on the AC (700T). The results revealed that N 1s was detected on the surface of AC (700T) (Table 4.2), and this may imply that nitrogen atoms were chemically bonded with the surface functional groups of AC (700T). The increased adsorption capacity not only would permit greater uptake of pollutants from water, but would also positively influence the kinetics and extent of photocatalytic efficiency of the N-TiO₂/AC composites.

Figure 4.12 Adsorption isotherm of BPA on various N-TiO₂/AC composites and AC (note: error bars denote standard deviation of triplicates).

Table 4.2 Adsorption parameters derived from the best-fitted Langmuir isotherm model (note: values denote average $\pm$ standard deviation of triplicates)

Sample	Adsorption capacity		
	$S_{\max}$ (mg g ⁻¹)	K_{ads} (L mg ⁻¹)	R^2
N-TiO ₂ /AC (400M)	194 $\pm$ 2	0.69 $\pm$ 0.09	0.996
N-TiO ₂ /AC (400M-500T)	229 $\pm$ 4	0.73 $\pm$ 0.10	0.992
N-TiO ₂ /AC (400M-600T)	240 $\pm$ 3	0.82 $\pm$ 0.07	0.991
N-TiO ₂ /AC (400M-700T)	259 $\pm$ 4	1.22 $\pm$ 0.22	0.992
Virgin AC (as received)	250 $\pm$ 6	1.14 $\pm$ 0.03	0.992
AC (700T)	297 $\pm$ 5	6.92 $\pm$ 1.44	0.998

4.3.3.2 Adsorption isotherms in the presence of selected aqueous matrix species

Figure 4.13 depicts the effects of organic species, namely $\text{C}_2\text{O}_4^{2-}$ and CH_3OH on the adsorption of BPA as exhibited by N-TiO₂/AC (400M-700T) at circumneutral pH, and the corresponding S_{max} and K_{ads} values are presented in Table 4.3. Apparently, the effect of competitive sorption as induced by CH_3OH molecules was more prominent than that of $\text{C}_2\text{O}_4^{2-}$ ions. The pK_{a1} and pK_{a2} for BPA is 9.6 and 10.2 (Kosky et al., 2002), respectively while the pH_{IEP} for N-TiO₂/AC (400M-700T) was determined to be 6.7 (Table 4.1). The initial pH for both $\text{C}_2\text{O}_4^{2-}$ and CH_3OH systems was 6.0 ± 0.4 , and at this pH, the net surface charge of N-TiO₂/AC (400M-700T) was positive. By law of electrostatic interactions, the composite was expected to adsorb $\text{C}_2\text{O}_4^{2-}$ to result in reduced BPA sorption. However, the results revealed that BPA was less adsorbed in the presence of CH_3OH instead. This suggests that electrostatic charge interaction was not the predominant governing factor. By virtue of chemical affinity, N-TiO₂/AC (400M-700T) would preferentially adsorb CH_3OH due to the presence of specific sorption sites viz. C-C bond and hydroxyl functional groups. Moreover, CH_3OH (a co-solvent) could induce greater solubility of BPA into the aqueous solution, thus decreasing the BPA affinity for N-TiO₂/AC (400M-700T) composite.

Figure 4.13 Adsorption isotherm of BPA as exhibited by AC (700T) and N-TiO₂/AC (400M-700T) in UPW and in the interferences of $\text{C}_2\text{O}_4^{2-}$ and CH_3OH at circumneutral pH (note: error bars denote the standard deviation of triplicates).

Table 4.3 Adsorption capacity of N-TiO₂/AC (400M-700T) in the presence of various aqueous matrix species

Experimental conditions		Adsorption capacity		
Matrix species	Solution pH	S _{max} (mg g ⁻¹)	K _{ads} (L mg ⁻¹)	R ²
UPW (control)	6.0 ± 0.4	259 ± 4	1.22 ± 0.22	0.992
HCO ₃ ⁻ (100 mM)	7.6 ± 0.4	240 ± 3	0.60 ± 0.04	0.991
C ₂ O ₄ ²⁻ (100 mM)	6.0 ± 0.4	252 ± 7	0.95 ± 0.07	0.991
CH ₃ OH (100 mM)	6.0 ± 0.4	250 ± 6	0.70 ± 0.02	0.991

4.3.4 Photocatalytic degradation efficiency in ultrapure water

The corresponding kinetic constants for BPA degradation as exhibited by the various as-synthesized N-TiO₂/AC composites are compared in Table 4.4. The experimental data were fitted into Langmuir-Hinshelwood (L-H) kinetic model (Herrmann, 2005), as shown below:

$$r = -\frac{dC}{dt} = -k \left[\frac{KC}{1 + KC} \right] = -k_{app}C \quad (\text{when } KC \ll 1) \quad (4.1)$$

where r = reaction rate, k = rate constant, K = equilibrium adsorption constant and C = instantaneous concentration.

Since L-H kinetic model was suitable for describing the kinetics of BPA degradation as exhibited by various photocatalysts such as P25, TiO₂ and N-TiO₂, the L-H model would also be suitable to be adopted for the case of N-TiO₂/AC composite because BPA degradation occurred on the surface of N-TiO₂. Since the initial BPA concentration used in this study represented a diluted solution (0.16 mM) and that minimal BPA adsorption on N-TiO₂ was observed, hence it is reasonable to assume that $KC \ll 1$. Accordingly, the L-H equation may be further simplified into pseudo first-order kinetic model with pseudo first-order rate constant (k_{app}). The PCD efficiency for BPA removal was represented by the initial k_{app} . The initial k_{app} was determined from the experimental data obtained throughout the 3-h of light irradiation time because subsequent data seemed to deviate from the linear plot of $\ln(C/C_0)$ vs. t , owing to the significantly decreased BPA concentration in the photoreactor.

Table 4.4 PCD efficiency as exhibited by various samples under full solar spectrum irradiation

Sample	PCD efficiency under full solar spectrum	
	Initial k_{app} (h^{-1})	R^2
P25	0.20	0.961
Hombikat (Sigma-Aldrich)	0.19	0.979
TiO ₂ (400M-700T-N ₂)	0.05	0.949
N-TiO ₂ (400M-700T)	0.06	0.911
N-TiO ₂ /AC (400M)	0.32	0.935
N-TiO ₂ /AC (400M-500T)	0.47	0.930
N-TiO ₂ /AC (400M-600T)	0.52	0.947
N-TiO ₂ /AC (400M-700T)	0.67	0.905
N-TiO ₂ (400M-700T) + AC (700T)	0.15	0.968
P25 + AC	0.44	0.996
Hombikat (Sigma-Aldrich) + AC	0.42	0.987

4.3.4.1 Effect of calcination condition

Figure 4.14a shows the effect of N-TiO₂/AC calcination condition on the PCD performance with respect to BPA removal. As presented in Figure 4.14b, the plot of $\ln(C/C_0)$ vs. irradiation time was linear for the initial 3 h of light irradiation. It was observed that the composites which underwent two-stage calcination exhibited enhanced efficiency for BPA degradation, with the highest removal (> 90%) being exhibited by N-TiO₂/AC (400M-700T) within 8 h of simulated solar irradiation. The remarkable PCD performance of bifunctional N-TiO₂/AC (400M-700T) could be ascribed to the synergistic effect of adsorption-photocatalysis. This is because during the adsorption in the dark, the AC would concentrate high amounts of BPA to be near the surface of the supported N-TiO₂. Upon light irradiation, photocatalysis process would occur and thus, highly oxidizing species such as h^+ or $\bullet OH$ would be produced and these species served to efficiently degrade BPA on the surface of N-TiO₂.

The production of highly crystalline nitrogen-doped anatase-rutile mixture for N-TiO₂/AC (400M-700T) is desirable. The anatase-rutile mixture is well known for its good photocatalytic activity. To date, two mechanisms have been suggested for the synergistic effect of anatase-rutile mixture, namely (1) the e^- in the anatase conduction band could be transported to the rutile conduction band (Schindler and Kunst, 1990; Bickley et al., 1991), or (2) the e^- in the rutile conduction band could be transported to

the lower energy anatase trapping sites (Hurum et al., 2003). It has been reported that nitrogen doping could induce the generation of localized states within the bandgap (slightly above the valence band maximum), and these states could serve as trapping sites for photogenerated holes for efficient photocatalytic reactions (Beranek et al., 2007; Di Valentin et al., 2007). Therefore, N-doped anatase-rutile mixture potentially further enhanced the photocatalytic activity because the occurrences of charge carriers recombination were effectively minimized. Furthermore, by having the first stage of calcination in the air atmosphere, organic residuals from sol-gel synthesis technique can be eliminated, thus permitting a greater exposure of N-TiO₂ surface to receive the incident light. Thus, N-TiO₂/AC (400M-700T) was used for further investigations.

Figure 4.14 The examination of photocatalytic degradation performance of BPA, as exhibited by various N-TiO₂/AC composites: (a) the effect of calcination condition, and (b) plot of ln(C/C₀) vs. irradiation time for the initial 3 h of light irradiation.

4.3.4.2 Effect of composite dosage

The influence of composite dosage on the PCD efficiency of BPA is presented in Figure 4.15. The observation of turbidity of N-TiO₂/AC (400M-700T) suspension with respect to the investigated dosage in the absence and presence of simulated solar light is shown in Figure 4.16a and 4.16b, respectively. The turbidities of the suspension with the dosage of 0.15, 0.25 and 0.35 g L⁻¹ were ca. 85, 120 and 160 NTU, respectively. Thus, the turbidity level for the dosage of 0.25 g L⁻¹ was larger than that of 0.15 g L⁻¹ by a factor of ca. 1.4, while smaller than that of 0.35 g L⁻¹ by a factor of ca. 0.8. In the case of 0.15 g L⁻¹ dosage, although the light distribution in the whole photoreactor was least hindered, the amounts of N-TiO₂ were unlikely to be adequate for optimum PCD rate. On the other hand, while 0.35 g L⁻¹ of dosage provided a greater amount of N-TiO₂ particles, the high turbidity in the solution resulted in the greatest light attenuation in the photoreactor. Thus, 0.25 g L⁻¹ was identified to be the optimum dosage for the subsequent PCD examinations.

Figure 4.15 Effect of N-TiO₂/AC (400M-700T) composite dosage on the PCD performance.

Figure 4.16 The observation of turbidity of N-TiO₂/AC (400M-700T) suspension with respect to the different dosages used (a) when the simulated solar light was turned off, and (b) when the simulated solar light was turned on.

4.3.3.3 Effect of light wavelength spectrum

The effect of various types of light wavelength spectra on BPA degradation with N-TiO₂/AC (400M-700T) is shown in Figure 4.17. Importantly, the light intensities of the simulated solar light, UV, and visible-light were ca. 1000, 65, and 400 W m⁻², respectively. It can be seen that the composite exhibited satisfactory photocatalytic activity for all ranges of light spectrum investigated, i.e. the simulated solar spectrum, UV (280-400 nm) and visible-light (420-630 nm), with initial k_{app} of 0.67 h⁻¹, 0.44 h⁻¹, and 0.29 h⁻¹, respectively. TOC analysis at the end of the experiments revealed that the reductions of total organic carbon species also followed similar trend, i.e. 72%, 60% and 45% for irradiations under the simulated solar light, UV and visible-light, respectively. Under the simulated solar light, the photolytic removal of BPA was negligible (ca. 10% within 8-h of irradiation). For comparison, a separate study was also carried out to determine the effect of simulated solar light on two different photocatalytic systems: (i) unsupported photocatalyst systems involving TiO₂ (400M-700T-N₂), N-TiO₂ (400M-700T), and P25, and (ii) binary mixture systems of titania

and AC, namely N-TiO₂ (400M-700T) + AC (700T), P25 + AC and Hombikat (Sigma-Aldrich) + AC. The obtained results are compared in Table 4.4. It can be observed that under the simulated solar light irradiation, N-TiO₂/AC (400M-700T) composite exhibited a greater efficiency of BPA degradation as compared to that of the unsupported photocatalysts and the binary mixtures of titania and AC, indicating the evidence of synergistic adsorption-photocatalysis processes, as exhibited by the N-TiO₂/AC (400M-700T) composite.

Figure 4.17 Effect of light wavelength spectrum on governing the photocatalytic activity, as exhibited by N-TiO₂/AC (400M-700T).

4.3.3.4 Repeated usage under simulated solar light irradiation

The performance of repetitive usage, as exhibited by the N-TiO₂/AC (400M-700T), is presented in Figure 4.18. It can be observed that the composite exhibited a satisfactory PCD performance, whereby ca. 80% of degradation efficiency (as compared to the 1st run) could be maintained at the end of 6th experimental run. This suggests that the composite might have a reasonably well physical stability, in which the good adherence of N-TiO₂ nanoparticles on AC surface could preserve the synergistic effect of adsorption-photocatalysis processes.

Figure 4.18 Performance of repetitive use of N-TiO₂/AC (400M-700T).

4.3.5 Photocatalytic degradation efficiency in the presence of aqueous matrix species

As shown in Figure 4.19, the investigated inorganic anions, organic anion, photocatalysis inhibitor (CH₃OH) and oxidant (H₂O₂) were found to exhibit different influences on the rates of BPA degradation, and these impacts were concentration dependent. From Figure 4.20, it can be observed that while PCD efficiency for BPA degradation was only marginally affected over the pH range 4 to 10 in the case of UPW, introduction of interfering species resulted in mainly inhibitive effect. A comparison of PCD efficiency for BPA removal as exhibited by N-TiO₂/AC (400M-700T) and N-TiO₂ (400M-700T) at selected concentrations of the matrix species at circumneutral pH is provided in Table 4.5. On the basis of k_{app} , it is evident that N-TiO₂/AC (400M-700T) exhibited superior PCD performance than that of N-TiO₂ (400M-700T) in UPW and also in the presence of various aqueous matrix species (except H₂O₂ which shall be discussed later). In addition, for the experimental condition of UPW at circumneutral pH, the BPA degradation efficiency as exhibited by N-TiO₂/AC (400M-700T) composite was 3.4 times higher than that of P25 (Table 4.4). These results thus proved that the synergistic effect of adsorption-PCD processes was greater than the sole effect of PCD process. In the following sections, a detailed

discussion is provided from the mechanistic point of view to further comprehend the underlying factors in play.

Figure 4.19 Effect of aqueous matrix species on BPA degradation as a function of species concentration.

Figure 4.20 Effect of aqueous matrix species on BPA degradation as a function of pH.

Table 4.5 Comparison of PCD efficiency between N-TiO₂/AC (400M-700T) and N-TiO₂ (400M-700T) in the presence of various aqueous matrix species at circumneutral pH

Experimental conditions		N-TiO ₂ /AC (400M-700T)			N-TiO ₂ (400M-700T)		
Matrix species	Solution pH	Initial k_{app} (h ⁻¹)	R ²	Removal efficiency at 3 h (%)	Initial k_{app} (h ⁻¹)	R ²	Removal efficiency at 3 h (%)
UPW (control)	6.0 ± 0.4	0.667	0.905	82.8	0.057	0.911	14.5
Cl ⁻ (100 mM)	6.0 ± 0.4	0.534	0.937	76.3	0.048	0.934	12.1
NO ₃ ⁻ (100 mM)	6.0 ± 0.4	0.560	0.932	77.6	0.163	0.959	35.9
SO ₄ ²⁻ (100 mM)	6.0 ± 0.4	0.558	0.931	76.9	0.022	0.912	5.8
HCO ₃ ⁻ (100 mM)	7.6 ± 0.4	0.350	0.973	62.2	0.032	0.912	8.0
H ₂ PO ₄ ⁻ (0.1 mM)	6.5 ± 0.2	0.708	0.930	85.4	0.066	0.982	16.9
C ₂ O ₄ ²⁻ (100 mM)	6.0 ± 0.4	0.169	0.996	40.4	0.045	0.986	12.7
Silica (10 mM)	6.8 ± 0.2	0.467	0.986	73.4	0.039	0.979	11.8
CH ₃ OH (100 mM)	6.0 ± 0.4	0.197	0.980	42.3	0.012	0.993	3.3
H ₂ O ₂ (100 mM)	6.0 ± 0.4	0.408	0.905	66.3	2.309	0.978	99.9

4.3.5.1 Effect of inorganic anions

Apparently from Figure 4.19, all anions resulted in some extent of detrimental effects on the BPA degradation as exhibited by N-TiO₂/AC (400M-700T), except H₂PO₄⁻. Since PCD processes are predominantly driven by the highly oxidizing species, viz. photogenerated h⁺ or •OH, scavengers of these oxidizing species would present inhibitory effect on photocatalysis. Many anions can scavenge h⁺ and •OH via the following reactions (Rincón and Pulgarin, 2004; Zhang et al., 2005a):

Production of these less reactive radicals may thus decrease BPA degradation efficiency. In addition, surface deposition of certain species (i.e. SO₄²⁻, H₂PO₄⁻, and silica) on the composite was confirmed using XPS analysis and it was found that these surface-bound species could influence the efficiency of BPA degradation (as shall be discussed later). It is worth noting that prior to the XPS analysis, the recovered samples after photocatalytic reaction were thoroughly washed in order to remove the loosely attached anions.

In the presence of Cl⁻ and SO₄²⁻, the reduction in BPA degradation efficiency as exhibited by N-TiO₂/AC (400M-700T) as a function of concentration (0.1 to 100 mM) appeared to be relatively small. For Cl⁻, the fact that the experiments were carried out at the circumneutral pH was one factor which reduced the deactivation of the composite, since Cl⁻ has been reported to exhibit deleterious effects only at the acidic condition (pH 3 to 4) (Abdullah et al., 1990; Wang et al., 1999). Interestingly, comparison of SO₄²⁻ influences on BPA degradation as exhibited by N-TiO₂/AC (400M-700T) and N-TiO₂ (400M-700T) demonstrated a significant contradictory effect. At 100 mM of SO₄²⁻ concentration, the k_{app} (N-TiO₂/AC (400M-700T))/k_{app} (UPW) value was greater than the k_{app} (N-TiO₂ (400M-700T))/k_{app} (UPW) by a factor

of 2.2, indicating that the AC support had induced a positive role in abating the detrimental effects of SO_4^{2-} species. It has been reported that SO_4^{2-} can adhere to the surface of TiO_2 via van der Waals forces and hydrogen bonds, and that SO_4^{2-} may displace some surface hydroxyl groups of TiO_2 (e.g. Ti-OH) via ligand exchange mechanism (Rincón and Pulgarin, 2004). The XPS results confirmed the presence of SO_4^{2-} deposition on both N- TiO_2/AC (400M-700T) and N- TiO_2 (400M-700T) through the detection of S 2p peak (BE at ca. 169 eV) and O 1s peak (BE at ca. 532 eV) (Jung and Grange, 2001). The area for O 1s at ca. 532 eV constitutes 20.5% and 69.7% of the total O element for N- TiO_2/AC (400M-700T) and N- TiO_2 (400M-700T), respectively. Moreover, the area for O 1s at ca. 530 eV (assigned to Ti-O-Ti) comprises 79.5% and 25.0% of the total O element for N- TiO_2/AC (400M-700T) and N- TiO_2 (400M-700T), respectively. These results indicated that a comparatively thicker deposition of SO_4^{2-} was formed on N- TiO_2 (400M-700T), thus blocking substantial active sites of the photocatalyst. Hence, by reducing the deposition of SO_4^{2-} on N- TiO_2 (400M-700T), AC support could abate the detrimental effects of SO_4^{2-} on BPA degradation.

As NO_3^- concentration was increased from 0.1 to 100 mM, the detrimental effect observed for BPA degradation using N- TiO_2/AC (400M-700T) was not prominent. Since NO_3^- could serve as UV absorber, one possible reason for the observed slight improvement of k_{app} beyond 1 mM NO_3^- was that additional $\bullet\text{OH}$ was produced through the photolysis of NO_3^- in the photocatalytic system via the following mechanism (Goldstein and Rabani, 2008):

where the wavelengths that can drive the above-mentioned reaction = 205 to 300 nm (Goldstein et al., 2007; Goldstein and Rabani, 2007)

To ascertain the promotional role of NO_3^- at high concentrations on BPA degradation, an auxiliary experiment was also conducted using N- TiO_2 (400M-700T) with 100 mM NO_3^- as the interfering species. The results revealed that the initial k_{app} was enhanced by a factor of 2.8 as compared to the case of UPW (Table 4.5). Such enhancement was not manifested in the case of N- TiO_2/AC (400M-700T), because the light intensity was

reduced in the turbid solution containing the composites. However, PCD efficiency for BPA removal as exhibited by N-TiO₂/AC (400M-700T) was still superior to that of N-TiO₂ (400M-700T), since the composite could exhibit synergism of adsorption-PCD.

At low concentrations of HCO₃⁻, BPA degradation efficiency as exhibited by N-TiO₂/AC (400M-700T) was not significantly inhibited. However, beyond 1 mM HCO₃⁻, a more obvious reduction in k_{app} was observed. Further increase of the HCO₃⁻ concentration from 10 to 100 mM resulted in a continual reduction of k_{app} from 0.39 to 0.35 h⁻¹. From the practical application point of view, these results indicate that N-TiO₂/AC (400M-700T) is more suitable to be employed in surface waters, since groundwaters in some parts of the world contain high HCO₃⁻ concentrations (> 200 mg L⁻¹) (Stamatis et al., 2001; Özcan et al., 2007; Karthikeyan et al., 2010). In addition, CO₃•⁻ could also be generated in the solution via the following equation (Rincón and Pulgarin, 2004):

Since both HCO₃• and CO₃•⁻ radical species are less reactive as compared to •OH, this would thus decrease the PCD efficiency for BPA removal. It is worth noting that the circumneutral pH of HCO₃⁻ system was 7.6 ± 0.4. Since pH_{IEP} of N-TiO₂/AC (400M-700T) was 6.7, it was possible that the negatively-charged composite had a lesser adsorption capacity for BPA, thus resulting in decreased BPA degradation performance. To confirm this phenomenon, an auxiliary equilibrium batch adsorption experiment for BPA was conducted in the presence of HCO₃⁻ species using N-TiO₂/AC (400M-700T) and the result is shown in Table 4.3. The results confirmed that the S_{max} for BPA in the presence of 100 mM HCO₃⁻ was considerably decreased as compared to the case of UPW. The presence of HCO₃⁻ in the solution is pH dependent, and the pK_{a1} and pK_{a2} for HCO₃⁻/CO₃²⁻ system is 6.3 and 10.3, respectively (Sawyer et al., 1994). From Figure 4.20, it can be observed that k_{app} values for HCO₃⁻/CO₃²⁻ system increased when initial pH was varied from 6.3 to 10. The enhancement of BPA degradation in the alkaline condition is because the increased production of •OH with increasing pH had overwhelmed the detrimental effect of HCO₃⁻/CO₃²⁻ anions.

Usually, the deleterious effect of H_2PO_4^- on PCD efficiency was because H_2PO_4^- could serve as a h^+ or $\bullet\text{OH}$ scavenger. However, in the present study, a slight enhancement effect in BPA degradation was observed instead in the presence of 0.01 to 0.1 mM H_2PO_4^- (Figure 4.19). Furthermore, it was found that 0.1 mM H_2PO_4^- enhanced the BPA removal efficiency by a factor of 1.2 in the case of N-TiO₂ (400M-700T) system (Table 4.5). Zhao et al. (2008) had reported that phosphate-modified TiO₂ could increase PCD performance because of the increased production of free $\bullet\text{OH}$ occurring in the photocatalytic system. The XPS results obtained in the present study revealed the formation of bidentate P on Ti surface sites for the composite at BE ca. 134 eV (Zhao et al., 2008). Hence, the enhanced BPA removal in the H_2PO_4^- system was confirmed to be mainly due to $\bullet\text{OH}$ attack. From Figure 4.20, the promotional effect of phosphate was comparatively enhanced under alkaline condition, suggesting that BPA was predominantly photooxidized by $\bullet\text{OH}$.

Figure 4.19 also depicts the effect of silica concentration in governing the efficiency of BPA degradation as exhibited by N-TiO₂/AC (400M-700T). The speciation of silica in aqueous phase is governed by silica concentration and solution pH (Yang et al., 2008b). In the case of N-TiO₂/AC (400M-700T), BPA degradation was suppressed when silica concentration was varied from 0.1 to 10 mM, with the initial k_{app} reduced from 0.54 to 0.47 h⁻¹. Inhibitory effect was also observed for the N-TiO₂ (400M-700T) system, whereby the initial k_{app} decreased by a factor of 0.68 in the presence of 10 mM silica. It has been reported that silica could induce the ligand-exchange mechanism through the formation of inner-sphere surface complexes on hydrous oxide surfaces (Doelsch et al., 2003). The obtained XPS results revealed the detection of Si 2p peak at BE ca. 103.5 eV, which is assigned to Si-O linkages (Wagner et al., 1979). Formation of surface-bound silica species may induce considerable light screening effect and thus reduced the BPA degradation efficiency. As shown in Figure 4.20, silica did not induce significant variation in the BPA degradation over the pH range from 4 to 10. In this study, the solution pH was investigated until pH 10. This is because the author had found that pH 11 would inhibit the adsorption of the deprotonated BPA onto N-TiO₂/AC composite (due to the effect of electrostatic repulsion), thus decreasing the PCD efficiency (Yap et al., 2010). The gradual enhancement of BPA degradation in the alkaline condition was due to the enhanced production of $\bullet\text{OH}$ in the aqueous system. In the acidic condition, silica mainly exists as a neutral molecule, thus

reduction in the electrostatic interactions between silica and the positively-charged surface of N-TiO₂/AC (400M-700T) was likely to inhibit the deleterious effect of silica.

4.3.5.2 Effect of organic anion

C₂O₄²⁻ is a widely recognized h⁺ scavenger and it has been reported to be used as a molecular probe species to determine the occurrences of direct h⁺ oxidation in a photocatalytic system (Mao et al., 1991; Yoon and Lee, 2005). As C₂O₄²⁻ is quite commonly found in wastewater effluents at different level of concentrations, thus the influence of C₂O₄²⁻ on the BPA degradation, as exhibited by the N-TiO₂/AC (400M-700T), was examined over a wide range of concentration, i.e. from 0.1 to 100 mM. As shown in Figure 4.19, the k_{app} for BPA degradation was consistently reduced with increasing concentration of C₂O₄²⁻. From 0.1 to 10 mM of C₂O₄²⁻ concentration, the corresponding k_{app} values were reduced in a linear fashion. Beyond 10 mM, the detrimental effect of C₂O₄²⁻ on BPA removal was more pronounced. Additionally, IC analysis revealed that the final C₂O₄²⁻ concentrations in the solutions were reduced. Thus, the results of this investigation suggest that BPA could also be degraded through direct h⁺ oxidation pathway. From Figure 4.20, the k_{app} values increased almost linearly from pH 4 to 10 for the C₂O₄²⁻ system. In the acidic condition, the positively-charged surface of N-TiO₂/AC (400M-700T) composite was likely to exhibit a stronger attraction towards C₂O₄²⁻, thus resulting in the decreased BPA degradation. In the alkaline condition, the greater electrostatic repulsion of C₂O₄²⁻ from the negatively-charged surface of composite and the increased amount of OH⁻ in the bulk solution resulted in the enhanced PCD efficiency for BPA removal.

4.3.5.3 Effect of photocatalysis inhibitor

CH₃OH is a common organic solvent and it is also a biological degradation byproduct widely found at varying concentrations in wastewaters. Thus, the effect of CH₃OH on the BPA degradation, as exhibited by the N-TiO₂/AC (400M-700T), was investigated over a broad range of concentration, ranging from 0.1 to 100 mM. From Figure 4.19,

the initial k_{app} decreased from 0.40 to 0.22 h^{-1} when the CH_3OH concentration was varied from 0.1 to 10 mM. However, further increase of CH_3OH concentration beyond 10 mM resulted in only a small decrease of initial k_{app} to 0.20 h^{-1} , indicating that the effect of PCD inhibition had reached a limit. Two reasons may account for the detrimental effect induced by CH_3OH . First, CH_3OH could scavenge both h^+ and $\bullet OH$ (Tamaki et al., 2005; Yoon and Lee, 2005). Second, due to the effect of competitive adsorption as induced by CH_3OH (Figure 4.13 and Table 4.3), the lesser adsorption of BPA onto the composite would also decrease the BPA degradation efficiency. From Table 4.5, it can be observed that in the presence of 100 mM CH_3OH system, the k_{app} (N-TiO₂/AC (400M-700T))/ k_{app} (UPW) and k_{app} (N-TiO₂ (400M-700T))/ k_{app} (UPW) values are 0.30 and 0.21, respectively. This slight improvement in the BPA degradation efficiency as exhibited by N-TiO₂/AC (400M-700T) over that of the N-TiO₂ (400M-700T) was because some amount of CH_3OH was adsorbed by the composite. The increase of pH from 4 to 6 in the presence of CH_3OH led to only some improvements for BPA degradation, with the initial k_{app} varied from 0.34 to 0.40 h^{-1} (Figure 4.20). Further increase in pH resulted in enhancement of PCD efficiency with the initial k_{app} being improved to 0.68 h^{-1} at pH 10. This indicates that BPA degradation in the presence of CH_3OH at the alkaline condition was likely to be due to $\bullet OH$ attack.

4.3.5.4 Effect of oxidant

Addition of H_2O_2 is expected to induce some interesting results because H_2O_2 is a strong oxidant. Interestingly, the BPA degradation was inhibited in the presence of H_2O_2 (0.1 to 100 mM). To understand the effect of H_2O_2 on unsupported N-TiO₂, PCD experiments were carried out using the N-TiO₂ (400M-700T) (with comparable photocatalyst loading) and the findings are presented in Figure 4.21. The results revealed that PCD performance was slightly improved with addition of 0.1 mM H_2O_2 , but beyond this concentration, prominent enhancement for BPA degradation was observed. Hence, the promotional role of H_2O_2 for N-TiO₂ (400M-700T) system was confirmed. It was hypothesized that H_2O_2 may have oxidized AC surface to some extent. To confirm this hypothesis, an auxiliary study investigating the effect of H_2O_2 on the photochemical stability of virgin AC was carried out (described previously in

Section 3.3.7). The results revealed that dissolved TOC increased with increasing concentration of H_2O_2 . Thus, it can be deduced that for the case of N-TiO₂/AC (400M-700T), some of the adsorbed BPA was released back into the bulk solution. The effect of pH on BPA degradation in the presence of 0.1 mM H_2O_2 is presented in Figure 4.20. At acidic condition, the combined effects of insufficient OH^- and reduced sorption of BPA molecules on the surface of positively charged N-TiO₂/AC (400M-700T) decreased the BPA degradation. At alkaline condition, the slight improvement in PCD efficiency was because BPA removal rate was adequate to overcome the accumulation rate of desorbed BPA. However, since this composite was engineered with the aim to reduce chemical usage, the addition of H_2O_2 as PCD promoter is not required. Thus, any associated adverse effects on PCD efficiency as induced by H_2O_2 can be avoided.

Figure 4.21 Enhancement of initial k_{app} (h^{-1}) for BPA degradation as exhibited by N-TiO₂ (400M-700T) under the influence of various H_2O_2 concentration.

4.4 Conclusions and environmental implications

Various types of bifunctional N-TiO₂/AC composites were prepared via the sol-gel technique with the incorporation of single-stage and two-stage calcinations, respectively. The N-TiO₂/AC composites were thoroughly characterized using XRD, porosimetry, electrophoretic mobility measurement, UV-Vis spectrophotometry, XPS,

SEM/EDX, and TEM. The composites prepared via two-stage calcination were superior to that of the composite prepared via single-stage calcination. The best performing composite was N-TiO₂/AC (400M-700T), which was prepared via the first-stage calcination in a muffle furnace at 400°C for 2 h under air atmosphere, and the second-stage calcination in a tube furnace at 700°C for 2 h under NH₃/N₂ atmosphere. N-TiO₂/AC (400M-700T) composite exhibited a high adsorption affinity for BPA, enhanced photocatalytic activity under all investigated ranges of light wavelength spectra (i.e. simulated solar light, UV, and visible-light), and it also demonstrated the potential for reuse. N-TiO₂/AC (400M-700T) also exhibited superior PCD performance as compared to all the unsupported photocatalysts (including commercial titania) and binary mixtures of titania and AC powders. The N-TiO₂/AC composite was also photostable under high-intensity UV irradiation. In the presence of various dissolved aqueous matrix species, the N-TiO₂/AC system generally demonstrated significantly higher PCD performance than that of the unsupported N-TiO₂ system. With the introduction of the AC support, the detrimental effects of sulfate on BPA degradation could be abated. Using oxalate as a molecular probe, BPA degradation pathway was found to proceed via both mechanisms of direct h⁺ oxidation and •OH attack. The BPA degradation efficiency as exhibited by the N-TiO₂/AC was not prominently affected by the presence of low concentration of silica from pH 4 to 10. Since the addition of H₂O₂ into the N-TiO₂/AC system apparently increased the BPA concentration in the bulk solution, this actually highlights the salient feature of this composite because exclusion of H₂O₂ usage would present significant environmental and economic merits. This study may also serve as a guide for employing N-TiO₂/AC in different water systems with varying dissolved species concentration and pH, and identifying the necessary water pre-treatment steps. Indeed, N-TiO₂/AC composite is promising for realizing a viable hybrid adsorption-solar photocatalysis treatment technology for water reclamation as compared to other photocatalyst systems.

Chapter 5 Solar Regeneration of Spent N-TiO₂/AC

5.1 Introduction

In Chapter 4, the adsorptive-solar photocatalytic characteristics of various N-TiO₂/AC composites synthesized via single-stage and two-stage calcinations were evaluated. The aqueous media were UPW and solutions containing different dissolved species. The best performing composite was N-TiO₂/AC (400M-700T) which exhibited strong affinity for BPA adsorption and the highest solar photocatalytic activity in degrading BPA. The findings indicate potential application of the composite in water reclamation. However, it is anticipated that over a prolonged usage of the composite, it would eventually be saturated with the pollutants, especially when used in the dark. Thus, it is essential to examine the technical feasibility of solar photocatalytic regeneration of the spent composite.

Traditionally, the spent AC used for pollutants removal has to be disposed of as hazardous waste or regenerated for reuse. Thermal regeneration is the widely adopted spent AC regeneration technique but it has several disadvantages because: (a) it requires off-site regeneration, (b) it merely transfers the pollutant from one phase to another phase, (c) it results in appreciable carbon lost (5-15%) (Sheintuch and Matatov-Meytal, 1999), and (d) it may affect the microporous structures of AC. Although chemical regeneration of the spent AC could yield high regeneration efficiencies (Leng and Pinto, 1996; Guo et al., 2011), this technique has its drawbacks including non-destructive pollutant removal, significant chemical consumption and generation of secondary waste streams. Microbial regeneration is generally environmentally friendly and of low cost (Coelho et al., 2006) but it usually requires a long treatment duration and is limited to removing biodegradable organic compounds. Other regeneration techniques have been proposed as potential alternatives for regenerating the spent AC, e.g. ultrasound regeneration (Lim and Okada, 2005), electrochemical regeneration (Ania and Béguin, 2008) and microwave regeneration (Foo and Hameed, 2009), Fenton-based regeneration (Kan and Huling, 2009), and

photocatalytic regeneration (Crittenden et al., 1997; Liu et al., 2004; Tao et al., 2006; Park et al., 2010) have been studied as regeneration techniques for the spent AC.

In general, the above-mentioned regeneration techniques for the spent AC entail large carbon footprint, consume chemicals or require expensive facilities, and thus have limited appeal for industry application. In view of the various limitations associated with the current regeneration techniques for the spent AC, it is compelling to develop a more environmentally-friendly and cost-effective regeneration technique. Most of the previous studies on the photocatalytic regeneration studies of the spent AC were about granular AC, and the light sources used were often UV lamps. Thus far, there has been very few well-documented works that report the performance of photocatalytic regeneration of the spent AC as induced by the solar light irradiation.

Solar photocatalytic regeneration (SPR) is potentially a green technology to regenerate the spent AC, because (a) it does not entail carbon footprint and chemical consumption during the AC regeneration, and (b) photocatalysis can non-selectively degrade various recalcitrant pollutants and the by-products are usually more environmentally benign or biodegradable. To the best knowledge of the author, there appears to be no well-documented reports thus far which describe the solar regeneration of the spent powdered AC employing a visible-light photoresponsive photocatalyst. Thus, the aims of this study were: (1) to examine SPR performance of the spent N-TiO₂/AC composites, and (2) to establish a versatile kinetic model for predicting the regeneration efficiency.

In this study, three recalcitrant organic contaminants of varying molecular properties and hydrophobicities, i.e., BPA, SMZ and CFA were investigated as the model pollutants. BPA is a plasticizer and also an EDC (Staples et al., 1998; Kang et al., 2007). SMZ is a type of heterocyclic sulfonamide drug and veterinary/human antibiotic which has been found to induce thyroid tumors in mice and rats at high dosages (Poirier et al., 1999). CFA is a lipid regulator and agent for treatment of heart disease (Tixier et al., 2003; Doll and Frimmel, 2005). It has been reported to induce ecotoxicity effect when it co-exists with other pollutants in water (Cleuvers, 2003). The physico-chemical properties of these pollutants are compared in Table 5.1. In this study, several important governing factors which might influence the efficiency of

regeneration were systematically studied. These include light intensity, areal loading of N-TiO₂/AC composite under solar irradiation, N-TiO₂ loading in the composite, and temperature. Reusability of the regenerated N-TiO₂/AC composite was examined over several cycles of regeneration.

Table 5.1 Comparison of physico-chemical properties of the investigated pollutants

Pollutant	Molecular weight (g mol ⁻¹)	Solubility in water (mg L ⁻¹)	pK _a or pK _{bH⁺}	Log K _{ow}	Henry's constant (atm·m ³ mol ⁻¹)
Bisphenol-A (BPA)	228	120 ^a	9.6, 10.2 ^b	3.40 ^c	1.00 x 10 ⁻¹⁰ ^a

Sulfamethazine (SMZ)	278	1500 ^d	2.7, 7.4 ^d	0.89 ^e	3.05 x 10 ⁻¹³ ^f

Clofibric acid (CFA)	215	583 ^g	3.2 ^h	2.57 ^e (-0.23) ⁱ	2.19 x 10 ⁻⁸ ^j

^a Howard (1989)

^b Kosky et al. (2002)

^c Leverkusen (1989)

^d Lertpaitoonpan et al. (2009)

^e Beausse (2004)

^f Hansch et al. (1995); Lissemore et al. (2006)

^g Meylan et al. (1996)

^h Doll and Frimmel (2004)

ⁱ Hu et al. (1998) for the equation of K'_{ow} = K_{ow} / (1 + 10^(pH-pK_a)), calculated at pH = 6.0

^j Meylan and Howard (1991)

5.2 Experimental section

The materials and methods used in this study have been described in Chapter 3. The bifunctional composites used were prepared via two-stage calcination technique that produced N-TiO₂/AC (400M-700T) composite (Section 3.1.3). Three different N-TiO₂/AC composites with varying N-TiO₂ loadings were synthesized. The as-synthesized N-TiO₂/AC composite is denoted by N-TiO₂/AC (x%), whereby x denotes the weight percentage (wt%) of N-TiO₂ in the composite. In the first part of this study, various factors which could influence the RE (Eq. 3.2) were investigated. In the second part, a kinetic model was established in order to predict the transient adsorbate concentration remaining in the spent composite during the time course of solar photocatalytic regeneration.

5.3 Results and discussion

5.3.1 Characteristics of N-TiO₂/AC composites

The crystallography, surface chemistry and textural properties of AC, AC (700T) and various as-synthesized materials are compared in Table 5.2. The S_{BET} decreased in tandem with the decreasing pore volume when the N-TiO₂ loading in the composite increased.

Table 5.2 Physico-chemical properties of various samples

Material	Structural and mineralogy	Surface chemistry	Textural properties	
	Crystallite size ^a (nm)	N ^b (at%)	S_{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
N-TiO ₂ /AC (20%)	23.9	1.57	678	0.33
N-TiO ₂ /AC (37%)	24.4	1.43	536	0.25
N-TiO ₂ /AC (50%)	24.7	1.31	434	0.21
N-TiO ₂	25.1	0.35	2.76	0.01
Virgin AC (as received)	-	-	799	0.39
AC (700T)	-	1.84	810	0.35

^aAnatase crystallite size estimated using the Scherrer's equation (Debye and Scherrer, 1917)

^bDetermined via XPS analysis

The XRD pattern (Figure 5.1) shows that the N-TiO₂ crystal phase in the composite comprised anatase-rutile mixture. In general, the introduction of AC support for the composite baffled the growth of N-TiO₂ crystallites. In addition, AC support also baffled the transformation of anatase to rutile. The anatase-rutile mixed crystal phase has been reported to yield synergistic effects for enhanced photocatalytic degradation efficiency (Zachariah et al., 2008) and thus it is beneficial for greater performance of pollutant removal. Interstitial N-doping occurred for the N-TiO₂/AC composite because the N 1s peak was detected at ca. 400 eV (Di Valentin et al., 2007) (Figure 5.2). In general, lower N-TiO₂ loading led to the increased amount of nitrogen being doped into the TiO₂ because AC could concentrate NH₃/N₂ gas onto the composite surface. More details of this phenomenon have been discussed in Section 4.3.1.

Figure 5.1 XRD pattern for various N-TiO₂/AC composites with different N-TiO₂ (%) loading.

Figure 5.2 Deconvoluted XPS spectra of N 1s for various N-TiO₂/AC composites.

5.3.2 Adsorptive characteristics of N-TiO₂/AC composites

Adsorption kinetics study revealed that 1.5 h was sufficient to achieve equilibrium adsorption of BPA, SMZ and CFA on the as-synthesized N-TiO₂/AC composites. The adsorption isotherms of BPA, SMZ and CFA on various N-TiO₂/AC composites, virgin AC (as received) and AC (700T) can be well-fitted with Langmuir adsorption model (Figure 5.3) ($R^2 > 0.99$, Table 5.3). The $S_{\max}$ of the composites decreased progressively with increased N-TiO₂ loading (Table 5.3), which is consistent with decreasing S_{BET} (Table 5.2). The adsorption capacity of N-TiO₂ for the respective pollutants (i.e. BPA, SMZ or CFA) was insignificant ($< 5 \text{ mg g}^{-1}$). The adsorption capacity of AC (700T) was higher than that of virgin AC because surface functionalization of AC under the influence of NH₃ gas could induce a greater adsorption affinity for various organic compounds (Quinlivan et al., 2005; Przepiórski, 2006).

Table 5.3 Langmuir adsorption parameters for various samples

Material	$S_{\max}$ (mg g ⁻¹)	K_{ads} (L mg ⁻¹)	R^2
<i>BPA</i>			
N-TiO ₂ /AC (20%)	272 ± 5	1.50 ± 0.34	0.991
N-TiO ₂ /AC (37%)	259 ± 4	1.22 ± 0.22	0.992
N-TiO ₂ /AC (50%)	231 ± 3	0.85 ± 0.11	0.997
Virgin AC	250 ± 6	1.14 ± 0.03	0.992
AC (700T)	297 ± 5	6.92 ± 1.44	0.998
<i>SMZ</i>			
N-TiO ₂ /AC (20%)	201 ± 2	4.39 ± 0.20	0.999
N-TiO ₂ /AC (37%)	188 ± 2	3.20 ± 0.10	0.997
N-TiO ₂ /AC (50%)	155 ± 3	1.77 ± 0.41	0.999
Virgin AC	168 ± 2	2.28 ± 0.23	0.997
AC (700T)	222 ± 5	15.00 ± 0.33	0.999
<i>CFA</i>			
N-TiO ₂ /AC (20%)	64 ± 2	5.64 ± 0.87	0.999
N-TiO ₂ /AC (37%)	55 ± 2	4.15 ± 0.54	0.998
N-TiO ₂ /AC (50%)	45 ± 2	1.92 ± 0.36	0.999
Virgin AC	50 ± 2	2.26 ± 0.54	0.994
AC (700T)	77 ± 1	8.91 ± 0.96	0.997

The N-TiO₂/AC composites exhibited adsorption affinity for the investigated pollutants in the following order: BPA > SMZ > CFA. The heteroatoms in AC (e.g. oxygen, sulfur, nitrogen) are bonded to the peripheral of the carbon planes, forming various surface functional groups (i.e. acidic or basic) on the AC surface (Yin et al., 2007). In general, complex interplay of various governing factors is involved in the AC adsorption process. Thus, BPA, SMZ and CFA could be adsorbed on AC via several mechanisms (Newcombe and Drikas, 1997; Radovic et al., 1997; Rivera-Utrilla and Sánchez-Polo, 2002), such as: (a) electrostatic interactions between the AC and adsorbates, (b) hydrogen bonding between the surface functional groups of AC and those of the adsorbates, (c) π - π dispersive interactions between the electrons in the AC basal planes and those of the aromatic rings of adsorbates, and (d) hydrophobic interaction between the graphitic AC surface and the hydrophobic functional groups of the adsorbates. At pH 6.0, BPA is present as neutral molecule, SMZ exists as predominantly neutral, while CFA ($pK_a = 3.2$) (Doll and Frimmel, 2004) is fully in anionic form. Thus, the adsorptions of BPA and SMZ on the composite were significantly higher as compared to that of CFA, probably because of weaker hydrophobic interaction between the latter and AC.

Figure 5.3 Langmuir adsorption isotherm as exhibited by various samples for the investigated pollutants: (a) BPA, (b) SMZ, and (c) CFA (note: error bars denote standard deviations of triplicates).

5.3.3 Evaluation of solar photocatalytic regeneration efficiency

5.3.3.1 *Effect of light intensity*

The effect of light intensity on the RE of the spent N-TiO₂/AC composite is depicted in Figure 5.4. The RE increased considerably with increasing solar light intensity, indicating the importance of sufficient intensity of solar irradiation for SPR process. Nevertheless, even at a low solar light intensity of 250 W m⁻², there was still appreciable regeneration of the spent composites achieved within one day. The RE decreased in the order of: CFA > SMZ > BPA, as opposed to their order of adsorption. It was hypothesized that the regeneration process was primarily governed by the desorbability of the pollutants from AC. To confirm this hypothesis, auxiliary desorption experiments were conducted at different temperatures. At equilibrium, the extent of pollutant desorption consistently followed the order of CFA > SMZ > BPA at various temperatures (Figure 5.5).

Adsorption sites on AC consist of both high-energy and low-energy sorption sites (Pikaar et al., 2006) and the molecular adsorbate-adsorbent thermodynamic interactions may be represented by the change in Gibbs free energy (ΔG) (van Noort, 2006). Since the spent composite was loaded with pollutants to its maximum loading possible, it is expected that both high- and low-energy sorption sites were significantly occupied. In general, the high-energy sorption sites are likely to induce irreversible sorption and thus rate-limiting the regeneration process. It is worth noting that with the incorporation of solar photocatalysis, continual pollutant desorption could be still achieved over a prolonged regeneration period and thus enhanced the RE (Figure 5.6).

Figure 5.4 Effect of light intensity on the RE of spent N-TiO₂/AC (37%) composite loaded with BPA, SMZ or CFA (note: error bars denote the maximum and minimum values for $n = 2$).

Figure 5.5 Effect of temperature on the desorption (in the dark) of various pollutants in water as exhibited by spent N-TiO₂/AC (37%) composite.

Figure 5.6 Regeneration efficiency of the spent N-TiO₂/AC composite as a function of time.

To investigate the susceptibility of these pollutants to photocatalytic degradation under solar irradiation and to analyze the intermediates and by-products produced, photocatalytic degradation experiment was conducted using the as-synthesized N-TiO₂ powder. For this study, Newport solar simulator was used as the solar light irradiation source. The results showed that the solar photocatalytic degradation for the pollutants followed the order of efficiency: CFA > SMZ ≥ BPA (Figure 5.7), with k_{app} of 0.53 h^{-1} , 0.22 h^{-1} , and 0.20 h^{-1} , respectively. It is worth noting that the above-mentioned order of efficiency is in agreement with the ranking of RE for the three pollutants.

The concentrations of acetate, formate, sulfate and chloride (which were the products of photocatalysis) were determined using ion chromatograph. Concentrations of acetate and formate were found to increase initially and then decreased with prolonged irradiation time, while both sulfate and chloride concentrations increased progressively with irradiation time. These results indicated the merit of SPR technique over other regeneration techniques for spent AC since solar photocatalysis is a greener technique that could also induce mineralization of the pollutants.

Figure 5.7 Photocatalytic degradation efficiency as exhibited by the as-synthesized N-TiO₂ for the degradation of BPA, SMZ and CFA, respectively.

5.3.3.2 Effect of areal loading of the spent composite under solar irradiation

Areal loading of composite under solar irradiation is an important SPR operational parameter because it determines the areal footprint required for AC regeneration. Figure 5.8 shows that RE decreased significantly when the areal loading of the spent N-TiO₂/AC composites was increased from 0.007 to 0.035 kg m⁻², for the three pollutants. This was due to light-shielding effect by the top layer of the N-TiO₂/AC composites. In practice, however, the above-mentioned effect can be minimized by increasing surface renewal rate through frequent intermittent mixing. Although the areal loading of 0.035 kg m⁻² yielded the least RE among the three areal loadings studied, it actually yielded the largest mass of pollutant removal per unit area. For example, for the three pollutants, the masses removed in the case of 0.035 kg m⁻² were around two times higher than those achieved using 0.007 kg m⁻² areal loading. Thus, to optimize the usage of land area, it is worth to consider using a high areal loading over a longer SPR duration and with frequent surface renewal.

Figure 5.8 Effect of areal loading of the spent composite under solar irradiation on the RE of spent N-TiO₂/AC (37%) composite loaded with BPA, SMZ or CFA (note: error bars denote the maximum and minimum values for $n = 2$).

5.3.3.3 Effect of temperature

Figure 5.9 depicts that the RE for all pollutants increased noticeably with temperature. It has been reported that the apparent activation energy (E_a) for photocatalysis is usually very small for the temperature range of 20-80°C (a few kJ mol⁻¹) (Herrmann, 2005). However, the desorption of pollutants increased with temperatures (Figure 5.5), indicating endothermic desorption process. In addition, the mass transfer of the pollutants can be also enhanced by increasing temperature. Thus, the observed temperature-dependent RE can be attributed to the desorption characteristics of the respective pollutants from the composite to the aqueous phase. This implies that solar heating could also synergistically promote the SPR efficiency.

Figure 5.9 Effect of temperature on the RE of spent N-TiO₂/AC (37%) composite loaded with BPA, SMZ or CFA (note: error bars denote the maximum and minimum values for $n = 2$ or 3).

5.3.3.4 Effect of N-TiO₂ loading

Photocatalysis exhibited by the N-TiO₂/AC composites involved only the illuminated N-TiO₂ particles which were deposited on the surface of AC. Thus, a larger surface covering with N-TiO₂ (or the composite with a higher N-TiO₂ loading) would therefore induce a higher photocatalytic degradation rate for the pollutants and thus a higher RE. The above-mentioned phenomenon was confirmed in this study (Table 5.4). It is also worth noting that for the optimal use of the bifunctional N-TiO₂/AC composite for pollutant removal from waste streams, the composite needs to have a good adsorption capacity for various pollutants. The adsorption capacities of N-TiO₂/AC (50%) with respect to BPA, SMZ and CFA were 15-30% lower than those of N-TiO₂/AC (20%) (Table 5.3), while its REs were 25-40% higher than the latter (Table 5.4). Apparently, an N-TiO₂ mass loading within 20-50% of the composite would exhibit the optimal bifunctionality for use as a competent pollutant adsorbent and meanwhile being effectively solar regenerable.

Table 5.4 Comparison studies with different regeneration systems

System	RE (%)		
	BPA	SMZ	CFA
^a N-TiO ₂ /AC (20%)	38.2 ± 4.9	40.3 ± 5.6	65.2 ± 4.3
^a N-TiO ₂ /AC (37%)	45.9 ± 6.4	50.5 ± 5.8	77.4 ± 5.2
^a N-TiO ₂ /AC (50%)	51.6 ± 3.5	56.9 ± 4.5	82.5 ± 4.7
^b P25 + spent AC	32.1 ± 4.2	38.5 ± 4.4	68.7 ± 4.3
^c Solvent extraction (Methanol)	62.4 ± 2.3	67.0 ± 3.0	45.5 ± 2.7
^c Solvent extraction (Ethanol)	60.8 ± 2.1	64.9 ± 3.4	21.8 ± 3.3
^c Solvent extraction (Ethyl acetate)	58.6 ± 2.5	73.2 ± 2.4	20.5 ± 1.8

^aSPR experimental condition was light intensity (765 W m⁻²), irradiation duration (8 h), areal loading (0.007 kg m⁻²) and temperature (40 ± 5°C)

^bSPR experimental condition was light intensity (765 W m⁻²), irradiation duration (8 h), areal loading (0.007 kg m⁻²) and based on comparable photocatalyst mass loading of 37% and temperature (40 ± 5°C)

^cSolvent extraction involved the mass ratio of spent AC to solvent (1:750) and extraction time was 9 h under continuous vigorous mixing

5.3.3.5 Effect of cycles of reuse

For cost-effective application of N-TiO₂/AC composite for pollutant removal, it is essential that the regenerated composite demonstrates minimal loss in SPR efficiency even after several cycles of reuse. This favorable characteristic was also exhibited by the N-TiO₂/AC (Figure 5.10). The REs achieved in the 3rd cycle were 75%, 83% and 93% of those achieved in the 1st cycle for BPA, SMZ, and CFA, respectively. This indicates the high adherence stability of N-TiO₂ nanoparticles on AC, since dislodgement of N-TiO₂ would cause significant loss in photocatalytic activity of the composite and consequently their decreased RE. In addition, the author's earlier study revealed that the N-TiO₂/AC composite was photostable (Section 4.3.2), hence the synergism of adsorptive-photocatalytic characteristics for pollutant removal could be still preserved over the repetitive use.

Figure 5.10 Effect of cycles of reuse on the RE of spent N-TiO₂/AC (37%) composite loaded with BPA, SMZ or CFA (note: error bars denote the maximum and minimum values for $n = 2$).

5.3.3.6 Examination of solar photocatalytic regeneration kinetics and mechanisms

The time-dependent SPR performance as exhibited by the spent N-TiO₂/AC (37%) composite revealed that the regeneration rates for the composites loaded with different pollutants were consistently high for the first two hours of SPR, and subsequently the regeneration process continued gradually with irradiation time (Figure 5.6). The fast regeneration during the initial stage was assumed to be due to the rapid degradation of adsorbate bound to the N-TiO₂ particles on the exterior surface of AC. The REs for control studies (in the dark for 8 h) were lower than the REs achieved under solar light irradiation for the three pollutants, thus confirming the promotional effect of photocatalysis during the SPR process. In order to determine the rate-limiting step during the SPR process, auxiliary studies on desorption kinetics of the pollutants were conducted using the spent powdered AC (without N-TiO₂). Generally, the desorption process reached a plateau around 1 h of desorption period, and the overall release of the pollutants from the powdered AC was insignificant. The above-mentioned findings suggest that the rate-limiting step during the spent composite regeneration process was primarily desorption into the interfacial film, followed by diffusion within the

powdered AC. Photocatalytic degradation of the released pollutants which have migrated to the surface of N-TiO₂/AC was rapid compared to interfacial film transportation.

A predictive kinetic model is needed to verify the hypothetical controlling rate-limiting step. During the SPR of the spent powdered AC with photocatalytic surface sites, the main processes involved can be conceptualized into four sequential steps: (1) desorption of adsorbate from the interior AC sorption sites, (2) diffusion through interfacial stagnant film, (3) intraparticle diffusion of adsorbate across the macropores to the exterior surface of spent composite, and (4) rapid degradation of adsorbate at the exterior surface due to the production of highly reactive $\bullet\text{OH}$ in proximity. The above processes are schematically illustrated in Figure 5.11.

Figure 5.11 Schematic illustration of adsorbate mass transfer as conceptualized in the proposed kinetic model for solar photocatalytic regeneration.

Eqs 5.1 to 5.5 (based on modified film theory for mass transfer) represent the kinetic model which predicts the transient concentration of adsorbate remaining in the spent composite during the course of SPR process. The following are the assumptions:

- (1) The rate-limiting process is desorption (especially when water is used as solvent) and followed by interfacial film diffusion within the powdered AC.

(2) The powdered AC of the composite was initially loaded uniformly since a 12-h adsorption equilibrium time for adsorbate loading to the composite was adopted in this study.

(3) C_{pore} (macropores or near exterior surface) $\approx C_{\text{bulk water}} < \text{limit of detection (0.01 mg L}^{-1}\text{)}$ because (a) it was confirmed through analysis of the concentrations of the pollutants present in the bulk aqueous phase during the SPR experiment, (b) powdered AC has a short intraparticle migration pathlength which justifies its less-important intraparticle diffusion in macropores compared to that occurring in the granular AC, and (c) outward radial dilution resulting in significant reduction of C_{pore} towards the direction of exterior surface.

$$J = \frac{1}{A} \frac{dM_t}{dt} = \frac{D_L}{\delta_L} (C_{\text{if}, t} - C_{\text{pore}, t}) \quad (5.1)$$

$$\frac{dM_t}{dt} = -k_L A C_{\text{if}, t} \quad (5.2)$$

$$\frac{dS_t}{dt} = -k_L \left(\frac{A}{m} \right) C_{\text{if}, t} = -k_L S_{\text{BET}} C_{\text{if}, t} \quad (5.3)$$

$$\frac{dS_t}{dt} = -k_L S_{\text{BET}} \left(\frac{S_t}{b'(S_{\text{max}} - S_t)} \right) \quad (5.4)$$

Integrating from the initial adsorbate concentration (S_o) to the transient concentration at time t of regeneration (S_t)

$$\ln \left(\frac{S_t}{S_o} \right) - \frac{S_t}{S_{\text{max}}} = - \left(\frac{k_L S_{\text{BET}}}{b' S_{\text{max}}} \right) t - \frac{S_o}{S_{\text{max}}} = -K t - \frac{S_o}{S_{\text{max}}} \quad (5.5)$$

where:

J = mass flux [$\text{M L}^{-2} \text{T}^{-1}$]

M_t = transient mass of adsorbate in the spent composite [M]

m = mass of spent composite used [M]

S_t = transient adsorbate concentration during regeneration [-]

S_o = initial adsorbate concentration [-]

$S_{\max}$ = maximum adsorption capacity of the fresh composite as derived from Langmuir isotherm [-]

S_{BET} = BET specific surface area [$\text{L}^2 \text{M}^{-1}$]

b' = Langmuir desorption constant [$\text{L}^3 \text{M}^{-1}$]

A = surface area of spent composite [L^2]

D_L = diffusion coefficient of adsorbate [$\text{L}^2 \text{T}^{-1}$]

δ_L = thickness of interfacial film [L]

$k_L = D_L/\delta_L$ = mass transfer coefficient [L T^{-1}]

$C_{\text{if}, t}$ = transient interfacial concentration of adsorbate on interior composite surface [M L^{-3}]

$C_{\text{pore}, t}$ = transient concentration of adsorbate in the interior pore water at time t [M L^{-3}]

$C_{\text{bulk water}}$ = concentration of adsorbate in the exterior bulk water [M L^{-3}]

K = regeneration rate constant [T^{-1}]

As presented in Figure 5.12, the experimental results of SPR kinetics could be well-fitted with the proposed model (Eq. 5.5). Thus, the model can provide a reasonable first-cut estimate of the regeneration efficiency of a spent N-TiO₂/AC composite with respect to various organic pollutants, through comparing their diffusion coefficients (D_L) and Langmuir desorption constants to those of a reference pollutant which has been previously investigated for its K value.

Figure 5.12 The linear form of the proposed kinetic model with experimental data-fitting (note: experimental condition was material used: N-TiO₂/AC (37%), areal loading: 0.007 kg m⁻², temperature: 40 ± 5°C, and light intensity: 765 W m⁻²).

The model also allows prediction of time-series adsorbate concentration (which indicates regeneration efficiency) in the spent composite with respect to various initial adsorbate loadings (S_0), as illustrated in Figure 5.13. The figure shows that the regeneration rate of the spent composite would decrease with decreasing S_0 and decreasing K . This agrees with the reduced concentration gradient that limit the desorption rate across the AC particle. In this study, the K for the pollutants was in the following order: CFA > SMZ > BPA and this order is in agreement with the order of pollutant desorbability from the spent composite. While the SPR rates appear to be slower for the composites loaded with highly hydrophobic organics, a prolonged solar irradiation would continue to improve their RE over time. Thus, the SPR technique is versatile for regenerating photocatalytic AC composites used for removing various organic pollutants. Nevertheless, it is worth noting that for practical application of SPR, tap water or other water matrix would be used as the aqueous solution. In the presence of dissolved species, the solar photocatalytic activity of the N-TiO₂ could be lower due to the presence of radical and hole scavengers in the solution (Lim et al., 2011).

Figure 5.13 Predicted time-series regeneration efficiency for various initial degrees of composite saturation and adsorption affinities for pollutants.

5.3.3.7 Comparative regeneration studies

For comparison, regeneration studies were also conducted using (1) a binary mixture of P25 TiO_2 and the pollutants-loaded powdered AC (with a comparable photocatalyst loading), and (2) solvent extraction technique for spent powdered AC using various organic solvents (methanol, ethanol and ethyl acetate). The solvent extraction technique was performed with a 1:750 mass ratio of spent AC to solvent, and extraction time was 9 h under continuous vigorous mixing. The system of binary mixture of P25 and AC has been investigated by previous researchers (Gulyas et al., 2009; Ocampo-Pérez et al., 2011) and it was found to be superior to that of a bare TiO_2 system in removing aqueous organic pollutants. In this study, the spent N- TiO_2 /AC composite consistently exhibited higher REs as compared to those achieved by the binary mixture of P25 and the spent AC, for the three pollutants (Table 5.4). This is mainly because P25 is only photoresponsive to UV (ca. 5% of the solar irradiation). Additionally, in practical application, the micron-size N- TiO_2 /AC composite could be more easily recovered from the slurry (e.g. using microfiltration membrane) (Lim et al., 2011) but it would be difficult to recover the nano-size P25.

A comparison between SPR technique and the solvent extraction technique (i.e. using various organic solvents) revealed that the findings were pollutant-dependent. For example, the RE obtained from SPR technique for CFA was superior to that of the solvent extraction technique. CFA is a polar pollutant which deprotonates at circumneutral pH, and its ionized form generally has a limited solubility in organic solvents. On the other hand, BPA and SMZ are more hydrophobic at circumneutral pH compared to the ionized CFA, thus their solvent extractions were more efficient compared to the 8-h SPR. Nevertheless, a prolonged SPR would outperform the solvent extraction technique.

5.4 Conclusions and practical significance

In general, the N-TiO₂/AC composites exhibited higher adsorption affinity for both BPA and SMZ than that of the CFA. This is because BPA and SMZ are more hydrophobic and less polar organic compounds as compared to CFA. The RE was generally enhanced with the increase in the light intensity, N-TiO₂ loading, and temperature. The RE was pollutant-dependent, and it was the highest for the case of CFA-loaded N-TiO₂/AC. This was due to the greater extent of CFA desorption from the interior AC adsorption sites. Desorption of pollutant from the AC adsorption sites was the rate-limiting process. A versatile kinetic model was established to predict the transient adsorbate remaining in the spent N-TiO₂/AC composite during the solar regeneration process, and this model would be applicable for various organic pollutants. The SPR technique was more efficient and environmentally-friendly as compared to the solvent extraction technique for regenerating spent AC loaded with CFA. The SPR technique has its practical and environmental merits because it requires only basic facility and simple operation and maintenance, allows on-site AC regeneration, and does not consume chemical and energy during the regeneration. Since the N-TiO₂/AC composite developed in this study remained photostable, its bifunctionality during solar regeneration could be preserved. Thus, its multiple cycles of reuse are possible and this will reduce the production of waste stream. The bifunctional characteristics of the N-TiO₂/AC composite potentially allow the in-line and in-situ regeneration of the composite during daytime, without operational downtime. Thus, the SPR technique is a greener and sustainable option compared to conventional spent AC regeneration techniques.

Chapter 6 Bimodal N-doped P25-TiO₂/AC Composite: Characteristics, Physical Stability, and Synergistic Removal of Sulfamethazine

6.1 Introduction

In Chapter 4, the N-TiO₂/AC prepared via the two-stage calcination manifested enhanced adsorptive-solar photocatalytic removal of BPA in water. In Chapter 5, the SPR technique was promising in regenerating the spent composites loaded with BPA, SMZ or CFA. Although the N-TiO₂/AC as prepared via multiple coatings and two-stage calcination exhibit synergistic effect of adsorption-photocatalysis processes, the synthesis technique may incur substantial cost. In view of the need for scale-up production, it is imperative to develop a synthesis technique for the composite which is less costly. Currently, various commercial titania are readily available in the market and they are proven to have high photocatalytic activity under UV irradiation. Thus, the development of a N-TiO₂/AC composite comprising commercial titania with effective N-doping technique is desirable.

In recent years, synthesis involving the integration of titania (sol) and commercial titania has been attempted because of the potential for enhanced photocatalytic performances or photoelectrochemical applications (Chen and Dionysiou, 2008; Chen et al., 2009). In addition, it has been reported that the incorporation of Degussa P25 powders into TiO₂ thin films as produced via alkoxide sol-gel technique yielded thicker and harder TiO₂ thin films (Balasubramanian et al., 2003). These TiO₂ thin films enriched with P25 powders exhibited good photocatalytic activity for degradation of 4-chlorobenzoic acid (Balasubramanian et al., 2004). The above-mentioned studies thus suggest that the incorporation of commercial titania into the TiO₂ sol will yield a hybrid photocatalyst that exhibits enhanced photocatalytic activity for efficient aqueous organic pollutant removal.

The commercial titania Degussa P25 is the most widely used photocatalyst which exhibits remarkable photocatalytic activity under UV irradiation, due to the synergism of its anatase-rutile phase. Hence, it potentially offers enhanced photocatalytic activity after incorporation into the TiO_2/AC composite. Nevertheless, it is imperative to narrow the bandgap energy of the P25, to induce more photoresponsiveness of the photocatalyst under the solar irradiation. It is also essential that the P25 powders are firmly coated onto the surface of AC particles in order to induce and maintain the synergistic adsorption-photocatalysis processes. In this regard, the incorporation of N- TiO_2 (sol) is still required and there is a need to obtain the most optimal weight distribution of N-P25 to N- TiO_2 (sol) which will lead to the enhanced photocatalytic activity for the composite.

In this study, a novel bimodal mesoporous photocatalytic composite, namely nitrogen-doped bimodal titania coated on powdered activated carbon (N-P25- TiO_2/AC), was synthesized through facile preparation route. The technique involved a lesser number of steps and amount of chemicals used as compared to that of the synthesis technique requiring multiple-coatings and the single-stage and two-stage calcinations. SMZ was chosen as the model pollutant. Its properties and environmental concern have been discussed in Section 5.1 and Table 5.1. Several governing factors for the solar photocatalytic degradation efficiency using the as-synthesized N-P25- TiO_2/AC were examined. These include the total loading of N-doped titania, sol-gel synthesis technique, weight distribution between N-P25 and N- TiO_2 (sol), composite dosage, light wavelength spectrum and solution pH.

6.2 Experimental section

The chemicals used, synthesis protocol, characterization equipments used and the analytical procedures employed in this study have been described in Chapter 3. The composites used were the bimodal N-P25- TiO_2/AC prepared via the facile modified sol-gel techniques (Section 3.1.4). The variances in the sol-gel techniques include the technique of anchoring the titania onto the AC, and also the procedure of nitrogen-doping process. In the first part of this study, the adsorption performances of the

bimodal N-P25-TiO₂/AC composites in UPW were examined. In the second part of this study, the physical stability of this composite was assessed using the ultrasonication disruption technique. In the third part of this study, a comprehensive investigation on the photocatalytic activity of the various bimodal composites with respect to SMZ degradation was conducted. The N-P25 and N-TiO₂ (sol) powders (without AC support) were also prepared by direct calcination of P25 and titania sol, respectively, under mixed NH₃/N₂ atmosphere at 700°C in a tube furnace. These samples are denoted as N-P25 (700T-H) and N-TiO₂ (sol) (700T-H), respectively, whereby H represents the calcination duration (in h). Virgin AC which was directly calcined at 700°C under NH₃/N₂ atmosphere for 4 h was denoted as AC (700T-4).

6.3 Results and discussion

6.3.1 Characteristics of N-P25-TiO₂/AC composites

As shown in Table 6.1, an increased N-doped titania loading also resulted in a reduction of both S_{BET} values and pore volumes. There were slight decreases in the pore volumes of the as-synthesized composites. For example, based on the content of N-doped titania in the N-P25-TiO₂ (25+10)/AC composite, the theoretical pore volume was calculated as 0.30 cm³ g⁻¹, while the as-determined pore volume was 0.23 cm³ g⁻¹. This indicates that some degrees of pore blocking occurred in the AC support, but the extent was marginal.

Table 6.1 Physico-chemical characteristics of various samples

Sample	Compositional property	Textural properties		Surface chemistry
	Total loading of N-doped titania in composite ^a (wt%)	S_{BET}^b ($\text{m}^2 \text{g}^{-1}$)	V^c ($\text{cm}^3 \text{g}^{-1}$)	N/Ti ^d (Atomic ratio)
P25	-	57.8	0.14	-
N-P25 (700T-4)	-	27.0	0.09	0.006
N-TiO ₂ (sol) (700T-4)	-	3.3	0.02	0.013
N-P25-TiO ₂ (5+15)/AC	20	666	0.33	0.358
N-P25-TiO ₂ (20+15)/AC	35	584	0.27	0.195
N-P25-TiO ₂ (20+15)/AC-U	35	593	0.25	0.223
N-P25-TiO ₂ (20+15)/AC-Pseudo	35	535	0.24	0.185
N-P25-TiO ₂ (25+10)/AC	35	575	0.23	0.186
N-P25-TiO ₂ (15+20)/AC	35	544	0.28	0.213
N-P25-TiO ₂ (35+15)/AC	50	462	0.22	0.086
Virgin AC	-	799	0.39	-
AC (700T-4)	-	881	0.42	-

(-), data not available or not determined

^a Composition of N-doped titania in the bimodal composite, as determined using gravimetry method

^b BET specific surface area

^c BJH total pore volume

^d Determined using XPS

The nitrogen adsorption-desorption isotherm for the N-P25-TiO₂ (25+10)/AC composite (Figure 6.1) was of Type IV and the type of hysteresis loop appeared to be of Type H4 loop (Sing et al., 1985). Apparently, there was some extent of capillary condensation which occurred in the mesopores of the bimodal composite, leading to the hysteresis loop as observed in the adsorption-desorption isotherm. This implies that the bimodal composite is likely to contain a large number of narrow slit-like pores in its AC pore structures. The predominant pore size for the N-P25-TiO₂ (25+10)/AC composite was ca. 3.8 nm (shown as inset in Figure 6.1), thus indicating that this composite was mainly mesoporous (Sing et al., 1985).

Figure 6.1 Nitrogen adsorption-desorption isotherm analysis for N-P25-TiO₂ (25+10)/AC (inset: the corresponding pore size distribution of the composite).

Figure 6.2a depicts the XRD patterns for various N-P25-TiO₂/AC composites with different total loadings of N-doped titania. The estimated percentages of rutile in the anatase-rutile mixtures (as determined using Spurr's and Myer's equation (Spurr and Myers, 1957)) for the N-P25-TiO₂ (5+15)/AC, N-P25-TiO₂ (20+15)/AC, N-P25-TiO₂ (35+15)/AC were ca. 25, 30 and 40 wt%, respectively. Apparently, a higher total loading of N-doped titania on AC was less efficient in baffling the transformation of anatase to rutile. This result indicates that AC served to baffle anatase phase transformation to rutile at high calcination temperatures. For the case of bare titania (Figure 6.2b), both the N-P25 (700T-4) and N-TiO₂ sol (700T-4) had rutile as the predominant phase. It is worth noting that the rutile content in P25 (Figure 6.2b) was ca. 20 wt%, as determined using Spurr's and Myer's equation (Spurr and Myers, 1957). This value is comparatively lower than the rutile content in the bimodal N-P25-TiO₂ (5+15)/AC, N-P25-TiO₂ (20+15)/AC, and N-P25-TiO₂ (35+15)/AC composites. The different contents of rutile phase present in photocatalyst of the bimodal composites are due to the fact that the amount of AC (as the support for the photocatalyst) was varied during the material synthesis.

Figure 6.2 XRD pattern for: (a) N-P25-TiO₂/AC with different total loadings of N-doped titania, and virgin AC, and (b) N-P25-TiO₂ (25+10)/AC, N-P25 (700T-4), N-TiO₂ (sol) (700T-4), and P25.

To investigate the suitable calcination duration for the bimodal composite, a systematic study was conducted and the results are shown in the UV-Vis absorbance spectra (Figure 6.3). In general, the first E_g for both N-P25 and N-TiO₂ (sol) decreased somewhat with increasing calcination time. The first E_g for N-P25 (700T-4) and N-TiO₂ (sol) (700T-4) was ca. 2.90 and 2.71 eV, respectively. Prolonging calcination duration from 2 to 4 h also improved the visible-light photoresponsiveness (in the wavelength region of 420-500 nm) for both types of N-doped titania. The N-P25-TiO₂ (25+10)/AC composite exhibited absorbance throughout the UV-Vis spectrum, in agreement with its black appearance as that of virgin AC (as received).

Figure 6.3 UV-Vis absorption spectra for various samples.

The FTIR spectra for N-P25-TiO₂ (25+10)/AC bimodal composite and virgin AC are depicted in Figure 6.4. The band for N-P25-TiO₂ (25+10)/AC composite at ca. 520 cm⁻¹ is associated with Ti-O stretching vibration (Liu et al., 2007a), thus confirming the coating of N-doped titania onto AC (Figure 6.4a). In general, it could be observed that most of the bands associated with surface functional groups of AC were considerably reduced in the case of the bimodal composite. The differences between the bands assigned to cyclic ethers (1400-1100 cm⁻¹), lactones (1730-1705 cm⁻¹), and phenols groups (3600-3000 cm⁻¹) (Cordero et al., 2007a) for that of the composite and AC are shown in the corresponding figures (Figure 6.4b, c and d). This indicates the

deposition of titania onto AC surface, which is likely to form new chemical bonds with these AC surface functional groups.

Figure 6.4 FTIR spectra of N-P25-TiO₂ (25+10)/AC and AC, respectively: (a) titania surface functional groups (520 cm⁻¹), (b) cyclic ethers surface functional groups (1400-1100 cm⁻¹), (c) lactones surface functional groups (1730-1705 cm⁻¹), and (d) phenols surface functional groups (3600-3000 cm⁻¹).

The deconvoluted XPS spectra for the N-P25-TiO₂ (25+10)/AC are presented in Figure 6.5. From Figure 6.5a, the detection of N 1s peaks at binding energy (BE) 399.2 eV indicates interstitial nitrogen doping (Asahi et al., 2001; Di Valentin et al., 2007). From Figure 6.5b, there was no observed C 1s peak ca. 281.8 eV, thus indicating that Ti-C bond was undetectable (Zhang and Koka, 1998), and carbon doping into the TiO₂ lattice was insignificant. The C1s peak detected at 288.9 eV is assigned to carboxylic acid groups (Moreno-Castilla et al., 2000). From Figure 6.5c, it was confirmed that the photocatalyst was titania because (i) the difference in BE

between Ti $2p_{3/2}$ and Ti $2p_{1/2}$ is ca. 5.7 eV, thus verifying that Ti element existed as Ti^{4+} (TiO_2) (Fu et al., 2004) and (ii) there are no Ti peaks at BE 455 eV (assigned to Ti^{2+}) and 456.7 eV (assigned to Ti^{3+}) (Zhang et al., 2006). As shown in Figure 6.5d, the observed O 1s peak at 530.4 eV can be associated with the Ti-O-Ti linkages (Zhao et al., 2008), while O 1s peak at 532.1 eV is attributed to the oxygen atoms in hydroxyl and ether groups in the AC (Boyano et al., 2008).

Figure 6.5 Deconvoluted XPS spectra for N-P25-TiO₂ (25+10)/AC: (a) N 1s, (b) C 1s, (c) Ti 2p, and (d) O 1s.

The SEM micrograph along with the elemental mapping and EDX spectra for N-P25-TiO₂ (25+10)/AC composite are depicted in Figure 6.6. The fact that C element (Figure 6.6b) was noticeable indicates that some exterior surface adsorption sites of AC were still exposed. The Ti element (Figure 6.6c) was detected on the surface of AC, indicating the titania deposition on AC.

Figure 6.6 EDX spectra for N-P25-TiO₂ (25+10)/AC, with insets (a), (b), and (c) depicting the SEM micrograph of the composite, C element distribution and Ti element distribution, respectively.

Figure 6.7a shows the TEM image for the N-P25-TiO₂ (25+10)/AC composite. In general, the titania nanoparticles were reasonably well anchored on the surface of AC. To verify the titania and AC, selected area electron diffraction (SAED) was performed and the results are presented in the insets (i) and (ii) (Figure 6.7a), respectively. The SAED pattern for the N-doped titania comprised concentric rings, which indicates the good crystallinity of the photocatalysts. By close examination, it could be observed that there were some differences in the morphologies and the particle sizes of the titania, thus confirming the presence of the bimodal titania. The SAED pattern for AC, however, was without the concentric rings, thus confirming the amorphous state of the carbon and negligible interstitial N-TiO₂ particles in the AC pores. From the high resolution TEM (HRTEM) image in Figure 6.7b, the d spacing of ca. 0.35 nm (from $\frac{1.77}{5} = 0.354$ nm) in the lattice fringes corresponds to the (101) plane of anatase (Xie et al., 2009). In addition, the d spacing of ca. 0.32 nm (from $\frac{3.24}{10} = 0.324$ nm) in the lattice fringes corresponds to the (110) plane of rutile (Fei et al., 2006) (as shown in

Figure 6.7c). This confirms the presence of anatase-rutile mixture in the bimodal composite.

Figure 6.7 TEM image for N-P25-TiO₂ (25+10)/AC composite depicting: (a) the anchorage of N-doped titania on activated carbon with the respective SAED patterns for (i) N-doped bimodal titania and (ii) activated carbon, (b) the lattice parameters for anatase as obtained using HRTEM, and (c) the lattice parameters for rutile as obtained using HRTEM.

6.3.2 Physical stability

To evaluate the disintegration of the composite or the dislodgement of N-TiO₂ particles as induced by the ultrasonication, specific ultrasonic energy which denotes the amount of energy supplied per unit mass of treated particles in the suspension was adopted as the operational parameter (Bougrier et al., 2005; Khanal et al., 2007).

The effect of ultrasonication disruption on the physical stability of the N-P25-TiO₂ (20+15)/AC and N-P25-TiO₂ (20+15)/AC-Pseudo composite is compared in Figure 6.8. The particle size distribution of the virgin AC was observed as ranging from 0.83 to 60.3 μm . Since there were no AC particles detected below 0.83 μm , it is assumed in this study that the particle sizes less than 0.83 μm would be attributed to the dislodged N-doped titania from the composite. The quantitative analysis of the dislodged N-doped titania (volume cumulative percentage) for both the N-P25-TiO₂ (20+15)/AC and N-P25-TiO₂ (20+15)/AC-Pseudo composites is presented in Table 6.2.

Table 6.2 Effect of specific ultrasonic energy on the cumulative particle size ($< 0.83 \mu\text{m}$) for N-P25-TiO₂ (20+15)/AC and N-P25-TiO₂ (20+15)/AC-Pseudo bimodal composites

Specific energy (kJ g^{-1})	Cumulative particle size $< 0.83 \mu\text{m}$ (Vol %)	
	N-P25-TiO ₂ (20+15)/AC	N-P25-TiO ₂ (20+15)/AC-Pseudo
0 (Baseline)	0.63	0.80
250	1.86	3.68
500	2.10	4.03
750	2.18	4.62
1000	2.54	5.82

For the baseline particle size distributions (i.e. without ultrasonic disruption) of N-P25-TiO₂ (20+15)/AC and N-P25-TiO₂ (20+15)/AC-Pseudo composites, the particle size in the range of ca. 60–830 μm represented the agglomerated portions of the bimodal composites. The small percentages of dislodged titania ($< 0.83 \mu\text{m}$) were also present, which could be resulted from hand-grounding the dried composites (using agate mortar and pestle prior to use). It is worth noting that for the baseline cases, the amount of N-doped titania dislodged from N-P25-TiO₂ (20+15)/AC-Pseudo was higher than that of N-P25-TiO₂ (20+15)/AC (Table 6.2). This could serve as a preliminary indication that the latter had a greater physical stability against abrasion.

When a specific ultrasound energy of 250 kJ g^{-1} (corresponding to 3 min of ultrasonication period) was applied to both of the composites, noticeable deagglomeration for particles in the range of 60-830 μm occurred. This indicates that ultrasonication disruption technique is powerful enough to be used for assessing the physical stability of bimodal composite. At 250 kJ g^{-1} , the dislodgement of N-doped titania nanoparticles was greater for N-P25-TiO₂ (20+15)/AC-Pseudo than that of N-P25-TiO₂ (20+15)/AC by a factor of 2.0. Furthermore, when the specific energy was gradually increased to eventually reach 1000 kJ g^{-1} , N-P25-TiO₂ (20+15)/AC also exhibited greater resistance to titania dislodgement as compared to N-P25-TiO₂ (20+15)/AC-Pseudo (Table 6.2). This implies that the synthesis technique for N-P25-TiO₂ (20+15)/AC was better than that of N-P25-TiO₂ (20+15)/AC-Pseudo in producing a physically stable composite, which is likely to be due to the stronger chemical bonding formed between the N-P25 and N-TiO₂ (sol) during the sol-gel synthesis.

It is worth noting that for practical application of the bimodal composite in water treatment and reclamation plants, it is unlikely that the hydrodynamic shearing in water treatment tanks could induce destabilization effect on the composites as high as the acoustic cavitation energy (ultrasonication) introduced in this study. In other words, the investigation of the physical stability of the composites via ultrasonication disruption technique in this study represented the worst case scenario. Thus, the bimodal composites synthesized in this study via sol-gel routes would have a good physical stability when used in water treatment plants. The good physical stability of the bimodal composites is crucial as it would ensure the synergistic effect of adsorption-solar photocatalysis processes.

Figure 6.8 Effect of specific ultrasonic energy on the dislodgement of N-doped bimodal titania from (a) N-P25-TiO₂ (20+15)/AC composite, and (b) N-P25-TiO₂ (20+15)/AC-Pseudo composite (note: the virgin AC was as received).

6.3.3 Adsorption characteristics of N-P25-TiO₂/AC composites

In general, the adsorption experiments revealed that 1.5 h was sufficient to achieve adsorption equilibrium of SMZ on the bimodal composites, as show in Figure 6.9 below:

Figure 6.9 Adsorption kinetics of AC (700T-4) and various as-synthesized bimodal N-P25-TiO₂/AC composites.

The adsorption isotherms of various as-synthesized N-P25-TiO₂/AC composites are presented in Figure 6.10, while the $S_{\max}$ and K_{ads} are compared in Table 6.3. The $S_{\max}$ decreased with increasing N-doped titania loading. For the composites having a comparable total titania loading (e.g. 35%), the differences in the $S_{\max}$ was insignificant. It is worth noting that $S_{\max}$ of AC (700T-4) was considerably higher than that of the virgin AC (as received) (Table 6.3). This is because studies have shown that AC being treated with NH₃ gas would exhibit higher affinity for various organic pollutants, due to the surface functionalization of the AC (Dimotakis et al., 1995; Cheng et al., 2005; Quinlivan et al., 2005; Przepiórski, 2006). The bimodal composites, despite having reduced $S_{\max}$ as compared to the AC (700T-4), could still exhibit good adsorption capacities for the removal of SMZ.

Figure 6.10 Adsorption isotherm for N-P25-TiO₂/AC with different total loadings of N-doped titania (note: error bars denote standard deviation of triplicates).

Table 6.3 Adsorption capacity for various samples

Sample	Adsorption capacity		
	$S_{\max}$ (mg g^{-1})	K_{ads} (L mg^{-1})	R^2
N-P25 (700T-4)	-	-	-
N-TiO ₂ (sol) (700T-4)	-	-	-
N-P25-TiO ₂ (5+15)/AC	207 ± 3	5.76 ± 1.15	0.997
N-P25-TiO ₂ (20+15)/AC	195 ± 2	3.27 ± 0.57	0.994
N-P25-TiO ₂ (20+15)/AC-U	198 ± 2	4.27 ± 0.47	0.996
N-P25-TiO ₂ (20+15)/AC-Pseudo	183 ± 3	2.68 ± 0.12	0.992
N-P25-TiO ₂ (25+10)/AC	194 ± 3	3.24 ± 0.05	0.995
N-P25-TiO ₂ (15+20)/AC	188 ± 2	3.08 ± 0.23	0.993
N-P25-TiO ₂ (35+15)/AC	166 ± 2	1.91 ± 0.11	0.995
Virgin AC (as received)	168 ± 2	2.28 ± 0.23	0.997
AC (700T-4)	230 ± 2	22.9 ± 1.02	0.999

(-), data not available or not determined

Solution pH is an important governing factor for adsorption because it governs the protonation/deprotonation of the target pollutant, surface TiOH group of titania and adsorption sites of AC. The effect of solution pH on adsorption of SMZ, as exhibited by N-P25-TiO₂ (25+10)/AC, generally follows the order: pH 6.0 ($194 \pm 3 \text{ mg g}^{-1}$) $\sim$ pH 3.0 ($183 \pm 3 \text{ mg g}^{-1}$) $>$ pH 10.0 ($103 \pm 2 \text{ mg g}^{-1}$). In this study, the pH_{IEP} of the N-P25-TiO₂ (25+10)/AC was ca. 6.0. The protonation/deprotonation of the SMZ under different pH conditions has been reported previously (Ingerslev and Halling-Sorensen, 2000). The amino group of SMZ will only protonate below pH 2.7. Thus, at pH 3.0

and 6.0, SMZ remains as predominantly neutral. Accordingly, adsorption of SMZ on the composite at pH 3.0 and 6.0 was quite comparable (Figure 6.11). It is also worth noting at pH 6.0, the adsorption capacity of the N-P25-TiO₂ (25+10)/AC composites for SMZ removal was marginally higher than that of the N-TiO₂/AC (37%) composite (i.e. the composite discussed for Figure 5.3b in Chapter 5). This is because the former were calcined for 4 h under mixed NH₃/N₂ gas, as opposed to only 2 h of calcination under mixed NH₃/N₂ gas for the latter. At pH 10.0, the SO₂NHR (sulfonamide group) is fully deprotonated and SMZ is in anionic form. Thus, at pH 10.0, the electrostatic repulsion between the negatively-charged surface of bimodal composite and the anionic SMZ resulted in the least adsorption of SMZ on the composite.

Figure 6.11 Adsorption isotherm for N-P25-TiO₂ (25+10)/AC at various pH values (note: error bars denote standard deviation of triplicates).

6.3.4 Evaluation of photocatalytic degradation efficiencies

The derived kinetic constants for SMZ degradation by the N-P25 (700T-4), N-TiO₂ (sol) (700T-4) and various types of bimodal N-P25-TiO₂/AC composites, are presented in Table 6.4. All the experimental data were fitted into the Langmuir-Hinshelwood (L-H) kinetic model. The simplification of the L-H model into pseudo first-order kinetic model with pseudo first-order rate constant (k_{app}) has been discussed

in Section 4.3.4. The k_{app} was determined using experimental data obtained throughout the 4 h of light irradiation time.

Table 6.4 Comparison of PCD efficiency under solar light irradiation for various samples

Sample	PCD efficiency under solar light irradiation	
	k_{app} (h^{-1})	R^2
N-P25 (700T-4) ^a	0.10	0.989
N-TiO ₂ (sol) (700T-4) ^a	0.04	0.991
N-P25-TiO ₂ (5+15)/AC	0.27	0.996
N-P25-TiO ₂ (20+15)/AC	0.39	0.997
N-P25-TiO ₂ (20+15)/AC-U	0.36	0.998
N-P25-TiO ₂ (20+15)/AC-Pseudo	0.31	0.998
N-P25-TiO ₂ (25+10)/AC	0.48	0.996
N-P25-TiO ₂ (15+20)/AC	0.34	0.997
N-P25-TiO ₂ (35+15)/AC	0.32	0.996
P25 + AC	0.43	0.995

^a Photocatalyst dosage of 0.1 g L⁻¹ was used

The N-P25 (700T-4) exhibited a greater solar photocatalytic activity for SMZ degradation as compared to that of N-TiO₂ (sol) (700T-4), where the k_{app} exhibited by the former to be 2.5 times higher than that of the latter (Table 6.4). This may be due to two reasons: (1) N-P25 (700T-4) exhibited greater ability to baffle anatase phase transformation to rutile, as can be confirmed from the XRD patterns in Figure 6.2b, and (2) the S_{BET} for N-P25 (700T-4) was ca. 8 fold higher than that of N-TiO₂ (sol) (700T-4) (Table 6.1), thus presenting more adsorption sites for target pollutants. On this basis, it was postulated that the composite would also exhibit greater PCD efficiency for SMZ degradation if N-P25 was incorporated as part of the supported N-doped titania. Although N-TiO₂ (sol) was not as photocatalytically active as N-P25, it was still essential to bind the N-P25 onto the AC support. Hence, the above-mentioned findings serve as a good motivation to investigate the solar photocatalytic activity of bimodal composites.

6.3.4.1 Effect of total loading of bimodal N-doped titania

As shown in Figure 6.12 and Table 6.4, the PCD efficiency for SMZ degradation under solar light irradiation, as exhibited by the bimodal composites of the same N-

TiO₂ (sol) content decreased in the following order: N-P25-TiO₂ (20+15)/AC > N-P25-TiO₂ (35+15)/AC > N-P25-TiO₂ (5+15)/AC. The effect of photolysis was insignificant (ca. 5%) over the 4-h solar irradiation. The photocatalytic activity of the N-P25-TiO₂ (5+15)/AC composite was the least efficient because it had the lowest N-doped titania content. Although N-P25-TiO₂ (35+15)/AC composite possessed the highest amount of N-doped titania, it also had the highest rutile content (ca. 40%) (Figure 6.2a). It has been reported that the charge carriers recombination in rutile is considerably higher than that of anatase, because the h⁺ trapping in anatase is 10-fold more efficient than in rutile (Riegel and Bolton, 1995). In addition, for the case of a bifunctional adsorptive-photocatalytic composite, the PCD efficiency for SMZ degradation is synergistically enhanced by the adsorption process under well-mixed conditions in water. In other words, an optimal content of AC as the titania support is important to induce a rapid adsorption-photocatalytic degradation process for efficient SMZ removal. Thus, the results suggest that the optimal total loading of N-doped titania on AC was 35%.

Figure 6.12 Effect of total N-doped titania loading but a constant N-TiO₂ (sol) content on the photocatalytic degradation of SMZ.

6.3.4.2 *Effect of sol-gel synthesis technique*

The type of sol-gel synthesis technique employed may influence the photocatalytic activity of the bimodal composites and thus this effect was investigated. It is worth noting that the provision of urea during the sol-gel synthesis route could serve as the alternative source of N-dopant for titania, as confirmed by the author's earlier study (Yap et al., 2011). Hence, it is important to examine the effect of the additional N-doping as provided by urea (i.e. in addition to the N-doping as provided by the 4-h calcination under mixed NH_3/N_2 gas) on the photocatalytic removal of SMZ. The PCD efficiency for SMZ removal under solar light irradiation as exhibited by the N-P25- TiO_2 (20+15)/AC was comparable to that of N-P25- TiO_2 (20+15)/AC-U, but 1.3 times higher than that of N-P25- TiO_2 (20+15)/AC-Pseudo (Figure 6.13 and Table 6.4). This indicates that the addition of urea might not increase the PCD efficiency, while the lower photocatalytic activity of N-P25- TiO_2 (20+15)/AC-Pseudo composite could be due to its relatively weaker physical stability (Figure 6.8b). The findings suggest that the type of sol-gel synthesis technique employed could have an important influence on PCD efficiency of the as-synthesized composite. Indeed, it could be inferred that the titania sol played an essential role to improve the binding of P25 onto the bimodal composite to further enhance the photocatalytic activity of the composite. In addition, the results also revealed that the more cost-effective sol-gel synthesis was through the single-step sol-gel route (i.e. direct addition of P25 to the titania sol), rather than the two-step pseudo sol-gel route (i.e. subsequent addition of P25 to the pre-coated composite in aqueous solution).

Figure 6.13 Effect of sol-gel techniques on the photocatalytic degradation of SMZ.

6.3.4.3 Effect of weight distribution between N-P25 and N-TiO₂ (sol)

To further explore possible improvements on the solar photocatalytic activity of the N-P25-TiO₂ (20+15)/AC composite, the influence of weight distribution between N-P25 and N-TiO₂ (sol) was investigated and the results are shown in Figure 6.14. Apparently, the results indicate that at a constant total loading of N-doped titania, a higher ratio of N-P25: N-TiO₂ (sol) would be advantageous for SMZ degradation. The PCD performance of the bimodal composites decreased in the following order: N-P25-TiO₂ (25+10)/AC > N-P25-TiO₂ (20+15)/AC > N-P25-TiO₂ (15+20)/AC. This result is in agreement with the results of the author's earlier investigations (as described in the preceding discussions in Section 6.3.4), whereby the N-P25 (700T-4) was more photocatalytically active than that of the N-TiO₂ (sol) (700T-4). Nevertheless, recapitulating the importance of incorporating titania (sol) for the bimodal composite (as described in the preceding discussions in Section 6.3.2), a minimum amount of N-TiO₂ (sol) content should be present. In this study, for a 35 wt% of total N-doped titania loading, a minimum of 10 wt% N-TiO₂ (sol) in the bimodal titania was necessary to yield the enhanced PCD efficiency of the N-P25-TiO₂ (25+10)/AC composite.

Figure 6.14 Effect of weight distribution between N-P25 and N-TiO₂ (sol) on the photocatalytic degradation of SMZ.

The proposed photocatalytic mechanism of the bimodal composite is schematically illustrated in Figure 6.15. First, it involved the adsorption of SMZ from the bulk aqueous solution to the surface of the N-P25-TiO₂/AC composite, due to the affinity of the composite for SMZ and also the large S_{BET} of AC. Second, upon excitation by photonic energy greater than the bandgap energy of N-doped titania, highly oxidizing $\bullet\text{OH}$ would be produced at both the surfaces of N-P25 and N-TiO₂ (sol) to participate in photocatalytic redox reactions for SMZ degradation. The $\bullet\text{OH}$ is a non-selective and highly reactive species, with a standard redox potential of +2.8 V versus NHE (normal hydrogen electrode) (Egerton and Christensen, 2004). For the N-P25-TiO₂ (25+10)/AC composite, the crystal phase was predominantly anatase, whereby the rutile content was ca. 33% (as estimated using the Spurr and Myers equation (Spurr and Myers, 1957)). This crystal phase distribution is similar to that of P25. For P25, its remarkable photocatalytic activity is attributed to the efficiency of spatial charge-carrier separation, as induced by its anatase-rutile mixture that can prolong e^-/h^+ lifetimes (Schindler and Kunst, 1990; Bickley et al., 1991; Hurum et al., 2003). Two mechanisms have been proposed for the efficient charge-carrier separation in P25: (1) the e^- in the anatase conduction band can be transferred to the rutile conduction band (Schindler and Kunst, 1990; Bickley et al., 1991), and (2) the e^- in the rutile

conduction band can be transferred to the anatase trapping sites (Hurum et al., 2003), as revealed by a study conducted using electron paramagnetic resonance spectroscopy. Accordingly, an optimum rutile content in the anatase-rutile mixture (for the as-synthesized mixed-phase titania) would lead to the highest photocatalytic activity (Zachariah et al., 2008). Thus, for this bimodal composite, the presence of anatase-rutile mixture (with predominant anatase phase) was advantageous for efficient SMZ degradation.

In addition, AC support could also reduce the agglomeration of the supported N-doped titania nanoparticles, thus improving the PCD efficiency. The doping of titania with nitrogen would also induce additional benefits such as: (a) the N-P25 exhibited enhanced visible-light photoresponsiveness as compared to P25, and (b) the creation of localized states within the titania bandgap could act as trapping sites for photogenerated h^+ for enhanced PCD performances (Beranek et al., 2007; Di Valentin et al., 2007). Since N-P25-TiO₂ (25+10)/AC composite exhibited the greatest degradation efficiency for SMZ, it was thus the focus of subsequent investigations and discussions.

Figure 6.15 Schematic illustration of the proposed photocatalytic mechanisms of N-doped bimodal titania supported on activated carbon.

6.3.4.4 Effect of composite dosage

The effect of composite dosage is depicted in Figure 6.16. The k_{app} decreases in the following order of dosages: $0.20 \text{ g L}^{-1} > 0.30 \text{ g L}^{-1} > 0.10 \text{ g L}^{-1}$. The turbidities of the suspension with the dosage of 0.10, 0.20 and 0.30 g L^{-1} were ca. 60, 105 and 150 NTU, respectively. In general, the composite dosage determined both the extent of light attenuation and amount of N-doped titania in the photoreactor. Thus, there would be a compromise between the two above-mentioned factors, leading to an optimal dosage that would yield the highest photocatalytic activity. In this study, 0.20 g L^{-1} was the optimal dosage for SMZ degradation.

Figure 6.16 Effect of N-P25-TiO₂ (25+10)/AC composite dosage on the photocatalytic degradation of SMZ.

6.3.4.5 Effect of light wavelength spectrum

Figure 6.17 depicts the influence of three different light wavelength spectra, namely solar, UV (280-400 nm) and also visible-light (420-630 nm) on the photocatalytic removal of SMZ. It is worth recapitulating that the light intensities of the simulated solar light, UV, and visible-light were ca. 1000, 65, and 400 W m^{-2} , respectively. The

PCD performance as exhibited by the N-P25-TiO₂ (25+10)/AC composite was in the following order: solar light ($k_{app} = 0.48 \text{ h}^{-1}$) > UV ($k_{app} = 0.35 \text{ h}^{-1}$) > visible-light ($k_{app} = 0.13 \text{ h}^{-1}$). The TOC removal in the solution after 4 h of irradiation were ca. 50%, 40% and 12% for the experiment conducted using solar light, UV and visible-light, respectively. Nevertheless, prolonging the irradiation time of UV to 6 h and that of visible-light to 8 h further increased the TOC removal to ca. 50% and 25%, respectively. Thus, the bimodal composite was photoresponsive under the three different wavelength spectra, which is appealing for potential application under solar irradiation.

Figure 6.17 Effect of light wavelength spectrum on the photocatalytic degradation of SMZ, as exhibited by the N-P25-TiO₂ (25+10)/AC composite.

A separate study examining the case of binary mixture of unsupported bimodal N-doped titania, i.e. N-P25 (700T-4) and N-TiO₂ (sol) (700T-4), was conducted. The results revealed that the k_{app} obtained from this photocatalytic system was only 0.05 h^{-1} under solar irradiation. The PCD performance as exhibited by the bimodal composite system was also better than that of the binary mixture of P25 + AC system (Table 6.4). Thus, it is evident that the bimodal system was superior to that of the unsupported photocatalyst system and the binary mixture system, and this could be attributable to its synergistic adsorption-solar photocatalysis processes. In addition,

auxiliary experiments were conducted to examine the performance of P25 + AC under UV and visible-light irradiation, respectively. The results revealed that the k_{app} values as achieved by the P25 + AC system were 0.31 h^{-1} and 0.02 h^{-1} under UV and visible-light irradiations, respectively. Importantly, the N-P25-TiO₂ (25+10)/AC exhibited ca. 6.5 fold higher SMZ degradation efficiency under visible-light irradiation than that of the P25 + AC system. To confirm the photocatalytic mineralization of SMZ, an auxiliary study was conducted using the unsupported photocatalyst system. The results revealed that sulfate concentration increased progressively, in tandem with the decreasing TOC during the SMZ degradation. Besides, acetate and formate were also detected in the solution. Thus, prolonged irradiation time would eventually lead to the significant mineralization of SMZ.

6.3.4.6 Effect of solution pH

The effect of solution pH on the SMZ degradation efficiency under solar light irradiation using the N-P25-TiO₂ (25+10)/AC composite is presented in Figure 6.18. The PCD efficiency follows the order of: pH 6.0 ($k_{app} = 0.48\text{ h}^{-1}$) $\sim$ pH 3.0 ($k_{app} = 0.44\text{ h}^{-1}$) $>$ pH 10.0 ($k_{app} = 0.21\text{ h}^{-1}$). Apparently, the acidic and circumneutral conditions did not induce significant differences in the SMZ removal. The capacity of SMZ adsorption at pH 3.0 and pH 6.0, as exhibited by N-P25-TiO₂ (25+10)/AC was also comparable (Figure 6.11). Since $\bullet\text{OH}$ concentration would be decreasing towards the acidic region, the fact that the PCD efficiency was insignificantly affected at pH 3.0 suggests other possible governing factors. It has been reported that the carboxylic functional groups on the AC surface can promote photocatalytic activity of the TiO₂-AC system because of the generation of common contact interface which can prolong the photogenerated e^{-}/h^{+} lifetime (Cordero et al., 2007b). Recapitulating that the presence of carboxylic groups on the bimodal composite was confirmed by XPS analysis (Figure 6.5b), thus, it is possible that the photocatalytic activity of the bimodal composite in the acidic condition was somewhat promoted through the above-mentioned charge separation mechanism. At pH 10.0, though OH^{-} concentration was comparatively the highest, the strong electrostatic repulsion between the anionic form of SMZ and the negatively-charged surface of bimodal composite limited the extent of $\bullet\text{OH}$ attack on the deprotonated SMZ.

Figure 6.18 Effect of solution pH on the photocatalytic degradation of SMZ, as exhibited by N-P25-TiO₂ (25+10)/AC.

6.4 Conclusions and practical significance

Several types of bimodal N-P25-TiO₂/AC composites were synthesized using facile preparation techniques, comprising a variance of sol-gel routes and nitrogen-doping processes. The adherence of the N-P25-TiO₂ bimodal titania on the AC support was evaluated using the ultrasonication disruption. The bimodal N-doped titania were reasonably robust to resist dislodgement from the AC support. Apparently, the sol-gel synthesis technique could influence the physical stability of the bimodal composites as the N-P25-TiO₂ (20+15)/AC exhibited greater physical stability as compared to that of the N-P25-TiO₂ (20+15)/AC-Pseudo. This good physical stability is necessary for inducing and maintaining the synergistic adsorptive-solar photocatalytic characteristics of the composites over prolonged usage. N-doping into the AC-supported bimodal P25-TiO₂(sol) could be induced through calcination in NH₃/N₂ atmosphere which also simultaneously enhanced AC adsorption capacity. The optimum total loading of N-doped titania was 35%. The best performing bimodal composite was the N-P25-TiO₂ (25+10)/AC, which comprised 25% of N-P25 and 10% of N-TiO₂ (sol) by weight

content. This composite exhibited a high affinity for SMZ adsorption. It also demonstrated the most efficient solar photocatalytic removal of SMZ and was photoresponsive under the visible-light irradiation. This is due to the effect of N-doping which increased its visible-light photoresponsiveness and also the synergistic effect of its mixed anatase-rutile phase which enhanced its photocatalytic activity. Due to its facile preparation, production of the bimodal composite may be potentially upscalable at a more competitive cost as compared to the N-TiO₂/AC prepared through multiple-coatings and two-stage calcination.

Chapter 7 Conclusions and Recommendations

7.1 Conclusions

Several types of N-TiO₂/AC bifunctional composites were prepared via the sol-gel technique incorporating either single-stage or two-stage calcinations. The N-TiO₂/AC (400M-700T) composite demonstrated high affinity for BPA adsorption and enhanced BPA degradation efficiency under simulated solar light irradiation as compared to all other types of N-TiO₂/AC composites. It was also photocatalytically active under the irradiation of UV and visible-light. N-TiO₂/AC (400M-700T) was superior to that of the unsupported photocatalysts (including commercial titania) as well as binary mixtures of titania and AC. The composite was photostable. In the presence of various solution matrix species, the photocatalytic removal of BPA was considerably higher in the N-TiO₂/AC system than in the unsupported N-TiO₂ system. Provision of AC support abated the deleterious effects of sulfate. Besides •OH attack, the BPA degradation pathway could also occur via direct h⁺ oxidation.

The SPR technique was examined for its technical feasibility to regenerate the spent N-TiO₂/AC composite, as like a spent AC. The composite exhibited varying degrees of adsorption affinity for BPA, SMZ, and CFA, because of the different hydrophobicities of the pollutants. In general, the SPR efficiency could be improved by increasing the light intensity, N-TiO₂ loading, and temperature. The highest RE was achieved by using the CFA-loaded N-TiO₂/AC. Owing to the long-term photostability of the N-TiO₂/AC composite, subsequent cycles of reuse were viable. The rate-limiting factor was the desorption of pollutant from the interior AC adsorption sites. A kinetic model was established to predict the solar regeneration efficiency of the spent composite. A different order of RE was observed for the three pollutants by comparing the findings obtained from the SPR technique and solvent extraction technique, respectively.

Various types of novel bimodal N-P25-TiO₂/AC composites were prepared via the facile sol-gel synthesis techniques. The optimum amount of total N-doped titania in

the bimodal composite was 35 wt%. The best performing composite was N-P25-TiO₂ (25+10)/AC and it exhibited a high adsorption affinity for SMZ. It also demonstrated enhanced solar photocatalytic removal of SMZ as compared to the other types of bimodal composites. It was photoresponsive under UV and visible-light irradiation. This was attributed to the effect of N-doping and the synergism of its mixed anatase-rutile phase for enhanced PCD efficiency.

7.2 Recommendations

To further capitalize on the advantages of these bifunctional composites and extend their potential practical application in water treatment and reclamation, there are several recommendations for the future study, as proposed below.

The synthesis techniques for preparing N-TiO₂/AC can be further improved. Importantly, the new syntheses should aim at the following objectives: (a) explore novel preparation techniques which may potentially enhance the performance of the composite, e.g. by tailoring the sol-gel routes with the incorporation of both metal alkoxides and inorganic precursors, (b) promote green chemistry synthesis by reducing the toxic chemicals used in synthesis, and (c) consider important factors for practical application, e.g. reproducibility, cost-effectiveness, and up-scalability.

The N-TiO₂/AC composites can also be examined using other types of characterization techniques to gain in-depth insights into their characteristics. For example, photoluminescence spectra can be conducted to investigate the efficiency of charge separation, which is directly correlated to the PCD efficiency. In addition, several analyses using highly-advanced characterization equipments can be conducted. For example, using field-emission scanning electron microscopy (FESEM) to examine the morphology of the composite at higher magnification, nuclear magnetic resonance to determine the localized metal environment, electron paramagnetic resonance to measure titanium valence and amorphous content, electron spin resonance (ESR) spectroscopy to measure the formation of •OH radicals, and time-resolved diffuse reflectance to examine the reactivity of photogenerated e^-/h^+ .

Since the real wastewater comprises various aqueous matrix species of diverse characteristics, it is important to investigate the removal efficiency of other classes of recalcitrant organic pollutants using the N-TiO₂/AC composite. Examples include disinfection-by-products (such as N-nitrosodimethylamine, formaldehyde, bromoform, and trichloroacetonitrile) and personal care products (such as ethylene glycol and ethylene oxide). It will be both interesting and useful to establish the pathways of degradation for a comprehensive range of recalcitrant organic pollutants. In addition, initial concentration of the pollutant is another parameter of study which may be evaluated. To understand the effect of temperature on the adsorption performance of the N-TiO₂/AC, it will be useful to examine the adsorption thermodynamics of the composite for a wide range of recalcitrant aqueous organic pollutants.

Future researchers may also examine the performances of the N-TiO₂/AC composites by using real sunlight (e.g. outdoor experiments conducted at the roof-top of buildings or field-scale studies incorporating solar collectors) to treat real wastewaters (e.g. the water after ultrafiltration membrane treatment). Another recommendation for the future study is the evaluation of the N-TiO₂/AC efficiency using a continuous flow reactor integrated with a membrane separation system as this hybrid treatment system is more relevant for practical application. For this proposed study, several important operating parameters or governing factors such as hydraulic residence time, mixing mode, light attenuation, composite separation, and the potential of membrane fouling, may be investigated.

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