Solar photocatalytic activity of anatase TiO₂ nanocrystals synthesized by non-hydrolitic sol–gel method

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Received 30 August 2013; received in revised form 18 December 2013; accepted 4 January 2014
Available online 28 January 2014
Communicated by: Associate Editor Gion Calzaferri

Abstract

Nanocrystalline anatase TiO₂ was prepared through modified non-hydrolitic sol–gel method by reacting TiCl₄ with benzyl alcohol at room temperature. The as synthesized anatase TiO₂ was calcined at 450°C for 5 h. The size and morphology of the as synthesized and calcined TiO₂ nanoparticles were characterized using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM) and BET surface area analysis. The band gap energy was measured using Kubelka-Munk function and the electronic state of the prepared TiO₂ was determined by X-ray photoelectron spectroscopy (XPS). The photocatalytic activity of the prepared samples was investigated by degrading 50 mg/L of 2,4-dichlorophenol (2,4-DCP) under natural sunlight as a source of irradiation. The obtained XRD patterns of both as synthesized and calcined TiO₂ matches completely with the tetragonal anatase phase of TiO₂. The as synthesized sample showed higher surface area (147.34 m²/g) with particles size ranging between 3 and 6 nm than the calcined titania (64.92 m²/g) of particle size ranging between 11 and 15 nm. Both the TiO₂ samples showed excellent photocatalytic activity for the degradation of 2,4-DCP under natural sunlight irradiation. The complete removal of 2,4-DCP is obtained after 2.5 h for calcined TiO₂ and 3.5 h for as synthesized TiO₂ suggests that the prepared photocatalysts have the potential to degrade the organic pollutants. The degradation of 2,4-DCP followed first order kinetics.

Keywords: Non-hydrolitic sol–gel method, Anatase TiO₂; Heterogeneous photocatalyst; 2,4-DCP degradation; Natural sunlight

1. Introduction

In recent years, considerable attention has been focused on the possibility of combining heterogeneous catalysis with solar technologies to achieve the degradation or mineralization of organic and inorganic pollutants present in water and wastewater (Wang et al., 2012). Heterogeneous solar photocatalysts effectively utilize the ultraviolet (UV) energy from the sunlight, a renewable energy, for the photocatalytic reactions that can potentially reduce the treatment costs (Serk et al., 2013; Xiao et al., 2008; Ioannou et al., 2011; Senthilnathan and Philip, 2012; Vineetha et al., 2013; Magalhaes and Lago, 2009). In addition, the UV part of the sunlight depends on the latitude, elevation, cloud amounts, time of the year and time of the day. The solar ultraviolet index (UVI) describes the level of solar UV radiation at the Earth’s surface. An approximate measure for the UVI is measured and published by the Malaysian Meteorological Department (MMD) that indicates that the northern region and few places in East Malaysia have the highest potential for solar...
energy application due to its high solar radiation throughout the year (Azhari et al., 2008).

Typically, semiconductor powders have been extensively studied as photocatalysts over the past five decades and TiO$_2$ has been recognized as promising photocatalyst due to its high oxidative power (high photocatalytic activity), nontoxic nature, photostability, chemical and thermal stability, low cost and favorable optoelectronic properties (Christensen et al., 2003; Stoyanova et al., 2010). It is well known that TiO$_2$ occurs in nature as three distinct crystallographic phases namely anatase, rutile and brookite. Among the three crystalline phases, anatase TiO$_2$ has promising photocatalytic activity, especially anatase nanoparticles (<14 nm) is more dominant for photocatalysis due to its high surface area (Hyun and Kang, 1996; Kermanpur et al., 2008; Samunova et al., 1993; Stoyanova et al., 2010). In general, the photocatalytic activity of the TiO$_2$ depends on several factors such as crystalline phase, crystal size and specific surface area as well as depends on other factors such as production capacity of electron–hole pair, separation efficiency of the photogenerated charge pair and the transfer efficiency to compounds adsorbed on the TiO$_2$ surface (Kavan et al., 1996; Li and Zeng, 2011; Zhang et al., 1999, 2001; Li et al., 2009; Mir and Salavati-Niasari, 2012). In addition, the photoactivity of TiO$_2$ also depends on the preparation method, thermal treatment, concentration of the pollutant and concentration of the photocatalyst. A good photocatalyst should possess high surface area and crystallinity. Few researchers attempted to increase the crystallinity through calcination and found both constructive and destructive photocatalytic activity due to increase in crystallinity and decrease in surface area, respectively (Ba-Abbad et al., 2012; Wu et al., 2013). Many researchers decreased the band gap of TiO$_2$ either by doping with metals (such as Ag, Au, Pb and Pt) or non-metals (such as C, N, F, P and S) to reduce the threshold energy for excitation that enhances the absorption of visible light spectrum resulting in improved photocatalytic activity (Asahi et al., 2001; Mrowetz et al., 2004; Thompson and Yated, 2006; Chen et al., 2010; Wang et al., 2011; Liu et al., 2012a; Bokare et al., 2013).

Numerous synthesis methods have been practiced by researchers such as inert gas condensation (Siegel et al., 1988), flame synthesis by oxidation (Morrison et al., 1997), oxidation–hydrothermal (Chen et al., 1995) and hydrolysis precipitation (Wang and Ying, 1999) of titanium alkoxides or inorganic salts. Different precursors (both alkoxides and inorganic salts) have been employed for the synthesis of TiO$_2$ nanoparticles such as titanium (IV) butoxide [Ti(OC$_4$H$_9$)$_4$] (Supphasrirongjaroen et al., 2008; Zukalova et al., 2010; Aziz et al., 2012a, b; Liu et al., 2012b), titanium tetraisopropoxide [Ti(OCH(CH$_3$)$_2$)$_4$] (Soares et al., 2011; Sridharan et al., 2013; Zhang et al., 2004; Hamadanian et al., 2013; Adan et al., 2007), titanium (IV) sulfate [Ti(SO$_4$)$_2$] (Kawasaki et al., 2009; Ren et al., 2009), titanium tetrachloride [TiCl$_4$] (Lao et al., 2005; Charbonneau et al., 2009; Di Paola et al., 2008; Barakat et al., 2005), titanyl sulfate [TiSO$_4$$_2$] (Ngamta et al., 2013) and titanyl nitrate [TiO(NO$_3$)$_2$] (Nagaveni et al., 2004). Numerous research works have been conducted to obtain uniform sized nanoparticles by controlling the reaction rate through modified or alternate synthesis route. The investigation on nonhydrolytic synthesis route revealed that the formation of nanosized titania with higher uniformity attributed to better control over the reaction rate (Niederberger and Garnweiter, 2006). Besides that, the solvent in the reaction system not only act as oxidizing agent but also contribute for the enhanced morphology (Stoyanova et al., 2010). Most of the photocatalytic degradation studies have been conducted using TiO$_2$ synthesized from alkoxide precursor rather than inorganic salt precursor attributed to the difficulty in the removal of anoins such as NO$_3^-$, Cl$^-$, SO$_4^{2-}$, which may hinder the catalytic activity. Although many photocatalytic degradation studies have been conducted for phenolic compounds using artificial UV and visible light as a source of irradiation, the reports are scarce for natural solar light as a source of irradiation (Han et al., 2010; Chen et al., 2009; Liu et al., 2012b; Aziz et al., 2012a, b; Bayarri et al., 2005; Barakat et al., 2005; Doong et al., 2001; Liu et al., 2008; Sun et al., 2003). Only a limited investigation has been found for the degradation of 2,4-dichlorophenol (2,4-DCP) using as-synthesized and calcined anatase TiO$_2$ photocatalyst under natural solar light irradiation.

Thus the present work is focused to investigate the photocatalytic activity of anatase TiO$_2$ synthesized through modified nonhydrolytic route at room temperature using TiCl$_4$ as a precursor. Both the TiO$_2$ samples, as-synthesized and calcined, were characterized with various analytical characterization techniques for their phase, morphology, elemental composition, surface properties, electronic configuration, optical property and bandgap energy. Furthermore, photocatalytic activity of the synthesized anatase TiO$_2$ photocatalysts was evaluated by degrading 2,4-DCP under natural solar light irradiation. In addition, the experimental photocatalytic degradation data were fitted with first order kinetics to determine the degradation mechanism.

2. Experimental

2.1. Materials

Titanium (IV) chloride (99.9%) and benzyl alcohol (99.8%, anhydrous) were procured from Aldrich and tetrahydrofuran (THF) from Fluka. All chemicals were analytical grade and used as received without any further purification.

2.2. Synthesis of titanium dioxide nanoparticles

Synthesis of anatase nanocrystalline TiO$_2$ at room temperature by nonhydrolytic polycondensation between
titanium chloride and anhydrous benzyl alcohol was performed in a glass beaker at controlled inert gas (nitrogen) atmosphere. One mL of TiCl₄ was added drop wise into 20 mL of anhydrous benzyl alcohol under vigorous stirring. The reaction is vigorous in nature; the solution initially turns to dark red color and then to orange color. After complete addition of TiCl₄ with continuous stirring yields yellowish colored solution with white precipitate at the bottom of the beaker. Stirring was continued for 24 h and the solution is aged for 21 days at room temperature.

The slow ageing process at room temperature ensures the formation of more uniform TiO₂ nanoparticles of smaller size rather than heating at higher temperature (generally practiced to reduce the ageing time). Furthermore aging dissolves any fluffy white precipitate. The resulting white precipitate after aging was recovered by centrifugation at 3000 rpm for 30 min and thoroughly washed with 20 mL of ethanol followed by 20 mL of tetrahydrofuran (THF) for 2 times. The washing step was repeated for 3 times and after every washing step, the solvent was removed by centrifugation. This ensures the complete removal of excess Cl⁻ anions. After washing, the obtained TiO₂ white powder was dried at room temperature and the sample is designated as TiO₂ as synthesized. On the other hand, the as synthesized sample was calcined at 450 °C for 5 h and is designated as calcined TiO₂.

2.3. Characterization

Both the TiO₂ samples (as synthesized and calcined TiO₂) were analyzed for their crystallite phase with Bruker AXS instrument using Cu Kα (λ = 1.5406 Å) radiation operating at 40 kV and 40 mA for the angle of diffraction 20 between 5° and 70° with an angular step of 0.05°/s. Raman spectra was obtained using Renishaw in Via Raman microscope with a solid state diode laser operating at a wavelength of 532 nm. Field emission scanning electron microscope (FESEM) (Hitachi SU-8000 attached with Zeiss Auriga) and transmission electron microscope (TEM) (Philips CM-12) were used to investigate the morphology of the photocatalyst. Energy dispersive X-ray spectroscopy (EDS) using Zeiss Auriga to determine the compositions of the TiO₂ photocatalysts. Brunauer–Emmett–Teller (BET) surface area, pore volume, and Barret–Joyner–Halenda (BJH) pore size distribution based on nitrogen adsorption–desorption isotherms were analyzed with TriStar II 3020 surface area and porosity system. Prior to surface area analysis, the samples were degassed at 120 °C for 5 h under nitrogen atmosphere. X-ray photoelectron spectra (XPS) were obtained with Axis Ultra DLD instrument of Kratos using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV). The binding energy (BE) of adventitious Cl⁻ (284.9 eV) was used as reference. UV–Vis diffuse reflectance spectroscopy of the samples was performed through Shimadzu UV-2600 UV–Vis–NIR scanning spectrophotometer using BaSO₄ as a reference.

2.4. Photocatalytic experiments

Photocatalytic activity of both as synthesized and calcined TiO₂ was evaluated by degrading the recalcitrant pesticide 2,4-DCP. The experiments were carried out in a batch reactor of 500 mL capacity with a working volume of 250 mL (initial concentration of 2,4-DCP = 50 mg/L) under continuous stirring in the presence of natural sunlight by adding 1 g of synthesized photocatalyst. The sunlight intensity during the experimentation was between 60,000 and 140,000 lx (which is approximately between 88 and 205 W m⁻²). Since the photocatalytic reactions occur in the adsorbed phase, dark experiments were carried out prior to photocatalytic experiments to substantiate the possibility of parallel removal of contaminant molecule (2,4-DCP) by adsorption. Additional control experiments were carried out with zero photocatalyst (as synthesized or calcined TiO₂) condition to ensure the degradation was only due to presence of photocatalyst. Three replicates of all experiments were performed at identical conditions to perform error analysis. The samples were drawn out at regular intervals (30 min) and analyzed for residual concentration of 2,4-DCP using ultrahigh performance liquid chromatography (Acquity UPLC H-Class, Waters). The column employed was C18 column (2.1 × 50 mm, 1.7 µm particle size) with acetonitrile/water (60/40) as the mobile phase (flow rate = 0.4 mL/min) with an injection volume of 20 µL. The detector was set to a wavelength of 285 nm. The degree of mineralization of 2,4-DCP during photocatalytic experiment was estimated from the amount of Total Organic Carbon (TOC) before and after photocatalytic degradation process using O. I Analytical Aurora 1030 W TOC Analyzer.

3. Results and discussion

3.1. Structural and morphology properties

Fig. 1 depicts the XRD patterns of the titania nanoparticles. The obtained diffraction peaks were matched very well with the JCPDS Card No.: 21-1272 indicating the body-centered tetragonal anatase phase of TiO₂. The diffraction peaks at 2θ = 25.25° (101), 47.98° (200), 53.59°(106), 37.82° (004) and 62.36° (215) were all correspond to the lattice plane of only anatase phase. The absence of the diffraction peaks at 2θ = 27.5° (110) and 30.8° (121) corresponds to rutile and brookite phase confirms both the synthesized TiO₂ was pure anatase nanoparticles (Por kodi and Arokiamary, 2007). As synthesized TiO₂ showed a wide peak (25.25°) with more background disturbance indicates that the amorphous nature of the nanomaterials. A sharp and more intense peak (Fig. 1b) obtained for the calcined TiO₂ was attributed to heat treatment that increases the crystallinity and crystallite size (Li and Zeng, 2011). The crystallite sizes were calculated from the broadening of the anatase (101) peaks using Scherer’s formula.
where $D$ is the crystallite size (nm), $K$ is the shape constant $(0.9)$, $\lambda$ is the wave length of Cu K$_{\alpha}$ radiation $(1.5406 \text{ Å})$, $\theta$ is the diffraction angle ($^\circ$) and $\beta$ is the full width at half maximum. The crystallite size of as synthesized and calcined anatase TiO$_2$ was found to be 4.65 and 14.8 nm, respectively. The obtained result suggests that the room temperature synthesis resulted in uniform nanosized TiO$_2$ particles. Fig. 2 shows the Raman spectra for both as synthesized and calcined TiO$_2$. Two broad bands at 425 and 609 cm$^{-1}$ of Raman spectrum of the as synthesized TiO$_2$ confirms the presence of amorphous anatase TiO$_2$. On the other hand, the bands at 399, 515 and 639 cm$^{-1}$ of calcined TiO$_2$ corresponds to the characteristic bands of crystalline anatase TiO$_2$. The shift in the Raman spectrum after calcination is attributed to increase in the crystallite size and crystallinity. The absence of bands at 445 and 612 cm$^{-1}$ indicates the absence of rutile phase in the calcined TiO$_2$. The Raman spectrum of both the samples confirms that the synthesized TiO$_2$ photocatalysts were in the complete anatase phase without any phase impurities (Li and Zeng, 2011; Tompsett et al., 1995; Zeng et al., 1998).

Morphology of the pure anatase titania nanoparticles were shown in Fig. 3a–f. The amorphous nature of as synthesized TiO$_2$ was clearly observed from the Fig. 3a–c and the particles were in uniform spherical shape and agglomerated in nature. The observation of calcined TiO$_2$ confirms the spheroid shaped uniform size particles distributed homogeneously (Fig. 3d and e). Higher magnification images clearly illustrates the amorphous nature of as synthesized TiO$_2$ (Fig. 3c) and crystalline nature of calcined TiO$_2$ (Fig. 3f). FESEM showed a higher particle size due to agglomeration of the nanoparticles. The actual sizes of the titania nanomaterials were measured using TEM images and presented in Fig. 4a and b. The diameter of the as synthesized TiO$_2$ was ranging between 3 and 6 nm (see Fig. 4a). Similarly the diameter of the calcined TiO$_2$ was ranging between 11 and 15 nm. The increase in particle size was attributed to the temperature effect and the obtained results were very well matched with the crystallite size measured by XRD analysis. Although the shape and size of the as synthesized and calcined TiO$_2$ were different, the particles were more uniform in nature. The EDX spectra of the as synthesized and calcined TiO$_2$ were analyzed and the spectra showed only the presence of Ti and O elements (figure not shown). The absence of the Cl$^-$ ion confirms the adopted washing procedure was more effective in the removal of the unwanted anion (Cl$^-$) that may interfere with the photocatalytic activity.

### 3.2. BET analysis

Nitrogen adsorption–desorption isotherms and corresponding pore size distribution of both as-synthesized and calcined TiO$_2$ was depicted in Fig. 5. Both the TiO$_2$ samples revealed a stepwise adsorption and desorption branch represented by type IV isotherms according to the IUPAC classification. The hysteresis loops indicates the slit-shaped pores for as-synthesized TiO$_2$ and cylindrical shaped pores for calcined TiO$_2$. The BET surface area of the as-synthesized TiO$_2$ was found to be 147.34 and 64.92 $\text{m}^2/\text{g}$, respectively. A decrease in the BET surface area of the calcined TiO$_2$ was ascribed to the gradual increase in grain size during calcination. In addition, the average pore diameter, determined by Barrett–Joyner–Halenda (BJH) method using the desorption isotherm (inset of Fig. 5), was found to be increased during calcination. The pore size distribution indicates that the as-synthesized TiO$_2$ has a smaller pore size $(3.46 \text{ nm})$ than calcined TiO$_2$ $(9.24 \text{ nm})$. A bimodal pore size distribution observed for calcined TiO$_2$ was attributed to the uncontrollable pore collapse during calcination, which have detrimental effect in
photocatalytic applications. In general, mesoporous anatase TiO$_2$ having both high surface area and crystallinity possess good photocatalytic properties and employed for photocatalytic applications (Zhang et al., 2011). Although the surface area of the calcined TiO$_2$ was low compared to as-synthesized TiO$_2$, the increased crystallinity of calcined TiO$_2$ has salutary effect in photocatalytic activity. In addition, solar energy conversion efficiency may vary based on the particle size and pore size distribution (Parmar et al., 2010). At times, very small average pore size of anatase TiO$_2$ would hinder the access of organic pollutants resulting in poor degradation. Hence both the anatase TiO$_2$ nanoparticles were experimented for their photocatalytic activity under the natural sunlight irradiation.

3.3. XPS analysis

High resolution XPS spectra of both the anatase nanoparticles were shown in Fig. 6. Both the TiO$_2$ nanoparticles exhibited similar pattern. The Ti 2p shell element found in the titania nanoparticles. In general, the Ti 2p peak was varied between 456 and 464 eV. The obtained broad peak at 463 eV and a sharp narrow peak at around 458 eV for both the as synthesized and calcined TiO$_2$ indicate the presence of Ti and Ti$^{4+}$ species (Fig. 6). These peaks are attributed to an active site which improves the photocatalytic activity, especially under the solar light irradiation (Aziz et al., 2013).

3.4. UV–Vis absorption spectra and band gap energy

The UV–Vis absorption spectra of the anatase TiO$_2$ samples were shown in Fig. 7. The obtained spectrum depicts the response of the prepared TiO$_2$ in both UV and visible light spectrum. From the spectrum, it is also evident that a strong increase in absorption appears at 425 nm caused by excitations of electrons from the valence band to the conduction band of titania. Kulbeka-Munk equation was used to obtain the accurate band gap energy of TiO$_2$ nanoparticles. The reflectance data was converted to the absorption coefficient $\alpha(R_\infty)$ values (Burgeth and Kirsch, 2002; Lin et al., 2006; Valencia et al., 2010):
\[ F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \]  

where \( R_\infty \) is the diffused reflectance of at the given wavelength

\[ E (\text{eV}) = \frac{hc}{\lambda} \]  

where \( h \) is the Planck’s constant \((6.626 \times 10^{-34} \text{ J s})\), \( C \) is the speed of light \((3.0 \times 10^8 \text{ ms}^{-1})\) and \( \lambda \) is the wavelength (nm). From the Kulbeka-Munk analysis, the band gap energy of the as synthesized and calcined TiO\(_2\) was found to be 3.1 eV and be 3.25 eV, respectively (Fig. 8). The increase in band gap energy for calcined TiO\(_2\) was attributed to increase in the crystallinity of calcined TiO\(_2\) than the as synthesized TiO\(_2\). Similar values of band gap energy were reported in literature for TiO\(_2\) nanoparticles synthesized by different methods and different precursors (Stone and Davis, 1998; Eufinger et al., 2007; Ba-Abbad et al., 2012; Wu et al., 2013; Zhang et al., 2001).

### 3.5. Photocatalytic activity

The results of control experiments and photocatalytic degradation experiments of 50 mg/L (250 mL solution) of 2,4-DCP on as synthesized and calcined TiO\(_2\) under the solar light irradiation were depicted in Fig. 9. All the experimental data were statistically significant and the standard deviation was found to be less than 0.05. The obtained results suggests that a complete degradation of 2,4-DCP was achieved using both the TiO\(_2\) photocatalysts with variation in time duration. The control experiments confirms that only a limited amount of 2,4-DCP was removed (<1%) in the absence of the TiO\(_2\) photocatalysts by direct photolysis. From the dark reactions (see Fig. 9), it was clear that a modest removal of 2,4-DCP was occurred due to adsorption (10–12% for as synthesized TiO\(_2\) and 18–20% for calcined TiO\(_2\)). Similar results have been reported by other researchers on TiO\(_2\) photocatalysts (Fabbri et al., 2006; Ba-Abbad et al., 2012). Almost complete degradation
(99–100%) was achieved for both the catalyst under solar light radiation, however, the as synthesized TiO\textsubscript{2} took longer period (3.5 h) than the calcined TiO\textsubscript{2} (2.5 h). According to the optical spectra and band gap energy value the as synthesized TiO\textsubscript{2} was expected to possess better photocatalytic activity than the calcined TiO\textsubscript{2}. However, the obtained upturned observance might be due to various reasons. In general, the photocatalytic activity depends on the efficiency of utilization of the fraction of the incident radiation absorbed by the catalyst (Dolat et al., 2012; Ahn et al., 2003; Pupo Nogueira and Guimaraes, 2000; Siero et al., 2011). In an irradiated suspension of photocatalyst particles photons were absorbed and scattered. Due to amorphous nature of the as synthesized TiO\textsubscript{2} photocatalyst the scattering of incident solar light energy was more than the absorbed energy (results in decreased formation of electron and hole pairs) as compared to that of calcined TiO\textsubscript{2}, which
may be resulted in decreased photocatalytic activity. In addition, amorphous surface has many defects that acts as recombination centers for the photo generated electrons and holes, which also decreases photocatalytic activity. Furthermore, when particle size become extremely small (i.e. \( \leq 5 \) nm in diameter), most of the generated electron and hole pairs may quickly reach the surface and undergo a rapid surface recombination that reduces the photocatalytic activity of the as synthesized TiO\(_2\) (Hines and Guyot-Sionnest, 1996; Serpone et al., 1995). The other possibility for decreased photocatalytic activity of as synthesized TiO\(_2\) might be due to overloading of the photocatalyst (excess of photocatalyst particles scatters the sunlight) and also due to agglomeration of particles that hinders the penetration of sunlight.

From the dark reactions, it was clear that the adsorption capacity of 2,4-DCP was higher in calcined TiO\(_2\) than the as synthesized TiO\(_2\). Although the as synthesized TiO\(_2\) has higher surface area than the calcined TiO\(_2\), the high adsorption capacity was attributed to the surface charge characteristics. During calcination, the increase in crystallinity increases the surface charge of the anatase TiO\(_2\), which lead to more adsorption of 2,4-DCP. Thus in the calcined TiO\(_2\) the photogenerated electrons were readily trapped on Ti\(^{4+}\) sites and form Ti\(^{3+}\) that traps the electrons and readily scavenged by oxygen. Hence, the localized holes can be scavenged by either reacting with hydroxide ions or through electron transfer with water to form hydroxyl radicals and super oxide radicals, which were strong oxidants that enhances the photocatalytic degradation of 2,4-DCP (Almquist and Biswas, 2002; Ilisz et al., 2002; Li Puma and Yue, 2002; Lin et al., 2006). In the case of as synthesized TiO\(_2\), the same number or more electrons and hole pairs were generated, however due to lower amount of 2,4-DCP on the surface, smaller particle size and higher surface area favors the recombination of the generated electron and hole pair resulted in decreased photocatalytic activity than the calcined TiO\(_2\). Thus the photocatalytic activity of as synthesized TiO\(_2\) was lower even though the band gap energy is lower (3.1 eV) compared to that of calcined TiO\(_2\). Photocatalytic degradation potential of the as synthesized and calcined TiO\(_2\) was compared with different phenolic compounds under various irradiation sources and listed in Table 1. It was clear from the Table 1, that the UV as a source of irradiation resulted in better photocatalytic performance than visible light irradiation attributed to the band gap energy of the TiO\(_2\) photocatalysts that can utilize only the wavelength less than 380 nm. It was also evident from the Table 1 that the synthesized photocatalysts has the potential to utilize the solar energy emerged with higher photocatalytic activity to completely degrade the 2,4-DCP in a reasonable time.

### 3.6. Total Organic Carbon (TOC)

The degree of mineralization of 2,4-DCP during the photocatalytic degradation was analyzed as a function of TOC and depicted in Fig. 10. An efficiency of 73.5% was

<table>
<thead>
<tr>
<th>TiO(_2) photocatalyst</th>
<th>Model pollutant</th>
<th>Dosage (g)</th>
<th>Initial concentration (mg/L)</th>
<th>Irradiation source</th>
<th>Photocatalytic efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra butyl titanate as precursor</td>
<td>2,4-DCP</td>
<td>0.01</td>
<td>50.00</td>
<td>UV (30 W Hg lamp at ( \lambda_{max} = 254 ) nm)</td>
<td>45.0% in 2 h</td>
<td>Han et al. (2010)</td>
</tr>
<tr>
<td>Ti(OC(_4)H(_9))(_4) as precursor</td>
<td>2,4-DCP</td>
<td>1.00</td>
<td>15.00</td>
<td>UV (20 W Germicidal lamp with main ( \lambda = 254 ) nm)</td>
<td>100% in 3 h</td>
<td>Liu et al. (2012)</td>
</tr>
<tr>
<td>Ti(OC(_4)H(_9))(_4) as precursor</td>
<td>2,4-DCP</td>
<td>1.00</td>
<td>50.00</td>
<td>Visible light (diffused light)</td>
<td>90.0% in 5 h</td>
<td>Aziz et al. (2012a,b)</td>
</tr>
<tr>
<td>Ti(OC(_4)H(_9))(_4) as precursor</td>
<td>2,4-DCP</td>
<td>1.00</td>
<td>50.00</td>
<td>Visible light (diffused light)</td>
<td>100% in 3 h</td>
<td>Aziz et al. (2012a,b)</td>
</tr>
<tr>
<td>TiCl(_3) as precursor</td>
<td>Phenol</td>
<td>0.20</td>
<td>50.00</td>
<td>UV (Philips 125 W high-pressure mercury lamp)</td>
<td>100% in 3 h</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>2,4-DCP</td>
<td>0.10</td>
<td>100.00</td>
<td>Visible light (1000 W Iodine tungsten lamp with a glass filter)</td>
<td>39.3% in 4 h</td>
<td>Chen et al. (2009)</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>2,4-DCP</td>
<td>2.00</td>
<td>125.00</td>
<td>Solar energy (Philips 1500 W xenon lamp)</td>
<td>99.9% in 6 h</td>
<td>Bayarri et al. (2005)</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>2-CP</td>
<td>1.00</td>
<td>100.00</td>
<td>Visible light (100 W medium pressure mercury lamp)</td>
<td>50.0% in 2.5 h</td>
<td>Doong et al. (2001)</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>Phenol</td>
<td>0.20</td>
<td>100.00</td>
<td>Visible light (200 W medium pressure mercury vapor quartz lamp with pyrex filter ( \leq \lambda = 320 ) nm)</td>
<td>60.0% in 3 h</td>
<td>Sun et al. (2003)</td>
</tr>
<tr>
<td>TiCl(_4) as precursor</td>
<td>2-CP</td>
<td>0.01</td>
<td>75.00</td>
<td>UV (100 W mercury lamp)</td>
<td>78.0% in 3 h</td>
<td>Barakat et al. (2005)</td>
</tr>
<tr>
<td>TiCl(_4) as precursor</td>
<td>2,4-DCP</td>
<td>1.00</td>
<td>50</td>
<td>Solar energy</td>
<td>100% in 2.5 h</td>
<td>Present study</td>
</tr>
</tbody>
</table>

Note: 2,4-DCP: 2,4 dichlorophenol, 2-CP: 2 chlorophenol.
achieved for as synthesized TiO$_2$ while 61.5% for calcined one, respectively. A higher degree of mineralization was achieved for as synthesized TiO$_2$ (73.5%) compared to that of calcined TiO$_2$ (61.5%) was attributed to its smaller crystallite size and larger surface area. Similar observations were reported by other researchers (Zhang et al., 2000; Zhu et al., 2000). Only a significant mineralization occurred during dark experiment (<9.0%) and control experiment (<1.0%) confirms that the mineralization was attributed to photocatalytic degradation of the synthesized TiO$_2$ photocatalysts.

3.7. Kinetics of degradation

The degradation kinetics of 2,4-DCP on as synthesized and calcined TiO$_2$ heterogeneous catalysts is explained by the first-order kinetics (Kumar et al., 2008). The first-order expression is given below.

$$-\ln \frac{C}{C_0} = k_1 t$$

where $C_0$ is the initial concentration of 2,4-DCP (mg/L) and $C$ is the concentration 2,4-DCP at time $t$ and $k_1$ represents the rate constant of first order reaction (min$^{-1}$). The obtained experimental data were fitted with first order kinetics and presented in Fig. 11. Higher correlation coefficients ($r^2 > 0.97$) obtained for both the TiO$_2$ photocatalysts indicates that the degradation of 2,4-DCP follows first-order kinetics. The first order reaction rate constants ($k_1$) was found to be 0.017 and 0.028 min$^{-1}$ for as synthesized and calcined TiO$_2$, respectively. Higher rate constant value of calcined TiO$_2$ indicates its potential for higher photocatalytic activity than the as synthesized TiO$_2$. The obtained results suggest that the decreased photocatalytic activity of as synthesized TiO$_2$ was attributed to the surface recombination and the higher photocatalytic activity of calcined TiO$_2$ was attributed due to increase in the crystallinity.

4. Conclusion

The present study exemplifies the successful synthesis of pure anatase titania nanoparticles through non-hydrolitic sol–gel method at room temperature. The structural and morphological studies confirmed that both the as-synthesized and calcined TiO$_2$ photocatalysts were pure anatase phase. The calcined TiO$_2$ exhibited good crystallinity whereas the as synthesized TiO$_2$ exhibited higher surface area. The synthesized photocatalysts demonstrated an excellent photo response towards the sunlight irradiation by successfully degrading 2,4-DCP in shorter duration. The band gap energy of the as synthesized and calcined TiO$_2$ was found to be 3.1 eV and be 3.25 eV, respectively. The lower band gap energy of as synthesized TiO$_2$ expected to possess more photocatalytic activity; however, the exhibited lower photocatalytic activity was attributed to the surface recombination of the photogenerated electron and hole pairs. Correspondingly, the higher photocatalytic activity of calcined TiO$_2$ was attributed to increased crystallinity that increases the formation of hydroxyl radicals and super oxide radicals. The kinetics of photocatalytic degradation confirms that the process follows the first order kinetic pathway. This study provides a versatile approach of utilizing solar energy for complete degradation of phenolic pollutant (2,4-DCP) using pure anatase TiO$_2$ photocatalysts synthesized from TiCl$_4$ precursor. Hence, the synthesized photocatalysts can be effectively used for water and wastewater treatment under solar light irradiation.

Acknowledgements

The first author is grateful to University of Malaya for the Bright Spark Fellowship. This work was supported
by University of Malaya Research Grant, UMRG (RG167/12SUS) and Postgraduate Research Grant, PPP (PG022-2013A).

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