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Photocatalytic activity of TiO$_2$ containing anatase nanoparticles and rutile nanoflower structure consisting of nanorods

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Abstract
A series of TiO$_2$ with different crystal phases and morphologies was synthesized via a facile hydrothermal process using titanium n-butoxide and concentrated hydrochloric acid as raw materials. The photocatalytic activity of the samples was evaluated by degradation of Methyl Orange in aqueous solution under UV-Visible light irradiation. On the basis of detailed analysis of the characterizing results of high-resolution transmission electron microscopy, X-ray powder diffraction measurements, X-ray photoelectron spectroscopy and Brunauer-Emmett-Teller measurement, it was concluded that the photo-activity of the catalyst is related directly to the 3D morphology and the crystal phase composition. An excellent catalyst should have both a rutile 3D flower-like structure and anatase granulous particles. The 3D flower-like structure could enhance light harvesting, as well as the transfer of reactant molecules from bulk solution to the reactive sites on TiO$_2$. In addition, the optimum anatase/rutile phase ratio was found to be 80:20, which is beneficial to the effective separation of the photogenerated electron–hole pairs.

Key words: photocatalysis; TiO$_2$; anatase nanoparticles; rutile nanoflowers; simulated solar light illumination.

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Introduction
Fujishima and Honda (1972) discovered the photocatalytic splitting of water on TiO$_2$ electrodes. Since then, TiO$_2$ has been the subject of intensive investigation as a semiconductor photocatalyst owing to its high level of photo-activity, photodurability, chemical and biological inertness, mechanical robustness as well as low cost (Anpo et al., 1987; Hoffman et al., 1995; Linsebigler et al., 1995; Srisong et al., 2012). Usually, the photocatalytic performance of TiO$_2$ depends strongly on its morphological, structural and textural properties. Therefore, much work has been devoted to the synthesis of TiO$_2$ with different structures and morphologies.

Until now, 1D TiO$_2$ nanostructures of nanotubes, nanorods and nanowires, 2D TiO$_2$ nanosheets and 3D TiO$_2$ nanostructures have been fabricated by various techniques (Chen and Mao, 2007). Of these, 3D TiO$_2$ assembled with ordered nanostructures has attracted great interest; its dimensions and large surface area make it promising for potential applications in photocatalysts, dye-sensitized solar cells and gas sensors (Sarkar et al., 2012). For instance, when used as a photocatalyst, the nanometer-scale unit in the 3D TiO$_2$ geometric architecture could be responsible for the high level of photocatalytic ability; meanwhile, the micrometer-scale structure favors light-harvesting and separation of the powders from the solution compared to nanometer-scale powders (Dong et al., 2009; Wu et al., 2011).

Recently, studies using only concentrated HCl as the morphological/crystallographic controlling agent have been focused on preparing 3D TiO$_2$ microparticles self-assembled from nanostructured sub-units, including nanorods and nanoparticles (Phan et al., 2009; Sarkar et al., 2012). These studies demonstrated that the crystalline structure and morphology of the TiO$_2$ nanoscale materials is governed largely by hydrothermal temperature and the starting concentration of HCl. However, these studies were based mainly on the growth mechanisms of the 3D TiO$_2$ structures and few of them considered the optical property of the catalysts, especially photocatalytic activity in the degradation of organic pollutants.

The main objective of this work was to correlate the 3D nanoflower morphology and crystal structure of TiO$_2$ with its photocatalytic activity under simulat-
ed solar light irradiation, based on characterization of the catalysts with high-resolution transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD) measurements, X-ray photoelectron spectroscopy (XPS), and Brunauer-Emmett-Teller (BET) measurement. The 3D TiO$_2$ was synthesized via a simple hydrothermal process in which only titanium n-butoxide (Ti(OBu)$_4$) and concentrated HCl were used, and we selected Methyl Orange (MO) as a model compound.

1 Materials and methods

1.1 Reagents

All chemicals used in this study were of analytic grade and used without further purification. Ti(OBu)$_4$ and concentrated HCl used for the preparation of the 3D TiO$_2$ nanoflowers were purchased from Huadong Medicine Co. Ltd., China. MO was produced from Shanghai Sanais Reagent Co. Ltd. Doubly distilled water was used for all processes.

1.2 Preparation and characterization of 3D TiO$_2$

The 3D TiO$_2$ nanoflowers were synthesized via a facile hydrothermal method similar to that described elsewhere (Phan et al., 2009; Xiang et al., 2010). In a typical synthesis, 50 mL of Ti(OBu)$_4$ and the appropriate amount of concentrated HCl were mixed in a Teflon-lined autoclave of 200 mL capacity at room temperature. Subsequently, the autoclave was sealed and heated at various temperatures for 24 hr then allowed to cool to room temperature. The resulting white precipitate was recovered by centrifugation and washed several times with absolute ethanol and then water. Finally, the products were dried at reduced pressure for 10 hr at 60°C. The nomenclature used for the catalysts is nHCl-TiO$_2$-T, where n (mL) is the amount of concentrated HCl added and T (°C) is the temperature of the hydrothermal synthesis. For comparison, control samples (denoted as pure-TiO$_2$-180) hydrothermally treated at 180°C were prepared by using 6 mL of H$_2$O instead of 6 mL of HCl under the similar conditions.

The XRD patterns were obtained using a diffractometer (Model ARL X'TRA, Thermo Electron Corporation, USA) and a Cu K$_\alpha$ radiation source at 45 kV and 40 mA over the 20 range 10–80°. The microstructure of the products was further analyzed using HRTEM ( Tecnai G2 F-30, FEI Company, Holland) at an accelerating voltage of 300 kV with 0.2 nm point resolution. XPS analysis was done using a photoelectron spectrometer (RBD upgraded PHI-5000C ESCA system, PerkinElmer, USA) equipped with a non-monochromatic Mg K$_\alpha$ radiation of 1253.6 eV. The BET surface areas of the spent catalyst and pretreated samples were determined by nitrogen adsorption/desorption at ~196°C (Model ASAP 2010, Micromeritics Instrument Corporation, Norcross, GA, USA), and the desorption isotherm was used to determine the pore size distribution by the Barrett-Joyner-Halenda (BJH) method.

1.3 Measurement of photocatalytic activity

For the measurement of photocatalytic activity of the 3D TiO$_2$ nanoflowers, 0.3 g of TiO$_2$ catalyst was added to 300 mL of 10 mg/L aqueous MO in a water-jacketed cylindrical Pyrex glass reactor (diameter 10 cm; height 11 cm; total capacity 500 mL) equipped with a 500 W xenon lamp (Beijing Electric Light Sources Research Institute, China) that was positioned 20 cm above the top of the mixture. The solution was stirred continuously and the temperature of the suspension system was controlled at (20 ± 1)°C by a thermostatically controlled water bath (THD-2015, Tianheng Instrument Factory, China). At preset intervals, a sample of 5 mL suspension was taken and centrifuged at 12,000 r/min for 5 min and then filtered through a 0.45 μm membrane filter. The reduction of color of the dye solution was examined by determining the residual concentration of MO with a UV-Visible light spectrophotometer (T6, Beijing Purkinje General Instrument Co., Ltd., China) in the wavelength range 200–900 nm. The efficiency of decolorization was calculated by measuring the change in intensity of the characteristic absorption peak of MO at 465 nm.

2 Results and discussion

2.1 Characterization of catalysts

2.1.1 Transmission electron microscopy

TEM allows imaging of the crystallographic structure of a sample at an atomic scale. As shown in Fig. 1, all samples, except pure-TiO$_2$-180 and 3HCl-TiO$_2$-180, have 3D flower-like morphology with a diameter of 800 nm, co-existing with finely dispersed nanoparticles. Yet the number of nanoflowers varies, increasing with increased concentration of HCl and decreasing with increased hydrothermal temperature. At higher magnifications, the nanoflower is seen to consist of nanorods growing evenly and radially from the center, with typical widths of 7–20 nm and lengths of 60–80 nm.

To improve our understanding of the single crystal nature of TiO$_2$, an HRTEM image of a typical TiO$_2$ nanorod from a nanoflower is illustrated in Fig. 1c. Lattice fringes of 0.33 nm and 0.29 nm correspond well to an interplanar distance of (110) and (001) planes of rutile TiO$_2$ (JCPDS 21-1276). In addition, the lattice fringes of the grains of pure-TiO$_2$-180 have a spacing of 0.35 nm, which is very close to the lattice spacing of (101) planes of anatase TiO$_2$ (JCPDS 21-1272). Therefore, the hydrothermal products in the present study contain a mixture of rutile and anatase, and have rodlike (rutile) and granulous (anatase) morphology.

It is well known that TiO$_2$ has three commonly encountered crystalline polymorphs: anatase, brookite, and rutile, which grow from the fundamental structural unit.
of the TiO$_6$ octahedron (Yoshida et al., 2009; Ren et al., 2010). However, their modes of arrangement and linkage are different. Formation of rutile proceeds by vertex-shared bonding, whereas formation of anatase proceeds by edge-shared bonding (Fei et al., 2006; Wang et al., 2007). In this study, HCl containing 62%–64% H$_2$O was introduced as the acid medium before hydrothermal treatment. Ti(OBu)$_4$ dissolved in the HCl aqueous solution was assumed to generate a complex of type [Ti(O-C$_4$H$_9$)$_{4-n,m}$(OH)$_m$Cl$_n$], where $n$ and $m$ are associated with the acidity and [Cl$^-$] in the reaction system, respectively (Phan et al., 2009). Generally, more OH ligand in [Ti(O-C$_4$H$_9$)$_{4-n,m}$(OH)$_m$Cl$_n$] promoted generation of the anatase phase. By contrast, the presence of Cl$^-$ in the complex species suppressed edge-shared bonding but enhanced vertex-shared bonding, favoring the formation of rod-like rutile titania (Izumi, 1978; Gopal et al., 1997; Wang et al., 2007). In other words, as $m$ increases, the probability of the formation of rutile TiO$_2$ increases. Rutile usually crystallizes in a rod-like shape because of its 4 screw axes along the crystallographic c-axis (Wu et al., 2002). The screw structure will promote crystal growth along this direction, leading to a crystal morphology dominated by the [110] facets (Li et al., 2007). Next, the rutile nanorods tend to aggregate on the (001) plane in spite of the repulsive force originating from the adsorbed Cl$^-$ on the (110) plane, because the (001) plane possess the highest surface energy among the low-index planes of the TiO$_2$ single crystal (Perron et al., 2007; Zhou et al., 2011). As a result, a radially aligned structure consisting of nanorods is formed, minimizing the surface area and reducing the total free energy.

In conclusion, high contents of HCl in the starting reactants play a positive role in enhancing the agglomeration of nanorods and thus formation of nanoflowers. Hence, as shown in Fig. 1, the agglomeration phenomenon is stronger and is accompanied by a smaller number of nanoparticles dispersed homogeneously around the nanorods when the initial acid content was increased from 3 to 9 mL.

The hydrothermal temperature is another important factor during the fabrication of various morphologies of TiO$_2$. Figure 1 shows that the density and size of the nanorods could be varied by changing the hydrothermal temperature of the growth solution. Elevating the temperature rapidly accelerated the hydrolysis of the [Ti(O-C$_4$H$_9$)$_{4-n,m}$(OH)$_m$Cl$_n$] complex; thus, more Cl$^-$ ligand in the complex is substituted gradually by the OH$^-$ ligand (Cheng et al., 1995), leading to a less dense distribution of the nanorod arrays, as shown in Fig. 1. Also, the diameter of the nanorods increased from 7–20 nm with increasing treatment temperature from 120 to 200°C. This could be due to the fact that high temperature can promote grain growth.

2.1.2 XRD
XRD is an established non-destructive method for qualitative and quantitative analysis of the phase composition of TiO$_2$. Figure 2 shows the XRD patterns of the prepared samples treated hydrothermally at different temperatures, as well as in various concentrations of the starting HCl solution. All peaks are clearly assigned to either the anatase or the rutile phase of titania, and no characteristic peak of crystalline phase relating to chlorine is visible. The sharp peaks at 20 values of 25.17°, 37.60°, 47.76°, 54.01° and 62.60° are a good match with the characteristic peaks of (101), (004), (200), (105) and (204) planes of the anatase phase of TiO$_2$ (JCPDS no. 21-1272), and the peaks at the 20 values of 27.38°, 36.10°, 41.24°, 54.28° and 62.67° fit well with the (110), (101), (111), (211) and (002) planes of the rutile phase of TiO$_2$ (JCPDS no. 21-1276). The anatase and rutile contents are calculated from the XRD intensity of the anatase (101) and rutile (110) reflections (Zhang and Banfield, 2000):

$$W_A = \frac{K_A I_A}{(K_A I_A + I_R)}$$

Fig. 1 TEM images of pure-TiO$_2$-180 (a), 3HCl-TiO$_2$-180 (b), 6HCl-TiO$_2$-180 (c), 9HCl-TiO$_2$-180 (d), 6HCl-TiO$_2$-120 (e), 6HCl-TiO$_2$-150 (f) and 6HCl-TiO$_2$-200 (g). The insets are enlarged TEM and HRTEM images of the corresponding samples.
The results given in Table 1 indicate that the crystalline phase of TiO$_2$ can be converted easily by varying the acid content. An increase in the volume of concentrated HCl in the reaction medium inhibited the formation of the anatase phase and favored the formation of the rutile phase. For example, the fraction of rutile phase was 17% in the presence of 3 mL of HCl, which was increased to 56% in the presence of 9 mL of HCl. The crystallization behavior in the present study was consistent with the literature, where a strong acidic medium is reported to favor the formation of rutile TiO$_2$ and relatively weak acid conditions favor the formation of anatase TiO$_2$ (Cheng et al., 1995; Izumi, 2007). In addition, by applying the Scherrer formula (Patterson, 1939) to the rutile (110) and anatase (101) diffraction peaks, the average crystallite sizes were found to be 12.8, 13.4 and 20.5 nm for rutile nanorods, and 7.3, 8.2 and 12.5 nm for anatase nanoparticles in 3HCl-TiO$_2$-180, 6HCl-TiO$_2$-180 and 9HCl-TiO$_2$-180, respectively. This indicates that the crystal sizes of both the resulting rutile nanorods and the anatase nanoparticles increased with increasing amounts of HCl. Thus, the use of more acid causes an increase in crystallinity and subsequently the nanocrystallite growth of TiO$_2$. The pH dependence on the phase composition of TiO$_2$ products should be ascribed to the coordination group of the Ti(IV) complex of [Ti(O-C$_4$H$_9$)$_{4-}$_{m-}$(OH)$_n$Cl$_n$], which is generated by the hydrolysis of Ti(OBu)$_4$. The lower the content of HCl in the starting reactants, the greater the number of OH ligands in [Ti(O-C$_4$H$_9$)$_{4-}$_{m-}$(OH)$_n$Cl$_n$]. Thus, the probability of edge-shared bonding is greater and the formation of anatase is easier (Cheng et al., 1995; Phan et al., 2009).

Following hydrothermal treatment, all samples clearly possessed mixed crystals consisting of anatase and rutile except pure-TiO$_2$-180, and the proportions of these crystalline phases depend on the hydrothermal temperature. As the hydrothermal temperature was increased from 120 to 200°C, the fraction of the rutile phase decreased gradually from 86% to 9%. Crystallite sizes of 6HCl-TiO$_2$-120, 6HCl-TiO$_2$-150, 6HCl-TiO$_2$-180 and 6HCl-TiO$_2$-200 powders were 7.4, 9.2, 12.8 and 14.9 nm for rutile nanorods and 7.7, 7.9, 8.2 and 10.1 nm for anatase granulous TiO$_2$ respectively. As described for the TEM analysis, lowering the temperature retarded the hydrolysis process, decreasing the $n$ value in [Ti(O-C$_4$H$_9$)$_{4-}$_{m-}$(OH)$_n$Cl$_n$] (Cheng et al., 1995). The edge-shared bonding is suppressed and the vertex-shared bonding is enhanced. Finally, titania with more rutile and less anatase was obtained.

### 2.1.3 XPS

XPS is able to identify the surface chemical composition and chemical states of a material. The XPS spectrum of the samples after calcination at 500°C in air showed the C 1s peak due to the adventitious carbonaceous species at 284.6 eV, the O 1s peak due to the adventitious oxygen at 531.8 eV, and the Ti 2p peak due to the adventitious TiO$_2$ at 457.8 eV. The Ti 2p peak shifted to lower binding energy with increasing HCl content, indicating the formation of Ti(III) species. The C 1s and O 1s peaks were not observed, indicating the removal of adventitious contaminants. The Ti 2p peak was deconvoluted into two components: the Ti 2p$_3/2$ peak at 457.8 eV and the Ti 2p$_1/2$ peak at 460.5 eV, corresponding to the Ti(IV) and Ti(III) species, respectively. The Ti(III) content increased with increasing HCl content, indicating the formation of Ti(III) species. The O 1s peak shifted to lower binding energy with increasing HCl content, indicating the formation of Ti-OH species. The C 1s peak was not observed, indicating the removal of adventitious contaminants.
6HCl-TiO$_2$-180 is shown in Fig. 3. For comparison, XPS was used with pure-TiO$_2$-180.

XPS spectra of the Ti 2p region of 6HCl-TiO$_2$-180 and of pure-TiO$_2$-180 are shown in Fig. 3b. The Ti 2p1/2 and Ti 2p3/2 spin-orbital splitting photoelectrons for both samples are located at binding energies of 458.5 and 464.2 eV, respectively, which can be fit to the peaks centered at 458.6 eV and 464.4 eV, assigned to the Ti$^{4+}$ species, and the peaks centered at 457.3 eV and 463.2 eV, assigned to the Ti$^{3+}$ species (Zhang et al., 2012).

The Cl/Ti molar ratio on the surface of 6HCl-TiO$_2$-180 is about 0.56:100, which is much lower than the molar ratio of HCl/Ti(OBu)$_4$ (50:100). Moreover, a weak peak corresponding to Cl 2p is located at a binding energy of 199.2 eV, which was previously attributed to chemisorbed chlorine (Xu et al., 2008; Wang et al., 2012). No signal assigned to the substitutional Cl (peak located at 198.2 eV) was found (Chen et al., 2006). Thus, our results are different from those reported by earlier studies, where some of the anionic Cl was believed to be incorporated into TiO$_2$ through substitution of the lattice oxygen atoms, and the others are present as adsorption chloride or the interstitial chlorine in the crystal cell (Chen et al., 2006; Xu et al., 2008; Wang et al., 2012). This could be because the earlier studies used the sintering process at high temperature, resulting in chlorine entering the crystal lattice and replacing oxygen. By contrast, we infer that the detection of trace quantities of Cl in this study can be associated with incomplete washing with ethanol and water. A similar result was reported by Phan et al. (2009).

### 2.1.4 Brunauer-Emmett-Teller measurement

The nitrogen adsorption-desorption isotherms and BJH pore size distributions derived from the desorption branch of the adsorption isotherms of the prepared samples are shown in Fig. 4. All the samples can be categorized as isotherms of type IV, indicating the presence of mesoporous materials according to the International Union of Pure and Applied Chemistry classification (Sing et al., 1985). Nevertheless, the hysteresis loops of various samples are qualitatively different. The hysteresis loop of pure-TiO$_2$-180, 3HCl-TiO$_2$-180, 6HCl-TiO$_2$-180 and 6HCl-TiO$_2$-200 fit well to type H2, which is characteristic for mesoporous materials with ink-bottle pores. Unlike the above catalysts, well-defined H3-type hysteresis loops were obtained for 6HCl-TiO$_2$-120, 6HCl-TiO$_2$-150 and 9HCl-TiO$_2$-180, implying the formation of slit-like pores that are associated with aggregates of nanorods in our experiments (Sing et al., 1985). The result given above is in accord with the TEM results. Samples containing more nanorods exhibit a hysteresis loop of type H3, whereas more nanoparticles lead to the H2-type hysteresis loop.

Also, two distinct capillary condensation steps derived from the structure of bimodal pore-size distributions compared to pure-TiO$_2$-180 can be observed: the first at a relative pressure ($P/P_0$) range of 0.13–0.40 correspond to mesoporous at 5–10 nm according to the BJH analysis of pore size distribution from the desorption branch of the isotherm, which is related to finer intra-aggregated pores within the primary agglomerated particles. The second was located at $P/P_0 > 0.45$, which corresponds to 15–20 nm mesopores, and is associated with a larger inter-aggregated pore between the secondary aggregated particles; namely, the pores among the nanoflowers (Yu et al., 2003).

The textural properties, such as BET surface area and average pore volume obtained from nitrogen adsorption-desorption analysis, are summarized in Table 1. The BET surface areas for 6HCl-TiO$_2$-120, 6HCl-TiO$_2$-150, 6HCl-TiO$_2$-180 and 6HCl-TiO$_2$-200 were 142, 185, 165 and 154 m$^2$/g, respectively. Hydrothermal temperature displays...
a significant influence on the BET surface area of the samples, which first increased and then decreased as the hydrothermal temperature was varied from 120 to 200°C. On the basis of the results given above, two types of agglomeration were identified in our samples; namely, agglomeration of rutile TiO$_2$ nanorods forming nanoflowers and agglomeration of anatase nanoparticles. It is widely accepted that increasing the hydrothermal temperature increases the grain size and enhances the agglomeration of the nanoparticles, but weakens the agglomeration forces of the nanorods as mentioned above. Consequently, the maximum BET surface area is observed for the 6HCl-TiO$_2$-150 catalyst. Moreover, the surface area of 3HCl-TiO$_2$-180, 6HCl-TiO$_2$-180 and 9HCl-TiO$_2$-180 were 193, 165 and 68 m$^2$/g. Combined with the results of the TEM analysis, it can be deduced that the more rutile nanorods and the larger their diameters, the smaller the BET surface area of the catalyst.

2.2 Photocatalytic activity

We evaluated photocatalytic activity by the decolorization of a representative model pollutant of MO in the presence of as-prepared TiO$_2$, and in the absence of catalysts under UV-visible light irradiation, as well as the absorption of MO on 6HCl-TiO$_2$-180 in darkness. A control experiment was done with the commercial catalyst Degussa P25, which is commonly used as the basis for comparison with titania photocatalysts prepared by other procedures.

No decolorization of MO was observed with 6HCl-TiO$_2$-180 in darkness or without catalysts under UV-visible light irradiation (Fig. 5a). The removal efficiency of dark adsorption and the direct photolysis of MO within 60 min are 8% and 5%, respectively, indicating that MO is stable under UV-visible light irradiation and the adsorption dependence can be considered negligible. In addition, the 6HCl-TiO$_2$-180 catalyst exhibits a slightly higher level of photo-activity than that of Degussa P25. To ascertain whether the photocatalyst of 6HCl-TiO$_2$-180 has a response in the visible light region, a similar degradation experiment was done by placing a UV cut-off filter between the Xe lamp and the sample suspension to prevent the passage of light of $<400$ nm wavelength. Figure 5a shows that the removing rate of MO was similar.
to that of dark adsorption, suggesting that visible light contributes little to the photochemical process.

The photocatalytic activity of TiO$_2$ might depend on the morphology of catalysts, which can be controlled by changing the starting concentration of HCl. Figure 5b shows the photodegradation of MO as a function of time for catalysts prepared from different concentrations of HCl. The starting concentration of HCl has a crucial role in determining the photocatalytic activity. We found that with an increasing concentration of HCl, the photocatalytic activity of the catalysts increases and then decreases, exhibiting a maximum decolorization efficiency of 98% for 6HCl-TiO$_2$-180 after 60 min reaction (Table 1).

Note that a similar composition was observed for the catalysts 3HCl-TiO$_2$-180 and 6HCl-TiO$_2$-180, consisting of 80% anatase and 20% rutile, and 6HCl-TiO$_2$-180 had a smaller BET surface area than that of 3HCl-TiO$_2$-180. However, the 6HCl-TiO$_2$-180 catalyst had a photocatalytic activity relatively higher than that of 3HCl-TiO$_2$-180 in the decolorization of MO under UV-Visible light irradiation. The greater photocatalytic activity of 6HCl-TiO$_2$-180 can be attributed to the 3D morphology that was observed by TEM, because the significant difference between the two samples is that the 3D flower-like morphology is present in 6HCl-TiO$_2$-180, whereas 3HCl-TiO$_2$-180 consists of dispersed nanorods and nanoparticles. The enhancement effect derived from the special hierarchical structure can be attributed to light-scattering induced by the nanorods within the nanoflowers, which in turn cause the light to be multiply absorbed during the transporting process. As a result, the absorption of photons and thus the production of photocarriers are improved significantly. In addition, the unique flower-like structure facilitates the formation of extra-large textural mesopores (Fig. 1c), providing more efficient transport channels for the reactant molecules to contact the reactive sites on nanoparticles (Bagshaw et al., 1995; Yang et al., 1997; Pauly et al., 1999). On the basis of the discussion above, the 6HCl-TiO$_2$-180 catalysts appear to have greater photocatalytic activity than 3HCl-TiO$_2$-180. The weak MO decolorization rate with 9HCl-TiO$_2$-180 is ascribed to the unfavorable composition of anatase and rutile, which will be discussed below.

In addition, the hydrothermal temperature has a significant influence on the crystalline phase composition, surface area and morphology of the TiO$_2$ nanostructure. Here, the degradation efficiency of MO increased as the hydrothermal temperature increased from 120 to 180°C, whereas a further increase in the hydrothermal temperature from 180 to 200°C produced a negative effect on the degradation efficiency (Fig. 5e). These results can be ascribed to the different anatase/rutile ratios of the samples.

Figure 5c shows 6HCl-TiO$_2$-200 has greater photocatalytic activity than pure-TiO$_2$-180 in UV-visible light. Almost the same surface areas of 6HCl-TiO$_2$-200 (154 m$^2$/g) and pure-TiO$_2$-180 (163 m$^2$/g) were calculated by referring to BET. As found by TEM, few 3D nanoflowers can be observed for 6HCl-TiO$_2$-200, as well as pure-TiO$_2$-180. Thus, the effect of BET specific surface and morphology can be ignored in this experiment.

Pure-TiO$_2$-180 is composed of pure anatase, whereas 6HCl-TiO$_2$-200 contains mainly anatase and a little rutile (the ratio of anatase/rutile was 91:9). We can infer that pure anatase would not be the most active TiO$_2$ sample, and the existence of rutile TiO$_2$ is a significant factor in promoting the removal of MO. The phase-dependence of TiO$_2$ on photo-activity is still under dispute. Anatase is often considered to be the most active because it has a slightly higher Fermi level, a higher degree of hydroxylation and a lower capacity to adsorb oxygen (Gerischer and Heller, 1992). A similar or even higher photocatalytic activity for rutile is also reported (Andersson et al., 2002). However, some researchers claim that the coexistence of anatase and rutile is more active than pure anatase or pure rutile (Bickley et al., 1991; Ohno et al., 2001). The role of rutile in photocatalytic reaction is to separate the electrons from the holes. Electrons that are photo-excited in rutile can migrate to the conduction band of anatase leaving the holes remaining in the rutile, resulting in effective suppressing the recombination of photogenerated electrons and holes (Li et al., 2008). Until now, the optimum ratio of anatase to rutile for the photocatalysis is still variable and controversial (Ohno et al., 2003; Li et al., 2008; Hsu et al., 2010; Su et al., 2011). In this study, we synthesized a series of TiO$_2$ catalysts containing both anatase and rutile by systematically adjusting hydrothermal temperature. As given in Table 1, the anatase content ranged from 14% to 91% as the hydrothermal temperature was increased from 120 to 200°C, corresponding to a decrease in the content of rutile from 86% to 9%. In this study, photocatalytic degradation of MO was used to investigate the influence of the anatase/rutile ratio on photoactivity. The maximum activity was obtained with 6HCl-TiO$_2$-180, a catalyst with an anatase content of 82% and a rutile content of 18%; that is, an anatase/rutile ratio of approximately 80:20. Any higher or lower anatase content leads to decreased performance and this composition is consistent with that of commercial TiO$_2$ photocatalyst powder (Degussa P25).

As mentioned above, the nanorods constituting nanoflowers are rutile, while other granulous particles are anatase. Regarding morphology-dependent photocatalytic performance, TiO$_2$ with a high level of photo-activity should have an appropriate ratio of rutile 3D flower-like structure and anatase granulous particles, because the optimum anatase/rutile ratio is found to be 80:20.

3 Conclusions

In summary, titania has been fabricated by a simple hydrothermal route using Ti(OBu)$_4$ as the Ti source and HCl as the growth additive. The hydrothermal
and starting concentration of HCl influence the crystalline phase and the morphology of TiO$_2$ species. Coexistence of the rutile 3D flower-like structure and the anatase granular particles favors improvement of the mass transfer of organics, the harvesting of light, and retarding the recombination of photo-excited electrons and holes. We believe that this photocatalyst is a promising candidate for possible photocatalytic applications using solar energy and warrants further investigation and improvement.

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References


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