Comparative study of photocatalytic performance of titanium oxide spheres assembled by nanorods, nanoplates and nanosheets

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TiO\textsubscript{2} spheres assembled by nanorods, nanoplates and nanosheets were fabricated by facile hydrothermal/solvothermal methods. The three samples were thoroughly characterised by scanning electron microscopy, X-ray diffraction, the Brunauer–Emmett–Teller method and UV spectroscopy. The surface area of spheres assembled by nanosheets was 83.9 m\textsuperscript{2}g\textsuperscript{-1}, which is larger than that obtained for nanorods (10.8 m\textsuperscript{2}g\textsuperscript{-1}) and nanoplates (6.31 m\textsuperscript{2}g\textsuperscript{-1}). Their photocatalytic performance was evaluated in terms of the decomposition rate of methyl orange in these three samples under UV irradiation. The best photoactivity was observed in the samples constructed from nanosheets.

Keywords: titanium oxide; hierarchical spheres; photocatalyst

1. Introduction

As an important n-type semiconductor, titanium oxide (TiO\textsubscript{2}) has gained increasing attention because of its applications in many fields, such as photocatalysis, sensors, dye-sensitised solar cells and self-cleaning coatings [1–5]. Photocatalysis on the surface of semiconductors is among the most promising technologies for converting solar energy into chemical energy [6–14]. There are four processes in a typical photocatalytic reaction, i.e. the generation of electrons and holes by photoexcitation, migration of the photogenerated charge carriers to the surface, subsequent reduction/oxidisation of the adsorbed reactants directly by electrons/holes and recombination of the photogenerated electron–hole pairs [11]. It is widely accepted that a structure with a high specific surface area can promote photocatalytic processes, such as P25 nanocrystallines [11]. However, for random nanocrystallines, the benefit from the size reduction would be cancelled out by the higher electron–hole recombination rate, since the photogenerated electrons and holes may not be efficiently migrated to the surface [11,12]. To suppress this recombination process, several strategies have been proposed. Wu \textit{et al.} fabricated anatase TiO\textsubscript{2} nanobelts and they found that the one-dimensional structure exhibits a lower electron–hole recombination rate than the nanospheres [11]. Yang \textit{et al.} introduced a stable phase interface by designing a core–shell structure, monoclinic TiO\textsubscript{2} nanofibres coated with a thin shell of anatase TiO\textsubscript{2} nanocrystals, and thus enhanced the photocatalytic activity of the nanofibres [12].
Recently, surface scientists found that surface energy has an important impact on the physical properties of materials [15]. The order of the average surface energies of anatase TiO_2 is 0.90 J/m^2 for \{001\} > 0.53 J/m^2 for \{100\} > 0.44 J/m^2 for \{101\} [15–18]. Several studies have demonstrated that the highly active (001) facets of anatase TiO_2 nanosheets exhibit excellent photocatalytic activity [17,18]. One problem for these nano unit applications is the difficult separation from the solution after the photocatalytic reaction. The construction of hierarchical structures of micro size could solve this nano size problem [19]. Furthermore, the hierarchical structures not only can keep the superior merits from nano unit but also can produce new collective properties and advanced tuneable functions arising from nano unit ensembles [20]. Therefore, much attention has been paid to the self-assembly and transformation of nano units into highly ordered superstructures with controllable architectures and several methods have been developed, such as oriented attachment and spontaneous assembling [21–23].

In this work, we prepared micro spherical TiO_2 architectures constructed by three different nanosized subunits (nanorods, nanoplates and nanosheets) through simple hydrothermal/solvothermal methods. The comparative photocatalysis reaction in these three architectures has been studied.

2. Experimental section

2.1. Materials synthesis

2.1.1. TiO_2 spheres assembled by nanorods (sample I)
In a typical process, 15mM titanium isopropoxide (Sigma-Aldrich), 10 ml hydrochloric acid (32 wt %) and 20 ml deionised water were mixed in a Teflon-lined stainless steel autoclave (45 ml volume, Parr Instrument Co.). The synthesis was conducted at 180°C for 14 h in an electric oven, and then the autoclave was cooled to room temperature naturally. The as-collected powders were washed by deionised water and ethanol for several times, and dried at 80°C for 5 h.

2.1.2. TiO_2 spheres assembled by nanoplates (sample II)
The synthesis procedure has been reported in our previous work [8]. Briefly, one piece of Ti foil and 15 ml mixed solution of deionised water and dilute hydrofluoric acid (0.2% by weight) were placed into a Teflon-lined stainless steel autoclave. The hydrothermal synthesis was conducted at 130°C for 10 h in an electric oven.

2.1.3. TiO_2 spheres assembled by nanosheets (sample III)
The nanosheets structure was prepared by a solvothermal method [16]. In a typical process, 1.15 ml titanium isopropoxide (Sigma-Aldrich), 32 ml isopropanol and 0.02 ml diethylenetriamine (DETA) were mixed in a Teflon-lined stainless steel autoclave (45 ml volume, Parr Instrument Co.). The synthesis was conducted at 200°C for 24 h in an electric oven, and then the autoclave was cooled to room temperature naturally. The as-collected powders were washed by deionised water and ethanol for several times, and then dried at 80°C for 5 h. To increase the crystallinity, some samples were heated at 400°C for 3 h in a muffle furnace.

2.2. Materials characterisation
The crystal structure of the as-prepared powders was characterised by X-ray diffraction (XRD, PANanalytical Xpert Pro diffractometer) with Cu Kα radiation (\(\lambda = 1.5418 \text{ Å}\))
in the 2θ range 10–70°. The morphology of the as-prepared powders was observed by scanning electron microscopy (SEM, FEI Quanta 200). The samples were sputter-coated with gold for 2 min before the observation and an accelerating voltage of 25 kV was used. Transmission electron microscopy (TEM, Philips CM200) was also used to characterise the detailed morphology. Nitrogen sorption isotherms were measured by volumetric method on an automatic adsorption instrument (Micromeritics, Tristar 3000) at liquid nitrogen temperature (77 K). Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method from the data in a \( P/P_0 \) range between 0.01 and 0.25. UV–visible absorption spectra were recorded using a UV–visible–NIR spectrophotometer (Varian Cary 5000).

2.3. Photocatalysis experiments

The photocatalysis experiments were carried out in a photoreactor equipped with six tubular Hg lamps (NEC, FL20SBL) of 20 W, and the peak of the wavelength was at about 350 nm. A total of 10 mg of TiO\(_2\) catalysts was added to a 10 ml solution of 20 mg/l methyl orange (MO) in a 15 ml polyethylene tube. At different time intervals of irradiation, the tubes were unloaded and then centrifuged at 10,000 rpm for 3 min to separate the supernatant and the catalysts. The supernatants were collected and analysed by recording the characteristic absorption peak of MO (464 nm) using a UV–visible spectrometer (Varian Cary 100). According to the calibration plot of the UV absorbance as a function of the remaining MO concentration, the efficiency of the MO decomposition was calculated.

3. Results and discussion

The morphologies of the samples were examined by SEM and the results are shown in Figure 1. As depicted in Figure 1a, sample I consisted of spheres with an average size of about 3 \( \mu \)m. From the high-magnification image shown in Figure 1b, it can be observed that the spheres are assembled by nanorods. It has been proposed that the chlorine system can help produce nanorods [7,8,24]. In this system, the nanorods with smaller dimensions are first formed under the current hydrothermal conditions. To reduce the surface energy, these small nanorods tend to aggregate together to form spheres of micro size.

The nanoplates in sample II are shown in Figures 1c and d. These nanoplates are well-defined quadrilateral platelets with a smooth surface. The nanoplates are 1–2 \( \mu \)m in size and around 50 nm in thickness, and they self-assemble into micro spheres with a diameter of about 4 \( \mu \)m. It has been suggested that the presence of fluorine can promote the formation of reactive {001} facets [15,17]. On the basis of the shape-dependent thermodynamic model, the stable exposed facets are {101}, while F-terminated surfaces could result in a (001) surface that is more stable than (101) surfaces [15]. Consequently, spheres assembled by the nanoplates with reactive {001} facets are obtained in this fluorine-assisted hydrothermal system.

Figures 1e and f illustrate the morphology of sample III, which consists of interesting prickly sphere-like structures. The size of the spheres is around 1–3 \( \mu \)m in diameter. It can be seen that the spheres are composed of nanosheets from the high-magnification TEM image shown in Figure 1f. The thickness of nanosheets is around 10–20 nm. Chen et al. reported that tridentate DETA could stabilise the high-energy (001) surfaces and produces ultrathin nanosheets [16]. In this solvothermal system, with increasing the reaction time the nanosheets self-assembled into hierarchical micro spheres to further reduce the high surface energy. The images of the spheres heated at 400°C for 3 h are shown in Figures 1g and 1h. It can be seen that the spherical structure remains unchanged and that the diameter of these spheres is around 2–3 \( \mu \)m, but these spheres aggregate more closely compared...
Figure 1. SEM images of spherical architectures of TiO$_2$ constructed by different sub units: (a, b) nanorods; (c, d) nanoplates; (e) nanosheets; (f) TEM image of TiO$_2$ spheres assembled by nanosheets; (g, h) SEM and TEM images of TiO$_2$ spheres assembled by nanosheets after being heated at 400 °C for 3 h.
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Figure 2. XRD patterns of spherical architectures of TiO$_2$ with three different sub units: nanorods, nanoplates and nanosheets, and TiO$_2$ spheres constructed by nanosheets heated at $400^\circ$C for 3 h.

to those spheres without heat treatment. In Figure 1h, nanosheets can be clearly observed, indicating that heating does not damage the highly active facets.

The crystal phases of the as-prepared samples were confirmed by XRD measurements, as shown in Figure 2. Sample I has a rutile phase with tetragonal structure, space group $P4_2/mmm$ (JCPDS card, No. 21-1276), while the other two samples contain pure anatase phase with tetragonal structure, space group $I4_1/amd$ (JCPDS card, No. 71-1169). The diffraction peak intensity from sample I and sample II is much higher than that from sample III. To increase the crystallinity in sample III, the samples were heated at $400^\circ$C for 3 h. It can be observed that the heat treatment results in a significant increase of crystallinity in sample III, as shown in Figure 2. Generally, the rutile phase is less active than the anatase phase due to a lower surface affinity for many organic compounds and a higher rate of recombination of photogenerated charge pairs. Recently, it was found that the mixed TiO$_2$ phases exhibit much higher catalytic activity than the individual phases [12,14]. The well-known P25 nanocrystal is a prime example, which consists of 80% anatase and 20% rutile and shows superior photocatalytic activity. Therefore, these two different phases were used to study its influence on the photocatalytic behaviour.

The surface area of the three samples was measured using the BET method. As shown in Figure 3, the surface area of sample I and sample II are quite low, 10.8 m$^2$g$^{-1}$ and 6.31 m$^2$g$^{-1}$, respectively. Sample III exhibits a type II adsorption isotherm and gives rise to a relatively high BET specific surface area of 83.9 m$^2$g$^{-1}$.

The photocatalytic degradation mechanism of MO by TiO$_2$ under UV irradiation is illustrated in Figure 4. TiO$_2$ is a photosensitive material, and when it is irradiated with UV light, electrons in the valence band absorb the photon energy and jump to the conduction band, leaving holes in the valence band [12]. The photogenerated hole can be captured by OH$^-$ or H$_2$O to produce hydroxyl radicals. These hydroxyl radicals then oxidise the MO with the formation of low molecular weight by-products. Generally, the bandgap of anatase TiO$_2$ is around 3.2 eV and rutile TiO$_2$ is around 3.0 eV [12].
The optical properties of TiO$_2$ spheres with different subunits were also studied in this work. As shown in Figure 5, the absorption edge of samples I, II and III is about 517 nm, 437 nm and 403 nm, respectively, and the corresponding bandgaps are 2.40 eV, 2.84 eV and 3.08 eV. The absorption edge of sample III after heating at 400°C is around 393 nm and the corresponding bandgap is about 3.16 eV. Although both sample II and III are anatase phase, the absorption edge of sample III takes an obvious blue shift, around
Figure 5. UV spectra of TiO$_2$ spheres constructed by nanoplates, nanorods and nanosheets and TiO$_2$ spheres constructed by nanosheets heated at 400 °C for 3 h.

32 nm, compared with that of sample II. This may be caused by the quantum effect of the nanosheets shown in Figure 1f. However, the absorption edge of sample III after heating at 400°C does not take an obvious shift. But in the visible light region, it is clear that there is a significant difference.

The photocatalytic performance of the three samples for degradation of MO in an aqueous solution under UV irradiation is shown in Figure 6. Apparently, sample III exhibits a much higher degradation efficiency compared to samples I and II. In Figure 6, it can be seen that MO is almost completely degraded by sample III after UV irradiation of 2 h. The surface area of sample III is about 7.8 and 13.3 times larger than that of the sample I and sample II, respectively. The high photocatalytic activity of sample III may be attributed to its large surface area and/or its unique structure with highly active (001) facets. To study which contributes more to the excellent performance, we calculated the MO degradation concentration with irradiation time for per unit surface area, and the results show that sample III is not the best photocatalyst among those three samples. Therefore, the conclusion can be drawn here that the surface area is the most significant factor influencing the activity. The higher surface area of a sample, the more active sites it provides for the degradation reaction and the better performance it shows. Note that although the surface area of sample I is larger than sample II, its photocatalytic activity is lower than that of sample II. Considering the considerably low surface area for sample I (10.8 m$^2$g$^{-1}$) and sample II (6.31 m$^2$g$^{-1}$), here the high active (001) facets may play an important role in enhancing the photocatalytic activity. Xiang and co-workers reported that this nanoplate structure exposes highly active (001) facets with an exposure rate of nearly 30% and exhibits superior photocatalytic activity towards decomposition of azo dyes in water [19]. Furthermore, the rutile structure in sample I may also be responsible for deteriorating the photocatalytic performance due to the strong recombination rate [11,12].
In summary, TiO₂ spheres individually constructed by nanorods, nanoplates and nanosheets were prepared by simple hydrothermal and solvothermal methods. The photoactivities show that the spheres constructed by nanosheets exhibit the best photocatalytic performance. This may be attributed to their large surface area and to highly active (001) facets. This study offers more insights about the effect of structures on the photocatalytic performance.

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