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A facile synthesis of rutile-rich titanium oxide nanoparticles using reverse micelle method and their photocatalytic applications



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ABSTRACT

Flower-like shaped rutile-rich TiO_2 nanoparticles were synthesized by the reaction of HCl with titanium diisopropoxide bis(acetylacetonate) immobilized in reverse micelles composed of oleic acid, water, and xylene. Brunauer Emmett Teller (BET) analysis showed large surface area of the synthesized TiO_2 nanoparticles of 177.8 m²/g. We investigated the effect of the concentration of Ti precursor and role of oleic acid in the formation of TiO_2 nanoparticles. Rutile-rich TiO_2 nanoparticles with large surface area showed better photocatalytic activity in decomposing methyl orange under visible-light irradiation than anatase and rutile mixed phase TiO_2 particles.

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Introduction

Titania (TiO₂) is an n-type wide band-gap semiconductor material and has been used in a wide variety of applications such as dye-sensitized solar cells (DSSCs) [1–5], photochromic devices [6], and lithium batteries [7]. TiO₂ has been widely investigated as photocatalysts due to high photo-activity, low cost, low toxicity and good chemical and thermal stability [8–10]. TiO₂ nanoparticles have been synthesized by various methods, including solution precipitation [11], solvothermal synthesis [12], polyol reaction [13,14], and sol–gel reaction [15]. However, these syntheses often suffer from harsh reaction conditions including high reaction temperature (more than 200 °C), high pressure, inert atmospheric conditions, and post-synthetic heat treatment due to poor crystallinity of the products. It remains a challenge to develop a simple and reliable route to the synthesis of TiO₂ nanoparticles under mild and ambient reaction conditions.

A reverse micelle method provides a simple route for producing various metal oxide nanoparticles including Fe_3O_4 [16,17], Mn_3O_4 [18], and TiO_2 [19–21] in which reverse micelles formed in an organic medium serve as nanoreactors for the formation of

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nanoparticles. A typical reverse micelle synthesis for nanoparticles involves the following steps: (i) surfactants are dissolved in an organic solvent; (ii) an aqueous solution containing metal precursor is added to the surfactant solution to produce reverse micelles acting as nanoreactors; (iii) nanoparticles grow inside the micelles through the reaction of the metal precursor upon the addition of a reactant. Typically, polymers which have long hydrocarbon chain or organic molecules having charged functional group are used as surfactants to form reverse micelles in an organic solvent, for example, P123 and cetyltrimethylammonium bromide. Here we report a reverse micelle route to the synthesis of TiO₂ nanoparticles using oleic acid, which is one of the natural fatty acid, as a surfactant. Flower-like shaped rutile-rich TiO₂ nanoparticles were synthesized by the reaction of HCl with titanium diisopropoxide bis(acetylacetonate) immobilized in reverse micelles composed of oleic acid, water, and xylene. We also investigated the effect of the concentration of Ti precursor and role of oleic acid in the formation of TiO₂ nanoparticles. Photocatalytic activity of the product TiO₂ nanoparticles was evaluated in decomposing methyl orange dye under visible-light irraditional.

Experimental

Synthesis of rutile-rich TiO₂ nanoparticles

9.765 ml of titanium diisopropoxide bis(acetylacetonate) (Aldrich, 75 wt% in isopropanol) was added to a mixture solution

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containing *p*-xylene (75.8 ml, Aldrich) and oleic acid (21.16 ml, Aldrich). After stirring for 2 h, 5 ml of deionized water was added to form a reverse micelle and the mixture solution was then heated to 90 °C. 4.715 ml of hydrochloric acid (HCl, 35%, Daejung) was added and the resulting solution was refluxed at 90 °C for 3 h. The final product was collected by repeating centrifugation and washing with ethanol three times to remove the excess reagents.

Characterization

The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured using a JEM-2100F microscope operated at 200 kV. Powder X-ray diffraction (XRD) patterns were obtained using a D8 Advance (Bruker) diffractometer at 40 kV and 40 mA. The UV-vis spectra were recorded using an Agilent Cary60 (Agilent) UV-vis spectrophotometer within a range of 250–850 nm. N₂ adsorption–desorption isotherms and Brunauer–Emmett–Teller (BET) surface area were analyzed using an ASAP 2020 (Micromeritics). Thermo gravimetric analysis (TGA) of the sample was carried out using Q50 (TA Instrument).

Measurements of photocatalytic properties

Photocatalytic activity of the sample was evaluated by decomposition of methyl orange (MO, Daejung Co.) under visible-light irradiation with 400 W mercury lamp. UV cut-off filter was used to eliminate the UV light (<420 nm). The initial concentration of MO was 15 mg/l. TiO₂ sample (0.1 g) was dispersed in 100 ml of 15 mg/l MO aqueous solution by sonication. The reactor temperature was kept at $25 \,^{\circ}\text{C}$ using circulating water. Before the lamp was on, the suspension was stirred in the dark for

60 min to establish adsorption–desorption equilibrium. During the photodegredation process, the concentration of MO solution was analyzed every 1 h by UV–vis spectrometer (Optizen POP, Mecasys Co.). For comparison, photocatalytic activity measurement was conducted using a commercial TiO_2 (P25, Degussa AG).

Results and discussion

Rutile-rich TiO₂ nanoparticles were synthesized from the reaction of HCl with titanium diisopropoxide bis(acetylacetonate) immobilized in reverse micelles composed of oleic acid, water, and xylene, without any additional heat treatment process. Upon the addition of an HCl solution, the color of the reaction solution immediately turned from yellowish brown to ivory, indicating the formation of nanoparticles. A typical transmission electron microscopy (TEM) image of the product reveals the formation of flower-like nanoparticles with an average sizes of around 250 nm (Fig. 1A and B). A high-resolution TEM (HRTEM) image of a single nanoparticle shows a cross-lattice pattern, which demonstrates that it has a good crystalline nature (Fig. 1C). The HRTEM result also indicates the formation of polycrystalline nanoparticles, as shown in Fig. 1C. The powder X-ray diffraction (XRD) pattern (Fig. 1D) of the nanoparticles is consistent with the rutile crystal structure (*a* = 4.517 Å and *c* = 2.940 Å, JCPDS Card No. 88-1175). The small characteristic peaks of anatase TiO₂ structures were also observed in the XRD patterns, demonstrating that the product contained a small amount of anatase TiO₂. The grain size of the TiO₂ nanocrystals, calculated by using the Scherrer formula, was 7.5 nm.

The percentage yield of TiO_2 nanoparticles was calculated by using TGA in a nitrogen atmosphere at a heating rate of 20 °C/min.



Fig. 1. (A and B) TEM images, (C) HRTEM image, and (D) XRD pattern of TiO₂ nanoparticles (Black arrows indicate the presence of anatase crystal structure.) synthesized by the reaction of HCl with titanium diisopropoxide bis(acetylacetonate) immobilized in reverse micelles composed of oleic acid, water, and xylene.



Fig. 2. (A) TGA thermogram and (B) N_2 adsorption-desorption isotherm of the TiO₂ nanoparticles shown in Fig. 1. (Inset shows the pore size distribution.) (C) UV-vis spectra and (D) Plots of $(Ah\nu)^2$ versus photon energy $(h\nu)$ of TiO₂ nanoparticles and commercial TiO₂ (P25). (E) Room-temperature PL spectra of TiO₂ nanoparticles.

Oleic acid stabilized TiO_2 nanoparticles shows around 10% weight loss at a temperature of as high as 410 °C (Fig. 2A). Based on the calculation using TGA data, we could conclude that the percentage yield of TiO_2 nanoparticles came out to be greater than 85%. Fig. 2B shows N₂ adsorption–desorption isotherm of the sample. According to BDDT classification [22], the sample shows type IV isotherm with type H3 hysteresis loop, indicating the presence of mesopores (2–50 nm). Due to the small particle size and mesoporisity, the produced TiO₂ nanoparticles showed large surface area of 177.8 m²/g with an average pore size of 3.8 nm. On the contrary, P25 showed small surface area of 49.3 m²/g. It is attributed to the fact that P25, produced through hydrolysis of TiCl₄ in a hydrogen flame, has relatively larger particle size and does not contain pores in each TiO₂ crystallites [23,24]. The band gap of metal oxide nanocrystals has a significant impact on their electronic, optical, and photocatalytic properties. For instance, it has been shown that

a reduced band gap can enhance the photocatalytic efficiency of metal oxide nanostructures [25-27]. Fig. 2C shows the absorption spectra recorded from aqueous suspensions of the TiO₂ nanoparticles and P25. The optical band gap energy (E_g) for direct transitions can be determined from the following relation, $\alpha \propto (h\nu - E_g)^{1/2}/h\nu$, where α is the optical absorption coefficient [28]. Because the optical absorption coefficient (α) is linearly proportional to the absorbance (A) of a sample, the intersection of the extrapolated linear portion in the plot of $(Ah\nu)^2$ versus the photon energy $(h\nu)$ gives the band gap energy (E_{σ}) for direct transitions (Fig. 2D). The measured band gap was approximately 3.0 eV for the rutile-rich TiO₂ nanoparticles, slightly smaller than that of P25 (3.18 eV) consisting of 22.4 wt% of rutile and 77.6 wt% of anatase. Room-temperature photoluminescence (PL) spectra of the rutile-rich TiO_2 nanoparticles are shown in Fig. 2E, revealing the green band emission at around 460 nm.

Fig. 3A shows the XRD patterns of the TiO₂ nanoparticles synthesized with different Ti precursor concentration and commercial P25. All synthesized TiO₂ nanoparticles mostly consist of rutile phase with a small trace of anatase phase, whereas P25 had a mixed phase of anatase and rutile showing 22.4% of rutile [24]. When the amount of titanium diisopropoxide bis(acetylacetonate) was increased from 9.765 ml (Ti-1-TiO₂) to 19.53 ml (Ti-2-TiO₂) and 39.06 ml (Ti-4-TiO₂), the surface area of the synthesized TiO₂ nanoparticles decreased from 177.8 to 140.3 and 122.1 m²/g, respectively, revealing the reduction of surface area of TiO₂ nanoparticles while maintaining similar rutile crystal structure. All synthesized TiO₂ nanoparticles showed much higher surface area than that of commercial P25 (49.3 m²/g).

We investigated the photocatalytic activities of the rutile-rich TiO₂ nanoparticles by degradation of methyl orange (MO) under visible-light irradiation in the presence of TiO₂ nanoparticles, which was demonstrated to be useful for the analysis of the photocatalytic activity [29]. Before the lamp was on, Ti-1-TiO₂ and P25 samples showed 30% and 10% decrease in MO concentration in the dark due to the adsorption-desorption equilibrium. It might be due to the different surface areas of each sample. All synthesized TiO₂ nanoparticles show much higher photocatalytic activity than reference P25 under visible light due to the difference in phases, which causes reduction of band gap energy (Fig. 3B). In catalytic reactions, modulating surface area of catalyst is one of the most critical factors to enhance the catalytic properties. Although Ti-1-TiO₂, Ti-2-TiO₂, and Ti-4-TiO₂ samples have very similar rutile crystal structures, Ti-1-TiO₂ sample showed the highest photocatalytic activity as high surface area is advantageous to photocatalytic reactions in view of active sites. In addition, we believe that small portion of anatase TiO₂ in the nanoparticles would improve the catalytic activity by the formation of phase junction between anatase and rutile crystal structures [30–34].

Controlling the crystal structure of TiO₂ nanoparticles also plays an important role for the enhancement of photocatalytic properties [35]. When the synthesis was conducted under the small amount of oleic acid (10%) while keeping the other experimental conditions unchanged, synthesized TiO₂ nanoparticles (oleic-0.1-TiO₂) contained a large portion of anatase (around 30%, Fig. 4A). Surface area of the anatase-rich-TiO₂ nanoparticles calculated using BET analysis was 201.9 m²/g, lager than that of the rutile-rich TiO₂ nanoparticles (oleic-1-TiO₂). However, the photocatalytic



Fig. 3. (A) XRD patterns of the TiO_2 nanoparticles shown in **Fig. 1** ($Ti-1-TiO_2$) and the samples synthesized with 2 times ($Ti-2-TiO_2$) and 4 times ($Ti-2-TiO_2$) larger amount of Ti precursors. (B) Degradation profile of methyl orange with $Ti-1-TiO_2$, $Ti-2-TiO_2$ and $Ti-4-TiO_2$ samples under visible-light irradiation.



Fig. 4. (A) XRD patterns of the TiO_2 nanoparticles shown in Fig. 1 (oleic-1-TiO₂) and a sample synthesized under the same conditions as those in Fig. 1 except that small amount of oleic acid (10%) was used (oleic-0.1-TiO₂). (B) Degradation profile of methyl orange with oleic-0.1-TiO₂ and oleic-1-TiO₂ samples under visible-light irradiation.

activity of oleic-0.1-TiO₂ sample was lower than that of oleic-1-TiO₂ sample due to the large amount of anatase phase. In summary, the rutile-rich TiO₂ nanoparticles with large surface area are preferable for photocatalysis under visible-light irradiation to mixed phase TiO₂ particles.

Conclusions

We have demonstrated a facile synthesis of rutile-rich TiO₂ nanoparticles with flower-like shapes based on a reverse micelle method by using the reaction between Ti precursors and HCl in the presence of oleic acid as surfactants. The synthesized rutile-rich TiO₂ nanoparticles had large surface area of $177.8 \text{ m}^2/\text{g}$. The surface area of the nanoparticles were controlled by varying the concentration of Ti precursor. Interestingly, we were also able to control the crystal structure of TiO₂ nanoparticles. Anatase-rich TiO₂ nanoparticles were synthesized when the synthesis was conducted under low concentration of oleic acid. Rutile-rich TiO₂ nanoparticles with large surface area were more active in decomposing methyl orange under visible-light irradiation than anatase and rutile mixed phase TiO₂ particles. The presented synthetic procedure is readily applicable to the large-scale synthesis for the industrial applications due to their simplicity and the mild reaction conditions including the low reaction temperature, the air atmosphere, and the use of nontoxic and cheap reagents. Furthermore, we expect that this synthetic strategy can be extended to large-scale synthesis of other metal oxide nanoparticles, including CeO₂, Y₂O₃, and ZrO₂.

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