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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 m^2/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.

Introduction

Titania (TiO_2) 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]. TiO_2 has been widely investigated as photocatalysts due to high photo-activity, low cost, low toxicity and good chemical and thermal stability [8–10]. TiO_2 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 TiO_2 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 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 TiO_2 nanoparticles using oleic acid, which is one of the natural fatty acid, as a surfactant. 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. We also investigated the effect of the concentration of Ti precursor and role of oleic acid in the formation of TiO_2 nanoparticles. Photocatalytic activity of the product TiO_2 nanoparticles was evaluated in decomposing methyl orange dye under visible-light irraditional.

Experimental

Synthesis of rutile-rich TiO_2 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. N_2 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. TiO_2 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 °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 TiO_2 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 TiO_2 structures were also observed in the XRD patterns, demonstrating that the product contained a small amount of anatase TiO_2. The grain size of the TiO_2 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.

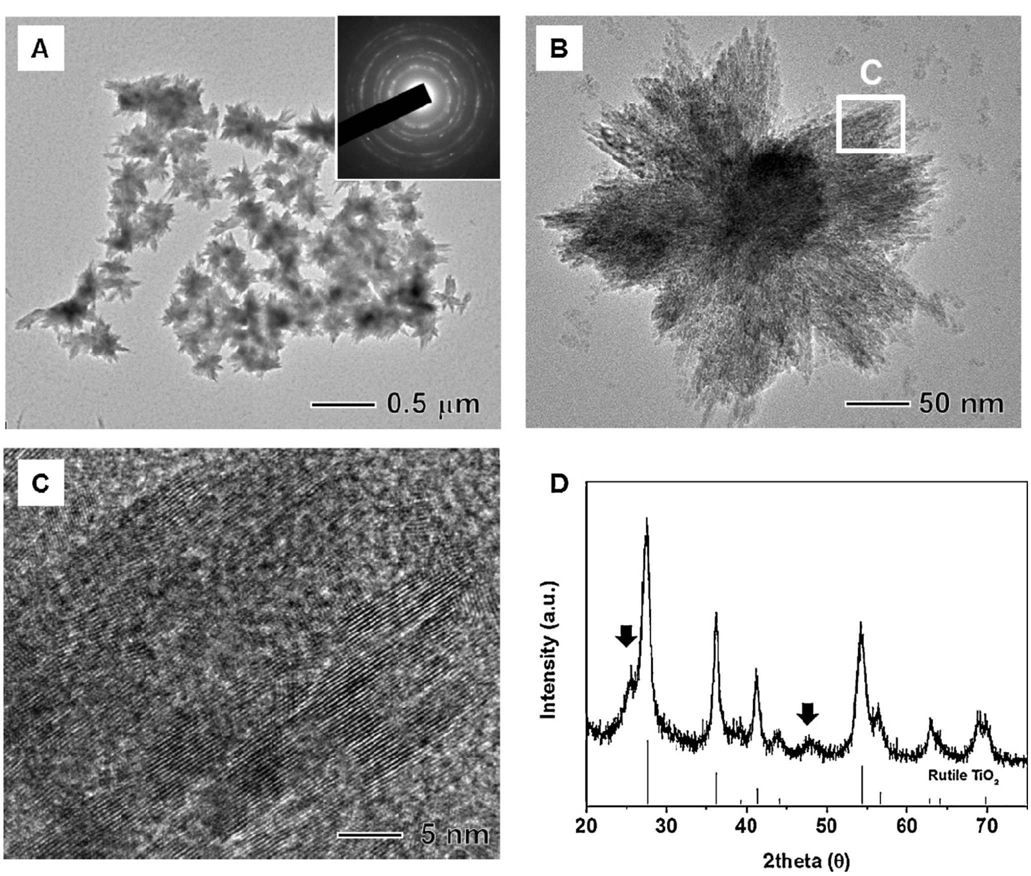

Fig. 1. (A and B) TEM images, (C) HRTEM image, and (D) XRD pattern of TiO_2 nanoparticles (Black arrows indicate the presence of anatase crystal structure.) synthesized by the reaction of HCl with titanium diisopropoxide bis(acetylacetonate) immobilized in reverse micelles composed of oleic acid, water, and xylene.