



Synthesis of anatase titanium dioxide nanocaps via hydrofluoric acid etching towards enhanced photocatalysis



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ARTICLE INFO

Article history:

Received 17 May 2015

Received in revised form 11 October 2015

Accepted 27 October 2015

Available online 31 October 2015

Keywords:

Semiconductors

Chemical synthesis

X-ray diffraction

Crystal structure

Catalytic properties

ABSTRACT

Anatase titanium dioxide (TiO_2) nanocaps were created via a four-step process including the preparation of SiO_2 spheres, the deposition of a TiO_2 layer to fabricate $\text{SiO}_2/\text{TiO}_2$ composite spheres, the calcination for obtaining the crystal structure of anatase phase, and hydrofluoric acid (HF) etching to dissolve SiO_2 cores. The $\text{SiO}_2/\text{TiO}_2$ spheres calcined at 700°C revealed fine photocatalytic activity. Interestingly, most of samples transformed into TiO_2 nanocaps via HF etching, and TiO_2 nanocaps prepared using optimal conditions exhibited quick degradation (k is 0.052 min^{-1}) compared with commercial P25 (k is 0.030 min^{-1}) and the TiO_2 nanostructures etched by a NaOH solution. The excellent photocatalytic performance is attributed to its unique hollow hemispherical nanocaps structure, which is in favor of making full use of incident light. The photocatalysis phenomenon in visible light was also observed after depositing Au nanoparticles on anatase TiO_2 nanocaps.

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1. Introduction

With the rapid development of economy, environmental pollution and energy shortage has become the most important problem needed to be solved in the near future. The traditional treatment of these problems is inefficient and easy to bring secondary pollution. In recent years, owing to the photochemical reaction can directly be driven by solar energy at room temperature, photocatalytic technology is recognized as the most ideal environment pollution control technology and clean energy production. Among various catalysts, titanium dioxide (TiO_2), a semiconductor catalyst with a broad band energy of 3.2 eV, due to its non-toxicity, self-cleaning, high thermal and chemical stability [1–3], and excellent photocatalytic performance, is widely studied in environmental and energy issues [4–8], especially in the photocatalytic degradation of organics, solar cells, and electrochemical photolysis of water [7–12]. However, the high recombination rate of photo-generated charge carriers of TiO_2 materials results in the low quantum yield, which affected its applications [13–15]. The crystalline property and surface state of TiO_2 catalysts are crucial for their photocatalysis performance. It is imperative to prepare TiO_2 with high quantum yield and fast response ability in a photolysis process. Therefore, the modification of TiO_2 catalyst has become a hot topic in photocatalytic degradation of organics.

So far, the photocatalytic ability of TiO_2 has been gradually improved and a significant breakthrough in terms of preparation method, morphology, and structure control has been made. It mainly focus on eight aspects below: (i) the deposition of noble metal [16–18], (ii) metal ion doping [19–22], (iii) nonmetallic ion-doping [23,24], (iv) semiconductor compound [25–27], (v) sensitization of TiO_2 [28,29], (vi) control of crystal facets of TiO_2 [30–33], (vii) immobilization [34], (viii) the preparation of special morphological TiO_2 [35–39]. The morphology of TiO_2 is one of the most essential factors affecting photocatalytic activity. For instance, one dimensional (1D) TiO_2 nanowires, nanobelts or nanorods; 2D TiO_2 nanosheets or thin films; and 3D TiO_2 solid or hollow nanospheres, have conspicuous differences in their properties. Among these morphologies, hollow TiO_2 nanostructures owing to its high surface area and well controlled size/morphology, regarded as an efficient semiconductor photocatalyst [40]. The preparation methods of hollow TiO_2 spheres are various, such as sol–gel, hydrothermal, solvothermal, self-assembly, hard template, and free-template method. Among them, template method by virtue of its good controllability for the morphology and size of resulting samples, have been widely studied. A variety of templates have already been studied, such as, polymers, CuO nanostructures, carbon spheres, and silica (SiO_2) spheres [41]. SiO_2 is commonly used as sacrificial template due to its low cost, strong adsorption, and thermal stability. But the removal of templates still exists the disadvantages of low efficiency and complicated operation, which needs further improvement.

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In this work, we successfully developed a feasible approach to synthesize anatase TiO_2 nanocaps by using SiO_2 spheres as templates and hydrofluoric acid (HF) as etching agent. HF-assisted chemical etching of SiO_2 templates extremely improved the photocatalytic behavior of anatase TiO_2 nanocaps and provided a new idea for the template synthesis of hollow structures. We also explored the effect of calcination temperature and HF amounts on the photocatalytic properties of $\text{SiO}_2@\text{TiO}_2$ (ST) samples. We found that the ST composite spheres calcined at 700°C (ST-700 $^\circ\text{C}$) had much high photocatalytic activity. Etched sample using 0.2 mL HF solution (EST-3) exhibited the best ability of photocatalytic degradation of Rhodamine B (RhB) under UV light. In order to improve its photocatalytic performance in visible light, Au nanoparticles (NPs) were deposited on the sample of EST-3. The result indicated that the deposition of noble metal is effective in improving photocatalysis under visible light.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) and ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25 wt %) were purchased from Sinopharm Chemical Reagent Company. Tetrabutyl titanate (TBOT) and hydroxypropyl cellulose (HPC) were purchased from Aladdin Reagent Company. Ethanol (AR, $\geq 99.7\%$) was taken from Tianjin Chemical Reagent Company. The deionized (DI) water (resistivity $\sim 18\text{ M}\Omega\text{ cm}$) was obtained from a Milli-Q synthesis system. All chemicals were used directly without further purification.

2.2. Synthesis of SiO_2 spheres

The preparation of monodispersed SiO_2 spheres was carried out using a modified Stöber method [2]. Briefly, 100 mL of anhydrous ethanol and 10 mL of DI water were mixed together. 3.0 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ was then dropwised in the mixture with stirring for 30 min. After that, 1 mL of TEOS was added slowly. After stirring for 6 h, samples were centrifuged, washed, and redispersed in 20 mL of anhydrous ethanol.

2.3. Fabrication of ST composite spheres

The above SiO_2 spheres (168 mg) were dispersed into a mixture of 20 mL of anhydrous ethanol, 0.2 mL of DI water, and 100 mg of HPC with vigorous stirring for 60 min. 0.2 mL of TBOT was added into the mixture within 30 min. The obtained uniform solution were shifted into a 50 mL Teflon-lined stainless steel autoclave heat-treated at 180°C for 180 min. The product was washed with ethanol and DI water for 6 times, and dried at 60°C for 10 h. Finally, the obtained ST composite spheres were calcined in a muffle furnace at different temperature with a heating rate of $5^\circ\text{C}/\text{min}$

and kept at that temperature for 90 min to obtain the final ST-temp products.

2.4. SiO_2 Etching

Anatase TiO_2 nanostructures were obtained by etching sample ST-700 $^\circ\text{C}$. The SiO_2 cores were dissolved with different amounts of HF solution at room temperature. 30 mg of sample ST-700 $^\circ\text{C}$ was dispersed in 2 mL of DI water, ultrasound for 10 min. 0.05, 0.1, 0.2, and 0.3 mL of diluted HF solution was then added with stirring, respectively. The obtained samples were denoted as EST-1, EST-2, EST-3 and EST-4, respectively.

2.5. Deposition of Au NPs on sample of EST-3

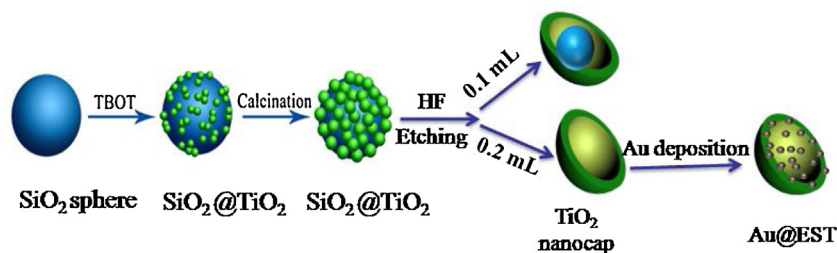
The deposition of Au NPs on EST-3 was carried out by a traditional chemical reduction method [17]. 20 mg of EST-3 was dispersed into 35 mL of DI water with stirring for 30 min. 35 μL of $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$ (50 mM) were added into the mixture solution with stirring for further 30 min. 0.15 mL of NaBH_4 solution was injected into above solutions. Because of NaBH_4 solution added, the color of the solution became pink.

2.6. Characterization

The morphology and size of samples can be observed by a field emission scanning electron microscope (FESEM, QUANTA250 FEG, FEI, USA) and a transmission electron microscope (TEM, JEM-2010). A high resolution transmission electron microscope (HRTEM, Tecani F20, FEI) was used to get TEM images with high resolution. A powder X-ray diffractometer (Bruker D8-Advance, Germany) was used to confirm the phase structure of samples. Nitrogen adsorption isotherms were obtained using a multi-function adsorption instrument (MFA-140 of Beijing Builder Company). Before measurement, the samples were firstly degassed under vacuum at 110°C for 2.5 h. Fourier transform infrared spectroscopy (FTIR) spectra were collected on a Fourier infrared spectrum instrument (Nicolet 380). Diffuse reflectance spectra (UV-vis) and absorption spectra of samples were measured using a traditional UV-vis spectrometer (Hitachi U-4100).

2.7. Photocatalytic tests

Photocatalytic degradation of RhB under UV light (20 W) and Visible light (18 W) was carried out as follows: the distance between light source and samples was 20 cm. 10 mg of sample was dispersed into 25 mL of RhB solution (10 mg/L). In order to guarantee the equilibrium of adsorption and desorption, the samples were firstly treated in dark for 30 min before the light turned on. After that, taking a sample at 30 min intervals during reaction, followed by centrifugation, the absorbance of the samples were measured using a UV-vis spectrometer.



Scheme 1. Formation illustration of anatase TiO_2 nanocaps.

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