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Full Length Article

Construction of anatase/rutile TiO_2 hollow boxes for highly efficient photocatalytic performance

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ABSTRACT

Hollow TiO_2 hierarchical boxes with suitable anatase and rutile ratios were designed for photocatalysis. The unique hierarchical structure was fabricated via a Topotactic synthetic method. $CaTiO_3$ cubes were acted as the sacrificial templates to create TiO_2 hollow hierarchical boxes with well-defined phase distribution. The phase composition of the hollow TiO_2 hierarchical boxes is similar to that of TiO_2 P25 nanoparticles (~80% anatase, and 20% rutile). Compared with nanaoparticles, TiO_2 hollow boxes with hierarchical structures exhibited an excellent performance in the photocatalytic degradation of methylene blue organic pollutant. Quantificationally, the degradation rate of the hollow boxes is higher than that of TiO_2 P25 nanoparticles by a factor of 2.7. This is ascribed that hollow structure provide an opportunity for using incident light more efficiently. The surface hierarchical and well-organized porous structures are beneficial to supply more active sites and enough transport channels for reactant molecules. The boxes consist of single crystal anatase and rutile combined well with each other, which gives photon-generated carriers transfer efficiently.

1. Introduction

Recently, it has attracted a great deal of attention for developing highly active photocatalysts, aiming to solve the increasing serious environmental and energy crises [1–5]. Owing to its unique advantages of low cost, environmentally-friendly, and high thermal and chemical stability, titanium dioxide (TiO_2) has drawn great interests as a photocatalyst since 1972 [6–8]. Commonly, TiO_2 has three crystal forms of anatase, rutile, and brookite. Among them, anatase and rutile both with tetragonal structure, are the most generally used in photocatalytic reactions [9–13]. Anatase and rutile phase have different bad gaps of 3.2 and 3.0 eV, respectively. When the two kinds of phase formed heterostructure, internal electric field was built due to the difference work function of anatase and rutile, which facilitates the charge carries transfer across the interface [14]. The results display enhanced photocatalytic performance of heterostructure over pure anatase or rutile [15].

As we all know, TiO_2 P25 consisted of 80% anatase and 20% rutile with the nanocrystal size of about 20–30 nm, has high-performance photocatalytic activity [16]. Unfortunately, the cycling performance of the P25 was not entirely satisfied, which limits its practical application due to aggregation of nanoparticles. It is worth noting that hollow microstructure constructed by primary nanoscale subunits has also been proved to be an effective way to overcome above aggregation problem [17–19]. Furthermore, hollow structures allow multiple reflections of light within the interior cavity, which enhances the effectiveness of light utilization [20–22]. Due to the excellent physical and chemical properties of hierarchical structured semiconductor materials with unique porous structure, they can help substances diffusion and transport [23–27], designing hierarchical structure with special ratio of phase composition is essential for the improved photocatalytic system.

The ratio of phase composition is very important for the photocatalytic performance [28–31], which easily regulated by simply mechanical mixing treatment method. However, mixing does not guarantee the two phases do really get into contact with each other, causing electron-hole pair cannot separate effectively by synergetic effect between the interface of anatase and rutile. Annealing is another synthetic method to vary the anatase-to-rutile ratio of the samples [32]. Rutile phase, the most stable structure of TiO_2, is obtained from metastable phase in thermodynamics of anatase through high temperature (e.g. 500–700 °C) annealing treatment [33]. However, particles are easily to sinter together, enlarged the particle size and weaken the photocatalytic activity. In order to reduce the sintering temperature, NO_3^-, SO_4^{2-}, and Cl^-, et al. have been used as additives in the reaction precursor [32]. Unfortunately,

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it may be bring in impurities, which increased the recombination rate of electron-hole pairs and declined the performance.

In this paper, a Topotactic synthetic method [34–36], also named as self-generated sacrificial template method, was used to fabricate TiO_2 hollow hierarchical boxes consist of anatase and rutile phases. $CaTiO_3$ cubes were obtained firstly, and then in situ transformed into TiO_2 through EDTA-2Na chelation reaction [37]. TiO_2 anatase and rutile phases are all appeared at the same time, which makes the two phases connect well with each other. In order to enhance the crystalline of the sample, low temperature annealing facilitates aqueous titanium acid compounds transformed into high crystalline TiO_2 with the particle size slightly changed. Then photocatalytic activity for degradation of methylene blue (MB) under low-power ultraviolet (UV) light were investigated. The results demonstrate that TiO_2 hollow boxes with hierarchical structures exhibited an excellent performance over than that of TiO_2 P25 nanoparticles. The reason attributed to the full use of incident light with hollow structure, as well as single crystal and biphases connect well with each other facilitate photo-generated electron-hole pair separation.

2. Experimental section

2.1. Synthesis of $CaTiO_3$ microcube precursors

In a typical synthesis, 0.11 g of calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$) was dissolved in 1 mL of poly(ethylene glycol) (PEG-200) and 19 mL of ethanol mixture solution. 0.33 mL of titanium *n*-butoxide (TBT) was injected in the above mixture solution and then added 0.24 g of sodium hydroxide (NaOH) as a mineralizer [38,39]. After vigorous stirring for homogeneous solution, the feedstock was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and heated at 180 °C for 15 h in an oven. The obtained samples were washed with water and dried.

2.2. Synthesis of TiO_2 hollow hierarchical boxes

As-synthesized $CaTiO_3$ sample (75 mg) and 0.34 g of EDTA-2Na were dispersed in the 10 mL of EG and 30 mL of deionized water (DI water, resistivity 18 MW cm^{-1}) mixture solution. The mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at the transformation temperature of 180 °C for 12 h. The obtained samples were washed with water and dried for the following step. The obtained powders were calcined at 400 °C for 2 h with a temperature rising rate of 5 °C min^{-1}.

2.3. Characterization

The crystal structure and phase composition of samples were characterized by X-ray diffraction measurements (XRD, Bruker D8-Advance X-ray diffractometer, Germany). The morphology of samples was observed by a field-emission scanning electron microscope (FESEM, QUANTA 250 FEG, FEI, USA). The images of high-resolution transmission electron microscopy (HRTEM) were recorded by a transmission electron microscope (FEI Tecani F20 TEM). The UV/vis absorption spectra and diffuse reflectance spectra (DRS) of samples were recorded by using a conventional UV/vis spectrometer (Hitachi U-4100, Japan). The nitrogen adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution were obtained at 77 K by using a multifunction adsorption instrument (MFA-140, Builder Company, Beijing). Photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (Hitachi F-4600, Japan) with an excitation light source at 325 nm and a 350 nm light filter. The width of excitation and emission slits was both 10.0 nm. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Fisher Scientific Escalab 250 spectrometer. Fourier transform infrared spectroscopy (FTIR) spectra were measured by using a Fourier infrared spectrum instrument (Nicolet 380). Raman spectra were observed by using a high-resolution Raman spectrometer (LabRAM HR Evolution, HORIBA JOBIN YVON SAS).

2.4. Photocatalytic tests

The photocatalytic activity of TiO_2 samples were evaluated under 20 W ultraviolet (UV, low power) lamp, and the optical irradiance at the samples was 0.23 mW/cm^2. 10 mg of photocatalyst was dispersed in a 10 mg L^{-1} of MB solution. The suspension was stirred in the dark to reach the adsorption–desorption equilibrium. The concentration of MB was measured by a UV/vis spectrometer at a wavelength of 664 nm. The photocatalytic degradation rate is in accordance with a pseudo-first order reaction, and its kinetics is expressed as following formulas: $\ln(C_0/C) = kt$, where C_0 and C are initial and reaction concentration at a certain time of the MB solution, respectively.

2.5. Photoelectrochemical measurements

Photocurrent measurements were conducted on an electrochemical station (CHI660E, China). These measurements were conducted with a standard three-electrode assembly. TiO_2 samples were deposited on the indium tin oxide (ITO) glass surface as the working electrode, a platinum foil as the counter electrode, and Ag/AgCl as the reference electrode. A sodium sulfate aqueous solution (1 mol of Na_2SO_4) was used as the electrolyte, and a 300 W xenon arc lamp was used as light source.

Electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660E electrochemistry workstation (ZAHNER Elektrik). TiO_2 samples were coated on the fluorine doped tin oxide (FTO) glass as the working electrode, a platinum foil as the counter electrode. The measurement was performed using a 5 mV AC (alternating current) amplitude under open circuit potential with a frequency range from 0.05 to 10^5 Hz.

3. Results and discussion

3.1. Morphology and mcrostructure

$CaTiO_3$ microcubes were successfully obtained by mineralization reaction. As shown in Fig. 1a, all of the diffraction peaks are well corresponding to the $CaTiO_3$ (JCPDF no. 22-0153). There are no impurities peaks appeared in the XRD pattern [38,39]. As shown in Fig. 1b, it is observed that many mono-dispersed cube $CaTiO_3$ with smooth surface have a size of about 1150 nm.

After the second step of chelation reaction by EDTA-2Na, $CaTiO_3$ cube transformed into TiO_2 or titanic acid hydrate, which was consisted of small size nanoparticles. As shown in Fig. 2, the surface becomes coarse but the morphology still keeps the cube structure. The XRD pattern of the sample in Fig. 4a shows that anatase and rutile phases are co-existed in the sample. Other than the two kinds of phases, impurities peaks of titanic acid hydrate have also been detected.

In order to improve the crystallinity of the sample and facilitate titanic acid hydrate transforming into TiO_2, annealing treatment is necessary [40,41]. Herein, the optimal annealing temperature controlled at a relative low temperature of 400 °C, which not only avoids grain size grow large but also prevents anatase phase transform into rutile phase. As shown in Fig. 3a, it is found that the profile of the sample becomes more clearly, which like nanoparticles assembled together into TiO_2 hollow hierarchical structure, but the synthetic method provides an opportunity for anatase and

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