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Synthesis and photoactivity of anatase porous single crystals with different pore sizes

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Abstract

In this paper, anatase porous single crystals (PSCs) with different pore sizes were hydrothermally synthesized by using silica spheres as template. The products exhibit uniform porous structure which is consistent with silica template dimensions. Sharp Laue diffraction patterns, uniform lattice fringes in different regions and occurrence of partial porous single crystal unequivocally prove monocrystalline nature of the samples. All PSC samples display high degree of crystallinity. Specific surface area increases with decrease of pore size and adsorption–desorption isotherms of type IV further confirm porous structure of PSCs. All samples show the strong absorption of ultraviolet light, the extent of which increases with decrease of pore size. Photoluminescence intensity decreases as pore size decreases, however, the intensity for S1 sample with minimum pore size is somewhat higher than that of S2. Photocatalytivity tests show the similar results which may be attributed to the combined effect of the surface active sites, the exchange between species in holes and those outside of PSCs, and electron mobility in framework. Moreover, the "seeding template-crystallization" mechanism for PSCs formation was discussed in detail. Based on these results, PSCs anatase with different purposes can be achieved by means of precise adjust for pore dimension and surface area.

Keywords: Anatase; Porous single crystal; Pore size; Photocatalytivity

1. Introduction

As one of the most important semiconductors, titanium dioxide (TiO_2) is usually applied in many different fields including photovoltaics, photo/electrochromics, photocatalysis, photonics, sensors, and smart surface coatings [1–4]. TiO_2 has three main polymorphs (anatase, rutile and brookite) in which the most widely used in energy and the environment field is anatase. The common preparation methods for anatase include hydrothermal, solvothermal, sol–gel, micelles, microwave, vapor deposition and high temperature oxidation [5]. However, most of products from these methods are nanoparticles, and TiO_2 single crystals with large size, high purity, active surface, and well defined shape can be not easily prepared [6].

Yang et al. [7] first synthesized the high purity anatase single crystals with large size using titanium tetrafluoride (TiF_4) as titanium source and hydrogen fluoride as morphology control agent, and the proportion of the active surface can be adjusted by changing reaction conditions for example the type and amount of titanium source and capping agent. The TiO_2 single crystals by controllable preparation provides model single crystal for fundamental studies in surface science, and has promising application in energy conversion and environmental governance, however, small specific surface area limits further improvement of performance.

If the TiO_2 single crystal has porous structure, not only the shortcoming of small specific surface area can be overcome, but also the good performance of the bulk crystal can be retained which is very suitable for the separation and recovery of

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photocatalyst in aqueous solution [8]. Crossland et al. [9] successfully prepared anatase PSCs with uniform morphology using silica spheres as a template by first seeding and then nucleation and growth in dilute solution. The single crystals displayed higher conductivity and electron mobility than conventionally nanocrystalline, and were applied to fabricate all-solid-state, low-temperature sensitized solar cells that attained a record 7.2% efficiency. Furthermore, Zheng et al. [10] and Jiao et al. [11] prepared porous single crystals of rutile, Fang et al. [12] synthesized fluorine-doped porous single crystal nanorods of rutile, and these PSC rutile all exhibited more excellent photocatalytic and photoelectrochemical performance than the bulk single crystal did.

The successful synthesis of porous TiO_2 single crystals, not only contributes to the further development for traditional TiO_2, but also provides the basis for the synthesis of other similar porous materials [13]. This instantly opens up possibilities for this subject and has important research prospects. For example, by adjusting the particle size of silica template sphere, porous single crystals with different pore sizes can be achieved, this will favor their use under different conditions. But so far, a systematic comparison study of PSC anatase with different pore sizes has not been found.

In this paper, we prepared a series of anatase PSCs with different pore sizes by the silica-templated hydrothermal method and then first investigated the influence of pore size on morphology, structure and photoreactivity by field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED), powder X-ray diffraction (PXRD), Brunauer–Emmett–Teller (BET) specific surface area analyzer, UV–Vis diffuse reflectance spectroscopy (DRS) and photoluminescence spectra (PL). At the same time, the formation mechanism of PSCs was discussed in detail.

2. Experiments

All the chemicals are analytical grade reagents and used as received except tetraethyl orthosilicate (TEOS) was vacuum distilled before use. Titanium tetrafluoride (TiF_4) was purchased from Alfa Aesar, ammonia water (NH_4OH, 30%), ethanol, TEOS, titanium tetrachloride ($TiCl_4$), hydrochloric acid (HCl, 37%), ionic liquid (1-methyl-imidazole tetrafluoroborate), sodium hydroxide (NaOH), terephthalic acid (TA) were purchased from Sinopharm.

2.1. Preparation of seeded silica templates

Silica template sphere was synthesized following the modified Stöber method [14]. In a typical process, 42 nm silica spheres were synthesized by adding 12 ml deionized water, 5 ml ammonia water and 28 ml TEOS to 205 ml ethanol and stirred at 700 r.p.m. for 24 h at 50 °C translucent solid was prepared by centrifugation of the reaction solution (10,000 r.p.m. for 30 min). The solid was sintered at 500 °C for 30 min to obtain the final close-packed template. The detailed reactant concentrations for the preparation of a series of samples are listed in Table 1.

The template was seeded with microscopic nucleation sites for crystal growth. 10 ml of $TiCl_4$ was added to 35 ml H_2O containing 0.1 ml HCl in an ice bath, then the solution was diluted to prepare 15 μM aqueous $TiCl_4$. 1 g of the sintered template was immersed in 6.6 ml of aqueous $TiCl_4$ and held at 70 °C for 1h followed by thorough rinsing with 1 l of H_2O. The dried template was resintered at 500 °C for 30 min.

2.2. Synthesis of PSCs

PSC anatase was synthesized by a hydrothermal method [15]. 40 mM TiF4 solution was prepared in deionized water after first adjusting the pH to 2.1 by addition of HCl. 1.67 ml of the ionic liquid, and 650 mg of the pre-treated silica template were added to 50 ml of TiF_4 solution in a Teflon-lined stainless autoclave. The sealed vessel was held at 180 °C for 12 h. The template product was formed on the bottom of the vessel and rinsed with H_2O by vacuum filtration. Then the silica template was selectively etched in aqueous 2 M NaOH at 80 °C for 10 h. The remaining TiO_2 was collected by centrifugation (10,000 r.p.m. for 30 min) and washed with H_2O and ethanol several times and dried at 80 °C for 12 h. The as-obtained samples are denoted as S1, S2, S3, S4 and S5 according to the corresponding size of silica template spheres, 23, 42, 64, 118 and 160 nm respectively. In the control experiments, solid TiO_2 single crystals were prepared in the same hydrothermal system without the addition of seeded silica template, is denoted as S0.

2.3. Characterization

The crystal structures of the synthesized samples were characterized by XRD (Bruker D8 Advanc with Cu*K*α radiation at 40 kV and 30 mA). The dimension, morphology, and structure of the samples were examined by using FE-SEM (JOEL 6700F) and HR-TEM (FEI JEOL2010) equipped with a selected area electron diffraction (SAED). The BET specific surface area and pore size were determined by nitrogen adsorption–desorption isotherm measurements at 77 K on a BELSORP-max system. DRS were performed on a Varian Cary 300 UV/Vis spectrophotometer, equipped with an external integrating sphere, by using $BaSO_4$ as the reference. PL spectra were measured on a fluorescence spectrophotometer (Varian Cary-Eclipse 500). The exciting wave-length

Table 1
Sizes of silica spheres synthesized under different experimental conditions (minimum 50 samples).

TEOS concentration (M)	H_2O concentration (M)	NH_3 concentration (M)	Size of silica spheres (nm)
0.5	2	0.4	23
0.5	3	0.4	42
0.5	4	0.4	64
0.5	5	0.4	118
0.5	6	0.4	160