Microporous and Mesoporous Materials 186 (2014) 65–72

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Nanoporous SnO_2 prepared by a photochemical strategy: Controlling of specific surface area and photocatalytic activity in degradation of dye pollutants

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ARTICLE INFO

Article history:
Received 28 August 2013
Received in revised form 11 November 2013
Accepted 19 November 2013
Available online 28 November 2013

Keywords:
Porous SnO_2
Specific surface area
Photocatalytic degradation
Dye pollutant
UV-light

ABSTRACT

Nanoporous SnO_2 fine particles with controlled specific surface area were prepared in the $SnSO_4$ and H_2SO_4 mixed solutions by a simple photochemical method for the first time. Compared with other solution methods, the controlling of surface area can be manipulated at room temperature without the addition of any surfactant or template. Only by controlling the concentration of H_2SO_4, the specific surface area of the product could be tuned in the range of 13–203 $m^2 g^{-1}$. They showed high activity and can be applied to efficient photocatalytic degradation of dye pollutants under a low power (8 W 254 nm) UV lamp. It was found the activity gradually increased with the increase of the specific surface area or the increase of the concentration of H_2SO_4 employed in the preparation process. The formation of SnO_2 and pore structures, the morphologies, the compositions and the photocatalytic degradation mechanisms were systematically studied.

1. Introduction

Tin dioxide (SnO_2), an n-type semiconductor with a wide band gap of 3.6 eV, is one of the most promising materials for the applications in gas sensing [1,2], photocatalytic removal of pollutant [3–6], photo-electrochemical devices [7,8], energy conversion [9,10], Li-ion battery [11,12], etc. The surface area as well as surface characters of the materials is vital to these applications, because they include the adsorption and reaction of chemicals on the SnO_2 surface. Many SnO_2 nanostructured materials with various morphologies such as nanoparticles [13], nanorods [14], nanowires [15], nanobelts [16], hollow spheres [17] and hollow SnO_2 supersymmetric nanostructures [18] have been obtained to increase the surface areas and maximize their performances. An alternative way to increase the surface areas is the generation of pores in nanometric scales [19]. Porous structures also give desired properties in high and fast adsorption capability of chemicals and facilitated surface reactions [20]. Controllability in surface areas of the porous materials would be evidently advantageous for the optimizations of functional materials in practical applications.

There have been some typical methods to construct porous SnO_2 including the polymer microsphere template induced solution/sol–gel method [1,21–24], surfactant template method [25–28] and nanocasting-replication method based on the mesoporous silica [29,30]. However, by the polymer microsphere template method, only macroporous structures were obtained, which is less helpful to the increase of the specific surface area. In reality, few works had increasingly focused on the surface area of such material. By the other two methods, although nanoporous SnO_2 with large specific surface area and even perfect ordered porous structures could be constructed, complicate designs and multi-step manipulations, at least including the fine choice of surfactant or the preparation of casting template and removal of them, had to be employed in the preparation process. Moreover, heat treatments at high temperatures (>400 °C) were necessary to obtain the SnO_2 porous structures, which not only increased the cost and the manipulation steps, but also removed some beneficial groups, for example, hydroxyl groups, for adsorption and photocatalysis. We have ever reported a photochemical method [31] to directly obtain nanoporous SnO_2 on the surface of the aqueous solution. However, the specific surface area was not tuned, limiting the optimization of catalyst in photocatalytic removals of pollutants. The production of SnO_2 was only controlled at the air–water interface by a special design, and the reactions in the solution were ignored, which added difficulty in collecting the products and

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1387-1811/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2013.11.030

reduced the practicality of the preparation method. In addition, variations of catalytic activity of SnO_2 with specific surface area as well as the photocatalytic mechanism remain problems to be solved.

In the present work, the nanoporous SnO_2 prepared by a practical photochemical strategy with simplified procedures was introduced. The control of the specific surface areas and the variations of photocatalytic activities of these materials in photodegradation of dye pollutant under a practicable low power UV lamp were focused on.

2. Experimental section

2.1. Preparation of nanoporous SnO_2

All chemicals used in this study were received from Tianjin-Damao Chemical Regent Factory of China without further purification. In a typical synthesis of nanoporous SnO_2 samples, 2.68 g of $SnSO_4$ was dissolved in 250 mL H_2SO_4 aqueous solution with different concentration at room temperature. The concentration of H_2SO_4 aqueous solution was controlled in the range of 0.1–0.8 M. Subsequently, the solutions were transferred into the ordinary Petri dishes (Φ = 150 mm) and then placed under UV tube-like lamps (Philips, 254 nm, 8 W). After irradiated at room temperature for 15 h, the whole product including precipitates and films on surface of the solution were collected, washed repeatedly with deionized water until no SO_4^{2-} ions were detected in the filtrate, then dried at 100 °C for 6 h. Powder samples of nanoporous SnO_2 were obtained eventually. In order to easily distinguish these samples, they were marked as SN-1, SN-2, SN-3, SN-4, SN-5, SN-6, SN-7 and SN-8, respectively, which were in accordance with the concentration of H_2SO_4 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 M in the precursor solution.

2.2. Characterization of nanoporous SnO_2

The morphological characters of the samples were investigated using field emission scanning electron microscope (FESEM, ZEISS Ultra 55). The crystal phases were determined by X-ray diffractometer (XRD, BRUKER D8 ADVANCE) with Cu-Kα radiation. UV–vis diffuse reflectance spectra using a UV-2501PC spectrometer. The chemical structures of the nanoporous SnO_2 was demonstrated by FD-5DX Fourier-transform infrared spectroscopy (FT-IR). The specific surface areas and porous structures of the samples were calculated by a multipoint Brunauer-Emmett-Teller (BET) analysis of the nitrogen adsorption isotherms recorded on a surface area analyzer (Micromeritics ASAP 2020M).

2.3. Photocatalytic degradation of dye pollutants

The photocatalytic degradation of eosin B was taken as a representative example. 0.05 g SnO_2 powder was added to 200 mL 20 mg L^{-1} of eosin B aqueous solution in a column glass reactor and magnetically stirred. A UV tube-like lamp (Philips, 254 nm, 8 W) was placed right above the reactor as the light source. Opening the magnetic stirrer and turning the lamp on, then the photocatalytic reaction was started. Every twenty minutes of irradiation time, a 5 mL aliquot of the reaction mixture was taken out and centrifuged immediately to separate the suspended solid, the total reaction time was 2 h. The upper solution was monitored by a UV–visible spectrophotometer (Cary 300, Varian, USA) at a wavelength of 517 nm, corresponding to the maximum absorption wavelength of eosin B. Photocatalytic degradation of other dye pollutants (e.g. rhodamine B and methylene blue) followed the same procedures.

3. Results and discussion

3.1. Characterizations of nanoporous SnO_2

Figs. 1A–H show SEM images of the powder samples (SN-1, SN-2, SN-3, SN-4, SN-5, SN-6, SN-7 and SN-8) which were prepared in the precursor solution containing 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 M H_2SO_4, respectively. Different concentrations of H_2SO_4 evidently induced different productions and morphologies. When the concentration of H_2SO_4 was controlled in 0.1 and 0.2 M, the products were composed principally of spherical particles smaller than 250 nm (Fig. 1A and B). Almost all adjacent particles were adhered to each other by undiscerned fine tiny particles (gel-like substance). As the concentration of H_2SO_4 increased to 0.3–0.5 M (Fig. 1C–E), some spherical particles could also be discerned, while many bigger particles with irregular shape and coarse surface were observed, small spherical particles adhered to the bigger particles, and there was no gel-like substance among the particles. The proportion of bigger particles in the products increased with the increase of the concentration of H_2SO_4. When the concentration of H_2SO_4 was controlled in 0.6, 0.7 and 0.8 M (Fig. 1F–H), respectively, there was nearly no discernible spherical particle found but irregular particles existed in the products. Especially, some sheet-like particles were found in the sample from the 0.8 M H_2SO_4. It's worth noting that the concentration of H_2SO_4 has significant impact on the conversion of Sn^{2+} into SnO_2. With the increase of the concentration of H_2SO_4 from 0.1 to 0.8 M, the conversion was gradually reduced (Fig. 2I). When the concentration of H_2SO_4 dropped below 0.1 M, no clear precursor solution could be obtained to prepare SnO_2. On the contrary, when it was higher than 0.8 M, nearly no product was seen in the solution.

Fig. 2A shows the XRD patterns of all as-prepared samples (from SN-1 to SN-8). These samples have similar patterns. Peaks at 26.3°, 33.9°, 51.7° and 65.5° correspond to the (1 1 0), (1 0 1), (2 1 1) and (3 0 1) crystal faces of SnO_2 with the tetragonal cassiterite structure (JCPDS No. 21–1250), respectively. With the increase of the concentration of H_2SO_4, the intensity of the {1 1 0} crystal plane diffraction peak (at 26.3°) was gradually increased and the full width at half maximum was narrowed, explaining the crystallization of the SnO_2 particles became better and the mean particle sizes were increased [32]. This could be proved by the SEM images of the products (Fig. 1). Fig. 2B shows the UV–visible spectra of the samples. An absorption peak appeared at ~254 nm for all samples, and the intensity increased with the increase of the concentration of H_2SO_4. Because of the gradually increased size of particles from SN-1 to SN-8, the adsorption edge of the samples red-shifted from ~415 to ~500 nm [33]. To further probe into the structure and the fine composition of the products, FTIR spectra were measured and shown in Fig. 2C. As a control subject, the spectrum of a sample (CSN-1) prepared by calcining of SN-1 at 800 °C was also recorded. The broad intense band at around 592 cm^{-1} is the characteristic absorption band of SnO_2 attributed to the O–Sn–O vibrations [34]. The intensity of other absorption bands or peaks in the spectrum of the calcined sample had decreased or disappeared, explaining they should be related to the hydroxyl groups that could be removed at high temperature. The absorption band at around 3471 cm^{-1} [υ_{OH} (H_2O)] and the peak at 1628 cm^{-1} [δ_{OH} (H_2O)] are attributed to the O–H vibrations of the absorbed water in the samples [35]. The peaks at 2400, 1146, 1028 and 952 cm^{-1} are assigned to the scissoring vibrations [δ_{OH} (Sn-OH)] of surface hydroxyl groups on SnO_2 [36]. This indicates the surface of the SnO_2 is terminated with many –OH groups.

The N_2 adsorption–desorption isotherms of the representative as-prepared SnO_2 samples (SN-1, SN-3, SN-5 and SN-8) are presented in Fig. 3a. The inset shows the magnified isotherm of