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ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 1813−1818
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Facile synthesis of tin oxide nanocrystals and their photocatalytic activity

Zhi-qian JIA[1], Hui-jie SUN[1], Yan WANG[1], Tian-li ZHEN[1], Qing CHANG[1,2]

1. College of Chemistry, Beijing Normal University, Beijing 100875, China;
2. Science and Technology on Remanufacturing Laboratory, Academy of Armored Forces Engineering, Beijing 100072, China

Received 26 June 2013; accepted 23 January 2014

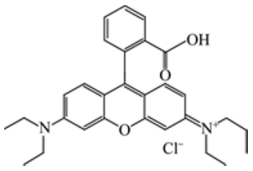
Abstract: Tin oxide nanocrystals with diameters smaller than 10 nm were synthesized using Na_2SnO_3 and CO_2 as reactants and cetyltrimethylammonium bromide (CTAB) as stabilizer under mild conditions. As a mild acidic gas, CO_2 is favorable for the accurate adjustment of pH value of Na_2SnO_3 solution. Stannate salt is stable, cheap and easy in operation. The effects of Na_2SnO_3 concentration, CTAB concentration, aging temperature, and aging time on the nanocrystals were studied. It was found that, with the increasing Na_2SnO_3 concentration, aging temperature and aging time, SnO_2 nanocrystals size decreases. The formation of SnO_2 nanocrystals can be interpreted by electrostatic-interaction mechanism. SnO_2 nanocrystals show high photocatalytic activities in the degradation of Rhodamine B solution. The catalytic activity of small nanocrystals is higher than that of large ones.
Key words: tin oxide nanocrystals; facile synthesis; photocatalytic activity

1 Introduction

As a wide band-gap n-type semiconductor (E_g = 3.6 eV at bulk state), tin oxide has drawn considerable attention owing to its various applications such as catalysts for oxidation of organic compounds [1], solid-state gas sensors for reducing gases [2], rechargeable Li-batteries [3,4], optical electronic devices [5], photocatalysts [6]. The size of tin oxide particles has been shown to drastically affect their properties due to surface and/or spacial confinement effects. Various methods have been developed for the synthesis of tin oxide nanocrystals, including thermolysis of organometallic precursors, sol−gel [7], hydrolysis of $SnCl_2$ [8,9] or SnF_2 [10], sonochemistry, and hydrothermal synthesis [11,12]. However, the fabrication of tin oxide nanocrystals with diameter smaller than 10 nm is still a challenge. Recently, WU et al [13] reported a lysteine-assisted hydrothermal route for generating SnO_2 nanocrystals (<10 nm). But the conditions (120−240 °C) are very harsh. JUTTUKONDA et al [14] employed stannate salt, carbon dioxide and fourth-generation dendritic polymers for the synthesis of tin oxide nanocrystals (<10 nm). Nevertheless, the dendritic polymers are very expensive due to the difficulty in synthesis.

In this work, tin oxide nanocrystals with diameters smaller than 10 nm were synthesized using Na_2SnO_3 and CO_2 as reactants and cetyltrimethylammonium bromide (CTAB) as stabilizer under mild conditions. Firstly, Na_2SnO_3 aqueous solution was carbonated by CO_2 to generate stannate acid. Then, CTAB solution was added, which interacted with stannate anions via electrostatic interaction. After aging, filtration, washing, drying and calcinations, tin oxide nanocrystals (<10 nm) were obtained. Compared with strong or moderate acids such as hydrochloric acid, H_2SO_4 or H_3PO_4, CO_2 is a mild acidic gas and is favorable for the accurate adjustment of pH value of Na_2SnO_3 solution, as well as for the emission reduction of greenhouse gas [15]. Meanwhile, in contrast with moisture-sensitive reagents (e.g. tin chloride), stannate salt is stable, cheap and easy in operation. In addition, the CTAB stabilizer is much cheaper than most of the other stabilizers. The effects of Na_2SnO_3 concentration, CTAB concentration, aging temperature, and aging time on the nanocrystals were studied. The photocatalytic activity of the SnO_2 nanocrystals in the degradation of Rhodamine B (RhB, Scheme 1) aqueous solution was evaluated.

Foundation item: Projects (20676016, 21076024) supported by the National Natural Science Foundation of China
Corresponding author: Zhi-qian JIA; Tel: +86-10-58802945; E-mail: zhqjia@bnu.edu.cn
DOI: 10.1016/S1003-6326(14)63258-1



Scheme 1 Rhodamine B

2 Experimental

2.1 Materials

The chemical reagents, including Na_2SnO_3 and CTAB, were in analytical grade and used as-received without further purification. The fresh Na_2SnO_3 solution was prepared with degassed pure water prior to the reaction.

2.2 Preparation of tin oxide

In a typical synthesis, CO_2 gas was bubbled into 250.0 mL of Na_2SnO_3 solution in a stirred tank at ambient temperature until a certain pH was attained. Then CTAB solution was added to precipitate the stannate acid, and the white turbid suspension was aged at design temperature for a certain time. After centrifugation, the as-obtained precipitate was washed with pure water and alcohol, dried at room temperature and then at 110 °C for 2 h. Last, the white powder was calcinated at 150 °C in Muffle furnace for 2 h and at 400 °C for another 2 h to remove CTAB completely.

2.3 Analysis

The products were observed on a transmission electron microscope (JEM 2010, Japan). In each image, more than one hundred particles were measured to determine the average size. The XRD pattern was analyzed by monochromatized Cu K_α incident radiation (Shimadzu XRD−6000). Nitrogen absorption−desorption isotherms were measured at 77 K by a volumetric technique (V-Sorb 4800P, Beijing), and the surface area was calculated by the Brunaner−Emmett−Teller (BET) method.

2.4 Photocatalytic activity

The photocatalytic activities of the SnO_2 nanocrystals in the degradation of RhB aqueous solution were evaluated. First, 50.0 mL of 1×10^{-5} mol/L RhB solution (containing 50.0 mg of SnO_2 sample) was stirred in a vessel (*d*115 mm) for 30 min at room temperature to attain an adsorption−desorption equilibrium. Then, a 500 W high-pressure mercury lamp (Beijing Tianmai Henghui Co. Ltd) was employed to irradiate the stirred RhB solution, and the distance between the lamp and the solution was 45.0 cm. The concentration of RhB was monitored by an UV-vis spectrometer (Cintra 10e, Australia) during UV irradiation.

3 Results and discussion

3.1 Evolution of pH value during carbonation

Figure 1 shows the pH evolution of Na_2SnO_3 solution during carbonation. The pH value drops quickly in the initial period (pH>10) and then declines slowly (8<pH<10). In the initial period, the dissolved CO_2 reacts with the excess alkaline in Na_2SnO_3 reagent, resulting in the rapid decline of pH value. The reactions can be expressed as follows [16]:

$$CO_2+OH^- =HCO_3^- \quad (1)$$

$$HCO_3^-+OH^- =CO_3^{2-}+H_2O \quad (2)$$

Then, with the consumption of OH^-, Na_2SnO_3 hydrolyzes and generates stannate acid and OH^-, leading to the slow decline of pH values. The hydrolyzation of Na_2SnO_3 is written as follows:

$$SnO_3^{2-}+3H_2O=Sn(OH)_4+2OH^- \quad (3)$$

$$2Sn(OH)_4=(OH)_3Sn—O—Sn(OH)_3+H_2O \quad (4)$$

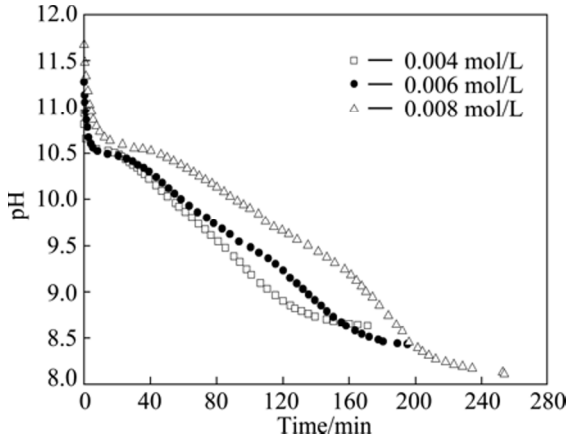


Fig. 1 Evolution of pH values in carbonation for various Na_2SnO_3 concentrations

3.2 Effects of reaction conditions on SnO_2 nanocrystals

The effects of Na_2SnO_3 concentrations were carried out at carbonation pH of 9.0, 0.0033 mol/L CTAB, aging temperature of 110 °C for 24 h, Na_2SnO_3 concentrations of 0.004, 0.006 and 0.008 mol/L, respectively. Figures 2(a), (b) and (c) show that with the increasing Na_2SnO_3 concentration, the SnO_2 nanoparticles size decreases from 5.8 nm to 4.9 nm and 4.5 nm, respectively. Electron diffraction (ED) of nanoparticles exhibits polycrystalline rings (Fig. 2(d)). In contrast, the effects of CTAB concentrations (0.0011, 0.0020 and 0.0033 mol/L) on the nanoparticles are found to be not significant.