



Facile synthesis of antimony selenide with lamellar nanostructures and their efficient catalysis for the hydrogenation of p-nitrophenol



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ABSTRACT

Antimony selenide (Sb_2Se_3) composed of numerous lamellas with average thickness of circa (ca.) 10 nm have been fabricated through a hydrothermal method, in which ethylene diamine tetraacetic acid disodium salt (Na_2EDTA) is selected as complex agent. Experimental parameters such as concentration of reactants and alkaline condition play crucial roles in determining the morphologies and homogeneity of the final products. Interesting self-assemble process and color change in stock solution has been observed, and a possible growth mechanism of Sb_2Se_3 with distinctive morphologies is proposed and discussed in detail. Importantly, the as-prepared products show efficient catalytic performance for reduction of p-nitrophenol to p-aminophenol at room temperature.

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1. Introduction

It is well known that inorganic materials with the desired structure and morphology have attracted considerable interest because the physical and chemical properties of materials are intensively dependent on their shape and texture [1–4]. And a lot of efforts have been made to explore the dimensional regime of nanomaterials by chemists and material scientists. Among these materials, V_2VI_3 -type semiconductors have attracted considerable attention because of their photovoltaic [5,6] and thermoelectric properties [7]. In particular, the antimony selenide (Sb_2Se_3), as an important member of V–VI binary chalcogenides, has attracted increasing attention due to excellent chemical stability, photovoltaic [8], electrochemical hydrogen storage properties [9] and thermoelectrical [10]. Inspired by its remarkable characteristics, in recent years, various routes have been developed for the synthesis of Sb_2Se_3 nanomaterials, such as solvothermal/hydrothermal methods [11–16], chemical bath deposition [17], pulsed laser deposition [18] and thermal evaporation [19,20]. Guo and his co-workers have synthesized Sb_2Se_3 submicron tetragonal tubular crystals through a microwave-assisted polyol method [21]. Yang et al. have fabricated Sb_2Se_3 nanowires by a pulsed vapor–liquid–solid growth of nanostructures from gaseous precursor molecules [22]. To our knowledge, the synthesis of Sb_2Se_3 with lamellar nanostructures by a one-pot hydrothermal method has not been reported. And

to exploit a facile solution route suitable for selectively fabricating Sb_2Se_3 with novel nanostructures still remains a great challenge.

The catalytic reduction of p-nitrophenol (4-NP) to p-aminophenol (4-AP) is very meaningful, because 4-AP has important applications as an analgesic and anti-pyretic drug, such as acetanilide, phenacetin, paracetamol, and so on [23,24]. Furthermore, 4-AP is also widely used as a corrosion inhibitor in paints, a dyeing agent, an anticorrosion-lubricating agent and a photographic developer in fuels for two-cycle engines [25]. Recently, the work of developing new nanocatalysts for catalytic reduction of 4-NP has aroused a big attention. For instance, Wang and co-workers prepared dendritic platinum nanoparticles with high activity for both methanol oxidation and p-nitrophenol reduction [26]. Du et al. reported that $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -Ag nanocomposites could be used as catalyst for the reduction of 4-NP to 4-AP with conversion of 95% within 14 min in the presence of an excess amount of NaBH_4 [27]. Huang et al. synthesized Cu–Ag nanocomposites with enhanced catalytic activity for 4-NP to 4-AP via the one-pot route [28]. However, the problems are that there is a high cost due to the usage of noble metal. Thus, with the aim of finding potential industrial applications, a stable and low-cost catalyst for catalytic hydrogenation of 4-NP is always in demand. At present, the catalytic performance of Sb_2Se_3 for catalytic hydrogenation of 4-NP to 4-AP has not been reported yet.

In this work, we report the synthesis of the Sb_2Se_3 nanostructures which are composed of numerous self-assembled lamellas with average thickness of about 10 nm through a simple hydrothermal route. Some reaction parameters, such as roles of Na_2EDTA

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and ammonia water, are investigated. The structure and morphology of the as-synthesized Sb_2Se_3 can be changed, simply by adjusting the concentration of Na_2EDTA and reactants. Moreover, the as-prepared Sb_2Se_3 nanomaterials show high catalytic activity for reduction of 4-NP to 4-AP at room temperature.

2. Experimental section

2.1. Materials

The reagents used include antimony trichloride SbCl_3 (AR), sodium selenite Na_2SeO_3 (AR), hydrazine hydrate $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (85%, wt.%), ammonium hydroxide $\text{NH}_3\cdot\text{H}_2\text{O}$ (25%–28%, wt.%), ethylene diamine tetraacetic acid disodium salt (Na_2EDTA) (AR), sodium borohydride NaBH_4 (AR), sodium hydroxide NaOH (AR). All chemical reagents used were analytical grade in this experiment and used as received, without further purification.

2.2. Synthesis of the Sb_2Se_3 with lamellar nanostructures

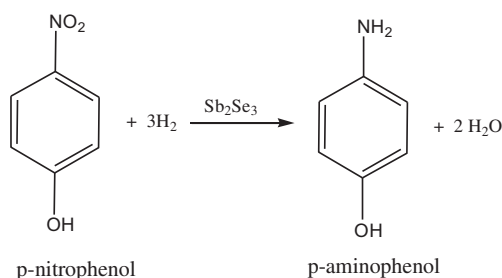
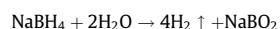
In a typical procedure, 0.08 mmol SbCl_3 (0.0182 g) was dispersed in distilled water (12 mL) by ultrasound to form white turbid liquid, then 0.0800 g Na_2EDTA was added, and a clear solution was obtained. Meanwhile, Na_2SeO_3 (0.0207 g, 0.12 mmol) were dissolved in the mixed solvent including 40 mL of the concentrated $\text{NH}_3\cdot\text{H}_2\text{O}$ and 16 mL of hydrazine hydrate, and another clear solution was obtained. After stirring each for 2 min, the above two clear solutions were mixed together and then stirred for 2 min to produce another white turbid liquid. Finally, the white turbid liquid was transferred into a Teflon-lined stainless-steel autoclave of 100 mL capacity, which was filled to ca. 80% of the total volume. The autoclave was maintained at 180 °C for 1 h and then cooled to the specified temperature. The resulting black product was collected by centrifuging the reaction mixture and washed with distilled water and absolute ethanol 3 times each and dried at 60 °C for 6 h.

2.3. Instruments and characterization

The samples were characterized by different analytic techniques. X-ray powder diffraction (XRD) was obtained on a Rigaku D/max-RAX-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). Scanning electron microscopy (SEM, S4800, Hitachi, Japan, at 5.0 kV), transmission electron microscopy (TEM, JEM-2100, JEOL, Japan, at 200 kV) and the selected area electron diffraction (SAED) were used to characterize the morphologies and structures of the samples. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method. The X-ray photoelectron spectra (XPS) were taken on an ESCALab MKII X-ray photoelectron spectrometer to obtain further evidence for the purity and composition of the as-prepared products, using Al K α radiation as the exciting source. UV–vis spectroscopic measurements of the samples were carried out with the UV–vis spectrometer (Shimadzu UV-3600 PC) operated at a resolution of 2 nm. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out with a Shimadzu Corporation TGA-60 thermal analyzer using a 10 °C/min heating rate in flowing nitrogen atmosphere.

2.4. Catalytic hydrogenation of p-nitrophenol

To test the catalytic activities of the as-prepared Sb_2Se_3 nanomaterials, the catalytic reduction of p-nitrophenol (4-NP) to p-aminophenol (4-AP) was employed as a model reaction [29,30]. The reduction reaction of 4-NP to 4-AP by the catalysis of the Sb_2Se_3 was studied in a standard quartz cuvette in the presence of an excess amount of NaBH_4 and measured by a UV–vis absorption spectroscopy at room temperature (see Scheme 1).



Scheme 1. The reaction equation for catalytic hydrogenation of p-nitrophenol to p-aminophenol.

In a typical process, 0.1 mL 0.005 mol/L 4-NP solution, 2.0 mL distilled water, and 1.0 mL 0.1 mol/L freshly prepared NaBH_4 aqueous solution were added into the quartz cuvette in sequence, and the solution color turned to bright yellow rapidly. Subsequently, 1.0 mg of the as-prepared Sb_2Se_3 was added to the solution. Immediately after the addition of Sb_2Se_3 , UV–vis spectra of the solution were recorded every 1 min in the scanning range of 200–500 nm. The rate constant of the reaction was determined by measuring the change of the absorbance at 400 nm as a function of time.

3. Results and discussion

3.1. Structure and morphology

Antimony selenide with lamellar nanostructure was synthesized under hydrothermal conditions at 180 °C for 1 h. The XRD pattern of the obtained samples was recorded in a 2θ range of 10–70°, as shown in Fig. 1. All detectable diffraction peaks could be indexed to an orthorhombic Sb_2Se_3 phase (JCPDS Card No. 15-0861); the lower diffraction intensity indicates that the crystallinity of the as-prepared samples was comparatively poor. No other impurity peaks were detected from the XRD pattern, which indicated the as-prepared products with high purity. Fig. 1b was a representative EDS spectrum conforming the composition of the as-prepared samples, and the result displayed that the diffraction peaks of only Sb and Se with an atomic ratio of 2.0:3.1 were detected, which atomic ratio was very close to the stoichiometric composition of the antimony selenide (2:3). The copper element in EDS was from copper mesh as a sample substrate.

The morphology and structure of the obtained samples were investigated by FE-SEM and TEM, as shown in Fig. 2. The low-magnification SEM image (Fig. 2a) shows that the as-synthesized Sb_2Se_3 products are homogeneous and well-defined. The high-magnification FE-SEM image (Fig. 2b) shows that the obtained Sb_2Se_3 nanostructures are composed of numerous lamellas with the average thickness ca. 10 nm and lengths of up to 1.0 μm . The TEM images provide further insight into the micro-structural details of the as-synthesized Sb_2Se_3 nanostructures (Fig. 2c and d).

Furthermore, the selected area electron diffraction (SAED) analysis (the inset of Fig. 2d) exhibits the poly-crystalline nature of the as-synthesized Sb_2Se_3 . The lattice fringe spacings are 0.312 nm, 0.219 nm, 0.184 nm, corresponding to the (211) (250) and (441) planes of orthorhombic Sb_2Se_3 , respectively.

3.2. Nitrogen sorption and XPS analysis

Nitrogen adsorption and desorption isotherms were used to investigate the specific surface area and porosity of the as-prepared Sb_2Se_3 nanomaterials, as shown in Fig. 3a. The N_2 isotherms are close to Type IV with an evident hysteresis loop in the 0.45–1.0 range of relative pressure. The Brunauer–Emmett–Teller (BET) specific surface area of the as-synthesized Sb_2Se_3 samples is 16.8 m^2g^{-1} by calculating from nitrogen adsorption. The high specific surface area of the Sb_2Se_3 nanostructures will provide more active sites for catalytic behaviors. Meanwhile, the pore size distribution curve is determined by the Barrett–Joyner–Halenda (BJH) method in the inset of Fig. 3a, and the peak at 12.4 nm can be observed, which can be attributed to the interparticle spaces.

The chemical state and composition of the as-synthesized Sb_2Se_3 products were further examined by X-ray photoelectron spectra (XPS). The values of the binding energy were calibrated using the C 1s peak (284.6 eV) as the inner label. Fig. 3b shows a typical survey spectrum of the Sb_2Se_3 synthesized under hydrothermal conditions at 180 °C for 1 h, which displays the peaks of C 1s (284.8 eV), N 1s (398.0 eV), Sb 3d, Sb 4d and Se 3d. Since the position of Sb 3d5 binding energy (529.4 eV) is superposed

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