Materials Research Bulletin 48 (2013) 955–960

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Modification of MoO_3 matrix with Fe_xO_y by using metal–ligand complex as template

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ARTICLE INFO

Article history:
Received 5 June 2012
Received in revised form 6 October 2012
Accepted 12 November 2012
Available online 22 November 2012

Keywords:
A. Inorganic compounds
A. Semiconductor
B. Chemical synthesis

ABSTRACT

We report a template route to modify MoO_3 molecules with Fe_xO_y by using metal-complex of Fe-phenanthroline (Fe-phen) as template. Fe-phen complex self-assembled with polyoxomolybdate into a Fe-phen/polyoxomolybdate hybrid easily and this hybrid decomposed into $FeOOH/MoO_3$ nanocomposite after calcinations. Single crystalline MoO_3 nanoparticles have been obtained with FeOOH doped in it. By this method the semiconductor MoO_3 molecules have been successfully modified with Fe_xO_y. This research makes it possible to prepare magnetic-semiconductor nanomaterial by using metal–ligand complex as template via in situ self-assembly route very easily in future and also supplies new techniques to prepare organic–inorganic hybrid materials via a green and efficient way.

1. Introduction

Semiconductor nanomaterials have called numerous attentions in the past decades due to their quantum size effects and wide applications in photochemistry and heterogeneous catalysis [1,2]. Metal/semiconductor, magnetic material/semiconductor and other semiconductor hybrid materials have been widely investigated because these hybrid materials combine both the metal (or the magnetic material) and semiconductor on one particle and thus greatly enhance the functionality of the system [3–7]. Among these hybrid materials, magnetic-semiconductor nanomaterials have called extensive attention due to their novel opotomagnetic properties and the great potential application as ideal components for the storage and processing of information for electronic devices. Scientists have tried numerous methods to obtain hybrid magnetic-semiconductor nanomaterials with controllable sizes and properties. Fe_xO_y-semiconductor hybrid nanomaterial has been fabricated. However, so far the only route to prepare Fe_xO_y-semiconductor is the seeding growth method, which requires multiple steps and elaborate experimental operations. Novel reaction routes are required to obtain controllable Fe_xO_y-semiconductor nanomaterials easily and efficiently.

MoO_3 is a wide band gap semiconductor material and has been extensively used in rechargeable lithium battery electrodes, smart windows, display devices, sensors and also catalysts. Its typical layered molecular structure makes it a wonderful host for intercalating guest molecules such as amines, aromatic polymers, and metals [8–12]. To obtain these hybrid materials, usually three steps are required: (1) preparation of alkali bronze gels; (2) swelling of the alkali bronze to expand its interlayer spacing; and (3) mixing of the expanded alkali bronze layered gels with appropriate guest species for ion exchange. The above process usually takes about several days and so far very few examples have been reported to fabricate modified MoO_3 semiconductor nanomaterials. The key problem lies in the insufficient exchange ability of the alkali bronze gels and also its low reaction rate in an inhomogeneous reaction environment. To obtain novel hybrid materials based on molybdenum oxide, new synthetic routes are required.

In this paper, we report a novel self-assembly route to prepare Fe_xO_y/MoO_3 nanocomposite by using metal–ligand complex as template in homogenous aqueous solution. Polyoxomolybdate molecules self-assembled with metal-complex of Fe-phenanthroline (Fe-phen) into a Fe-phen/polyoxomolybdate hybrid, in which the Fe-phen molecules and polyoxomolybdate molecules were dispersed on the molecular level. By this method the polyoxomolybdate molecules have been modified with the Fe-phen molecules. This hybrid later hydrolyzed into $Fe(OH)_x$-phen/polyoxomolybdate after being heated. Experiments proved that the polyoxomolybdate in this hybrid induced the unusual hydrolysis of Fe-phen complex. The hydrolysis product decomposed into $FeOOH/MoO_3$ nanocomposite after calcinations. Single crystalline MoO_3 nanoparticles have been obtained with FeOOH

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0025-5408/$ – see front matter.
http://dx.doi.org/10.1016/j.materresbull.2012.11.071

doped in it. By using Fe-phen complex as template, Fe_xO_y-modified semiconductor nanoparticles have been obtained. Compared with the usual seeded growth method, this template route is highly efficient. We believe that this research opens a easy self-assembly route to obtain Fe_xO_y-semiconductor hybrid by using metal–ligand complex as precursor template. This research will also benefit fabrication of novel organic–inorganic hybrid materials in future.

2. Experimental

2.1. Preparation of Fe-phen/polyoxomolybdate hybrid

7.0 g ammonium molybdate was dissolved in 250 ml deionized water by heating. HCl was used to adjust its pH value to 1. 0.65 g $FeSO_4$ and 1.5 g phen were put into 280 ml deionized water and dissolved by ultrasonic treatment. Dark red solution of Fe-phen complex was obtained. This red Fe-phen solution was added into acidified ammonium molybdate and copious red precipitate appeared immediately. After being heated at 90 °C for several minutes, the precipitate was filtered and washed with deioned water. Dark red mud-like product was obtained. This compound was named compound 1.

2.2. Transformation of the red Fe-phen/polyoxomolybdate hybrid into blue $Fe(OH)_x$-phen/polyoxomolybdate

The above red composite of Fe-phen/polyoxomolybdate hybrid was put in neutral deionized water and heated for 10 min. The red composite turned blue. The blue precipitate was filtered, washed with deionized water and dried in air. This compound was named compound 2.

2.3. Preparation of the phen/polyoxomolybdate hybrid

0.75 g phen was dissolved in 150 ml deionized water by ultrasonic treatment. Its pH value was adjusted to 2. 3.5 g ammonium molybdate was dissolved in 100 ml deionized water by ultrasonic treatment and its pH value was adjusted to 1. Once the two solutions were mixed, copious red precipitate was obtained. After being heated for half an hour, the precipitate was filtered and washed with deioned water. Thus obtained compound was named compound 3.

2.4. Transformation of $Fe(OH)_x$-phen/polyoxomolybdate into $FeOOH/MoO_3$ by calcinations

Thus obtained $Fe(OH)_x$-phen/polyoxomolybdate composite (compound 2) was calcined in air at 500 °C for 3 h. Light brown powder was obtained.

2.5. Transformation of $Fe(OH)_x$-phen/polyoxomolybdate into MoO_2 by calcinations

Thus obtained $Fe(OH)_x$-phen/polyoxomolybdate hybrid (compound 2) was calcined in N_2 at 500 °C for 3 h. Dark black powder was obtained.

2.6. Characterization

The obtained compounds were identified by TEM measurements (FEI Tecnai G2 F30 and Tecnai G2 F20 U-TWIN), SEM measurements (S-3400N(II)), UV–vis analysis (UV-2501PC) and XRD analysis with a diffraction meter using Cu Kα irradiation (D8ADVANCE). X-ray photoelectron spectroscopy (XPS) measurement was carried out on X-ray photoelectron spectrometer (ULVAC-PHI 1800).

3. Results and discussion

3.1. Self-assembly of Fe-phen complex and polyoxomolybdate into Fe-phen/polyoxomolybdate hybrid and its hydrolysis into $Fe(OH)_x$-phen/polyoxomolybdate

The molecular structure of the Fe-phen complex is drawn in Scheme 1, in which three phen molecules bond with the Fe^{2+} ion via 6 Fe–N metal–ligand bonds. The reaction product of Fe-phen complex with polyoxomolybdate is a red hybrid (compound 1), as shown in the HR-TEM images (Fig. 1). Lamellar microstructures can be observed, about 10–100 nm in width and 100–1000 nm in length (Fig. 1a). In this hybrid the polyoxomolybdate molecules (the hydrolysis result of ammonium molybdate under

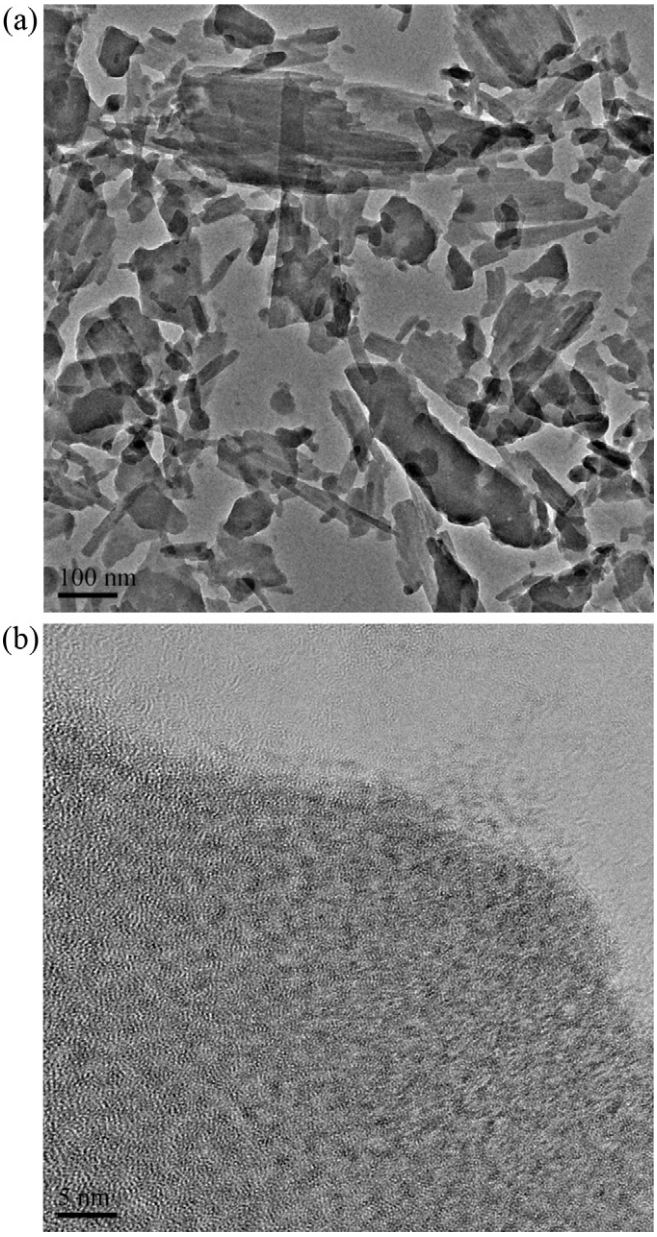

Fig. 1. HR-TEM images of compound 1.