

Selective synthesis and novel properties of single crystalline α -CoMoO₄ nanorods/nanowhiskers

Yumei Kong, Jun Peng^{*}, Zhifeng Xin, Bo Xue, Baoxia Dong, Fengshan Shen, Li Li

Institute of Polyoxometalate Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, P. R. China

Received 29 November 2005; accepted 10 August 2006

Available online 1 September 2006

Abstract

The selective controlled syntheses of crystalline CoMoO₄ nanorods (rod-CoMoO₄)/nanowhiskers (whiskers-CoMoO₄) by using reverse micelles in different molar ratios (w) of [H₂O]/[CTAB] under mild hydrothermal conditions are reported for the first time. The obtained rod-CoMoO₄/whiskers-CoMoO₄ have a monoclinic structure (α -CoMoO₄), with diameter range from 10 to 80 nm and their lengths range from several tens of nanometers to 1 μ m. The synthesis conditions and formation mechanism of the nanorods/nanowhiskers were discussed. The electrochemistry behaviors of Co²⁺ and CoMoO₄ in nanoscale and in macroscale are compared, from which an interesting result is obtained. Furthermore, the efficient antibacterial property of the nanorods against *Escherichia coli* (*E. coli*) was first found.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Molybdates; Nanorods/nanowhiskers; Selective synthesis; Antibacterial property

1. Introduction

Among various metal oxides, molybdates play an important role in technological applications such as catalysts [1], optical materials [2,3], electrode materials [4], and so on. A great deal of molybdates [5–9] and their composites [10,11] in macroscale were synthesized by diversified methods. Furthermore, nanomaterials with sizes between 1 and 100 nm attract extensive interest in recent years due to their inimitable properties of photochromic, electrochromic and magnetism. Some researches were distributed to the preparation of nanosized molybdates. In previous papers, Pramanik et al. [12] reported the nanocrystalline powders of metal molybdate, AMoO₄ (A = Ca^{II}, Co^{II}, Cu^{II}, Ni^{II} and Zn^{II}) prepared from the complete evaporation of polymer-based metal–complex precursor solutions. Later, the La₂(MoO₄)₃:YbEr nanocrystals, with an average diameter of 50 nm, were prepared via the hydrothermal method, whose fluorescent intensity was much stronger than that of the bulk materials [13]. A simple processing route that leads to nanostructures of mixed cobalt–nickel molybdates, Co_{1-x}Ni_xMoO₄, was devel-

oped by David Vie et al. It was based on the use of precursors resulting from the freeze-drying of aqueous solutions of the appropriate common metal salts. The Co_{1-x}Ni_xMoO₄ grains were aggregates of nanoparticles (with diameters typically around 30–40 nm). The performance of these nanostructure catalysts for the oxidative dehydrogenation of propane was higher than that reported for homologous oxides prepared through conventional procedures [14]. It has been demonstrated that many properties of nanomaterials are strongly related to their sizes and morphologies. In particular, the catalytic properties and the optical properties of nanomaterials are enormously affected by their shapes and sizes. Therefore, further exploration for the function of nanostructure molybdates is a challenging subject due to the intimately morphology-dependent characteristic of their properties. However, only few reports dealt with the preparation of molybdates with one-dimensional nanostructures such as nanorods, nanowires/nanobelts, and nanotubes. For example, Cui and co-workers have recently reported that selective synthesis of uniform single crystalline silver molybdate/tungstate nanorods/nanowires in large scale can be easily realized by a facile hydrothermal recrystallization technique [15]. Herein we report for the first time the preparation of crystalline CoMoO₄ nanorods with an average diameter of 10 nm in reverse micelles under

^{*} Corresponding author. Tel./fax: +86 431 5099667.

E-mail address: jpeng@nenu.edu.cn (J. Peng).

hydrothermal conditions. The electrochemistry, magnetism and antibacterial activity are also presented.

2. Experimental section

All of the chemical reagents used were of analytical grade, and commercially obtained. In a typical synthesis process, two solutions were first prepared. Solution A was obtained by adding 1 ml of 1 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into a 30 ml microemulsion containing cyclohexane, *n*-butanol, 0.1 M cetyltrimethylammonium bromide (CTAB) and water, with stirring for 30 min. The molar ratio (w) of H_2O to CTAB was 28.5. Solution B was obtained by the same method while 1 ml of 1 M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was used instead of 1 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Then solutions A and B were mixed and continuously stirred for another 30 min, and its color turned into dark purple (final pH 7–8). The as-prepared microemulsion mixture was then transferred into a stainless Teflon lined autoclave and heated at 120 °C for 24 h. The resulting suspension was naturally cooled to room temperature. The black precipitates of crystalline cobalt molybdate nanorods (rod- CoMoO_4) were collected by centrifugation, washed with absolute ethanol, and hexane and dried at room temperature.

XRD analysis of the obtained powder was performed using a Rigaku D/max-IIB X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=0.15408$ nm) at a scan rate of 4° per minute. The morphology and selected area electron diffraction (SAED) of the samples were observed on a JEM-2010 electro-microscope using an accelerating voltage of 200 kV. The cyclic voltammogram (CV) of the samples was studied in the rod- CoMoO_4 -CPE (carbon paste electrode) system (CHI 660 electrochemical workstation, conventional three-electrodes, SCE, Pt). The rod- CoMoO_4 -CPE electrode was prepared according to the method of Ref. [16]. The magnetic measurements were carried out using Quantum Design MPMS-XL SQUID magnetometer.

3. Results and discussion

In many trials it was found that the pH value was crucial for the preparation of pure crystalline cobalt molybdate either in nanorod morphology or in nanowhiskers morphology. The CoMoO_4 monoclinic phase can be obtained in a neutral aqueous solution (pH ~ 7). While under acidity conditions (pH 2–3), some un-identified cobalt molybdates were obtained. It was also found that crystalline CoMoO_4 in different morphologies could be isolated by adjusting the w . When w was 28.5, pure rod- CoMoO_4 was obtained, while when w was 18.5, pure whiskers- CoMoO_4 was obtained.

The crystalline phase of the rod- CoMoO_4 is verified by powder XRD (Fig. 1). The diffraction patterns in $2\theta=15\text{--}70^\circ$ are in good agreement with the standard values of the pure crystal CoMoO_4 monoclinic phase [space group: $C2/m$ (12)], with lattice constants: $a=9.666$ Å, $b=8.854$ Å, $c=7.755$ Å, and $\beta=113.82^\circ$ (Joint Committee on Powder Diffraction Standards, JCPDS 73–1331). Accordingly, the nanorod sample (rod- CoMoO_4) is assigned to the α - CoMoO_4 phase [17]. The XRD patterns of the whiskers sample (whiskers- CoMoO_4) have a w of 18.5, which is quite similar to that of the rod- CoMoO_4 , so that both samples possess the same CoMoO_4 monoclinic phase (α - CoMoO_4 phase).

The morphologies of the rod- CoMoO_4 /whiskers- CoMoO_4 are obtained by transmission electron microscopy (TEM). Fig. 2a shows

the TEM image of the rod- CoMoO_4 with a smooth surface and an average diameter of 10 nm. The ratio of diameter to length is 1:5. Fig. 2b shows the TEM image of the whiskers- CoMoO_4 with an average diameter of 30 nm and the ratio of diameter to length is 1:3. This indicates that the aspect ratio of the prepared 1D nanostructure is dependent on the $[\text{H}_2\text{O}]/[\text{CTAB}]$ molar ratio and exchangeable water molecules in the microemulsions are of key importance for the formations of nanorods/nanowhiskers [18]. Scheme S1 illustrates schematically a possible mechanism of the formation process of the rod- CoMoO_4 and whiskers- CoMoO_4 . When the concentration of CTAB is lower, as in the case of $w=28.5$, it is favorable to form the rod- CoMoO_4 via pathway 1, otherwise, the formation of the whiskers- CoMoO_4 is dominant via pathway 2, as in the case of $w=18.5$.

The morphology and microstructure of the obtained rod- CoMoO_4 were further characterized by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). Fig. 2c shows the typical TEM image of a representative nanorod with a uniformity diameter of 10 nm. The SAED pattern of the rod- CoMoO_4 (the upper inset in Fig. 2c) taken from the single nanorod suggests that the nanorods prepared were single crystal with uniform lattice. The HRTEM image (the lower inset in Fig. 2c) shows that the nanorod is structurally uniform with an interplanar spacing of about 0.375 nm, which corresponds to the [021] lattice spacing of the monoclinic phase CoMoO_4 . In addition, an angle of 105° between the normal direction of [021] and the long axis direction of the nanorod is observed, indicating that the nanorod grows along that direction at an angle of 105° from the normal direction of [021].

Electrochemical behavior of the rod- CoMoO_4 was studied by cyclic voltammogram measurement of the rod- CoMoO_4 -CPE, see Fig. 3. Under an acidic condition (1 M H_2SO_4 solution), no response was observed in the potential range -1500 to $+1000$ mV, while under basic condition (1 M NaOH solution), a reduction peak at about -910 mV, which was assigned to the reduction of Mo (VI) to Mo (IV), and a pair of redox waves with the mean peak potential $E_{1/2}=(E_{pa}+E_{pc})/2=-0.30$ V, corresponding to the two-electron processes of Co^{2+}/Co , and an oxidation peak at -0.15 V, attributed to the one-electron process of $\text{Co}^{2+}/\text{Co}^{3+}$ were observed (see Fig. 3a). The peak currents were proportional to the scan rates, indicating that the reduction processes are diffusion-controlled [19]. To make a comparison, the cyclic voltammogram of CoMoO_4 -CPE, in which the purple CoMoO_4 salt was obtained by simply mixing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solution, was carried out under the same conditions. Interestingly, no redox peaks related to cobalt were observed (see Fig. 3b). The different electrochemical behaviors between them, we conjecture, may arise from the nano-effect of the rod- CoMoO_4 , which is further studied.

The plot of the product $\chi_m T$ vs T is shown in Fig. S1. The $\chi_m T$ value is 2.75 emu K mol^{-1} at 300 K. The value 2.75 emu K mol^{-1} for the ambient temperature and pressure leads to an effective magnetic moment of $\mu_{\text{eff}}(\text{Co}^{2+})=4.7$ μB , corresponding to those obtained for

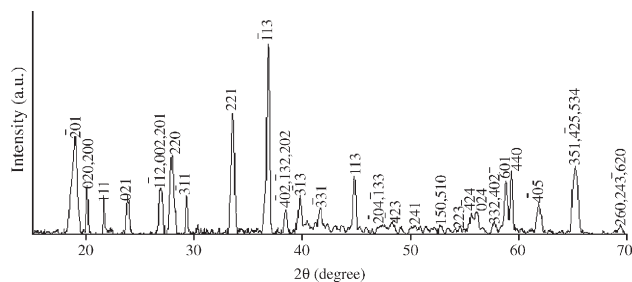


Fig. 1. XRD pattern of the rod- CoMoO_4 .

Download English Version:

<https://daneshyari.com/en/article/1652752>

Download Persian Version:

<https://daneshyari.com/article/1652752>

[Daneshyari.com](https://daneshyari.com)