Synthesis and characterization of silver molybdate nanowires, nanorods and multipods

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Abstract. Silver molybdate nanowires, nanorods and multipods like structures have been prepared by an organic free hydrothermal process using ammonium molybdate and silver nitrate solutions. The powder X-ray diffraction (PXRD) patterns reveal that the silver molybdate belongs to anorthic structure. The thickness, 200–500 nm, for silver molybdate nanorods/wires and 2–5 μm for microrods are identified from SEM images. UV-visible spectrum of silver molybdate nanorods/nanowires shows maximum absorbance at 408 nm. Photoluminescence (PL) spectrum exhibits UV emission at 335 nm, violet emission at 408 nm and a weak green emission at 540 nm. The influence of hydrothermal synthesis conditions on silver molybdate nanowires, nanorods and multipods compositions were established.

Keywords. Silver molybdates; hydrothermal; multipods; nanorods; photoluminescence.

1. Introduction

Strategies for obtaining nanosized building blocks such as nanorods, nanowires, nanotubes and nanobelts have received extensive attention because of their distinctive geometries, novel physical and chemical properties and potential applications in nanodevices (Cui *et al* 2004). Low-dimensional systems represent one of the important frontiers in advanced materials research (Liao *et al* 2000). Various methods have been developed to synthesize 1-D nanomaterials (Klein *et al* 1993; Dai *et al* 1995; Morales and Lieber 1998; Pan *et al* 2001). In contrast, the solution approaches have been proved to provide an alternative route for the synthesis of 1-D nanomaterials (Buhro *et al* 1996; Holmes *et al* 2000; Peng *et al* 2000; Peng and Peng 2001, 2002). The template method is known to be a very effective method for the fabrication of the desired materials (Torigoe and Esumi 1995; Nagappa *et al* 2005). However, it is interesting to explore the solution-based synthesis of nanomaterials without the presence of pre-formed templates (Liao *et al* 2000; Nagaraju *et al* 2007). As a simple, cost-effective and efficient synthesis route, the hydrothermal process has been demonstrated as a versatile pathway toward the size and morphology-controllable nanomaterials (Wu *et al* 2006). Synthesis of 1-D metal molybdates (Guo *et al* 1995; Liao *et al* 2000; Mougín *et al* 2000; Cui *et al* 2004) have attracted recent interest due to their strong application potential in various fields such

as photoluminescence (Kozma *et al* 2002), microwave applications (Van Uitert and Preziosi 1962), optical fibres (Wang *et al* 1992), scintillator materials (Wang *et al* 1994), humidity sensor (Qu *et al* 2000), magnetic properties (Ehrenberg *et al* 1997), and catalyst (Driscoll and Ozkan 1994). Lamellar oxide of transition metals, particularly silver molybdate, shows a high temperature friction coefficient without decomposition during melting (Gulbinski *et al* 2003). These materials have high electrical conductivity and usually have found important applications in conducting glass. For example, silver based superionic glasses and crystals whose conductivity differs by more than 11 orders of magnitude are found to be fast ionic conductors (Adams and Swenson 2000). Most previous approaches for preparation of these families of molybdates need high temperature reaction (Swanson *et al* 1963). Few reports are related to the synthesis of metal molybdates through solution methods (Sen and Pramanik 2002; Beale and Sankar 2003). Silver molybdates of different phases were traditionally synthesized by the reaction of MoO_3 with Ag_2O (Wenda 1998). Cui *et al* (2004) prepared silver molybdate nanowires through hydrothermal method using HCl or NaOH to control pH of the solution. Recently, Brechignac *et al* (2004) prepared silver molybdate clusters by laser annealing method.

In this paper, we report the synthesis of silver molybdate nanorods/nanowires/multipods through a simple hydrothermal approach. In order to understand the habits of one-dimensional silver molybdate nanorods/nanowires/multipods, the influence of reaction time, temperature and concentration of the precursor on their morphology have been investigated.

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2. Experimental

2.1 Synthesis

In a typical procedure, 0.61 g ammonium molybdate heptahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ was dissolved in 10 mL distilled water and 0.08 g silver nitrate was dissolved in 10 mL distilled water. Then silver nitrate solution was slowly added into ammonium molybdate solution under magnetic stirring to form a homogeneous greenish-yellow precipitate. The resulting precipitate was transferred into a Teflon-lined stainless autoclave. The autoclaves were sealed and maintained at different temperatures (140–200°C) for several hours (12–72 h). After the hydrothermal process the autoclaves were cooled and the resulting greenish-yellow products were retrieved from the solution by centrifugation, washed with distilled water followed by ethanol to remove the ions possibly remaining in the end product and finally dried in air.

2.2 Characterization

Powder X-ray diffraction data were recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) with Ni filter. The Fourier transform infrared spectrum of the sample was collected using Nicolet FTIR spectrometer. The absorption spectrum of the sample was measured on a UV-3101 Shimadzu UV-visible spectrometer. SEM images of

the samples were recorded by JEOL JSM-840 A scanning electron microscope. Photoluminescence spectrum was examined at room temperature by Perkin Elmer spectrometer using Xe lamp with an excitation wavelength of 330 nm.

3. Results and discussion

Phases and purities of the samples were investigated by PXRD analysis. Figure 1 shows the PXRD patterns of the silver molybdate nanorods/multipods. Hydrothermal treatment of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ with AgNO_3 led to the formation of mixture of phases including $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ (JCPDS Card: 72-1689, $a = 7.59$, $b = 8.31$, $c = 11.42 \text{ \AA}$, $\alpha = 82.6$, $\beta = 102.9$, $\gamma = 106.48$), $\text{Ag}_2\text{Mo}_2\text{O}_7$ (JCPDS Card: 75-1505, $a = 6.095$, $b = 7.501$, $c = 7.681 \text{ \AA}$, $\alpha = 110.4$, $\beta = 93.3$, $\gamma = 13.58$) and $\text{Mo}_{17}\text{O}_{47}$. With increase in temperature, disappearance of $\text{Mo}_{17}\text{O}_{47}$ peaks is observed as shown in figure 1a.

Figure 1. XRD patterns of the products obtained at different conditions: (a) 180°C for 24 h, (b) 180°C for 72 h and (c) 200°C for 24 h. (○, $\text{Ag}_2\text{Mo}_2\text{O}_7$; ▼, $\text{Mo}_{17}\text{O}_{47}$; □, $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$).

Figure 2. FT-IR spectrum of silver molybdate nanorods prepared at 180°C for 48 h.

Figure 3. UV-visible spectrum of silver molybdate prepared at 180°C for 48 h.

Figure 4. SEM images of the silver molybdate multipods prepared at 180°C for 48 h.

Figure 5. SEM image of silver molybdate nanowires prepared at 200°C for 63 h.

Some key structural information was deduced from the FTIR spectrum, which is shown in figure 2. The most important feature is a relatively sharp band at 987 cm^{-1} , characteristic of the stretching of $\text{M}=\text{O}$ double bond which is also found in orthorhombic $\alpha\text{-MoO}_3$ indicating a terminal oxygen in the framework. The bands below 1000 cm^{-1} are assigned as $\text{O}-\text{Mo}-\text{O}$ bond stretching and bending with different $\text{Mo}-\text{O}$ bond lengths (Guo *et al* 1995). UV-visible absorption spectroscopy is a useful technique to monitor the size-dependent optical properties of the nanomaterials, due to the quantum confinements of the photo-generated electron-hole carriers in the particles. Nanostructured materials generally exhibit the blue shift behaviour in the

absorption measurement due to the size-dependent band-gap structure (Khiew *et al* 2004). The UV-visible diffuse reflection spectrum of the sample is recorded in the range 200–800 nm on a Shimadzu spectrophotometer, and representative spectrum is shown in figure 3. It shows that the samples absorb in the spectral region between 250 and 450 nm and a maximum absorbance around 405 nm corresponds to a bandgap of 3.05 eV.

Figures 4–8 show the SEM morphologies of the sample prepared at 140–200°C for 12–72 h. By controlling the experimental conditions (concentration, temperature and duration), we have successfully prepared silver molybdate nanowires, nanorods and multipods of various morphologies through hydrothermal method. SEM images shown in figure 4 shows that the products synthesized at 180°C for 48 h composed of silver molybdate multipods structures, which look like flowers in which each pod radially grows from one centre. A high-magnified SEM image shows that the diameter of each pod of these structures is quite uniform along its length, and the typical diameters of the pods range from 3–6 μm . The length of each pod is about 10–30 μm . The description of the flower-like silver molybdate structures comes from the geometrical similarity to flowers. Bundles of silver molybdate protrude from the root of the flower-like silver molybdate microrods. In our experiments, it is impossible that the aggregation resulted in the flowerlike structures, because long time ultrasonic treatment could not destroy the structures. Figure 5 shows the SEM morphologies of the sample prepared at 200°C for 63 h. The thickness of the nanowires is found to be in the range 200–400 nm and length is about several micrometers. The thickness of nanowires is found to be almost uniform along its entire length. By doubling the concentration of any one of the reactants (ammonium molybdate and silver nitrate), silver molybdate nanorods

Figure 6. SEM images of silver molybdate nanorods prepared at 180°C for 48 h by doubling the concentration of both (a) ammonium molybdate and (b) silver nitrate.

Figure 7. SEM images of the silver molybdate nanorods and nanowires prepared at (a) 140°C for 24 h and (b) 140°C for 12 h.

Figure 8. SEM image of silver molybdate nano/micro spheres obtained at 180°C for 48 h by dissolving silver nitrate in 10 mL ethyl alcohol.

(figures 6a and b) of uniform diameter of about 200–500 nm are obtained at 180°C for 48 h. When both temperature and treatment time are reduced to 140°C for 24 and 12 h, by keeping concentration of the precursor constant, nanorods and nanowires of about 300–600 nm diameter are obtained as shown in figures 7a and b. Silver nitrate crystals are dissolved in 10 ml ethyl alcohol instead of water by keeping all the above parameters the same and nano/micro spheres are obtained as shown in figure 8.

In order to assess the crystalline quality and investigate the optical properties of the silver molybdate micro/nanorods, PL spectrum of 320 nm is taken using Xe lamp as the excitation source. Figure 9 shows photoluminescence spectrum of the sample prepared at 180 °C for 48 h. It is generally assumed that the measured emission spectrum of silver molybdate complex is mainly attributed to the charge-transfer transitions within the molybdate complex. It shows UV emission at 335 nm, violet

Figure 9. Photoluminescence spectrum of silver molybdate multipods.

emission at 408 nm and a weak green emission at 540 nm. The emission in the UV region is attributed to the recombination between electrons in the conduction band and holes in the valence band (Gao *et al* 2006). Violet emission at 408 nm is attributed to the exciton transition (Wang and Gao 2003). Weak and broad green emission at 540 nm can be ascribed to a defect structure. The strong UV emission and weak green emission in PL spectrum indicate that the silver molybdate nano/microrods have a good optical quality with few oxygen vacancies (Monticone *et al* 1998). Oxygen vacancies have been considered as the most common defects and usually act as radiative centres in luminescence process. In addition, silver molybdate with high aspect ratio should also favour the existence of large quantities of oxygen vacancies.

4. Conclusions

In summary, by means of an organic-free hydrothermal process, silver molybdate nanowires, nanorods and multipods like structures have been successfully prepared. It is found that concentration of the precursor, reaction temperature and treatment time have significant influence on the morphology of silver molybdate nanowires, nanorods and microrods. PXRD results show the formation of mixed phases of silver molybdates. SEM images reveal that the thickness of the nanowires/rods is in the range of 200–500 nm and microrods are in the range of 3–6 μm . UV-vis spectrum of silver molybdate nanorods/nanowires shows maximum absorbance at 405 nm corresponding to a bandgap of 3.05 eV. The PL spectra of the silver molybdate microrods consist of UV emission at 335 nm and violet emission at 408 nm.

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