Synthesis of SrCrO_4 nanostructures by onion inner-coat template and their optical properties

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MS received 18 November 2007

Abstract. This paper describes a bio-template method of the squama inner coat of onion for preparing the SrCrO_4 nanostructures including nanospheres, nanorods and dumbbell-shaped superstructure. The method is able to make SrCrO_4 nanoparticles with average diameters in the range of 90–170 nm, SrCrO_4 nanorods with length in the range 0.70–2 μm , width in the range of 80–180 nm, and SrCrO_4 dumbbell-shaped superstructure with length in the range 10–14 μm . The dumbbell-shaped superstructures are assembled by many SrCrO_4 nanowires with length in the range 10–14 μm and width in the range 30–50 nm. The products were characterized by transmission electron microscope, powder X-ray diffraction, UV-Vis spectroscopy and luminescence spectrophotometer. A possible formation mechanism was also proposed. In the preparation, the SrCrO_4 nanostructures were synthesized at room temperature without any surfactants. This new bio-template method will have potential applications in preparation of the nanoscale materials with different morphologies.

Keywords. Inorganic compounds; nanostructures; optical properties; SrCrO_4 ; inner coat of onion.

1. Introduction

As is well known, nanomaterials have attracted great interest in the past decade because of their marvellous characteristics that are different from those of bulk materials (Alivisatos 1996; Nie and Emery 1997; Link and El-Sayed 1999; Guo *et al* 2005). One-dimensional nanoscale materials such as nanorods, nanowires and nanobelts, may have wide potential and practical applications because of their unique chemical and physical properties and have attracted wide attention (Hu *et al* 1999; Vayssieres 2003). Strontium chromate (SrCrO_4) is of importance owing to its important optical behaviour, structural properties and potential applications. Especially, Zou *et al* recently developed MCrO_4 ($\text{M} = \text{Ba}, \text{Sr}$) catalyst, which may have promising application in the photocatalyst (Schenker *et al* 1998; Yin *et al* 2003). Up to now, considerable efforts have been focussed on the properties of SrCrO_4 . However, to the best of our knowledge, there are several reports on the synthesis of SrCrO_4 nanostructures. For example, Chen *et al* (2006) reported the surfactant-assisted synthesis of SrCrO_4 nanostructures by microemulsion-based technique. Wang *et al* (2006) reported the synthesis of SrCrO_4 nanowires by a solution-phase method. Recently, our team has successfully prepared SrCrO_4 crystals with different morphologies (Yang *et al* 2007).

Now it is very important to develop facile and green technologies in nanomaterials synthesis (Sastry *et al* 2003; Gericke and Pinches 2006; Mandal *et al* 2006; Huang *et al* 2007). In the past several years, there have been some reports on the synthesis of inorganic materials using biological systems (Li *et al* 2004; Zhang *et al* 2006). An onion is a traditional vegetable and is available in the supermarkets in many countries. Its squama consists of larger amounts of celluloses, proteins and many kinds of amino acids (Kopsell and Randle 1997; Luan 2002). In principle, these various functionalities such as hydroxyl, carboxylate and amine groups should offer a wide variety of nucleation sites for surface controlled inorganic deposition, and could be used in the synthesis of inorganic materials. It is very inexpensive and, though thin, a squama inner coat of onion is stable in a solution (Luan 2002). A squama inner coat of onion probably is an ideal biological template for the synthesis of inorganic materials.

In this work, we present a novel and simple route using the squama coat of onion as template for the preparation of SrCrO_4 nanostructures including SrCrO_4 nanospheres, nanorods and dumbbell-shaped superstructure. The products were characterized by scanning electron microscope (SEM), powder X-ray diffraction (XRD), UV-Vis spectroscopy and luminescence spectrophotometer (PL). In the synthesis, the nanomaterials were synthesized at room temperature without use of surfactants. This new bio-template method will have potential applications in preparation of the other nanoscale materials, especially super-

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structure nanomaterials. The as-prepared SrCrO_4 nanostructures may be used in optical and electronic devices.

2. Experimental

2.1 Reagents and equipment

All the reagents used were of analytical purity and used without further purification. K_2CrO_4 and SrCl_2 were purchased from Shanghai Chemical Reagent Factory, China.

The scanning electron microscopic (SEM) images were acquired on a scanning electron microscope. XRD pattern of the sample was measured on a Rigaku X-ray diffraction with $\text{CuK}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$ (Japan)). The optical properties of the products were studied by an Agilent UV-Vis spectroscopy. PL spectra were obtained using a Perkin-Elmer LSS-55 luminescence spectrophotometer (USA).

2.2 Synthesis

The synthesis of SrCrO_4 was simply achieved by the reaction between strontium and chromate ions. In a typical preparation (figure 1), a fresh onion was washed and the squama inner coat was separated from it. The inner coat was immersed in deionized water for 5 min. Then it was fastened in a reactor and separated the reactor into two compartments. A solution of K_2CrO_4 (25 mL) and a solution of SrCl_2 (25 mL) were respectively placed on both sides of the coat in a vertical direction. The system was kept at a certain temperature. Then the products appeared in the two compartments of the reactor. The solution containing products was centrifugally separated, and washed in turn with deionized water and absolute alcohol, and the final products were obtained.

Figure 1. Scheme of the reacting cell.

2.3 Characterization

The morphologies of the final product were observed using SEM. The structures were characterized by XRD using a Japan Rigaku X-ray diffractometer, and the optical properties of the product were studied by fluorescence and UV-Vis spectrophotometers.

3. Results and discussion

3.1 Structures and morphologies

The overview morphologies and size of the products were observed by SEM. Figure 2 presents the SEM images. When the concentration of SrCl_2 and K_2CrO_4 was both 0.1 mol/L, the SEM image of product is as shown in figure 2a, which shows that the obtained products are of SrCrO_4 nanoparticles with average diameters in the range 90–170 nm. When the concentration of SrCl_2 and K_2CrO_4 was both 0.4 mol/L, the SEM image of product is as shown in figure 2b. Figure 2b shows that the obtained products are of one-dimension SrCrO_4 nanorods with length in the range 0.70–2 μm and width in the range 80–180 nm. Figure 2c presents SrCrO_4 dumbbell-shaped superstructure with length in the range 10–14 μm , which was obtained when the concentration of SrCl_2 and K_2CrO_4 was both 0.2 mol/L. Figure 2d is the high magnification SEM image of the dumbbell-shaped superstructure. The dumbbell-shaped superstructures are assembled by many SrCrO_4 nanowires with length in the range 10–14 μm and width in the range 30–50 nm. All the SrCrO_4 nanostructures were obtained when the reaction time was 28 h. The as-prepared SrCrO_4 nanorods and dumbbell-shaped superstructure may be used in optical and electronic devices in the future. Figure 3 shows the SEM image of product when the SrCl_2 and K_2CrO_4 are directly mixed together with a concentration of 0.2 mol/L. From figure 3, irregular K_2CrO_4 rods can be seen. This indicates that the squama inner coat of onion plays a key role in the preparation of SrCrO_4 nanostructures.

Figure 4 shows typical XRD patterns of the as-prepared SrCrO_4 nanorods. The XRD patterns show that the SrCrO_4 nanorod has a monoclinic structure (JC-PDS no. 35-0743) belonging to $P21/n$ (14) group. The XRD patterns of the as-prepared SrCrO_4 nanospheres and dumbbell-shaped superstructure are similar to that of the nanorods.

3.2 Optical properties of products

The optical properties of nanoscale materials are the most important ones. For SrCrO_4 , the conduction band is composed of the Cr (VI) 3d orbital and the valence band is composed of the O 2p orbital. Because of the electronic excitation from the O 2p state to the Cr (VI) 3d⁰ state, the optical absorption produces in the region of UV-visible

Figure 2. SEM micrographs of SrCrO_4 nanospheres (a), nanorods (b), dumbbell-shaped superstructure (c) and dumbbell-shaped superstructure (magnified) (d) (a. 0.1 mol/L K_2CrO_4 , 0.1 mol/L SrCl_2 , 28 h; b. 0.4 mol/L K_2CrO_4 , 0.4 mol/L SrCl_2 , 28 h; c and d. 0.2 mol/L K_2CrO_4 , 0.2 mol/L SrCl_2 , 28 h).

Figure 3. SEM micrographs of the products when 0.2 mol/L SrCl_2 and 0.2 mol/L K_2CrO_4 are directly mixed together.

light. UV-Vis and photoluminescence properties of the as-prepared SrCrO_4 nanostructures were carefully researched. UV-Vis spectra of SrCrO_4 nanostructures are shown in figure 5. It can be seen that the SrCrO_4 nanostructures exhibit a broad, strong optical absorption in the region of UV-visible light. In figure 5a, SrCrO_4 nano-

spheres showed maximum absorption peak at about 374 nm. UV-visible absorption spectra of the SrCrO_4 nanorods (figure 5b) showed maximum absorption peak at about 389 nm. The products of SrCrO_4 dumbbell-shaped superstructure have strong absorption peaks at 384 nm (figure 5c). Compared with the results of Yin *et al* (2003), the SrCrO_4 nanospheres, nanorods and dumbbell-shaped superstructure show obvious blue shift in UV-visible absorption. Compared with SrCrO_4 nanorods and SrCrO_4 dumbbell-shaped superstructure, SrCrO_4 nanospheres showed blue shift at 15 nm and 11 nm, respectively. Compared with SrCrO_4 nanospheres, SrCrO_4 nanorods show broader UV-visible absorption.

The photoluminescence properties of the SrCrO_4 nanostructures are shown in figure 6 with a 220 nm excitation line at room temperature. Figures 6a–c show the photoluminescence properties of the SrCrO_4 nanospheres, nanorods and dumbbell-shaped superstructure. SrCrO_4 nanospheres have shown a strong emission band peaking at 505 nm and two weak emission bands peaking at 484 nm and 531 nm, respectively. SrCrO_4 nanorods have shown a strong emission band peaking at 504 nm and two weak emission bands peaking at 486 nm and 530 nm, respectively. SrCrO_4 dumbbell-shaped superstructures

have shown a strong emission band peaking at 507 nm and two weak emission bands peaking at 486 nm and 530 nm, respectively.

3.3 Effect of preparation parameters of SrCrO_4 nanostructures

Many experiments have been performed to explore the preparation condition of the SrCrO_4 nanostructures. Results show that the reaction solution concentration and system temperature can affect the products. Experimental results show that the reaction solution concentration plays a key role in preparation (figure 2). When the concentration of Sr^{2+} ion and CrO_4^{2-} ion was lower, the products obtained are the SrCrO_4 nanospheres. When the medium reaction

solution concentration is selected, the dumbbell-shaped superstructures are obtained. But, when the concentration of Sr^{2+} and CrO_4^{2-} ions was higher, the SrCrO_4 nanorods were obtained. By altering the reaction solution concentration, the SrCrO_4 nanospheres, nanorods and dumbbell-shaped superstructure can be obtained.

Effect of temperature on the SrCrO_4 nanostructures also was studied. Experimental results show that when the temperature is lower than 15°C , the products cannot be obtained in 28 h. The reason probably is functional groups of a squama inner coat of onion can lose active ability. Figure 7 shows the SEM micrographs of SrCrO_4 products when the temperature is 35°C . The products are irregular nanospheres. When the temperature is higher than 37°C , a squama inner coat of onion is not stable and

Figure 4. XRD patterns of SrCrO_4 nanorods.

Figure 5. UV-Vis spectra of SrCrO_4 nanospheres (a), nanorods (b) and dumbbell-shaped superstructure (c). (a. 0.1 mol/L K_2CrO_4 , 0.1 mol/L SrCl_2 , 28 h; b. 0.4 mol/L K_2CrO_4 , 0.4 mol/L SrCl_2 , 28 h; c. 0.2 mol/L K_2CrO_4 , 0.2 mol/L SrCl_2 , 28 h).

Figure 6. Fluorescent spectra of SrCrO_4 nanospheres (a), nanorods (b) and dumbbell-shaped superstructure (c). (a. 0.1 mol/L K_2CrO_4 , 0.1 mol/L SrCl_2 , 28 h; b. 0.4 mol/L K_2CrO_4 , 0.4 mol/L SrCl_2 , 28 h; c. 0.2 mol/L K_2CrO_4 , 0.2 mol/L SrCl_2 , 28 h).

Figure 7. SEM micrographs of SrCrO_4 products (0.1 mol/L K_2CrO_4 , 0.1 mol/L SrCl_2 , 35°C).

Figure 8. a. SEM micrograph of the squama inner coat of onion and b. schematic of biological membrane (nonsymmetric trilayer model, P: protein).

Figure 9. Schematic of the possible mechanism.

easily ruptured in a solution. In our research, 25°C was selected.

3.4 Possible mechanism

Figure 8a shows the scanning electron micrograph of the surface of squama inner coat of onion. It can be seen that the squama inner coat of onion is made up of nearly hexagonal cells, which are arranged closely. Figure 8b shows schematic of the cell membrane of the nearly hexagonal cells (non-symmetric trilayer model, P: protein). The bio-

logical membrane mainly contains three layers: sugar-chain layer, lipid layer and protein layer. The sugar-chain layer of the cell membrane and cellulose and glucoprotein system of the cell wall, which contain abundant functional groups play a key role in the formation of SrCrO_4 nanostructures. The template of squama inner coat of onion includes abundant organic groups. The main groups are hydroxyl and carboxylate. These various functionalities can offer a wide variety of nucleation sites for surface controlled inorganic deposition, which could be exploited in the bio-template synthesis of inorganic materials.

Figure 10. SEM micrograph of SrCrO_4 product (0.2 mol/L K_2CrO_4 , 0.2 mol/L SrCl_2 , 20 h).

A probable mechanism for the development of the SrCrO_4 nanostructures is proposed. The schematic of the development of the SrCrO_4 nanospheres is shown in figure 9. First, according to the theory of hard and soft acids and bases, Sr^{2+} ion belongs to Lewis acid, which preferentially combine with Lewis alkaline groups, such as oxygen in the hydroxyl and carboxylate groups. Therefore, Sr^{2+} ions first can pass the cell membrane by permeation and combine on the wall of the squama inner coat of onion containing many hydroxyl groups mainly by electrostatic attraction. Second, when the CrO_4^{2-} ions meet Sr^{2+} ions, the Sr^{2+} ions reacted with CrO_4^{2-} ions near the surface of the squama inner coat of onion to form SrCrO_4 crystal nuclei. Then the crystal nuclei were continuously produced on the interface and induced to grow into nanoparticles as time increases. Especially, during nucleation, the sugar-chain layer of the template is dominant in the nucleation positions through special confinement. The sugar-chain layer can supply an adequate site to have attractive action with Sr^{2+} ions and then the nanoparticles were formed.

The control of the template of squama inner coat of onion is very important in the formation of the SrCrO_4 nanostructures. When the concentration of Sr^{2+} and CrO_4^{2-} ions was lower, on the control of the template of squama inner coat of onion, the SrCrO_4 crystal nuclei could not grow in bulk unlimitedly and the growth rates in all the crystal faces were almost the same, so the SrCrO_4 nanospheres can be gained. But, when the concentration of Sr^{2+} and CrO_4^{2-} ions was higher, on the control of the template of squama inner coat of onion, the SrCrO_4 nanospheres first produce, then many nanospheres can assemble in the one-dimensional direction. Therefore, the SrCrO_4 nanorods came into being. This can be supported by figure 10, which shows the SEM micrograph of SrCrO_4 product when the concentration of Sr^{2+} ion and CrO_4^{2-} ion was both 0.4 mol/L and reaction time was 20 h. When the medium reaction solution concentration is selected, on

the control of the template of squama inner coat of onion, the SrCrO_4 little nanospheres first produce, then many of the little nanospheres can assemble in the one-dimensional direction. So, the SrCrO_4 nanowires came into being. Then many SrCrO_4 nanowires can self-assemble and the dumbbell-shaped superstructures are produced. Currently, it should be pointed out that the process remains highly speculative, and the detailed mechanism needs to be further investigated in future work.

4. Conclusions

In this paper, a simple and effective approach has been developed for the preparation of the SrCrO_4 nanorods, nanospheres and dumbbell-shaped superstructure using the bio-template technique, without any surfactants. Because the method is simple, effective, mild and green, it will have potential application in synthesizing the other nanomaterials. However, in order to fully understand the mechanism for the formation of nanomaterials under the control of squama inner coat of onion, more studies will be done in the future.

Acknowledgements

The authors are grateful to the financial support of the National Natural Science Foundation of China (Nos 50772074 and 20571051) and the Nano-Foundation of Shanghai in China (No: 0652nm007).

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