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Synthesis and characterization of manganese oxide and cobalt oxide nano-structure

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Abstract

The preparation of nanostructure type manganese oxide and cobalt oxide materials with the smallest particle size is reported here. The nanorod manganese oxide and cobalt oxide nanotube were prepared via a sol-gel reaction in reverse micelles from $KMnO_4$ and $CoCl_2$ with respectively source at room-temperature. The structure and surface morphology of the obtained manganese oxide were studied by means of X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and transmission electron microscopy.

1. Introduction

In recent years, there has been an increasing interest in developing materials with low dimensional nanostructure such as nanotubes and nanorods due to their potential technological application in nano scale devices. Also, it has been obvious that their properties depend sensitively on their size and shape. Therefore, the challenges in nanocrystal synthesis are to control not only the crystal size but also the shape and morphology [1,2]. In order to produce the desired nanostructural materials, various method have been developed, such as electrodeposition [3, 4], molecular beam epitaxy (MBE) [5], hydrothermal methods [6], chemical reactions [7], homogeneous precipitation

[8], sol–gel [9] and deposition on a support [10]. Cobalt oxide is an important functional material for a wide range of technological applications such as heterogeneous catalysts, anode materials in Li-ion rechargeable batteries, solid-state sensors, magnetism, and optical devices [11–14]. Owing to the influence of particle size and morphology on the properties of materials, the controlled preparation of cobalt oxide particles of different sizes and morphologies is always the researcher's purpose. Up to now, cobalt oxide particles with various morphologies, such as nanotubes [11], nanorods [11], nanosheets [12], hollow nanospheres [13] and nanocubes [14], have been prepared.

Although different morphologies of cobalt oxide nanostructure were synthesized, the preparation methods need either complicated technique or rigorous conditions. Here in, we describe a simple way to generate cobalt oxide nanotubes. In our experiments, cobalt oxide nanotubes are acquired, at nano and micro reverse micelles by using basic cobalt (III) chloride precursor and purified soybean oil as organic phase.

Moreover in this study, manganese oxide nanorods with narrow size distributions and non-aggregation characteristics were prepared by acidic deposition of MnO_x nanoparticles from $KMnO_4$ solution containing Twien 80. Manganese oxides including MnO, MnO_2, Mn_3O_4 and Mn_2O_3 etc. have a wide range of applications such as adsorption, catalysis, batteries and functional materials [15, 16]. Many studies have reported the formation of manganese oxide from the thermal decomposition of $KMnO_4$ [17]. The manganese oxide formed during decomposition of solid $KMnO_4$ in concentrated sulfuric acid has not been characterized due to the abandonment of this reaction because of its explosive nature.

2. Experimental

2.1. Preparation of nanostructured Co_2O_3

$CoCl_2$, NaOH, purified soybean oil, Tween 80 and distilled water were used in the experiments. Nanotube were synthesized by the following steps: 0.30 g of $CoCl_2$ in 1 mL of water and 4% Tween 80 were added into 30 mL of purified soybean oil under mechanical stirrer with 2000 rpm until obtaining a nearly clear emulsion. this solution was referred to as solution A. 0.16 g of NaOH was dissolved into 3.5 mL of water was added into solution A under mechanical stirrer with 2000 rpm for 4 h at 20-25 °C and then the reaction mixture was filtrated. The precipitates were washed and dried.

2.2. Preparation of nanostructured manganese oxide

Tween 80 and distilled water were used in the experiments. Manganese oxide nanorod was synthesized by the following steps: 0.79 g of $KMnO_4$ and 40% Tween 80 were added into 8 mL of water under stirrer until obtaining a nearly clear solution. this solution was referred to as solution A. 1mL of water HCl 8 mmol was added into solution A under stirrer for 10 h at 20-25 °C and then the reaction mixture was dried. The precipitates were reflux with diethyl ether and ethanol for 10 h and 5 h respectively and dried at room temperature.

The powder X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a Cu Kα radiation (λ = 1.54056 Å) with a MINIPROP detector and operating at 40 kV and 40 mA. X-ray diffraction patterns were recorded between 2θ =5° and 79° with a step of 0.04° and a time of 0.8 s by step. The crystallographic data of the resulting Cr_2O_3 powders were collected by using the PC-APD, Diffraction software.

Surface morphologies of the specimens were observed with a scanning electron microscope (SEM, PHILIP XL-30).

3. Results and discussion

Aqueous precipitation is commonly used to synthesize oxides, but the powders with small size obtained by this process are often heavily aggregated. The main reason for the aggregation is caused by the absorbed water and the surface hydroxyl group in the precipitated hydroxide precursors besides the particle aggregation occurring when the precipitated precursors are dried, milled and calcined. In this work, we provide a liquid system to manganese oxide and cobalt oxide nanostructure's synthesis.

$CoCl_2$, NaOH, purified soybean oil, Tween 80 and distilled water were used for precipitation of cobalt oxide nanotubes. Fig.1. shows the scanning electron microscopy (SEM) images of cobalt oxide nanotubes indicating the homogeneous size and high purity of the product. The TEM image of cobalt oxide (Fig. 2) shows that the materials have nanotube like shape. The length of nanotube is 200–550 nm but the average lengths are around 261 nm and the diameters of them are about 58 nm. The synthesized cobalt oxide shows good nanotubes structure and are stable in hydrocarbon solvents against air oxidation.

The phase composition and structure of obtained samples were examined by X-ray powder diffraction (XRD).

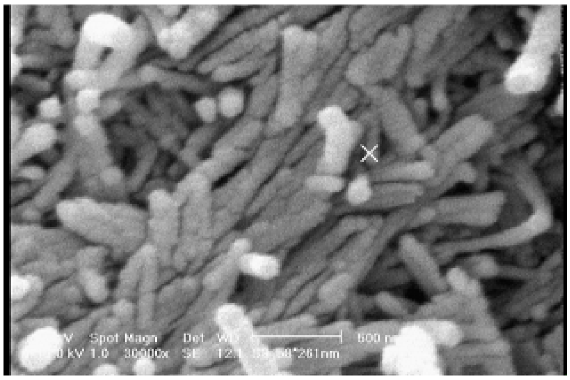

Fig. 1: SEM image of the cobalt oxide nanotube.

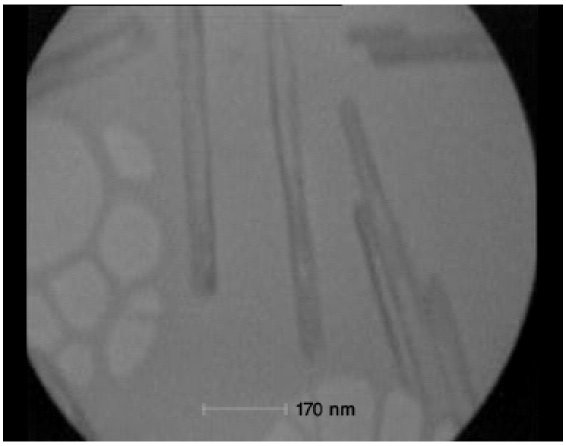

Fig. 2: TEM image of the cobalt oxide nanotube.

The XRD patterns of cobalt oxide nanotubes products are shown in Fig. 3. According to standard Co_3O_4 XRD pattern (JCPDS card no. 43-1003), All the peaks of cobalt oxide can be indexed to cubic phase (Fd 3m). In our case, cobalt oxide formation in this process may proceed through two steps. Firstly, $Co(OH)_2$ is formed in aqueous solution when $CoCl_2$ is dissolved in H_2O, and a fraction of $Co(OH)_2$ is oxidated to $Co(OH)_3$ by the oxygen in the environment. Secondly, $Co(OH)_2$ and $Co(OH)_3$ deposit with each other in the basic conditions and then cobalt oxide nanostructures are obtained. This process is presented as chemical equations as follows:

$$CoCl_2 \xrightarrow{H_2O} Co(OH)_2 \xrightarrow[H_2O]{O_2} Co(OH)_3$$

$$4\,Co(OH)_3 + 2\,Co(OH)_2 \xrightarrow{NaOH} 2Co_3O_4 + 8H_2O$$

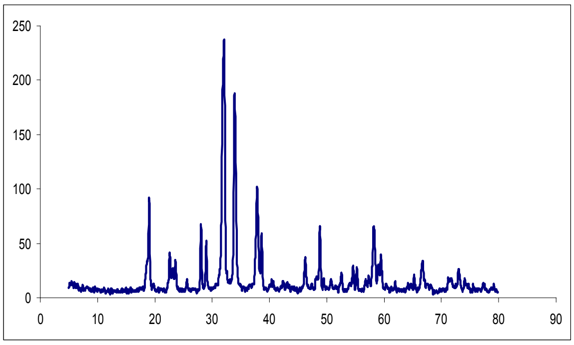

Fig. 3: XRD pattern of the cobalt oxide nanotube.

Fig. 4 shows the TEM images of the manganese oxide formed under deposition conditions. The linear structure of each particle is nanorod (diameter: ca10–15 nm, length: 60–90 nm).

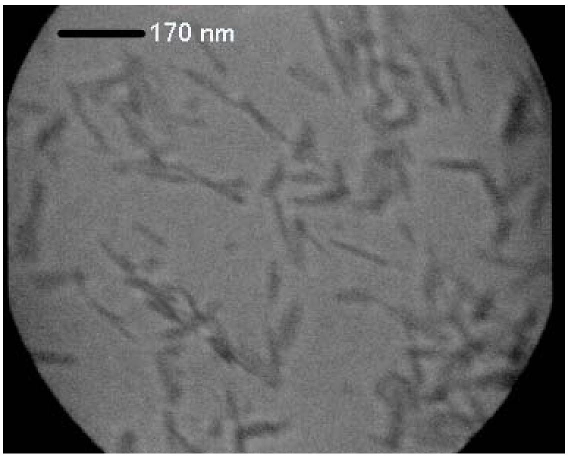

Fig. 4: TEM image of the manganese oxide nanorod.

The synthesis of nano manganese oxide was carried out with the concurrent addition of KMnO4 and 40% Tween 80 and increasing the stirring time, to prevent excessive grain growth and aggregation of nanoparticles. This is a multi-step process that involves the transformation of the $KMnO_4$ to $Mn(OH)_7$ followed by the dehydration to form Mn_2O_7 intermediate. Mn_2O_7 decomposes and products are amorphous manganese oxide phase (The XRD spectra of powders are shown in Fig. 5) reaction is shown below:

$$2KMnO_4 + 2HCl \rightarrow Mn_2O_7 + H_2O + 2KCl$$
$$Mn_2O_7 \rightarrow \text{Decomposes to } MnO_X$$

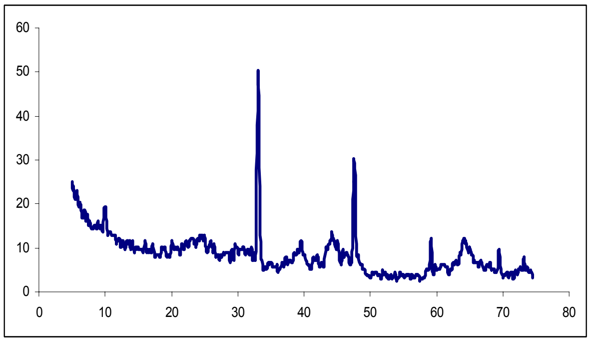

Fig. 5: XRD pattern of the manganese oxide nanorod.

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