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Original Article

Synthesis and Characterization of Co_3O_4 Nanotubes to Prepare Variety of Electrochemical Biosensors

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Abstract

Cobalt (II) Chloride was used as a precursor to prepare Co_3O_4 nanotubes in reverse micelles. Tween 80 was added as surfactant. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy. The diameter of Co_3O_4 nanotubes was about 58 nm and the average length of them was around 261 nm. The study provides a simple and efficient route to synthesize Co_3O_4 nanotubes at room temperature. Tremendous demands for electrochemical biosensors with high sensitivity and reliability, fast response and excellent selectivity have stimulated intensive research on developing versatile materials with ultrahigh electrocatalytic activity.

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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]. Co_3O_4 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 Co_3O_4 particles of different sizes and morphologies is always the researcher's purpose. Up to now, Co_3O_4 particles with various morphologies, such as nanotubes and nanorods [11], nanosheets [12], hollow nanospheres [13] and nanocubes [14], have been prepared.

Although different morphologies of Co_3O_4 nanostructure were synthesized, the preparation methods need either complicated technique or rigorous conditions. Here in, we describe a simple way to generate Co_3O_4 nanotubes. In our experiments, Co_3O_4 nanotubes are acquired, at nano and micro reverse micelles by using basic cobalt (II) chloride precursor and purified soybean oil as organic phase. Electrochemical biosensors, which have been widely employed in clinical, environmental, industrial and agricultural applications, recognize biological analytes through a catalytic or binding event occurring at the interface of electrodes [15–20].

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic head regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre. This phase is caused by the packing behavior of single-tail lipids in a bilayer. The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle. This type of micelle is known as a reverse micelle.

The shape and size of a micelle are a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength.

In this article, we describe the use of organic anionic surfactants that stabilize reverse (water-in-oil) micelles containing transition metal water-soluble salts. The particles obtained by reactions of the reverse micelles at room temperature are evaluated as active variety of electrochemical biosensors.

Materials and Methods

Chemicals and apparatus

All Chemical reagents ($CoCl_2$, NaOH, Tween 80) and solvents in high purity were purchased from the Merck Chemical Company. All materials were commercial reagent grade and used without further purification. The purity determination of the substrates and reaction monitoring were accomplished by thin layer chromatography (TLC) on silica gel polygram SILG/UV 254 plates. Scanning electron microscope (SEM) was performed with a PHILIP XL-30, operated at 30 KV. Transmission electron microscopy (TEM) was performed with ZeissEM10C-80 KV, operated at 80 KV. X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a Cu Kα radiation (λ = 1.54056 A°) with a MINIPROP detector and operating at 40 kV and 40 mA.

Preparation of nanotube

$CoCl_2$, NaOH, purified soybean oil, Tween 80 and distilled water were used in the experiments. Nanotubes 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 dissolved into 1.5 ml of water was added into solution A under mechanical stirrer with 2000 rpm for 2 h at room temperature and then the reaction mixture was filtrated. The precipitate was washed with absolute water (300 ml) for 3 times. This material was calcinated in electronic oven at 200 °C for 1 h. The resulting powder X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a Cu Kα radiation (λ = 1.54056 A°) with a MINIPROP detector and operating at 40 kV and 40 mA. X-ray diffraction patterns were recorded between $2\theta = 5^{\circ}$ and 79° with a step of 0.04° and a time of 0.8 s by step. The crystallographic data of the resulting Co_3O_4 powders were collected by using the PC-APD, Diffraction software. Surface morphologies of the specimens were observed with a scanning electron microscope (SEM, Philips XL-30). The ordered nano structures of Co_3O_4 can be further confirmed by transmission electron microscope (TEM, Philips KV-120).

Results

Figure 1 shows the scanning electron microscopy (SEM) images of Co_3O_4 nanotubes indicating the homogeneous size and high purity of the product. This some nanotubes which were broken during the SEM sample preparation can be seen and they are straight and uniform along their lengths. The nanotubes are arranged in a parallel and well-ordered way. The morphology and structure of individual Co_3O_4 nanotubes have been characterized in further detail using transmission electron microscopy (TEM). The TEM image of Co_3O_4 (Fig. 2) shows that the materials have single nanotube like shape. The length of nanotubes is 200–550 nm but the average lengths is 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. It can be seen that the nanotube is straight and uniform along its whole length. The outer diameter and wall thickness of the nanotube are about 261 and 10 nm, respectively. Figure 3 shows a typical XRD pattern of the Co_3O_4 nanotube. All diffraction peaks can be indexed as cubic structure Co_3O_4 with lattice constant of a = 8.08 Å, which is consistent with the standard value for bulk Co_3O_4 (JCPDS 9-418). Using the Scherrer equation, the average sizes of the nanoparticles composing the nanotubes were roughly estimated to be 280 nm. The phase composition and structure of obtained samples were examined by X-ray powder diffraction (XRD). 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 (Fig. 3).

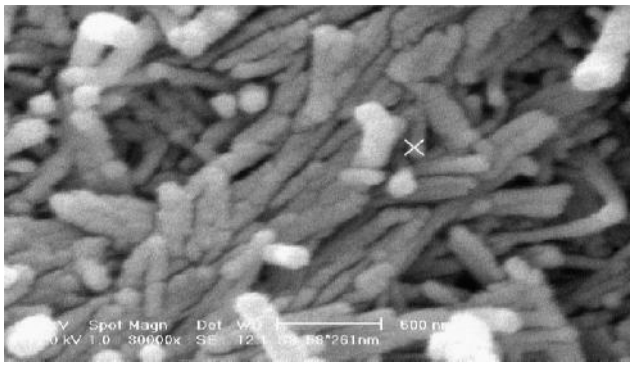

Figure 1. SEM image of the Co_3O_4 nanotube

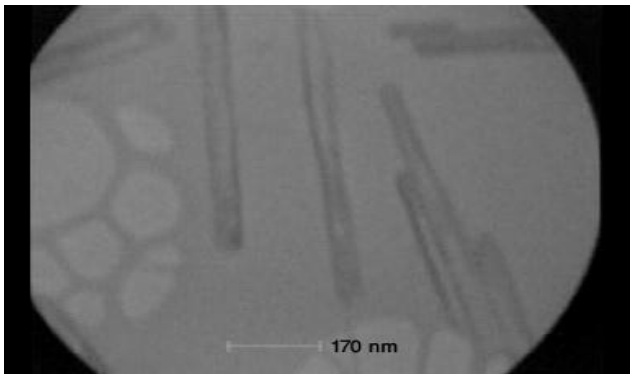

Figure 2. TEM image of the Co_3O_4 nanotube

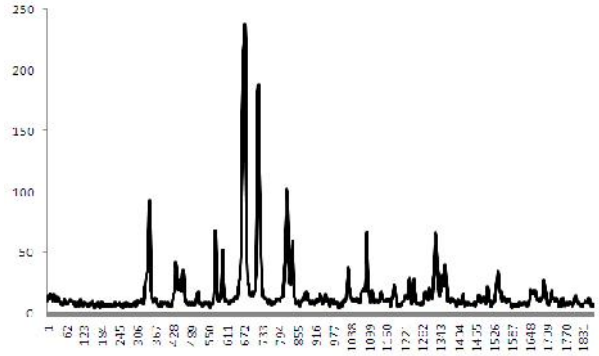

Figure 3: XRD pattern of the Co_3O_4 nanotube

Discussion

In our case, Co_3O_4 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 oxidized 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 Co_3O_4 nanostructures are obtained. This process is presented as chemical equations as follows.

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

$$\left.\begin{matrix} 4\,Co(OH)_3 \\ 2\,Co(OH)_2 \end{matrix}\right\} \xrightarrow{NaOH} 2Co_3O_4 + 8H_2O$$

.

Conclusion

We have described the use of an inorganic phase in water-in-oil (w/o) microemulsion that has received considerable attention for preparing cobalt oxide nanotubes via a sol-gel reaction in reverse micelles from $CoCl_2$ source at room-temperature. The nanotubes with diameters of 58 nm and lengths of 261 nm have been characterized by SEM, TEM and the XRD. In addition, the easily controllable conditions with using low cost cobalt source is merit to be considered for scaling up by industrial researchers.

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