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Short communication

Biomolecule-assisted synthesis of cobalt sulfide nanowires for application in supercapacitors

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Abstract

A biomolecule-assisted hydrothermal process is developed to synthesize cobalt sulfide (CoS), in which L-cysteine is used as the sulfide source and directing molecule. By controlling the synthesis conditions, CoS nanospheres and nanowires can be assembled. The as-synthesized samples are characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are used to study the effects of microstructure and morphology of the samples on their capacitance and conductivity. A specific capacitance, as high as 508 F g^{-1}, is achieved for CoS nanowires. This is very competitive with the best supercapacitor material, RuO_2 (720–760 F g^{-1}), but its cost is remarkably lower than RuO_2. Thus the nanowires are a promising material for low-cost, high-performance supercapacitors. This method could provide a universal green chemistry approach to synthesize other metal sulfides.

Keywords: Supercapacitor; Cobalt sulfide; Hydrothermal synthesis; Biomolecule; Nanowire

1. Introduction

Due to concerns over environmental pollution and the depletion of fossil fuels, the development of alternative energy conversion/storage systems with high specific power and energy is of great importance. Among the different technologies, electrochemical capacitors (ECs) or supercapacitors (SCs) that have higher specific power and longer cycle-life than secondary batteries and higher specific energy than conventional electrical double-layer capacitors are attracting much attention [1]. The supercapacitors are being developed for a variety of applications such as mobile electronic devices, back-up power supplies, and hybrid electric vehicles [1–3]. Prototypes made with hydrous ruthenium oxide (RuO_2) exhibit the highest specific capacitance, i.e., 720–760 F g^{-1}, and such performance has enhanced the research and development of ECs [4,5]. Unfortunately, the high cost of RuO_2 greatly limits its commercialization. Hence, extensive studies have been conducted to explore alternative, economic supercapacitor materials.

In the last few years, nanostructured metal sulfides have been investigated as a new type of energy storage materials and have achieved good performance, of which sponge-like Ni_3S_2 [6] and 'flower-like' Bi_2S_3 [7] demonstrate their hydrogen storage capability, while ZnS [8] and CoS nanoparticles [9,10] are used in ECs or rechargeable lithium batteries. Nevertheless, the synthesis of one-dimensional metal sulfide nanomaterials requires expensive and toxic organic agents, as well as high reaction temperatures, and produces pungent H_2S from the sulfur sources used (thioactamide, thiourea, sodium thiosulfate, Na_2S or H_2S) [6,7]. A new, environment-friendly, biomolecule-assisted synthesis method, a green chemistry approach, has recently been developed to produce different sulfur-based nanomaterials, such as ZnS and Bi_2S_3 [7,11–14].

In the work reported here, a simple and efficient biomolecule-assisted hydrothermal process is developed to produce cobalt sulfide (CoS) for the first time. This method is used not only to fabricate nano-CoS, but also to tailor its nanostructure for superior physical and chemical properties. Different nanostruc-

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tured CoS can be produced simply by altering the polarity of the precursor solution through addition of ethanol. The possible formation mechanisms of CoS under different conditions are proposed. The electrochemical properties of different nanostructured CoS materials are studied systematically for their use as EC electrodes. It is discovered that the morphology has a remarkable effect on the capacitive behaviour of the samples, among which CoS nanowires provide good conductivity and large capacitance.

2. Experimental

2.1. Material preparation

All chemical reagents were analytical grade and used as-received. The synthesis was performed via a simple hydrothermal process, in which 3 mmol L-cysteine was dissolved in 45 mL de-ionized water and 3 mmol $CoCl_2 \cdot 6H_2O$ was dissolved in 45 mL de-ionized water or ethanol, respectively. Then the $CoCl_2$ solution was added to the L-cysteine solution with constant and vigorous stirring. After 15 min, the resulting mixture was transferred into a Teflon-lined stainless-steel autoclave, that was then sealed and maintained at 190 °C for 6 h followed by cooling down to room temperature. The prepared products were washed three-times with de-ionized water and ethanol, respectively, followed by drying in a vacuum oven at 50 °C for overnight.

2.2. Material characterization

The crystal structure of the product was characterized by X-ray diffraction (XRD, Bruker AXS X-ray diffractmeter). The morphology and microstructure of the synthesized materials were examined by field-emission scanning electron microscopy (FESEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, Hitachi 600, Japan).

2.3. Electrochemical measurements

The working electrodes of the ECs were fabricated by mixing the prepared powder with 15 wt.% acetylene black and 5 wt.% polytetrafluorene-ethylene (PTFE) binder. A small amount of distilled water was added to the mixture to produce a more homogeneous paste. The mixture was pressed on to nickel foam current-collectors (1.0 cm × 1.0 cm) to make electrodes. Before the electrochemical test, the prepared electrode was soaked overnight in 3 M KOH solution. Electrochemical characterization was carried out in a conventional three-electrode cell with 3 M KOH as the electrolyte. Platinum foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All electrochemical measurements were conducted with a CHI 660 electrochemical workstation (CH Instruments Inc., Texas, USA).

3. Results and discussion

3.1. Characterization of materials

The synthesized new materials were first examined by XRD. As shown in Fig. 1, all of the diffraction peaks for both samples synthesized from different solutions can be indexed to a hexagonal phase of CoS, which is well-matched with its standard XRD pattern (ICSD No. 029305). No impurity peaks are observed, which indicates that pure CoS is produced by the biomolecule-assisted hydrothermal method in different solutions.

The prepared products were examined further by FESEM. As shown in Fig. 2, the microstructure and morphology of the products synthesized with different conditions is very distinctive, of which the CoS obtained from aqueous solution is uniform spheres (Fig. 2a) constructed by interleaving rice-like rods (Fig. 2b). Interesting morphology and microstructures are illustrated in Fig. 2c and d, in which the low-magnification FESEM images (Fig. 2c) show that the material formed in the ethanol aqueous solution is produced as nanowires. The higher magnification FESEM image in Fig. 2d reveals its detailed nanostructure, in which the CoS nanowires are shown to consist of many interconnected, small, flower-like particles formed by interleaving nanoflakes.

TEM was employed to study the synthesized products, which were dispersed completely using sonication for 1 h in ethanol prior to examination. CoS made from the aqueous solution (Fig. 3a) is seen to be composed of small particles, while CoS synthesized from ethanol aqueous solution (Fig. 3b) has a nanowire structure even after sonication. The results are in agreement with the SEM images.

3.2. Formation mechanism of different structured CoS

On the basis of the FESEM and TEM analyses, a possible mechanism is proposed to explain the formation of different nanostructured CoS. Functional groups, such as $-NH_2$, $-COOH$ and $-SH$ of the L-cysteine molecule, have a strong tendency to coordinate with inorganic cations and metals, as demon-

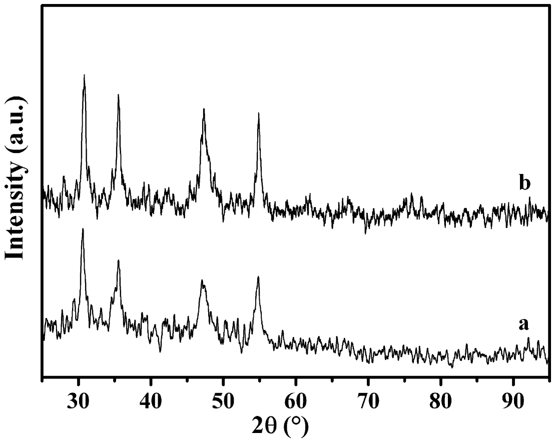

Fig. 1. XRD patterns for (a) sample obtained in aqueous solution and (b) sample obtained by ethanol aqueous solution.