



Rapid synthesis of three-dimensional flower-like cobalt sulfide hierarchitectures by microwave assisted heating method for high-performance supercapacitors



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ABSTRACT

In this study, a novel facile and rapid method to prepare three-dimensional (3D) flower-like CoS hierarchitectures by microwave assisted heating has been developed. The 3D flower-like CoS architectures are constructed by two-dimensional nanopetals intertwined with each other and the formation mechanism are studied. The pseudo-capacitive properties of the CoS material are evaluated by cyclic voltammetry and galvanostatic charge-discharge tests in 6 M KOH solution. A specific capacitance of 586 F g⁻¹ is obtained at a charge-discharge current density of 1 A g⁻¹. The CoS nanostructure exhibits excellent cycling stability and it maintains 91% of its initial specific capacitance after 1000 cycles. It also exhibits excellent rate capability, improved energy density and power density.

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1. Introduction

Electrochemical capacitors (ECs), also called ultracapacitors or supercapacitors, have attracted intense attention due to their features of high specific power density, fast charge and discharge rates, long durability, and environmental friendliness [1–3]. To date, ECs have been developed for a variety of applications such as mobile electronic devices, back-up power supplies, and hybrid electric vehicles. ECs can be classified into two types based on their charge-storage mechanism, electrical double-layer capacitors dominated by electrostatic charge diffusion and accumulation at the interface of the electrode/electrolyte and pseudocapacitors governed by Faradaic reactions at the electrode materials [4–6]. The most widely investigated metal oxide for pseudocapacitors is unequivocally RuO₂, which displays a fairly high specific capacitance, good electronic conductivity, and high electrochemical stability [7,8]. However, the high cost and toxic nature of RuO₂ has prompted the search for other transition metal oxides/hydroxides, such as Co₃O₄ [9,10], NiO [11–13], MnO₂ [14,15], Co(OH)₂ [16,17], Ni(OH)₂ [18–22], etc. Compared with these widely used electrode materials, some metal sulfides are receiving increasing attention as

supercapacitor electrode materials in view of their interesting intrinsic properties and excellent performance [23,24].

As an important class of transition metal chalcogenides, cobalt sulfides exist in several phases, such as Co₄S₃, Co₉S₈, CoS, Co_{1-x}S, Co₃S₄, Co₂S₃, and CoS₂. Cobalt sulfides are versatile materials with potential applications in supercapacitors [25–31], lithium-ion batteries [32–34], alkaline rechargeable batteries [35], magnetic materials [36], solar cells [37,38] and catalysts [39]. Up to now, different CoS nanostructures have been reported. However, the controlled synthesis of CoS with high purity and well-defined complex morphology without templates or surfactants still faces grand challenges. First, other complicated phases are easy to form because cobalt sulfides have a number of chemical compositions. Second, cobalt oxide or cobalt hydroxide impurities are hard to remove because cobalt ion has a very strong affinity to oxygen. Third, reaction temperature is hard to control because cobalt sulfides possess a complicated phase diagram.

Microwave assisted heating (MWH) is a promising preparation method because the microwave synthesis process is of fast heating and high reaction rate, and capable of saving energy and dramatically reducing reaction time, and thus can lower the cost of final products. Besides, MWH also has many other unique advantages, such as the high penetration depth of microwave, homogeneous volumetric heating, and high selectivity. Due to these advantages, MWH has aroused extensive enthusiasm in the synthesis of various inorganic/organic materials [40–42]. In this work, we report a facile

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and large-scale production strategy for the synthesis of high purity and three-dimensional (3D) flower-like CoS hierarchitectures using nickel nitrate hexahydrate, citric acid and thioacetamide in ethylene glycol solution, assisted with MWH. It was found that the electrode based on CoS in alkaline solution could display excellent electrochemical behavior with a specific capacitance of 586 F g^{-1} at 1 A g^{-1} and still maintained 91% of initial specific capacitance after 1000 charging-discharging cycles.

2. Experimental

2.1. Preparation of 3D flower-like CoS hierarchitectures

All of the chemicals were of analytical grade and used without further purification. The 3D flower-like CoS hierarchitectures were prepared by a facile and rapid MWH method. In a typical procedure, 5 mmol nickel nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 5 mmol citric acid (H_3Cit) and 15 mmol thioacetamide (CH_3CSNH_2) were added to 50 mL ethylene glycol (EG) solution. Stirred for a while, the solution was treated in the microwave oven and the reaction was conducted for 5 min at 700 W. At the end of the reaction, the black precipitates were collected and washed with distilled water and absolute ethanol to remove the residues, and then the final products were dried in vacuum at 50°C for overnight.

2.2. Characterization of the 3D flower-like CoS hierarchitectures

The crystal structures of CoS were analyzed by a Tongda TD-3500 X-ray powder diffractometer (Liaoning, China) with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15148 \text{ nm}$) operating at 30.0 kV and 20.0 mA. Field emission scanning electron microscopy (FESEM) images and energy dispersive spectra (EDS) were obtained from a Hitachi S4800 scanning electron microscope (Tokyo, Japan). Transmission electron microscopy (TEM) studies were conducted using a Hitachi H-800 microscope operated at 200.0 kV. The X-ray photoelectron spectra (XPS) were acquired on a Kratos XSAM 800 spectrometer (Manchester, U.K.) with a $\text{Mg-K}\alpha$ X-ray (1253.6 eV) excitation source running at 15.0 kV, a hemi-spherical electron energy analyzer and a multichannel detector.

2.3. Preparation of the electrodes and electrochemical measurement

To evaluate the electrochemical properties of the resultant CoS material, working electrodes were prepared as follows. CoS, acetylene black as the conducting material, and poly (vinylidene fluoride) as the binder, were mixed in a weight ratio of 80: 15: 5 to yield a paste. N-Methyl-2-pyrrolidone (NMP) was used as the solvent. The slurry was loaded onto the nickel foam substrate (surface, $1.0 \text{ cm} \times 1.0 \text{ cm}$) with a spatula, and followed by pressing under a pressure of 10 MPa. The CoS-modified electrode was dried at 60°C for 12 h in a vacuum oven. The mass loading of active materials was between $2.0\text{--}3.0 \text{ mg cm}^{-2}$ on Ni foam substrate.

Cyclic voltammetry (CV) and galvanostatic charge/discharge tests were performed on an Autolab PGSTAT 302 electrochemical workstation (Eco Chemie B.V., Amsterdam, the Netherlands) using a conventional three-electrode system with the CoS-modified electrode, a graphite sheet ($1 \text{ cm} \times 1 \text{ cm}$) and a Hg/HgO (1.0 M NaOH) electrode as the working, counter and reference electrodes, respectively. EIS measurements of the working electrode were carried out in a frequency range 100 kHz–10 mHz at open circuit potential with an ac perturbation of 10 mV. All measurements were performed using 6 M KOH as the electrolyte.

3. Results and discussion

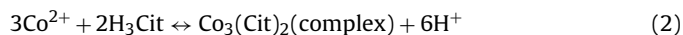
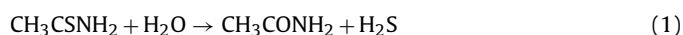
3.1. Characterization of 3D flower-like CoS hierarchitectures

Typical 3D flowerlike CoS hierarchitectures are displayed in Fig. 1. As the XRD pattern revealed in Fig. 1a, the diffraction peaks at $2\theta = 30.6^\circ, 35.3^\circ, 47.0^\circ, 54.4^\circ$ and 74.7° correspond to the respective (100), (101), (102), (110) and (202) planes of the hexagonal CoS phase (JCPDS card No. 65-8977). No characteristic peaks from other phases were detected, indicating the high purity of the products. Fig. 1b displays the EDS of the CoS material, which shows only the Co and S elements. This result is in accordance with the XRD. The SEM image shown in Fig. 1c reveals that the as-prepared CoS product is composed of flower-like microspheres with a mean diameter of 600 nm. It is clearly observed that these 3D flower-like architectures are constructed by two-dimensional (2D) nanopetals intertwined with each other, and the 2D nanopetals thickness is as thin as ca. 50–60 nm. Furthermore, the morphology and structure of the CoS material were further characterized with TEM techniques. As shown in Fig. 1d, the TEM image reveals that the as-obtained sample exhibits some apparent nanoplates in the surface of the microspheres. The internal cross-linked structure of the nanopetals would effectively maintain the long-standing existence of the architectures. It was found that the flowerlike hierarchitectures tend to cluster in groups in the TEM image, which confirmed the image of SEM.

To further identify the chemical composition of the as-prepared CoS product, XPS measurements were carried out. As shown in the $\text{Co } 2p$ spectrum (Fig. 2a), the main peak located at the lower binding energy value (777.9 eV) and a shake-up feature at higher binding energies can be assigned to Co^{2+} in CoS according to the literature [27]. Furthermore, Fig. 2b shows that the binding energy value of $\text{S } 2p$ in the product is around 162.5 eV, indicating that most of the S species exist as S^{2-} in the product. There is also a peak at 168.5 eV for O impurity [27], due to the surface absorption of the samples exposed to air during processing. These results indicate most definitely that CoS composed of interlaced nanosheets was successfully synthesized via the facile MWH method.

3.2. Formation mechanism of 3D flower-like CoS hierarchitectures

In order to investigate the evolution of the 3D flower-like CoS architecture, a series of time-dependent experiments were carried out, during which samples were collected at different time intervals (2 min, 3 min, and 5 min). As we known, Co^{2+} could react with H_3Cit to form a $\text{Co}_3(\text{Cit})_2$ complex. Meanwhile, H_2S is released gradually, as the decomposition product of thioacetamide with increasing temperature. Then, the $\text{Co}_3(\text{Cit})_2$ complex and H_2S react to form the CoS original nucleus, which can be expressed as:



at the initial stage, thioacetamide, as the water-soluble sulfur source whose C=S bonds are easily attacked by oxygen atoms of H_2O , can release H_2S slowly. The relatively free H_2S can react with the vicinal $\text{Co}_3(\text{Cit})_2$ complex to form numerous tiny CoS crystalline nuclei. With the reaction proceeding, these tiny nuclei grow larger so that the particles with different sizes appear in the solution. Driven by the minimization of surface free energies, the larger particles grow at the cost of the smaller ones, based on a typical Ostwald ripening process [43]. In the subsequent process, the primary particles diffuse and aggregate together to form solid microspheres and

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