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ScienceDirect

Cite this article as: New Carbon Materials, 2016, 31(3): 336-342

RESEARCH PAPER

A hierarchically porous CuCo$_2$S$_4$/graphene composite as an electrode material for supercapacitors

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Abstract: A CuCo$_2$S$_4$/graphene composite was synthesized using a simple hydrothermal method. The sample was characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction, nitrogen adsorption and electrochemical tests. The composite had a hierarchical porous structure with micropores of 0.7-1.2 nm, mesopores of 2-10 nm and a total pore volume of 0.1 cm$^3 \cdot$g^{-1}, and the CuCo$_2$S$_4$ had a nano-belt structure. As the electrode of a supercapacitor the composite showed a high specific capacitance of 665 F/g at 7.5 mV/s, and excellent rate capability and cycling stability.

Key Words: Graphene; Metal sulfide; Composite; Micropore; Mesopore; Supercapacitor

1 Introduction

Supercapacitors (SCs), a class of energy storage devices, can store a large amount of energy and then release when it is needed by a faradaic and non faradaic electrochemical reactions. They have attracted great attention owing to their fast charging–discharging rates, high power density and long cycle lifespan, high reliability and low cost[1-3]. They are promising in the areas of uninterruptible power supplies, hybrid electric vehicles, aerospace, emergency lighting and renewable energies[4-8]. Generally, SCs are classified into two types based on the charge storage mechanisms, non-Faradaic double layer capacitors (EDLCs) or reversible Faradaic redox electrochemical capacitors (pseudocapacitors) [9-10]. The pseudocapacitors with metal oxides, metal sulfides and conductive polymers as active materials can provide much higher specific capacitance and higher energy density than EDLCs, attracting widespread attentions[11-13].

Transition-metal oxides, hydroxides, and conducting polymers are applied in supercapacitors with their pseudocapacitive properties[14-18]. More recently, metal sulfides have attracted extensive attention owing to their high specific capacitance, low cost, safety and environment benignity and high electrochemical activity. They have the very potential applications such as catalysis, sensors, solar energy and batteries[19-28]. However, most of metal sulfides posses low electronic conductivity and undergo a large volume change during repetitive cycling. To overcome these problems, one of most effective way is to combine metal sulfides with carbon matrix[29].

In carbon-based composite electrodes, two dimensional (2-D) graphene (GR) is flexible to integrate with metal compounds. GR nanomaterials serve as the conductive support to prevent electroactive nanomaterials from agglomerating. Moreover the notable synergistic effect between the graphene and electroactive nanomaterials can improve the diffusion rate of ions, leading to a high specific capacitance and rate capability[30]. Thus, efforts have been devoted to GR-based electrode materials of SCs.

Because of the richer redox reactions and high conductivity of GR based metal sulfide than the mono-metal sulfide, there are numerous research studies concerning the preparation of ternary compounds for supercapacitors[31-33]. A combination of the metal sulfides and graphene synergizes the electrochemical properties of the ternary metal sulfide/graphene composite. Therefore, it is of significant importance and challenging to exploit multi-component materials for SCs[34]. Several metal sulfides were synthesized by a hydrothermal anion-exchange reaction method[35]. However, this anion exchange method is difficult to control the nanostructure because the uncontrollable exchange reaction dislocates the crystal growing significantly. Here we proposed a method to control the nanostructure and synthesized a uniform nano-belt- like nanocomposites.

Among metal sulfides, a few researches reported on the synthesis of copper and cobalt-based sulfide nanomaterials recently. Moosavifard et al. prepared Ni-foam templated nanoneedle array[36]. Shen et al. fabricated three dimensional nanocomposite with graphene and CNTs[37]. It is necessary to

DOI: 10.1016/S1872-5805(16)60017-3

explore their properties for capacitive performance. In this work, we prepared nanoporous $CuCo_2S_4$/rGO nanocomposite with a nano-belt structure by a facile hydrothermal method and used the material as supercapacitor electrode. Electrochemical tests showed that the $CuCo_2S_4$/rGO electrode had a maximum specific capacitance of 525 F·g^{-1} at 1 A·g^{-1} and a capacitance retention of 58% at 20 A·g^{-1}. A capacitance retention of 83% after 1000 charge–discharge cycles at 4 A·g^{-1} indicated their excellent cycling stability. The hierarchically nanoporous structure of the $CuCo_2S_4$/rGO nanocomposites would be advantageous for such an excellent electrochemical performance.

2 Experimental

2.1 Materials and reagents

Co(acetate)·4H$_2$O, Cu(acetate)·H$_2$O, Sodium carbonate (Na$_2$CO$_3$), Na$_2$S·9H$_2$O, potassium hydroxide(KOH), N-methyl-2-pyrrolidone (NMP) and polyvinylidene fluoride (PVDF) were purchased from Aladdin, China. Trimethylamine (TMA) was purchased from Sinopharm Co., Ltd in analytical grade. All chemcals were used without further purification. Distilled water was used in this work.

2.2 Preparation of CuCo₂S₄/rGO nanocomposite

$CuCo_2S_4$/rGO nanocomposites were prepared by a hydrothermal synthesis method as follows. Graphene oxide (GO) was synthesized from graphite powder by the improved Hummers'method[38,39]. 3 mg·mL^{-1} GO was dispersed in 15 mL distilled water by sonication for 3 h to obtain a homogeneous dispersion. 5 mM of Cu(acetate)·H$_2$O and 10 mM of Co(acetate)·4H$_2$O were dissolved in 15 mL ethanol. The above metal ion solution was slowly dropped into the GO dispersion under vigorous stirring. Then 68 mM Na$_2$CO$_3$ and 1.5 mL TMA were added drop wise into the above solution and stirred for 1 h at room temperature. The reaction mixture was transferred into a Teflon-lined autoclave and heated to 453 K for 12 h. After cooled down to room temperature, the composite precursors were obtained by washing with distilled water and ethanol separately, dried at 313 K and annealed at 573 k for 3 h in air. The annealed composites were dispersed in water at a concentration of 1 mg·mL^{-1} and Na$_2$S·9H$_2$O water solution was added under stirring. The mixture was then treated at 453 K for 6 h in the autoclave. The product was

washed with water, ethanol and dried at 313K to obtain the $CuCo_2S_4$/rGO nanocomposite.

2.3 Characterization

The field emission scanning electron micrographs (FE-SEM) of the sample was obtained by a JSM-6700 (JEOL) scanning electron microscope, operating at 5 kV. Transmission electron micrographs (TEM) were obtained on a TecnaiF20 (Philips) transmission electron microscope, operating at 100 kV. Before the test, sample was dispersed in ethanol and placed in TEM grid. The powder X-ray diffraction (XRD) patterns were obtained on a M18XHF X-ray automatic diffractometer (MacScience) using a monochromatized X-ray 25 beam from nickel-filtered Cu $K\alpha$ (λ=0.154050 nm) radiation and operated at 50 kV and 250 mA from 10-70° at 0.2 °/min. The nitrogen adsorption isotherms were measured at 77 K using a ASAP2020 (Micromeritics) gas adsorption analyzer. The samples were evacuated at 10^{-4} Pa and 393 K for 2 h before the measurement.

To test the electrochemical performance of the $CuCo_2S_4$/rGO nanocomposite, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) were conducted in 3M KOH between the potential range of 0.01 to 0.6 V with a conventional three-electrode cell using a CHI 660E electrochemical workstation (Shanghai CH Instruments, China). Active material and polyvinylidene difluoride (PVDF) binder were uniformly mixed in the weight ratio of 80:10 and made as a slurry using N-methyl 2-pyrrollidone. The slurry was coated on 1 cm^2×1 cm^2 Ni-foam, dried in vacuum oven at 343 K overnight and then pressed under 5 MPa. As-prepared active material electrode, Hg/HgO electrode, and a platinum electrode were used as the working electrode, reference electrode and counter electrode, respectively.

The capacitance of the electrode can be evaluated according to the following equations:

$$C_s=[(\int IdV)/2(S*\Delta V*m)]$$

$$C_p = I\,\Delta t/m\,\Delta v$$

Where both C_s and C_p (F·g^{-1}) are the specific capacitance, $\int IdV$ is the area under the CV curve, I (A) is the current during the discharge process, Δt (s) is the discharge time, ΔV (V) is the potential window and m (g) is the mass of the active materials. S (mV·s^{-1}) is the scan rate.
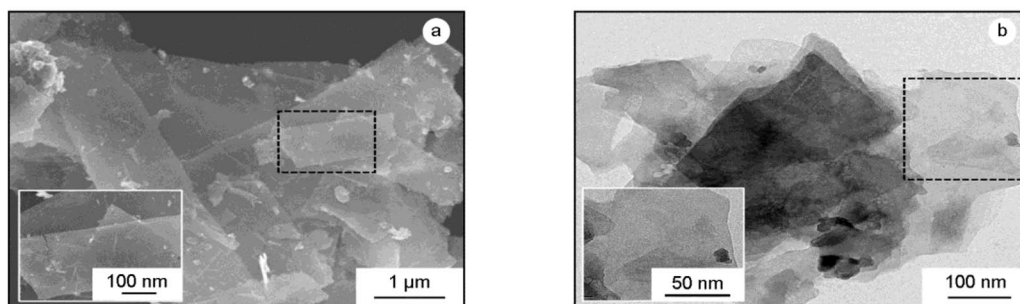

Fig. 1 (a) FE-SEM image and (b) TEM image of the $CuCo_2S_4$/rGO composite. Insets in (a) and (b) are the high magnification images of dotted line in the corresponding images.