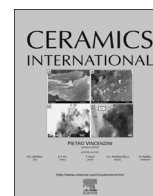




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Synthesis of hierarchical carbon sphere@NiMoO₄ composite materials for supercapacitor electrodes



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ABSTRACT

In this work, hierarchical Carbon sphere@NiMoO₄ (C@NiMoO₄) composite was successfully synthesized by cost-effective two-step hydrothermal method. The samples were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction analysis and Thermogravimetric analysis. The Electrochemical measurement demonstrated that hierarchical C@NiMoO₄ electrode materials exhibited good specific capacitance (Csp) of 268.8 F g⁻¹ at a current density of 1 A g⁻¹ in 2 M NaOH aqueous electrolyte solution, as well as good cycling stability (88.4% retention after 2000 cycles). Compared to pure NiMoO₄, the excellent capacitive properties and stability suggest that the hierarchical structure C@NiMoO₄ could be promising electroactive material for supercapacitors.

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1. Introduction

Supercapacitors, also named as electrochemical capacitors (ECs) or ultra-capacitors, are widely recognized as promising energy storage devices due to their excellent specific capacitance, high power density, long cycle life, environmental friendliness, safety [1]. In term of storage mechanisms, supercapacitors can be classified as two categories: electrical double layer capacitors (EDLCs) and pseudocapacitors [2]. The EDLCs, usually depended on the porous carbon materials, have been widely applied in different fields, but usually restricted by the limited effective surface area of active materials, which eventually suffer from poor capacitance performance [3]. Pseudocapacitors are dominated by reversible Faradaic reactions on the surface of electrode materials. Compared with EDLCs, pseudocapacitors present better specific capacitances and higher energy density, but usually suffer from poor rate capacity and low cycling stability because of inherently slow reaction kinetics and terrible volume expansion during charge-discharge process [4]. Recently, hybrid nanomaterials for supercapacitors have been an intense exploration trend in view of their synergistic reaction [5–7].

To date, binary metal oxides, such as NiMoO₄, CoMoO₄, and MnCo₂O₄, combine the advantages of different metal cations and possess higher electrochemical activity, which have been widely investigated [8–10]. Among these candidates, NiMoO₄ is a particularly promising electrode material due to its extremely high

redox activity and low cost [11,12]. For instance, Seyyed Ebrahim Moosavifard et al. synthesized 3D ordered porous NiMoO₄, which features specific capacitance of 4.25 F cm⁻² at 3 mA cm⁻² [13]. Ghosh et al. reported one dimensional NiMoO₄ nanorods synthesized by hydrothermal method could deliver a specific capacitance of 161 F g⁻¹ at a current density of 5 A g⁻¹ [14]. However, NiMoO₄ often suffers from the drawbacks of low rate capability and poor cycling stability due to inherently poor electronic conductivity, slow reaction kinetics and severe morphology collapse during repeated discharge-charge cycles [15]. To solve these critical problems, hybridization with carbonaceous materials such as carbon spheres (CSs), graphene, CNT can increase the unite load of active materials, electro conductivity and buffer the volume change during repetitive cycling, leading to good cycling performances and high rate capabilities [16–18].

Herein, We report a two-step hydrothermal method to synthesize the hierarchical C@NiMoO₄ electrode materials. Based on the hierarchical structure, as-synthesized core-shell C@NiMoO₄ shows high specific capacitance and attractive rate capability, as well as excellent cycling stability, compared with bare NiMoO₄ and previous reported C@NiMoO₄, which predicts its potential application for supercapacitor.

2. Experimental section

2.1. Synthesis of CSs

All of the chemicals used in the experiment were of analytical

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grade and used without further purification. CSs were synthesized by hydrothermal method: Firstly, 4 g glucose were dissolved in 160 ml of deionized water under vigorous stirring, and kept this process at 35 °C for 30 min to form homogeneous dispersion. Then the clear solution was transferred into 200 ml Teflon-lined autoclave and kept in 200 °C for 10 h and then cooled to room temperature naturally. The as-obtained brown-black precipitate was collected by filtration and washed with deionized water and ethanol for several times. The resulting final product was dried at 60 °C overnight.

2.2. Synthesis of C@NiMoO₄

The as-prepared CSs materials were dissolved in mixed solution of 30 ml ethanol and 30 ml deionized water under vigorous stirring, followed by addition of 1 mmol Ni(NO₃)₂ and 1 mmol Na₂MoO₄. The mixture was forcefully stirred for a further 1 h and then transferred into 100 ml Teflon-lined autoclave and kept in 160 °C for 8 h and then cooled to room temperature naturally. The as-obtained grey-black precipitates were collected by ultracentrifugation and washed with deionized water and ethanol for several times and then dried overnight. Finally, the dried precipitates were annealed at 450 °C under argon atmosphere for 2 h (ramp rate: 3 °C min⁻¹) to obtain the C@NiMoO₄ samples. For comparison, NiMoO₄ samples were also made in the same hydrothermal process without the adding of CSs.

2.3. Structural characterization

The structure of the fabricated samples were examined by X-ray diffraction analysis (XRD) (Rigaku, model D/max-2500 system at 40 kV and 100 mA of Cu Kα). The X-ray photoelectron spectroscopy (XPS) spectra was tested by an ESCALab 250 electron spectrometer (Thermo Scientific Corporation). The samples morphologies were inspected on a field emission scanning electron microscopy (FESEM, USA, Tecnai F30 G2 FEI CO). Thermogravimetric analysis (TGA, Q500) was conducted with a heating rate of 10 °C min⁻¹.

2.4. Electrochemical measurements

The working electrode materials were prepared by mixing the obtained sample, acetylene black and Polyvinylidene fluoride (PVDF) in a mass ratio of 80:10:10. The hybrid was mixed with little N-methyl-2-pyrrolidone (NMP) for homogeneity and then coated on nickel foam substrates (1 cm × 1 cm) as the working electrode and dried at 60 °C for 12 h, the as-prepared electrodes loaded with the hybrid were then pressed at 10 MPa for 60 s. The typical mass loading of the sample in each electrode is in the range of 4–6 mg. Electrochemical measurements were performed on an Autolab Electrochemical Workstation (PGSTAT302N) by the three-electrode system, platinum electrode and the standard calomel electrode (SCE) were used as the counter and reference electrodes respectively. 2 M KOH solution was served as the electrolyte at room temperature. Cyclic voltammogram (CV) was recorded between -0.1 and 0.40 V at scan rates ranging from 1 to 40 mV s⁻¹. Galvanostatic charge/discharge testing was conducted at different current densities from 0.5 to 10 A g⁻¹ between 0 and 0.4 V. The test of cycle life for 2000 cycles at 1 A g⁻¹ was operated on a LAND battery program-control test system. The electrochemical impedance spectroscopy (EIS) measurements were manipulated in a frequency range from 10⁻² Hz to 100 kHz with potential amplitude of 5 mV. The device specific capacitance was calculated from the charging-discharging curve by the following equation:

$$C_{sp} = \frac{I \times t}{\Delta V \times m} \quad (1)$$

where C_{sp} (F g⁻¹) is the gravimetric capacity, I (A) is the current, ΔV (V) is the potential window, m (g) is the mass of the active material and t (s) is the discharging time.

3. Results and discussion

The schematic diagram of the synthetic procedure and morphologies of hierarchical structure C@NiMoO₄ is presented in Fig. 1. Firstly, CSs are obtained by the polymerization and carbonization process of glucose monomers. Some oxygenous functional groups are existed in the surface of CSs served as nucleation sites. Followed by the addition of nickel salt and molybdate, which are absorbed on the surface of CSs owing to the interaction with oxygenous functional groups. Then Ni²⁺ and MoO₄²⁻ ions combine to form self-assembly during the hydrothermal condition. Finally, hierarchical structure C@NiMoO₄ composite which uniformly distributed NiMoO₄ nanograins anchored on the surface of CSs are obtained.

The morphologies and nanostructures of CSs, NiMoO₄ and C@NiMoO₄ can be characterized by morphological examination. Fig. 2(a,c) depict representative SEM images of CSs, it can be seen that the bare CSs with smooth surfaces have a diameter about 2–4 μm. In Fig. 2(b,e), the NiMoO₄ rods have an average diameter of 200 nm and length up to around 4 μm. Fig. 2(c,f) displays the SEM morphologies of C@NiMoO₄ composite materials. One can see that NiMoO₄ nanograins anchored on the surface of CSs present nanosized agglomerated morphology and irregular shape composed of numerous nanoparticles, forming a rather rough silkworm-cocon-like compound. Note that the change of morphology is ascribed to the involvement of CSs backbone and may work in favor of high loading capability of the active materials and facilitate more efficient charge transportation [19]. Both the results from the EDS spectrum (Fig. 2g) and the elemental mapping (Fig. 2i) images confirm that Ni, Mo, C and O elements are not only contained but also homogeneously distributed throughout the whole material.

The phase structures of the samples are disclosed by powder X-ray diffraction (XRD). Fig. 3a shows the XRD patterns of CSs, NiMoO₄ and C@NiMoO₄ samples. For the CSs, two peaks at about 26.8° and 43° can be attributed to the (002) and (101) planes of graphite. For the NiMoO₄ and C@NiMoO₄, the similar diffraction

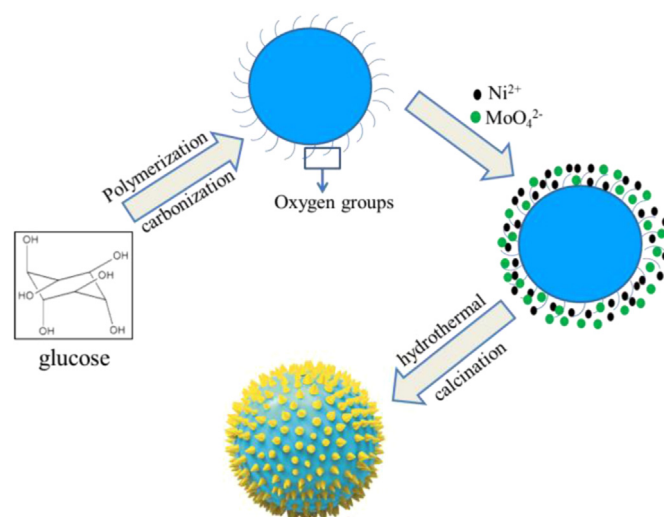


Fig. 1. The schematic illustration for the preparation of uniform hierarchical C@NiMoO₄ sample.

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