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An asymmetric supercapacitor with ultrahigh energy density based on nickle cobalt sulfide nanocluster anchoring multi-wall carbon nanotubes hybrid

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HIGHLIGHTS

- $NiCo_2S_4$/MWCNTs hybrids were fabricated *via* simple solvothermal reaction.
- The capacitive behaviors of the hybrids were explored.
- An asymmetric supercapacitor cell was assembled and tested.
- The cell exhibited a superior energy-storage capacity.

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ABSTRACT

The development of novel electrode materials with high energy density and long cycling life is critical to realize electrochemical capacitive energy storage for practical applications. In this paper, the hybrids of nickle cobalt sulfide/multi-wall carbon nanotubes ($NiCo_2S_4$/MWCNTs) with different contents of MWCNTs are prepared using a facile one-pot solvothermal reaction. As novel active materials for supercapacitors, the electrochemistry tests show that the hybrid of $NiCo_2S_4$/MWCNTs-5 is able to deliver a high specific capacitance of 2080 F g^{-1} at the current density of 1 A g^{-1}, even superior rate capability of 61% capacitance retention after a 20-fold increase in current densities, when the content of MWCNTs is up to 5%. More importantly, an asymmetric supercapacitor assembled by $NiCo_2S_4$/MWCNTs-5 as positive electrode and reduced graphene oxide (rGO) as negative electrode delivers a high energy density of 51.8 Wh Kg^{-1} at a power density of 865 W kg^{-1}, and 85.7% of its initial capacitance is retained at the current density of 4 A g^{-1} after 5000 charge-discharge cycles, exhibiting potential prospect for practical applications.

1. Introduction

In recent years, exploring electrode materials for supercapacitors with high energy and power density, excellent rate capability and long lifespan has stimulated extensive research interest, and realizing the fast energy storage and conversion would make supercapacitors accessible upon practical applications, such as hybrid vehicles, portable electronic devices and back-up sources [1–5]. In general, depend on energy storage mechanism, supercapacitors can be classified into two categories: the electrical double-layer capacitors (EDLCs) by electrostatic interactions in carbonaceous materials at the electrode/electrolyte interface and the pseudocapacitors by faradaic redox reaction [6,7]. In the past decade, advanced carbon-based materials (such as graphene, CNTs, porous carbon etc. [8–11]) for EDLCs and transition metal-oxides (such as RuO_2, Mn_3O_4, Co_3O_4, NiO etc. [12–15]) for pseudocapacitors have been employed to explore the electrochemical performance. However, the limited specific capacitances of carbon-based materials make them deliver the relatively low energy density, while the poor conductivity of transition metal-oxides makes them suffer from low rate capability and inferior cycle lifespan, despite being superior in specific capacitance than carbon-based materials [8,10,13,15].

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Furthermore, transition-metal sulfides, such as CoS_x and NiS_x, also have been explored extensively due to their thermal stability and more higher theoretical capacitance in supercapacitors [16–18]. Unfortunately, the contribution of simplex metal ion is still restricted because of intrinsically low surface area and inactive ions transport, even though the much efforts on the design and synthesis of metal sulfides with a large surface area and well-defined morphology, including nanosheets [19], nanorods [20], and nanoparticles [17], has been devoted to improving the performance of supercapacitors. Recently, ternary metal sulfides of $NiCo_2S_4$ have attracted intense investigations owing to their higher electric conductivity, richer redox reactions and more prominent specific capacitances than single component cobalt sulfides and nickel sulfides [21]. Therefore, several works about $NiCo_2S_4$ have been reported for supercapacitors. Ji's group prepared mesoporous $NiCo_2S_4$ nanoparticles *via* solvothermal route with a specific capacitance of 1440 F g^{-1} at the current density of 3 A g^{-1} [22], and Xiao's group developed $NiCo_2S_4$ nanowires on nickel foam by two steps hydrothermal reaction to deliver a ultrahigh specific capacitance of 2415 F g^{-1} at the current density of 2.5 mA cm^{-2} [23], even further, shape-controlled $NiCo_2S_4$ with urchin-, flower-, tube-, and cubic-like morphology were also fabricated, and the results indicated that the tube-like $NiCo_2S_4$ exhibited a promising specific capacitance of 1048 F g^{-1} at the current density of 3.0 A g^{-1} [24]. Xu and coworkers constructed 3D porous $NiCo_2S_4$ nanonetworks showing a specific capacitance of 1501.2 F g^{-1} at the current density of 1 A g^{-1} [25]. Nevertheless, it can be perceived that the bare $NiCo_2S_4$ still offers restricted energy-storage capacibility, despite varying architectures developed. Moreover, the electroactive materials grown directly on nickel foams substrate often present a small mass loading, which leads to hurdle for their implementation in practical applications and the tedious operations also resulted in energy consumption and time waste. Therefore, the further elevation of the specific capacitance and improvement of the electrical conductivity as well as the promotion of rate property are still needed for practical applications. Integrating $NiCo_2S_4$ with carbon-based materials has been considered as one of effective strategies, because of carbon materials possessing large surface area, high stability and good electric conductivity. Very recently, in *situ* growth of $NiCo_2S_4$ nanosheets on graphene for supercapacitors has been reported, delivering a specific capacitance of 1451 F g^{-1} at the current density of 3 A g^{-1} [26], and $NiCo_2S_4$ grown in *situ* on carbon fibers for supercapacitors has been fabricated, achieving a specific capacitance of 0.83 F cm^{-2} at the current density of 25 mA cm^{-2} [27]. However, to the best of our knowledge, no work was available to investigate the supercapacitive properties of $NiCo_2S_4$/multi-walled carbon nanotubes (MWCNTs) hybrids. Thus, it is presumed that the growth of $NiCo_2S_4$ nanoparticles on MWCNTs matrix could lead to superior supercapacitive performance.

Herein, we reported the synthesis of $NiCo_2S_4$/MWCNTs hybrid *via* one pot solvothermal reaction and explored its electrochemical performance. The nanoclusters consist of $NiCo_2S_4$ nanoparticles were anchored randomly on MWCNTs matrix all around. The as-fabricated $NiCo_2S_4$/MWCNTs was able to deliver ultrahigh specific capacitances (2080 F g−1 and 1270 F g^{-1} at a current density of 1 A g^{-1} and 20 A g^{-1}, respectively), outstanding rate capability and excellent cycling stability. Furthermore, an asymmetric capacitor device was assembled using the $NiCo_2S_4$/MWCNTs as the positive electrode and reduced graphene oxide (rGO) as the negative electrode. The as-fabricated asymmetric supercapacitor device exhibited a high specific energy (51.8 Wh Kg^{-1}) and excellent cycle life (92% retention after 5000 cycles).

2. Experimental

2.1. Materials

Nickel acetate tetrahydrate ($Ni(OAc)_2{\cdot}4H_2O$), cobalt acetate tetrahydrate $Co(OAc)_2{\cdot}4H_2O$, triethylamine (Et_3N), thiourea ($SC(NH_2)_2$), ethylene glycol (EG), and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd (China), MWCNTs were purchased from Suzhou Crystal Silicon Electronics & Technology Co. Ltd (China). All the reagents used are of analytical grade and used without further purification.

2.2. Fabrication of $NiCo_2S_4$/MWCNTs hybrids

The fabrication of $NiCo_2S_4$/MWCNTs hybrids were realized by one pot solvothermal reaction. In a typical procedure, MWCNTs oxidized mildly according to our previous report were used [28]. $Ni(OAc)_2{\cdot}4H_2O$ (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (2.0 mmol) and $SC(NH_2)_2$ (10 mmol) were added into 50 mL EG and 30 mL deionized (DI) water, following with MWCNTs (37.5 mg, 5 wt% based on the total mass of metal salts). The mixture was ultrasonicated for 30 min to ensure the dissolution of salts and dispersion of MWCNTs. Then, Et_3N (2.0 mL) was injected, and a lots of flocculents were emerged immediately. The flocculents was utralsonicated for 10 min with manual stirring. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave with a volume capacity of 100 mL. After sealing, the autoclave was heated to 200 °C for 24 h and cooled naturally to room temperature. Finally, the resulting precipitate was filtered off and soaked with ethanol and DI water several times to remove the residuals, and then dried in a vacuum oven at 60 °C for 6 h. The as-prepared hybrid was denoted as $NiCo_2S_4$/MWCNTs-5. For the other hybrids with MWCNTs (0, 2 wt% and 8 wt%) were fabricated using the same condition and denoted as $NiCo_2S_4$/MWCNTs-0, $NiCo_2S_4$/MWCNTs-2, $NiCo_2S_4$/MWCNTs-8, respectively.

2.3. Characterization

The morphologies and composition of the samples were characterized by transmission electron microscope (TEM, FEI Tecnai G2 F20) working at 200 kV. The crystallographic phase of the samples was analyzed by X-ray diffraction (XRD, Rigaku D/Max-2400 diffractometer using Cu-Kα radiation and graphite monochrometer, $\lambda = 1.54056$ Å) over the 2θ ranging from 5° to 80°. The chemical composition was analyzed by in situ energy dispersive X-ray spectroscopy (EDX) using an instrument equipped in the TEM. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) with an Al Kα(mono) anode at an energy of 150 W in a vacuum of 10^{-7} Pa. The specific surface area of the samples was measured by nitrogen adsorption at 77 K using an automated gas sorption analyzer (Micromeritics ASAP 2020 apparatus) and calculated according to the Brunauer-Emmett-Teller (BET) method. The content of MWCNTs in the hybrids was calculated by thermogravimetric analysis (TGA, STA 449 F3) with a rate of 10 °C/min.

2.4. Electrochemical measurements

Electrochemical measurements were performed using a CHI 660C electrochemical workstation. The active material, acetylene black, and poly(tetrafluoroethylene) (PTFE) in a mass ratio of 85:10:5 were mixed to form a homogeneous slurry. Then the slurry was coated onto the Ni foam current collector as the working electrode with an area of 1 × 1 cm^2, and dried at 70 °C for 12 h, then the working electrode was pressed under a pressure of 10 MPa. The