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Construction of hierarchical nickel cobalt selenide complex hollow spheres for pseudocapacitors with enhanced performance

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ABSTRACT

Construction bimetallic transition metal selenides with complex hollow structures is of significant importance but also extremely challenging. In this work, starting form metal-organic frameworks (MOFs), we have successfully synthesized the unique hierarchical $(Ni_{0.33}Co_{0.67})Se_2$ complex hollow spheres (CHSs), which manifest high specific capacitance as well as excellent rate performance and cycling stability, making them promising electrode materials for pseudocapacitors. The hierarchical $(Ni_{0.33}Co_{0.67})Se_2$ CHSs display a high specific capacitance of 827.9 F g^{-1} at the current density of 1 A g^{-1} and can still retain 646.2 F g^{-1} at a very high current density of 30 A g^{-1}. Besides, a high capacitance of 865.8 F g^{-1} is obtained after cycling at 6 A g^{-1} for 2000 cycles, indicating good cycling stability. The excellent electrochemical performance could be owing to their high electrical conductivity and hierarchical complex hollow structure. Furthermore, an asymmetric supercapacitor (ASC) device employing $(Ni_{0.33}Co_{0.67})Se_2$ CHSs as positive electrode and activated carbon (AC) as negative electrode is also fabricated, which displays a high energy density of 29.1 Wh kg^{-1} at a power density of 800 W kg^{-1}. These electrochemical results indicate the hierarchical $(Ni_{0.33}Co_{0.67})Se_2$ CHSs could be promising electrode materials for pseudocapacitors. The present work might also contribute to the rational construction of metal selenides with complex hollow structures for high-performance energy storage.

1. Introduction

Supercapacitors, also named electrochemical capacitors, have received considerable attentions owing to their advantages such as high power density, fast charging and discharging, long lifespan and environmentally friendly [1–3]. According to the different charge storage mechanism, supercapacitors can be generally divided into electrical double layer capacitors (EDLCs) and pseudocapacitors [4]. Pseudocapacitors employing fast surface or near surface redox reactions of the active materials can obtain significant higher charge storage compared to the EDLCs. In the past decade, transition metal oxides/hydroxides including MnO_x, CoO_x, NiO, $Ni(OH)_2$, $NiCo_2O_4$, etc. have been widely studied as electrode materials for pseudocapacitors [5–8]. Unfortunately, their practical applications is seriously hindered by the unsatisfactory rate capability and cycling stability resulted from the low electrical conductivity. Therefore, it is urgent necessary to explore new advanced electrode materials with desirable pseudocapacitive properties, including high specific capacitance, superior rate performance and excellent cycling stability.

Recently, metal-like transition metal selenides have shown promising potential for energy storage-related applications in view of their high electrical conductivity [9–11]. In the periodic table, selenide (Se) is located at the same sixth group with oxygen (O), and the elemental Se has high electrical conductivity of about 1×10^{-3} S m^{-1}, which endows the transition metal selenides with superior electrical conductivity [12]. Among them, bimetallic nickel cobalt selenides have attracted particularly interest as new type electrode materials for pseudocapacitors with good performance. The coexistence of nickel and cobalt cations could enable multiple redox reactions, resulting in better electrochemical activity than monometallic nickel or cobalt selenides [13–16]. Besides, previous studies have confirmed that the incorporation of nickel into cobalt

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selenides could greatly increase the electrical conductivity [17]. As a good example, Chen et al. first reported that the bimetallic nickel cobalt selenides exhibited enhanced pseudocapacitive performance than the monometallic nickel or cobalt selenide [16]. Thereafter, nickel cobalt selenide nanotubes, hollow nanoparticles, nanowires, nanorods etc. have also been demonstrated as advanced electrode materials for pseudocapacitors [18–21]. Despite these progress that has been achieved, the researches on bimetallic nickel cobalt selenides for pseudocapacitors are still quite limited.

As we know, it is well accepted that the electrochemical properties of the electrode materials are greatly depended on the morphology and structure. Among various nanostructures, hollow structures especially those with structural and composition complexity, have recently attracted tremendous research interest owing to their unique features. Complex hollow structures have more electroactive sites and better structural robustness, which often exhibit improved performance compared with simple hollow counterparts [22–31]. For instance, Lou et al. reported the Co_3O_4/$NiCo_2O_4$ double-shelled nanocages for pseudocapacitors, which displayed higher specific capacitance and improved rate capability compared to their simple counterparts [26]. Wang et al. demonstrated that the unique septuple-shelled $(Co_{2/3}Mn_{1/3})$ $(Co_{5/6}Mn_{1/6})_2O_4$ hollow spheres exhibited the optimal performance, which delivered a high specific capacity of 236.39 mAh g^{-1} at the current density of 1 A g^{-1}, as well as excellent rate and cycling performance [27]. In this regard, it should be quite meaningful to construct bimetallic nickel cobalt selenides with complex hollow structures and investigate their electrochemical properties. However, current researches about complex hollow structures are mainly concentrated on metal oxides, while the bimetallic nickel cobalt selenides with complex hollow structures have not been reported so far.

In this work, for the first time, we develop a facile ion-exchange strategy to synthesize the hierarchical $(Ni_{0.33}Co_{0.67})Se_2$ complex hollow spheres (CHSs) with unique hierarchical outer shells. Starting from metal-organic frameworks (MOFs), $NiCo_2O_4$ multishelled hollow spheres (MHSs) are synthesized as the templates and then transformed to hierarchical $(Ni_{0.33}Co_{0.67})Se_2$ CHSs through a simple hydrothermal selenization method. When evaluated as electrode materials for pseudocapacitors, the hierarchical $(Ni_{0.33}Co_{0.67})Se_2$ CHSs exhibit significant improved electrochemical performance compared with the $NiCo_2O_4$ MHSs. For real applications, an asymmetric supercapacitor (ASC) device employing $(Ni_{0.33}Co_{0.67})Se_2$ CHSs as the positive electrode and activated carbon (AC) as the negative electrode is also fabricated, which can display a high energy density of 29.1 Wh kg^{-1} at a power density of 800 W kg^{-1} and still retain 23.0 Wh kg^{-1} at a high power density of 6400 W kg^{-1}.

2. Experimental section

2.1. Materials preparation

2.1.1. Synthesis of Ni-Co-MOF precursor

In a typical procedure [31,32], 154.9 mg of nickel nitrate hexahydrate and 309.8 mg of cobalt nitrate hexahydrate were dissolved in 30 mL of *N*,*N*-dimethylformamide (DMF) to a clear green solution under stirring. Then, 1 g of polyvinylpyrrolidone (PVP, K30) and 150 mg of trimesic acid were added to the above solution with vigorous stirring for 30 min before transferred to the Teflon-lined stainless autoclave and then maintain at 150 °C for 6 h in an oven. The resulting pink product was centrifuged at 8000 rpm for 7 min and washed with alcohol at least three times. Finally, the product was dried in a vacuum oven at 70 °C for 12 h.

2.1.2. Synthesis of $NiCo_2O_4$ MHSs

The resulting final pink product was placed in a tube furnace, followed by annealing at a temperature of 400 °C for 2 h in air with a ramp-rate of 2 °C min^{-1}. After cooling to room temperature, the final black product was obtained.

2.1.3. Synthesis of $(Ni_{0.33}Co_{0.67})Se_2$ CHSs

Typically, 2.857 g of NaOH and 0.228 g of Se powder and 25 mL deionized water were stirred for 1 h and then poured into a 50 mL Tefoln-lined stainless autoclave. The autoclave was sealed and kept at 200 °C for 20 h. After the autoclave was cooled down to room temperature, 14 mg of the $NiCo_2O_4$ MHSs was added into the as-obtained solution. After that, the autoclave was sealed again and kept at 140 °C for 12 h. The final products were washed and centrifuged with deionized water and alcohol, and finally dried at 80 °C under vacuum overnight.

2.2. Materials characterization

The morphology and structure properties of the prepared products were obtained by the scanning electron microscopy (SEM, Supra55, Zeiss) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin, FEI). The crystalline structures were characterized using X-ray diffraction (XRD, D/max-UltimaIII, Rigaku) equipped with Cu Kα radiation (λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was also conducted to obtain the surface compositions and chemical states. Nitrogen adsorption/desorption isotherms (3Flex Surface Characterization Analyzer) was tested to obtain the specific surface area and pore-size distribution.

2.3. Electrochemical measurements

All electrochemical data were measured using the Shanghai Chenhua Electrochemical Workstation CHI 760 E. The electrochemical performance were measured using a three-electrode connection method in which the 3 M potassium hydroxide solution as the electrolyte, platinum plate as the counter electrode and the saturated calomel electrode as the reference electrode. The working electrodes were prepared by coating the slurry on the nickel foam and then dried at 80 °C under vacuum for 12 h. The slurry was made up of 70 wt% of active materials, 20 wt% of conductive carbon black and 10 wt% of polyvinylidene fluoride (PVDF). The mass loading of the active materials on the electrodes was about 1.0–2.0 mg. The specific capacitance of the electrodes can be calculated according to the galvanostatic charge and discharge (GCD) curves based on the following formula [33,34]:

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

where I is the discharge current, t was the discharge time, ΔV was the potential window, and m was the mass of the electroactive materials.

In the two-electrode system, $(Ni_{0.33}Co_{0.67})Se_2$ CHSs acted as the positive electrode and activated carbon (AC) acted as the negative electrode, respectively. The charges in negative (Q_-) and positive (Q_+) electrodes were balanced to follow $Q_+ = Q_-$, which was based on the following equations:

$$Q = C \times \Delta V \times m \quad (2)$$

$$\frac{m+}{m-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (3)$$

The energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) for the ASC device were obtained from the following formulas: