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$NiCo_2S_4$ hollow microsphere decorated by acetylene black for high-performance asymmetric supercapacitor

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ABSTRACT

High-rate acetylene black (AB) decorated $NiCo_2S_4$ hollow microsphere is prepared via a gas bubble soft template and hydrothermal methodology. Benefiting from the combined advantages of the AB with high conductivity and the nanopetals assembled $NiCo_2S_4$ with unique hollow micro-/nano- structures, abundant porosity and high conductivity, the as-obtained composites are found to exhibit high specific capacitances (768 F g^{-1} at 2 A g^{-1}) and remarkable rate capabilities (92.2, 80.1 and 70.3% of capacity retention rate at 20, 50 and 100 A g^{-1}). The fabrication mechanism of the AB-$NiCo_2S_4$ composite is also proposed. Furthermore, an asymmetric supercapacitor is fabricated by using the AB-$NiCo_2S_4$ composite as a positive electrode and activated carbon as a negative electrode. Owing to the excellent electrochemical properties of the AB-$NiCo_2S_4$ electrode, the asymmetric device delivers high energy density (24.7 Wh kg^{-1}) at a power density of 428 W kg^{-1} or high power density (17.12 kW kg^{-1}) at a reasonable energy density of 7.1 Wh kg^{-1}, and exceptional cycling stability (105.6% of the initial capacity retention at 5 A g^{-1} over 5000 cycles). These results above demonstrate the significance and great potential of mesoporous $NiCo_2S_4$ hollow microsphere-based composites in the development of high-performance energy-storage systems.

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1. Introduction

Supercapacitors (also named electrochemical capacitors or ultracapacitors) have attracted considerable attention in recent years due to their high power density and long cycling lifespans compared to secondary batteries [1–3]. The performance of supercapacitors is largely determined by the properties of their active electrode materials [4]. So far, these electrode materials can usually be divided into three types: carbon materials, conducting polymers and transition metal oxides. Among them, transition metal oxides have been widely investigated because they usually possess multiple oxidation states that are especially in favor of fast redox reaction leading to a much higher specific capacitance [5,6]. RuO_2 (especially hydrous and amorphous RuO_2) shows the best electrochemical properties due to its good electrical conductivity, reversible charge-discharge properties and high specific capacitance (as high as 1580 F g^{-1}) [7]. Nevertheless, the rareness of Ru and the toxic nature of RuO_2 have prevented its practical application in supercapacitors [8,9]. The applications of other metal oxides, such as MnO_2, NiO and Co_3O_4, are mainly restricted by their poor electrical conductivity and low energy density [10–12]. Hence, it is imperative to develop cost-effective, environmentally friendly and high-performance alternative electrode materials for supercapacitors.

Since the pioneering work of ternary $NiCo_2O_4$ (1400 F g^{-1} at 25 mV s^{-1}) reported in 2010 by Hu et al. [9], it has sparked worldwide interest as a pseudocapacitive electrode material for supercapacitor applications due to its many intrinsic advantages [13–16]. Firstly, it possesses several other inherent advantages, such as low cost, abundant resources and good environmental benignity. Secondly, it exhibits multiple oxide states that enable rich redox reactions originating from both nickel and cobalt ions. More significantly, it possesses at least two orders of magnitude higher conductivity and a higher electrochemical activity than single NiO and Co_3O_4. These attractive features are of huge benefit for the development of high-performance, especially high-rate supercapacitors. Unfortunately, the rate performance and the utilization rate of active materials of $NiCo_2O_4$ are still unsatisfactory despite its extremely attractive theoretical capacity value [17,18]. It is well known that the rate capability of the electrode material is mainly determined by the kinetics of ion diffusion and electronic conductivity [19,20]. Very recently, $NiCo_2S_4$ has been found to show much lower optical band gap energy and higher

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conductivity compared to $NiCo_2O_4$. The as-obtained $NiCo_2S_4$ reported by Chen et al. exhibits much higher rate capability than those of $NiCo_2O_4$ [21]. Additionally, Li et al. reported that Ni-Co sulfides show even twice higher specific capacitance than Ni-Co sulphides [22]. The enhancement of electrochemical performances of Ni-Co sulfides is ascribed to the fact that the replacement of oxygen with sulfur may create a more flexible structure because the electronegativity of sulfur is lower than that of oxygen, preventing the disintegration of the structure by the elongation between layers and making it easy for electrons to transport in the structure [23]. Therefore, $NiCo_2S_4$ is a promising candidate for high-performance supercapacitor applications. Although $NiCo_2O_4$ has been intensely researched recently [24–29], there are not many reports for the synthesis of $NiCo_2S_4$ as supercapacitor electrode materials.

In recent years, hollow micro-/nanostructures have attracted significant interest because they possess many inherent advantages such as large surface area, low density, a kinetically favourable open structure and surface permeability [30,31]. Moreover, it is generally accepted that micro-/nanostructures as electrode materials are one of the best systems in the field of supercapacitors [16,32,33]. These structures offer the exceptional advantages of both nanometer-sized building blocks and micrometer-sized assemblies. In particularly, when hierarchical hollow micro-/nanostructures, especially with complex shell and interior structures are well constructed, remarkable electrochemical performances are exhibited because of the large active specific surface area, short electron and ion transport pathways, and desirable hierarchical porosity (that is, meso- and macroporosity) [34]. Note that mesoporous materials with high surface areas also have been demonstrated as a promising candidate for energy storage, and their high surface areas can not only increase the electroactive sites, but also alleviate the volume change during the charge-discharge process [24,35]. This is especially useful for supercapacitors, where hollow structures with large surface areas and abundant porosities can provide rich electroactive sites and short diffusion paths for charge carriers, which are required in the Faradaic redox reactions [36,37]. Some very recent literatures about $NiCo_2S_4$ hollow structures (such as hollow tubular structures, ball-in-ball hollow spheres) have been successfully reported as the excellent electrode materials for application in supercapacitors [38,39]. Therefore, excellent electrochemical performances of the as-fabricated mesoporous $NiCo_2S_4$ hollow micro-/nanostructures, as reported here, can be expected. In order to further enhance the electrochemical properties of single $NiCo_2S_4$, an effective method is to introduce carbon materials, which serve not only as a conductive agent to raise the conductivity, but also as a physical buffer for the volume expansion [40,41]. The most common utilised carbon materials are carbon nanotubes and graphene. Although their composites have been reported to show the improved electrochemical properties compared with pure metal oxides due to the enhancement of conductivity [40,41], their high cost seriously hinders their practical applications. In the present work, acetylene black (AB) is used to fabricate the AB-$NiCo_2S_4$ composites because of its advantages of low cost, high conductivity and uniform small particle sizes. Thus, acetylene black is beneficial to improve the electrochemical performances of $NiCo_2S_4$, especially the rate capability and cycling stability. To the best of our knowledge, there is no report for the AB decorated mesoporous $NiCo_2S_4$ hollow microsphere composite as supercapacitor electrode materials. More significantly, in considering practical applications, a novel asymmetric supercapacitor was firstly fabricated by using the AB decorated mesoporous $NiCo_2S_4$ hollow microsphere composite and activated carbon (AC) as the positive and negative electrodes, respectively.

Herein, we report the first report of a gas bubble soft template synthesis of a new mesoporous $NiCo_2S_4$ hollow microsphere/AB composite via a facile hydrothermal route. The formation mechanism of the AB-$NiCo_2S_4$ composite is proposed. Compared with just $NiCo_2S_4$, the fabricated composite manifests an improved electrochemical performance when tested as an electrode for electrochemical evaluation in a three-electrode system. It is encouraging that the rate capability of the composite is superior to the other $NiCo_2S_4$-based supercapacitors that have been reported so far. Furthermore, an asymmetric supercapacitor with excellent electrochemical performances has been fabricated based on mesoporous $NiCo_2S_4$ hollow microsphere/AB composite as a positive electrode and AC as a negative electrode. Due to the excellent electrochemical property of mesoporous $NiCo_2S_4$ hollow microsphere/AB composite, the asymmetric device exhibits high energy density of 24.7 Wh kg^{-1} at a power density of 428 W kg^{-1}, high power density of 17.12 kW kg^{-1} at a reasonable energy density of 7.1 Wh kg^{-1} and exceptional cycling stability with 105.6% of the initial capacity retention at 5 A g^{-1} over 5000 cycles, which is promising for practical application in supercapacitors.

2. Experimental section

2.1. Materials and Chemicals

All the chemicals used in the experiments were analytical grade and were used without further purification. $Ni(NO_3)_2{\cdot}6H_2O$ (analytical grade) was purchased from Fengchuan Chemical Reagent Co., Ltd, Tianjin. $Co(NO_3)_2{\cdot}6H_2O$ was obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. CS $(NH_2)_2$ (analytical grade) was bought from Xilong Chemical Co., Ltd. Ethylenediamine (analytical grade) was obtained from the Hengxing Co., Ltd, Tianjin. All solutions were prepared with distilled water of resistivity not less than 18.2 MΩ cm (Synergy UV, Millipore).

2.2. Materials synthesis

AB was activated by using concentrated nitric acid. 0.5 g AB and 100 mL concentrated nitric acid were dispersed in an ultrasonic bath for 30 min, and then refluxed at 120 °C for 12 h. After being cooled to room temperature, the black powder was washed thoroughly with distilled water until the pH was close to 7, and further dried in vacuum at 80 °C for 24 h.

For the synthesis of mesoporous $NiCo_2S_4$ hollow microsphere/AB composite, 0.378 g $Ni(NO_3)_2{\cdot}6H_2O$ and 0.757 g $Co(NO_3)_2{\cdot}6H_2O$ and 2.6 mL ethylenediamine (EN) were dissolved in 40 mL distilled water and stirred for 30 min at room temperature. Then, 100 mg activated AB and 0.396 g thiourea (CS $(NH_2)_2$) were respectively added into the mixed solution under stirring. After stirring for another 30 min, the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 24 h. The final product was washed with distilled water and ethanol several times and dried in vacuum at 80 °C for 12 h. For comparison, the mesoporous $NiCo_2S_4$ hollow microsphere was synthesized without AB via the same route.

2.3. Materials characterization

The X-ray diffraction (XRD) patterns of the samples were obtained on a Rigaku D/max 2550 VB^+ 18 kW X-ray diffractometer with Cu Ka radiation at a scanning rate of 0.1° 2θ s^{-1}. Field emission scanning electron microscopy (FSEM, MIRA3), Transmission electron microscopy (TEM, JEM-2100F), High resolution transmission electron microscopy (HRTEM, JEM-2100F) and the corresponding selected area electron diffraction (SAED) were used to characterize the morphology and structure of the samples. The

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