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Full Length Article

Ni_3S_2 nanorods and three-dimensional reduced graphene oxide electrodes-based high-performance all-solid-state flexible asymmetric supercapacitors

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ABSTRACT

Exploring efficient all-solid-state flexible supercapacitors is particularly attractive to face the rapid growing demand of powers for flexible and wearable energy storage devices. Herein, we report a novel strategy to prepare high-performance all-solid-state flexible asymmetric supercapacitors based on nanostructured Ni_3S_2 nanorods as positive electrode and three-dimensional reduced graphene oxide (3DrGO) as negative electrode. Due to the tunable morphological structures and novel electronic properties of heazlewoodite phase Ni_3S_2 and interconnected porous 3DrGO, the synthesized electrode materials exhibit high specific capacitances, excellent rate performance and cycling stability. Furthermore, combining capacitive and faradaic energy storage mechanisms, the constructed asymmetric supercapacitor can work complementarily in separate operating voltage, thus leading to substantially enhanced energy and power densities. Remarkably, the optimized device is able to be cycled reversibly in the voltage range of 0–2.2 V, but still delivers high energy density (70.58 W h kg^{-1}), high power density (33.0 kW kg^{-1} at 52.44 W h kg^{-1}), and excellent cycling stability (with 90.4% specific capacitance retained even after 5000 cycles). Moreover, the device exhibits good flexibility without performance degradation. Significantly, the conception of the combining capacitive and faradaic energy storage mechanisms in this work undoubtedly enables new perspective in exploring high-performance energy storage systems.

1. Introduction

With the increased demand for portable and clean energy, supercapacitors (SCs, namely electrochemical capacitors), have attracted worldwide attention as power sources since they have much greater power density and cyclability than Li batteries [1–3]. Generally, an integrated SC device includes three most influential components, i.e. a negative electrode, electrolyte, and a positive electrode. Energy storage of SCs are in principle based on either ion adsorption (double-layer capacitance) or redox reactions (pseudocapacitors) at or near the electrode/electrolyte interfaces in the device. Therefore an ideal electrode material for SCs should exhibits high effective specific surface area, good electrical conductivity, and well-matched with electrolyte [4]. Depending on the type and nature of the two electrodes, SCs can be briefly classified as symmetric configurations and asymmetric configurations [5]. Asymmetric configurations are usually associated to the combination of capacitive and faradaic energy storage mechanisms, that is to say a faradaic materials as the positive electrode (energy source) and a capacitive materials as the negative electrode (power source). Therefore, constructing asymmetric supercapacitors (ASCs) is one of the best choices to design and optimize the high performance electrochemical SCs. In terms of application, all-solid-state ASCs based on solid or semi-solid electrolytes have emerged as promising energy supplies in flexible and stretchable electronics because they can effectively avoid the electrolyte leakage issue that occurs in conventional aqueous-electrolyte ASCs [6]. However, the ionic conductivity of (semi) solid electrolytes is usually lower than liquid electrolyte at room temperature [7]. Therefore, for all-solid-state ASCs to achieve the optimized overall performance, the compatibility or the possible interaction between the electrolyte and electrodes must be taken into consideration during device design.

Nanostructured faradaic materials, featured with high capacitance

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for storing electrical charge, low cost, great reversibility and environment friendly, have been widely studied for high performance pseudocapacitance [8]. The nanostructured heazlewoodite phase Ni_3S_2 is among the most promising electrode materials for SCs due to its novel atomic structures and electronic property [9]. The Ni_3S_2 exhibits metallic behavior but the bonding in its structure is more covalent compared with metal oxides [10], resulting in high electronic conductivity and more corrosion resistant as an electrode material for SCs. Great effort has been devoted to exploring varieties of Ni_3S_2 nanostructures for high-performing SCs in the last decade, such as thin film [11], nanosheets [12], nanorods [13], as well as in some hybrid nanostructures forms with CNTs [14], or rGO [15]. However, it is still a significant challenge to fabricate a perfect heazlewoodite phase Ni_3S_2 nanostructure with controllable composition and morphology.

Graphene is an important capacitive electrode materials in SCs as a result of its high ion-accessible surface area, low ion transport resistance, chemical stability, as well as excellent electrical and thermal conductivity. However, due to the strong interlayer π-π stacking and van der Waals interactions, graphene sheets tend to form irreversible agglomerates. Therefore, the area of effective contact between graphene electrode and electrolyte is decreased greatly and thus leads to the decay of its capacitive performance [16]. At present, advancing toward facile use, various three-dimensional (3D) porous and interconnected graphene materials (such as graphene foam, graphene hydrogels, and sponges) have been successfully designed and synthesized to improve the capacitive performance of SCs [17–19]. In particular, 3D reduced graphene oxide (3DrGO) with interconnected network structures as capacitive electrodes for SCs not only deliver a high specific capacitances, but also exhibit excellent rate performance and cycling stability [20,21]. Considerable researches suggest that binder- and conductive-agent-free interconnected 3DrGO can further improve overall SCs performance, because of the significantly decreased contact resistance, and improved the relative weight of the active materials compared to the introduction of conductive agent or a binder [19]. Therefore, it is important to develop effective and standardized methods to prepare binder- and conductive-agent-free interconnected 3DrGO for high-performance SCs applications.

In the present work, we developed a novel all-solid-state flexible ASC device based on home-made Ni_3S_2 positive electrode, 3DrGO negative electrode and PVA/KOH gel electrolyte. The heazlewoodite phase Ni_3S_2 nanorods are successfully grown on Ni foam (NF) scaffold through an optimized electrodeposition followed by a thermal annealing process. Simultaneously, the unique binder- and conductive-agent-free 3DrGO negative electrodes without current collector are synthesized by using NF as sacrificial templates. Moreover, the rational combination of electrodes with faradaic and capacitive storage mechanisms in the designed all-solid-state device leads to higher operating voltage as well as improved electrochemical capacitive performance and energy density. Finally, the optimized all-solid-state ASCs can be cycled reversibly between 0 and 2.2 V in PVA/KOH gel electrolyte and exhibit excellent electrochemical and mechanical behavior, including ultra-high energy density (70.58 Wh kg^{-1}), tremendous power density (33.0 kW kg^{-1} at 52.44 Wh kg^{-1}), excellent cycling stability (with 90.4% specific capacitance retained even after 5000 cycles at a constant current density of 5 A g^{-1}), and flexibility.

2. Experimental

2.1. Fabrication of samples

Preparation of Ni_3S_2 materials. The Ni_3S_2 nanorods are grown on Ni foam by a simple electrodeposition followed by a post annealing treatment. Ni_3S_2 nanorods are electrodeposited on Ni foam in a three-electrode electrochemical system. The precursor solution for electrodeposition of Ni_3S_2 is consisted of $NiCl_2{\cdot}6H_2O$ and thiourea (TU). In order to obtain the optimized Ni_3S_2 electrode, the concentration of the precursor solution for electrodeposition can be changed, but keeping the molar ratio of $NiCl_2{\cdot}6H_2O$ (as Ni source) to thiourea (as S source) is 1:20. A clear Ni foam sheet (1.0 × 1.0 × 0.1 cm), a Pt sheet (1.0 × 1.0 × 0.1 cm^2) and a saturated Ag/AgCl act as the working electrode, counter electrode and reference electrode, respectively. Ni-S nanorods precursor are electrodeposited by the cyclic voltammetry method, where the potential range from −1.2 to 0.2 V and the sweep rate is 5 mV per second. Three different concentration of $NiCl_2{\cdot}6H_2O$ and TU are prepared (25 mM $NiCl_2{\cdot}6H_2O$ and 0.5 M TU, 50 mM $NiCl_2{\cdot}6H_2O$ and 1 M TU, 100 mM $NiCl_2{\cdot}6H_2O$ and 2 M TU), suggesting that the optimal concentration of $NiCl_2{\cdot}6H_2O$ and TU are 50 and 1 M, respectively. The reaction between $NiCl_2$ and thiourea (TU) can be described as: $Ni^{2+} + 2e^- \rightarrow Ni$; $TU + Ni^{2+} \rightarrow (NiTU)^{2+}$; $TU + 2e^- \rightarrow S^{2-} + CN^- + NH^{4+}$; $2S^{2-} + O_2 + 2H_2O + 3Ni \rightarrow Ni_3S_2 + 4OH^-$. In order to obtain high crystallization feature of the heazlewoodite phase Ni_3S_2 nanorods, the as-prepared samples are annealed at 300 °C for 4 h with the ramp rate of 5 °C min^{-1} under the protection of argon.

Preparation of 3DrGO materials. The 3DrGO is synthesized by graphene oxide nanosheets deposited and coated onto the surface of Ni foam (as sacrificial templates), then etch the Ni foam templates by aqueous $FeCl_3$ solution at room temperature and reduce the GO into 3DrGO by ascorbic acid. A cleared Ni foam sheet (1.0 × 1.0 × 0.1 cm) is immersed into a GO dispersion (2 mg mL^{-1}) for 5 min. Then the Ni foam is taken out and dried for 5 h at room temperature. The dipping and drying process is repeated three times to increase the mass of GO. Then, the nickel foam sheet coated with GO is immersed into 1 M $FeCl_3$ at 60 °C for 72 h to completely dissolve the Ni foam. Finally, the as-prepared sample is transferred 20 ml of ascorbic acid aqueous solution (10 mg ml^{-1}) and maintain at 60 °C in a water bath for 5 h. Then, the sample is washed in sequence with absolute ethanol and deionized water.

Preparation of the all-solid-state flexible ASC device. The all-solid-state flexible ASC is made by using the Ni_3S_2 as positive electrode and the 3DrGO as negative electrode in PVA/KOH gel with one piece of filter paper (NKK TF45, 40 μm) as the separator. 3.0 g of KOH is added into 50 mL of deionized water, then 6.0 g of poly (vinyl alcohol) (PVA) powder is added. The solution is then stirred at 90 °C for 30 min. After that two pieces of the Ni_3S_2 and 3DrGO electrodes (1.0 × 1.0 cm) are immersed into the PVA/KOH gel for 10 min, they are removed and assembled into all-solid-state symmetric supercapacitor with a filter paper (NKK TF45, 40 μm) as the separator until the water evaporates.

2.2. Characterization

The morphology of samples is characterized by scanning electron microscopy (SEM, Hi-tachiS3400, Japan) and transmission electron microscopy (TEM, JEOL-2100F, Japan). X-ray diffraction (XRD) patterns are measured on an Xray diffraction instrument (X'TRA, Thermo ARL X'TRA, Switzerland). X-ray photoelectron spectroscopy (XPS) analysis is carried out using a Phi 5000 Versa Probe Scanning ESCA Microprobe (Ulvac-Phi, Inc., Japan). Raman spectra are recorded on a Raman spectrometer (LabRAM HR, Horiba Jobin Yvon Inc., France) using a 632.8 nm wavelength laser. Electrochemical performance measurements are measured on an electrochemical workstation (CHI 660D, Chenhua Instruments, China).

2.3. Electrochemical measurement

Electrochemical measurements are performed using an electrochemical workstation (CHI660D) at room temperature. For three-electrode systems tests, Ni_3S_2 materials and 3DrGO materials are directly used as the working electrode. A Pt foil (1.0 × 1.0 × 0.1 cm) and a standard calomel electrode (SCE) are used as the counter electrode and the reference electrode, respectively. A KOH aqueous solution (6M) is used as the electrolyte. The gravimetric specific capacitance in the three-electrode system is obtained from the discharge process by