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Dual support ensuring high-energy supercapacitors via high-performance $NiCo_2S_4@Fe_2O_3$ anode and working potential enlarged MnO_2 cathode

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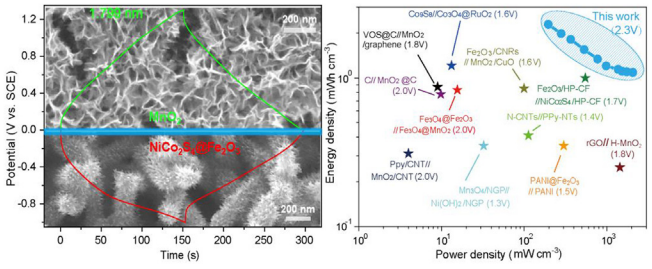
HIGHLIGHTS

- An asymmetric $NiCo_2S_4@Fe_2O_3$// MnO_2 supercapacitor is reported for the first time.
- Hierarchical $NiCo_2S_4@Fe_2O_3$ nanoarray with a capacitance of 342 F/g was used as anode.
- MnO_2 nanoarray with enlarged working potential to 1.3 V was used as cathode.
- The device was operated stably in 0 −2.3 V in neutral aqueous electrolyte.
- The device delivered high energy density (2.29 mWh cm^{-3}) at high power density.

GRAPHICAL ABSTRACT



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ABSTRACT

Development of high-energy and high-power asymmetric supercapacitors (ASCs) is still a great challenge due to the low specific capacitance of anode materials (carbon materials of about 100–200 F g^{-1}) and limited voltage window (<2 V) in aqueous electrolytes. Herein, we demonstrate the rational design of the hybrid $NiCo_2S_4@Fe_2O_3$ nanoneedle array anode with large specific capacitance (342 F g^{-1} at 5 mV s^{-1}) and MnO_2 nanosheet array cathode working in wide potential window (0–1.3 V *vs.* SCE) for high-energy and high-power ASCs. The unique core-shell hierarchical nanoarchitecture of the hybrid $NiCo_2S_4@Fe_2O_3$ nanoneedle arrays not only provides large surface area for charge storage but also facilitates fast charge transport in the electrode. Moreover, the extended potential window of the MnO_2 cathode can effectively increase the device voltage of the as-assembled ASC up to 2.3 V, resulting in significantly increased energy density. The obtained ASC device can deliver a high volumetric energy density of 2.29 mWh cm^{-3} at 196 mW cm^{-3} and retain 1.08 mWh cm^{-3} at 2063 mW cm^{-3}, providing new opportunity for developing high-performance ASCs.

1. Introduction

Intensive efforts have been stimulated to explore new charge storage devices by increasing power capability and energy density for portable electronic devices and hybrid electrical vehicle systems

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[1,2]. Asymmetric supercapacitors (ASCs), also known as an efficient strategy to boost energy density of supercapacitors (SCs), typically consist of a cathode and an anode working in separate potential windows [3–6]. As the key to realize high-performance ASCs, the development of high-performance electrodes has inspired many researchers to explore various electrode materials. High specific capacitance has already been achieved by advanced cathode materials in recent years. The anode materials (mainly carbon materials), however, haven't yet been fully explored and their limited specific capacitance cannot match the high specific capacitance of the cathode. In addition, the working voltage of the as-assembled ASCs is usually below 2 V, which is limited by the stable potential windows of cathode and anode in aqueous electrolytes. Therefore, it is still a great challenge to develop high voltage ASCs in aqueous electrolytes with high energy density and power density.

Transition metal oxides (TMOs) are of particular interests owing to their variable oxidation states which enable more readily accessible redox couples when utilized as anode or cathode materials. In past decades, great achievements have been made in developing various TMOs for supercapacitors [7–9]. Among these materials, Fe_2O_3 is considered as a promising anode material for ASCs due to following significant merits: a) rich redox pairs, such as Fe^0/Fe^{2+}, Fe^0/Fe^{3+}, and Fe^{2+}/Fe^{3+}, enabling high pseudocapacitance and wide working potential window; b) comparable costs with commercial activated carbon (less than $1 per kg for Fe_2O_3) [8]; c) and environmental benignity [10]. Nevertheless, the relatively low specific capacitance and poor cycling stability of Fe_2O_3 anodes deteriorate their performance and applicability in ASCs. This can be attributed to the intrinsically poor electrical conductivity and poor structural stability of Fe_2O_3. Several approaches including the construction of nanostructured Fe_2O_3 electrodes, making Fe_2O_3-based composite electrodes, and introduction of oxygen vacancy have been developed to alleviate these problems [5,11–14]. For Fe_2O_3-based composites, various conducting nanostructures (graphene [15–17], carbon nanotube (CNT) [18], highly conductive metal or metal oxides [19,20], *etc.*) have been used as scaffolds to load Fe_2O_3 materials. Notably, several issues about previous reported scaffolds should be taken into consideration: a) Yields and costs of carbon nanomaterials such as CNT and graphene may limit their practical applications. b) Metal nanomaterials such as porous Au [21] and Ni [22] lead to dead volume (no capacitance contribution) in the electrodes. c) Some TMOs such as CoO_x [23] and NiO [24] exhibit high capacity but fairly poor stability. Therefore, it is still a great challenge to develop appropriate conducting matrix for developing high-performance Fe_2O_3-based composite as anode material for ASCs.

In this work, we designed a hierarchical heterostructure consisting of highly conductive $NiCo_2S_4$ nanoneedle arrays (NNAs) core and Fe_2O_3 nanorods (NRs) shell (<5 nm in diameter). $NiCo_2O_4$ is well known to possess high electronic conductivity, which is twice higher than that of nickel oxides and cobalt oxides. Significantly, $NiCo_2S_4$ exhibits an electronic conductivity ~100 times higher than that of $NiCo_2O_4$ [25,26]. Therefore, $NiCo_2S_4$ NNAs could be perfect conductive scaffold for Fe_2O_3 by supplying fast electron transport. Significantly, a large specific capacitance (up to 342 F g^{-1}) as well as good rate capability has been achieved by the hierarchical $NiCo_2S_4@Fe_2O_3$ core-shell NNAs. Additionally, MnO_2 nanosheet arrays (NSAs) with enlarged stable working potential window (0–1.3 V *vs.* SCE) was prepared as cathode. Finally, a 2.3 V ASC device was constructed by using $NiCo_2S_4@Fe_2O_3$ anode and MnO_2 cathode, achieving a maximum volumetric energy density of 2.29 mWh cm^{-3} and a maximum volumetric power density of 2063 mW cm^{-3}.

2. Experimental section

2.1. Synthesis of the $NiCo_2S_4$ NNAs

Typically, a clear pink solution was firstly obtained by dissolving $NiCl_2 \cdot 6H_2O$ (5 mM), $CoCl_2 \cdot 6H_2O$ (10 mM), and urea (35 mM) in deionized water (40 mL). The as-prepared solution together with cleaned titanium (Ti) substrates was transferred into a Teflon-lined (50 mL) stainless-steel autoclave, which was heated to 120 °C for 6 h in an oven. After cooling down to room temperature, the Ti substrates with grown Ni-Co carbonate hydroxide NNAs were cleaned with the deionized water and ethanol, and then dried in air at 60 °C for 12 h. The as prepared Ni-Co carbonate hydroxide NNAs were put into a 50 mL Teflon-lined stainless steel autoclave containing 0.1 M Na_2S solution (40 mL) for further sulfuration (90 °C for 9 h). The final samples were washed with deionized water and ethanol for several times, and then dried at vacuum oven for further use.

2.2. Synthesis of $NiCo_2S_4@Fe_2O_3$ core-shell NNAs

The $NiCo_2S_4$@FeOOH NNAs were synthesized through a simple electrodeposition method. The electrodeposition is performed in a standard three electrode cell with the $NiCo_2S_4$ NNAs as the working electrode, Ag/AgCl (sat. KCl) as the reference electrode, and Pt foil as the counter electrode. The FeOOH electroactive materials were deposited at a constant potential of 1.5 V (vs. SCE) in 40 mL of 20 mM $FeCl_2$ solution at 75 °C for 10 min. After that, the samples were rinsed with deionized water and ethanol for several times, and dried at vacuum oven. Finally, the samples were annealed in Argone (Ar) gas at 300 °C for 2 h to obtain the $NiCo_2S_4@Fe_2O_3$ core-shell NNAs for further characterization.

2.3. Materials characterization

The crystallographic information and phase purity of the products were investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The XRD patterns were performed by a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα radiation between 20 and 80°. XPS was recorded on an ESCA Lab MKII X-ray photoelectron spectrometer with non-monochromatized Mg Kα X-ray as the excitation source. The morphology and microstructure of the samples were investigated by scanning electron microscopy (SEM, Hitachi S4300) and transmission electron microscopy (TEM, FEI-Philips CM300 UT/FEG). Brunauer-Emmet-Teller (BET) specific surface areas of the samples (scratched from the substrates) were determined from N_2 adsorption-desorption isotherms by using a Micromeritics ASAP 2010 (Micromeritics Instrument Corp) analyzer at liquid nitrogen temperature.

3. Results and discussion

As illustrated in Fig. 1a, free-standing Ni-Co carbonate hydroxide NNAs were firstly grown on the Ti substrate for the following anion exchange to form $NiCo_2S_4$ NNAs (Fig. S1 in Supporting Information (SI)). The Ti substrate was covered by uniform $NiCo_2S_4$ NNAs with diameters of 50–100 nm and length of ~800 nm (Fig. 1b and Fig. S2 in SI). Then a simple hydrothermal method was adopted to synthesize FeOOH NRs (~5 nm in diameter and 5–15 nm in length, see Figs. S3–4 in SI) on $NiCo_2S_4$ as precursor of Fe_2O_3. The $NiCo_2S_4@Fe_2O_3$ core-shell NNAs were finally obtained via annealing the $NiCo_2S_4$@FeOOH core-shell NNAs in Ar atmosphere. Fig. 1c shows the SEM image of the $NiCo_2S_4@Fe_2O_3$ core-shell NNAs, revealing no obvious morphological change and good thermal stability.