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Construction of hierarchical zinc cobalt sulfide@nickel sulfide core-shell nanosheet arrays for high-performance asymmetric solid-state supercapacitors

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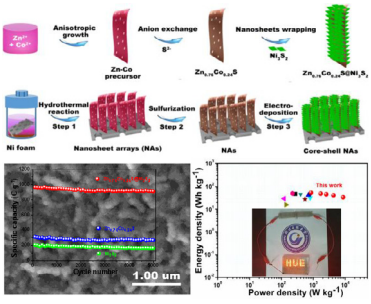
HIGHLIGHTS

- Hierarchical $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSNAs on NF have been designed and synthesized.
- Ni_3S_2 nanosheets were electrochemically deposited onto $Zn_{0.76}Co_{0.24}S$ NAs.
- Such CSNAs exhibited a high specific capacity of 1209 C g^{-1} at 2 A g^{-1}.
- The assembled ASSC could deliver an energy density of 53.8 W h kg^{-1} at 853 W kg^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

To fulfill the promise of high-performance supercapacitors (SCs) with a high specific capacitance, superior rate capability, long cycling life, and high energy density, it is desirable to rationally construct core-shell composite electrode materials with tailored architectures and components. In this reported study, hierarchical $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ core-shell nanosheet arrays (CSNAs) on Ni foam are designed and synthesized, in which interconnected $Zn_{0.76}Co_{0.24}S$ nanosheet cores are initially constructed through a hydrothermal reaction combined with a sulfurization process. These nanosheet cores are then uniformly wrapped by a Ni_3S_2 nanosheet shell using an electrochemical deposition reaction. The hierarchical structure of nanosheets@nanosheets together with the synergistic effect between the $Zn_{0.76}Co_{0.24}S$ and Ni_3S_2 components, enables the composite electrode to exhibit a large specific capacity (1209 C g^{-1} at 2 A g^{-1}), good rate capability (78.6% capacity retention at 20 A g^{-1}), and remarkable cycle stability (94.9 capacity retention after 5000 cycles at 20 A g^{-1}). Furthermore, the fabricated $Zn_{0.76}Co_{0.24}S@Ni_3S_2$//active carbon (AC) asymmetric solid-state supercapacitor cell (ASSC) can deliver a high energy density of 53.8 W h kg^{-1} at a power density of 853 W kg^{-1}. These results showcase the great application potential of the novel core-shell composite electrode in high-performance SCs, and they also provide an alternative method for constructing metal sulfide-based composite electrodes with optimum electrochemical performance.

1. Introduction

Nowadays, SCs have emerged as very attractive devices to meet the increasing demands of portable electronic devices, hybrid electric vehicles, and energy storage systems, because of their quicker charge-discharge rate, larger power density, and better cycle stability than Li-

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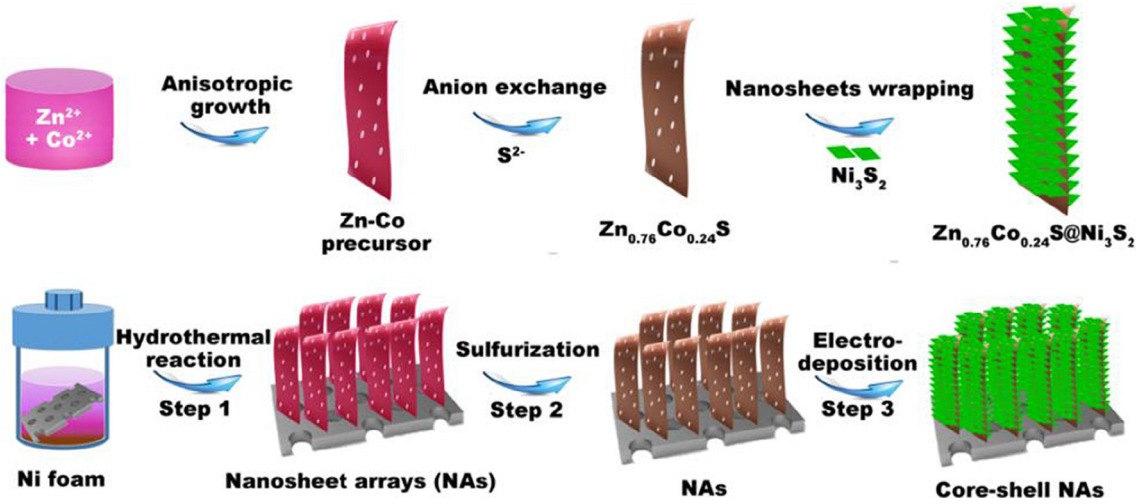

Fig. 1. Schematic illustration of the synthesis of $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSNAs on Ni foam by a stepwise fabrication procedure.

ion batteries and fuel cells [1–11]. In particular, the ASSC is very intriguing due to their systemic advantages such as environmental friendliness, portability, flexibility, and reliability [12–17]. These devices are fabricated by using a pseudocapacitive material as the energy source and electric double layer capacitance (EDLC) material as the power source, which can deliver high energy density as well as high power density to the whole cell [18,19]. Despite these desirable features, the ASSC still suffers from the major issue of low energy density in large-scale practical applications. Therefore, significant challenges still remain in enhancing the energy density of ASSC, while retaining its high power density and long cycle stability to satisfy the practical application requirements in electric vehicles and electronic devices.

In this regard, considerable attention has thus been to paid to investigate pseudocapacitive electrodes with excellent electrochemical performance. Recently, transition metal sulfides (TMSs), including monometal sulfides M_xS_y (M = Ni, Co, Cu, Mo, etc.) [20–26] and bimetal sulfides ($NiCo_2S_4$ [27,28], $MnCo_2S_4$ [29], $CuCo_2S_4$ [30], etc.), have been studied as a novel class of SC electrode materials, considering their high electrical conductivity and excellent redox performance in comparison to the corresponding transition metal oxides. Although great technical progress has been achieved, it is still important to optimize the compositions and microstructures of the TMSs-based electrode materials to improve them for use as electrode materials in high-performance SCs.

It has been clearly established that several desirable features are essential for high-performance pseudocapacitive electrodes, including good electrical conductivity, a large electroactive surface area, high electrochemical activity, and a stable integrated architecture. It has been postulated that these prerequisites can be achieved by constructing the electrodes as the core-shell heterostructure nanoarrays (CSHNs) that could significantly improve the electrochemical performance. This conclusion is based on the belief that this CSHNs structure would provide an abundance of accessible redox reaction sites, a short path length for ion diffusion, and synergistic effects offered by the core and shell materials [31–35]. To date, reports have emerged of various CSHNs that have been built by combining TMSs with metal hydroxides, metal oxides, conductive polymer, or different TMSs. These various CSHNs have been reasonably designed and have been reported to exhibit superior electrochemical performance [36–41]. For example, Zhu et al. reported on the synthesis of $Co_9S_8@Ni(OH)_2$ nanotubes arrays with a specific capacity of 149.44 mAh g^{-1}, which is about two times more than the single Co_9S_8 electrode [36]. This same study also found that this novel material exhibited 50.2% capacity retention at 10 A g^{-1}. Yan et al. reported the preparation of a $NiCo_2S_4$@polypyrrole core-shell heterostructure nanotube array that exhibited 39% capacitance retention at 50 mA cm^{-2} with a specific area capacitance of 9.781 F/cm^2, which was two times greater than the single $NiCo_2S_4$ nanoarray [37]. Wang et al. synthesized $Ni_3S_2@MoS_2$ core-shell nanorod arrays with a 46.6% capacity retention at 20 A g^{-1}, and a specific capacitance of 848 F g^{-1} that was twice that of the single Ni_3S_2 nanoarray [38]. Despite these considerable accomplishments, a major challenge still remains to finely tailor the specific components and engineer the microstructures of TMSs-based CSHNs to produce optimum electrochemical performance for the practical application of SCs.

Zinc cobalt sulfides (ZCSs), such as $Zn_{0.76}Co_{0.24}S$, have drawn much attention as a potential low-cost, competitive electrode material for SCs [42–45]. Compared to either single zinc or cobalt sulfide or the zinc cobalt oxide, ZCSs possess higher electrical conductivity and more energetic reactions, all of which endow ZCS with better electrochemical performance. Nickel sulfide, such as Ni_3S_2, is also of interest as an electrode material with a number of advantages such as high theoretical capacitance (2400 F g^{-1}), good conductivity (1.8×10^{-5} Ω cm^{-1}), and low cost [46,47]. Therefore, by combining the advantages of these two materials, it has been anticipated that the unique $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSHNs might be a promising candidate for high-performance SCs. Moreover, until now, there has been no reported research on the electrochemical performance of the integrated $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSHNs electrode.

Herein, we detail the design and preparation of $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSNAs by electrodepositing Ni_3S_2 nanosheets onto $Zn_{0.76}Co_{0.24}S$ nanosheet arrays (NAs) on a Ni foam. As shown in Fig. 1, Zn-Co precursor NAs were prepared using a hydrothermal reaction, which was followed by a sulfurization process that was performed to form $Zn_{0.76}Co_{0.24}S$ NAs as a result of an anion exchange reaction. Finally, Ni_3S_2 nanosheets were electrodeposited onto the surface of $Zn_{0.76}Co_{0.24}S$ nanosheets to produce the target $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSNAs. It was found that, compared to the single $Zn_{0.76}Co_{0.24}S$ or Ni_3S_2 electrodes, the prepared $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSNAs as an electrode for SCs demonstrated remarkably improved electrochemical performance. This performance included a high specific capacity of 1209 C g^{-1} (2.23 C cm^{-2}) at 2 A g^{-1} (3.7 mA cm^{-2}), a good rate capability with 78.6% capacity retention at 20 A g^{-1}, and high cycle stability with 94.9% capacity retention after 5000 cycles at 20 A g^{-1}. This superior electrochemical performance was probably due to the nanosheets@nanosheets CSHNs and the synergistic effects of the $Zn_{0.76}Co_{0.24}S$ core and Ni_3S_2 shell. Moreover, the ASSC fabricated with $Zn_{0.76}Co_{0.24}S@Ni_3S_2$//AC exhibited an energy density of 53.8 W h kg^{-1} at a power density of 853 W kg^{-1}. These results aptly demonstrate the competitive nature of $Zn_{0.76}Co_{0.24}S@Ni_3S_2$ CSNAs for use in high-performance SCs electrodes, but also offer an effective way to design and construct TMSs-