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Rational construction of nickel cobalt sulfide nanoflakes on CoO nanosheets with the help of carbon layer as the battery-like electrode for supercapacitors

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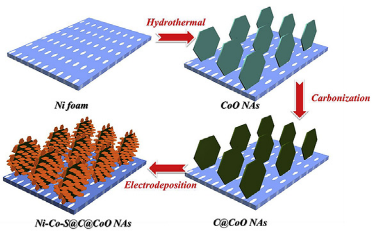
HIGHLIGHTS

- Hierarchically structured Ni-Co-S@C@CoOnanosheet arrays are fabricated on Ni foam.
- The synergistic effect of each component results in achieving excellent electrochemical performance of Ni-Co-S@C@CoO.
- High specific capacitance, good rate capability and excellent cycling stability are achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, binder-free hierarchically structured nickel cobalt sulfide nanoflakes on CoO nanosheets with the help of carbon layer (Ni-Co-S@C@CoO NAs) are fabricated *via* hydrothermal synthesis, carbonization treatment and electrodeposition, where three key components (CoO nanosheet arrays, a carbon layer and Ni-Co-S nanoflakes) are strategically combined to construct an efficient electrode for supercapacitors. The highly well-defined CoO nanosheets are utilized as ideal conductive scaffolds, where the conductivity is further improved by coating carbon layer, as well as the large electroactive surface area of Ni-Co-S nanoflakes. Furthermore, self-supported electrodes are directly grown on Ni foam without conductive additives or binders, which can effectively simplify the whole preparation process and achieve excellent electrical contact. Benefiting from the unique structural features, the hierarchically structured Ni-Co-S@C@CoO NAs exhibit high specific capacitance up to 4.97 F cm^{-2}, excellent rate capability, and maintains 93.2% of the initial capacitance after 10000 cycles. Furthermore, an asymmetric supercapacitor using the Ni-Co-S@C@CoO NAs electrode and activated carbon is assembled, which achieves a high energy density (49.7 W h kg^{-1}) with long cycling lifespan. These results demonstrate the as-fabricated Ni-Co-S@C@CoO NAs can be a competitive battery-like electrode for supercapacitors in energy storages.

1. Introduction

Supercapacitor, known as one promising energy storage device, has been extensively studied because of the high power density, rapid charge-discharge rate and good cycling stability [1–4]. In

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general, there are two kinds of supercapacitors according to the charge storage mechanisms, including electrochemical double layer capacitors (EDLCs) and pseudocapacitors [5–7]. Recently, many research works have been devoted to pseudocapacitors, which offer variable oxidation states for reversible faradaic redox reactions and deliver a higher specific capacitance than that of EDLCs [8].

Till now, transition metal sulfides, especially ternary nickel cobalt sulfides (Ni-Co-S), have been promising candidates for supercapacitor electrodes and achieving in better electrochemical performance, due to the higher conductivity and richer electroactive sides [9–11]. Furthermore, various kinds of Ni-Co-S nanomaterials such as nanowire, nanotube, nanosheet arrays have been successfully synthesized in order to fully achieve better electrochemical performance [12–15]. However, the structural instability of free-standing Ni-Co-S nanomaterials brings about a detrimental effect on the cycling performance, which may be due to the mechanical stress and strain, or the volume change associated with ion insertion-desertion process [16,17]. In order to overcome the aforementioned drawback and improve the utilization of active materials, various Ni-Co-S based configurations have been constructed [18–20]. In particular, developing the core-shell structure is an effective approach for better electrochemical performance because such unique structure can provide numerous redox reaction sites, efficient ion diffusion pathway, as well as inherit advantages from individual components [21–23]. For example, Yang et al. has successfully fabricated one-dimensional $NiCo_2S_4$@MnO_2 core-shell heterostructures using a simple hydrothermal route [22]. Compared with pure $NiCo_2S_4$, the resulting $NiCo_2S_4$@MnO_2 possesses a maximum capacitance up to 1337.8 F g^{-1} and retains 82% after 2000 cycles. Wan et al. have fabricated three dimensional (3D) $NiCo_2S_4$@Ni-Mn layered double hydroxide (LDH) on graphene sponge, where $NiCo_2S_4$ nanotube acts as backbones for supporting Ni-Mn LDH [23]. This unique core-shell heterostructure can optimize the electrochemical performance of 3D structural electrodes, resulting in higher specific capacitance up to 1.7 F cm^{-2}. Consequently, elaborately designing the core-shell structure of Ni-Co-S based electrodes is regarded as a fascinating and effective strategy for improving their electrochemical properties.

With respect to construct core-shell structure, it is vital to make use of 3D hierarchical materials such as carbon nanomaterials and metal oxides, as backbones for supporting Ni-Co-S to enhance the performance [12,15,23,24]. Among these materials, metal oxide nanowires or nanosheets (e.g., CoO, Co_3O_4, and MnO_2) are promising core materials, which can be simply and directly synthesized on substrates without binders (e.g., Ti foil, Cu and Ni foam) [23–25]. Further, well-define metal oxides with three-dimensional structure can not only create an effective electron transport path, but also maximize the loading of active material for increasing the area-normalized capacitances [25,26]. Due to the high theoretical specific capacitance, low cost, and environmentally friendly nature, CoO is a promising candidate as backbones for core-shell structure [27]. However, the poor electrical conductivity of CoO may show some disadvantages on the capacitive performance of Ni-Co-S hybrid electrodes [28]. It is generally accepted that amorphous carbon layer shows much higher electrical conductivity that of CoO [29]. Thus, introducing amorphous carbon layer to form hybrid cores can effectively enhance electrical conductivity of the whole entity and maintain the structural stability. Therefore, new designs of high-performance Ni-Co-S based electrodes must feature with a desired combination of three-dimensional structured Ni-Co-S and a good electrical conductivity with the help from of conductive additives.

Herein, we have successfully designed and synthesized hierarchically structured Ni-Co-S@C@CoO nanosheet arrays (NAs) *in situ* on Ni foam and directly used as the battery-like electrode for supercapacitors. Above all, the well-defined CoO nanosheets serve as backbones for Ni-Co-S nanoflakes, and maximize the loading of Ni-Co-S nanoflakes and increase the area-normalized capacitances. Then, the carbon layer on CoO nanosheets can enhance the conductivity of the whole entity and maintain the structural stability. Additionally, ultrathin Ni-Co-S nanoflakes can provide large surface area with the electrolyte and shorten ion diffusion paths. More importantly, the self-supported Ni-Co-S@C@CoO NAs on Ni foam without non-conducting organic binders can achieve excellent electrical contact and make each component fully participate in electrochemical reactions. Owing to the synergistic contribution from individual constituents and elaborately designed configuration, the resulting Ni-Co-S@C@CoO NAs exhibit the high specific capacitance up to 4.97 F cm^{-2}, good rate capability and maintains excellent cycling performance. Furthermore, the as-assembled Ni-Co-S@C@CoO NAs//AC device exhibits relatively high energy density as well as good cycling performance.

2. Experimental

2.1. Preparation of carbon-coated CoO nanosheet arays (C@CoO NAs)

The nickel foams (80–100 pores per inch, 0.25 mm average hole diameter and 1.6 mm thick, Hefei Ke Jing Materials Technology Co. Ltd., China) were used as the substrates. The self-supported CoO NAs were directly grown on Ni foam using a hydrothermal method [30]. Firstly, $Co(NO_3)_2 \cdot 6H_2O$ (3.5 mmol) and hexamethylene tetramine (HMTA, 7 mmol) were dissolved in 35 mL of deionized water to form pink solution. Subsequently, the obtained solution and Ni foam were transferred into a Teflon-lined stainless steel autoclave and was heated to 95 °C for 8 h. When cooled down to room temperature, the obtained samples were washed using deionized water and ethanol for several times. Finally, the samples were annealed at 400 °C for 2 h at Ar atmosphere to obtain self-supported CoO NAs. To fabricate carbon-coated CoO NAs, the obtained CoO NAs were immersed in 0.05 M aqueous glucose solution at 80 °C for 5 h, followed by carbonization at 400 °C at Ar atmosphere for 2 h, resulting in C@CoO core-shell NAs.

2.2. Preparation of Ni-Co-S@C@CoO hybrid nanosheet arrays (Ni-Co-S@C@CoO NAs)

Ni-Co-S@C@CoO NAs were prepared using C@CoO NAs as backbones by an electrodeposition process [3,30]. The electrodeposition solution contains $NiCl_2 \cdot 6H_2O$ (5 mmol), $CoCl \cdot 6H_2O$ (5 mmol) and $CS(NH_2)_2$ (0.75 M). The electrodeposition was performed via cyclic voltammetry (CV) at 10 mV s^{-1} for 20 cycles from −1.2 V to 0.2 V. After that, the obtained samples were washed several times and dried at 80 °C for 8 h. The mass loadings of CoO, C@CoO, Ni-Co-S, Ni-Co-S@CoO and Ni-Co-S@C@CoO are calculated to be ~0.95 mg cm^{-2}, ~1.24 mg cm^{-2}, ~1.93 mg cm^{-2}, ~2.27 mg cm^{-2} and ~2.54 mg cm^{-2}.

2.3. Materials characterization

Scanning electron microscopy (SEM, JEOL JSM-6700F), transmission electron microscopy (TEM) and high resolution TEM (HRTEM) (HRTEM, FEI F30) were conducted to characterize the morphologies and structures of obtained samples. Further, X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) and Raman spectroscopy (Renishaw inVia) were also conducted.