



Mesoporous composite nickel cobalt oxide/graphene oxide synthesized via a template-assistant co-precipitation route as electrode material for supercapacitors



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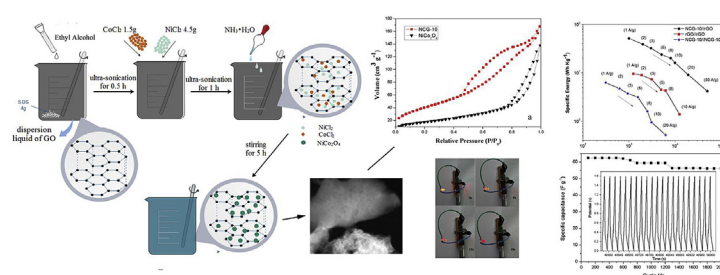
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HIGHLIGHTS

- A simpler chemical route was utilized to prepare composite NiCo₂O₄/GO.
- The abundant mesopores and channels are boosted by the substantial function of SDS.
- NiCo₂O₄/GO delivers good specific capacitance and cycling stability.
- NiCo₂O₄/GO//rGO demonstrates remarkable energy density and power density.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple co-precipitation method utilizing SDS (sodium dodecyl sulfate) as template and ammonia as precipitant is successfully employed to synthesize nickel cobalt oxide/graphene oxide (NiCo₂O₄/GO) composite. The as-prepared composite (NCG-10) exhibits a high capacitance of 1211.25 F g⁻¹, 687 F g⁻¹ at the current density of 1 A g⁻¹, 10 A g⁻¹ and good cycling ability which renders NCG-10 as promising electrode material for supercapacitors. An asymmetric supercapacitor (ASC) (full button cell) has been constructed with NCG-10 as positive electrode and lab-made reduced graphene oxide (rGO) as negative electrode. The fabricated NCG-10//rGO with an extended stable operational voltage of 1.6 V can deliver a high specific capacitance of 144.45 F g⁻¹ at a current density of 1 A g⁻¹. The as-prepared NCG-10//rGO demonstrates remarkable energy density (51.36 W h kg⁻¹ at 1 A g⁻¹), high power density (50 kW kg⁻¹ at 20 A g⁻¹). The retention of capacitance is 88.6% at the current density of 8 A g⁻¹ after 2000 cycles. The enhanced capacitive performance can be attributed to the improved specific surface area and 3D open area of NCG-10 generated by the pores and channels with the substantial function of SDS.

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1. Introduction

Currently, with the soaring energy consumption and the

subsequently increased demand for alternative energy sources, the urgent development of energy storage devices has drawn enormous attention with regard to their nature of both desirable energy density and high power density. Supercapacitors, exhibiting fast charge/discharge capability and long cycle life, are becoming the promising candidates for energy storage devices. However, the key limitation for its further application is the relatively lower energy

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density than traditional batteries [1–3]. To solve the problem, a general strategy is to prepare hybrid material, as positive electrode, composed of carbon-based material and pseudocapacitive component [4,5].

Transition metal oxides and hydroxides were reported as the most commonly-used pseudo-capacitive materials for high energy density storage systems because of their desirable theoretical capacitance, such as RuO_2 , MnO_2 , Co_2O_3 , NiO , $\text{Ni}(\text{OH})_2$ etc., but the high cost of RuO_2 hinders its practical application despite its excellent capacitive performance. Besides, most of transition metal oxides are faced with the challenges of poor cycling stability [6–9]. The fabrication of binary oxides has thus attracted extensive investigations in recent years, among which NiCo_2O_4 has been reported to show superior electrochemical performance and attain increasing attention. Sama B. et al. reported a mixed electrode Co_2O_3 – NiCo_2O_4 obtaining specific capacitance ($>400 \text{ F g}^{-1}$) under the scan rate of 20 mV s^{-1} [10]. Porous nickel–cobalt layered hydroxide synthesized via a facile hydrothermal method by X.T. Zheng et al., delivers a significantly enhanced specific capacitance (2184 F g^{-1} at 1 A g^{-1}) owing to the pronounced synergistic effect between Ni^{2+} and Co^{2+} , retaining 88.5% of the initial capacitance after 2000 cycles [11].

Carbon-based material, such as graphene which presents many edges, like notably high electrical conductivity, and large SSA (specific surface area) (over $2600 \text{ m}^2 \text{ g}^{-1}$), makes itself good support for pseudo-capacitors in energy storage [12]. B. Wei et al. reports the MnO_2/rGO composites displayed an excellent cycling (2.3% loss after 1000 cycles) [13]. The $\text{C}/\text{CoNi}_3\text{O}_4$ composite possesses a specific capacitance of 1299 F g^{-1} and excellent rate capability (78% retention at the large discharge current) [14]. It can be seen that the capacitive performance can be considerably improved, especially the cycling stability with the help of the carbon-based material [15].

Herein, in this study, we demonstrate a simple co-precipitation method combined with calcination to fabricate $\text{NiCo}_2\text{O}_4/\text{GO}$ (NCG) composites with the assistance of anionic surfactant SDS. Compared with other fabrication methods, including chemical vapor deposition [16], electrodeposition [17], hydrothermal synthesis [2,14], sol–gel method [18], electrospinning [19], and electrophoretic deposition (EPD) calcination method [20], co-precipitation is a facile, and cost-effective way to prepare binary oxides with short reaction durations [21]. Meanwhile, Supported by the previous reports (shown in Table S1), the as-prepared composite is somehow competitive in electrochemical properties which also delivers a higher specific capacitance than either pure NiCo_2O_4 particles or graphene oxide.

To further ensure the facile synthetic method can serve as an attractive route to fabricate the potential asymmetric electrodes in practical application, an asymmetric supercapacitor (ASC) has been constructed with NCG-10 as positive electrode and lab-made reduced graphene oxide (rGO) as negative electrode. The fabricated ASC enlarges the voltage window to 1.6 V, delivers relatively high specific capacitance, and demonstrates remarkable energy density ($51.36 \text{ W h kg}^{-1}$ at 1 A g^{-1}), high power density (50 kW kg^{-1} at 20 A g^{-1}). In terms of the employed surfactant SDS, the long molecular chains can prevent solute from getting together by reducing the surface tension of particles and provide more active rooms to enhance capacitive performance [22]. The decomposition of SDS can create pores, change the morphologies, and increase the specific surface area as well as improve the electrochemical behavior of the samples [23–25]. The physicochemical characteristics and electrochemical properties of the prepared products were studied to prove that the enhanced capacitive behavior was stimulated by the porous structure due to the decomposition of the template SDS. The simple and environmentally-benign method

employing the most common alkali (Ammonia) is demonstrated to serve as a promising route for synthesizing promising electrode material for supercapacitors.

2. Experiment

2.1. Synthesis of graphene oxide and reduced graphene oxide

Graphene oxide was prepared by a modified Hummers method [26]. Graphite powder (3.0 g) was first added with stirring into concentrated H_2SO_4 (24 mL), in which $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g) and P_2O_5 (2.5 g) were dissolved at 80°C in advance. The mixture was stirred for 4.5 h at 80°C in oil bath. After cooling down to room temperature, the solution was diluted with distilled water and settled overnight. The as-prepared product was collected by filtration and washed by distilled water, and then dried at 80°C for 10 h. Then the pre-oxidized graphite (2.5 g) and NaNO_3 (1.25 g) were mixed and put into concentrated H_2SO_4 (115 mL) in a flask with ice bath. KMnO_4 (7.5 g) was gradually added into the mixture with vigorous stirring to keep the temperature below 20°C . After removing the ice bath, the mixture was stirred at 35°C for 0.5 h followed by addition of H_2O (300 mL). The color of the solution turned to yellow after additional stirring at 98°C for 1 h. Then the solution was further diluted with distilled water and H_2O_2 (30%, 30 mL) was added into it. After being settled overnight, the remaining product was centrifuged and washed with distilled water until the pH became neutral. Then dry in vacuum to get the brown flake graphene oxide (GO). rGO can be obtained simply by a reduction reaction with the help of hydrazine hydrate as reductant.

2.2. Synthesis of $\text{NiCo}_2\text{O}_4/\text{GO}$ composite

The $\text{NiCo}_2\text{O}_4/\text{GO}$ composite was prepared by a facile chemical co-precipitation route. Sodium dodecyl sulfate (4 g) and 5 mL ethanol were added to 100 mL of 1 mg mL^{-1} GO suspension, and then stirred for 30 min to form homogenous solution. Next, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (4.5 g) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5 g) (Ni:Co = 3:1) were dissolved in the solution with ultra-sonication for 1 h to make ions adsorbed on the surface of GO sheets. The pH value of the mixture was adjusted to 9 by adding slowly 5 wt. % $\text{NH}_3 \cdot \text{H}_2\text{O}$ at room temperature. After 5 h stirring, the dark green precipitate was filtered, repeatedly washed by deionized water until pH reach 7 and then washed by absolute ethyl alcohol and finally dried in a vacuum oven at 70°C for 0.5 h. The precursor was calcined at 250°C for 3 h in air to obtain the $\text{NiCo}_2\text{O}_4/\text{GO}$ composite (See Scheme 1).

In light of comparison, different $\text{NiCo}_2\text{O}_4/\text{GO}$ composites can be obtained by changing the feeding weight ratio of GO and then calcined under different temperatures. For referring convenience, all the as-prepared composite products $\text{NiCo}_2\text{O}_4/\text{GO}$ (at Ni:Co = 3:1, calcined at 250°C , with SDS) are termed as NCG-r, with r denoting the content of GO.

In addition, pure Ni–Co binary oxide were also synthesized using the same procedure at other molar ratios (Ni:Co) of 1:1, 1:2, 1:3, 1:10, 10:1 and 2:1, for comparison with NiCo_2O_4 (prepared at Ni:Co = 3:1).

2.3. Physicochemical characterization

The surface morphology of the products was characterized by field emission scanning electron microscopy (FESEM, Ultra 55, Germany). Transmission electron microscopy (TEM, JEM 2011, Japan) and high-resolution transmission electron microscopy (HRTEM) were also utilized to characterize the microstructure of the products. The crystal structure was analyzed by X-ray diffraction (XRD, D8 Advanced, Germany) using $\text{Cu K}\alpha$ radiation. Raman

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