

DNA-templated synthesis of nickel cobaltite oxide nanoflake for high-performance electrochemical capacitors



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ABSTRACT

NiCo₂O₄ nanoflake composites were synthesized by using DNA molecules as templates via in-situ assembly and subsequent thermal treatment. The obtained NiCo₂O₄ composites were characterized by scanning electron microscopy, energy dispersive spectroscopy, X-ray powder diffraction, thermogravimetric analysis, and X-ray photoelectron spectroscopy. Cyclic voltammetry and chronopotentiometry tests were used to investigate the electrochemical properties of the as-prepared composites. Superior performances with a good specific capacitance (1468 F/g), an extraordinary rate capability (64.9% capacity retention at 16 A/g) and an excellent cycling stability (85.5% retention after 5000 cycles) were achieved. The DNA templates were introduced as the binder of NiCo₂O₄ and as the conductive matrix to facilitate the electron transmission between electroactive materials and outside current collectors, which resulted in the excellent electrochemical performances of the synthesized NiCo₂O₄ composites. It is believed that our NiCo₂O₄ nanocomposites could be used as effective electrode materials for supercapacitors.

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1. Introduction

Considerable effort has been devoted to develop advanced energy storage device and management systems to address the ever worsening energy depletion and the environmental issues [1–4]. Electrochemical capacitors (ECs), known as supercapacitors, have received considerable attention as a promising energy storage device, due to their highly specific power and energy density, fast charge and discharge rates, long cycle life, and low maintenance cost [5–7]. ECs store energy depending on either ion adsorption (electrical double-layer charge storage, which are most carbonaceous supercapacitors [8,9]) or fast reversible multi-electron surface redox Faradaic reactions (pseudocapacitors, fabricated by transition metal oxides or hydroxides with variable valence [10–13]). Among various EC electrode materials, transition metal oxides are considered as a kind of ideal material which can offer rich redox reactions. Up to now, it is well established that RuO₂ is a prominent electroactive material showing a remarkably high specific capacitance (SC) and an excellent reversibility [14,15]. However, several disadvantages like the high cost, the rarity and the toxic nature of RuO₂ limit its wide applications. Therefore, in recent years,

low-cost and environmentally friendly transition metal oxide materials including nickel oxide [16], cobalt oxide [10], manganese oxide [11], iron oxide [17] and their composites [18] have been extensively investigated to explore alternative and effective electroactive materials for high-performance supercapacitors.

Cobalt and/or nickel oxides have been widely applied in many fields, for instance, supercapacitors [19], lithium-ion batteries [20,21], magnetic materials [22], electrocatalysts [23], and chemical sensors [24]. Recently, hierarchically cobalt-nickel oxides with controllable dimensions have attracted much interest because of their improved electrochemical activity compared to the single-element materials. It was reported that the spinel binary NiCo₂O₄ showed two orders of magnitude higher electronic conductivity than that of only nickel oxides or cobalt oxide [25]. The co-contribution of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺ redox couples are responsible for variety of redox reactions, and result in highly specific capacitance and good electrochemical stability [26]. These attractive features are of great benefits for the development of high-rate supercapacitors.

Recently, researchers have utilized many methods to prepare a lot of binary NiCo₂O₄ nanomaterials with different controllable morphologies including spinel nanostructures [27], nanosheets [28], nanoneedle arrays [29], nanowires [30,31], and nanotubes [32]. For example, Lou's group obtained ultrathin mesoporous NiCo₂O₄ nanosheets by thermal treatment of Ni-Co hydroxide

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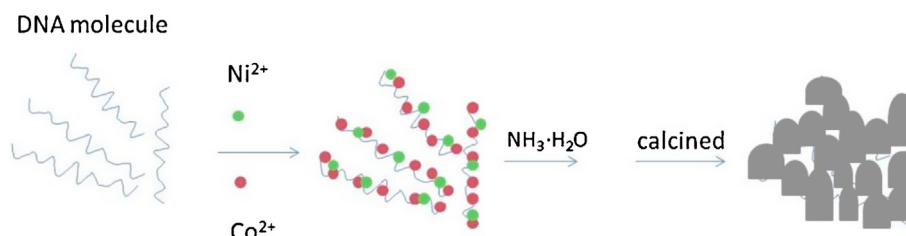


Fig. 1. The scheme illustration of the synthesis process for NiCo₂O₄ nanoflakes by DNA template.

co-electrodeposited on Ni foam [28], and they also obtained single-crystalline NiCo₂O₄ nanoneedle arrays through a solution reaction and subsequent post-annealing treatment [29]. Yuan *et al.* constructed ultralayered mesoporous NiCo₂O₄ nanowires from quasi-single-crystalline NiCo₂O₄ nanosheet building blocks [30]. Although different structures of NiCo₂O₄ have been fabricated, the rate capability and cycling stability of the material still need to be improved.

It is well-known that DNA molecules have been used as building blocks for controlled assemblies of complicated nanostructures [33–36]. Recently, DNA molecules have been introduced to polymers or carbon nanotubes (CNTs) to improve their electrochemical properties in supercapacitors [37,38]. However, the preparation of metal oxide supercapacitors by using DNA molecules has not been reported so far. In addition, DNA molecules show several advantages in constructing nanomaterials for supercapacitor. DNA molecules could easily bind with metal ions due to they have plenty of phosphate backbone and bases. Furthermore they could produce metal oxide nanomaterials with large surface area, which is favorable for ion diffusion throughout the porous materials. At the end, DNA is a kind of conductive macromolecule, and it may improve electrical conductivity of the metal oxide nanomaterials.

Here, for the first time, we reported a facile strategy to prepare NiCo₂O₄ nanoflake composites by using DNA molecules as templates through an in-situ assembly and subsequent thermal treatment procedure. Ni²⁺ and Co²⁺ ions were firstly adsorbed on DNA molecules backbones; further reacted with ammonia solution and then produced Ni-Co hydroxide nanoflakes on DNA molecules. After thermal treatment, Ni-Co hydroxide was transferred to NiCo₂O₄ composites. The synthesis process of NiCo₂O₄ composites by DNA template was schemed in Fig. 1. In the composites, NiCo₂O₄ nanoflakes interconnect with each other to afford porous nanostructure, and the open space among the nanoflakes can greatly enlarge the contact area and shorten the diffusion path between the electrode materials and electrolyte. DNA is introduced as the binder of NiCo₂O₄ and the conductive matrix to facilitate the electron transfer between electroactive materials and outside current collectors. The electrochemical measurements demonstrated that NiCo₂O₄ nanoflake composites exhibited high pseudocapactive performance, extraordinary rate capability and good cyclability, indicating its potential applications as high-performance supercapacitor electrode materials.

2. Experimental

2.1. Materials

Nickel chloride hexahydrate (NiCl₂·6H₂O, 99.95%, metal basis), cobalt chloride hexahydrate (CoCl₂·6H₂O, 99.95%, metal basis), ammonia solution (NH₃·H₂O, 25%), potassium hydroxide (KOH) and absolute ethanol were purchased from the Beijing Chemical Co. (Beijing, China). Calf thymus DNA (fibers) was purchased from Sigma-Aldrich Chemical Co., and was dissolved to 0.2 mg/mL by tris-HCl buffer (pH = 8.23). Nickel foam with a purity of ≥ 99.6%

was purchased from Changsha Lyrun Material Co., Ltd., China. All of these reagents were of analytical grade and used without further purification. Ultrapure water (18.2 MΩ cm) produced by a Milli-Q system was used as the solvent throughout this work.

2.2. Synthesis of Ni-Co hydroxide nanoflakes

100 mL of 0.01 M NiCl₂ and 0.02 M CoCl₂ mixture was added to the beaker and stirred for 5 min. Then, different quantity of DNA was added to the solution and stirred for another 5 min. Finally, 600 μL of ammonia solution was diluted 10-fold, and added dropwise into the above solution under vigorous stirring. The obtained solid product was centrifuged, washed several times with distilled water and alcohol, and dried at 60 °C.

2.3. Synthesis of the DNA-NiCo₂O₄ composites

The above black precipitate was heated at 200 °C for 6 h in an air atmosphere, resulting in the formation of the DNA-NiCo₂O₄ composites. For the synthesis of DNA-NiCo₂O₄ composites with different amounts of NiCo₂O₄, the volumes of the DNA: 100 μL, 500 μL, and 2 mL were denoted as NC1, NC5, and NC20, respectively. The pure NiCo₂O₄ was prepared in the same procedure, without the addition of DNA (denoted as NC0).

2.4. Characterization techniques

X-ray diffraction (XRD) patterns were recorded with a Rigaku-D/max 2500 V X-ray diffractometer equipped with a CuK_α radiation source (λ = 1.54178 Å). Scanning electron microscopy (SEM), and X-ray energy dispersive spectroscopy (EDS) characterizations were obtained on an XL30 ESEM FEG scanning electron microscope equipped with an energy dispersive X-ray analyzer at an accelerating voltage of 20 kV. AFM imaging was performed on a Digital Instruments multimode AFM controlled by a Nanoscope V apparatus (Veeco Instruments, USA) equipped with an E scanner. A standard silicon cantilever tip from Digital Instruments was used. The scan rate was 1 Hz. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were carried out using a TECNAI G2 high resolution transmission electron microscope with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) data were measured from 23 to 900 °C at 10.0 °C/min under flowing air on Netzsch Sta 449F3 (Germany). Nitrogen adsorption and desorption isotherms were measured at 77 K with a Quadrachrome Adsorption Instrument. X-ray photoelectron spectroscopy (XPS) was performed using an ESCA-LAB-MKII spectrometer (VG Co., United Kingdom) with Al K_α X-ray radiation as the source for excitation.

2.5. Electrochemical Measurement

The working electrodes were prepared with the as-obtained materials, acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 75:20:5. Then, a small amount of ethanol was

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