



Intimately coupled hybrid of carbon black/nickel cobaltite for supercapacitors with enhanced energy-storage properties and ultra-long cycle life



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ABSTRACT

An intimate hybrid of carbon black/nickel cobaltite (CB/NCO) is rationally designed and successfully synthesized via a facile two-step method. Due to the unique nanostructure and strong synergistic effects between individual components, the CB/NCO hybrid electrode delivers distinctly enhanced energy-storage properties, including a high specific capacity (604.4C g^{-1} at 0.5A g^{-1}) and excellent rate capability ($\sim 77.3\%$ and 62.4% of initial capacity at 10A g^{-1} and 20A g^{-1} , respectively). The excellent energy-storage properties of this low-cost hybrid can stand comparison with the hybrids of NiCo_2O_4 with various costly nanocarbons. An asymmetric supercapacitor (ASC) is constructed using CB/NCO hybrid and activated carbon as the positive and negative electrode, respectively. The assembled ASC device exhibits a maximum energy density of 33.7Wh kg^{-1} and a high power density of 12.2kW kg^{-1} . Meanwhile, the ASC device also shows a satisfactory long cycle-life and long-term stability ($\sim 90\%$ capacitance retention after 50,000 charge-discharge cycles at 5A g^{-1}). On the premise of cost control, such a strategy may enlighten new design opportunities for high-performance energy storage devices based on inexpensive carbon-based materials.

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1. Introduction

The soaring energy demand and the imminent exhaustion of limited fossil fuels have stimulated tremendous interest in developing eco-friendly and cost-effective energy storage devices. Supercapacitors, as one of the important energy storage devices, have received growing attention because their power delivery performance fills the gap between traditional dielectric capacitors (high power output) and batteries (high energy storage). Moreover, they possess the features of high specific power, fast charge/discharge rate, long cycle life, safe operation, low maintain cost and so on [1,2].

As is well known, the nature of electrode materials can significantly impact the electrochemical performance of supercapacitors, thus there is a strong demand for the development of high-performance and low-cost electrode materials [3]. Based on the charge storage mechanism, supercapacitors can be generally

divided into two types: electrical double-layer capacitors (EDLCs, mainly porous carbonaceous materials) and pseudocapacitors (mainly transition metal oxides/hydroxides and conductive polymers) [1]. The EDLCs store charges through purely electrostatic charge accumulation around the electrode/electrolyte interfaces without involving chemical reactions during charging/discharging processes and exhibit high power density and remarkable cycling durability. Whereas, the relatively limited specific capacitance and energy density still restrict the further development of EDLCs to some extent [3]. Consequently, plenty of efforts are put in the enhancement of carbon-based electrode materials. There into, rational design and proper introduction of active components with high specific capacity onto nanocarbon substrates to construct robust hybrid materials have been reported as one promising strategy [3,4]. Through the effective hybridization, the resultant hybrid may deliver significantly enhanced electrochemical performance owing to the distinguished synergistic effects between each component [4,5]. Accordingly, the selection of suitable carbon substrates and active components for supercapacitors are of great importance, especially, variety of electrode materials based on nanocarbons have been reported, such as graphene [2,6], carbon nanotubes (CNTs) [7,8], carbon

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nanofibers (CNFs) [9,10] and so forth. Nevertheless, in view of the large-scale commercial popularization, cost controlling must also be taken into account. Commercial carbon black (CB) is a conventional material and often used as conductive additive in working electrodes for supercapacitor. It should be noted that CB only plays an auxiliary role in some reported CB-containing hybrids, such as graphene/CB hybrid film [11,12], graphene/MnO₂/CB hybrid film [13,14], acetylene black modified NiCo₂S₄ [15], rGO/PANI/CB [16] and so on. As reported, CB can also be qualified to serve as a suitable substrate on account of its unique turbostratic structures with relatively large specific surface area, excellent electric conductivity and prominent physicochemical stability to ensure good electrochemical properties [17,18]. Notably, the easy availability and relatively low cost of CB make it more competitive with those costly nanocarbons. Recently, several composites using CB as substrate have been reported, such as CB/MnO₂ [19], CB/MnFe₂O₄/PANI [17], CB/PANI [20], CB/PPy [21], CB/NiMn-LDH [22] and so on. Nevertheless, there are still some big challenges such as relatively low specific capacitances and energy densities. Therefore, there is great interest to design and fabricate a novel CB-based hybrid with high energy-storage performance, such as high specific capacity and energy density, as well as excellent rate capability and cycling stability.

Among various supported active components, spinel-type nickel cobaltite (NiCo₂O₄) has been widely studied due to its high theoretical specific capacity, rich electrochemical activity, achievable cost, natural abundance and strong corrosion resistance in alkaline solutions [23,24]. Heretofore, numerous explorations about NiCo₂O₄ loaded onto various carbonaceous substrates, such as graphene [25–28], CNTs [7,8,29], CNFs [30–32] and so on have been demonstrated. To the best of our knowledge, very little attention has been paid to constructing the CB/NiCo₂O₄ hybrid nanostructure for energy storage devices so far. It is expected that both CB and NiCo₂O₄ in the CB/NiCo₂O₄ hybrid can play their respective advantages, such as high redox activity, good conductivity, rapid penetration of electrolyte and low diffusion resistance of protons/cations, and so forth. If that can be realized, it is possible to pave the way for a new approach to the high-performance electrode materials for energy storage devices based on low-cost carbon-based materials.

Herein, we report a low-cost carbon black/NiCo₂O₄ hybrid (CB/NCO) prepared via a facile two-step method including simple chemical co-precipitation followed by thermal treatment. It is found that the well-dispersed ultrafine NiCo₂O₄ nanoparticles are strongly coupled with CB substrate to form a stable hybrid system. In view of the unique structural characteristics and the significant concerted effects between individual components, the CB/NCO hybrid exhibits remarkably enhanced energy-storage performance, including superior specific capacity and rate capability. Notably, the excellent electrochemical properties of the CB/NCO hybrid with low-cost CB can be comparable to those NiCo₂O₄ composites with various costly nano-carbon materials. Moreover, an asymmetric supercapacitor (ASC) device was constructed using CB/NCO hybrid and commercial activated carbon (AC) as positive and negative electrode materials, respectively. The assembled device exhibits high energy density and power density as well as extraordinary long-term stability.

2. Experimental section

2.1. Materials

Vulcan XC-72 carbon black (CB) was obtained from Cabot Corporation and pretreated with concentrated nitric acid via a hydrothermal process as previously reported [18]. During the acidification, numerous oxygen-containing functional groups were

introduced to the surface of CB, which can not only distinctly improve the dispersibility of CB, but also act as robust nucleation sites for the subsequent deposition of NiCo₂O₄ nanoparticles [17]. All other reagents were of analytical grade and directly used as received without any purification. Nitric acid (HNO₃, 65–68%), ethylene glycol (EG, 99.0%), nickel chloride (NiCl₂·6H₂O, 98%), cobalt chloride (CoCl₂·6H₂O, 99%) were purchased from Sino-pharm Chemical Reagent Co., Ltd. Concentrated ammonia (NH₃·H₂O, 28.0–30.0%) and potassium hydroxide (KOH, 95%) were supplied by Aladdin Industrial Cooperation. To assemble the asymmetric supercapacitor device, activated carbon (AC) YP-50F for the negative electrode was obtained from Kuraray Shanghai Co., Ltd.

2.2. Synthesis of carbon black/NiCo₂O₄ hybrid

The carbon black/NiCo₂O₄ hybrid was synthesized with a two-step strategy consisting of a simple chemical co-precipitation followed by a thermal treatment. In a typical procedure, the reaction solvent was prepared in advance by uniformly mixing EG and deionized water with the volume ratio of 1:2. 120 mg of acid-treated CB was fully dispersed into 120 mL of premixed solvent in a 250 mL round-bottom flask via ultrasonication under stirring for 2 h. The flask was then placed into water bath at 40 °C with continuously vigorous stirring. Metallic salt solution (30 mL) containing well-mixed NiCl₂·6H₂O (0.5 mmol) and CoCl₂·6H₂O (1 mmol) was also prepared with the premixed solvent and then added into CB dispersion dropwise under stirring. After that, the reaction mixture was kept stirring for 4 h. Whereafter, 0.56 mL of concentrated NH₃·H₂O (~28%) was dropped into the mixture slowly under stirring and maintained stirring for 24 h at 40 °C. The as-obtained precursor was fully washed with deionized water for several times, collected by centrifugation and freeze-dried. The dried precursor was put into the tube furnace and heated to 300 °C with a heating rate of 1 °C min⁻¹ for 2 h in air and then cooled to room temperature with a cooling rate 2 °C min⁻¹. The ultimate product was labeled as CB/NCO. Besides, pure NiCo₂O₄ was also prepared for comparison via a similar procedure without using CB.

2.3. Materials characterization

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM-2100 microscope operating at 200 kV. The surface morphologies were characterized by a field emission scanning electron microscopy (FESEM, HITACHI S-4800 II). Powder X-ray diffraction (XRD) analyses were performed using a powder X-ray diffraction system (XRD, Bruker D8 Advance, Cu K α , λ = 1.5406 Å) with the scanning angles (2θ) ranging from 10° to 80°. To investigate the thermal property of the samples and estimate their composition, thermogravimetric (TG) analyses were carried out using a TGA/SDTA 851e thermogravimetric analyzer from 50 to 750 °C with a heating rate of 5 °C min⁻¹ under air atmosphere. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 FTIR spectrophotometer with the wavenumber ranging from 4,000 to 400 cm⁻¹. Raman spectra were collected using a Britain Renishaw InVia Raman spectrometer with an excitation wavelength of 514 nm. X-ray photoelectron spectra (XPS) were measured by a Thermo ESCALAB 250 spectrometer using Al K α as excitation source (1486.6 eV). The surface area was measured by Brunauer-Emmet-Teller (BET) adsorption-desorption isotherms at 77 K on a Micromeritics Tristar II 3020 analyzer and the corresponding pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model.

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