



Facile Assembly of Co-Ni Layered Double Hydroxide Nanoflakes on Carbon Nitride Coated N-doped Graphene Hollow Spheres with High Electrochemical Capacitive Performance



Xiaoqiong Hao^{a,b}, Zhongqing Jiang^{b,*}, Xiaoning Tian^b, Xiaogang Hao^{a,**}, Zhong-Jie Jiang^c

^a Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

^b School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315211, Zhejiang, China

^c New Energy Research Institute, College of Environment and Energy, South China University of Technology, Guangzhou 510006, China

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ABSTRACT

High specific capacitance, large surface area, good flexibility and super durability are recognized as advantageous characteristics to acquire ideal supercapacitor, but it is a great challenge to realize them at the same time. Here, a novel cobalt-nickel layered double hydroxide nanoflakes grow on carbon nitride coated N-doped graphene hollow spheres is successfully assembled by a facile chemical bath deposition method. The carbon nitride coated N-doped graphene hollow spheres scaffold not only possesses large surface area for increasing loading of electroactive material but also has hollow structure for accelerating electron and ion transport. Owing to synergistic contributions, the resulting Co₂Ni₁ layered double hydroxide nanoflakes on carbon nitride coated N-doped graphene hollow spheres with large surface area of 268 m²g⁻¹ exhibited enhanced specific capacitance (1815 Fg⁻¹ at 1 Ag⁻¹) and excellent cycling stability (82.1% retention after 4,000 cycles even at 20 Ag⁻¹). In addition, the capacitance retention still keeps 90.7% after rolling-up about 360° due to wonderful flexibility. Finally, an asymmetric supercapacitor is assembled to further investigate its practical application, which exhibited high energy density of 28.9 Wh kg⁻¹ at an average power density of 1875 W kg⁻¹ and outstanding capacitance retention (no any losses of initial specific capacitance after 10,000 cycles). These advantageous characteristics demonstrate that the new electrode gives a comprehensive application prospect in miniaturized and flexible energy storage.

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1. Introduction

Depleting fossil resources, increasing concerns of serious environmental problems and portable electronic devices miniaturization have spurred global interest in developing advanced energy storage and conversion devices [1]. In recent years, supercapacitor has become a potential candidate which attract substantial attention and extensive study due to rapid charge-discharge rate, ultra-high power density, greater energy density, as well as excellent cycle stability [2,3]. The exploration of optimal electrode materials is the key prerequisite for the properties of supercapacitor. Generally, supercapacitor can be classified into two major types in terms of the mechanism of energy storage: (i)

electrochemical double-layer capacitors (EDLCs); (ii) pseudocapacitors which depend on faradaic redox reaction. Up to date, different electrode materials have been used for developing supercapacitor, such as porous carbon materials (carbon nanofiber [4,5], activated carbon [6,7], carbon nanotube [8,9], and graphene [2,10–13]), conducting polymer materials [14,15] and transition metal oxides/hydroxides [5,16,17], etc. However, porous carbon materials are seldom separately utilized for electrode materials because of its low specific capacitance. Although conducting polymer materials have high proton conductivity, the most prominent shortcoming is that they often produce the volume expansion and shrinking during long period of charge and discharge, which result in poor stability [18]. In contrast, transition metal oxides/hydroxides exhibit remarkable redox properties and outstanding theoretical specific capacitance values [19]. A general formula of layered double hydroxide (LDH) is [M²⁺_{1-x}M³⁺_x(OH)₂]^{x+} [Aⁿ⁻_{x/n}]^{x-}·m H₂O (where M²⁺, M³⁺ and Aⁿ⁻ are divalent cation, trivalent cation and charge-balancing anion, respectively) [20,21]. The combination of two kinds of metal ions may enhance the active

* Corresponding author.

** Corresponding author.

E-mail addresses: zhongqingjiang@hotmail.com (Z. Jiang), xghao@tyut.edu.cn, tyutxghao@hotmail.com (X. Hao).

site density and led to much better electrochemical performance [22]. Especially, Co-Ni LDH with high theoretical capacitance and richer redox reactions has been widely studied. However, pure Co-Ni LDH often shows poor conductivity and low surface area since hydrogen bonding interaction of interlayer and particle aggregation [23,24]. In efforts to improve surface area and expose all active-sites, some great efforts have been made by introducing conductive carbonaceous components, which are low cost, low toxicity, better stability, and better electrical conductivity [23,25,26]. For example, Chen et al. reported Ni-Co hydroxide nanoflakes by using carbon nanotube as the supporter, delivering good capacitance of 1843 F g^{-1} at 0.5 A g^{-1} [8]. Cai et al. fabricated NiCo-layered double hydroxide nanosheets coated on graphene (RGO) sheets with high capacitance of 1911 F g^{-1} at 2 A g^{-1} [27]. Warsi et al. prepared CoNi-LDHs nanoflakes with carbon fibers as carrier, presenting ideal capacitance of 1938 F g^{-1} at 1 A g^{-1} [23]. In such reports, conductive carbonaceous materials play an important role, which possess proficient charge transport due to curvate electron and ion diffusion pathways. Compared with common carbon-based carriers, graphene hollow spheres (GHSs) are preferential supporter due to their three-dimensional and porous structure [28,29]. Firstly, deformation and collapse can not happen because of stretchy 3D hollow structure during repeated charge and discharge process, improving stability obviously. Secondly, coating of PANI on graphene hollow spheres not only avoid effectively the damage of the spherical shell in the process of deposition of LDH, but also help the nucleation and overgrowth of Co-Ni LDH by abundant embossments of CN_x on the outer surface of N-doped graphene hollow spheres (NGHSs), which are originating from the carbide of polyaniline in the process of roasting. Moreover the doping of heteroatoms (such as nitrogen atom) into 3-D structured carbon and GHSs can increase electron transfer capabilities by adjusting the carbon electron orbital energy [29,30].

In this work, nano structured $\text{Co}_x\text{Ni}_{1-x}$ LDH ($x = 0, 0.33, 0.5, 0.67, 1$) composites attached on three-dimensional carbon nitride coated N-doped graphene hollow spheres ($\text{CN}_x\text{@NGHSs}$) were prepared via chemical bath deposition (CBD) method [31]. By offering the conductivity network of $\text{CN}_x\text{@NGHSs}$, rapid transfer of electrons and fast diffusion of ions were realized. Under optimal composition, the Co_1Ni_1 LDH/ $\text{CN}_x\text{@NGHSs}$ electrode displayed an enhanced specific capacitance of 1815 F g^{-1} at a discharge current density of 1 A g^{-1} , a high rate capability, and an excellent cycling stability (After 4,000 cycles, 82.1% of the original capacitance could be retained at 20 A g^{-1}). In addition, the asymmetric supercapacitor, assembled with Co_1Ni_1 LDH/ $\text{CN}_x\text{@NGHSs}$ as positive electrode and $\text{CN}_x\text{@NGHSs}$ as negative electrode, presented high energy density of 41.2 Wh kg^{-1} at a power density of 425 kW kg^{-1} , suggesting their promising future for supercapacitors.

2. Experimental section

2.1. Materials preparation

2.1.1. Synthesis of carbon nitride coated N-doped graphene hollow spheres ($\text{CN}_x\text{@NGHSs}$)

Firstly, 100 mg dispersed graphene oxide solution (prepared by a modified Hummer's method as our previously reported [32]) and 2 g polystyrene spheres (PS) as template (the preparation procedure of the polystyrene spheres was described detailedly in the supporting information) were added to 100 mL HCl (0.5 M) and stirred at 25°C for 12 h, which led to the wrapping of GO onto the surface of PS by an electrostatic interaction [33]. To this solution, 3 g melamine was added. The obtained mixture solution was stirred at room temperature for 12 h, and subsequently, 0.004 mol FeCl_3 and 0.004 mol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were immersed. Meanwhile, the oxidative polymerization of 5 mL aniline monomers was initiated at 0°C by

dropwise adding 7.5 g ammonium persulfate solution. The reaction mixture was then stirred for 24 h at 0°C . Then, 0.25 mol urea and 0.1 mL hydrazine hydrate were dissolved into the above solution, heated up to 110°C and kept for 24 h. Furthermore, the product was freeze-dried. Whereafter, 5 g as-prepared samples were adequate immersed in 100 mL H_2O solution containing 3 g of melamine, which led to adsorb enough nitrogen. After being magnetically stirred for 12 h at room temperature, the resulting suspension was collected, dried and calcined at 420°C for 2 h and then 750°C for 1 h in the nitrogen atmosphere with a ramping rate of 5°C min^{-1} to get carbon nitride coated N-doped graphene hollow spheres. Finally, the samples were washed by 2 M sulfuric acid at 80°C for 8 h to remove residual reactants and dried at 80°C overnight.

2.1.2. Fabrication of the $\text{Co}_x\text{Ni}_{1-x}$ LDH/ $\text{CN}_x\text{@NGHSs}$

In a typical procedure, 2 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.5 g urea were dissolved in 50 mL H_2O to form a solution. After being magnetically stirred for 10 min, 74 mg preliminary product ($\text{CN}_x\text{@NGHSs}$) was then subjected to mix and heated to 120°C for 4 h. The produced precipitate was separated by filtration and washed with deionized water for several times, and then dried at 80°C overnight. For obtaining Co-Ni LDH/ $\text{CN}_x\text{@NGHSs}$ composites with different Co contents, the amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ used in the preparation was changed from 4 to 2.67, 2, 1.33 and 0 mmol, respectively, and correspondingly the amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was also changed to keep the total molar to be 4 mmol, which were denoted as $\text{Ni}(\text{OH})_2/\text{CN}_x\text{@NGHSs}$, Co_1Ni_2 LDH/ $\text{CN}_x\text{@NGHSs}$, Co_1Ni_1 LDH/ $\text{CN}_x\text{@NGHSs}$, Co_2Ni_1 LDH/ $\text{CN}_x\text{@NGHSs}$, $\text{Co}(\text{OH})_2/\text{CN}_x\text{@NGHSs}$. For comparison, pure Co_1Ni_1 LDH was also synthesized in the absence of $\text{CN}_x\text{@NGHSs}$ but with the other experimental condition constant.

2.2. Characterizations

An environmental scanning electron microscope (Model Quanta 650FEG) at an operation voltage of 20.0 kV was used to measure the morphology of the obtained samples. TEM measurements were conducted on a JEM-2100F high-resolution transmission electron microscope with an accelerating voltage of 200 kV. The X-ray diffraction (XRD) analysis was performed on a D/Max-III (Rigaku Co., Japan) using $\text{Cu K}\alpha$ radiation and operating at 40 kV and 30 mA. The 2θ angular regions between 5° and 85° were explored at a scan rate of 2° min^{-1} . The chemical compositions of the samples were determined by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 250 spectrometer (Thermo Electron, U. K.), using an Al $\text{K}\alpha$ X-ray source (1486 eV). The structure is also characterized by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum BX FTIR instrument), in the range of 4000–500 cm^{-1} . The specific surface areas of the samples were analyzed by a surface area analyzer (NOVA 2000, Quantachrome) using physical adsorption/desorption of N_2 at the liquid- N_2 temperature. The specific surface areas of the samples were calculated using the Brunauer–Emmett–Teller (BET) method with the adsorption data at the relative pressure (P/P_0) range of 0.05–0.20. And the pore size distributions were calculated using a slit/cylindrical NLDFT model.

2.3. Electrochemical measurements

Electrochemical measurements were tested in a conventional three-electrode electrochemical cell. A saturated Ag/AgCl electrode and a platinum wire served as reference and counter electrode, respectively. The working electrode was fabricated by combining active materials, polyvinylidene fluoride (PVDF) binder and acetylene black in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone, and then the slurry was dipped on precleaned nickel foam (surface area 1 cm^2). The loading mass of active materials was

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