Nickel–cobalt layered double hydroxide ultrathin nanoflakes decorated on graphene sheets with a 3D nanonetwork structure as supercapacitive materials

Yan Tao[a], Li Ruiyi[b], Li Zaijun[a,*]

[a] School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China
[b] The University of Birmingham, Edgbaston, Birmingham BI5 2TT, United Kingdom

ABSTRACT

The study reported a novel microwave heating reflux method for the fabrication of nickel–cobalt layered double hydroxide ultrathin nanoflakes decorated on graphene sheets (GS/NiCo-LDH). Ammonia and ethanol were employed as precipitant and reaction medium for the synthesis, respectively. The resulting GS/NiCo-LDH offers a 3D flowerclusters morphology with nanonetwork structure. Due to the greatly enhanced rate of electron transfer and mass transport, the GS/NiCo-LDH electrode exhibits excellent supercapacitive performances. The maximum specific capacitance was found to be 1980.7 F g^{-1} at the current density of 1 A g^{-1}. The specific capacitance can remain 1274.7 F g^{-1} at the current density of 15 A g^{-1} and it has an increase of about 2.9% after 1500 cycles. Moreover, the study also provides a promising approach for the design and synthesis of metallic double hydroxides/graphene hybrid materials with time-saving and cost-effective characteristics, which can be potentially applied in the energy storage/conversion devices.

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1. Introduction

With increasing energy crisis in the world, the concept of energy efficiency has been imbedded into the economical development. Supercapacitors as a promising energy storage device have attracted extensive attentions from global researchers because of their high capability and power density, rapid charge/discharge stability and long lifespans [1]. Currently, main supercapacitors electrode materials are carbon-based materials such as activated carbon [2,3], carbon nanotubes [4], graphene oxide [5] and graphene [6,7], whose charge storage relies on the principles of electrical double layer, and pseudocapacitive materials such as RuO$_2$ [8], metal oxides [9], nitrides [10], sulfides [11], hydroxides [12,13] and conducting polymers [14], whose capacitance results from reversible Faradaic reactions occurring at the interface between the electrode and the electrolyte. Commonly, the capacitance of pseudocapacitive materials is obviously higher than that of carbon-based materials [15,16]. For solving their drawback of inferior energy densities comparable to those of lithium ion batteries, there is great need to develop advanced pseudocapacitive materials for supercapacitors.

Metallic double hydroxides have been a hot research topic in the recent years due to high specific capacitance, low cost and environmental friendliness [13,17,18]. However, poor conductivity and structure stability result in a low power performance and short cycling lifespan. To build up various carbon-based hybrid materials is a solution way. Among carbon-based hybrid materials, the graphene-based hybrid materials have the priority owing to large surface area, good conductivity and excellent structural stability. Particularly, the unique architecture designed in metallic double hydroxide, including ultrathin nanostructure [12], specific three-dimensional structure [18,19], and nanonetwork structure [20], can effectively boost the rate of electron transfer and mass transport during the Faradaic redox process. On the one hand, the introduction of graphene gives a better conductive nanonetwork and structure stability, which can guarantee high electron transfer rate and long lifespans during the redox process [21]. On the other hand, the ultrathin nanostructure supplies more superficial electroactive species to participate in the Faradaic redox reactions. This will result in an enhanced faradic redox reaction. Moreover, the unique three-dimensional nanonetwork structure can provide the interconnected nanochannels and suitable mesopore distributions, which will help the diffusion and permeation of OH$^-$ ions between electroactive species and the electrolyte and benefits the mass transfer of electrolytes. Thus, graphene-based supercapacitors often show a high electrical double layer capacitance and

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long-term lifespans [22,23]. However, traditional hydrothermal method for the fabrication of graphene-based metallic double hydroxides hybrid materials is very time-consuming, energy-consuming and cannot meet the needs in practical applications. Recently, a simple and rapid microwave heating method has been employed for the synthesis of graphene-based metallic double hydroxides hybrid materials [24–26]. Compared with common hydrothermal method, microwave heating technology offers a lower temperature gradients, faster reaction rate and more excellent heating homogeneity, resulting in more homogeneous nucleation, shorter crystallization time and higher yield. More importantly, microwave-heating technology is a potential tool for the commercial production in a large scale.

In the study, we focus on building up nickel–cobalt layered double hydroxide ultrathin nanoflakes decorated on graphene sheets (GS/NiCo-DH) via a microwave heating method. The resulting GS/NiCo-LDH shows a three-dimensional flowerclusters morphology with a nanonetwork structure. Because of the greatly enhanced the rate of electron transfer and mass transport, the GS/NiCo-DH electrode exhibits excellent electrochemical performances, including high capacitance and rate capability, good charge/discharge stability and long cycle life. The study also provides a promising approach to design and synthesis of the advanced graphene-based materials with time-saving and cost-effective characteristics.

2. Experimental

2.1. Synthesis of graphene

Graphite oxide (GO) powder was made from modified Hummers method [27] and then irradiated in a domestic microwave oven operated at 1200 W for 1 min, resulting in the formation of a black and fluffy graphene powder with a large volume expansion (denoted as r-GO). To obtain the well-defined GS, the r-GO was further reduced by thermal annealing in Ar/H_2 (V:V = 95:5) environment under 800 °C for 1 h.

2.2. Synthesis of GS/NiCo-LDH

The GS/NiCo-LDH was synthesized by the microwave method. In a typical synthesis, 60 mg of the GS was dissolved in a 150 mL ethanol solution (98 wt% in water) by the ultrasonication with 30 min to form a homogeneous suspension. Subsequently, 582 mg of $Ni(NO_3)_2 \cdot 6H_2O$ and 375 mg of $Co(NO_3)_3 \cdot 6H_2O$ were dissolved in the GS suspension under ultrasonication. The suspension was transferred into the HWL07-3 experimental microwave reactor and heated to refluxing state under microwave power of 400 W. Then, the mixture of 9.5 mL ethanol and 0.5 mL ammonia was dropwise added into the above solution under continuous vigorous stirring. After that, the microwave power was rapidly adjusted to 300 W and remained for 0.5 h. The suspension was cooled down to room temperature and the sample was collected after the centrifugation, being washed with distilled ethanol, and dried in vacuum at 60 °C for 12 h. Furthermore, pure NiCo-LDH composites were also prepared via the similar procedure.

2.3. Materials characterization

Scanning electron microscope (SEM) analysis was carried out in a HITACHI S4800 field emission scanning electron microscope. SEM sample was prepared by placing a drop of dilute ethanol dispersion of the composites onto a copper plate attached to an aluminum sample holder, and the solvent was required to evaporate at room temperature. Transmission electron microscope (TEM) analysis was conducted on a JEOL 2010 (HR) transmission electron microscope at 200 keV. The sample was prepared by dispensing a small amount of dry powder in ethanol. Then, one drop of the suspension was dropped on 300 mesh copper. TEM grids covered with thin amorphous carbon films. X-ray diffraction (XRD) patterns were measured on a X-ray D8 Advance instrument operated at 40 kV and 20 mA and using Cu K_α radiation source with λ = 0.15406 nm. The impedance Z was expressed in terms of a real and an imaginary component. Impedance signal was recorded after reaction between the electrodes and the unstirred substrate solution for 10 min. Raman measurement was carried out using a InVia laser micro-Raman spectrometer. Infrared spectrum (IR) was recorded on a Nicolet FT-IR 6700 spectrometer. The specific surface areas were determined on ASAP 2020 Accelerated Surface Area and Porosimetry System (America, Micromeritics) according to Bru-nauer–Emmett–Teller (BET) plot of nitrogen adsorption isotherm at the relative pressure range of 0.05–0.3. Barrett–Jouner–Halenda (BJH) pore volume and NLDFT pore size distribution were obtained from the N_2 adsorption/desorption isotherms recorded at 77 K. Before BET measurements, the samples were degassed at 100 °C for 5 h.

2.4. Electrodes preparation

The working electrode was fabricated by a following procedure. The GS/NiCo-LDH or other electro-active materials, acetylene black, and poly(tetrafluoroethylene) were mixed in a mass ratio of 80:15:5 and dispersed in ethanol to produce a homogeneous paste. Acetylene black and poly(tetrafluoroethylene) were used as the conductive agent and binder. The slurry was coated on a nickel foam substrate (1 cm × 1 cm) and dried in a vacuum oven at 60 °C for 8 h. The as-formed electrode was then pressed at 10 MPa.

2.5. Electrochemical measurements

Electrochemical properties of the as-prepared products were investigated under a three-electrode electrochemical cell. The Ni foam coated with the GS/NiCo-LDH or other electro-active material was used as working electrode, and platinum foil (1 cm × 1 cm) and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrochemical mea-surements were carried out in a 6 mol L^{-1} potassium hydroxide aqueous electrolyte at room temperature. Cyclic voltammogram (CV) and galvanostatic charge/discharge curves were recorded on the CHI 660D electrochemical workstation. Galvanostatic charge/discharge curves were measured in the potential range of 0–0.4 V at different current density.

3. Results and discussion

3.1. Synthesis of GS/NiCo-LDH

The synthesis of GS/NiCo-LDH is schematically illustrated in Fig. 1. First, GO was made from the Hummers method and then irradiated in a domestic microwave oven to yield black and fluffy powders (r-GO). Subsequently, the r-GO was further reduced and exfoliated using a thermal annealing to obtain a well-defined GS. IR spectra and EIS patterns of the r-GO and well-defined GS were shown in Fig. 1. It is seen that IR spectra of the r-GO exists in three absorption peaks at 1734, 1518 and 1189 cm^{-1}, implying that the existence of carbonyl and epoxy groups. But for the well-defined GS, there is almost no peak on IR spectra, indicating that oxygen-containing groups in the r-GO have been completely reduced. In addition, Fig. 2b also shows the electron transfer impedance of the well-defined GS is obviously lower than that of the r-GO, this implies as-prepared well-defined GS has a more electrical conductivity. Next, NiCo-LDH was fabricated and anchored on