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One-pot Hydrothermal Synthesis of 3D Flower-like RGO/Co_3O_4/Ni$(OH)_2$ Composite Film on Nickel Foam for High-performance Supercapacitors

Shudi Min, Chongjun Zhao*, Guorong Chen, Zhuomin Zhang, Xiuzhen Qian

Key Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, P.R, China

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Reduced graphene oxide (RGO)/Co_3O_4/Ni$(OH)_2$ composites on nickel foam (NF) were hydrothermal-assisted synthesized by using a modified “active metal substrate” route, in which nickel foam acted as both a reductant of GO and Ni source, and a substrate for composite film. As-synthesized samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscope (FESEM), and transmission electron microscopy (TEM). The electrochemical performances of the supercapacitor with the as-synthesized RGO/Co_3O_4/Ni$(OH)_2$/NF electrodes are evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectrometry (EIS) in 1 M KOH aqueous solution. It is found that the RGO/Co_3O_4/Ni$(OH)_2$/NF electrode exhibits superior capacitive performance with high capability (10.24 F cm^{-2} at a current density of 11 mA cm^{-2}, i.e., 2133.3 F g^{-1} at 2.3 A g^{-1}), compared with the Co_3O_4/Ni$(OH)_2$/NF electrode (1.71 F cm^{-2}) and the RGO/Ni$(OH)_2$/NF electrode (0.95 F cm^{-2}) prepared under identical conditions.

1. Introduction

Supercapacitors have attracted intense attention because they can instantaneously provide a higher power density than secondary batteries, and also a higher energy density than conventional dielectric capacitors [1–3]. Therefore, supercapacitors are regarded as promising energy storage devices and power supplies for digital products, hybrid-electric vehicles and other portable electronic devices, which require high power density and long cycle life [4]. Furthermore, asymmetrical supercapacitors, consisting of pseudocapacitors using transition metal oxides/hydroxides and conducting polymers as active materials, have improved both energy and power density [2,5]. Among the wide range of explored pseudocapacitive transition metal oxides and hydroxide materials, Ni$(OH)_2$ is one of the most promising candidates, and has been attracting increasing attention over recent decades because of its low cost, environmentally-friendly nature, high theoretical capacitance and high stability in alkaline electrolyte [6–8]. However, some challenges still remain in the application of high capacity Ni$(OH)_2$ electrodes. For example, one of the major drawbacks for Ni$(OH)_2$ is its very low electrical conductivity ($\sim 10^{-17}$ S cm^{-1}) [9], and the supercapacitor of Ni$(OH)_2$ electrode sometimes experiences some problems, e.g., unsatisfied cycling stability [10], which will greatly limit its practical application.

Up to now, two main useful strategies have emerged to overcome the above disadvantages of pure Ni$(OH)_2$, i.e., to improve conductivity by introducing nanostructured carbon materials, including graphene, in the electrode [3,11], and to enhance electrochemical performance, especially the cycling stability by synthesizing composites with other metal oxides, i.e., MnO_2, Co_3O_4 [12–14]. In addition, a composite of Ni$(OH)_2$/CoO/RGO was designed and synthesized so that the improved electrochemical performance can meet the demand for practical application [10], facilitate the synergistic effect of two metal oxides [13], as well as enhance the effect of RGO on mechanical properties and conductivity to Ni$(OH)_2$ [10]. However, no further report was found.

On the other hand, from the viewpoint of electrodes, the fussy electrode process for powdery materials was not necessary, when the conductive Ni foam acted as support to deposit hybrid

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* Corresponding author. Key Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering East China University of Science and Technology Shanghai 200237, P.R. China. Tel.: +0086 21 6425 0838, fax: +0086 21 6425 0838.
E-mail address: chongjunzhao@ecust.edu.cn (C. Zhao).

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$Ni(OH)_2$/graphene during the preparation process [15,16]. However, in these cases, Ni foam was just used as inset support during the preparation of the $Ni(OH)_2$ composite, and subsequent current collector during the electrochemical test process, i.e., an extra Ni salt has to be added to supply the Ni ion source for $Ni(OH)_2$ [15,16]. As is commonly known, utilizing RGO is quite popular because its parent of GO can be easily produced at scale; thus, an additional reduction process and reductant is necessary [17]. At the same time, a precipitant, such as OH^- from alkali or urea, was added to react with the Ni ion from the Ni salt to form $Ni(OH)_2$. Here, it is obvious that, for Ni foam, the activity and its intrinsic Ni were totally neglected, i.e., the reductant for GO, precipitant, and Ni salt can be avoided when the redox of active Ni foam substrate and oxidative GO can be applied during preparation. This conjecture was confirmed in the previous work, in which $Ni(OH)_2$/RGO composite was *in-situ* produced on Ni foam through the redox reaction of Ni foam and GO [18].

In this study, the "active Ni foam substrate" route is further developed to prepare the composite of two metal oxides and RGO on Ni foam surface. Since Co_3O_4 is also a good candidate for electrode materials [19–21], RGO/Co_3O_4/$Ni(OH)_2$ composite was chosen, in which Ni foam acts as support, reductant of GO, and Ni source during the preparation process and, subsequently, the current collector in the electrochemical test. The electrode of as-prepared RGO/Co_3O_4/$Ni(OH)_2$/NF composite film exhibited improved supercapacitor performance, e.g., 10.24 F cm^{-2} at 11 mA cm^{-2}, and 95.7% capacity retention at 1,000th cycle 50 mA cm^{-2}. This synthesis route paved the way for the direct preparation of Ni foam-supported composite film of $Ni(OH)_2$/RGO, accompanied by a series of metal oxides, including Fe_2O_3, ZnO, MnO_2, Mn_3O_4, TiO_2, or metal hydroxides, such as $Co(OH)_2$.

2. Experimental

2.1. Materials and reagents

Pristine graphite powder, hydrogen chloride (HCl, 36.0-38.0 wt%), hydrogen peroxide (H_2O_2, 30.0 wt%), sulfuric acid (H_2SO_4, 98.0 wt%), potassium permanganate ($KMnO_4$, $\geq$ 99.5 wt%), phosphorus pentoxide (P_2O_5, $\geq$ 98.0 wt%), potassium persulfate ($K_2S_2O_8$, $\geq$ 99.5 wt%), ethanol (C_2H_5OH, $\geq$ 99.7 wt%), and cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, $\geq$ 99.0 wt%) were purchased from Sinopharm Chemical Reagent Company. Nickel foam (hereinafter referred to as NF) was obtained from Alfa Aesar. All chemicals were used as received without any further purification.

2.2. Synthesis of RGO/Co_3O_4/$Ni(OH)_2$, RGO/$Ni(OH)_2$, and Co_3O_4/$Ni(OH)_2$ composites on NF

GO was synthesized by a modified Hummer's method [18,22]. The synthesis of RGO/Co_3O_4/$Ni(OH)_2$ composites was carried out through a hydrothermal process, by immersing the cleaned Ni foam in the mixture solution of GO and cobalt salt. Typically, GO (30 mg) and $Co(NO_3)_2{\cdot}6H_2O$ (1 m mol) (or 1 m mol Co powder) was added in deionized water (50 ml) and dispersed in an ultrosonication bath for 30 min. The NF (1 × 2 cm^2) with the bared area of 1 × 1 cm^2 was then immersed in this aqueous solution. The mixture was loaded into a Teflon-lined stainless steel autoclave (100 ml in volume) for hydrothermal reaction at some temperature (i.e., 160 °C, 180 °C, 200 °C, 220 °C, and 240 °C, respectively) for 24 h (or 12 h for comparison). The final product was washed with water and ethanol in turn, and then dried in a vacuum oven at 80 °C for 12 h. The samples of RGO/Co_3O_4/$Ni(OH)_2$/NF composites were denoted as RCNN-160, RCNN-180, RCNN-200, RCNN-220, and RCNN-240 according to the hydrothermal treatment temperatures. RGO/$Ni(OH)_2$/NF-200 (RNN), Co_3O_4/$Ni(OH)_2$/NF-200 (CNN) and RGO/Co_3O_4/$Ni(OH)_2$/NF-200 with Co powder as Co source (RCNN-Co-200) composites were prepared under identical conditions (200 °C, 24 h).

2.3. Characterization

Wide-angle (10°-80°, 40 kV/200 mA) powder X-ray diffraction (XRD) was recorded using an X-ray diffractionmeter with Cu Kα (λ=0.15406 nm). Raman spectra were recorded on an INVIA Raman microprobe (Renishaw Instruments, England), with a 514 nm laser excitation. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250Xi (Thermo Fisher, U.S.A.) instrument. The morphology and elementary composition of the samples were investigated by field-emission scanning electron microscope (FESEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL JEM-2100), and energy dispersive spectrometer (EDS, Bruker, AXS, Quantax 400-30), respectively.

2.4. Electrochemical measurement

The electrochemical measurements were performed using a standard three-electrode cell in 1 M KOH aqueous solution. The composite samples with the apparent area of 1 × 1 cm^2 were used as working electrodes, as synthesized. Platinum foil (2 × 3 cm^2) and a saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. Cyclic voltammograms (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) were carried out using an electrochemical workstation (CHI660e, Shanghai). Impedance spectroscopy measurements were performed at open circuit potential, with a sinusoidal signal of 5 mV in the frequency range from 100 kHz to 0.01 Hz. The loading amount of RGO/Co_3O_4/$Ni(OH)_2$ (weight of active material) was determined by the weight difference of the above electrode before testing and after ultrasonic treatment [18].

3. Results and discussion

3.1. XRD patterns, Raman spectra, and XPS of RGO/Co_3O_4/$Ni(OH)_2$ composites

X-ray diffraction (XRD) patterns of pure NF, RGO/$Ni(OH)_2$/NF (RNN), Co_3O_4/$Ni(OH)_2$/NF (CNN), and RGO/Co_3O_4/$Ni(OH)_2$/NF (RCNN) prepared at 200 °C composites are shown in Fig. 1. Three peaks centered at 44.6°, 51.9°, and 76.4° assigned to the (111), (200), and (220) planes of metallic nickel (JCPDS No. 01-1258), respectively [23], are clearly observed in the patterns of both NF and all composite samples. Seven new characteristic diffraction peaks at 19.3°, 33.2°, 38.6°, 59.1°, 62.7°, 70.4°, and 72.6° in the RNN composites could be ascribed to the (001), (100), (101), (110), (111), (103), and (201) crystalline planes of the hexagonal β-phase $Ni(OH)_2$ (JCPDS No. 14-0117), respectively [18,24]. Referring to RCNN, in addition to the characteristic diffraction peaks of β-phase $Ni(OH)_2$, four additional peaks are observed at 31.3°, 36.9°, 38.5°, and 65.2°, which correspond to (220), (311), (222), and (440) of Co_3O_4 (JCPDS No. 42-1467), respectively [14]. Although the broad peak of RGO at 2θ=23.7° is negligible, the addition of GO enhanced the transformation of Ni to $Ni(OH)_2$ and Co^{2+} to Co_3O_4, for only partial weak peaks corresponding to $Ni(OH)_2$, and Co_3O_4 appears in the absence of GO [14,24], as shown in the XRD pattern of CNN. These indicate that the surface of Ni foam was well decorated with the $Ni(OH)_2$ and Co_3O_4 in the presence of GO.

The presence of RGO in the composite is confirmed by Raman spectroscopy, as shown in Fig. 2. The ratio of G band (~1597 cm^{-1}) corresponding to the in-plane bond-stretching motion of the pairs of C sp^2 atoms (the E_{2g} phonons) and the D band (~1345 cm^{-1})