

# Synthesis of poly(aniline-co-*m*-aminophenol)/graphene/NiO nanocomposite and its application in supercapacitors



Xiucui Ji<sup>a</sup>, Qiang Xu<sup>a</sup>, Ting Zhou<sup>b</sup>, Xiaotong Wang<sup>a</sup>, Hui Xu<sup>a,\*</sup>, Xue Yao<sup>a</sup>, Wei Lan<sup>a</sup>, Yong Kong<sup>b,\*</sup>

<sup>a</sup> College of Chemistry and Materials Science, Ludong University, Yantai 264025, China

<sup>b</sup> School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

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## ABSTRACT

Poly(aniline-co-*m*-aminophenol)(PANMA)/graphene/NiO nanocomposite was synthesized and applied as a supercapacitor electrode for the first time. Graphene/NiO nanocomposite was first synthesized via a hydrothermal synthesis method from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, urea, and graphite oxide. NiO nanoparticles were distributed uniformly on both sides of the graphene. Then, PANMA was deposited in situ on the surface of the graphene/NiO nanocomposite via the copolymerization of aniline and *m*-aminophenol. The obtained nanocomposite has a similar porous morphology with that of PANMA. Experimental results indicate that the synergistic contributions from PANMA, graphene and NiO enable the composite electrode with substantially improved energy storage performance metrics. The nanocomposite shows a high specific capacitance of 562 F g<sup>-1</sup> at a current density of 0.5 A g<sup>-1</sup>, a good rate capability even at high current densities and a better long-term cycling stability.

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## 1. Introduction

Supercapacitors, a class of modern energy storage devices with large power density, reasonable energy density, good operational safety and long cycling life, are of interest in a wide range of applications from consumer electronics to heavy electric vehicles, and industrial power management [1,2]. In the last three decades, it has been proposed that conducting polymer polyaniline (PANI) is an important and highly promising electrode material for energy storage applications due to its high pseudocapacitance originating from fast and reversible Faradic redox reactions [3,4]. However, PANI will lose its electrochemical activity when pH is higher than 5 [3,5], which limits its application range. Copolymerization of aniline with other monomers will extend the useful pH range of aniline-based conducting polymers [6,7]. And the applications of conducting copolymers in pseudocapacitors with improved performance have been reported previously by our group [8] and other group [9].

It is well-known that RuO<sub>2</sub> is the most promising electrode material of pseudocapacitors due to its high power density and high energy density. However, due to the fact that RuO<sub>2</sub> is toxic,

scarce and expensive [10,11], numerous efforts are made toward other alternative and cheap transition metal oxides such as Ni, Co, and Mn oxides, which have similar charge storage performances to RuO<sub>2</sub>. However, it is still a challenge to achieve good cycling stability for transition metal oxides-based pseudocapacitors owing to the low conductivity of transition metal oxides. To overcome the problem, one common strategy is to grow electroactive NiO nanostructures on conductive matrix such as graphene nanosheet. Graphene has been reported to be a competitive electrode material for supercapacitor applications owing to its specific properties such as high electrical conductivity, large surface area, and good chemical stability [12]. Although metal oxide/graphene [13–16] or conducting polymers/graphene binary hybrids [13,17] have been successfully prepared by various methods as supercapacitors electrodes, ternary hybrid structures including metal oxide/graphene/conducting polymer [18,19] have been recently explored as a promising electrode material that could combine the synergistic advantages of the three components in the system. In this work, synthesis and characteristics of a unique composite (constituted by PANMA, graphene and NiO, PANMA/graphene/NiO) material exhibiting an excellent specific capacitance of 562 F g<sup>-1</sup> are discussed. As a conductive matrix, graphene not only enhanced the electrical conductivity of electrode materials, but also acts as a barrier to prevent the aggregation of metal oxides particles during the charge–discharge process. At the same time, the existence of NiO prevents the graphene sheets from restacking. The ternary

\* Corresponding authors.

E-mail addresses: [xuhui235@163.com](mailto:xuhui235@163.com), [xhsinap@gmail.com](mailto:xhsinap@gmail.com) (H. Xu), [yzkongyong@126.com](mailto:yzkongyong@126.com) (Y. Kong).

hybrid exhibits synergistic pseudocapacitive contributions from PANMA and NiO and electrical double-layer capacitive contributions from graphene.

## 2. Experimental

### 2.1. Materials

PANI and *m*-aminophenol were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China).  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  were all analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nafion were purchased from Sigma. All solutions were prepared using double distilled water.

### 2.2. Preparation of graphene/NiO nanocomposite

Graphite oxide (GO) was prepared through a modified Hummers method [20,21]. The graphene/NiO nanocomposite was fabricated by combining hydrothermal synthesis and subsequent heat treatment. In a typical preparation process, 0.01 mol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.04 mol urea were mixed in 50 mL water, then the mixture was added into 30 mL of the GO dispersion with different concentrations (0–4 mg mL<sup>-1</sup>). After stirring for 1 h, the obtained mixture was heated for 16 h at 140 °C in a Teflon-lined autoclave vessel. The solid product obtained was washed using absolute ethonal and deionized water several times and dried at 50 °C for 24 h. Afterwards, the samples were calcined at 400 °C for 4 h to get graphene/NiO nanocomposite. The samples after calcination were denoted as 1<sup>#</sup>–5<sup>#</sup> sample, respectively, corresponding to the GO concentrations of 0–4 mg mL<sup>-1</sup>.

### 2.3. Preparation of graphene/NiO/PANMA nanocomposite

4<sup>#</sup> graphene/NiO of different masses (30 mg, 60 mg, 90 mg, 120 mg and 150 mg) was added to 30 mL of 1 M  $\text{H}_2\text{SO}_4$ , respectively. After sonication, aniline (final concentration 0.2 M) and *m*-aminophenol (final concentration 0.01 mol/L) were added and stirred. Afterwards, 30 mL of 0.2 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was added dropwise to the mixture and stirred for 12 h in an ice bath (0~5 °C). Finally, the obtained composite was filtrated and washed with absolute ethonal several times followed by water several times until the filtered fluid was colorless. The resulting sample was dried in a vacuum oven at less than 65 °C. The composite composed by 120 mg of 1<sup>#</sup>, 2<sup>#</sup>, 3<sup>#</sup> or 5<sup>#</sup> sample with PANMA was synthesized by the same procedure.

### 2.4. Fabrication of graphene/NiO/PANMA electrode

A glassy carbon electrode (GCE) (3 mm diameter) was polished with alumina slurry of 0.05 μm diameter on a polishing cloth and

then sonicated in absolute ethonal and deionized water bath for 10 min, respectively before use. 40 mg of graphene/NiO/PANMA nanocomposite was added into 2 mL deionized water and sonicated to obtain aqueous dispersion. A 10 μL aqueous dispersion of graphene/NiO/PANMA nanocomposite was dropped on the surface of GCE and then allowed to dry at room temperature. 10 μL Nafion (5 wt%) was dropped onto the surface of the electrode to form a graphene/NiO/PANMA modified GCE.

### 2.5. Materials characterizations

The morphologies of different samples were examined by field-emission scanning electron microscope (FESEM, Supra 55). Fourier transform infrared (FTIR) spectra of the products were obtained from KBr pellets in a FTIR-8400S spectrometer (Shimadzu, Japan) in the range from 4000 to 400 cm<sup>-1</sup>.

### 2.6. Electrochemical characterizations

All electrochemical experiments including cyclic voltammetry (CV), electrochemical impedance spectra (EIS) and galvanostatic charge/discharge testing were carried out with an electrochemical workstation (CHI 660D, Beijing, China) in 1 M  $\text{H}_2\text{SO}_4$  using a three electrode system, in which platinum and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively, the nanocomposite modified GCE as working electrode. The EIS measurements were performed at open circuit potential 0.2 V over the frequency range from 10 kHz to 10 mHz at an amplitude of 5 mV.

## 3. Results and discussion

### 3.1. Morphological analysis

The morphologies of PANMA, graphene/NiO and graphene/NiO/PANMA were recorded by FESEM. As shown in Fig. 1, NiO nanoparticles with diameters about 60–100 nm were well dispersed on the surface of graphene sheets (Fig. 1B), which prevents the restacking of graphene flakes. Compared with the FESEM image of pure PANMA (Fig. 1A), graphene/NiO–PANMA shows similar irregular coralloid structure, indicating that the polymerization of PANMA occurs outside the graphene/NiO and therefore the graphene/NiO is wrapped in the PANMA matrix. The porous structure of graphene/NiO/PANMA is advantageous to the penetration and transport of electrolyte ions during a rapid charge/discharge cycle.

Fig. 2 shows the FTIR of PANMA, graphene/NiO and graphene/NiO/PANMA. For graphene/NiO, the strong and wide band at 3442 cm<sup>-1</sup> is ascribed to the strong stretching vibrations of O–H functional group [22] from water adsorbed on the graphene/NiO powder surface. The peak at 1634 cm<sup>-1</sup> is due to the O–H bending

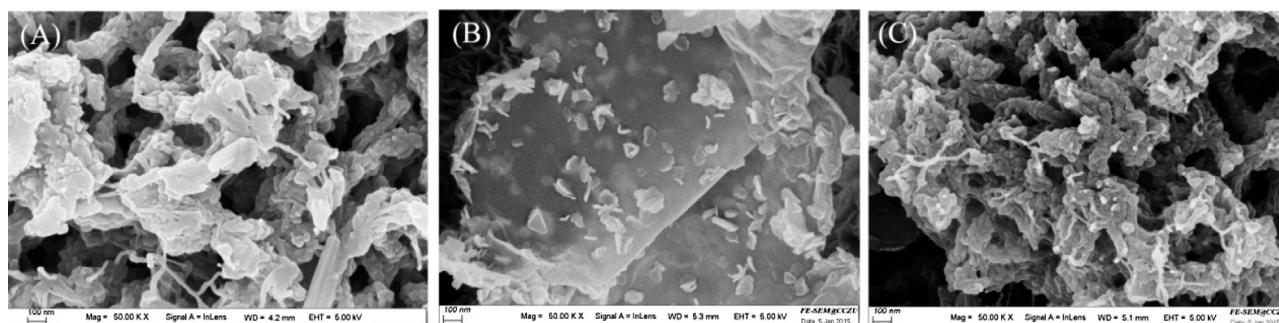


Fig. 1. The FESEM images of (A) PANMA, (B) graphene/NiO, (C) graphene/NiO–PANMA (sample 4<sup>#</sup> containing 120 mg of graphene/NiO).

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