

## Effect of Graphene Oxide as a Dopant on the Electrochemical Performance of Graphene Oxide/Polyaniline Composite

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A method for preparing a graphene oxide/polyaniline (GO/PANI) composite electrode was developed to investigate the effect of GO doped in PANI. PANI was first prepared by the polymerisation of aniline and then dedoped by  $\text{NH}_4\text{OH}$  to form emeraldine base (EB). The dedoped PANI and as-prepared GO were dissolved in N-methyl-2-pyrrolidone (NMP) to generate a homogeneous dispersion. The GO/PANI composites were redoped in HCl before use as electrode materials. These composites were characterised by Raman spectroscopy, X-ray diffraction, UV–vis adsorption spectroscopy, scanning electron microscopy, atomic force microscopy and electrochemical measurements. The GO/PANI composite electrode (containing 2.5% GO) has an initial gravimetric capacitance of  $896 \text{ F g}^{-1}$  at a scan rate of  $5 \text{ mV s}^{-1}$  and a retention life of 51% after 500 cycles, which is an improvement over that of pure PANI (23%). The results show that the synergy of GO and PANI attributes to the good electrochemical performance of the GO/PANI composite electrode.

**KEY WORDS:** Electrical properties; Carbon film; Capacitance; Materials synthesis

### 1. Introduction

Since their discovery in 1960, intrinsically conducting polymers (ICPs) have attracted enormous interest due to their potential for use in many areas, including as actuators<sup>[1]</sup>, electrochromic materials<sup>[2]</sup>, films<sup>[3,4]</sup>, supercapacitors<sup>[5]</sup>, biosensors<sup>[6]</sup>, electromagnetic shields and optical materials<sup>[7–9]</sup>. Among the ICPs, polyacetylene (PA), polypyrrole (PPy), polythiophene (PT), polyparaphenylene vinylene (PPV) and polyaniline (PANI), have been investigated. However, because of their low conductivity compared with metal, poor solubility in solvents, infusibility and low environmental stability, few large-scale applications have been performed. Of these polymers, PANI is the most promising because of its low cost, ease of synthesis, good stability<sup>[10]</sup>, high capacitive characteristics and fine-tuned properties<sup>[11–13]</sup>. In particular, advancements in doping technology yielding a suitable dopant and nanostructured forms of PANI or its composites<sup>[7,14,15]</sup> would accelerate progress in this field. Recently, PANI has been widely studied as an electrode material with better performance for supercapacitors.

Graphene and graphene oxide (GO) are two-dimensional carbon materials that have attracted great interest due to their high surface area, extraordinary electrochemical and mechanical properties. These advantages have led to various applications of graphene/PANI composites or GO/PANI composites<sup>[16,17]</sup>. These composites show enhanced electrochemical characteristics for energy storage devices. GO, which exhibits many oxygen functional groups on its basal planes and edges, is highly dispersible in water and thus a promising material for composites with PANI. In fact, the fabrication of many graphene/PANI composites has been performed by the reduction of GO/PANI composites. Most works employed *in situ* polymerisation approaches using aniline in the presence of GO, yielding high-performance electrodes<sup>[18,19]</sup>. In such a strategy, GO plays a dual role. On one hand, it acts as an efficient template for the nucleation and polymerisation of aniline<sup>[20]</sup>, which changes aniline's polymerisation characteristics, such as its morphology, molecular weight and the molar fraction of oxidised units in the PANI structure<sup>[21]</sup>. On the other hand, GO also acts as a dopant, affecting the electrochemical properties and conformations of the molecular chain. Both of these aspects affect electrochemical performance; however, how to understand the distinction between the two roles remains unclear. Regarding this problem, to our best knowledge, few studies have been reported<sup>[22]</sup> and further studies are required.

In this work, PANI was first synthesised by chemical polymerisation and then converted into emeraldine base (EB) after dedoping by 1 mol/L  $\text{NH}_4\text{OH}$  for 24 h. The EB and as-prepared

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GO were dissolved in N-methyl-2-pyrrolidone (NMP) to generate a homogeneous dispersion, which was attributed to good solubility of EB and the high degree of dispersion of GO in NMP. In this process, GO acted only as a dopant. The interaction between GO and PANI was investigated. The introduction of GO into PANI was found to enhance the electrochemical performance of PANI; thus, this composite was a promising electrode material.

## 2. Experimental

### 2.1. Materials

High-purity (99.5%) natural flake graphite (G) was purchased from Alpha. Other chemicals (analytical-grade reagents) were provided by Sinopharm Chemical Reagent Co., Ltd. and used without purification.

### 2.2. Preparation of GO

Based on the method of Hummers and Offeman<sup>[23]</sup>, a modified method was proposed for preparing a high-quality GO monolayer from G. The modified procedure involved an additional G pre-oxidation step. G (2 g) was pre-oxidized with a mixture of 20 mL of concentrated H<sub>2</sub>SO<sub>4</sub>, 5 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 5 g of P<sub>2</sub>O<sub>5</sub> at 80 °C for 6 h under stirring and then carefully diluted with distilled water, filtered, and washed until the pH of the rinse water was neutral. The product was dried in air at ambient temperature overnight. The peroxidised G powder (2 g) was added to concentrated H<sub>2</sub>SO<sub>4</sub> (0 °C, 80 mL). KMnO<sub>4</sub> (10 g) was then added slowly with stirring and cooling such that the temperature of the mixture remained below 10 °C with the aid of an ice bath. The mixture was then stirred at 35 °C for 3 h, after which distilled water (150 mL) was added and the temperature was allowed to rise to approximately 98 °C. After 15 min, the reaction was terminated by the addition of a large amount of distilled water (350 mL) and 30% H<sub>2</sub>O<sub>2</sub> solution (10 mL). The GO dispersion was centrifuged and then washed in succession with 300 mL of 5% HCl and distilled water. A 2% GO dispersion was prepared and subjected to dialysis for a week to completely remove metal ions and acids. Finally, solid GO was obtained after centrifugation and drying in a vacuum oven at 40 °C for 24 h.

### 2.3. Preparation of PANI

A typical preparation route is as follows. Aniline (5 mL) and hydrochloric acid (15 mL, 37%) were added to 190 mL of water with stirring. The dispersion was kept in an ice bath and the temperature was controlled between 2 and 4 °C. Chemical polymerisation was then performed by the slow addition of 20 mL of ammonium persulfate (APS) solution (molar ratio: APS/aniline = 1:1). The aniline polymerisation was appreciable as the dispersion turned green. 2 h later, the product (emeraldine salt) was filtered and washed with water and acetone. The as-prepared PANI was then dedoped by immersion in 1 mol/L NH<sub>4</sub>OH and stirring for 24 h. EB was obtained by filtering, washing with distilled water and then drying in a vacuum oven at 60 °C for 24 h<sup>[24]</sup>.

### 2.4. Preparation of electrodes

EB was dissolved in NMP to form an 82 mg/mL solution. GO was added to another NMP and ultrasonicated (250 W, 220 V)

for 1 h to obtain an exfoliated yellow-brown GO suspension with a concentration of 1.13 mg/mL<sup>[25]</sup>. These two solutions were then mixed in different ratios, and the dedoped GO/PANI composite dispersions were obtained by an additional 0.5 h of ultrasonication. The GO/PANI composite electrodes were prepared as follows. A stainless-steel mesh was cleaned in 1 mol/L H<sub>2</sub>SO<sub>4</sub> electrolyte by cyclic voltammetry (CV) with the potential range of -0.2 V and 0.8 V and used for preparing the working electrode<sup>[5]</sup>. It was first coated with the dedoped GO/PANI composite dispersion and then dried at 60 °C under vacuum to assure good electrical contact. The repeated coating and drying process ensures a high-quality product. The dedoped GO/PANI composite electrode was redoped with 1 mol/L HCl for 1 h. The working electrode has an area of approximately 2 cm<sup>2</sup>. The pure PANI electrode was prepared in the absence of GO *via* a similar procedure. The different GO/PANI composites were denoted as GO/PANI composite A, B, C and D, which contain 1.2%, 2%, 2.5% and 3% GO, respectively.

### 2.5. Characterisation of materials

GO, PANI and their composites were characterized by Fourier transform infrared (FT-IR) spectroscopy, UV-vis spectroscopy, atomic force microscopy (AFM), Raman spectroscopy, scanning electron microscope (SEM) and X-ray powder diffraction (XRD). FT-IR spectra were recorded with an FT-IR spectrophotometer (SHIMADZU FTIR-8400S) using KBr pellets. SEM images were obtained using the Hitachi S-4800. UV-vis absorption spectra were collected on a TU-1810 UV-vis spectrophotometer (Beijing Purkinje General Instrument, China) with standard 1-cm-optical-path quartz cells. Raman spectra were measured on a Renishaw Micro-Raman spectroscopy system. The excitation line, 514 nm, was provided by an argon ion laser. XRD was performed on a Bruker D8 Advanced X-ray diffractometer with CuK $\alpha$  radiation. AFM images were obtained using an SPA300HV (Seiko Instruments Inc.) instrument in tapping mode. AFM samples were prepared by drop-casting GO dispersions onto freshly cleaved mica substrates and drying in air. All electrochemical experiments were performed using a three-electrode setup with a CHI660C workstation, in which platinum was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte was 1 mol/L H<sub>2</sub>SO<sub>4</sub>. The electric conductivity measurements of compressed powder pellets of samples were performed using a four-probe method (SDY-4, China).

## 3. Results and Discussion

Fig. 1 shows typical XRD patterns for G, GO, PANI and the representative GO/PANI composite C, which has high electrochemical performance and will be discussed later. No characteristic G peaks are detected in GO, whereas a peak is observed for GO at 10.72° (2 $\theta$ ), corresponding to the (001) reflection of GO. This result indicates that a highly oxidised GO product has been synthesised<sup>[26]</sup>. As shown in Fig. 1, an intense peak around 2 $\theta$  = 25° and some weak reflections from PANI indicate some crystalline order in PANI. The relative intense peak of GO (2 $\theta$  = 10.72°) disappears in GO/PANI composite, which indicates that low-content GO is exfoliated and loosely dispersed in GO/PANI composite. XRD patterns of GO/PANI composite and PANI reveal their different crystalline forms. There is a new broad peak at 15°–30° existing in the XRD pattern of the GO/

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