



# Enhanced electrochemical behavior and hydrophobicity of crystalline polyaniline@graphene nanocomposite synthesized at elevated temperature



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## ABSTRACT

This paper reports a simple route for the synthesis of graphene (GN) using an electrochemical method as well as its composite with polyaniline (Pani). The resulting nanocomposite contained high crystalline regions due to the in-situ oxidative polymerization performed at elevated temperatures. Thus prepared GN, Pani and Pani@GN nanocomposite were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). Morphological studies showed that Pani formed a smooth coating over the surface of GN. A shift in the FTIR, Raman and XPS spectra of the Pani@GN nanocomposite also supports the strong interactions between Pani and GN, confirming the successful synthesis of the Pani@GN nanocomposite. XRD and selected area electron diffraction revealed the highly crystalline nature of Pani in the Pani@GN nanocomposite, highlighting the efficacy of the preparation method. The Pani@GN nanocomposite showed higher DC electrical conductivity and capacitance than Pani. The enhanced performance of the Pani@GN nanocomposite was attributed to the large surface area provided by GN, facilitating the rapid transport of electrolyte ions into the electrode during the redox process. The Pani@GN nanocomposite also exhibited better hydrophobicity due to the incorporation of GN.

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## 1. Introduction

The 1977 chemical communication report on conducting polyacetylene provided new insights into the bright and exciting world of conducting polymers [1]. Later, many other polymers, such as polyaniline (Pani), polythiophene, polypyrrole, etc., were also found to be conducting. Among all these polymers, Pani has attracted considerable attention because of its ease of synthesis, low cost, good environmental stability, interesting electroactivity, unusual doping/dedoping chemistry, and long shelf life [2–4]. On the other hand, Pani normally suffers from poor thermal stability and low capacitance. To improve the performance further or extend the functions of the devices, Pani normally needs to be nanostructured, i.e. synthesis of either nanometer-sized polymer particles or nanocomposites with conducting materials to improve the

conductive path structure. Small sized nanomaterials can provide high electroactive regions and a short diffusion path [5,6], which are essential for the effective access of an electrolyte to the electrode in both double-layer and redox mechanisms. The high conductivity of electroactive materials is another important parameter to meet the rapid electron transmission for the high rate redox reactions of Pani. Therefore, to achieve high capacitance, a nanocomposite of Pani with carbon based materials, particularly graphene (GN), can be effective owing to its high conductivity [7,8].

GN is comprised of  $sp^2$  hybridized aromatic carbon atoms arranged in a honeycomb network, and has unique electrical and thermal properties [9,10] as well as considerable mechanical strength [11]. For applications in supercapacitor systems, GN can provide good stability during the charge/discharge process. On the other hand, the capacitance achieved is generally low due to the unavoidable aggregation of nanosheets. Pani has been used as a supercapacitor material because of its high conductivity, high flexibility, low cost, and multi-redox state [12]. In addition, it has particularly high theoretical pseudocapacitance, but has limited

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applications as supercapacitors because of its poor stability during the charge/discharge process. Several studies have reported the incorporation of GN into Pani matrices to produce nanocomposites for supercapacitors electrodes. Nevertheless, the specific capacitance obtained is generally low, i.e. approximately 111 F/g for GN [13] and 233 F/g for Pani@GN composites [14]. The capacitance of the Pani@GN composites is dominated mainly by the pseudocapacitance from Pani. The electrical double-layer capacitors (EDLC) for GN are not high, possibly due to the agglomerated large numbers of layer-like structures of the GN sheets [15]. A few layered GN and its composite with Pani are expected to overcome the drawbacks of GN and Pani due to the synergism between the constituents, which might lead to good supercapacitor performance and better charge acceptance behavior.

This paper reports the synthesis of few layered GN nanosheets and highly crystalline Pani@GN nanocomposites via a simple in-situ oxidative polymerization technique. Aniline was polymerized by the drop wise addition of an oxidant, at 60 °C, which is considerably different from the conventional method of polymerization. The combination of GN and Pani resulted in a Pani@GN nanocomposite with enhanced capacitance (613 F/g) and super hydrophobic behavior compared to Pani because GN not only serves as a conducting support material, but also provides a large surface area. The electrochemical performance, morphology and chemical structure of the nanocomposite were also investigated.

## 2. Experimental

### 2.1. Materials

Aniline was acquired from Sigma Aldrich. Potassium persulfate (PPs), hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), ammonia solution (35%), sodium phosphate dibasic (Na<sub>2</sub>HPO<sub>4</sub>), methyl alcohol, and ethanol were purchased from Duksan Pure Chemicals Co. Ltd., South Korea. The graphite sheets for the synthesis of GN were supplied by KOMAX, South Korea. The water used in these experiments was de-ionized water obtained from a PURE ROUP 30 water purification system.

### 2.2. Methods

The microstructures of GN, Pani and Pani@GN were examined by scanning electron microscopy (SEM, HITACHI-S4800), and field emission transmission microscopy (FE-TEM, Tecnai G2 F20, FEI, USA) at an accelerating voltage of 200 kV. The mean diameter of the particles was calculated using image J software. Phase analysis was performed by X-ray diffraction (XRD, PANalytical, X'pert PRO-MPD, Netherland) using Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm). Raman spectroscopy was recorded on Lab Ram HR 800 UV Raman microscope (Horiba Jobin-Yvon, France,  $\lambda = 514$  nm). The Raman spectra were acquired at the Korea Basic Science Institute, South Korea. The functional groups and their interactions were examined by Fourier transform infrared (FTIR, Excalibur series FTS 3000 Bio-Rad spectrometer) spectroscopy. The UV–visible diffuse absorbance/reflection spectra were measured using an ultraviolet–visible–near infrared spectrophotometer (UV–VIS–NIR, Cary 5000, VARIAN, USA). X-ray photoelectron spectroscopy (XPS, K-ALPHA) was performed using a monochromatized Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV) with a 400  $\mu$ m spot size. Thermogravimetric analysis (TGA, Perkin Elmer, Pyris Diamond) was performed by heating the samples from 20 to 900 °C at 10 °C min<sup>-1</sup> at a N<sub>2</sub> flow rate of 200 mL min<sup>-1</sup>. Electrochemical studies, such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were carried out using a potentiostat (VersaSTAT 3, Princeton Research, USA). The DC electrical conductivity ( $\sigma$ ) was measured

using a 4-in-line probe electrical conductivity measuring instrument in a PID controlled oven (Scientific Equipment's, Roorkee, India), and were calculated using the following equation:

$$\sigma = [\ln 2(2S/W)]/[2\pi S (V/I)] \quad (1)$$

where I, V, W, and S are the current (A), voltage (V), thickness of the pellet (cm), and probe spacing (cm), respectively, and  $\sigma$  is the DC electrical conductivity in S/cm [16].

For the electrical conductivity studies, a pellet of Pani and the Pani@GN nanocomposite was prepared using a hydraulic pressure instrument at a 50 kN pressure for 10 min. All electrochemical measurements were performed using a potentiostat Versa STAT 3, Princeton Research, USA. The working electrode was prepared by casting a Nafion-impregnated sample into a carbon paper electrode with area of 1 cm<sup>2</sup>. In a typical process, 5 mg of each sample (GN, Pani and Pani@GN nanocomposite) was dispersed in 1 mL of an ethanol solution containing 5  $\mu$ L of a Nafion solution in an ultrasonic bath for 20 min and then coated on a carbon paper electrode. A three electrode cell system was used to evaluate the electrochemical performance by CV and EIS in 1 M H<sub>2</sub>SO<sub>4</sub> as the electrolyte. GN, Pani and the Pani@GN nanocomposite were coated separately on carbon paper and used as the working electrodes. Platinum gauze and Ag/AgCl (3.0 M KCl) were used as the counter and reference electrodes, respectively.

### 2.3. Electrochemical synthesis of graphene

The Pani@GN nanocomposite was synthesized using GN, which was prepared via electrochemical route and its subsequent polymerization with aniline by in situ oxidative polymerization technique. The electrochemical cell consisted of a graphite sheet and platinum gauze as the anode and cathode, respectively. The complete assembly was dipped in an aqueous electrolyte solution containing 100 mL of 1% H<sub>2</sub>SO<sub>4</sub> and 3 g of Na<sub>2</sub>HPO<sub>4</sub>. The electrodes were connected to the respective terminals of the electrochemical workstation at a fixed voltage of  $\pm 10$  V. Soon after the start of the reaction, the solution gradually turned gray and finally to an intense black. The graphite anode dissociated constantly into flaky GN and exfoliated graphite particles throughout the course of the reaction, which settled at the bottom of the bottle. After 1.5 h, the electrolyte solution containing exfoliated graphite and GN was centrifuged at 8000 rpm for 10 min to isolate GN, which was then washed with water and an excess of ethanol followed by drying in an oven at 80 °C.

### 2.4. Synthesis of the Pani@GN nanocomposite

The Pani@GN nanocomposite was synthesized via the simple in-situ oxidative polymerization of aniline in the presence of GN using PPs as an oxidizing agent. In a typical process, 0.1 g of GN was added to 500 mL of 1 M HCl followed by ultrasonic agitation for proper dispersion of the GN nanosheets, which was followed by the addition of 5 mL of the aniline monomer. The entire system was stirred vigorously on a hot plate at a constant temperature of 60 °C. A solution of the oxidant (0.5 M PP in 500 mL 1 M HCl) was added drop wise to the above dispersion of GN and aniline to initiate the polymerization of aniline on the GN nanosheets. The reaction mixture was then stirred constantly for 12 h, after which the solution was filtered. The Pani@GN slurry after filtration was washed with an excess of water and methanol to remove the residual PPs and Pani oligomers. The nanocomposite dedoped by 1 M ammonia solution and then washed sequentially with water and methanol. The prepared emeraldine base of the Pani@GN nanocomposite was doped with 100 mL of a 1 M HCl solution for 12 h, filtered and

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