



# Facile Preparation of Graphene/Polyaniline Composite and Its Application for Electrocatalysis Hexavalent Chromium Reduction



Ying Yang<sup>a,1</sup>, Mu-he Diao<sup>a</sup>, Ming-ming Gao<sup>a,\*</sup>, Xue-fei Sun<sup>a</sup>, Xian-wei Liu<sup>b</sup>, Guo-hui Zhang<sup>a</sup>, Zhen Qi<sup>a</sup>, Shu-guang Wang<sup>a,\*</sup>

<sup>a</sup> School of Environmental Science and Engineering, Shandong University, Jinan 250100, P.R. China

<sup>b</sup> The Biodesign Institute, Arizona State University, Tempe AZ 85287, USA

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## ABSTRACT

Herein, graphene–polyaniline (GR–PANI) composite were synthesized via a combination of electrochemical polymerization and chemical technique. This in-situ approach allows GR and PANI to combine efficiently and anchor on electrode steadily, and the attractive interactions enable GR–PANI to provide superior electrochemical activities on the basis of their respective functionalities. Detailed electrochemical studies indicate that the GR–PANI possesses high sensitive response to Cr(VI) and presents exceptional electrocatalytic performance toward Cr(VI) reduction, which is attributed to the increasing amount of active sites on the GR–PANI modified electrode and the effective electron transfer behavior on GR–PANI/Cr(VI) interface.

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## 1. Introduction

Graphene, a two-dimensional monolayer carbon material, has attracted increasing attention since its first discovery in 2004 [1], primarily due to its extraordinarily electronic property, thermal conductivity, and super mechanical strength. Approaches for GR preparation mainly include micromechanical exfoliation [1,2], solvent thermal reactions [3,4], and chemical vapor deposition [5] processes. Among them, chemical oxidation and reduction of graphite is an effective method which is not only productive but also provides multi-functional GR. Up-to-date, GR has been applied in various fields of investigation, such as sensors [6,7], energy storage devices [8,9], and electrocatalysts for oxygen reduction [10,11]. In addition, to improve the performance or extend the functions of GR, the fabrication of GR and polymers are of scientific interests for their enhanced mechanical and electrochemical properties arising from the incorporation of polymer chains [10,12,13]. Such GR–polymer composite always shows large specific area, high conductivity, well redox property, and enhanced electrocatalytic activity with broad applications [12–15]. Recently Stein et al. [16] prepared the ultralight graphene/carbon composite aerogels with a density as low as 3.2 mg/cm<sup>3</sup> or a surface area as high as 1019 m<sup>2</sup>/g

by assembly of graphene oxide and resol-type phenolic prepolymer. And Li et al. [17] revisit the capacitance of polyaniline (PANI) by using graphene hydrogels as a substrate, and very interestingly, the PANI on graphene hydrogels exhibit an excellent cycling performance compared with PANI capacitor. All of these studies show GR could provide well interaction with polymers, and hence to present novel property or dramatically expand each other's application field.

As a typical conducting polymer, PANI is generally believed to have good environmental stability, exceptional electroactivity, and well doping/dedoping character [18–20]. The synthesis of electrically conducted PANI can be readily accomplished either by chemical oxidation or electrochemical polymerization of aniline in acidic conditions. The reversible conductivity achieved by changing the oxidation state makes PANI a promising material for various applications including in sensors [21–23], separation membranes [24], and modified electrodes for electroreduction [25–27]. Recent reports demonstrated that PANI shows excellent electrocatalytic activity toward the reduction of Cr(VI), which reveals one promising process for treatment of Cr(VI) containing wastewater since it is efficient and selective as reported [28,29]. However, most of the previous studies focus on PANI films, which always have relatively small specific surface areas, typically up to 80 m<sup>2</sup>/g [30], and limited functional groups on the edge areas [31–33]. It may result in the relatively low electrochemical activity [27,30]. Hence preparation of composites based on PANI and GR may be a suitable candidate for electrochemical applications, especially for removal of toxic Cr(VI)

\* Corresponding author.

E-mail addresses: [mmgao@sdu.edu.cn](mailto:mmgao@sdu.edu.cn) (M. Gao), [wsg@sdu.edu.cn](mailto:wsg@sdu.edu.cn) (S. Wang).

<sup>1</sup> ISE member

in wastewater treatment. Overall, the incorporation of PANI into GR is expected to can both optimize the unique property and overcome the defects of two kinds of materials when applied in the field of electrocatalysis.

Attempts to combine GR and PANI have been made to prepare electrode materials as supercapacitor [26–32] and promising nanocomposite for ultrafast photonics [14]. Significant improvement have been observed in these composite materials with the incorporation of PANI which are considered to improve mechanical and thermal properties, enhance the electron transfer rate [27,28], and increase the basal spacing between GR layers [12]. Although the synthesis of GR–PANI composites have been achieved successfully, experimental investigation demonstrated that both the chemical and electrochemical methods have their own insufficiencies that the compound made by chemical process always showed unsatisfactory redox and electroactive properties, while the electrochemical synthesis employed graphite oxide rather than graphene as the starting material due to the hydrophobicity of GR [32]. Therefore, the improved fabrication of GR–PANI composite with large specific surface area, high electrochemical activities and desired functional groups through simple and efficient methods remains scientifically challenging.

In the present study, we report a facile approach for the synthesis of GR–PANI composite films by electrochemical polymerization and chemical interaction, which would be capable of enhancing electrocatalytic activity. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), flourier transform infrared spectroscopy (FT–IR), X–ray photoelectron spectroscopic (XPS) analysis were carried out to characterize the as–made composites. The edge and defective region of GR–PANI composites have large numbers of functional groups, which offers plenty of reaction sites for electron transfer reaction. In addition, there are strong interactions between GR and PANI, GR–PANI composite and reactant, which will greatly accelerate the electron transfer rate. In proof of this theory, the applications of various modified electrodes (GR, PANI, and GR–PANI) on Cr(VI) reduction and detection were investigated in details by cyclic voltammetry (CV), liner sweep voltammetry (LSV), electrochemical impedance spectrum (EIS), and chronopotentiometry.

## 2. Experimental Section

### 2.1. Materials

graphite powder (99.95% purity) was purchased from Aladdin. Other chemicals such as aniline, hydrazine hydrate, and N, N–dimethylformamide (DMF) were all of analytical grade and obtained commercially. Aniline was distilled for further purification and other chemicals were used as received.

### 2.2. Preparation of GR–PANI modified electrode

Graphene oxide (GO) was synthesized from graphite powder (99%, 40 nm, Aladdin) by Hummers method [33]. Briefly, 23 mL of 98% H<sub>2</sub>SO<sub>4</sub> was added into a mixture of 0.5 g of graphite powder and 0.5 g of NaNO<sub>3</sub> in the conditions of ice–water bath. Thereafter, 3 g of KMnO<sub>4</sub> was added slowly. The ice bath was then removed and the solution was kept at 35°C under vigorous stirring for 1 hour. Subsequently, 40 mL of water was added slowly and the solution was heated up to and kept at 90°C for 30 min. Eventually, 100 mL of water and 5 mL of H<sub>2</sub>O<sub>2</sub> was added, followed by water washing and filtration. To obtain GR then, the above mentioned GO was reduced by ammonia water and hydrazine hydrate.

The GR–PANI film was prepared through a stepwise method. Before polymerization, the GR dispersion was prepared as follows:

5 mg GR was added into a 1 mL dimethyl formamide (DMF) aqueous solution under ultrasonication for 2 h, and a stable mixture of was obtained. Consequently, PANI was coated on the electrode by an electrochemical process by CV for 5 cycles from an aqueous solution containing 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M aniline, in which the potential range was between –0.4 and 0.85 V and at a scan rate of 50 mV s<sup>–1</sup>. After polymerization, 5 μL GR (0.05 wt %) dispersion was dropped on the electrode immediately. After drying in an oven for 1 h, the working electrode was scanned by CV in the above aniline solution for 2 cycles again. Finally, the as prepared electrode was washed in distilled water carefully and dried in oven for 24 h.

Meanwhile, the GR and PANI modified electrode was prepared by dropping 5 μL GR (0.05 wt %) on the surface of the electrode, and CV scanning for 10 cycles in aniline contained electrolyte, respectively.

### 2.3. Characterization of GR–PANI modified electrode

The morphology of the as synthesized films was characterized by SEM (JSM–6700F, JEOL, Japan) and TEM (JEM–100 CXII, Japan). FT–IR spectra were recorded on an Avatar 370 Fourier transform infrared spectrophotometer (PerkinElmer, USA, frequency region between 2000 and 400 cm<sup>–1</sup>). XPS analysis was performed on an ESCALAB250 photoelectron spectrometer (Thermo, USA).

### 2.4. Electrochemical measurement

All electrochemical characterizations were conducted with a CHI 760 D electrochemical workstation (Shanghai Chenhua, Shanghai) and performed in a standard three–electrode system, where PANI/GR/GR–PANI modified glass carbon electrodes served as the working electrodes, a platinum electrode and a saturated calomel electrode (SCE) was used as counter and reference electrode, respectively. The electrochemical activities of the composite were studied by CV at 5 mV s<sup>–1</sup> in 0.1 M H<sub>2</sub>SO<sub>4</sub> with or without Cr(VI), the potential range was –0.2 to +0.7 V. Electrocatalytic reduction of Cr(VI) on GR–PANI modified electrode was conducted using CV and LSV. Electrochemical impedance spectrum was performed at the apparent formal potential (E<sup>0'</sup>) extrapolated from voltammograms, and EIS data were fitted by the Randles circuit.

### 2.5. Application of GR–PANI for Cr(VI) reduction

Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) was dissolved into deionized water to prepare Cr(VI) aqueous solution. A serial of experiments were conducted using deferent electrodes (GR, PANI, and GR–PANI) and the influence of initial pH values on the reduction rates are studied between the initial pH 0.5~2. Chronopotentiometry was carried out in a three–electrode system, a negative potential E = –0.1 V was applied. In order to clarify effect of the modified electrodes on the reduction of Cr(VI), the working electrode here was large–area wax–impregnated graphite electrodes (0.79 cm<sup>2</sup>) instead of glass carbon electrodes. A platinum electrode (2 cm<sup>2</sup>) and a saturated calomel electrode (SCE) served as counter and reference electrode, respectively.

## 3. Results and discussion

### 3.1. Synthesis and structural characterization of the GR–PANI film

In order to fabricate GR–PANI with enhanced electrochemical activity, the GR–PANI composite modified electrode was prepared through a three–step method, as shown in [Scheme 1A](#). First, GR was dispersed in DMF under ultrasonication to form a stable mixture suspension. Once the polymerization of PANI at the surface of the glass carbon electrode was realized for the first time, 5 μL

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