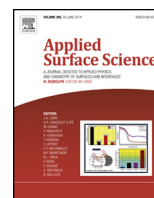




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# Fabrication of poly(*o*-phenylenediamine)/reduced graphene oxide composite nanosheets via microwave heating and their effective adsorption of lead ions

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## ABSTRACT

In this paper, we have demonstrated a microwave heating method to fabricate poly(*o*-phenylenediamine)/reduced graphene oxide (PoPD/RGO) composite nanosheets. During the reaction process, graphene oxide (GO) nanosheets were used as oxidant to polymerize *o*-phenylenediamine (*o*PD) monomer to form PoPD on their surface, while themselves were reduced. Transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, ultraviolet–visible (UV–vis) absorption spectroscopy, X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) indicate the successful production of PoPD/RGO composite nanosheets with crumpled morphology. The as-prepared PoPD/RGO composite nanosheets were tested and evaluated as a potential adsorbent for the removal of lead ions. The results showed that the adsorbent exhibited a favorable performance for the removal of lead ions and the adsorption processes were well fitted by pseudo-second-order kinetic model.

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## 1. Introduction

Conducting polymers have formed a new interdisciplinary field of research because of their unique physical and chemical properties, and many potential applications in electronic devices, supercapacitors, rechargeable batteries, functional electrodes, sensors, and so on [1–6]. Moreover, the effective adsorption performance of conducting polymers has made them to be promising adsorption materials especially in the removal of heavy metal ions [7]. For instance, the adsorption of metal ions by conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and their composites have been reported. PANI as synthesized from a traditional fashion typical approach with irregular particulate morphology has been used as adsorbent for the removal of Hg(II) from water [8]. The nanocomposites of PANI/activated carbon can effectively improve the adsorption performance of As(V) [9]. Recently, our group has prepared bamboo-like PPy nanotubes via a vapor phase polymerization approach by using V<sub>2</sub>O<sub>5</sub> nanofibers as oxidants and sacrificial templates. And the as-synthesized PPy

nanotubes have exhibited good adsorption performance toward Cr(VI) [10].

Recently, polymers based on aniline derivatives have attracted much interest for researchers because of their apparently different characteristics compared with those widely studied conducting PANI [11,12]. Moreover, some aromatic diamine polymers show highly reactive sensitivity to some metal ions, including Ag(I), Cu(II), Hg(II), Pb(II), and Cr(VI), through chelation or redox reaction with the amino/imino groups on the polymer chains [13,14]. For example, poly(*m*-phenylenediamine) (PmPD) has been shown powerful Ag<sup>+</sup> adsorption ability, fluffy poly(*o*-phenylenediamine) (PoPD) microspheres could be used in treatment of Cr(VI)-polluted waste waters, etc. [15,16].

The surface area of the sorbents plays a key role during the adsorption process. Therefore, it is necessary to prepare adsorptive materials with a large surface area to improve its adsorption efficiency [17]. In the past few years, graphene oxide (GO) nanosheets have received considerable interest for potential applications in many technological field due to the unique properties [18,19]. GO has a unique two-dimensional nature and contains a range of reactive oxygen functional groups on its surface, such as epoxide (C–O–C), hydroxyl (OH), carboxyl (COOH), and carbonyl groups, which render them a good candidate for supporting other functional nanomaterials [20,21]. In addition,

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the large surface area of GO enables graphene–polymer hybrids process a large adsorption capacity. In the past few years, various kinds of synthetic methods have been developed for the preparation of GO/conducting polymer or RGO/conducting polymer nanocomposites because of their unique properties such as good environmental stability, large adsorption ability, and excellent electrochemical activity [22,23]. Our group has reported for the preparation of PPy/GO composite nanosheets by using a simple and reliable sacrificial-template polymerization method. The as-prepared PPy/GO composite nanosheets exhibited an excellent adsorption performance for Cr(VI) ions [24]. Chen et al. have also reported the preparation of colloids of graphene monolayers by the heat treatment of *N,N*-dimethylformamide (DMF) solution containing GO and *p*-phenylenediamine (*p*PD) [25]. More recently, a novel method for preparation of graphene-conducting polymer hybrids through the redox reactions between GO and conducting polymer monomer has been reported because GO could be regarded as an oxidizing agent, which could initiate the polymerization of the conducting polymer monomer. By using such a strategy, PANI/RGO, PPy/RGO, poly(3,4-ethylenedioxythiophene) (PEDOT)/RGO and PpPD/RGO nanocomposites have been fabricated. These nanocomposites have exhibited widely applications in supercapacitors and electrochemical sensors [26–30].

In this study, we have reported the synthesis of poly(*o*-phenylenediamine)/reduced graphene oxide (PoPD/RGO) composite nanosheets by a one-step in-situ redox reaction through microwave heating. GO as an oxidant could be reduced to RGO, whereas *o*PD was polymerized in situ on the surface of the RGO. The as-prepared PoPD/RGO composite nanosheets with crumpled morphology have been tested for the adsorption of Pb(II) ions. The RGO is obtained by the reduction of GO, with a similar large theoretical surface area of GO and a large number of structural defects, leading to great potential application as an effective adsorbent for RGO itself. Furthermore, the RGO with a two dimensional structure could be well served as a support for loading the metal, metal oxide nanoparticles or polymers on its surface, improving the adsorption ability for heavy metal ions and dyes [31–33]. The adsorption process was well fitted by pseudo-second-order kinetic model. The adsorbent exhibited a favorable performance and its maximum adsorption capacity calculated by the Langmuir model was about 228 mg g<sup>-1</sup>.

## 2. Experimental

### 2.1. Chemicals and materials

Graphite powder and Pb(NO<sub>3</sub>)<sub>2</sub> were purchased from Sinopharm Chemical Reagent Co., Ltd. *o*PD was purchased from Tianjin Guangfu Fine Chemical Research Institute and all other chemicals (H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, NaNO<sub>3</sub>) were obtained from Beijing Chemical Corporation. The chemicals were analytical grade and used without further purification.

### 2.2. Preparation of PoPD/RGO composite nanosheets

GO was synthesized based on the modified Hummers and Offeman's method [34,35]. In a typical preparation of PoPD/RGO composite nanosheets, 30 mg of GO was dispersed in 25 mL H<sub>2</sub>O by ultrasonication for 4 h. Then 150 mg of *o*PD monomer dispersed in 5 mL H<sub>2</sub>O was added into the homogeneous GO dispersion and stirred for 30 min at room temperature. Because of the strong electrostatic adsorption between *o*PD monomer and GO, *o*PD/GO compounds were formed for the preparation of PoPD/RGO composite nanosheets. Then the mixture was placed into a microwave oven. PoPD/RGO composite nanosheets were obtained

after microwave heating (210 W) for 20 min. Finally, the products were collected by filtration, washed with water for three times.

### 2.3. Application of PoPD/RGO composite nanosheets for Pb(II) ions adsorption

The Pb(II) solution was prepared by dissolving lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) in aqueous solution. Adsorption kinetics was performed by using batch experiments as follow: 25 mg of PoPD/RGO composite nanosheets and 50 mL of 100 mg L<sup>-1</sup> Pb(II) solution was continuously stirred at room temperature under natural pH conditions. At various time intervals, the adsorbent was filtrated and the concentration of Pb(II) was determined using an inductive coupled plasma (ICP) emission spectrometer. For the effect of Pb(II) concentration of solution on the adsorption capacity experiment, 10 mg of PoPD/RGO composite nanosheets and 20 mL of Pb(II) solution with different concentrations were continuously stirred at room temperature under natural pH conditions. After 12 h, the adsorbents were filtrated and the concentrations of Pb(II) were determined using an ICP emission spectrometer. The adsorption capacity of Pb(II) ions could be calculated by the following formula:

$$q = \frac{(C_0 - C_e)V}{W}$$

where  $q$  (mg g<sup>-1</sup>) was the adsorption capacity,  $C_0$  (mg L<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) were Pb(II) ions concentrations before and after adsorption, respectively.  $V$  (L) was the initial volume of the Pb(II) ions solution, and  $W$  (g) was the weight of PoPD/RGO composite nanosheets added.

### 2.4. Characterization

Transmission electron microscopy (TEM) experiment was performed on JEM-1200 EX (JEOL) electron microscopes at 100 kV. FT-IR spectra were recorded on a BRUKER VECTOR22 spectrometer using KBr pellets. XRD patterns were obtained with a Siemens D5005 diffractometer using Cu K $\alpha$  radiation. Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB MKII instrument. The ultraviolet–visible (UV–vis) absorption spectroscopy was performed on SHIMADZU UV-2501 UV–vis spectrophotometer. The concentrations of Pb(II) ions were determined using an inductive coupled plasma emission spectrometer (ICP, PerkinElmer OPTIMA 3300DV).

## 3. Results and discussion

### 3.1. Morphology and structure

In this paper, we have used GO as oxidant to polymerize *o*PD, which GO was reduced to RGO to prepare PoPD/RGO composite nanosheets. A typical polymerization process for the formation of PoPD/RGO composite nanosheets by microwave heating of GO and *o*PD is shown in Scheme 1. The morphology of GO and PoPD/RGO composite nanosheets were characterized by TEM images. Fig. 1a presents the lamellar structure of the exfoliated GO nanosheets with a smooth surface. After the polymerization of *o*PD on the surface of GO nanosheets, a layer-like structure of PoPD was uniformly coated on the surface of the RGO nanosheets, which was similar with the previous report [29]. The crumpled morphology of the obtained PoPD/RGO composite nanosheets affords their good adsorption ability for the heavy metal ions.

The chemical structure of the as-prepared PoPD/RGO composite nanosheets was characterized by FT-IR measurement. The FT-IR spectra of the GO, PoPD/RGO composite nanosheets were present in Fig. 2. It was seen that GO nanosheets exhibit several obvious bands. The characteristic peak at 1725 cm<sup>-1</sup> is attributed to the

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