



# Sulfur-free exfoliated graphite with large exfoliated volume: Preparation, characterization and its adsorption performance



Qi Zhao<sup>d,1</sup>, Xiuwen Cheng<sup>a,b,c,1</sup>, Juan Wu<sup>b</sup>, Xiujuan Yu<sup>a,b,\*</sup>

<sup>a</sup> Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province, Xuefu Road 74, Nangang District, Harbin 150080, PR China

<sup>b</sup> Department of Environmental Science and Engineering, Heilongjiang University, Xuefu Road 74, Nangang District, Harbin 150080, PR China

<sup>c</sup> State Key Laboratory of Urban Water Resources and Environment (SKLUWRE), Department of Environmental Science and Engineering, Harbin Institute of Technology, Huanghe Road 73, Nangang District, Harbin 150090, PR China

<sup>d</sup> National Engineering Research Center of Urban Water Resource, Harbin Institute of Technology, Huanghe Road 73, Nangang District, Harbin 150090, PR China

## ARTICLE INFO

### Article history:

Received 23 November 2013

Accepted 2 January 2014

Available online 10 January 2014

### Keywords:

Exfoliated graphite  
Microwave exfoliation  
Adsorption capacity  
4-Chlorophenol  
Rodamine B

## ABSTRACT

Sulfur-free exfoliated graphite (EG) with large exfoliated volume ( $760 \text{ mL g}^{-1}$ ) was prepared through chemical oxidation, followed by microwave exfoliation. SEM results indicated that well-developed network pores in the worm-like structure of EG could be clearly observed. XPS results displayed that some functional groups were yielded on the surface of the as-prepared EG. Moreover, the capacity of EG was evaluated by the adsorption of rodamine B and 4-chlorophenol aqueous solution. Results showed that EG exhibited high adsorption capacity for RhB and 4-CP, which could be attributed to the functional groups and well-developed network pores in the worm-like EG.

© 2014 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, environmental endocrine disruptors (ECDs) have often been detected in the natural surface and ground water, leading to an increased issue of its monitor and treatment [1–3]. Because these substances are potential carcinogenic and refractory agent, which poses a significant health threat to human being. Thus, it's urgent to develop an environmental-friendly process or functional materials to solve the tough problem. Over the past few decades, a great deal of efforts has been made in attempts to eliminate the organic contaminants from aqueous solution [4,5]. Fortunately, the adsorption process has been proven to be an effective technology for the elimination of low concentration organic compounds from contaminated water and aqueous solutions. However, the efficient and functional adsorbent plays an important role in this process.

Exfoliated graphite (EG) is a new kind of functional nano-carbon-based material due to its lightweight, soft, porosity, high-surface area and high-surface activity [6], which has been widely prepared and used in gasket, electromagnetic interference shielding, vibration damping, electrochemical applications, stress sensing and thermal insulator [7–9]. Nevertheless, EG often comes from the graphite intercalation compounds (GICs) during the rapid heating process at high temperature in muffle furnace. Generally, sulfuric acid has usually been applied to fabricate GICs, thereby resulting in the residual of sulfur species in the as-fabricated EG samples, which limited its widely application [10]. Very recently, microwave exfoliation has been considered to be an effective approach to fabricate functional materials due to its homogeneous heating and energy-saving [11]. From then on, many attempts have been performed.

In the present work, sulfur-free exfoliated graphite (EG) with large exfoliated volume (EV) has been successfully prepared through chemical oxidation, followed with microwave exfoliation. The resulting materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectra and X-ray photoelectron spectroscopy (XPS). Further, the performance of EG was evaluated by the adsorption of colored rodamine B (RhB) and colorless 4-chlorophenol (4-CP) aqueous solution. As a result, EG sample exhibited superior adsorption efficiency for the organic contaminants from aqueous solution.

\* Corresponding author at: Department of Environmental Science and Engineering, Heilongjiang University, Xuefu Road 74, Nangang District, Harbin 150080, PR China. Tel.: +86 451 86608549; fax: +86 451 86413259.

E-mail addresses: [yuxjuan@hit.edu.cn](mailto:yuxjuan@hit.edu.cn), [yeqian04@126.com](mailto:yeqian04@126.com), [yuxjuan@sina.com](mailto:yuxjuan@sina.com) (X. Yu).

<sup>1</sup> Qi Zhao and Xiuwen Cheng are co-first authors, they contributed equally to the work.

## 2. Experimental

All reagents used in the experiments were purchased from Sinopharm Chemical Reagent Co. Ltd, which were analytical grade and employed without any further purification, and doubly deionized (DI) water was used throughout this study.

### 2.1. Sample preparation

The preparation process of EG went as follows: a mixture consisted of nature flake graphite (NG, 2 g) and potassium permanganate (KMnO<sub>4</sub>, 1 g) was added dropwise into perchloric acid (HClO<sub>4</sub>, 8 g) in a water bath at 308 K under stirring. Herein, perchloric acid was served as oxidant and inserting agent, while potassium permanganate as assistant oxidant. After continuously stirring for 40 minutes, graphite intercalation compounds (GICs) were successfully achieved. Subsequently, GICs were washed close to neutrality with DI water through a vacuum filter. Afterwards, the as-cleaned GICs were dried for 12 h in an oven at 353 K. Eventually, the worm-like EG was obtained after exfoliation in a microwave oven at 750 W for 20 s.

### 2.2. Characterization

In order to observe the porosity and morphology of the as-prepared EG, scanning electron microscopy (SEM) images were recorded using a XL-30-ESEM-FEG instrument. X-ray diffraction (XRD) measurement has been performed on a Rigaku D/max III apparatus using Cu K $\alpha$  radiation ( $k = 0.15406$  nm). The accelerating voltage and applied current were held at 40 kV and 30 mA, respectively. Raman spectra were conducted on a Jobin Yvon HR800 Raman spectrophotometer (Ar laser excitation wavelength was 457.9 nm). X-ray photoelectron spectroscopy (XPS) was conducted on a PHI-5700 ESCA system with Al K $\alpha$  X-rays source. All the binding energies (BE) were calibrated with respect to the C 1s peak at 284.6 eV of the surface adventitious carbon. The measurement of exfoliated volume (EV) was carried out according to our previous study, which has been described elsewhere [12].

### 2.3. Adsorption capacity

The performance of the as-prepared EG sample was evaluated by the adsorption of colored rodamine B (RhB) and colorless 4-chlorophenol (4-CP) aqueous solution. All the adsorption measurements were carried out at ambient conditions under stirring in the dark. In each run, 0.10 g EG was added into the 250 mL 4-CP or RhB of 10 mg L<sup>-1</sup>. At given time intervals, the collected samples were measured at their characteristic wavelengths with a model T6 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co. LTD., China) after centrifugation and filtration.

## 3. Results and discussion

### 3.1. SEM analysis

In order to observe the morphology of the as-prepared GICs and EG, SEM was conducted and shown in Fig. 1. Noticeable, as shown in Fig. 1a and c, the smooth interlayer between adjacent NG compacted together. However, after chemical reaction, a great deal of cracked fragments could be obviously observed (Fig. 1b). In addition, the distance between the adjacent layers of GICs was obviously increased (Fig. 1d). Moreover, slight distorted layers could be clearly observed. However, after microwave exfoliation, worm-like EG could be clearly observed (Fig. 1e). Meanwhile, the EV of EG could be increased by several hundred times because of the rapid decomposition and spill of intercalation compounds. As measured,

the EV of EG could be achieved to 760 mL g<sup>-1</sup>. Furthermore, it can be seen from the high magnification SEM images (Fig. 1f) that many of well-developed network pores in the worm-like EG could be clearly observed, revealing that the as-prepared EG should possess large surface area thereby exhibiting excellent adsorption ability.

### 3.2. XRD and Raman analysis

The XRD peaks at  $2\theta = 26.5^\circ$  and  $54.6^\circ$  were often taken as the characteristic diffraction peaks of graphite (0 0 2) and (0 0 4) crystal phase [13], respectively. Fig. 2A showed the XRD patterns of NG and EG samples. Clearly, as shown in Fig. 2A, the characteristic diffraction peak of NG was located at  $26.5^\circ$ , indicating that the typical interlayer distance ( $d_{002}$ ) was 0.3358 nm. In case of EG, the dominant diffraction peak shifted to lower angle, suggesting that the interlayer distance among adjacent graphite slightly increased to 0.3370 nm, which was attributed to the decomposition of the intercalation compounds, which was agreed with the SEM results. In addition, it can be apparently observed that EG exhibited relative weaker and narrower diffraction peaks present at  $26.3^\circ$  and  $54.4^\circ$  than that of NG, which was due to the preferred orientation (*c*-axis) of graphite platelets. Seredych [13] indicated that the decrease of relative intensity corresponds to the yield of lattice defects such as stacking disorder. Further, the crystal sizes could be calculated by the Scherrer's equation [14]. As calculated, the crystal size of NG and EG was 7.3 and 9.6 nm, respectively.

Raman spectroscopy is a powerful non-destructive technique to characterize the ordered and disordered structure of the graphite. Fig. 2B showed the Raman spectra of NG and EG. Clearly, it can be seen that both spectra of NG and EG were composed of a D-band, a G-band, and a 2D-band (G'). As known to us [15], D-band is associated with disorder-induced scattering resulting from imperfections or loss of hexagonal symmetry of disordered graphite. However, G-band corresponds to an  $E_{2g}$  mode of graphite and is related to vibration of sp<sup>2</sup>-bonded carbon atoms in a two-dimensional hexagonal lattice. By comparison, the G-band of EG was broadened and up-shifted to 1591 cm<sup>-1</sup> due to the presence of isolated double bonds that resonated at higher frequencies than that of NG. Meanwhile, the intensity of D band of EG at 1366 cm<sup>-1</sup> increased sharply, which was attributed to the microwave exfoliation.

### 3.3. XPS analysis

In order to investigate the chemical state of the as-prepared EG sample, XPS was performed and shown in Fig. 3. Seen from Fig. 3, EG only contained carbon and oxygen elements, indicating that the intercalation compounds in the interlayer of EG were completely decomposed after microwave exfoliation. In addition, it can be clearly seen from the C 1s spectra of EG (in the inset of Fig. 3) that the binding energy of 284.5 eV was attributed to the C–C bond. However, the deconvoluted peaks located at the binding energies of 285.4, 288.1 and 289.5 eV were assigned to the C–O, C=O, and O=C–O functional groups [16–18], which was beneficial for the adsorption of contaminants.

### 3.4. Mechanism

Based on the above analysis, we considered that chemical oxidation and microwave exfoliation were all contributing to the formation of EG material. The proposed scheme was shown in Fig. 4. This process contained two steps as follows: (i) The first step is to prepare GICs through chemical oxidation. Nature flake graphite (NG) compacted together. However, the interaction has been emerged under the reaction between strong acid (HClO<sub>4</sub>), oxidation agent (KMnO<sub>4</sub>) and graphite layer. Thus, the distance between adjacent graphite was greatly increased, along with slight

Download English Version:

<https://daneshyari.com/en/article/227526>

Download Persian Version:

<https://daneshyari.com/article/227526>

[Daneshyari.com](https://daneshyari.com)