



# Green fabrication of cellulose/graphene composite in ionic liquid and its electrochemical and photothermal properties



Weijie Ye<sup>a</sup>, Xiaoyun Li<sup>a</sup>, Hongli Zhu<sup>b</sup>, Xiaoying Wang<sup>a,\*</sup>, Suqing Wang<sup>c,\*</sup>, Haihui Wang<sup>c</sup>, Runcang Sun<sup>a</sup>

<sup>a</sup> State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

<sup>b</sup> Department of Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, USA

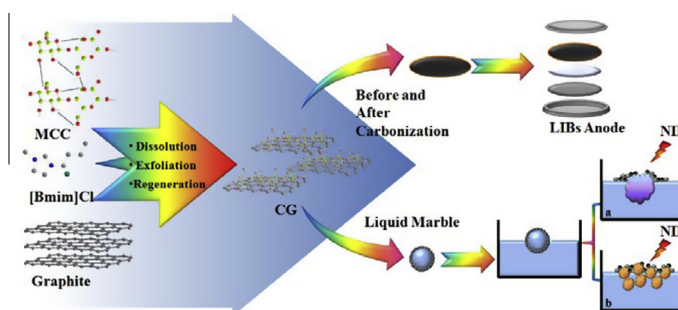
<sup>c</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

## HIGHLIGHTS

- Cellulose/graphene composite (CG) was obtained by exfoliating graphite in ionic liquid.
- Ionic liquid-cellulose complexes acted as exfoliating agent.
- The concentration of the obtained graphene was as high as 1.12 mg mL<sup>-1</sup>.
- Carbonized CG showed desirable electrochemical performance as anode materials.
- CG was made into liquid marble as a trigger to detect the chemical reactions.

## GRAPHICAL ABSTRACT

Schematic of CG preparation via direct liquid-phase exfoliation and applications as lithium ion battery anode and chemical reaction trigger.



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## ABSTRACT

In this work, cellulose/graphene composite (CG) was obtained by directly exfoliating graphite in ionic liquid in presence of microcrystalline cellulose. In an ideal solvent medium provided by ionic liquid, the ionic liquid-cellulose complexes acted as exfoliating agent. The concentration of the obtained graphene was 1.12 mg mL<sup>-1</sup>. The thickness of graphene sheets was ~1.25 nm, and the lateral size was ~1 μm. The graphene sheets were effectively stabilized by hydrogen bonds between cellulose and graphene. Moreover, the galvanostatic charge-discharge cycling measurements of CG before and after carbonization were evaluated. Carbonization improved the initial coulombic efficiency and the cycling performance. Furthermore, the photothermal conversion study showed that CG can availably convert the near-infrared irradiation into heat, and the measured temperature reached as high as 75 °C after 1 min of irradiation. Finally, CG was made into a near-infrared-responsive liquid marble as a trigger to detect the chromogenic chemical reactions. This study provided a green method to prepare graphene nanosheets with multifunctional applications.

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## 1. Introduction

Graphene, a 2D single layer of sp<sup>2</sup> carbons arranged in a hexagonal lattice, has demonstrated excellent electrical conductivity [1], outstanding thermal conductivity (5000 W m<sup>-1</sup> K<sup>-1</sup>) [2,3], and

\* Corresponding authors. Tel./fax: +86 20 87111861 (X. Wang), +86 20 87110131 (S. Wang).

E-mail addresses: [xyw@scut.edu.cn](mailto:xyw@scut.edu.cn) (X. Wang), [cesqwang@scut.edu.cn](mailto:cesqwang@scut.edu.cn) (S. Wang).

admirable fracture strength (125 GPa) and Young's modulus (1100 GPa) [4]. Enjoying the desirable properties, graphene becomes a pretty promising material in many applications, such as batteries [5,6], supercapacitors [7–9], sensors [10], and semiconductor materials [11]. Owing to the excellent properties and widespread applications, an inexpensive, efficient, and green method to produce graphene with ideal structure and desirable properties has gained much attention.

Direct liquid-phase exfoliation is a convenient method to produce graphene with less oxygen functional groups, in which organic solvents, surfactants, or ionic liquids (ILs) assist to exfoliate pristine graphite [12]. However, organic solvents, such as the widely used organic exfoliation medium N-methyl-2-pyrrolidone, ortho-dichlorobenzene and chloroform, may cause toxicity [13,14]. Water-surfactant solutions comprise a simple exfoliation system, but the surfactant are hardly to remove, which may produce undesirable bubbles and have a negative effect on the subsequent application [15]. ILs are regarded as desirable green solvents for graphite exfoliation, for reasons that the high surface tension of ILs are favorable for exfoliation and the imidazolium structure of ILs can conjugate with  $\pi$  electrons of graphite [16–18]. However, direct liquid-phase exfoliation in ILs has serious problems, including long time for sonication and instability of the prepared graphene dispersions [19]. Therefore, an efficient liquid-phase exfoliation to produce high-quality graphene is worth studying.

As a green material, microcrystalline cellulose (MCC) is the depolymerized cellulose, which is more convenient and accessible than synthetic polymer surfactants and considered as an almost inexhaustible raw material. Moreover, owing to the large specific surface area and submicroscopic porosity, MCC exhibits an unusual affinity for hydrophobic reactants like graphite [20]. Given the plentiful hydroxyl groups in MCC, this green material may stabilize graphene sheets by forming hydrogen bonds. Notably, MCC can be dissolved well in ILs without any modification. Based on the matter mentioned above, it provides a possibility to exfoliate graphite in ILs with MCC as co-exfoliating and stabilizing agent. To our knowledge, there was no report about the use of MCC in ILs to produce graphene.

Generally, graphene obtained by direct liquid-phase exfoliation retains the intact structure and thus provides excellent electrical conductivity, but cellulose may restrict the electrical property because of inherent insulation [21]. It is noted that carbonization is a straightforward method to convert cellulosic materials into carbon [22]. The resulting carbon materials exhibit improved electrical conductivity and larger specific surface area compared with the original cellulose [23,24]. Therefore, the carbonized composite can be used as an electrode material for energy storage, such as lithium ion batteries (LIBs) or supercapacitors [5]. Additionally, graphene has attracted great interest in photothermal application because of its high light irradiation absorption and thermal conversion [25,26]. Graphene provides an important idea for preparing a controllable near-infrared (NIR)-responsive liquid marble [27,28], which is rarely reported.

Herein, we proposed a promising way to prepare graphene nanosheets and explored its various applications (Fig. 1). In the present study, cellulose/graphene composite (CG) was obtained from natural flake graphite with MCC in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) under tip ultrasonication. The effects of different graphite concentrations and MCC contents on graphene exfoliation were studied. Furthermore, the electrochemical performance of the composite before and after carbonization was studied with CG as the anode electrode. The photothermal conversion performance of CG was also investigated, and CG was further introduced into a NIR-responsive liquid marble as a chemical reaction trigger.

## 2. Materials and methods

### 2.1. Materials

Natural flake graphite was provided by XFANO Materials Tech Co., Ltd. (Nanjing, China). MCC was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and its particle size was 20–100  $\mu\text{m}$ . [Bmim]Cl was purchased from Chengjie Chemical Co., Ltd. (Shanghai, China) (purity,  $\geq 99\%$ ). Polyvinylidene fluoride (PVDF) was supplied by Micxy Reagent Co., Ltd. (Chengdu, China). Other reagents and solvents were of analytical grade.

### 2.2. Preparation of cellulose/graphene composite

First, 0.01 g of natural flake graphite and 0.04 g of MCC were dispersed in [Bmim]Cl followed by stirring at 110 °C for 5 h. The mixture was subjected to tip ultrasonication for 120 min (JY92-IIDN, 900 W, 2 s on, 2 s off). The resulting dispersion was centrifuged at 15,000 rpm for 10 min to remove the bulk graphite, and the supernatant containing graphene sheets was collected and retained for UV-vis test. The samples with different graphite concentrations were labeled as CG1-1, CG1-2, CG1-3, CG1-4, and CG1-5 (Table S1 in the SI). Under the same ultrasonication condition, MCC and graphite were dissolved in [Bmim]Cl separately for comparison. The ultrasonicated graphite in water, ultrasonicated graphite in IL, ultrasonicated MCC in IL, and ultrasonicated IL were labeled as UGW, UGIL, UMCC, and UIL, respectively.

Second, the mixture with different mass ratio of MCC to graphite in [Bmim]Cl was subjected to tip ultrasonication for 180 min. The resulting dispersed sample was centrifuged at 15,000 rpm for 10 min, and the supernatant containing graphene sheets in IL was collected for UV-vis test. Then, deionized water was added to initiate the regeneration. After washing the residual with deionized water, the CG samples with different mass ratio were obtained after lyophilization at  $-40$  °C. These samples were labeled as CG2-1, CG2-2, CG2-3, CG2-4, and CG2-5 (Table S1 in the SI).

### 2.3. Carbonization of cellulose/graphene composite

The carbonized cellulose/graphene composite (CCG) was prepared in OTF-1200X tubular furnace (Hefei, China). The CG sample was heated from room temperature to 750 °C at the heating rate of 5 °C/min in high-purity flowing nitrogen atmosphere (50 mL/min). After carbonization at 750 °C for 2 h, the sample was cooled down to room temperature.

### 2.4. Characterizations

UV-vis spectra of the samples were measured with UV-1800 UV-vis spectrometer (Shimadzu, Japan). The results were the average of at least three measurements. Thermal analysis (TGA) was performed on a TGA Q500 (TA, USA). The samples were heated from room temperature to 700 °C at the heating rate of 10 °C/min in high-purity flowing nitrogen atmosphere (25 mL/min). X-ray diffraction (XRD) patterns were investigated using a D8 advance X-ray diffraction (Bruker, Germany) with a Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at 40 kV and 40 mA. Relative intensity was recorded in the scattering range of 5°–90° ( $2\theta$ ) at a scanning rate of 0.1 s/step. Raman spectra were obtained using the LabRAM Aramis Smart Raman Spectrometer (HORIBA Jobin Yvon, France), with He-Ne laser excitation at 632.8 nm and power at 20 mW. Fourier transform infrared (FT-IR) spectra were obtained using a Vector 33 spectrophotometer (Bruker, Germany) under a dry air atmosphere at room temperature via KBr pellets method. The

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