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Solvent-free mechanochemical reduction of graphene oxide

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ABSTRACT

We report a versatile and eco-friendly approach for the reduction of graphene oxide into high-quality graphene nanoplatelets by simple solid-state mechanochemical ball-milling in the presence of hydrogen. After the ball-milling process, the resultant graphene nanoplatelets show the efficient restoration of the graphitic structure completely free from any heteroatom doping (e.g., nitrogen, sulfur) and enhanced electrical conductivities up to 120 and 3400 S/m before and after an appropriate heat treatment (e.g., 900 °C for 2 h under nitrogen).

1. Introduction

Along with the recent explosive interest on graphene due to its outstanding mechanical, thermal and electrical properties [1–3], several synthesis methods have been developed to prepare graphene nanoplatelets (GnPs), including a simple mechanical exfoliation from graphite [4], chemical vapor deposition (CVD) [5], solvothermal synthesis [6], epitaxial growth [7], and graphitization of graphene oxide (GO) [8,9]. Among them, the chemical reduction of GO into reduced graphene oxide (RGO) has been the most widely investigated approach to GnPs with a good processability and scalability [1,8–10]. However, the preparation of RGO often involves the use of very toxic and hazardous reducing agents, such as hydrazine [9,11] and $NaBH_4$ [12,13]. In addition, the undesirable incorporation of heteroatoms from the reducing agent (e.g., nitrogen from hydrazine) into graphene network could significantly alter the electronic properties of GnPs produced by chemical reduction [9,14,15]. To address the aforementioned issues, several alternative approaches for the transformation of GO into RGO have been reported, including the reduction of GO by biomolecules as reducing agents [16–20], irradiations (e.g., laser [21,22], UV [23,24]), electrochemical method [25], and thermal treatments [26–28]. Like all other methods for reducing GO to RGO, however, these green reduction methods of GO are still suffered from an incompleted reduction, and hence a non-integrated graphitic network in the final products.

Recently, we have developed a simple, but efficient, approach to the large-scale production of edge-functionalized graphene nanoplatelets (EFGnPs) with minimal basal plane distortion by mechanochemical ball-milling of graphite [29,30]. The EFGnPs display promising properties, including high electrical conductivity and outstanding electrocatalytic

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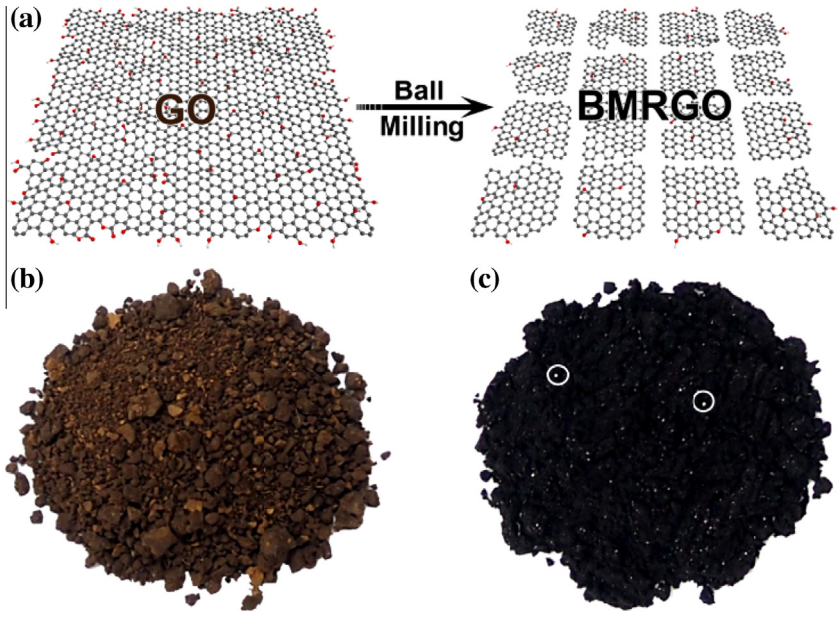

Fig. 1 – (a) A schematic representation of solvent-free mechanochemical reduction of graphene oxide (GO) in the presence of hydrogen. Photographs: (b) GO; (c) BMRGO. The color change from GO (brown) to BMRGO30 (dark black) is a visual indication of the mechanochemical reduction and the shiny light reflection (white circles) of BMRGO30 implies high crystallinity. (A colour version of this figure can be viewed online.)

activity toward oxygen reduction reaction (ORR) [31,32]. By ball-milling of graphite with different reactants, various chemically functionalized GnPs were produced [33–35].

To avoid the solution-based reduction process with multiple drawbacks (*vide supra*), we report here a simple method for eco-friendly, solid-state mechanochemical reduction of GO into GnPs by ball-milling of GO, instead of pristine graphite used for our previous reports [29–32], in the presence of hydrogen (Fig. 1). We found that the ball-milled reduced graphene oxide (BMRGO) pellets with an efficiently-restored graphitic structure free from any heteroatom doping exhibited electrical conductivities up to 120 and 3400 S/m before and after an appropriate heat treatment (e.g., 900 °C for 2 h under nitrogen, *vide infra*), respectively. Therefore, the solid-state ball-milling approach, involving no hazardous chemicals to generate undesirable contaminant(s), outperforms the commonly used solution-based reduction process for mass production of high-quality GnPs.

2. Experimental section

2.1. *Materials and preparation of ball-milled reduced graphene (BMRGO)*

Graphite (Alfar Aesar, natural graphite, 100 mesh, 99.9995% metal basis, Lot#F22U001) was used as the starting material in this study. Firstly, GO was prepared by the modified Hummers' method from graphite [36]. The ball-milling of GO to produce ball-milled reduced graphene oxide (BMRGO) was carried out in a planetary micro ball-mill machine (Pulverisette 7 premium line, Fritsch) at 900 rpm. In a typical experiment, 2.0 g of GO and hydrogen gas (10 bar, Daesung Industrial Gases Co., Ltd.) were charged into a stainless steel capsule containing stainless steel balls of 5 mm in diameter. The container was fixed in a planetary ball-mill machine and rotated at 900 rpm for a operation time ranging from 30 to 240 min to produce various ball-milled reduced graphene oxides (BMRGO), including BMRGO30, BMRGO60, BMRGO120, BMRGO180 and BMRGO240 (the digital number refers to 30, 60, 120, 180 and 240 min, respectively). After opening the container lid at the end of ball-milling, the resultant black powders were carefully collected and purified by Soxhlet extraction with a 1 M HCl solution to remove metallic impurities. The purified powders were washed with a plenty of water and methanol and the final products were dried in vacuum oven at 80 °C under a reduced pressure for 48 h to yield 1.15 g of BMRGO30, 1.09 g of BMRGO60, 1.05 g of BMRGO120, 1.03 g of BMRGO180 and 1.01 g of BMRGO240, respectively.

2.2. *Characterizations*

Elemental analysis (EA) was conducted with a Thermo Scientific Flash 2000. The surface area was measured by nitrogen-adsorption–desorption isotherms using the Brunauer–Emmett–Teller (BET) method on Micromeritics ASAP 2504N. Themogravimetric analysis (TGA) was conducted with a TA Q200 (TA Instrument) under air atmosphere at a heating rate of 10 °C min^{-1}. Solid-state 13C magic-angle spinning (MAS) NMR spectra were recorded on a Varian Unitylnova 600 (600 MHz) spectrometer, using a 5-mm probe spinning at 9 kHz. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin–Elmer Spectrum 100 using KBr pellets. Raman spectra were taken with a He–Ne laser (532 nm) as the excitation source by using confocal Raman microscopy (Alpha 300S, WITec, Germany), in conjunction with atomic force microscopy (AFM). X-ray diffraction (XRD) patterns were