Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors

Yanwu Zhu, Shanthi Murali, Meryl D. Stoller, Aruna Velamakanni, Richard D. Piner, Rodney S. Ruoff

Department of Mechanical Engineering and the Texas Materials Institute, The University of Texas at Austin, One University Station C2200, Austin, TX 78712-0292, USA

ABSTRACT

We report a simple yet versatile method to simultaneously achieve the exfoliation and reduction of graphite oxide. By treating graphite oxide powders in a commercial microwave oven, reduced graphite oxide materials could be readily obtained within 1 min. Extensive characterizations showed that the as-prepared materials consisted of crumpled, few-layer thick and electronically conductive graphitic sheets. Using the microwave exfoliated graphite oxide as electrode material in an ultracapacitor cell, specific capacitance values as high as 191 F/g have been demonstrated with KOH electrolyte.

First prepared almost 150 years ago [1], graphite oxide (GO) has re-emerged as an intensive research interest in recent years due to its role as a precursor for the affordable and large-scale production of graphene-based materials [2]. GO-derived materials include chemically functionalized [3] or reduced [4] graphene oxide (exfoliated from GO) sheets, assembled paper-like forms [5,6], and graphene-based composites [7]. Due to the attached oxygen functional groups, GO is electrically insulating and various reduction methods have been developed to restore its electrical conductivity. Chemical reduction using agents such as hydrazine or dimethylhydrazine [3,4,8,9], hydroquinone [10] and NaBH4 [11,12] have been used to reduce GO or graphene oxide exfoliated from GO. Direct thermal treatment at elevated temperatures provides yet another method to reduce GO while eliminating the use of potentially hazardous reducing agents. ‘Thermal shock’ of GO powders at temperatures up to ~1050 °C has been used [13,14] to obtain exfoliated and conductive graphitic materials. A flash-assisted reduction of films composed of graphene oxide platelets and their polymer composites has been reported [15].

As a convenient and rapid heating source, microwave irradiation has been used to prepare exfoliated graphite (EG) from a wide range of graphite intercalation compounds (GICs) [16-19]. EG has also been prepared by directly heating natural graphite with nitric acid and potassium permanganate in a microwave oven [20]. Recently, microwave assisted chemical reduction of graphene oxide has been realized by heating its suspensions in aqueous or organic media [21]. Herein, we report preparation of exfoliated and reduced GO by treating the GO precursor in a microwave oven for less than 1 min. This facile and efficient process has provided a straightforward method to generate what we will call MEGO (microwave exfoliated graphite oxide) that could be used, among other applications, as a high-performance electrode material in energy storage devices such as ultracapacitors.

GO powders (Fig. 1a) made from the modified Hummers method [22] were treated in a microwave oven (GE, Model...
Upon microwave irradiation, a large volume expansion of the GO powders, accompanied by ‘violent fuming’ was observed. As can be seen from Fig. 1b, the GO powder in the glass vial has dramatically expanded yielding a black and fluffy MEGO powder. Further treatment of the MEGO powders with the microwave induced sparking and even burning.

(Caution: gaseous species could be released from the GO during the microwave heating. A proper amount of GO sample and an appropriately sized container with a pressure release valve are suggested to minimize dangers. Carrying out the experiments in a chemical hood is preferred to avoid possible inhalation of MEGO powder and released gas). It was found that a minimum power of 280 W (40% of full power for the oven used) was necessary for the expansion of GO. The duration required for the expansion varied from 10 to 40 s depending on the microwave power and sample mass. In addition to GO powders, graphene oxide suspensions in organic solvents such as in propylene carbonate could also be reduced by microwave treatment (Fig. S1). The scanning electron microscopy (SEM, FEI Quanta-600) image in Fig. 1c shows that the MEGO obtained by treating GO powders with microwave irradiation has a “worm-like” morphology, similar to the EG obtained by microwave treatment of GICs [16–19]. A high magnification SEM image (inset of Fig. 1c) shows crumpled and curved MEGO sheets that are transparent to the electron beam. Transmission electron microscopy (TEM, JEOL 2010F 200 kV) was used to assess MEGO samples first dispersed in N,N-dimethylformamide (DMF) and then vacuum dried. A typical TEM image, Fig. 1d, shows that the MEGO sheets have many wrinkled and folded regions. The electron diffraction (inset of Fig. 1d) includes multiple hexagons, indicating an overlay of crystalline MEGO sheets in the sample. A high-resolution TEM (HRTEM) image (Fig. S2) from the same sample shows that the edge has a few irregularly stacked layers. From atomic force microscopy (AFM) studies (Fig. S3), both ‘thick’ (several nm) and ‘thin’ (~1 nm) MEGO sheets were observed. A N2 adsorption Brunauer–Emmett–Teller (BET, Micromeritics Tristar 3000) measurement on the as-prepared MEGO powders showed a specific surface area of 463 m2/g, 6–9 times higher than the typical values (50–77 m2/g) obtained from the EG prepared by treatment of GICs with microwave irradiation [18,19].

X-ray photoelectron microscopy (XPS, Kratos AXIS Ultra DLD, Al Kα) was performed on the as-prepared MEGO powders and the C1s spectrum is shown in Fig. 1e, with that of the GO precursor for reference. Clearly, the peaks with binding energies higher than for sp2-bonded carbon (284.5 eV) are smaller for this MEGO prepared by microwave irradiation than for the GO precursor. Since the peaks between 286 and 289 eV are typically assigned to epoxide, hydroxyl, carboxyl groups and so on [23–25], the XPS results suggest that the oxygen-containing groups have been significantly removed by the exposure to the microwave irradiation. A combustion elemental analysis (measured by Atlantic Microlab Inc., Norcross, GA) gave C/O ratios of 0.79 for GO powders and 2.75 for the MEGO made from microwave irradiation, respectively. Note that the
The reduced graphite oxide has a moderately high specific surface area and is electrically conductive. This simple preparation of reduced graphite oxide by rapid microwave irradiation can provide a promising route for the scalable and cost-effective production of processable graphene materials. To demonstrate one potential application, an ultracapacitor cell using this material as electrodes was constructed and tested, and yielded a specific capacitance value of 191 F/g using KOH electrolyte.

In summary, we report the simultaneous exfoliation and reduction of graphite oxide by rapid microwave irradiation. The reduced graphite oxide has a moderately high specific surface area and is electrically conductive. This simple preparation of reduced graphite oxide could provide a promising route for the scalable and cost-effective production of processable graphene materials. To demonstrate one potential application, an ultracapacitor cell using this material as electrodes was constructed and tested, and yielded a specific capacitance value of 191 F/g using KOH electrolyte.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.02.001.

REFERENCES