

(HK) methods. Further studies are needed to control the pore size distributions for specific applications, for example, increasing micropore volume for hydrogen storage.

In summary, using SiC_x fibres derived from the pyrolysis of the hybrid precursor fibres of PCS and pitch, a proper control of the activation conditions can yield the co-axial porous composite fibres with high SSA. The porosity and component of the activated fibres may be adjusted by facile control the activation conditions. This kind of core-shell structured fibres can be regarded as Si-substituted activated carbon fibres, which may be promising functional materials, for example, as potential hydrogen storage materials and catalyst supports. This approach can also be adopted for the preparation of M-substituted activated carbon fibres if M-containing polymers (or blends) are used as the starting material.

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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.2010.01.064.

REFERENCES

- [1] Mandal TK, Gregory DH. Hydrogen storage materials: present scenarios and future directions. *Annu Rep Prog Chem Sect A* 2009;105:21–54.
- [2] Lee J, Kim J, Hyeon T. Recent progress in the synthesis of porous carbon materials. *Adv Mater* 2006;18(16):2073–9.
- [3] Wang HL, Gao QM, Hu J. High hydrogen storage capacity of porous carbons prepared by using activated carbon. *J Am Chem Soc* 2009;131(20):7016–22.
- [4] Gogotsi Y, Welz S, Ersoy DA, McNallan MJ. Conversion of silicon carbide to crystalline diamond-structured carbon at ambient pressure. *Nature (London)* 2001;411(6835):283–7.
- [5] Thomas KM. Adsorption and desorption of hydrogen on metal – organic framework materials for storage applications: comparison with other nanoporous materials. *Dalton Trans* 2009;9:1487–505.
- [6] Chung TCM, Jeong Y, Chen Q, Kleinhammes A, Wu Y. Synthesis of microporous boron-substituted carbon (B/C) materials using polymeric precursors for hydrogen physisorption. *J Am Chem Soc* 2008;130(21):6668–9.
- [7] Mpourmpakis G, Froudakis GE, Lithoxoos GP, Samios J. SiC nanotubes: a novel material for hydrogen storage. *Nano Lett* 2006;6(8):1581–3.
- [8] Macia-Agullo JA, Moore BC, Cazorla-Amoros D, Linares-Solano A. Activation of coal tar pitch carbon fibres: physical activation vs. chemical activation. *Carbon* 2004;42(7):1367–70.
- [9] Chen XQ, Cantrell DR, Kohlhaas K, Stankovich S, Ibers JA, Jaroniec M, et al. Carbide-derived nanoporous carbon and novel core-shell nanowires. *Chem Mater* 2006;18(3):753–8.

Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors

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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.

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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 NaBH_4 [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 $\sim 1050^\circ\text{C}$ 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 graphene 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 JES0736SM1SS) in ambient conditions at 700 W for 1 min. 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

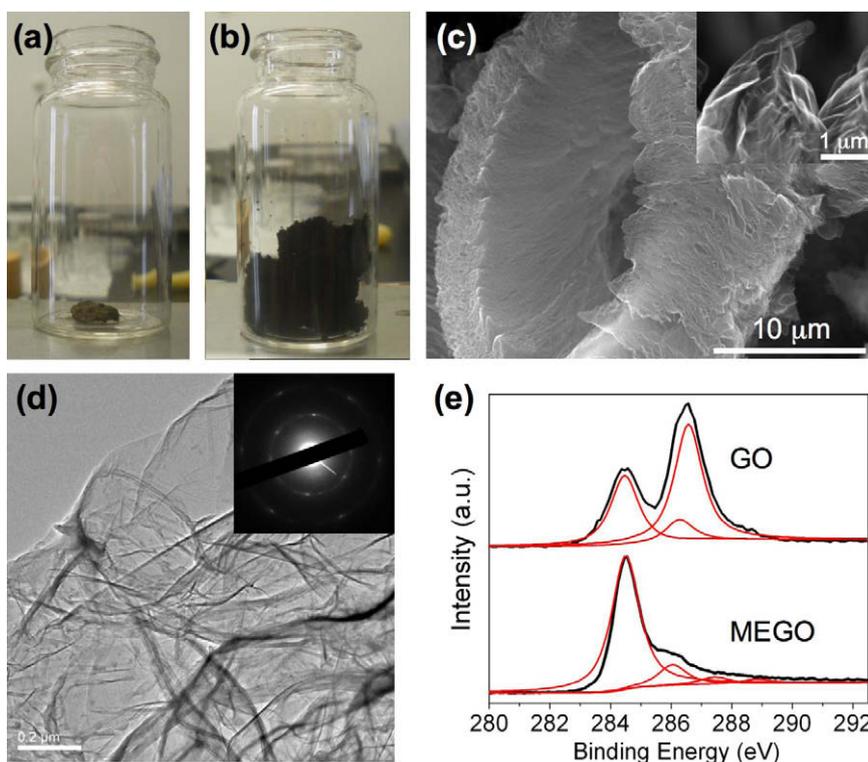


Fig. 1 – Optical photos of GO before (a) and after (b) treatment in a microwave oven for 1 min. (c) Typical SEM image of as-prepared MEGO by microwave irradiation with a high magnification SEM image in the inset showing the crumpled MEGO sheets. (d) Typical TEM image of the MEGO and the corresponding electron diffraction pattern. (e) XPS C1s spectra of GO and MEGO.

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 N_2 adsorption Brunauer–Emmett–Teller (BET, Micromeritics Tristar 3000) measurement on the as-prepared MEGO powders showed a specific surface area of 463 m^2/g , 6–9 times higher than the typical values (50–77 m^2/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 $K\alpha$) 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 sp^2 -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 oxygen content of GO may include the contribution from H_2O in GO (refer to the TGA results, described below). The reduction of GO was further confirmed by the improved conductivity of MEGO. The powder conductivity of the MEGO obtained has been measured to be about 274 S/m (Fig. S4), which is four orders of magnitude higher than that of GO and comparable to the values obtained for powders composed of agglomerated reduced graphene oxide platelets obtained by reduction of their aqueous suspensions with hydrazine followed by drying [4,26].

The structure of the MEGO made from microwave treatment was characterized by X-ray diffraction (XRD, Philips X’Pert PRO, $\lambda = 1.54 \text{ \AA}$), Raman (Witec Alpha 300, 532 nm laser wavelength) and thermogravimetric analysis (TGA, TGA 4000, Perkin Elmer) with the results from the precursor GO powder (the master batch) as a reference. From the XRD spectra (Fig. S5), a layer distance of 0.88 nm was calculated from the sharp peak at about 10° for GO. In contrast, this peak was absent for MEGO and a broad peak centered at around 25° was observed, corresponding to an interlayer spacing of about 0.36 nm. In contrast to Raman spectra of powders composed of agglomerated reduced graphene oxide platelets obtained

by reduction of their aqueous suspensions with hydrazine followed by drying [4], the Raman spectrum of MEGO (Fig. S6) clearly shows a smaller ratio of D band to G band intensities, indicating fewer defects in MEGO after microwave irradiation. From the TGA curves (Fig. S7), three significant weight loss events were observed for GO powders, corresponding to the evaporation of water (below 120 $^\circ C$) and the loss of ‘carbon oxide’ gas species (120–150 $^\circ C$ and 170–250 $^\circ C$) from the decomposition of labile oxygen functional groups [4,27]. In contrast, MEGO powders have less than 10% of weight loss below 300 $^\circ C$, suggesting substantial removal of water and oxygen-containing groups.

Powder composed of agglomerated and reduced graphene oxide platelets obtained by reduction of their aqueous suspensions with hydrazine followed by drying has been used as a promising electrode material for ultracapacitors due to its high surface area and good electrical conductivity [26,28]. The rapid exfoliation and reduction of GO by microwave irradiation described here may provide a facile and scalable method to prepare graphene-based materials for electrical energy storage. Using as-prepared MEGO powders as electrodes in a two-electrode ultracapacitor cell, the cyclic vol-

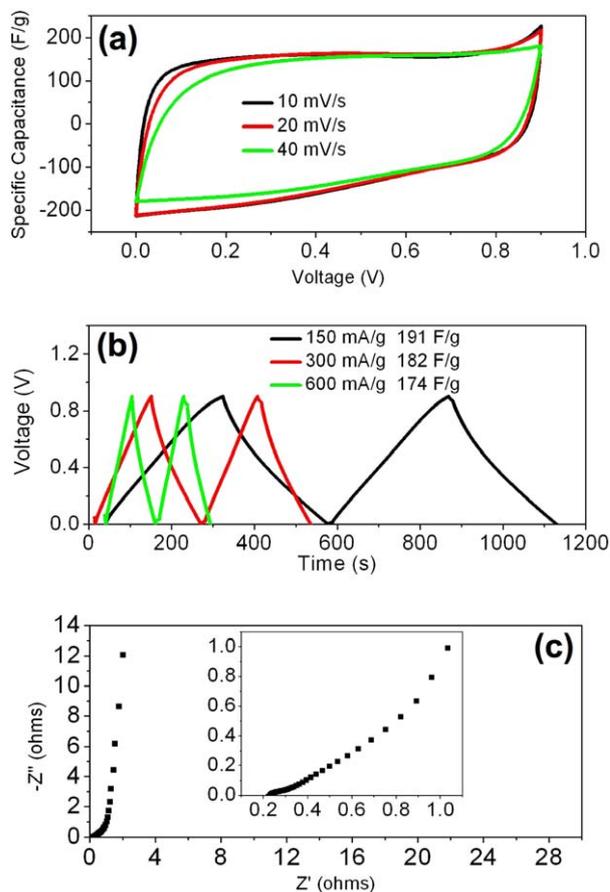


Fig. 2 – Ultracapacitor performance of the MEGO in KOH electrolyte; (a) CV curves. (b) Galvanostatic charge/discharge curves at different constant currents. Specific capacitance values are calculated from the discharge curve for each current. (c) Frequency response analysis with magnified high frequency range in the inset.

tammetry (CV), galvanostatic charge/discharge and frequency response performances of the ultracapacitor were tested in 5 M KOH electrolyte. The typical results are shown in Fig. 2. As seen from Fig. 2a, the CV curves have a rectangular shape, indicating a good capacitive behavior. A specific capacitance of 191 F/g was calculated from the galvanostatic discharge curve at a constant current of 150 mA/g (Fig. 2b). With the increase in the charge/discharge current to 600 mA/g, the specific capacitance decreased to 174 F/g, a reduction of only 9%. A nearly vertical Nyquist plot is observed in Fig. 2c, corresponding to a nearly ideal capacitor response of the cell. The resistance value at the intersection of the Nyquist plots and the real Z' axis was 0.23 Ω (18 kHz), suggesting a low series resistance of the cell. Compared with our previous report on ultracapacitors based on powder composed of agglomerated and reduced graphene oxide platelets obtained by reduction of their aqueous suspensions with hydrazine followed by drying [28], the MEGO obtained here by treating GO in a microwave oven yields an improvement of $\sim 40\%$ in terms of specific capacitance. This result (191 F/g @ 150 mA/g discharge current) is also comparable to the performance of other graphene-based electrodes (~ 205 F/g @ 100 mA/g discharge current) using KOH electrolytes [26].

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

- [1] Brodie BC. *Annales des Chimie et des Physique*. 1806;59:466–72.
- [2] Park S, Ruoff RS. Chemical methods for the production of graphenes. *Nat Nanotechnol* 2009;4(4):217–24.
- [3] Stankovich S, Piner RD, Nguyen ST, Ruoff RS. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. *Carbon* 2006;44(15):3342–7.
- [4] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, et al. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 2007;45(7):1558–65.
- [5] Chen CM, Yang QH, Yang YG, Lv W, Wen YF, Hou PX, et al. Self-assembled free-standing graphite oxide membrane. *Adv Mater* 2009;21(29):3007–11.
- [6] Dikin DA, Stankovich S, Zimney EJ, Piner RD, Dommett GHB, Evmenenko G, et al. Preparation and characterization of graphene oxide paper. *Nature* 2007;448(7152):457–60.
- [7] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, et al. Graphene-based composite materials. *Nature* 2006;442(7100):282–6.
- [8] Tung VC, Allen MJ, Yang Y, Kaner RB. High-throughput solution processing of large-scale graphene. *Nat Nanotechnol* 2009;4(1):25–9.
- [9] Park S, An JH, Jung IW, Piner RD, An SJ, Li XS, et al. Colloidal suspensions of highly reduced graphene oxide in a wide variety of organic solvents. *Nano Lett* 2009;9(4):1593–7.
- [10] Wang GX, Yang J, Park J, Gou XL, Wang B, Liu H, et al. Facile synthesis and characterization of graphene nanosheets. *J Phys Chem C* 2008;112(22):8192–5.
- [11] Si Y, Samulski ET. Synthesis of water soluble graphene. *Nano Lett* 2008;8(6):1679–82.
- [12] Shin H-J, Kim KK, Benayad A, Yoon S-M, Park HK, Jung I-S, et al. Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance. *Adv Funct Mater* 2009;19(12):1987–92.
- [13] McAllister MJ, Li JL, Adamson DH, Schniepp HC, Abdala AA, Liu J, et al. Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem Mater* 2007;19(18):4396–404.
- [14] Schniepp HC, Li JL, McAllister MJ, Sai H, Herrera-Alonso M, Adamson DH, et al. Functionalized single graphene sheets derived from splitting graphite oxide. *J Phys Chem B* 2006;110(17):8535–9.
- [15] Cote LJ, Cruz-Silva R, Huang J. Flash reduction and patterning of graphite oxide and its polymer composite. *J Am Chem Soc* 2009;131(31):11027–32.
- [16] Chung DDL. Exfoliation of graphite. *J Mater Sci* 1987;22(12):4190–8.
- [17] Kwon OY, Choi SW, Park KW, Kwon YB. The preparation of exfoliated graphite by using microwave. *J Ind Eng Chem* 2003;9(6):743–7.
- [18] Tryba B, Morawski AW, Inagaki M. Preparation of exfoliated graphite by microwave irradiation. *Carbon* 2005;43(11):2417–9.
- [19] Falcao EHL, Blair RG, Mack JJ, Viculis LM, Kwon CW, Bendikov M, et al. Microwave exfoliation of a graphite intercalation compound. *Carbon* 2007;45(6):1367–9.
- [20] Wei T, Fan ZJ, Luo GL, Zheng C, Xie DS. A rapid and efficient method to prepare exfoliated graphite by microwave irradiation. *Carbon* 2009;47(1):337–9.
- [21] Hassan HMA, Abdelsayed V, Khder AERS, AbouZeid KM, Turner J, El-Shall MS, et al. Microwave synthesis of graphene sheets supporting metal nanocrystals in aqueous and organic media. *J Mater Chem* 2009;19(23):3832–7.
- [22] Park S, An JH, Piner RD, Jung I, Yang DX, Velamakanni A, et al. Aqueous suspension and characterization of chemically modified graphene sheets. *Chem Mater* 2008;20(21):6592–4.
- [23] Zhou Y, Bao Q, Tang LAL, Zhong Y, Loh KP. Hydrothermal dehydration for the green reduction of exfoliated graphene oxide to graphene and demonstration of tunable optical limiting properties. *Chem Mater* 2009;21(13):2950–6.
- [24] Yang D, Velamakanni A, Bozoklu G, Park S, Stoller M, Piner RD, et al. Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy. *Carbon* 2009;47(1):145–52.
- [25] Fan XB, Peng WC, Li Y, Li XY, Wang SL, Zhang GL, et al. Deoxygenation of exfoliated graphite oxide under alkaline

-
- conditions: a green route to graphene preparation. *Adv Mater* 2008;20(23):4490–3.
- [26] Wang Y, Shi Z, Huang Y, Ma Y, Wang C, Chen M, et al. Supercapacitor devices based on graphene materials. *J Phys Chem C* 2009;113(30):13103–7.
- [27] Jeong HK, Jin MH, So KP, Lim SC, Lee YH. Tailoring the characteristics of graphite oxides by different oxidation times. *J Phys D –Appl Phys* 2009;42(6):065418-1–6.
- [28] Stoller MD, Park SJ, Zhu YW, An JH, Ruoff RS. Graphene-based ultracapacitors. *Nano Lett* 2008;8(10):3498–502.