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## Graphene reduced from magnesiothermic reaction

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5 We, for the first time, employ magnesiothermic reaction to convert microwave-irradiated graphite oxide to pure graphene. The magnesiothermic reaction raises the carbon to oxygen atomic ratio from 22.2 to 165.7 and maintains a high surface area. The new strategy demonstrates an efficient  
10 method for obtaining highly pure graphene materials.

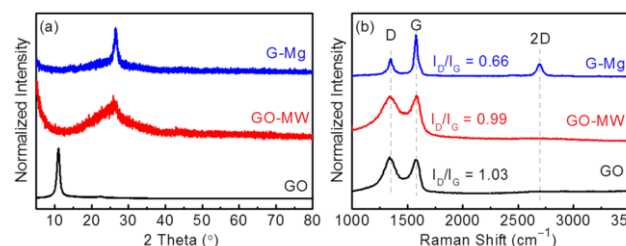
Recently, graphene, the one-atom-thick two-dimensional graphitic carbon system, has attracted tremendous attention due to its extraordinary physical, mechanical and chemical properties.<sup>1</sup> Considerable efforts have been devoted to producing  
15 large-quantity of graphene in recent years to meet the ever-increasing demand.<sup>2</sup> To date, graphene has been formed by physical exfoliation,<sup>3</sup> epitaxial growth,<sup>4</sup> solvothermal synthesis,<sup>5</sup> chemical vapor deposition,<sup>6</sup> or unzipping multiwalled carbon nanotubes.<sup>7</sup> Nevertheless, the low yield and expensive equipment  
20 or raw materials involved in these methods prevent a large-scale production of high-quality graphene. Very recently, intensive efforts have shifted to reducing graphite oxide (GO) for preparing graphene.<sup>8</sup> GO, the product obtained by oxidizing graphite, exhibits a similar layered structure as graphite.<sup>9</sup> With significant  
25 development in past decades, the yield of GO fabrication has been greatly improved, and the cost has been much decreased.<sup>10</sup> In contrast to graphite, GO is heavily decorated by oxygen-containing groups, including hydroxyl, epoxide, carbonyl and carboxyl groups.<sup>11</sup> By employing a reduction procedure, GO can  
30 be converted to graphene.

Rapid thermal annealing has been used to reduce GO to graphene.<sup>12</sup> The sudden temperature increase not only removes most oxygen contained in GO, but also efficiently expands the GO layers due to the prompt release of CO or CO<sub>2</sub> gases.<sup>13</sup>  
35 Recently, Ruoff *et al.* introduced microwave irradiation as a rapid, facile process to exfoliate and reduce GO.<sup>14</sup> The graphene products obtained by thermal annealing or microwave irradiation typically exhibit a modest carbon to oxygen atomic ratio (C/O) of ~ 20. As another strategy, chemical reduction by reagents was  
40 employed to form graphene from GO.<sup>15</sup> Among reagents, hydrazine and metal hydrides have been widely used at room temperature.<sup>16</sup> The as-synthesized graphene by these reducing reagents maintains large lateral sizes of GO but suffers a low C/O ratio of ~ 10. Moreover, the chemical reactions between GO and  
45 reducing reagents occurred in an aqueous suspension, which gives rise to agglomerated hydrophobic graphene sheets. Most recently, a combination of chemical reduction and thermal annealing has led to an almost complete reduction of GO with a

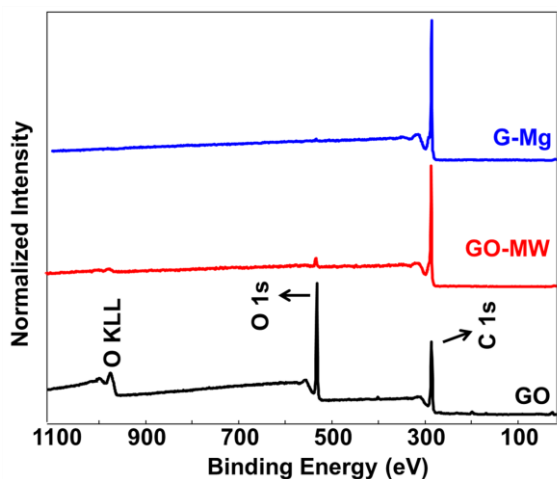
high C/O ratio of 246.<sup>17</sup> However, the toxicity of the reagents  
50 limits their large-scale applications. In short, it is still desirable to develop new reduction strategies to avoid the problems encountered in existing methods.

Magnesium metal is well-known as a strong reluctant that can efficiently convert SiO<sub>2</sub> to Si in magnesiothermic reactions.<sup>18</sup>  
55 Herein, we present a new strategy to convert GO to graphene using microwave irradiation followed by magnesiothermic reduction. Typically, GO film was first synthesized from natural graphite flakes via a modified Hummers method.<sup>19</sup> Microwave irradiation was then used to expand and partially reduce GO film  
60 to give an intermediate product that is referred to as GO-MW. Later, the GO-MW was heated with Mg powder in a tube furnace under Ar at 650 °C for 2 hrs. The mixture was stirred in an HCl aqueous solution to give a graphene product that is denoted as G-Mg. This two-step reduction renders the obtained G-Mg an  
65 ultrahigh C/O ratio of 165.7 with a surface area of 249.9 m<sup>2</sup> g<sup>-1</sup>.

The structural information of the as-prepared products was first investigated by X-ray diffraction (XRD). As shown in Fig. 1a, in the XRD pattern of GO, a well-resolved peak around 11.0° is attributed to an interlayer distance of 8.00 Å in GO crystals.<sup>17</sup>  
70 During the microwave irradiation, significant volume expansion of the GO sample and ‘violent fuming’ were observed, which had been reported before (see ref. 14a). In sharp contrast to GO, the XRD pattern of GO-MW exhibits a weak peak around 25.6° that corresponds to a d-spacing of 3.46 Å (Fig. 1a). With further  
75 reduction by Mg vapor, the broad peak of GO-MW turned sharper and slightly shifted to 26.3° (Fig. 1a). The layer distance of 3.37 Å was calculated for G-Mg, which is very close to the d-spacing in graphite (3.36 Å). The sharp decrease of layer spacing from GO to G-Mg should be attributed to the further removal of  
80 oxygen-containing groups by the magnesiothermic reduction. Fig. 1b compares the Raman spectra for GO, GO-MW, and G-Mg,



**Fig. 1** (a) XRD patterns and (b) Raman spectra of GO (down black), GO-MW (middle red) and G-Mg (up blue).



**Fig. 2** XPS spectra of GO (down black), GO-MW (middle red) and G-Mg (up blue).

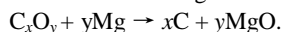
Sample Name	C (at%)	O (at%)	C/O ratio
GO	66.2	31.8	2.1
GO-MW	95.6	4.3	22.2
G-Mg	99.4	0.6	165.7

**Table 1.** Chemical compositions and C/O ratios of GO, GO-MW and G-Mg analysed by XPS.

presenting carbon features with peaks at  $\sim 1350\text{ cm}^{-1}$  (D-band) for  $\text{sp}^3$  configuration and  $\sim 1580\text{ cm}^{-1}$  (G-band) for  $\text{sp}^2$  graphitic configuration. The D/G band intensity ratio ( $I_D/I_G$ ) decreases from 1.03 for GO to 0.99 for GO-MW. Importantly, the  $I_D/I_G$  dramatically decreases to 0.66 after the magnesiothermic reaction, suggesting a much higher degree of graphitization in G-Mg. Moreover, a new peak at  $\sim 2700\text{ cm}^{-1}$  (2D-band) appeared in the Raman spectrum of G-Mg, providing an unequivocal evidence that the graphene sheets were restored upon magnesiothermic reduction.<sup>17</sup>

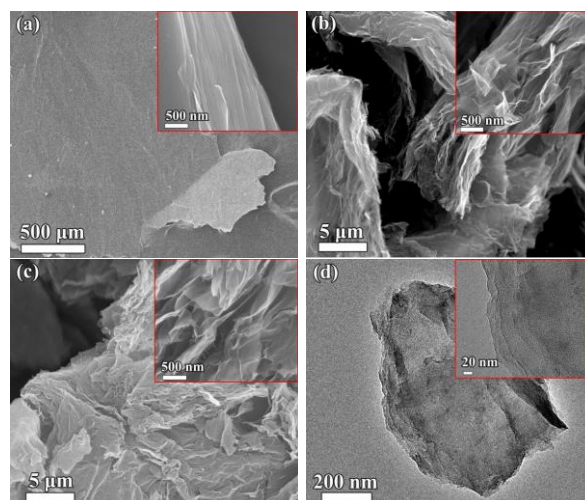
The chemical compositions of samples were examined by X-ray photoelectron spectroscopy (XPS). Fig. 2 compares the survey XPS spectra of GO, GO-MW and G-Mg, demonstrating a clear decrease of O 1s peak from GO to GO-MW and further to G-Mg. As summarized in Table 1, C/O ratios for GO, GO-MW and G-Mg are 2.1, 22.2, and 165.7, respectively.

With the above characterizations, we demonstrate that a more complete reduction of GO can be achieved by a combination of a microwave irradiation and a magnesiothermic reaction. This is the first time that GO is reduced to graphene by Mg vapor. We postulate the following reaction:

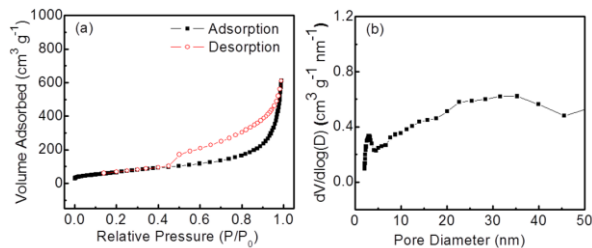


By forming very stable MgO as the product, this magnesiothermic reaction may release intense heat at the oxygen-containing defective sites, which may help restoration of the graphitic structures. This may explain the Raman results.

Fig. 3 shows the field-emission scanning electron microscopy (FESEM) images of GO, GO-MW and G-Mg. It can be seen that the GO sample exhibits a smooth surface morphology and large particle size (Fig. 3a). When zoomed in, it is evident that the GO crystal was assembled by a stacking of sheets (inset of Fig. 3a).



**Fig. 3** Low-magnification FESEM images of GO (a), GO-MW (b), and G-Mg (c). Insets are corresponding high-magnification FESEM images. (d) Low and high-magnification (inset) TEM images of G-Mg.



**Fig. 4** (a) Nitrogen adsorption/desorption isotherm of G-Mg and (b) the corresponding pore size distribution.

After the microwave irradiation, the big pieces of GO was distorted, and the closely stacked sheets became fluffier in GO-MW (Fig. 3b), resulting from the violent reaction and the release of  $\text{CO}_2$  or  $\text{CO}$ .<sup>14a</sup> With further reduction by Mg vapor, the porous structure of GO-MW was well-maintained in G-Mg. Transmission electron microscopy (TEM) image provides further information from the microstructure and morphology of G-Mg. Fig. 3d displays a typical bright-field TEM image of an individual graphene piece of  $\sim 400\text{ nm}$  in diameter. High-magnification TEM observation indicates G-Mg was assembled by 4-5 layers graphene sheets (Fig. 3d inset). The G-Mg was further characterized by nitrogen adsorption/desorption isotherms at 77 K. Fig. 4a shows a Type IV isotherm, indicative of a mesoporous structure in G-Mg. The Brunauer-Emmett-Teller (BET) surface area is calculated to  $249.9\text{ m}^2\text{ g}^{-1}$ , which is lower than that of GO-MW ( $380.6\text{ m}^2\text{ g}^{-1}$ ) (Fig. S1, see ESI†). This may be attributed to fewer defects resulted from the complete reduction by the magnesiothermic reaction. Moreover, the pore size distribution of G-Mg is shown in Fig. 4b. It can be seen that the sample possesses nanopores sized of  $\sim 3.0\text{ nm}$  and other pores larger than 10 nm. The mesoporous structure of G-Mg with a high surface area may attract potential applications, including batteries, capacitors and sensors.<sup>20</sup>

## 55 Conclusions

In summary, we present here a new fabrication strategy that employing a combination of a microwave irradiation and a magnesiothermic reaction to prepare graphene from GO. The two-step reduction gives the as-prepared graphene an ultra-high C/O ratio of 165.7. This is comparable to the highest reported C/O ratio of 246 (ref. 16a). Magnesiothermic reactions can be a promising reduction method for production of graphene from GO. The present results may open a new pathway for fabrication of graphene products from GO.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and N<sub>2</sub> adsorption/desorption isotherm of GO-MW. See DOI: 10.1039/b000000x/

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- 1 (a) S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature* 2006, **442**, 282; (b) D Li, M. B. Mueller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. nanotechnol.*, 2008, **3**, 101 ; (c) M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, 2009, **110**, 132.
- 2 (a) X. Huang, X. Qi, F. Boey and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 666; (b) N. O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang and X. Duan, *Adv. Mater.*, 2012, **24**, 5782.
- 3 (a) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666; (b) Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. McGovern, B. Holland, M. Byrne and Y. K. Gun'Ko, *Nat. Nanotechnol.*, 2008, **3**, 563.
- 4 (a) P. W. Sutter, J.-I. Flege and E. A. Sutter, *Nat. Mater.*, 2008, **7**, 406; (b) C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First and W. A. de Heer, *J. Phys. Chem. B*, 2004, **108**, 19912.
- 5 M. Choucair, P. Thordarson and J. A. Stride, *Nat. Nanotechnol.*, 2008, **4**, 30.
- 6 (a) K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi and B. H. Hong, *Nature*, 2009, **457**, 706; (b) Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei and H.-M. Cheng, *Nat. Mater.*, 2011, **10**, 424.
- 7 L. Jiao, L. Zhang, X. Wang, G. Diankov and H. Dai, *Nature*, 2009, **458**, 877.
- 8 (a) S. Pei and H.-M. Cheng, *Carbon*, 2012, **50**, 3210; (b) D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *Acs Nano*, 2010, **4**, 4806.
- 9 (a) N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771; (b) A. Lerf, H. He, M. Forster and J. Klinowski, *J. Phys. Chem. C*, 1998, **102**, 4477.
- 10 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228.
- 65 11 A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla and V. B. Shenoy, *Nat. Chem.*, 2010, **2**, 581.
- 12 H. C. Schniepp, J.-L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville and I. A. Aksay, *J. Phys. Chem. B*, 2006, **110**, 8535.
- 70 13 K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay and R. Car, *Nano Lett.*, 2007, **8**, 36.
- 14 (a) Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach and R. S. Ruoff, *Science*, 2011, **332**, 1537; (b) H. M. Hassan, V. Abdelsayed, S. K. Abd El Rahman, K. M. AbouZeid, J. Ternner, M. S. El-Shall, S. I. Al-Resayes and A. A. El-Azhary, *J. Mater. Chem.*, 2009, **19**, 3832.
- 15 (a) S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558; (b) W. Chen, L. Yan and P. Bangal, *J. Phys. Chem. C*, 2010, **114**, 19885. (c) W. Guo, Y. Yin, S. Xin, Y. Guo and L. Wan, *Energy Environ. Sci.*, 2012, **5**, 5221.
- 16 (a) Y. Sun, X. Hu, W. Luo and Y. Huang, *ACS Nano*, 2011, **5**, 7100; (b) Y. Sun, X. Hu, W. Luo and Y. Huang, *J. Mater. Chem.*, 2011, **21**, 17229; (c) Y. Liang, D. Wu, X. Feng and K. Müllen, *Adv. Mater.*, 2009, **21**, 1679.
- 85 17 W. Gao, L. B. Alemany, L. Ci and P. M. Ajayan, *Nat. Chem.*, 2009, **1**, 403.
- 18 (a) Z. Bao, M. R. Weatherspoon, S. Shian, Y. Cai, P. D. Graham, S. M. Allan, G. Ahmad, M. B. Dickerson, B. C. Church and Z. Kang, *Nature*, 2007, **446**, 172; (b) W. Luo, X. Wang, C. Meyers, N. Wannemacher, W. Sirisaksoontorn, M. M. Lerner and X. Ji, *Sci. Rep.*, 2013, **3**, 2222.
- 90 19 (a) W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339; (b) S. Zhu, J. Zhang, C. Qiao, S. Tang, Y. Li, W. Yuan, B. Li, L. Tian, F. Liu, R. Hu, H. Gao, H. Wei, H. Zhang, H. Sun and B. Yang, *Chem. Commun.*, 2011, **47**, 6858.
- 95 20 (a) H. Wang, L.-F. Cui, Y. Yang, H. Sanchez Casalongue, J. T. Robinson, Y. Liang, Y. Cui and H. Dai, *J. Am. Chem. Soc.*, 2010, **132**, 13978; (b) S. Vivekchand, C. S. Rout, K. Subrahmanyam, A. Govindaraj and C. Rao, *J. Chem. Sci.*, 2008, **120**, 9; (c) Z. Cheng, Q. Li, Z. Li, Q. Zhou and Y. Fang, *Nano Lett.*, 2010, **10**, 1864.
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