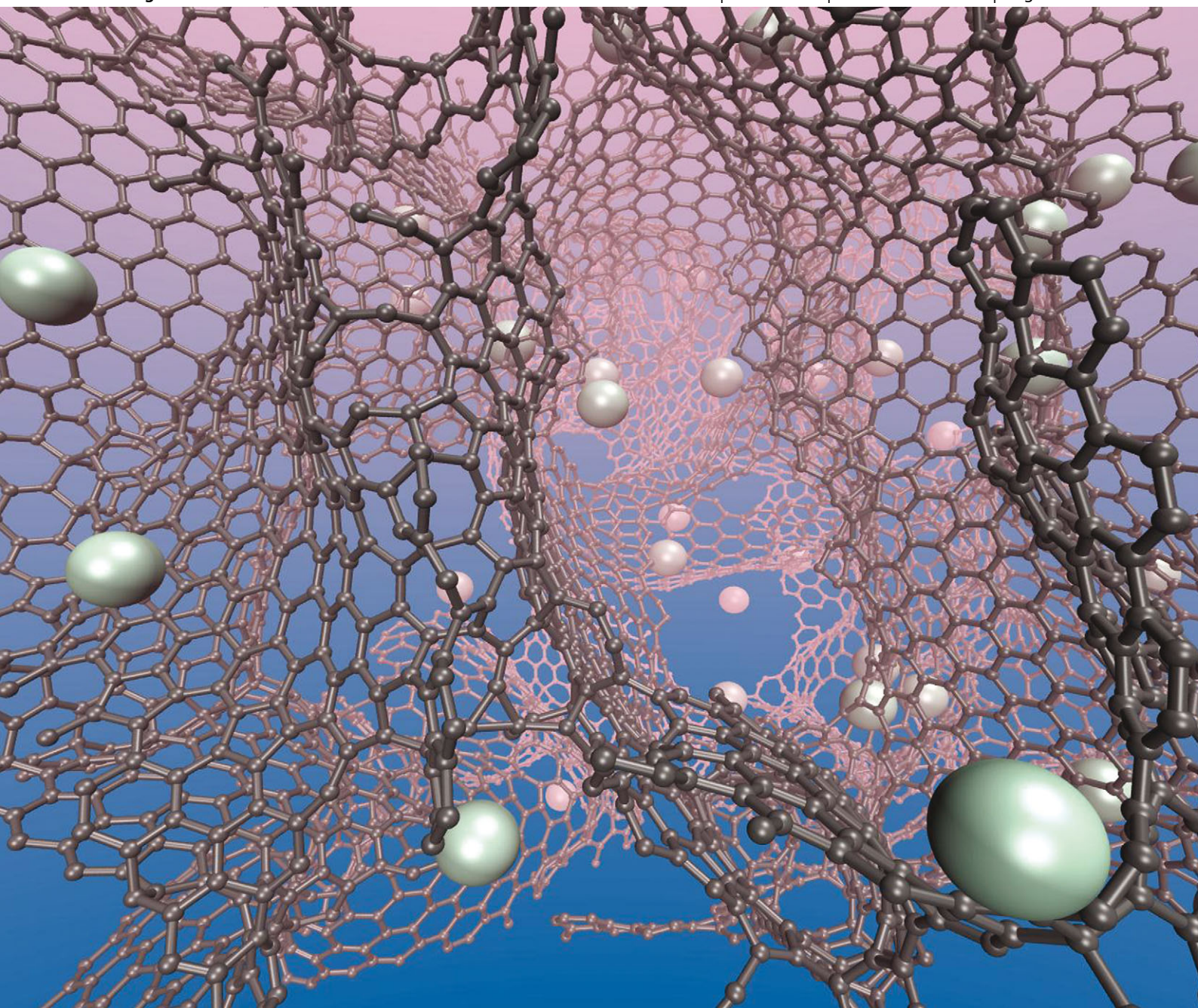


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Production of graphene by reduction using a magnesiothermic reaction



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Production of graphene by reduction using a magnesiothermic reaction†

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We have, for the first time, employed a magnesiothermic reaction to convert microwave-irradiated graphite oxide to pure graphene. The magnesiothermic reaction increases the carbon to oxygen atomic ratio from 22.2 to 165.7 and maintains a high surface area. The new strategy demonstrates an efficient 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.¹ Considerable efforts have been devoted to producing a large-quantity of graphene in recent years to meet the ever-increasing demand.² To date, graphene has been formed by physical exfoliation,³ epitaxial growth,⁴ solvothermal synthesis,⁵ chemical vapor deposition,⁶ or unzipping multiwalled carbon nanotubes.⁷ Nevertheless, the low yield and expensive equipment 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.⁸ GO, the product obtained by oxidizing graphite, exhibits a similar layered structure to graphite.⁹ With significant development in the past decades, the yield of GO fabrication has greatly improved, and the cost has been much decreased.¹⁰ In contrast to graphite, GO is heavily decorated by oxygen-containing groups, including hydroxyl, epoxide, carbonyl and carboxyl groups.¹¹ By employing a reduction procedure, GO can be converted to graphene.

Rapid thermal annealing has been used to reduce GO to graphene.¹² The sudden temperature increase not only removes most of the oxygen contained in GO, but also efficiently expands the GO layers due to the prompt release of CO or CO₂ gases.¹³ Recently, Ruoff *et al.* introduced microwave irradiation as a rapid, facile process to exfoliate and reduce GO.¹⁴ 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 employed to form graphene from GO.¹⁵ Among the reagents, hydrazine and metal hydrides have been widely used at room temperature.¹⁶ The as-synthesized graphene prepared using 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 reducing reagents occur 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 246.¹⁷ However, the toxicity of the reagents 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 reductant that can efficiently convert SiO₂ to Si in magnesiothermic reactions.¹⁸ Herein, we present a new strategy to convert GO to graphene using microwave irradiation followed by magnesiothermic reduction. Typically, the GO film was first synthesized from natural graphite flakes using a modified Hummers method.¹⁹ Microwave irradiation was then used to expand and partially reduce GO film 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 hours. 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 ultrahigh C/O ratio of 165.7 with a surface area of 249.9 m² g⁻¹.

The structural information of the as-prepared products was first investigated using X-ray diffraction (XRD). As shown in Fig. 1a, in the XRD pattern of GO, a well-resolved peak at around 11.0° is attributed to an interlayer distance of 8.00 Å in GO crystals.¹⁷ 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 at around 25.6° that corresponds to a *d*-spacing of 3.46 Å (Fig. 1a). With further reduction by Mg vapor, the broad peak of GO-MW turned sharper

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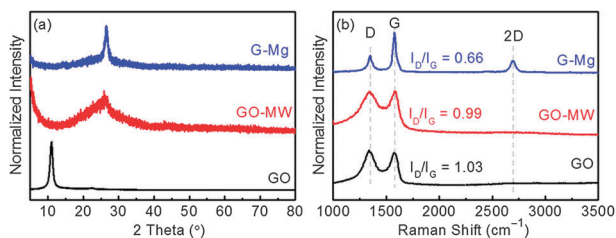


Fig. 1 (a) XRD patterns and (b) Raman spectra of GO (down black), GO-MW (middle red) and G-Mg (up blue).

and slightly shifted to 26.3° (Fig. 1a). The layer distance of 3.37 \AA was calculated for G-Mg, which is very close to the d -spacing in graphite (3.36 \AA). The sharp decrease of layer spacing from GO to G-Mg should be attributed to the further removal of oxygen-containing groups by the magnesiothermic reduction. Fig. 1b compares the Raman spectra for GO, GO-MW, and G-Mg, presenting carbon features with peaks at $\sim 1350 \text{ cm}^{-1}$ (D-band) for sp^3 configuration and $\sim 1580 \text{ cm}^{-1}$ (G-band) for 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 unequivocal evidence that the graphene sheets were restored upon magnesiothermic reduction.¹⁷

The chemical compositions of samples were examined using 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 characterization, we demonstrate that a more complete reduction of GO can be achieved by a combination of a microwave irradiation and a magnesiothermic reaction.

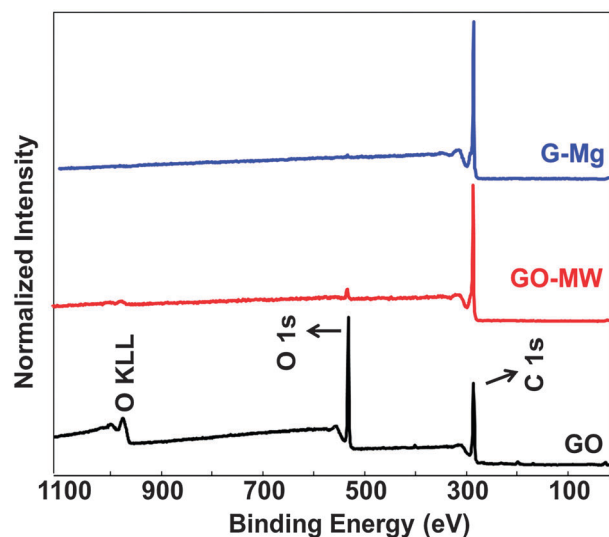
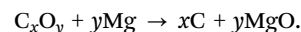


Fig. 2 XPS spectra of GO (down black), GO-MW (middle red) and G-Mg (up blue).

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

| 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 |

This is the first time that GO is reduced to graphene using 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). After the microwave irradiation, the big pieces of GO were distorted, and the closely stacked sheets became fluffy in GO-MW (Fig. 3b), resulting from the violent reaction and the release of CO_2 or CO .^{14a} With further reduction by Mg vapor, the porous structure of GO-MW was well-maintained in G-Mg. Transmission electron microscopy (TEM) images provide 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 $\sim 400 \text{ nm}$ diameter. High-magnification TEM observation indicates G-Mg was assembled using 4–5 layer 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 be

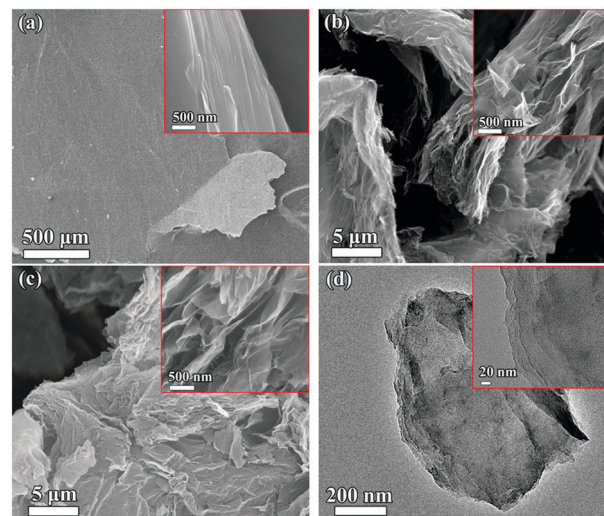


Fig. 3 Low-magnification FESEM images of GO (a), GO-MW (b), and G-Mg (c). Insets are corresponding high-magnification FESEM images. (d) Low and high-magnification (inset) TEM images of G-Mg.

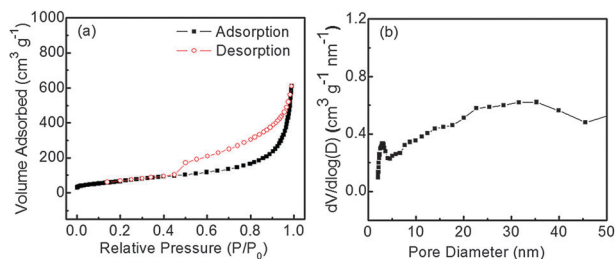


Fig. 4 (a) Nitrogen adsorption-desorption isotherm of G-Mg and (b) the corresponding pore size distribution.

249.9 m² g⁻¹, which is lower than that of GO-MW (380.6 m² g⁻¹) (Fig. S1, see ESI†). This may be attributed to fewer defects resulting 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 a nanopore size of ~3.0 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.²⁰

In summary, we present here a new fabrication strategy that employs 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. 17). Magnesiothermic reactions can be a promising reduction method for the production of graphene from GO. The present results may open a new pathway for the fabrication of graphene products from GO.

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