Conversion of carbon dioxide to few-layer graphene

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Burning magnesium metal in dry ice resulted in few-layer nanosheets of graphene in high yields. These carbon nanomaterials were characterized by Raman spectroscopy, energy-dispersive X-ray analysis, X-ray powder diffraction and transmission electron microscopy. This work provides an innovative route for producing one of the most promising carbon nanostructures by capturing carbon dioxide that is popularly known as the greenhouse gas.

Within the last few years, graphene has received special attention from the scientific world due to its unique mechanical and electrical properties.1 The widespread application of graphene is not just limited to the fields of sensors,2 nanoelectronics,3 composites,4 hydrogen storage,5 lithium-ion batteries,6 but also shown promise in medicine as antibacterial materials.7 The diversity of the technological applications of graphene materials drives the search for facile routes to produce graphenes in high yields. Recent research for synthesis of such materials involved either chemical or electrochemical reduction of exfoliated graphite oxide.8 Most of these techniques require the use of strong oxidizing agents, e.g., H2SO4/KMnO4, while some of them claimed to have utilized greener chemicals. A recent report described the production of graphene via reduction of CO using Al2S3.9 Nonetheless, a well-controlled large scale production protocol for graphene structures is still in great demand and thus we embarked on research involving graphene synthesis with a particular emphasis on green chemistry. Consequently, our work described here provides a new methodology that can be potentially scaled up in directly capturing CO2 to produce few-layer graphene as useful solid carbon materials.

Thus, burning magnesium metal in a CO2 environment produces carbon materials as shown in eqn. (1). Although the metal–CO2 propulsion system for Mars missions has been explored,10 the conversion of CO2 into solid nanostructured carbon materials has not been reported. Therefore, our approach involving combustion of magnesium metal in carbon dioxide to form few-layer graphene is unprecedented and provides further incentives for exploration of a number of environmentally friendly ways for capturing carbon dioxide.11

$$2\text{Mg}(s) + \text{CO}_2(g) \rightarrow 2\text{MgO}(s) + \text{C}(s) \quad (1)$$

In a typical experiment, 3 g of Mg ribbon was ignited inside a dry ice bowl, covered up by another dry ice slab. After the combustion of Mg in CO2 was completed, the black products were collected and transferred to a beaker containing 100 ml of 1 M HCl. The product was stirred in the acid solution at room temperature overnight to remove the MgO formed and any remaining Mg metal. Both Mg and MgO react with hydrochloric acid to form MgCl2 which is soluble in water and thus it can easily be removed to get pure carbon material as the product. The mixture was then filtered, washed with deionized water several times until the filtrate turned out to be of neutral pH. Finally, the isolated solid carbon product was dried under high vacuum overnight at 100 °C and the yield was 680 mg (92%). This product was characterized by transmission electron microscope (TEM, high-resolution TEM was done in a Philip CM-30 with an acceleration voltage of 250 kV and low-resolution TEM was performed in a Hitachi H-600 transmission electron microscope at an acceleration voltage of 75 kV), Raman spectroscopy (Renishaw system 2000 microfocus Raman spectrometer), Energy-dispersive X-ray analysis (EDX, studies done using field emission scanning electron microscope Hitachi S-4700-II) and X-ray powder diffraction (XRD, Rigaku MiniFlex, Cu, 30 kV, 15 mA X-ray) techniques.

Raman spectroscopy is considered to be an effective tool for characterization of mono- or few-layer graphenes, and several theoretical and experimental studies have been reported recently.12–16 Raman spectrum of the nanostructured carbon species obtained during our experiments is depicted in Fig. 1. The two major components of the spectrum consisted of peaks at 1570 cm−1 and 2645 cm−1, which are commonly designated as the G-band and the G’-band or 2D-band respectively. In a recent study on the structure of graphene, Ferrari et al. demonstrated clearly that the number of layers in a graphene structure can be revealed from the Raman peaks, and thus, graphite can be easily distinguished from graphenes.12,14 The position and shape of the G’ band in the Raman spectrum identify the presence and the number of layers of the graphene structures respectively. With a 633 nm Raman, the G’ band peak of graphene was found at about 2645 cm−1,12 which closely matches our finding as shown in Fig. 1. In the case of...
monolayer graphene, the $G'$ band is a sharp single peak; while in the case of bi- or multi-layer graphenes, there are splittings generated either from the phonon branches or the electronic bands. The $G'$ band shifted more towards 2700 cm$^{-1}$ in the case of graphenes with more than 7–10 layers, which is indistinguishable from graphite.$^{12}$ From the observed spectrum, splitting of the 2D band (inset of Fig. 1) and its position provided a strong evidence in favor of few-layer graphene as the major product. Moreover, the peak intensities of the G-band and the $G'$-band are also related to the number of layers of the graphene structures. Gupta et al. compared the peak intensities of different layer structures of graphene and found that with the number of layers of five or more the G-band grows higher with respect to the intensity than that of the $G'$-band,$^{13}$ which again was a confirmation of our product to be few-layer graphene. The other band found in the spectrum is the D-band at 1325 cm$^{-1}$, which is of significantly lower intensity and represents some lattice defects present in the structure.$^{17}$

Fig. 2a and b show TEM images of the few-layer graphene, prepared by our new method described above, in which graphene sheets with varying lengths between 50 nm and 300 nm have been found. While large crystalline graphene structures are evidently observed in Fig. 2c; high-resolution TEM (Fig. 2d) clearly exhibits the signature image of the few-layer graphene with the number of layers ranging from 3–7. The measured lattice space of this material is about 3.5 Å, which is in good agreement with the thickness of a mono-layer graphene (3.4 Å). The inset image in Fig. 2d, corresponding to the diffraction pattern of few-layer graphene, is indicative of the crystallization.

An X-ray diffraction pattern of our sample is described in Fig. 3. The prominent 002 peak at 26.3 degree is observed along with the 101 peak at 44.6 degree. The other characteristic peak for graphene structure is 100 peak located at 2$\theta$ of 43.2 degree, which is overlapped with one of MgO peaks. While we examined the purity of the product via EDX spectroscopy, the absence of any impurity other than a trace amount of Mg and O in the product was confirmed (Fig. 4). The trace amount of Mg (2.38 atomic weight percent) and O (7.30 atomic weight percent) is mainly due to the trapped MgO and some absorbed O$_2$. Therefore, the contribution of MgO to the peak at 2$\theta$ of 43.2 degree is small, and this peak can be readily assigned to 100 diffraction of graphenes.

Although the exact mechanism of the formation of graphene is still under investigation, the high temperature generated during the burning of magnesium metal undoubtedly plays a crucial role. It is possible that the combustion of the solid magnesium in gaseous CO$_2$ favors the rapid flee of the solid product from the reaction center. As such, the retention time of the sp$^2$ carbon atoms in the reaction core is not long enough to form multi-layer graphene (graphite). Instead, only few-layer graphene is kinetically favored. Experiments on the effect of catalysts on formation of monolayer graphenes with higher yields using similar techniques are presently underway in our laboratories.

In conclusion, the current methodology produces few-layer graphene captured directly from CO$_2$ by burning Mg in it. The structure of few-layer graphene product was confirmed by TEM, Raman spectroscopy and XRD and they are all consistent with the
data available in the literature. The synthetic process is cost effective and can be used to produce few-layer graphene in large quantities. Furthermore, the use of non-toxic chemicals and recyclable materials during the synthesis constitutes this work as part of green chemistry.

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Notes and references


Fig. 4 EDX spectrum of the graphene nanosheets, C 90.32 (atm wt%); Mg 2.38 (atm wt%); O 7.30 (atm wt%).