

A 'FLASH' in the synthesis of graphene

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Since the first report on the isolation of graphene, a single atomic plane of graphite, by Novoselov *et al.*¹ of Manchester University, United Kingdom in 2004 by a simple peeling of the top layer of a highly oriented pyrolytic graphite with a Scotch tape, graphene has become a hot area of research in physics, chemistry and materials science. Today, graphene is the most attractive nanomaterial not only because it is the thinnest known material in the universe and the strongest ever measured², but also due to its excellent electrical, thermal and optical properties, high-specific surface area, and ease of chemical functionalization which actually helps in tuning its properties^{3,4}. Graphene, the 2D nanomaterial, is considered to be the mother of all graphitic materials as it can be wrapped up into 0D fullerene, rolled into 1D carbon nanotube or stacked into 3D graphite⁵. The 'Scotch tape' technique, also known as micromechanical exfoliation method, yields very small amount of graphene. In view of the excellent properties and projected applications of graphene, several innovative methods^{3,4,6} for scaling up its production have been demonstrated among which, the reduction of graphite oxide (GO) appears to be simple and convenient. The production of GO involves oxidation of graphite in the presence of strong acids and oxidants³. GO is water dispersible due to the presence of oxygen-containing groups including carboxylic acid and hydroxyl moieties; it readily exfoliates upon sonication in water. It is also interesting to note that GO can be directly dispersed in several polar solvents like ethylene glycol, dimethylformamide, *N*-methylpyrrolidone and tetrahydrofuran. The dispersion of GO on chemical reduction using either hydrazine or dimethylhydrazine or hydroquinone or sodium borohydride yields chemically modified graphene in which a large portion of oxygen-containing functional groups is removed during reduction³. Thermal treatment of GO in inert or reducing atmosphere provides another route for graphene production⁴. However, it is desirable to search for feasible green methods that do not rely on the use of

chemicals or high temperature. In this context, the recent report by Cote *et al.*⁷ of the camera flash reduction of GO to produce graphene deserves attention.

A surge to study the influence of a consumer camera flash on nanostructured materials has been witnessed in recent years. A camera flashlight emulates sunlight minus the ultraviolet light. Ajayan *et al.*⁸ established that by exposure to a camera flash, single-walled carbon nanotubes (SWCNTs) can be ignited and reconstructed in air. This study motivated Guo *et al.*⁹ to generate hydrogen by splitting of water confined in SWCNT with visible light from a camera flash. Si nanowires also ignited in air to yield silicon oxide nanotubes and exhibited a large photoacoustic effect when exposed to a conventional photographic flash¹⁰. These studies on the effect of a camera flash on nanomaterials reveal that they undergo oxidation. Also, Huang and Kaner¹¹ have demonstrated that under camera flash irradiation, polyaniline nanofibres 'melt' to form a smooth and continuous film from an originally random network of nanofibres.

Cote *et al.*⁷ have demonstrated that a photographic close camera flash can trigger instantaneously the reduction of GO by photothermal heating. They used

both free standing GO films (1 μm thick) and also GO/polystyrene composite films. The typical Xenon flash energies applied to the samples were around 0.1–2 J/cm². When the brown and transparent film of GO was exposed to a camera flash (within 1 cm), it became black and opaque with a loud pop sound (video clip provided in ref. 7), which was attributed to the expansion of air near the surface (Figure 1a and b). The GO film after flash reduction (r-GO) expanded tens of times due to rapid degassing. The spectacular change of colour of the brown GO film into black (Figure 1a and b), the marked reduction of water contact angle for GO from 45° to 78° (inset, Figure 1), and the conversion of the insulating GO film to a conducting r-GO film vouch for the reduction of hydrophilic GO to hydrophobic graphene. The authors have also made use of other techniques like thermogravimetry, photoacoustic and infrared spectroscopy and XRD to provide unambiguous evidence for the flash reduction of GO to graphene. By studying the absorption spectrum of GO in the visible region and also from the differential scanning calorimetry investigation, it was concluded that the energy provided by the flashlight at a close distance (1 J/sq. cm at <2 mm) was sufficient to

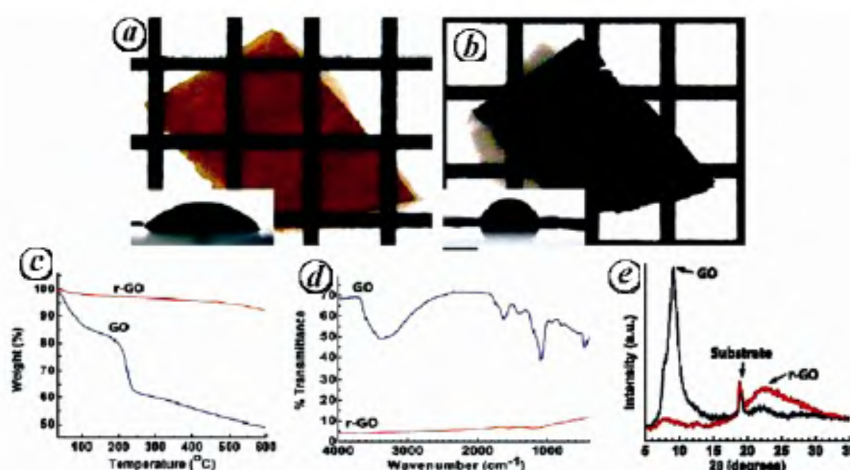


Figure 1. A GO paper (a) can be instantaneously reduced to r-GO (b) upon exposure to a photographic camera flash. The grids in the background are 1 mm \times 1 mm. The flash reduction of GO to r-GO was evident by the dramatic changes in colour (a, b), water contact angle (insets), (c) TGA (d) FTIR and (e) XRD pattern. Reprinted with permission from Cote *et al.*⁷. Copyright (2009) from American Chemical Society.

provide nine times the energy needed to heat the 1 μm thick GO film over 100°C for inducing the reduction.

Thermogravimetric analysis (TGA) of GO in nitrogen atmosphere exhibited 15% mass loss at 100°C due to water removal and another mass loss of about 25% at 220°C attributed to the loss of oxygen containing groups (Figure 1c). In contrast, the TGA curve of r-GO (Figure 1c) in nitrogen gas did not show any significant reduction in mass.

The absence of vibrational bands corresponding to carboxylic acid (1630–1730 cm^{-1}), phenyl hydroxyl (around 1100 cm^{-1}) and epoxide group (around 930 cm^{-1}) in the FT-IR spectrum of r-GO (Figure 1d) also confirmed the formation of graphene. The XRD spectrum of GO film (Figure 1e) showed one sharp peak at $2\theta = 9.12^\circ$ corresponding to 0.97 nm spacing between the stacked sheets but this peak was not observed in the XRD spectrum of r-GO and instead a new broad peak at 22.5° emerged which was at a slightly lower angle than graphite suggesting that the r-GO sheets were

exfoliated. Elemental analysis revealed C/O atomic ratio increased from 1.15 for GO to 4.23 for r-GO.

The prominent advantage of the flash reduction method of GO is that it readily allows photopatterning and thereby appears to be very promising in the fabrication of graphene-based functional devices. The authors demonstrated that unlike conventional photolithography, the flash reduction could be used to perform both patterning and etching in one experimental set-up. When the flash patterned film was exposed to a higher power flash, the exposed area was found to be etched because of rapid degassing and air expansion. A blend of GO and polystyrene was flash patterned for chemical vapour sensing. The presence of polystyrene helped in containing the agglomeration of graphene in solution and also acted as a heat sink during flash irradiation thereby preventing overexposure during patterning. Figure 2a and b show the SEM images of a blend of GO and polystyrene before and after flash irradiation respectively. After flashing, polystyrene was fused with r-GO to form a homogeneous composite. The heat generated during flash irradiation actually helped to induce welding between r-GO and polystyrene. The inset, a low magnification image of the blend before and after flash reduction clearly showed a brightness contrast due to the difference in the electrical conductivity between GO and r-GO. Figure 2c shows the TEM image of polystyrene particles deliberately sandwiched between two GO thin films prepared by layer-by-layer deposition. The softening of the polymer particles by the heat generated during flash irradiation can be observed in Figure 2d. In the absence of GO, flash irradiation had no effect on the colloids (Figure 2e and f), the reason being that polystyrene was transparent in the visible range and did not have a strong photo-thermal effect.

An interdigitated array of r-GO/polystyrene electrode fabricated on a flexible, nylon wafer by the flash patterning technique was used for the deposition of conducting polyaniline nanofibres which acted as a gas sensing material. Exposure of the sensor to 100 ppm NH_3 vapour resulted in good sensitivity and time response.

The environmental friendly camera flash reduction of GO is rapid and con-

verts the insulating GO to a highly conducting r-GO. The important outcome of the study by Cote *et al.*⁷ is that a variety of polymer composites of graphene can be processed from a blend of GO-polymer on flash irradiation. This innovative finding has also opened a way to fabricate new graphene-polymer composites for sensor devices to find applications from fire alarms to air pollution and from alcohol breath tests to detectors of dangerous gases. The search for new green methods to prepare graphene from graphene oxide has become a scientific quest and in this context it may be interesting to know that recently Guo *et al.*¹² have reported another facile green method for the synthesis of high-quality graphene nanosheets on a large scale through electrochemical reduction of exfoliated graphite oxide at a potential of -1.5 V in phosphate buffer at pH 5. The direct electrochemical method of preparation will be a boon for the fast exploitation of graphene in electrochemical device applications.

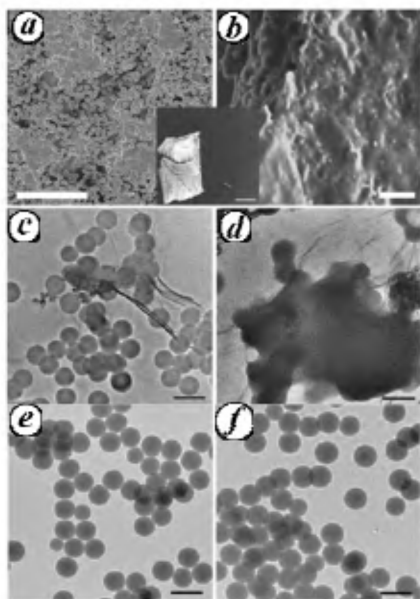


Figure 2. SEM (a, before; b, after) and TEM images (c, before; d, after) of a sandwiched GO/polystyrene/GO structure clearly showing the softening of the polymer colloids after flash. The presence of GO sheets can be identified by the wrinkles. Without GO, the polystyrene beads (e, before; f, after) did not appear to be affected by the same flash exposure. Reprinted with permission from Cote *et al.*⁷. Copyright (2009) from American Chemical Society.

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