

Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite

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Abstract: Graphite oxide (GO) is a promising precursor for the bulk production of graphene-based materials due to its relatively low cost of synthesis. The superior solvent processability of GO makes it particularly attractive for making composites by premixing with other materials. Typically, the reduction of GO has relied on either chemical agents or high temperature treatment. Here we report a room temperature, chemical-free flash reduction process where a photographic camera flash instantaneously triggers the deoxygenation reaction of GO by photothermal heating. Flash irradiation also rapidly creates a fused polymer composite from a random mixture of GO and polymer particles. Using a photomask, conducting patterns such as interdigitated electrode arrays can be readily made on flexible substrates.

Introduction

Graphite oxide (GO) is a promising precursor for bulk production of graphene-based materials, as it can be synthesized in large quantities from inexpensive graphite powders.¹ It is usually made by reacting graphite with strong oxidants followed by gentle exfoliation.² The reaction derivatizes graphene sheets with carboxylic acid, phenol hydroxyl and epoxide groups and thus breaks the π -conjugation in the two-dimensional carbon networks.^{3–5} Therefore, the resulting graphite oxide product is water dispersible, insulating, and light brown in color. The insulating GO can be reduced to form chemically modified graphene (a.k.a. reduced GO, r-GO), in which a large portion of oxygen-containing functional groups are removed by reactions with chemical reducing agents such as hydrazine or its derivatives,^{6–11} or by thermal treatment in various inert or

reducing atmospheres.^{12–15} Such deoxygenating treatments could be challenging if GO is to be blended with other materials, such as in composites since the polymer component may prevent the reducing agent from reacting with GO, or it may be unstable at the annealing temperature. Alternative reducing methods that do not rely on the use of chemicals or high temperature would maximize the advantage of GO's solvent processability. Here we report a flash reduction process where GO can be photo-thermally reduced upon exposure to a pulsed Xenon flash at ambient conditions. In addition, it enables patterning of GO or GO/polymer films by flashing through a photomask. Flash reduction is rapid, clean, and versatile and can be done with a consumer camera flash unit.

Experimental Section

Materials Synthesis. Graphite oxide was prepared using a modified Hummer's method from graphite powders^{2,7,8,16,17} (Bay carbon, SP-1) using NaNO₃, H₂SO₄, and KMnO₄ in an ice bath as reported in great detail elsewhere.¹⁶ A stock solution of GO single layers (0.17 mg/mL) was obtained after multiple sedimentation steps to remove unexfoliated materials. GO thin films were obtained by filtration or casting. To obtain free-standing films, the stock solution was filtered through a 47 mm diameter anodized aluminum oxide (AAO) membrane with a nominal pore size of 0.02 μ m. The GO thin film can be peeled off the AAO filter after drying in air. A thus-prepared free-standing GO film is 34 mm in diameter, 1 μ m in thickness, and typically weighed about 1.7 mg. Filtration using cellulose nitrate or Nylon filter papers gave supported GO thin films.

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Polystyrene colloids with average diameters of 300 nm were synthesized by suspension polymerization according to a reported procedure.¹⁸ A stock solution of about 1.4 wt % of polystyrene beads was obtained after purification. Since both GO colloids and polystyrene colloids are processable in water, they can be mixed with any fraction to produce a blend with nearly arbitrary GO loading. GO/polystyrene composite films were prepared by filtering their mixed colloidal dispersion through Nylon (0.45 μm pore size) or AAO filters (0.2 μm nominal pore size) and dried at room temperature. Before flashing, the films were dried for another 10 min in a 90 °C oven to remove residual water.

Flash Reduction of GO. Most of the flash reduction experiments were carried out in air. Under N₂ atmosphere inside a glovebox, it was found that lower flash energy (indicated by the *f*/stops on the flash units) was needed to achieve reduction. This was attributed to more effective heating of GO because of reduced water content in GO. Flash reduction of free-standing GO films can be done with a single, close-up (<1 cm) flash from the Xenon lamp equipped on a common digital camera. Most experiments were done with a Sunpak 383 stand-alone flash unit with a larger window size of around 30 mm \times 50 mm. The interdigitated electrodes arrays on the 1.5 in. diameter GO/polystyrene thin film (Figure 5) were flash-patterned using an Alien Bees B1600 unit equipped with a 7 in. diameter reflector. The flash energies were measured using a Gentec QE25ELP flash lamp measurement system. The typical flash energies applied to the samples were around 0.1–2 J/cm². In order to improve the uniformity and contrast of the patterns, multiple flashes of lower energy were applied until the desired color was reached. Supported GO films tended to form cracks when exposed to high power flashes due to volume shrinkage and rapid degassing. In order to obtain crack-free, uniform r-GO domains on the supported GO films, a low power, pulsed curing system (Xenon Corp., RC-250B) was used to obtain the N shaped pattern shown in the middle of Figure 3. This system emits relatively low energy pulses at a frequency of 120 Hz. The exposure time was adjusted to obtain the best reduced GO pattern. A few sequential pulses from the photographic units can often burn away the exposed area (Figure 3, right). GO/polystyrene blends tended to give better defined patterns and more durable reduced GO films due to the heat sink effect of the nonabsorbing polystyrene spheres, which melt to fuse with the r-GO sheets. Photomasks for flash patterning were either made by paper punches (Figure 3) or printed on overhead transparency thin films. The dose of exposure can be adjusted by changing the relative power range (the *f*/stops on the flash units) or the distance between the sample and the lamp, or by inserting light absorbing layers (e.g., glass slides) between the sample and the lamp.

Characterization. Thermogravimetric analysis (TGA) of the samples was carried out in a Mettler Toledo TGA/SDTA851 under N₂ atmosphere with a heating rate of 5 °C/min. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-7 under N₂ atmosphere with a heating rate of 5 °C/min. The Fourier transform infrared spectra (FTIR) were acquired in transmission mode on a Nicolet Nexus 870 FTIR spectrophotometer. X-ray diffraction (XRD) patterns were obtained using an INEL CPS120 powder diffractometer with Cu K α radiation. Water contact angle was measured using a Krüss DSA100 drop shape analyzer. Free-standing GO films of about 1.0 μm in thickness and their reduction products were used in all these characterization techniques. Scanning electron microscopy (SEM) images were taken on a FEI Nova 600 SEM. For the insulating GO/polystyrene particle samples, as the one shown in Figure 4a, a 10 nm Au/Pd layer was sputtered before imaging to avoid charging. Transmission electron microscopy (TEM) images were taken on a Hitachi H-8100 TEM at 200 kV. Optical microscopy studies were carried out on a Nikon Eclipse E600 POL microscope under reflectance mode. Sheet resistance

measurements were taken using the four-point probe technique with a Keithley 2601 source meter. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA, using combustion (carbon, hydrogen)- and pyrolysis (oxygen)-based analysis.

Ammonia Sensing. Polyaniline nanofibers were prepared according to previously reported methods.¹⁹ A drop of polyaniline nanofiber aqueous dispersion was cast on the fingers of a set of flash patterned, r-GO/polystyrene interdigitated electrodes. Ammonia-sensing experiments were conducted in a headspace system. The resistance of the polyaniline nanofibers was monitored using a Keithley 2601 source meter at 7 Hz data acquisition rate.

Results and Discussion

Figure 1a and 1b show the dramatic color change in a GO thin film before and after flash reduction. Upon a close camera flash (within 1 cm), the brown, transparent film (Figure 1a) instantaneously turned black and opaque (Figure 1b), accompanied by a loud pop sound (see Supporting Information, Video 1). The strong photoacoustic response suggested a rapid expansion of air near the surface of the film due to a heat pulse generated by photothermal energy conversion,²⁰ which effectively initiated the thermal deoxygenating reactions for reducing GO. The resulting black film became more hydrophobic (Figure 1, a and b insets). The water contact angle of the GO film increased from about 45° to around 78° after the flash, approaching the value measured on a piece of highly ordered pyrolytic graphite of 81°. This indicated the removal of the oxygen-containing groups, which was confirmed by several characterization techniques. Figure 1c shows the TGA heating curves of GO films before and after flash under N₂ atmosphere. GO showed mass loss of about 15% around 100 °C due to water removal, and a second mass loss of about another 25% around 220 °C, which has been attributed to the loss of oxygen-containing groups.⁷ The thermal behavior of our flash-reduced graphite oxide appeared the same as those made by high temperature annealing, with only <2% mass loss in the same temperature range.⁷ Since the oxygenated functional groups are IR active, FTIR spectra (Figure 1d) can give a qualitative measure of the deoxygenating reactions. The spectrum of the original GO film showed a rich collection of transmission bands corresponding to carboxylic acid (1630–1730 cm⁻¹), phenyl hydroxyl (around 1100 cm⁻¹), and epoxide groups (around 930 cm⁻¹),^{7,13} all of which were nearly eliminated after flashing. The flashed film also showed much decreased transmission in the IR spectra, which is characteristic of electrically conducting carbon²¹ that has been observed in HOPG. Elemental analysis showed that the C/O atomic ratio was increased from 1.15 for GO to 4.23 for flash-reduced GO.

The GO films typically expanded tens of times after flash reduction because of rapid degassing (Figure 1e). The thickness expansion of the flashed film suggested that the r-GO sheets were well exfoliated. This was confirmed by the XRD studies (Figure 1f). There is only one sharp peak centered at $2\theta = 9.12^\circ$ in the XRD pattern of the GO film, corresponding to a distance of 9.7 Å between the stacked GO sheets. This is consistent with the apparent thickness of a GO single layer, which was observed to be around 1 nm.^{7,8,16,22} It also suggests that our GO starting materials were free of unexfoliated or unreacted graphite. After flashing, the GO peak disappeared from the XRD pattern and a

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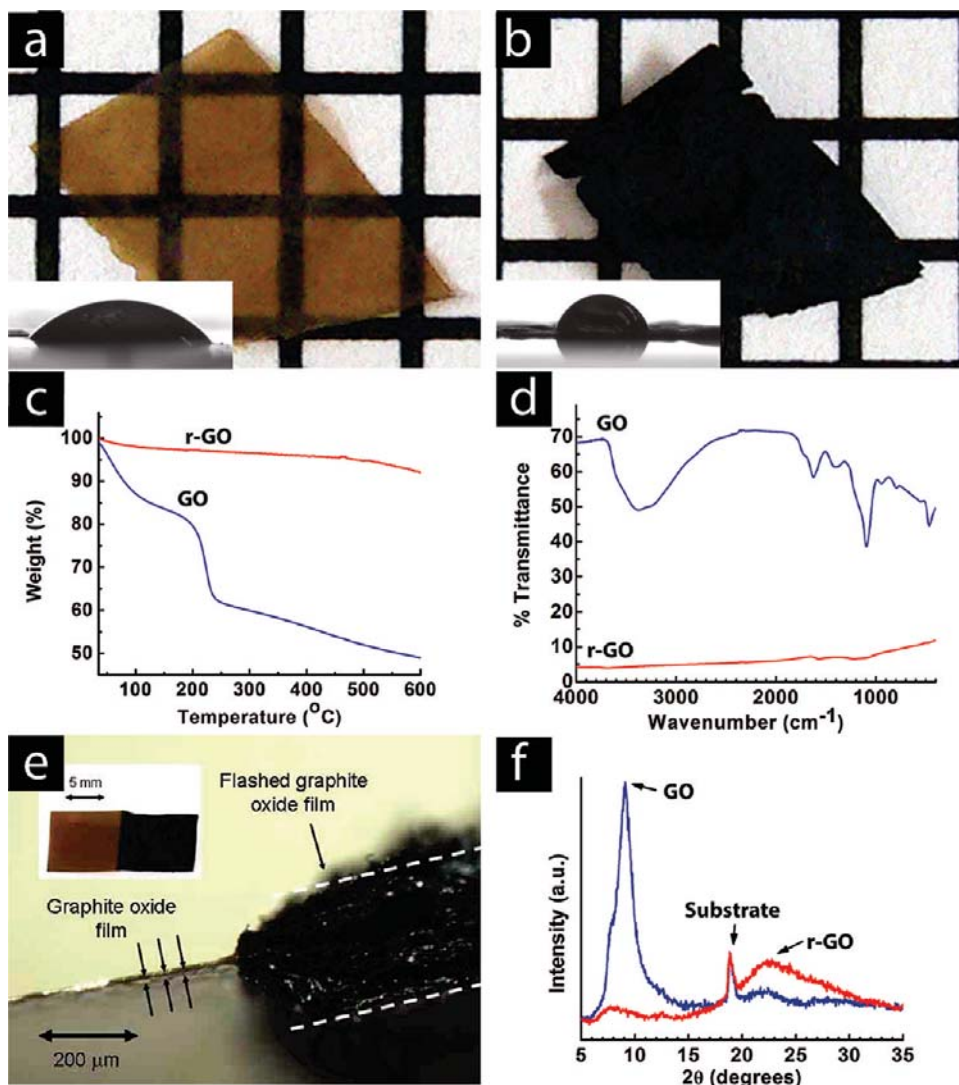


Figure 1. A graphite oxide (GO) paper (a) can be instantaneously reduced (b) upon exposure to a photographic camera flash. The grids in the background are $1\text{ mm} \times 1\text{ mm}$. The flash reduction of GO was evident by the dramatic changes in color (a, b), water contact angle (insets), (c) TGA, and (d) FTIR. In c, d, f, the blue lines correspond to GO and the red lines correspond to the flash reduced GO (r-GO). (e) Cross-sectional view of a GO paper showing large thickness expansion after flash reduction. Only the right half of the GO sample was flashed. The left part of the picture shows the cross-sectional view of the light brown colored GO film. The thickness increased by almost 2 orders of magnitude, resulting in a very fluffy and potentially high surface area film. (f) The lack of a graphitic peak in the XRD pattern of the reduced material suggests disordered packing of the r-GO sheets, consistent with the large volume expansion observed in e.

broad peak centered at 22.5° emerged, which is at a slightly lower angle than the peak for bulk graphite. The lack of a graphite peak suggests that the r-GO sheets stayed exfoliated and disorderly packed despite their strong π - π interaction.²³ This is not surprising since flash irradiation causes microscopically explosive reduction of GO that occurs *in situ* in solid state. The density of flash-converted graphene films were calculated to be around 0.14 g/cm^3 , which is 6% of the value for bulk graphite. The conductivities of flash-reduced GO films were measured to be around 1000 S/m using their much expanded thicknesses in the calculation. Note that the conductivity of reduced GO heavily depends on the processing history of the GO precursor, the reaction conditions, and densities of the final products. Although much higher values of conductivities have

been reported for GO coatings of tens of nanometers in thickness annealed at high temperature ($>500^\circ\text{C}$),^{12,15} for GO papers prepared under similar conditions, flash reduction produces products with comparable conductivities to those from chemical or thermal treatments.^{7,9,13,14,24–26} The open structure of the flash-reduced GO thin films should make them useful for applications favoring high surface area.²⁵

To understand the photothermal heating mechanism, we investigated the photo energy input from the camera flash unit and the thermal energy needed for heating GO films to thermal reduction temperature (Figure 2). The photo energy emitted by the flash lamp used for Figure 1 and Video S1 was measured to be around 1 J/cm^2 at close distances ($<2\text{ mm}$). Since the

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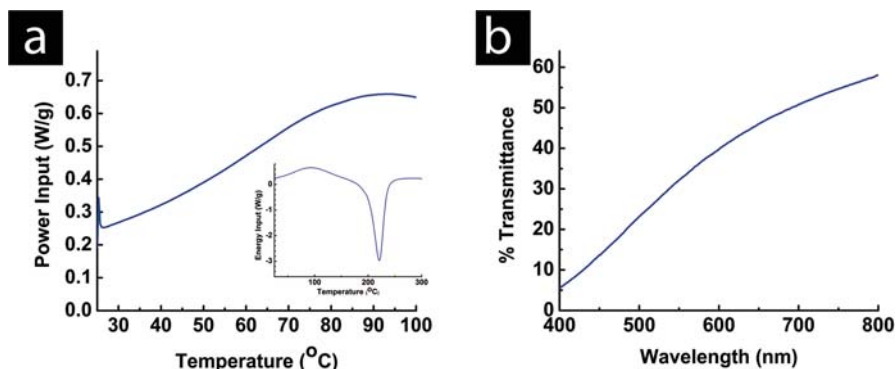


Figure 2. Energy analysis on the flash reduction of graphite oxide. (a) The closeup of the DSC data (inset) shows the heating curve of GO up to 100 °C. The total energy input can be calculated from the area under the heating curve. It took about 377 J/g (i.e., 70 mJ/cm²) of thermal energy to heat up the GO film from room temperature. (b) UV/vis spectrum of a 1 μm thick GO film. The average absorption over the visible range (400–800 nm) is 63%.

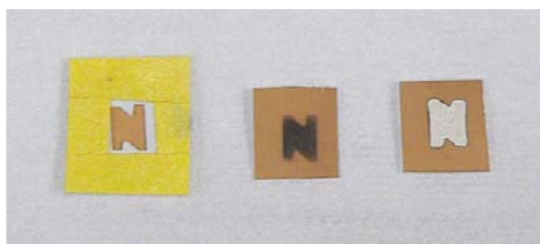


Figure 3. Dry flash lithography of GO. Left: A shadow mask defining an exposed area with “N” shape was taped onto a GO film supported by filter paper. Center: The black, N-shaped, r-GO pattern obtained after flash. Right: The exposed area was ablated by higher power flashes, leaving an etched “N” pattern on the film.

typical optical absorption of a 1 μm thick GO film is about 63% in the visible range, the total absorbed energy is about 630 mJ/cm². Using differential scanning calorimetry (DSC), the total thermal energy required to heat a 1 μm thick GO to 100 °C is calculated to be about 70 mJ/cm². Note that this value already includes the extra energy needed to heat and evaporate the 15% water in the GO film. Therefore, a single camera flash at this distance can provide 9 times the thermal energy needed for heating GO over 100 °C, which should be more than enough to induce deoxygenating reactions. This suggests that flash irradiation could lead to a much higher degree of reduction of GO if the photothermal conversion and heat absorption by GO are optimized. It was also found that much lower energy flashes (<200 mJ/cm², smallest f-stop value on the flash unit) can be used to convert films in a nitrogen atmosphere or predried films because of the lower water content in the films. Since both the optical absorption and heat consumption scale with the film thickness, the thickness term is normalized in the above calculation. This indicates that flash reduction is thickness independent up to the absorption limit. Note that the reduction of GO darkens its color, which leads to higher optical absorption in the visible range. This provides a positive feedback in the photothermal process for further heating. Therefore, a camera flash can rapidly deliver more than enough energy to photothermally reduce GO.

Since flash reduction is triggered by light, it has a great advantage over the conventional GO reducing processes in that it readily allows photopatterning. Using a photomask, conducting r-GO domains can be patterned on the insulating GO film. Compared to conventional photolithography, flash patterning has an additional advantage in that the exposed areas can also be removed directly by further flashing utilizing the enhanced photothermal effect of graphene or r-GO. Therefore, both

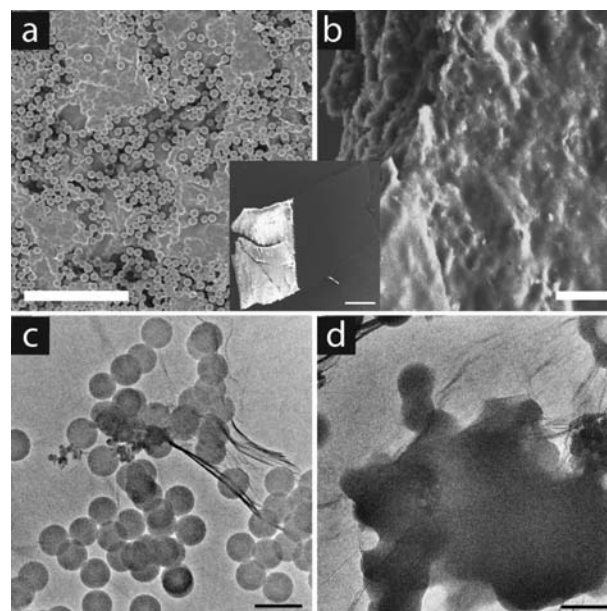


Figure 4. Flash reduction can be utilized to make r-GO/polymer composites from random GO/polymer particle blends as shown in this proof-of-concept experiment. A GO dispersion was mixed with a polystyrene colloidal solution with a predetermined fraction and then filtered to make a thin film. The SEM image (a) of such a film clearly shows a blend of GO sheets and polystyrene beads. After flashing, polystyrene was fused with r-GO to form a much more homogeneous composite as revealed by the SEM image (b). The inset is a low magnification SEM image showing such a film before (left) and after (right) flash reduction. A strong brightness contrast can be clearly seen because of the great difference in electrical conductivity before and after flash treatment. The TEM images (c: before; d: after) of a sandwiched GO/polystyrene/GO structure clearly show the softening of the polymer colloids due to flash photothermal heating of GO or r-GO. Scale bars in parts a and b, the inset, and parts c and d represent 3, 500, and 0.5 μm, respectively.

patterning and etching can be performed in one experimental setup by increasing the dose of flash irradiation. This concept was demonstrated using a photomask with a hollow letter “N” (Figure 3). First, the photomask was placed on top of a GO film supported by a piece of filter paper (Figure 3a, left). The exposed area was first flashed, creating a black N on the GO film (Figure 3a, center). When exposed to relatively higher power flashes, the exposed area can be ablated because of rapid degassing and air expansion, leaving an etched “N”-shaped mark in the GO film (Figure 3a, right).

The properties of GO and its reduction product contrast in many aspects, especially in their solvent processability. GO is

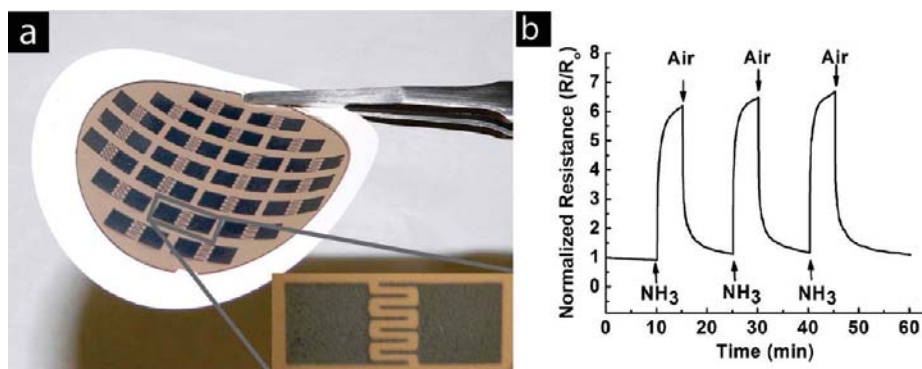


Figure 5. Scalable production of functional r-GO based devices on flexible substrates by flash patterning. (a) Arrays of r-GO/polystyrene interdigitated electrodes (IDE) were fabricated on a 1.5 in. diameter GO/polystyrene thin film deposited on a Nylon filter paper. The inset shows the close up view of one set of such IDE. The contact pads are 5 mm \times 5 mm. The electrode fingers are 100 μ m wide. As a proof of concept, the graphene IDEs were used to construct ammonia sensors with polyaniline as the selective layer. The response from such a metal-free, flexible sensor device on exposure to 100 ppm of ammonia vapor is shown in b.

well processable in water and alcohols because of the strong electrostatic repulsion between the single layers.^{8,16} But r-GO tends to agglomerate in solution because of π - π stacking, greatly limiting the concentration of single layer solutions. For making an r-GO/polymer composite, it would be ideal to make a GO/polymer blend first to take full advantage of the excellent processability of GO. r-GO/polymer composites with near arbitrary loading levels can be rapidly fabricated by flash reduction from a blend of GO and polymer particles. An additional advantage is that the excess heat generated can be utilized to induce welding between the polymer and the r-GO sheets. A proof-of-concept experiment was shown in Figure 4 where GO is flash-reduced and welded with polystyrene beads. First, GO single layers and polystyrene colloids were mixed in water with a predetermined fraction. Then films of a GO/polystyrene mixture were made by filtration. Such thin “filter cakes”, if detached from the filter paper, were brittle and cracked easily upon manipulation as shown in the low magnification SEM image (Figure 4a and 4b, inset). The SEM image also revealed a random blend of polystyrene beads with GO (Figure 4a). After flash irradiation, GO was reduced and the polystyrene particles and GO were fused together, leading to a continuous, conducting film (Figure 4b and inset). The deformation of polymer colloids can be clearly observed in the TEM images, where the polymer particles were deliberately sandwiched between two GO thin films using layer by layer deposition (Figure 4c). The spreading of molten polystyrene on the r-GO sheets was evident after flashing (Figure 4d). The thickness of each GO film is estimated to be no more than 35 nm based on the widths of the folds. Flash irradiation on these thin films was able to generate sufficient heat to soften the polystyrene beads. Without GO, flash irradiation had little effect on the colloids (see Supporting Information, Figure S2) since polystyrene is transparent in the visible range. In the GO/polystyrene films, the polymer particles can act as a heat sink to drain away the excess heat to avoid overexposure during patterning. This helps to improve the resolution of the patterns and the integrity of the reduced domains.

Because many properties of GO are altered after reduction such as color, electrical conductivity, thermal stability, surface energy, wettability and chemical reactivity, flash reduction, and patterning of GO is especially promising for fabricating functional surfaces and devices. For example, Figure 5a shows arrays of interdigitated r-GO/polystyrene electrodes fabricated on a flexible, 1.5 in. Nylon “wafer” upon flashing through a

mask printed on a sheet of overhead transparency. A GO/polystyrene blend was used as the precursor to improve the resolution and mechanical durability of the patterned films. The exposed areas became conducting with the sheet resistance decreased significantly from $2 \times 10^8 \Omega$ / to 9.5 k Ω /square. The flashed areas also became more hydrophobic. Such electrodes were used to construct chemical vapor sensors by depositing some conducting polymer polyaniline nanofibers. When exposed to 100 ppm NH₃ vapor, such all-organic, flexible sensors showed comparable sensitivity (Figure 5b) and time response (see Supporting Information, Figure S3) to those made with conventional metal electrodes and hard substrates.²⁷ The wettability contrast between the electrode fingers and the blank areas may be further utilized to fabricate microfluidic or electrowetting devices.

Advancement in the processing technique can usually bring breakthroughs and discoveries in the materials as seen in the development of carbon nanotubes^{28–30} and conducting polymers.³¹ Some inspiring results have been reported on flash treatment of nanomaterials such as single-walled carbon nanotubes, Si nanowires, and conducting polymer nanofibers.^{32–34} However, in all these cases it caused the degradation of electrical conductivity. Flash irradiation of GO makes an insulating material conducting, enhancing its electrical conductivity by many orders of magnitude. Therefore, it could lead to many more useful applications. Compared to chemical and high temperature thermal treatments, flash reduction is rapid, chemical-free, and energy efficient. It could be an enabling technique that holds great promise for patterning GO films in device and composite applications.

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Supporting Information Available: Video of flash reduction process; TEM images of GO/PS and PS before and after flash; more data on ammonia sensing using polyaniline nanofibers deposited on GO/PS electrodes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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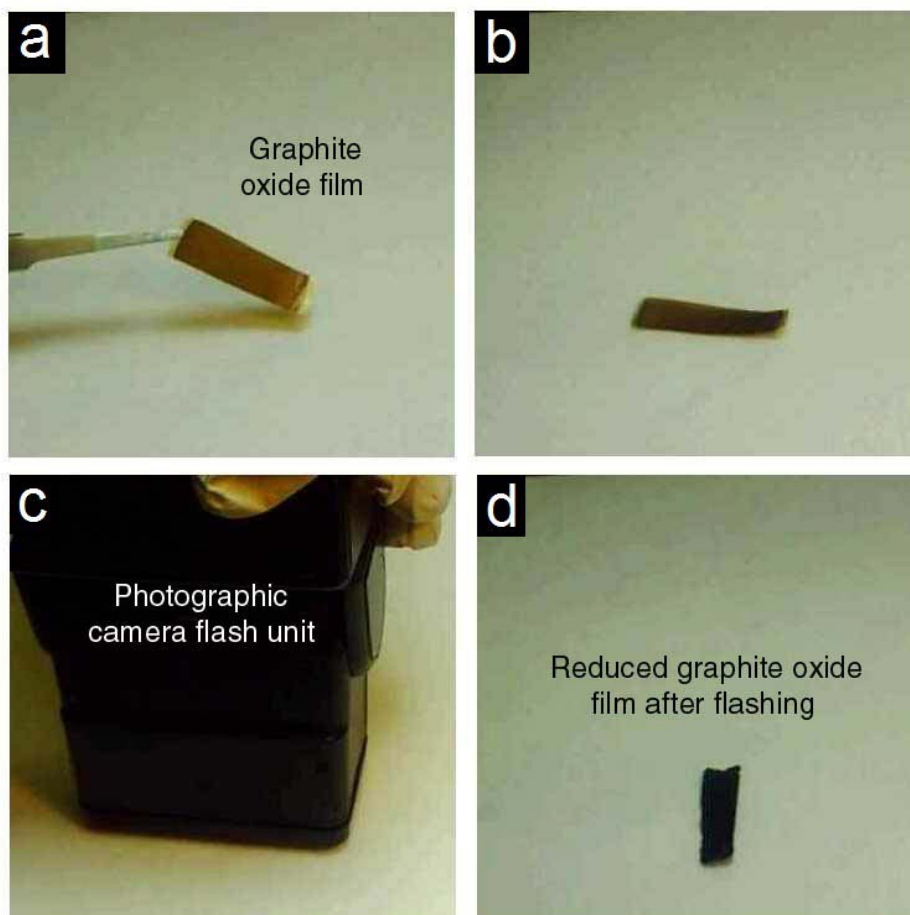
Supporting Information

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Video S1. Snapshots from Video S1 showing a typical flash reduction experiment.

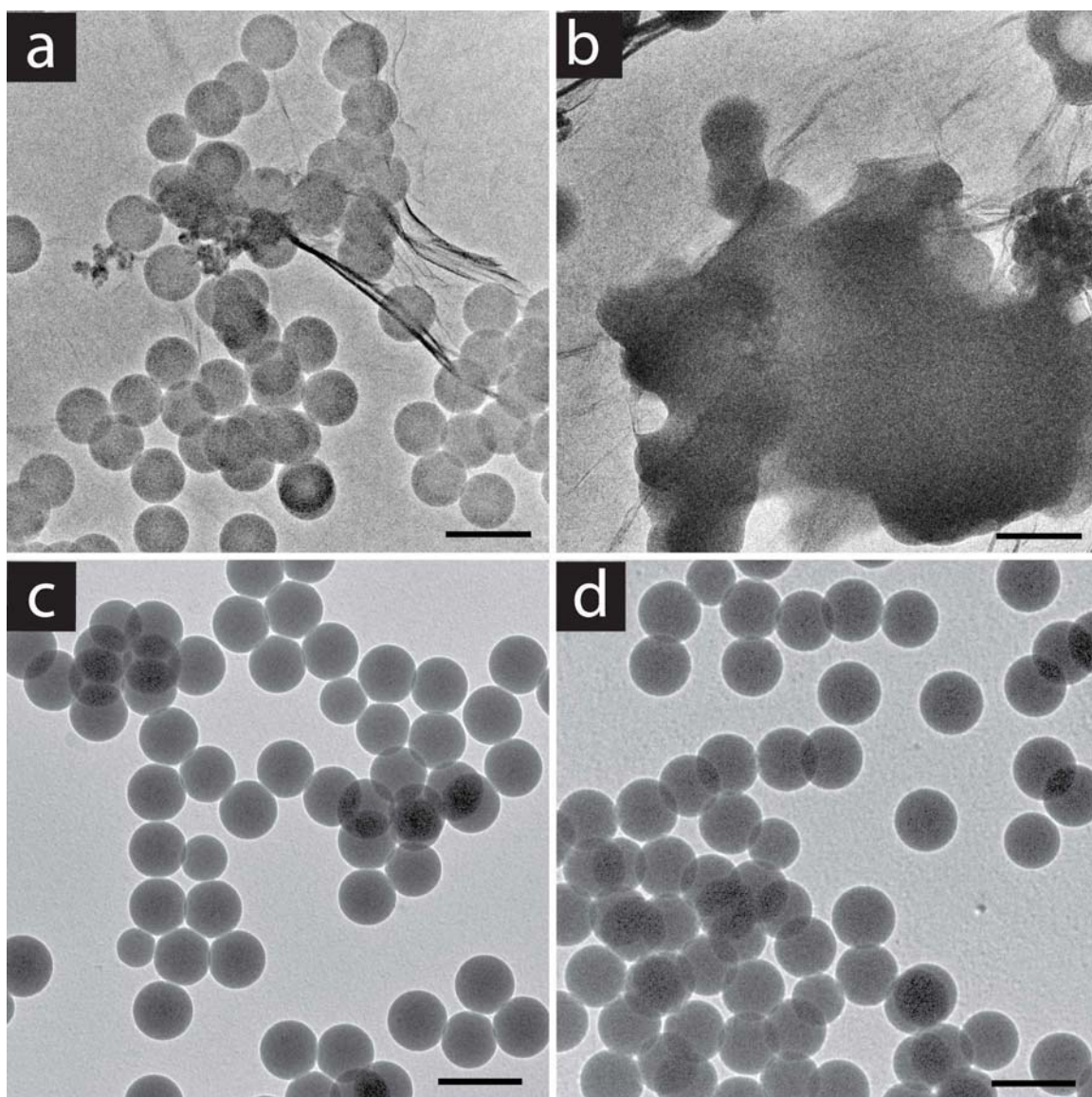


Figure S2. TEM images (a: before; b: after) of a sandwiched GO/polystyrene/GO structure clearly showing the softening of the polymer colloids after flash. The presence of GO sheets can be identified by the wrinkles. Without GO, the polystyrene beads (c: before; d: after) did not appear to be affected by the same flash exposure since polystyrene is transparent in the visible range, and therefore does not have a strong photothermal effect.

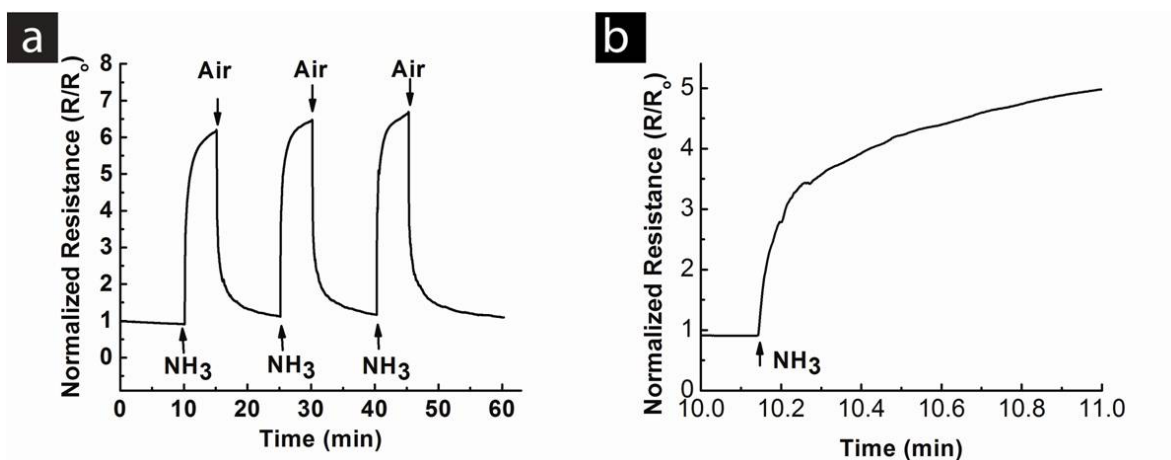


Figure S3. (a) Response of a polyaniline nanofiber sensor deposited on flash patterned r-GO/polystyrene interdigitated electrodes upon exposure to 100 ppm ammonia. (b) is a close up view of the onset of the first cycle, showing the time response. These results are similar to those obtained with conventional metal electrodes on hard substrates¹.

SI References

1. Huang, J.X., Virji, S., Weiller, B.H. & Kaner, R.B. *J. Am. Chem. Soc.* **125**, 314-315 (2003).