

PULSE PHOTOTHERMAL REDUCTION AND PATTERNING OF GRAPHITE OXIDE

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Introduction

Graphene, a single atomic layer of sp^2 hybridized carbon, has been an intensely researched material since its isolation in 2004 by Geim et al[1]. Graphene is largely explored for its electronic properties, mechanical durability, mechanical properties, and large aspect ratio[2]. One of the chief problems when exploring the possibilities of graphene in research and technology is the difficulty of scalable production of graphene. Existing methods include the epitaxial growth[1], chemical vapor deposition[3], and reduction of the more processible graphene oxide through thermal[4] or chemical[5,6] means. Here we report that thin films of graphite oxide can be instantaneously reduced by use of a high-power pulse of electromagnetic radiation such as a camera flash.

Experimental

Graphite Oxide (GO)[7] is prepared as prescribed by a modified version of the Hummer's method, a chemical synthesis that converts graphite into GO dispersed in aqueous solution[8]. After repeated steps of sedimentation for removal of unexfoliated GO, a 0.17mg/mL dispersion of monolayers was created. Thin films were created with vacuum filtration or casting. Free-standing films were created with a filtration through an anodized aluminum oxide filter (pore size 20 nm). After sufficient drying time, the film can be peeled from the filter disc. For a disk that is supported by a filter paper, nylon or cellulose nitrate was used.

Polystyrene colloids were prepared by a suspension copolymerization process. After purification, polystyrene beads of 300 nm diameter were produced, with a 1.4 weight percent composition. Colloidal dispersions of the polystyrene mixed with GO were filtered in either anodized aluminum oxide filters (200 nm pore size) for free standing films, or in nylon (450 nm pore size) for supported films. Samples were air dried and heated at 90°C for ten minutes prior to photo-thermal reduction.

Flash pulsing of most samples was performed with a Sunpack 383 standalone camera flash, at a distance of less than one centimeter. The GO-polystyrene composite films were flashed using an Alien Bees B1600 unit, with a 7" diameter hemispherical reflector. These composite films were patterned to make interdigitated electrode patterns, by placing a photopattern mask over the sample during the flashing process. Flash energies were found to be 0.1 – 2 J/cm² as measured by a Gentec QE25ELP, a flash energy density measurement device.

For a gradient reduction level, as indicated by color change, a series of lower-energy high-frequency flashes was used in patterning, for more uniform and precise treatment. A Xenon Corp. RC-250B flash pulse curing device, with a low energy per flash, and a frequency of 120 Hz, was used to controllably reduce a photopatterned design. Exposure time was experimentally optimized. Photomasks are created either by a cut-out shape from paper, or printed onto transparent plastic sheets. Exposure was controlled by relative power of the flashes, distance from light source, or placing an absorbing material such as glass between the GO film and light source.

Characterization includes thermogravimetric analysis, differential scanning calorimetry, Fourier transform infrared spectra, x-ray diffraction, water contact angle measurement, scanning electron microscopy, four-point probe sheet resistance measurements, optical microscopy, and elemental analysis by combustion.

Results and Discussion

It is shown in Figure 1 that there is a stark color change in the GO film as it transitioned to r-GO. With a close flash, a transparent brown GO film changes to a black, opaque reduced GO film. The transition was accompanied with an audible "pop" sound, suggesting a rapid gaseous expansion within the film. Hydrophobicity was also notably increased, with the contact angle changing from 45° to 78°. The measured value for pristine graphite is 81°. These factors are evidence of a removal of the functional groups that are present in GO.

TGA noted a mass loss of about 15% at 100 °C for water loss, and a second mass loss of 25% at 220 °C, for the loss of the oxygen-containing functional groups. A TGA of flash-produced r-GO showed little mass loss (under 2%). FTIR showed the removal of various functional groups, including carboxylic acid, phenyl hydroxyl, and epoxide. A decreased IR transmission is characteristic of electrically conducting carbon. Elemental analysis showed an increase in the carbon-oxygen ratio from 1.15 to 4.23 from before to after flashing.

The rapid degassing after flashing expands the film by tens of times, and exfoliates the films, as XRD evidence supports. The sharp GO peak was removed and replaced with broad peak centered at 22.5°, a slightly lower than the peak of graphite, because of high disorder and exfoliation of the sheets. This agrees with the density of 0.14 g/cm, which is only 6% of the density of bulk graphite. Conductivities measured were comparable to chemically and thermally reduced GO. It has been calculated that the flash provided about 1 J/cm² and is at least four times the necessary energy to heat GO to initiate the exothermic reduction. This value includes water removal, suggesting that there is sufficient energy for deoxygenating reactions. Until the absorption limit, it is expected that this reduction is independent of film thickness.

This light-induced method has an advantage over thermal reduction in that it can be used for photopatterning, using a

photomask to selectively reduce patterns into the GO film with multiple low power flashes. Also possible is etching, removal of exposed GO areas of the film by higher power flashes. This may allow for a single processing technique to both pattern reduced and etched regions in a film.

Composites of r-GO and polymers are also made easily processed by these techniques. GO is processable more easily than graphene, as it has high electrostatic repulsion, offsetting the Van der Waal's forces that make graphene and r-GO much more difficult to process. To make a well distributed composite, GO and polymer colloids were mixed before vacuum filtration, and the resulting films were flashed to create the r-GO/polymer composite. An archetype was created with polystyrene (PS) and GO. Colloids of the PS particles and GO sheets were mixed together, and filtered into a thin film. When flashed, the GO was reduced and made more conductive, and the excess heat blends the polymer particles with the GO. Without the GO, there is little change in the PS particles from the flashing, indicating the necessity of GO's absorption of the light into heat for the deformation of the PS.

Using a GO/PS blend, a film was patterned with interdigitated electrodes. Polyaniline nanofibers were drop cast onto the electrodes and successfully implemented as an ammonia detector, as a proof of concept for the potential applications of photopatterned GO/r-GO composite films.

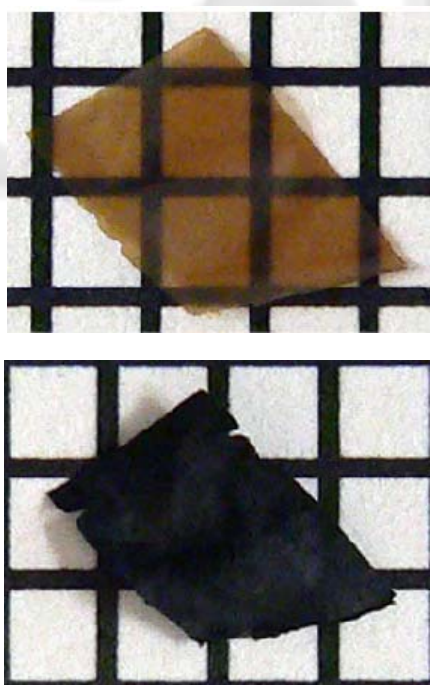


Fig. 1 GO Film (top) and flash reduced (r-GO) film (bottom)

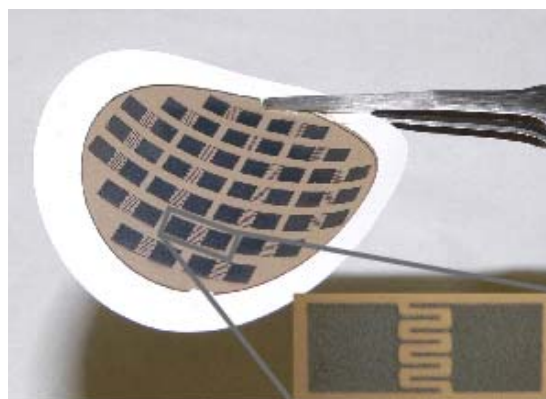


Fig. 2 GO/PS composite with an interdigitated electrode pattern. Electrode fingers are 100 microns wide.

Conclusions

GO can be photothermally reduced with a pulse of camera flash. This restores much of the conducting behavior, and allows for patterned electronic films without the use of expensive metallic components or complex and high-cost processing techniques[9]. Composite GO-polymer blends can be created, and with this flash mechanism reduced, welded, and used as an electrode material.

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