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Stenciling Graphene, Carbon Nanotubes, and Fullerenes Using Elastomeric Lift-Off Membranes

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Graphene, a 2D crystal comprised of single-atom-thick sheets of hexagonal sp^2 carbon atoms, has garnered much attention recently owing to potential applications in field-effect transistors (FETs), sensors, composite reinforcement, supercapacitors, and emissive displays.^[1–5] While other low-dimensional allotropes of carbon have been extensively studied since their discoveries over 20 years ago,^[6,7] graphene research is still in its infancy. Although many methods to synthesize these nanomaterials have been demonstrated, there are relatively few approaches to systematically organize these materials that meet the high

throughput requirements for practical device applications. In this Communication, we demonstrate that thin elastomeric membranes comprised of poly(dimethylsiloxane) (PDMS) can be utilized as physical stencils for patterning chemically converted graphene (CCG), carbon nanotubes (CNTs), and fullerenes, all of which can be dispersed in hydrazine. Furthermore, this method represents a simple and versatile process to selectively register these carbon nanomaterials into configurations suitable for nanoelectronic devices.

Patterning of Graphene, CNTs, and Fullerenes

Since the initial report of peeled graphene in 2004, researchers have looked for alternative routes to isolate single sheets. The original method was based on the mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) using cellophane tape.^[8] Despite many fundamental studies that have been enabled by this work, the peeling technique is unlikely to become an industrial scalable process because it is laborious and single sheets are difficult to isolate. Substrate-based approaches using molecular epitaxy^[9] or chemical vapor deposition have also been used to grow macroscale graphene sheets.^[10–12] Unfortunately, registration remains a challenge and the high-temperature process can complicate the precise growth of graphene onto many substrates.

Methods to arrange CNTs and fullerenes into a matrix have been extensively investigated.^[13–18] CNTs have been patterned through soft-transfer printing,^[13] spray-coating,^[14] ink-jet printing,^[15] and dielectrophoresis^[16] but low resolution and length limitations of the nanotubes can be problematic. Arrays of fullerenes have also been constructed, via physical vapor transport (PVT) onto self-assembled monolayers of octadecyltrichlorosilane.^[17,18] Fullerenes arranged by PVT have been utilized in organic FETs and in the photoactive layer of bulk heterojunction solar cells. While relatively large fullerene features on the order of $8\mu\text{m} \times 8\mu\text{m}$ can be obtained on silicon with PVT, the typical processing temperatures required for this technique ($425\text{--}500\text{ }^{\circ}\text{C}$) preclude the use of flexible plastics as substrates for device fabrication.

An alternative strategy to the aforementioned methods is to solution process these materials. Graphite oxide, a precursor to graphene, can be dispersed and simultaneously reduced in a solution of either dilute or pure hydrazine.^[19–22] We have previously demonstrated that the hydrazinium graphene formed can be deposited onto a variety of substrates with standard solution-processing techniques. Thermal annealing, carried out at relatively low temperatures ($150\text{ }^{\circ}\text{C}$), can then be used to drive off residual hydrazine.^[20] Additionally, our group has found that slightly oxidized CNTs readily disperse in hydrazine at a relatively high loading concentration (15mg mL^{-1}) and can be mixed with CCG for use as a conductive, transparent electrode material.^[5]

Here, we report that a fullerene derivative, phenyl- C_{60} -butyric acid methyl ester (PCBM) disperses in hydrazine to form a transparent yellow solution (Fig. 1) at a rather high loading concentration (17mg mL^{-1}). The compatibility of PCBM in hydrazine can be attributed to the functionality present on the fullerene, which also enables it to be dissolved in common organic solvents.^[17] Interestingly, while PCBM forms a solution in hydrazine, CNTs and CCG tend to form colloidal dispersions in hydrazine. The reason for this is likely due to

differences in size. The dimensions of a fullerene are within the nanometer regime, while the other two allotropes exhibit at least 1- μm dimensions.

When a 532 nm, green laser is projected through mixtures of CNTs (0.1mg mL^{-1}), PCBM (0.5mg mL^{-1}), and CCG (0.1mg mL^{-1}), respectively, light scatters differently based on the Tyndall effect. A beam of light traveling along a straight path will be scattered if it comes into contact with discontinuities such as colloidal particles in a suspension, as seen in Figure 1. A higher loading concentration of PCBM was used to enhance the yellow color of the solution, which may account for a modicum of light scattering that can be seen through the solution. Additionally, the glass vial diffracts some light around the edges. The difference in light-scattering intensity correlates with differences in particle size and dimensionality. Since a single-walled CNT can be thought of as a rolled-up graphene sheet, it is logical that they will absorb up to twice as much visible light. Likely for this reason, CNT dispersions appear darker and scatter the light more heavily than CCG colloids.

While the use of solution processing of CCGs has led to the fabrication of several CCG-based devices,^[2,4,5,20] this process relies on the manipulation of a random distribution of sheets. Recently we demonstrated the ability to soft-transfer CCG from glass to a silicon substrate.^[23] However, this method suffers from relatively low-resolution features and does not prevent the transfer of residual PDMS oligomers onto the substrate surface. Here, we describe a stenciling technique that circumvents these problems by removing most of the residual oligomers through a PDMS pre-treatment process as described elsewhere.^[24]

A physical mask can be used to arrange these materials into a matrix. Our group has explored using metal, photoresist, and polyimide masks but the chemical reactivity of hydrazine precludes these options. It is for this reason that we elected to use thin membranes comprised of PDMS to selectively register graphene, CNTs, and fullerenes. PDMS is an elastomeric material that has become ubiquitous in applications ranging from microfluidics, biomedical packaging, and the soft-lithographic patterning of a variety of materials including metals.^[24] PDMS is well suited as a mask material based on the ease with which it can be fashioned into many desired structures as well as its resistance to many chemical and physical processes.

Fabrication of Elastomeric Membranes and Stenciling of Carbon Nanomaterials

Templates for preparing PDMS membranes with defined cavities were fabricated using conventional photolithography. Figure 2 outlines the process used to mold an elastomeric membrane from the photolithographically prepared master and to stencil arrays of graphene, CNTs, or fullerenes from charge-stabilized solutions in hydrazine. Images of a typical PDMS membrane are provided in Figure 3 to illustrate the uniformity of the features. Once cured, PDMS membranes are cut from the mold using a clean razor and placed onto a substrate with fine tip tweezers, Figure 3a. These membranes are free-standing and not limited by the shapes described here. Furthermore, the master wafer is reusable several times over and fresh PDMS membranes can be readily fabricated, sidestepping the arduous task of prefabricating alignment markers prior to every deposition.

The thin PDMS sheet conforms to the substrate surface, as seen in Figure 3b, which shows the membrane resting on top of a silicon oxide surface with no visible air pockets. In instances where the membrane is very thin, a few drops of isopropyl alcohol (IPA) are used to temporarily lubricate the surface and prevent the membrane from adhering onto itself.

The wettability of the substrate surface plays a vital role in determining the uniformity of material coverage. For instance, a completely hydrophobic surface will limit the material to beaded regions along the corner of the substrate and virtually no deposition through the stencil. To reduce the surface tension we briefly expose our membrane-covered substrates to an oxygen plasma. After this treatment, the surface becomes temporarily hydrophilic, enabling the deposition of CNTs, CCG, or PCBM into the membrane cavities via spin-coating.

After deposition, the PDMS membrane is removed and defined arrays of CCG, CNTs, and fullerenes are revealed. The substrates are then thermally annealed to drive off any residual hydrazine. In Figure 4, arrays patterned from the hydrazinium solutions can be seen.

Characterization of Patterned Arrays

Raman spectroscopy was used to further demonstrate the presence of each graphitic material within the pre-determined locations, as seen in Figure 4. The Raman spectra of CCG shows the Gb and around 1600 cm^{-1} , while the spectra of CNTs have two peaks at the G band resulting from the semiconducting (larger) and the metallic (smaller) conformations.^[25] For PCBM, we resolved several peaks hidden beneath the strong fluorescing band as well as the characteristic 1450 cm^{-1} peak.^[26]

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images taken within the individual arrays provide a detailed overview of the surface coverage and nanotopology of the materials. Figure 5a shows the AFM step height of CCG to be $\sim 0.6\text{ nm}$, indicative of a single layer, as explained by Tung et al.^[20] We can control the amount of material deposited by changing the concentration of the dispersions as needed. In Figure 5a, we used a concentration of 0.1 mg mL^{-1} to deposit a single sheet of graphene. In Figure 5b and 5c the SEM and AFM images show bundles of single-walled CNTs and large round aggregates of coalesced PCBM, respectively. Similarly, few bundles of CNTs can be isolated through dilution of the graphitic dispersion.

We envision that this clean transfer process could be used in the low-temperature and high-throughput fabrication of FETs and organic light-emitting diodes (OLEDs). For nanoelectronic applications, patterned arrays of these carbon nanomaterials could reduce, if not eliminate, parasitic current paths (cross-talk) between neighboring devices.^[27]

In conclusion, we have demonstrated a simple and flexible method to stencil and solution-process a family of carbon nanomaterials that are dispersed in hydrazine. This method is certainly not limited to the materials described here and could be extended for patterning other solvent-dispersed derivatives of fullerenes, CNTs, and graphenes.

Experimental

Solution Preparation

Graphite oxide was prepared via a modified Hummer method [28]. Water dispersions (2% w/v) of GO were dried under vacuum using 0.22- μm alumina anodisc filter membranes. A thick, black paper-like material is produced after 24 h of drying under ambient conditions. P3 single-walled CNTs were purchased from Carbon Solutions Inc. These tubes were purified by refluxing for 1 h in ethanol followed by a mild oxidation in a 1 M nitric acid solution. The tubes were filtered and dried under vacuum for 24 h prior to exposure to hydrazine. [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) was purchased from Nano-C, Inc. and used as received. The materials were preweighed, transferred into a nitrogen glove box, dissolved into clear anhydrous hydrazine, and left to stir for at least 24 h. Effervescence of nitrogen gas occurred upon contact with hydrazine. CCG and CNT dispersed in hydrazine formed black colloids, while the PCBM dissolves in hydrazine to yield a dark yellow and translucent solution. CCG, CNTs, and PCBM hydrazinium dispersions were prepared in concentrations of 1mg mL⁻¹, 10mg mL⁻¹, and 17mg mL⁻¹, respectively, and subsequently purified to remove larger aggregates. Hydrazinium graphene and CNT suspensions were purified using centrifugation, dilution, and ultrasonication, while dispersions of PCBM are simply diluted to different loading conditions to vary the final thicknesses. A Heraeus Labofuge 400 was used for centrifugation, which removed any aggregates prior to spin-coating. Sonication was carried out using a VWR model 250D sonicator set at level 9 for 10 min.

Master Preparation

Test-grade silicon wafers were processed using standard piranha cleaning techniques. Transparency masks of the final designs are printed using a high-resolution printer. An array of raised photoresist features, on the master silicon wafers was generated using photolithography techniques. To inhibit SU-8 and PDMS delamination, the features are exposed to a tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane under vacuum for 1 h rendering the features hydrophobic. A Veeco Dektak profiler was used to measure the step heights of the SU-8 features to be 135–140 μm and the width to range between 75 and 200 μm . The features are produced by spin-coating SU-8 2100 onto a silicon wafer at 2000 rpm. Postannealing, the films are exposed to UV irradiation using a Karl Suss contact aligner and the nonexposed regions are developed away in SU-8 developer. The final designs are rinsed with isopropyl alcohol and hard baked.

Lift-Off Preparation

Sylgard 184, PDMS, elastomer was spin-coated over the master wafer at speeds of 2500–3000 rpm, which yielded membranes with thicknesses of 10–50 μm . Low-molecular-weight polymers are removed from the membranes by soaking for 2 h in dichloromethane and drying in a vacuum oven at 65 °C overnight. The treated membranes are finally rinsed with IPA and dried in a desiccator overnight.

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Figure 1. The Tyndall effect is observed upon shining a 532-nm green laser through a 0.1 mg mL^{-1} mixture of CNTs (left), 0.5 mg mL^{-1} PCBM (middle), and 0.1 mg mL^{-1} CCG (right) dispersed in hydrazine.

Figure 2.

A schematic diagram illustrating how to stencil carbon-based nanomaterials onto any substrate using an elastomeric lift-off membrane: Wafer view (left) and side view (right). a) A master silicon wafer with raised photoresist features is fabricated. b) A thin PDMS layer is then spin-coated onto the master wafer, which c) is subsequently removed, and d) placed onto a new silicon wafer with a 300-nm thermal-oxide coating. e) Carbon-based nanomaterials are then spin-coated over the entire membrane. f) The coated membrane is finally lifted off, leaving behind an array of carbon-based nanomaterials.

Figure 3.

a) A free-standing elastomeric membrane held by tweezers. b) Pores made from a silicon mold are clearly visible. An optical microscopy image of the membrane pores shows the silicon dioxide substrate beneath it. c,d) SEM images show the cross-sectional view of a folded membrane (c) and a magnified view of the membrane pores (d).

Figure 4.

Optical microscopy images on silicon oxide substrates show patterned arrays of carbon materials with representative Raman spectra below: a) CCG, b) single-walled CNTs, and c) PCBM.

Figure 5.

a) SEM (left) and AFM (right) images with corresponding line profile (inset) confirming a step height of less than 1 nm, indicative of CCG. b) An SEM (left) and an AFM (right) of a dense network of CNT bundles. c) An SEM (left) and an AFM (right) showing the topology of PCBM aggregates.