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Intact Pattern Transfer of Conductive Exfoliated Graphite Nanoplatelet Composite Films to Polyelectrolyte Multilayer Platforms

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Layer-by-layer (LBL) assembly of polyelectrolyte multilayers (PEM) has become a ubiquitous process for creating functional ultrathin films. Introduced by Decher, the simple deposition of two oppositely charged polyions can be performed on many types of surfaces giving them new functionality based on the type of polyelectrolytes utilized.^[1] Incorporating new functional materials such as nanoparticles, proteins, or medicine (therapeutic chemicals) to alter film properties has led to changes in mechanical,^[2,3] surface wetting,^[4,5] antireflective,^[6] and luminescent^[7] properties and resulted in applications as biosensors^[8,9] or in drug delivery.^[10,11] Exfoliated graphite has been incorporated into PEM and other polymer composite films for its unique mechanical, thermal and electrical properties, which are comparable to carbon nanotubes.^[12–18] Multilayer graphite, large stacks of sp^2 hybridized graphene sheets bound together by weak van der Waals interactions, is an ideal starting material because it is inexpensive and available in large quantities. To take advantage of these properties, oxidized graphite has been incorporated into PEM.^[15–18] Oxidized graphite is created by the acid treatment of graphite, which exfoliates the multilayered graphene sheets into platelets of only a few graphene layers thick, creates a negative charge so that they are stable in aqueous solutions, and renders the graphite nonconductive. LBL assembly with a positively charged polyelectrolyte allows for the formation of PEM. To make conductive films, the oxidized graphite must be reduced back to graphite, which is not cost-effective and can change the film morphology. To our knowledge no one has performed LBL assembly using exfoliated graphite that was not oxidized. Mass production of these films for electronic devices requires a patterned film on the substrate surface. Patterning a single layer of graphite does not result in a large enough surface coverage to surpass the

percolation threshold, which means a multilayer film is required for conductivity. Recently the direct transfer of multilayer films has been shown as a facile route to fabricate patterned films that would be difficult to form using other assembly and patterning methods.^[19–22]

In this Communication, we present a simple method of creating patterned conductive multilayered polymer/exfoliated graphite nanoplatelet (xGnP) nanocomposite films by using the LBL assembly of xGnP and the intact pattern transfer (IPT)^[19–22] of these films to a substrate. Multilayered graphite was exfoliated followed by milling to create size-controlled xGnP.^[14] The xGnP films were then coated with a negatively charged polymer to form a stable aqueous solution. The solution was used for electrostatic LBL assembly, with a positively charged polyelectrolyte as the counter ion, onto the surface of an uncharged hydrophobic elastomeric stamp. Once the film was formed, it was placed in direct contact with a substrate of the opposite charge to directly transfer the multilayer film. If enough layers of xGnP were adsorbed onto the stamp, the LBL film became conductive. Before LBL assembly, the elastomeric stamp is coated with a layer of polyelectrolyte using relatively weak hydrophobic interactions between the stamp and film. When the stamp is removed from the substrate, the strong electrostatic interactions between the oppositely charged films on the stamp and substrate hold the multilayer film on the substrate surface.

Our process is illustrated in Figure 1. Multilayered graphite was expanded using acid intercalation, followed by exfoliation using ultrasonication^[13,23,24] and finally milled to create xGnP nanoplatelets (few layer graphene particles with a thickness of 1–10 nm and a 100–1000 nm diameter). Since graphite is naturally hydrophobic, the xGnP needs to be further modified to be used in LBL assembly from aqueous solutions. To solve this problem, ultrasonication was used to disperse the xGnP in a solution containing a negatively charged polymer (sulfonated polystyrene, SPS). The SPS coats the xGnP through interactions between the sp^2 hybridized graphitic surface and the aromatic rings of the polymer.^[25] This coating facilitates the formation of a stable aqueous solution by preventing agglomeration of the SPS coated xGnP (xGnP-SPS) through like charge repulsion. This charge also enables the xGnP-SPS to be used for electrostatic LBL assembly. Zeta potential measurements confirm the negative charge of the xGnP-SPS. Before LBL assembly, topographically patterned uncharged hydrophobic poly(dimethylsiloxane) (PDMS) stamps were

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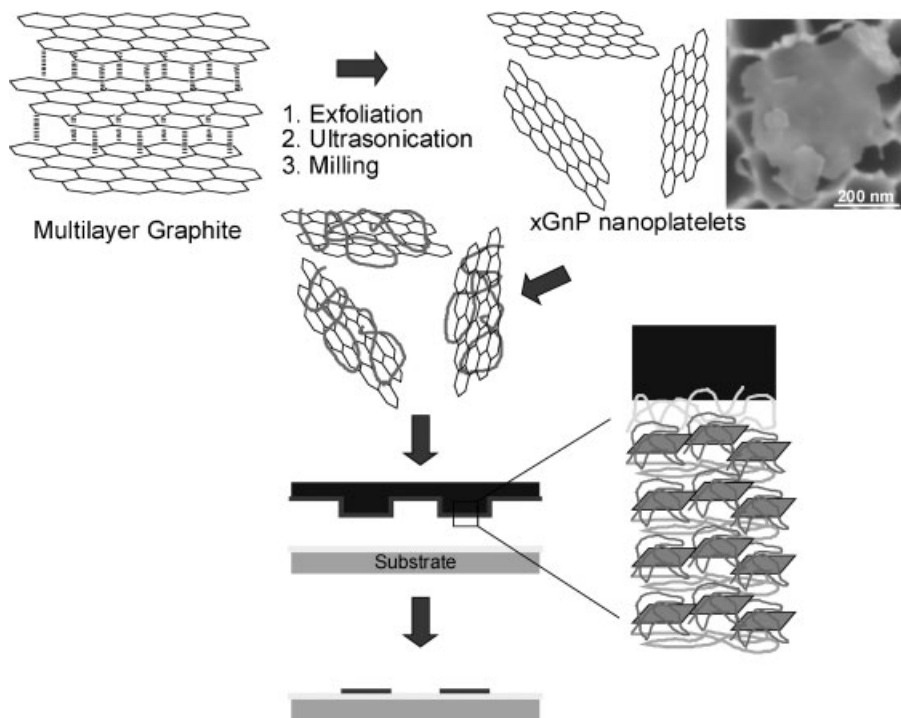


Figure 1. Illustration of the process to form xGnP, subsequent film formation on poly(dimethylsiloxane) and transfer to a PEM-coated substrate.

coated with poly(allylamine hydrochloride) (PAH) using hydrophobic interactions at a pH of 7.5 or 10. The PDMS substrates were then placed into a solution containing xGnP-SPS, where the xGnP-SPS electrostatically deposits onto the PAH-coated surface. After washing the sample is then placed into a solution containing positively charged poly-(diallyldimethylammonium chloride) (PDAC), where a second layer deposits on the surface. Repeated immersion into the xGnP-SPS and PDAC solutions creates multilayer films denoted as PAH/(xGnP-SPS/PDAC) $_n$ where n is the number of bilayers deposited on the PAH coated surface. The build-up of multilayered films was confirmed by the gradually increasing darkness of the deposited film. PDAC was typically the final layer adsorbed. After the film was fabricated it was removed from solution, gently blown dry, and placed in contact with a negatively charged PEM coated substrate. Contact times were typically one hour. However it was found to be critical for the film to be completely dry before the stamp was removed from the substrate. The IPT of the multilayers proved to be more reproducible than directly microcontact-printing the xGnP-SPS solution as a carbon ink. It was possible to obtain patterns of xGnP using the latter method; however the process was less reproducible and observation from by optical microscopy showed the patterns would not be conductive.

Figure 2 shows optical and scanning electron microscopy (SEM) images of the transferred patterns of the PAH/(xGnP-SPS/PDAC) $_4$ nanocomposite films using the IPT method. Films containing four and six bilayers could be patterned on areas as large as the stamp ($1.5 \times 3 \text{ cm}^2$) using this

technique. In the SEM image, Figure 2b, the xGnP are observed in multilayer stacks created by the LBL process. Additionally, the xGnP packed densely enough on the surface to conduct electrical current. Atomic force microscopy (AFM) analysis shows that the transferred four and six bilayer films have a thickness of 85 nm and 120 nm, respectively.

To ensure complete film transfer from the stamp, we used a negatively charged green fluorescent dye, 6-carboxyfluorescein (6-CF), to confirm total transfer of the xGnP-SPS containing films. Figure 3a shows the surface of a PDMS stamp that was placed in a 6-CF solution before patterning. Since PDAC was the last adsorbed layer in the composite film, the 6-CF was adsorbed to the outer surface and can be seen on both the peaks and valleys of the patterned stamp. A second stamp was also placed in the dye after patterning,

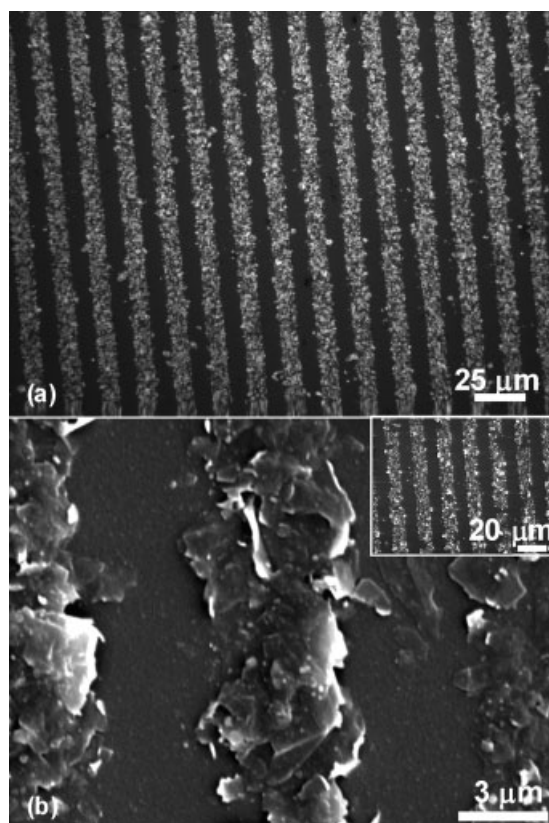


Figure 2. a) Optical microscopy and b) SEM images of PAH/(xGnP-SPS/PDAC) $_4$ films transferred to a PEM-coated substrate via IPT.

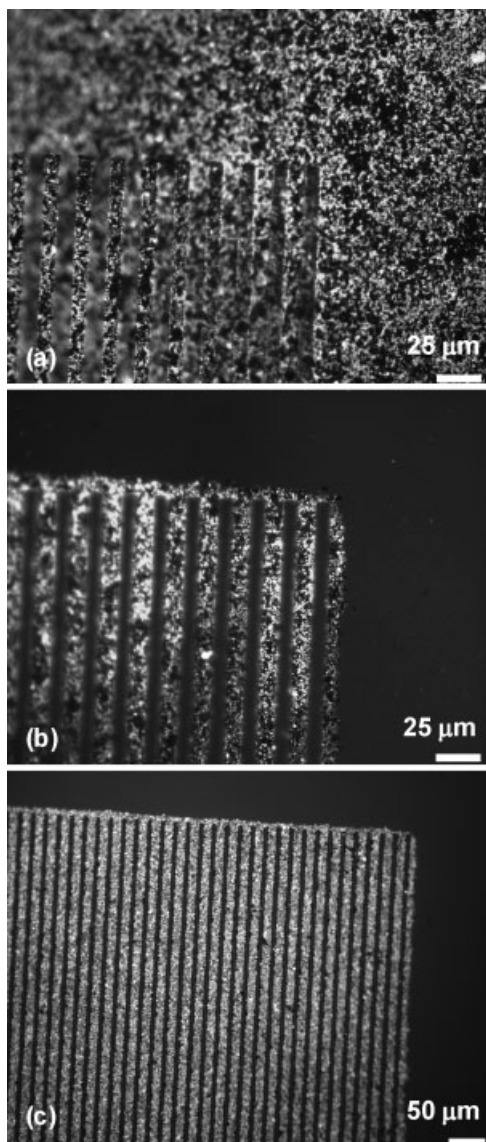


Figure 3. Fluorescent microscope images of PDMS stamps coated with PAH/(xGnP-SPS/PDAC)₄ films and dyed with 6CF a) before and b) after IPT stamping. c) An optical microscopy image of a stamp after the film is transferred.

Since the PAH/(xGnP-SPS/PDAC)₄ film was transferred to the surface, the dye can only be seen on the inset regions of the stamp surface shown in Figure 3b (the film on the large homogeneous area to the right transfers due to sagging of the stamp). The optical microscope image (Fig. 2c) also confirms that there were no xGnP-SPS on the raised regions of the stamp.

The electrical properties of the films were determined by measuring the surface resistance. Films of xGnP-SPS were created on PAH adhesion layers at a pH of 7.5 or 10. However, the films formed onto the layers formed at 7.5 had a higher resistance than films formed on adhesion layers adsorbed at a pH of 10. Figure 4 displays the results of measurements of

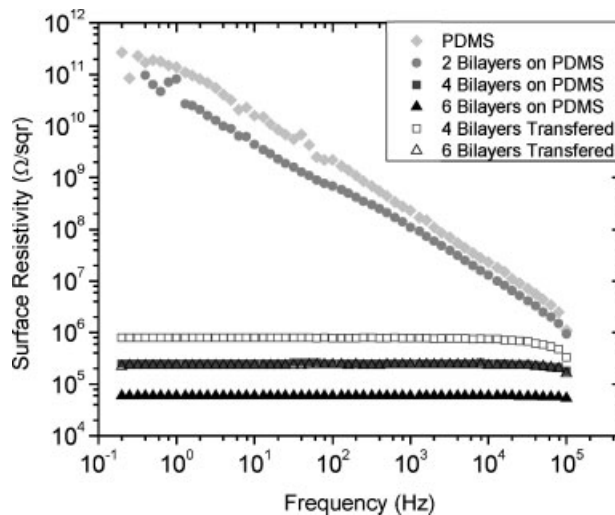


Figure 4. Surface resistance vs. frequency for various films on PDMS and films transferred to PEM surfaces.

xGnP-SPS films with an adhesion layer formed at a pH of 10. Uncoated PDMS substrates and two bilayers on PDMS were found to be nonconductive. (Samples on PDMS were measured without the final layer of PDAC.) However, when four bilayers are used, the percolation threshold is surpassed and the samples are found to be conductive. Six bilayer films on PDMS show the lowest surface resistivity of $5.8 \times 10^4 \text{ Ohm/square}$. This resistance is comparable to previous reports by Kotov et al. which used exfoliated graphite created by oxidation to create the film, followed by a reduction step to render the film conductive.^[15] However, our process does not include oxidation or reduction steps. In addition, we use a smaller number of layers, six instead of ten, to achieve nearly the same resistance. The addition of more bilayers could be used to further reduce the surface resistivity of the film. Four and six bilayer films were transferred from PDMS to PEM coated glass slides. The surface resistance of these transferred films increased slightly. The increase in resistance is caused by the presence of the dense 4–5 nm PAH layer which covers the xGnP-SPS layer.^[19,26] We attempted to lower the resistance of the transferred films by removing the layer of PAH. Soaking the samples in a high pH solution to cause charge screening and removal of the PAH was unsuccessful. Additionally plasma treatment did not remove the PAH layer. Heating the samples to 275 °C for 3 hours to burn out the polymers also did not lower the measured resistance of the transferred six bilayer films. Films with surface resistivities in this range are potentially useful for controlling electrostatic charge dissipation and preventing damage to surrounding electronic equipment.^[27,28]

In conclusion, we report a novel method to create and pattern conductive polymer-xGnP multilayered nanocomposite films using the IPT method. Conductive xGnP films were created on PDMS stamps without the use of oxidation/reduction steps. By first adsorbing a weakly bound PAH layer

onto a PDMS stamp the entire multilayer film can be completely transferred to a PEM coated substrate. This allows for these patterned films to be transferred to nearly any surface. The transferred films show excellent conductivity for electrostatic dissipation applications. However, further increasing the conductivity by incorporating conductive polyelectrolytes and measurement of the films anisotropic conductivity remains as future work.

Experimental

Materials: Poly(diallyldimethylammonium chloride) (PDAC, $M_w \sim 70,000$), sulfonated poly(styrene), sodium salt (SPS, $M_w \sim 150,000$), 6-carboxyfluorescein (6-CF) and nitrocellulose membranes (0.22 μm pore diameter) were purchased from Sigma–Aldrich (Milwaukee, WI) and used as received. Poly(dimethylsiloxane) (PDMS) was created using a Sylgard 184 kit from Dow Corning (Midland, MI). Poly(allylamine hydrochloride) (PAH, $M_w 60000$) was obtained from Polysciences, Inc. (Warrington, PA). Graphite Intercalate Compounds (GIC) were purchased from UCAR Inc. Purified deionized (DI) water was obtained from a Barnstead Nanopure Diamond (Barnstead International, Dubuque, IA, resistivity $>18.2 \text{ M}\Omega \text{ cm}$) and used exclusively for all experiments. All polymer solution concentrations were based on the repeat unit of the polymer.

xGnP Preparation: xGnP are created using a process developed in the Composite Materials and Structures Center and MSU [29, 30]. GIC which are acid intercalated graphite about 300 μm in size were expanded using microwave radiation. The microwaves cause the intercalated acids to evaporate quickly and expand the multilayered graphite. The expanded graphite is then ultrasonicated using a tip sonicator [23]. This creates xGnP of about 15 μm in diameter and 5–10 nm in thickness. The size of the xGnP is then reduced to a 0.5–1 μm diameter using ball milling [13, 14, 31]. xGnP used in the following experiments were 5–10 nm in thickness with a 0.5–1 μm diameter. 0.1 g of xGnP was added to a 100 mL aqueous solution containing 0.01 M SPS and 0.1 M NaCl. The solution was then tip sonicated with a Virsonic 100 (SP Industries Inc, Warminster, PA) for 30 min, agitated with stirring for 24 h and filtered using nitrocellulose membranes. The SPS coated xGnP were then redispersed in 100 mL of DI water and tip sonicated for 20 min. After sonication, any undispersed nanoplatelets on the surface of the solution were removed using wax paper. This xGnP-SPS solution was then used for LBL assembly.

Film Preparation on PDMS: PDMS stamps were fabricated by pouring a degassed 10:1 prepolymer/initiator mixture over a patterned silicon wafer (Keck Microfabrication Facility, Michigan State University) and curing overnight in an oven at 60 °C. The stamps were then placed in a 0.05 M solution of PAH at a pH of 7.5 or 10 for 20 min. The samples were then alternately dipped by hand into the xGnP-SPS solution (described above) and a solution containing 0.01 M PDAC and 0.1 M NaCl. The polymer dipping time was 20 min which was followed by two 5 min washing steps in water before the next polymer layer was adsorbed. Typically 4 or 6 bilayers were used which has a positively charged outer PDAC surface.

Substrate Film Preparation: A Carl Zeiss slide stainer (Richard-Allan Scientific, Kalamazoo, MI) was used to perform LBL assembly on glass microscope slides. Glass slides were prepared by bath sonication (Branson Ultrasonics Corporation, Danbury, CT) for 20 min in an aqueous Alconox (Alconox Inc., New York, NY) solution followed by bath sonication for 10 min in DI water. The slides were then dried with nitrogen and oxygen plasma cleaned in a Harrick Plasma cleaner (Harrick Scientific Corporation, Broadway Ossining, New York) for 10 min at a pressure of 125 mTorr. After plasma cleaning, LBL assembly of PDAC and SPS was performed using 20 minute immersion

times followed by two 5 min washing steps to form 10 bilayers with a negatively charged SPS outer surface denoted as (PDAC/SPS)¹⁰.

Intact Pattern Transfer (IPT): The coated stamps were removed from the washing solution and gently dried with nitrogen. The composite film formed on a PDMS stamp with an outer PDAC surface was misted with DI water from a spray bottle and placed in conformal contact with the outer SPS surface on the PEM coated substrate. After one hour of contact time the dry stamp was removed. The xGnP containing film transferred to the surface due to the strong electrostatic forces created during rearrangement of the polymer chains while the samples were still slightly moist from the DI water spraying.

Characterization: Optical and fluorescent microscope images were obtained using a digital camera mounted on a Nikon Eclipse ME 600 or ME 400 respectively. 6-CF was dissolved in 0.1 M NaOH and used to selectively bind to positively charged regions on the surface. SEM images were obtained using a JOEL 6400 V microscope equipped with a LaB6 filament and operated at 8 keV. AFM images were obtained in tapping mode using a Nanoscope IV multimode scope (Digital Instruments). The conductivity of the samples was measured using Impedance Spectroscopy. Two copper tape electrodes were attached to the surface of the film and the resistance (R) was measured using a 0.1 V potential. The resistances were normalized by the dimensions of the films and reported as a surface resistivity ($\rho_s = R \times L/D$) where L is the length between the electrodes and D is the width of the electrode [27, 28].

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