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Electrochemical fabrication of graphene nanomesh *via* colloidal templating[†]

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A simple electrochemical fabrication of graphene nanomesh (GNM) via colloidal templating is reported for the first time. The process involves the arraying of polystyrene (PS) spheres onto a CVDdeposited graphene, electro-deposition of carbazole units, removal of the PS template and electrochemical oxidative etching. The GNM was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy.

Discovered in 2004, graphene, with its long-range π -conjugation, has attracted tremendous attention for its exceptional structural, chemical, mechanical, thermal, electrical and even biomedical properties.¹ The mean free path for electron-phonon scattering in graphene is long (>2 mm) resulting in room temperature electronic mobility that could potentially exceed 200 000 cm² V⁻¹ s^{-1,2} Even with these outstanding charge-transport characteristics, graphene cannot be used as field-effect transistors (FETs) device operating at room temperature due to its zero band gap.² One way to open a band gap in graphene-based electronic systems was recently demonstrated through the fabrication of graphene nanomesh (GNM), a nano-perforated form of graphene. Processes such as block-copolymer lithography which are typically followed by reactive ion etching (RIE), and nanoparticle-assisted perforation were reported to have successfully opened a technologically relevant band gap for graphene. Though these methodologies are deemed to be scalable to batch-process large-area substrates while simultaneously achieving exceptionally small features $(<10 \text{ nm})^2$ the tedious and costly procedure opens an opportunity for simpler alternative techniques that are ideal for economies of scale. This work reports for the first time, a simple solution-processable electrochemical fabrication method of graphene nanomesh (GNM) via colloidal templating in tandem with electrochemical oxidative etching.

Apart from its important use in FET devices, GNM has been shown to exhibit interesting properties for a myriad of applications such as supercapacitor electrodes, surface enhanced Raman scattering (SERS), ferromagnetism, chemical sensors and *in vivo* photothermal therapy.³ More recently, GNM was decorated with materials such as DNA and Fe₂O₃ nanoparticles for the detection of chemical vapors (*e.g.* dimethyl methylphosphonate, dinitrotoluene, and propionic acid) and enhancement of electrode performance, respectively.⁴ With increasing interest on GNM's properties and applications, it is essential to devise methodologies that are simple, economical and offers facile control of mesh size.

In this contribution, we report the fabrication of GNM *via* a colloidal templating approach which offers a facile and accurate control of array formation by simply varying the size of the colloidal template.⁵ Also, this method is a room-temperature technique and does not involve intricate instrumentation. Electrochemical oxidative etching (EOE) was employed to puncture holes on the graphene sheet. EOE was recently shown to be effective in patterning single-walled carbon nanotube films.⁶ To the best of our knowledge, this is the first report on nanostructuring graphene, utilizing colloidal polystyrene (PS) spheres coupled with electrochemical etching.

Scheme 1 illustrates our approach in the fabrication of GNM. As a proof of concept, commercially available graphene film obtained by chemical vapor deposition (CVD) on a nickel substrate was used as a starting material. PS spheres were layered by the so-called Langmuir–Blodgett (LB)-like technique.⁵ The hexagonal arrangement of the PS particles serves as the template for the electrodeposition of the monomer we tagged as G1CbztEG ((2-(2-(2-(2-hydroxy)ethoxy)ethy)-3(4-(9H-carbazol-9-yl)butoxy)-5-(4-(9H-carbazol-9-yl)butoxy))-benzoate). The dissolution of PS in tetrahydrofuran (THF) affords the formation of hexagonal cavities exposing the graphene underlayer. EOE on the exposed graphene film was accomplished in three-electrode system. The formation of GNM was monitored by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Colloidal templating approach offers a facile and accurate control of the array by simply varying the shape of commercially

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Scheme 1 Colloidal templating. (a) Pristine graphene deposited by CVD. (b) PS microspheres are deposited on graphene. (c) Electropolymerization of the G1CbztEG monomer (d) into the interstitial spaces of the colloidal array forming a polymer network. (e) PS is selectively etched by the action of THF, resulting in the exposure of graphene. (f) Electrochemical oxidative etching (EOE) destroys the exposed graphene. (g) The polymer network is dissolved (h) by lift-off, free-standing graphene nanomesh is obtained.

available colloidal spheres. The formation of monolayer ordering is reported to be highly dependent on the vertical speed, particle and surfactant concentration.⁷ We have established the optimal conditions for colloidal layering on pristine graphene. Fig. 1a shows the pristine graphene sheet grown *via* CVD. It is noteworthy that not only PS spheres form a monolayer on the graphene surface, but the PS deposition also follows the groove or the curvature of the sheet (Fig. 1b). This is especially interesting because this suggests that PS nanoparticles can be easily deposited onto graphene and does not require a completely flat graphene surface. This extraordinary hexagonal array formation may be due to the strong π - π interaction of graphene and polystyrene. The line profile shows the diameter of the PS spheres corresponding to homogeneous 500 nm PS particles (Fig. 1c).

The monomer, G1CbztEg, was previously synthesized by our group. 8 We conjecture that the hydrophilic ethylene glycol



Fig. 1 Colloidal templating and electro-deposition (a) AFM image of CVD-grown graphene on a nickel substrate. (b) Monolayer ordering of 500 nm PS spheres on top of graphene. (c) Line profile of PS spheres. (d) CV profile of the electrodeposition of G1CbztEG. (e) Monomer-free scan operated under the same CV conditions.

moiety will facilitate the diffusion of ions during EOE. Owing to its carbazole group, the molecule can be electrodeposited into the interstices of the colloidal crystals forming a conducting polymer network upon cross-linking, which proceeds *via* radical cation mechanism whereby both inter- and intra-molecular cross-linking can occur.⁹ The electrodeposition was observed by the increasing redox peak (between 0.7 to 0.9 V) of the poly(carbazole) as the potential was swept from 0–1.1 V for 10 cycles (Fig. 1d). To ensure complete cross-linking, monomer free scan was performed. The redox peak of poly(carbazole) is apparent which fairly became constant from the 3rd to 10th sweeps, suggesting complete crosslinking (Fig. 1e).

The PS microspheres were then etched by THF to expose the graphene under-layer. It should be noted that the polymer network is not soluble in THF. The inverse colloidal crystals are intact and are also present on the curvature of the sheets (Fig. 2a), substantiating the fact that PS particles can be deposited regardless of the planarity of the graphene sheets. The now exposed graphene is available for different types of chemistry, in this case, oxidative etching. The electrochemical etching employed in this work was based on an earlier work where CNTs were electro-patterned in an aqueous solution with an optimal potential of 3 V.⁶ The underlying concept relies on the conversion of solid carbon to CO_2 . This electrochemical oxidation was also performed on other carbonaceous materials



Fig. 2 Electrochemical oxidative etching: (a) graphene sample after etching of PS (b) electrochemical set-up for oxidative etching. (c) Plot of current vs. time in response to applied potential (3 V) in 0.1 M NaCl electrolyte solution (inset: electrochemical etching of graphene).

like coal, carbon-black and diamond-like carbon.¹⁰ In this light, we devised a similar electrochemical set-up shown in Fig. 2b where the graphene deposited on nickel served as the working electrode, and platinum wire and Ag/AgCl as counter and reference electrodes, respectively. 0.1 M NaCl was used as a supporting electrolyte and a constant voltage of 3 V was applied. The shape of the *I*-*t* curve as shown in Fig. 2c is similar to that of SWCNTs oxidatively etched under the same conditions, where initially, there is a gradual increase in current and a sudden, fast current fall-off.⁶ During this oxidative process, the exposed graphene is converted to CO_2 . The overall reaction between graphene and water can be expressed as:

Graphene(s) + $2H_2O(l) \rightarrow CO_2(g) + H_2(g)$

SEM and AFM imaging were then used to visualize the resulting material after electrochemical oxidative etching. Fig. 3a displays the formation of graphene nanomesh (GNM). A large area AFM image of GNM can be found in Fig. S1 (ESI†). To further evidence the formation of GNM, height profiles as well as the RMS roughness were obtained by AFM measurements. After PS-etching (Fig. 3b), the line profile shows an approximate height of 5.5 nm. Subsequently after electrochemical etching, the height increased to approximately 8 nm (Fig. 3c). This result confirms the successful



Fig. 3 (a) SEM image of GNM. AFM topography image (b) after PSetching, (c) after electrochemical oxidative etching, and (d) after dissolving the poly(carbazole) network.

etching of the graphene underlayer as the perforations were deeper. After the dissolution of the colloidal pattern, an approximately 5 nm height (Fig. 3d) was observed. This decrease in height suggests that the polymer pattern on top of graphene was etched away. The small specks of material in Fig. 3d may have come from the polymer patterns that were not completely dissolved. We also utilized surface roughness data to furthermore confirm the formation of GNM. The RMS value (5.8 nm) after oxidative etching was roughly 4 nm higher than the un-etched film (Fig. 4b). The increase in roughness after oxidative etching is due to deeper perforations resulting from the removal of the graphene underlayer, thus making the film rougher than it used to be. Upon removal of the polymer pattern, the roughness value significantly lowered to 3.15 nm due to the decrease in height caused by the removal of the polymer pattern.

We also characterized the resulting GNM in terms of neck width (the smallest distance between pores), a characteristic that is inversely proportional to band gap opening.¹¹ In this method, it is obvious that such a property can be tuned by simply varying the size of PS spheres. The average neck width of the GNM fabricated herein is 94 ± 13 nm (Fig. 4a). This is fairly large compared to most of the GNMs fabricated in the past, but this is due to the fact that 500 nm PS spheres were used as templates.^{2,11} Lastly, Raman spectroscopy was utilized to characterize the resulting GNM. Raman spectroscopy is an indispensable technique for the study of the electronic and structural properties of graphene materials, and also surface defects. The Raman signature of the graphene sample is typically composed of a G-band arising from the first order scattering of the E_{2g} phonon of sp² carbon atoms and a disorder band or commonly known as the D-band which arises from the breathing mode of κ -point photons of A_{1g} symmetry.¹² The 2D band is related to the number of layers of graphene. A weak D band in graphene ($\sim 1450 \text{ cm}^{-1}$) indicates that the graphene used is of high-quality (Fig. 4b). After etching, it can be noticed that the D band in GNM significantly increased. This is expected since GNM has now a large density of edges, which further evidence the successful electrochemical etching. On the other hand, the G band for graphene and GNM is centered at 1582.3 cm⁻¹ suggesting that there is no change in the state of doping.¹¹ This is expected since the neck width is fairly large. However, what is interesting is the appearance of the peak



Fig. 4 (a) AFM topography image of GNM showing an average neck width of 94 \pm 13 nm and (b) Raman spectra of graphene before and after electrochemical etching.

at 1454.7 cm⁻¹ for GNM. This is a similar peak observed by Ren *et al.* for graphene nanoribbons (GNRs) which are stripes of graphene with a width typically smaller than 100 nm.¹³ This particular Raman signal arises from the localized vibration of the edge atoms of zigzag GNRs terminated with H atoms. Another interesting fact is that GNRs with zigzag-shaped edge are typically metallic with peculiar edge states on both sides of the ribbon regardless of their width. Jung *et al.* also noted that GNM can be thought of as many highly interconnected GNRs¹¹ and the similarities observed herein suggest that our fabricated GNMs may well behave just like GNR. However, further studies are necessary to evaluate this observed phenomenon. The fabrication and characterization of GNM with narrower neck widths using smaller PS spheres are currently underway.

In summary, we have demonstrated a simple and costeffective electro-patterning method in tandem with colloidal templating to afford the fabrication of GNM. The processes described herein are mainly solution processes that do not require intricate instrumentation. The technique presented is a promising route to fabricate GNMs as evidenced by SEM images, AFM topography, surface roughness and Raman spectroscopy. We envision that this patterning technique will facilitate the fabrication of graphene-based electronic devices and will be useful in other applications such as chemical sensors and supercapacitors.

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