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Deposition of bio-mimicking graphene sheets with lotus leaf-like and cell-like structures on the nickel substrate

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Bio-mimicking graphene films, deposited on textured nickel substrates, were synthesized by the following method: replicating the surface textures of the lotus leaf by polymer duplication, fabricating textured nickel substrates by electroplating on the polymer coated with a Au film, preparing bio-mimicking graphene oxide films on the nickel substrates by vacuum filtration, and electrochemical reduction. By controlling the vacuum filtration, this replica method can not only replicate the lotus leaf structure by a graphene film, but also can achieve a novel cell-like graphene film.

bio-mimicking, graphene film, lotus leaf-like structure, cell-like structure

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Since graphene was first isolated in 2004 with the help of Scotch Tape, researchers have excitedly turned to the material to discover its potential applications, which include nanoelectronics, sensors, batteries, supercapacitors, hydrogen storage and nanocomposites [1–5]. Based on the excellent flexibility and mechanical stiffness, graphene oxide (GO) and graphene sheets can indeed be assembled into paper-like materials through flow-directed assembly by vacuum filtration of their colloidal dispersions [6,7]. Also, employing their stretchable physical property, GO and graphene films can be transferred to an arbitrary substrate [8].

Biomimic micro textures, owing to their intrinsic geometric microstructure, bring about many unique properties [9–14]. It is well known that the lotus leaf structure, which includes micro-bumps and a thin wax film on the surface, has attracted much interest with its self-cleaning function and low hysteresis ability to carry effortlessly the contaminations attached to the leaf when the surface is slightly tilted. Accordingly, there has been much effort to design and synthesize multifunctional artificial materials by mimicking the surface of the lotus leaf [15–19]. It is expected that, if graphene sheets were assembled into bio-mimicking lotus leaf surfaces, it would stimulate some novel functional properties for various potential applications.

In this study, a preparation of the bio-mimicking graphene films with lotus leaf-like and cell-like structures on nickel substrates was first reported. A simple combination of duplication-electroplating resulted in fully duplicated surface micro textures of lotus leaf on nickel substrates. A controllable vacuum filtration realized the textured GO films on the bio-mimicking nickel substrates. Owing to the excellent flexibility and ultrathin structure of GO and graphene sheets, not only the morphology of bio-mimicking nickel substrates can be retained, also the original isolated micro-bumps on the surface can be linked with graphene sheets through prolonging the titration time during the vacuum filtration.

1 Experimental

A fresh lotus leaf was placed in a glass dish. Polydimethylsiloxane (PDMS) was poured over the leaf, held for 2 h at room temperature (RT) and then cured in a drying oven at 60°C for 10 h, to replicate the surface micro textures of the

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lotus leaf. The textured PDMS film was gently peeled off from the lotus leaf. After that, a gold coating with an approximate thickness of 100 nm was sputtered on the textured PDMS and then a nickel layer (the thickness was above 100 μm) was electrodeposited on the surface of the gold coating. The PDMS mold was peeled off from the textured nickel layer, to form a freestanding nickel slice. GO was prepared from natural graphite [20–22] (See the Supporting Information for details). A homogeneous GO aqueous suspension (0.5 mg/mL) was obtained with the aid of sonication using a high-power (800 W) ultrasonic pole at 0°C for 1 h, and then the suspension was centrifuged at 3000 r/min for 30 min. The resulting suspension was placed in a funnel and dropwise added (1 drop/min) on the textured nickel slice (1 cm×1 cm), which was fixed on the center of a Millipore filter (50 mm in diameter and 0.45 μm in pore size). The vacuum filtration experiment was carried out for different durations (2 and 4 d) to prepare bio-mimicking GO films with different surface textures. Finally, the textured GO films were electrochemically reduced in the 0.1 mol/L KCl solution using an Autolab Electrochemical Working Station. The textured GO and graphene films were characterized by field emission scanning electron microscope (FE-SEM, JSM-6701F) and Raman spectroscopy (JY-HR800, the excitation wavelength at 532 nm). The electrical conductivity was measured by a standard four-probe method.

2 Results and discussion

As shown in Figure 1, the success of the technique in the process flow sheet to create the graphene film of bio-mimicking lotus leaf requires four key steps. Firstly, a PDMS film is used to replicate the surface micro textures of the lotus leaf to obtain a negative impression of the bio-mimicking micro textures. Secondly, a nickel layer is electrodeposited on top of the textured PDMS film to obtain the positive replica of the lotus leaf after removing the textured polymer film. In this step, since the PDMS is an insulating material, a thin gold coating should be sputtered on the surface of the textured PDMS in advance, to aid the subsequent electroplating of nickel. Thirdly, a GO film is placed on top of the textured nickel substrate by vacuum filtration. In this step, through adjusting the titration time of the GO suspension during the filtration, two different morphologies can be obtained. Finally, the textured GO films are electrochemically reduced into textured graphene films at RT.

SEM images revealed the surface textures of the lotus leaf and its replicas. Figure 2(a) demonstrates the arrayed part of the bumps on the textured nickel surface as well as the one-dimensional order of the microstructure similar to that of the SEM image of the lotus leaf (shown in the inset). Figure 2(b) presents a typical low-magnification SEM image of the textured GO film when the copy of the structure

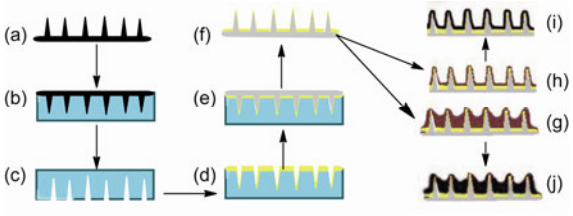

Figure 1 (Color online) The process of creating the graphene films with bio-mimicking textures: (a) the original lotus leaf; (b) replicating the surface micro textures of the lotus leaf with PDMS; (c) the PDMS film with a negative impression of the bio-mimicking textures; (d) sputtering gold on the textured PDMS film; (e) electrodepositing nickel layer on the surface of the textured PDMS film; (f) the nickel slice with the bio-mimicking textures; (g) and (i) the GO and graphene films with lotus leaf-like structures prepared by vacuum filtration followed by electrochemical reduction; (h) and (j) the GO and graphene films with cell-like structures prepared by vacuum filtration followed by electrochemical reduction.

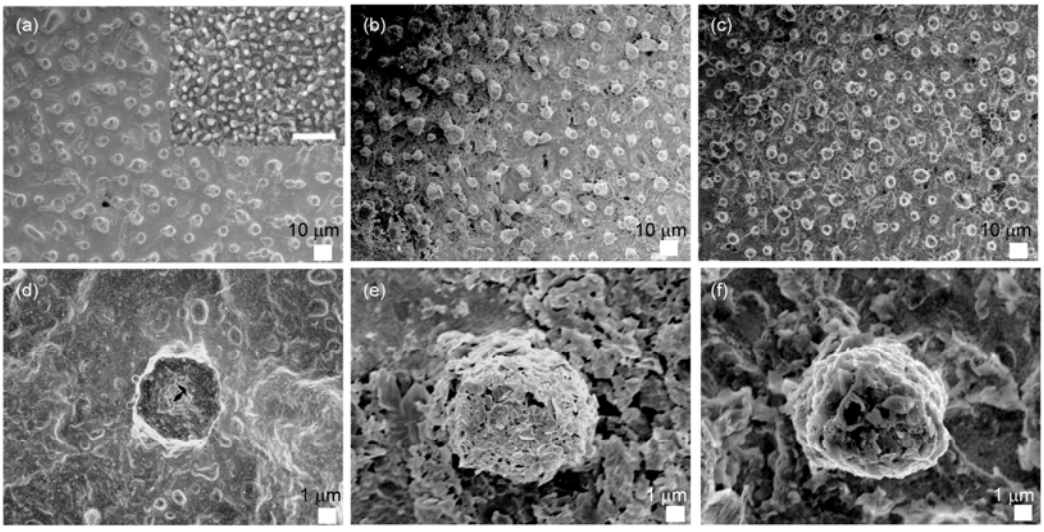

Figure 2 SEM images of top view of the textured nickel slice (a) and (d); the textured GO film with lotus leaf-like structures (b) and (e); and the textured graphene film with lotus leaf-like structures (c) and (f). The inset in (a) is the typical SEM image of the lotus leaf and the scale is 50 μm.

of the lotus leaf was completed. The textured GO film was then electrochemically reduced into the graphene film and the corresponding low-magnification SEM image is shown in Figure 2(c). It is clear seen that the surfaces of the as-obtained GO and graphene films were both composed of micro-scale bump arrays, which were in accordance with the surface morphology of the textured nickel slice. The average size the bumps was at about 3–6 μm and the distance between the adjacent bumps was of about 5–20 μm. Figure 2(d)–(f) shows the typical SEM images of the individual bumps on nickel, GO and graphene films. Owing to the wrapping of the GO and graphene, the sizes of the bumps on the textured GO and graphene films were larger than that of the bump on the textured nickel slice.

In our vacuum filtration step, through prolonging the titration time of GO suspension, another surface morphology was obtained on the GO film and on the subsequent graphene film. As shown in Figure 3(a) and (c), some two adjacent bumps were linked with GO sheets. Such morphology was also retained after the electrochemical reduction of GO (Figure 3(b) and (d)). In other words, some adjacent bumps were connected with graphene sheets, as a result of the formation of the textured graphene film with cell-like structures.

As shown in Figure 4, the Raman spectra of two textured GO films were identical, which presented two features: D peak at 1358 cm^{-1} and G peak 1605 cm^{-1}, i.e. assigned to sp^2-hybridized C–C bonds. Although the Raman spectra of two textured graphene films also had both D and G bands at the similar positions, the intensity ratio of D/G increased obviously in comparison with that of the GO spectra. It agreed well with the graphene materials prepared by hydrazine reduction [22,23], indicating the realization of deoxygenation in electrochemically reduced graphene films. In addition, the result of electrical conductivity measurements showed that the electrical conductivity of the textured graphene films was approximately 15 S/cm, which was much larger than that of the textured GO films (< 10^{-7} S/cm).

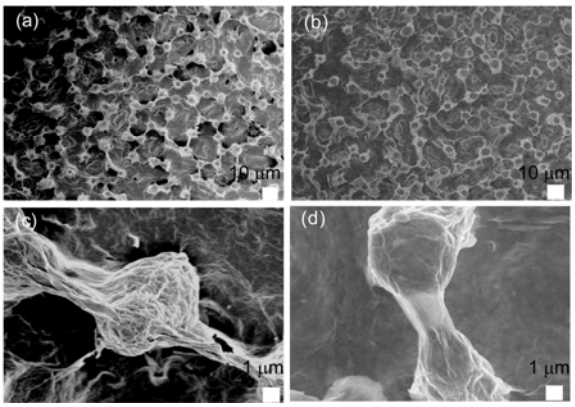

Figure 3 SEM images of top view of the textured GO film with cell-like structures (a) and (c); and the textured graphene film with cell-like structures (b) and (d).

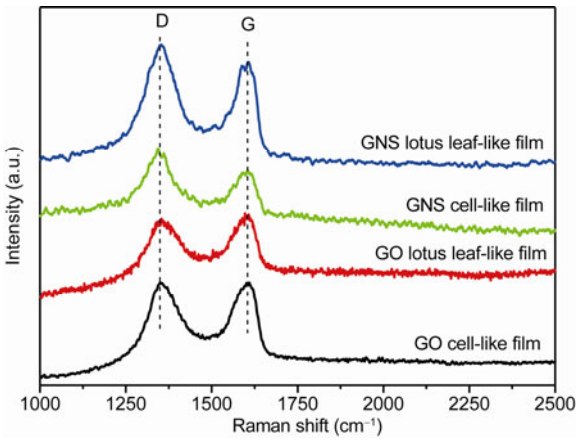

Figure 4 (Color online) Raman spectra of the bio-mimicking GO and graphene films with lotus leaf-like structures and cell-like structures.

X-ray photoelectron spectroscope further revealed that the GO film was deoxygenized by electrochemical reduction (see the Supporting Information for details). Therefore, electrochemical reduction of GO, using applied DC bias by scanning the potential at RT, is in favor of fabricating highly ordered and controllable graphene films on the electrode material [24].

3 Conclusions

It is well known that GO sheets have excellent flexibility and mechanical stiffness. In our synthesis, when the GO suspension was dropwise added on the textured nickel slice which was fixed on the Millipore filter, GO sheets were adsorbed onto the textured nickel surface and onto exposed filter surface through flow-directed assembly by vacuum filtration. Because of the relatively high pressure of vacuum filtration (0.08 MPa) and slow droplet rate, GO sheets adsorbed on the micro-scale bumps bent and then wrapped around the bumps under the flow-inductive force. As a result the morphology of the obtained GO film was in accordance with the textured nickel slice. With prolongation of titration time, the flow-inductive force became weaker and weaker. In this situation, the GO sheets freshly absorbed on the bumps, especially some large size GO sheets simultaneously contacted with the adjacent two bumps, failed to bend completely and wrap around the bumps. On the contrary, they merely linked with the adjacent bumps and other parts bent towards the flow direction, as a result of the formation of the cell-like structures. It should be mentioned that, the droplet rate and the total titration time of the GO suspension must be carefully controlled in the replication of the micro-scale bumps from nickel surfaces by using vacuum filtration. With the relatively short titration time of 2 d, the GO film with lotus leaf-like structures was formed; with the relatively long titration time of 4 d, the GO film with cell-like structures was formed.

The successful preparation of the textured GO and graphene films on nickel slices proved that the flow-directed assembly by vacuum filtration is an efficient approach to replicate the micro-scale bumps on the nickel surface. Furthermore, with the controlled droplet rate and calculated increase in the quantity of the GO suspension, the new cell-like GO and graphene films can be prepared. We believe that, this strategy can be used to prepare the textured GO and graphene films on different substrates with various geometric microstructures. Also, the textured graphene films with bio-mimicking structures are promising materials for various novel applications, such as nanoelectronics, electrodes, capacitors, batteries and culture of electrically excitable cells.

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Supporting Information

SI 1 Preparation of graphene oxide (GO)

SI 2 Structural characterization of GO and GNS

Figure S1 Characterization of GO: XRD patterns (a) and TEM image (b).

Figure S2 The C 1s XPS spectra of the textured GO film and the textured graphene film. It is revealed that the GO film was deoxygenized by electrochemical reduction.

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SI 1 Preparation of graphene oxide (GO)

In a typical synthesis, graphite powder (3 g, 325 mesh) was put into an 80°C solution of concentrated H_2SO_4 (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). The mixture was kept at 80°C for 4.5 h using a hotplate. Successively, the mixture was cooled to room temperature and diluted with 0.5 L of H_2O and left overnight. Then, the mixture was filtered and washed with H_2O using a 0.45 μm Millipore-filter to remove the residual acid. The product was dried under ambient condition. This pre-oxidized graphite was then subjected to oxidation by Hummers' method described as follows. Pretreated graphite powder was put into cold (0°C) concentrated H_2SO_4 (120 mL). Then, $KMnO_4$ (15 g) was added gradually under stirring and the temperature of the mixture was kept to be below 20°C by cooling. Successively, the mixture was stirred at 35°C for 2 h, and then carefully diluted with 250 mL of H_2O. After that, the mixture was stirred for 2 h, and then additional 0.7 L of H_2O was added. Shortly, 20 mL of 30% H_2O_2 was added to the mixture. The resulting brilliant-yellow mixture was filtered and washed with 10 wt% HCl aqueous solution (1 L) to remove metal ions followed by washed repeatedly with H_2O to remove the acid until the pH of the filtrate was neutral. The GO slurry was dried in a vacuum oven at 60°C and purified by dialysis for one week.

SI 2 Structural characterization of GO and GNS

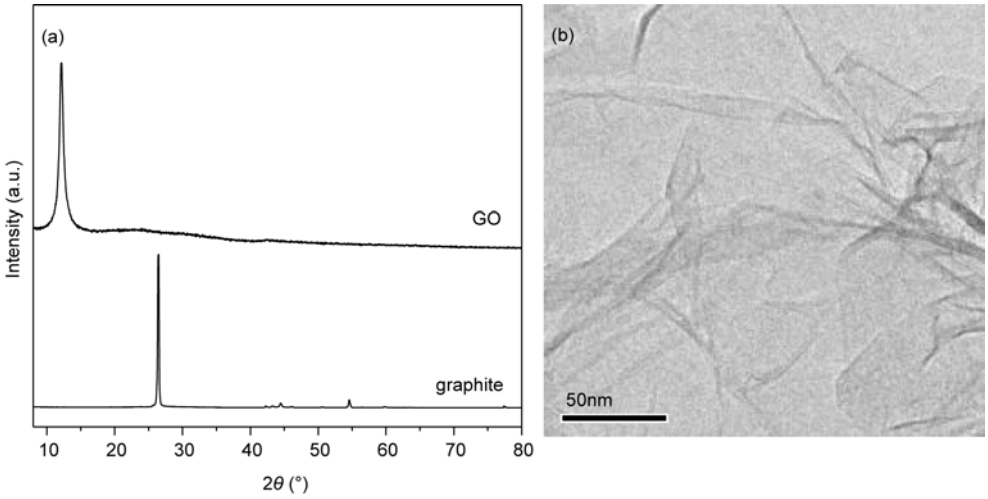

Figure S1 Characterization of GO: XRD patterns (a), and TEM image (b).

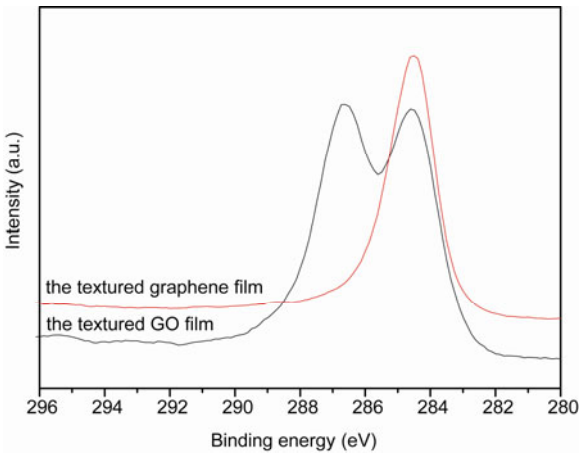

Figure S2 The C 1s XPS spectra of the textured GO film and the textured graphene film. It is revealed that the GO film was deoxygenized by electrochemical reduction.