Layer-by-layer assembly of graphene and gold nanoparticles by vacuum filtration and spontaneous reduction of gold ions†

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Layer-by-layer films comprised of alternating graphene and gold nanoparticle layers are readily produced by the two-step procedure involving the use of vacuum filtration of a reduced graphene oxide solution to fabricate the graphene thin film on the quartz substrate, followed by gold nanoparticle formation by spontaneous reduction of gold ions in a gold salt solution on the graphene films.

Graphene and its derivatives have attracted considerable attention in recent years because of their unique physical properties.[1,2] Owing to their two-dimensional plate-like structures, graphene and bilayers containing graphene are zero-gap semiconductors that exhibit larger aerial overlap than carbon nanotubes. It has been reported that hybridization of graphene with functional nanomaterials usually enhances the attributes of each of the components, as reflected in electrical, thermal, chemical, and mechanical properties.[3–6]

Previous methods to fabricate graphene hybrids involved mixing a graphite oxide dispersion and metal precursors, followed by reduction.[5,6] As in the construction of other self-assemblies, the control of the periodic structures of the hybrid graphene materials over large areas is essential for functional nanomaterial applications that require the integration of the properties of the disparate materials. Below, we describe the results of an investigation that has led to the development of a new method for the layer-by-layer (LbL) assembly of gold nanoparticle-decorated graphene thin films. Importantly, the technique does not require the use of added agents for the reduction of gold ions on graphene sheets, a distinct disadvantage over previously developed procedures. In this technique, a reduced-graphene oxide (RGO) thin film is prepared by vacuum filtering a solution containing a suspension of RGO. This is followed by deposition of the gold nanoparticles on the RGO film. Moreover, we have shown that it is possible to employ this method consecutively to construct LbL structures.

Scheme S1 (see ESI†) shows the overall process involved in fabricating the RGO-gold nanohybrid films and LbL assemblies. The graphite oxide used for this purpose was generated from natural graphite by using a modification of the method described by Hummers.[7–9] Reduction of graphene oxide (GO), which was made by the exfoliation of graphite oxide using sonication, was performed by mixing a homogeneous GO aqueous dispersion with solutions containing hydrazine (weight ratio of hydrazine to graphene oxide of 7 : 10)[10] and ammonia. The vacuum filtration method[11] was used to prepare a uniform LbL film of RGOs and gold nanoparticles. The RGO film on the quartz substrate was then immersed in an aqueous solution of $HAuCl_4 \cdot 3H_2O$. During the immersion process, gold nanoparticles were produced by spontaneous reduction of Au^{3+} on the RGO sheets by a mechanism that will be discussed below. A LbL assembly of RGO sheets and gold nanoparticles was fabricated by repetitive implementation of vacuum filtration and gold nanoparticle formation steps.

AFM, XPS, and UV-vis–NIR absorption spectroscopy were used to compare the structures and morphologies of the graphene before and after reduction. The absorption maxima in the UV spectra of the GO and RGO films are 227 nm and 268 nm, respectively (Fig. 1a). This finding means that the electronic conjugation within the graphene sheets is restored upon reduction.[10] In contrast to that of the GO film, the C 1s XPS spectrum of RGO film (lower spectrum in

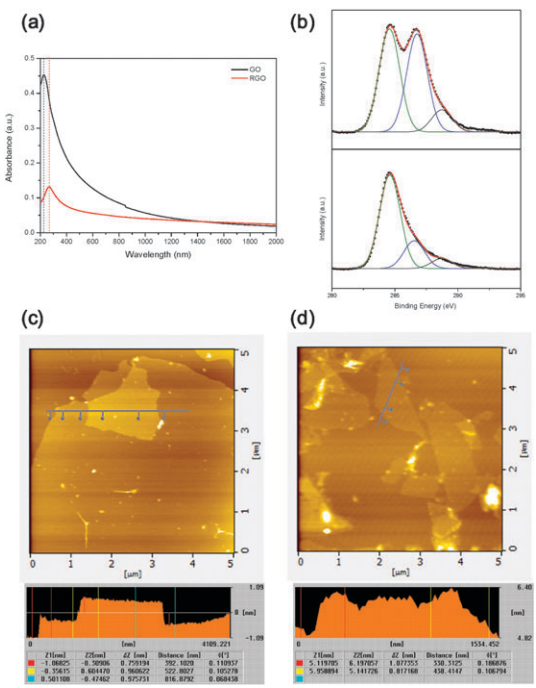

Fig. 1 (a) The UV-vis–NIR spectra of GO and RGO films. (b) The C 1s XPS spectra of GO (upper spectrum) and RGO (lower spectrum) films. AFM images and their height profiles of (c) GO and (d) RGO sheets.

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Fig. 1b) shows that fewer C–O (286.7 eV) and O–C=O (288.8 eV) bonds are present. This finding is consistent with observations made previously[12,13] and shows that reduction of GO has taken place. The AFM images and their corresponding height profiles, show that GO sheets (Fig. 1c) on a mica surface are flat (0.8–1.0 nm thick). In a manner that parallels previous results,[14,15] the thickness of graphene layers produced in the reduction process are the same as that of the oxide precursor, because a small number of C–O bonds still remained on the RGO surface (Fig. 1d). This observation suggests that the RGO sheets are dispersed uniformly in water with same exfoliation level as the GO sheets.

In order to demonstrate that gold nanoparticles have formed on the RGO sheets, the RGO-gold nanohybrid films were subjected to TEM, XPS, and UV-vis–NIR analysis. The plasmon absorption of gold nanoparticles in the gold nanoparticle-decorated RGO films appears at 585 nm in the UV-vis–NIR spectrum (Fig. 2a).[16–18] The XPS spectrum of the RGO-gold nanohybrid film displays a doublet for $4f_{5/2}$ (87.8 eV) and $4f_{7/2}$ (84.2 eV) in the gold nanoparticles on RGO sheets (Fig. 2b). Further analysis of the gold nanoparticles on RGO films by using EDS (data not shown) confirmed that Au^0 is present. Moreover, the results show that a large number of spherically shaped gold nanoparticles, size ranging from subnanometer to ~200 nm, are formed on the RGO sheets (Fig. 2c and 2d). The presence of gold nanocrystals was readily observed at higher magnification (inset of Fig. 2c). The measured regular *d*-spacing of the observed planes of the lattice are 2.35 ± 0.03 Å, which corresponds to a 2.355 Å spacing between the {111} planes of crystalline gold.[16]

The combined results demonstrate that the gold ions (Au^{3+}) are spontaneously reduced to gold nanoparticles (Au^0) on the RGO sheets in the absence of reducing agents and under the ambient condition. Unlike a previous report on the preparation of RGO-gold nanohybrids,[19] the method we have developed does not require a linker molecule (octadecylamine) and a reducing agent ($NaBH_4$) for the introduction of gold nanoparticle on RGO sheets. As a results, the method is not only simple but cost-effective, it uses RGO sheets which are more electrically conductive than GO sheets.[14] Consequently, the new material should be more applicable to sensors and electronic devices.

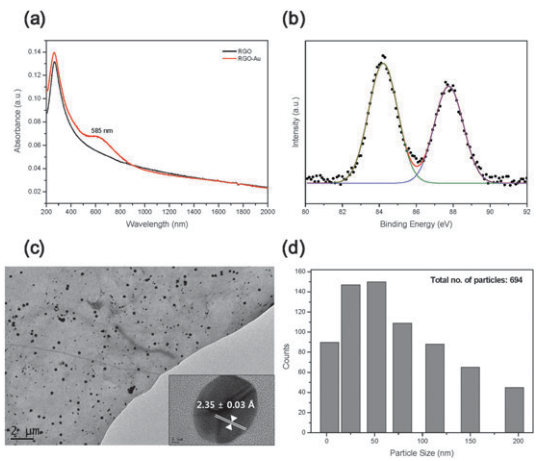

Fig. 2 (a) The UV-vis–NIR absorption spectra of RGO films before and after gold nanoparticle formation. (b) The XPS spectrum of RGO-Au. (c) TEM images of gold nanoparticle-decorated RGO films (inset: high resolution TEM image of a gold nanoparticle) and (d) particle size distribution histogram.

The mechanism of the reductive deposition process that generates gold nanoparticles on the RGO sheets likely involves Galvanic displacement[20,21] and redox reaction by relative potential difference.[11] Electrons in negatively charged substrate materials can participate in the reduction of metal cations.[21] In the same manner, gold nanoparticle deposition in the process we have developed can be promoted by electrons present in the negatively charged RGO sheets.[10] The zeta potential of the RGO dispersion at pH 7, measured by using a Zetasizer Nano-ZS analyzer (ZEN 3600; Malvern Instruments), was found to be −39 mV. To further support the evidence, we measured the work function of the RGO films by using an ultraviolet photoelectron spectroscopy (AC-2; RKI Instruments). The work function of the RGO was 4.88 eV. Thus, the reduction potential of the RGO is +0.38 V *vs.* SHE (standard hydrogen electrode) (see ESI†), which is much below as compared to that of $AuCl_4^-$ (+1.002 V *vs.* SHE).[22] Therefore, it is likely that gold cations (Au^{3+}) in a salt solution can be reduced spontaneously, because of the electrons donated from negative-charged RGO sheets and the lower reduction potential of RGO.

LbL films, consisting of RGO sheets and gold nanoparticles, can be fabricated by using the sequential vacuum filtration of RGO dispersion and spontaneous reduction of gold ions on RGO sheets in a repetitive manner. Fig. 3 shows the UV-vis–NIR absorption spectra measured after the construction of each bilayer in the LbL structure (*i.e.* the S-$(G/Au)_n$ films from n = 1–10). The absorbance in the entire spectral region is found to linearly increase with the number of bilayers. The inset in Fig. 3 indicates the linear relationship that exists between the absorbance at 268 nm and the number of bilayers formed. Also, the presence of shoulder peaks in the 585 nm region in the spectra of all bilayers indicates that gold nanoparticles are formed in each layer.

To characterize the LbL assemblies fully, the surfaces of S-$(G/Au)_{1,3,5,7,10}$ films were probed by using SEM. As can be seen by viewing Fig. 4a–e, thoroughly covering all films are a number of gold nanoparticles. Further evidence was made by

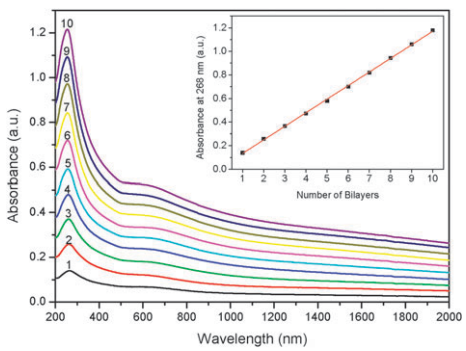

Fig. 3 The absorption spectra monitored during layer-by-layer construction of the structured films. The inset is a plot of absorbance at 268 nm *vs.* the number of bilayers.

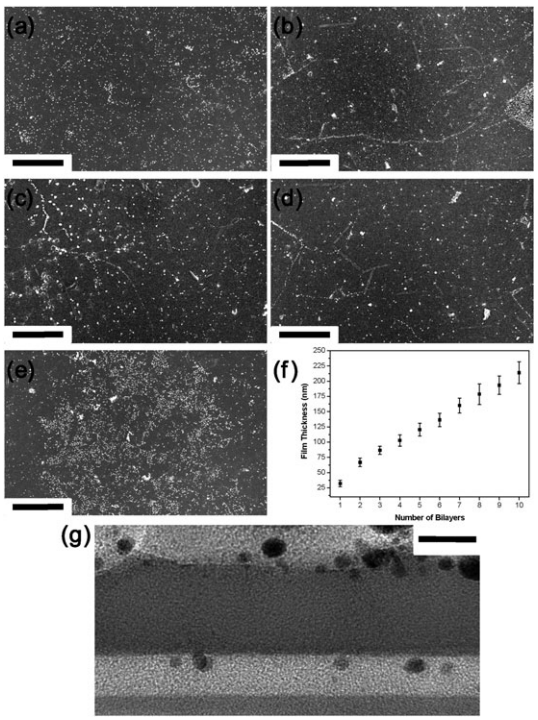

Fig. 4 SEM images of (a) S-$(G/Au)_1$, (b) S-$(G/Au)_3$, (c) S-$(G/Au)_5$, (d) S-$(G/Au)_7$ and (e) S-$(G/Au)_{10}$ film surfaces. The scale bar represents 20 μm. (f) A plot of the film thickness *vs.* the number of bilayers. (g) TEM image of the cross section of S-$(G/Au)_{10}$ film. The scale bar represents 20 nm.

measuring the thicknesses of S-$(G/Au)_{1-10}$ films by using surface profiler (Alpha-Step IQ; KLA Tencor) (Fig. 4f). The film thickness linearly increases with the number of bilayers, which is consistent with the UV-vis–NIR absorption spectra (Fig. 3). The side view of the LbL structure from the S-$(G/Au)_{10}$ film was obtained through sample cross-sectioning with the focused-ion beam. As shown in Fig. 4g, the 10th bilayer and the 9th bilayer (*i.e.* the 10th gold nanoparticle layer/10th RGO sheet/9th gold nanoparticle layer/9th RGO sheet from top to bottom layer) were imaged. The brighter region seen in the gold nanoparticle layers appears to be a gap between larger particles and smaller particles.

In summary, a novel method has been developed for constructing LbL assemblies of graphene and gold nanoparticles. The two-step procedure involves the use of vacuum filtration of a RGO solution to fabricate the graphene thin film on the quartz substrate. This is followed by gold nanoparticle formation by spontaneous reduction of gold ions in a gold salt solution on the RGO films. Sequential repetition of the two processes can be employed to make a 10th bilayer. By using this methodology, LbL films comprised of alternating RGO and gold nanoparticle layers are readily produced. It is believed that this method will enable production of transparent platforms that have high potential for use in a variety of sensor applications, including probes for DNA microarrays[23] and gold nanoparticle-oligonucleotide complexes for intracellular gene regulation.[24]

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