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Hollow Capsules of Reduced Graphene Oxide Nanosheets Assembled on a Sacrificial Colloidal Particle

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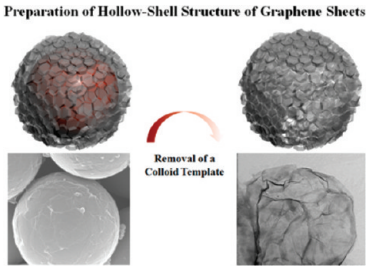
ABSTRACT We introduce a novel and versatile approach for preparing hollow multilayer capsules of graphene oxide nanosheets. Positively charged reduced graphene oxide (rGO-NH_3^+) and negatively charged reduced graphene oxide (rGO-COO^-) were used as building blocks for the layer-by-layer assembly of graphene multilayer films onto polystyrene (PS) colloids. After removing the PS colloids with THF treatment, hollow graphene capsules with necessary physical and chemical stabilities were prepared successfully. Furthermore, we expand this approach in incorporating a new functionality such as gold nanoparticles into a hollow graphene capsule. SEM and TEM analyses suggest the successful preparation of multilayers of hollow graphene capsules and integration of gold nanoparticles into a hollow graphene capsule.

SECTION Nanoparticles and Nanostructures



Graphene, a monolayer of an aromatic carbon lattice, has attracted a tremendous amount of attention in recent years because of its extraordinarily high electrical and thermal conductivities, mechanical properties, and large surface area.[1−4] Graphene has been explored for various applications in electronic and energy storage devices, biomedical devices, and ultrathin membranes.[5−9] In order to meet the demands of the variety applications, preparation of desired structures of graphene sheets with controlled dimension and architecture are of significant importance.

Taking full advantage of two-dimensional morphologies, the preparation of an assembled graphene sheet into a desired structure has been reported to produce the graphene oxide (GO) papers and membranes, transparent conducting electrode, and hybrid thin film. In particular, a stable suspension of GO is the common choice over pristine graphene with its facile synthetic nature in a controlled, scalable, and reproducible manner. For example, a number of approaches have been made to assemble well-dispersed oxidized or chemically reduced graphene oxide (rGO) nanosheets into thin films with tailorable properties, including vacuum filtration,[10] dip coating,[11] spin coating,[12] Langmuir−Blodgett assembly,[13] and direct chemical vapor deposition.[14,15] However, few papers have been reported on the preparation of hollow capsules of graphene through the controlled assembly of graphenes up to now.[16]

Alternatively, herein, we present a simple and facile approach of integrating exclusively graphene sheets onto the surface of a colloidal template based on the layer-by-layer (LbL) assembly.[17−20] The LbL assembly offers a variety of opportunities to prepare multilayer films of desired functions with a nanometer scale control over the composition and thickness. So far, various materials ranging from simple polyelectrolytes to nanoparticles, nanotubes, and biomaterials have been incorporated within the LbL films through the complementary interactions (i.e., electrostatic, hydrogen-bonding, covalent bonding).[19,21−24] In addition, LbL assembly enables preparation of conformal thin films onto virtually any substrate, irrespective of its size and shape, further expanding its potential in creating three-dimensional objects beyond the traditional thin films on a two-dimensional surface.

Therefore, here, we report a simple protocol to prepare hollow graphene capsules through LbL assembly of the stable rGO nanosheets with opposite charges onto a sacrificial polystyrene (PS) colloidal particle. Furthermore, we expand this approach in incorporating a new functionality such as gold nanoparticles (Au-NPs) into a hollow graphene capsule. Considering the broad range of potential applications of graphene sheets and LbL assembly, the approach developed here may lead to new possibilities for the fabrication of hollow graphene structures endowed with multiple functionalities.

To introduce the rGO nanosheet into an LbL assembly based on the electrostatic interactions, GO suspensions were initially prepared according to the modified Hummers method.[18,19] Following the sonication for exfoliation of graphite oxide, chemical functional groups introduced onto the surface of a graphene sheet, such as carboxylic acids (COOH), render the prepared GO negatively charged over wide pH conditions (GO-COO^-). Positively charged GO sheets were subsequently

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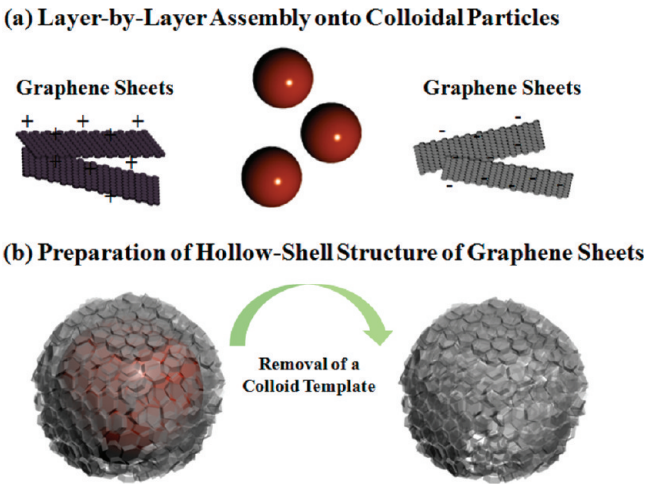
Scheme 1. Schematic Illustration of (A) the LbL Assembly of rGO Sheets onto PS Colloidal Particles and (B) the Preparation of rGO Multilayered Hollow Capsules with Removal of the Sacrificial Template



prepared by introducing amine groups (NH_2) on the surface of negatively charged GO sheets through the *N*-ethyl-*N*′-(3-dimethyl aminopropyl)carbodiimide methiodide (EDC)-mediated reaction between carboxylic acids (and/or epoxides) and excess ethylenediamine, which led to a positively charged stable GO suspension (GO-NH_3^+). Chemical reduction of the GO-COO^- suspension was carried out by adding hydrazine in the presence of ammonia to prevent the aggregation of the resulting rGO-COO^- suspensions, as reported previously.[25] The reduction of the positively charged GO-NH_3^+ suspension was identically carried out without mixing of the ammonia solution to prepare the rGO-NH_3^+ suspensions.

The hollow graphene capsules were assembled based on the electrostatic interactions by repeatedly layering the suspensions of rGO-NH_3^+ and rGO-COO^- onto a colloidal PS particle to afford the multilayer in the architecture of (rGO-NH_3^+/rGO-COO^-)$_n$ (n = number of bilayer) (Scheme 1a). After LbL deposition, as similarly demonstrated with other previous reports of using a sacrificial template to create the hollow nanostructure,[26] hollow capsules composed of rGO-sheet-paired multilayers were recovered by removing the PS colloidal particle substrates with THF exposure (Scheme 1b).

The formation of rGO sheet multilayer films requires that the two types of aqueous-solution-dispersed objects be oppositely charged at a given pH. Zeta-potential measurements for the reduced cationic rGO-NH_3^+ and reduced anionic rGO-COO^- indicate that each rGO suspension meets this necessary condition at pH 6 (29 ± 3.4 and -34 ± 6.3 mV, respectively). Given that the PS colloids are highly negatively charged under the same pH condition (-32 ± 1.4 mV), it was logical to initiate the multilayer deposition using complementary rGO nanosheets with opposite charges. As a result, the uniform adsorption of (rGO-NH_3^+/rGO-COO^-)$_n$ multilayers on the PS colloidal particles from the first layers to last six layers was monitored from the zeta-potential values of PS colloidal particles periodically oscillating from 19.4 ± 9.4 (from the first rGO-NH_3^+ layer) to -25.7 ± 11.5 mV (for the last rGO-COO^- layer) (Figure 1). These results of alternating surface charge imply the stable growth of multilayers of (rGO-NH_3^+/rGO-COO^-)$_n$ onto PS colloids (diameter of $2 \pm 0.020\,\mu$m) upon sequential adsorption of oppositely charged rGO nanosheets.

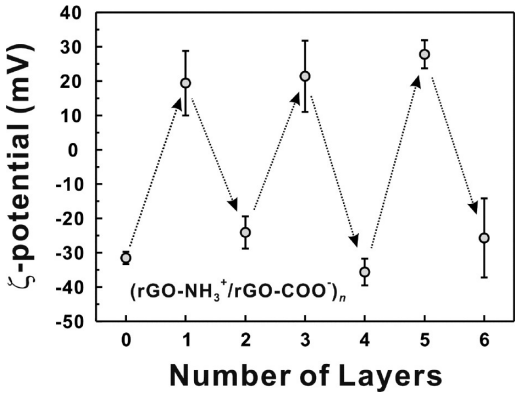


Figure 1. Zeta-potentials of PS colloids alternatively coated with rGO-NH_3^+(odd)/ rGO-COO^-(even) as a function of layer number.

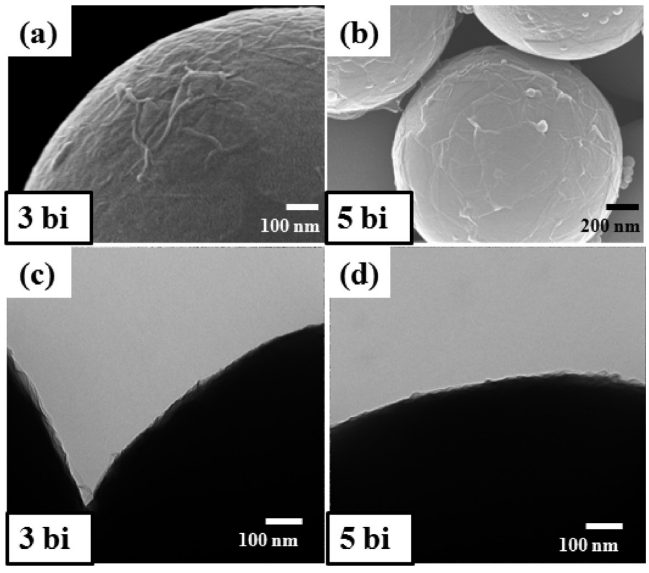


Figure 2. (a, b) SEM and (c, d) TEM images of (rGO-NH_3^+/rGO-COO^-)$_n$ multilayer films on a colloidal PS particle as a function of bilayer (n); (a,c) n = 3 and (b,d) n = 5.

On the basis of the stable growth of (rGO-NH_3^+/rGO-COO^-)$_n$ multilayers on colloids, we have investigated the morphology of PS colloids decorated with rGO sheets with scanning electron microscope (SEM) and transmission electron microscope (Figure 2). Although the first few bilayers of rGO sheets are hard to discern clearly due to the low contrast, we found that the graphene sheets are uniformly coated onto PS colloidal particles, yielding fairly smooth surface morphology (see also Supporting Information). It is very interesting to observe that the two-dimensional GO can conformally coat the curvature of the colloidal PS particles without much undulation. Though it was not possible to measure the film thickness of the graphene multilayer on the PS colloidal

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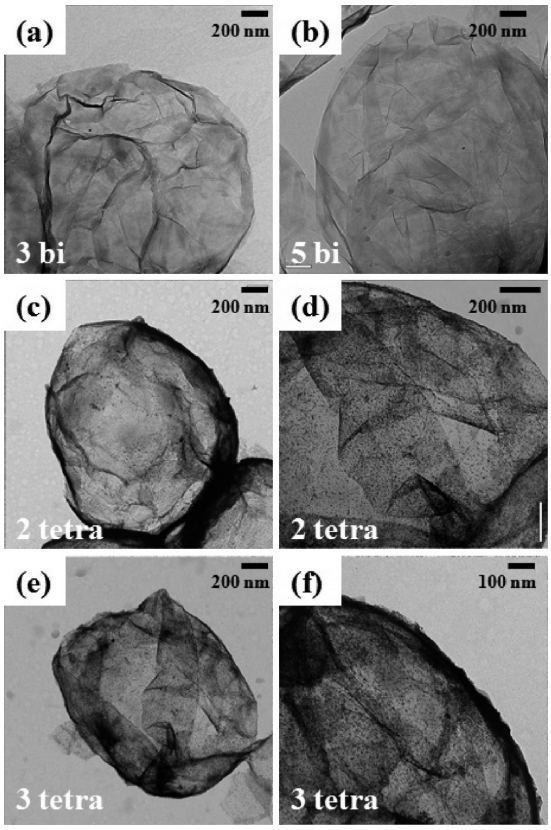

Figure 3. TEM images of hollow graphene capsules prepared from (a,b) $(rGO\text{-}NH_3^+/rGO\text{-}COO^-)_n$ (a) $n = 3$, (b) $n = 5$; (c–f) tetralayers with Au-NPs in an architecture of $(rGO\text{-}NH_3^+/rGO\text{-}COO^-/Au\text{-}NPs/rGO\text{-}COO^-)_n$ (c,d) $n = 2$, (e,f) $n = 3$. All images are obtained after the removal of sacrificial colloidal PS particles.

particles in the current experimental setup, the average thickness of a single bilayer of a $(rGO\text{-}NH_3^+/rGO\text{-}COO^-)_n$ film assembled on a flat silicon wafer corresponds to 1.36 nm measured from ellipsometry.[27]

After removing the PS colloidal particle substrates, the $(rGO\text{-}NH_3^+/rGO\text{-}COO^-)_n$ multilayers yielded hollow capsules with some wrinkles on the surface (Figure 3). The PS particles readily decomposed into their constituent oligomers upon treatment with extensive THF solvent. Further evidence for the production of the hollow rGO capsules was obtained from TEM images (see also Supporting Information). In this case, the surface coverage of the $(rGO\text{-}NH_3^+/rGO\text{-}COO^-)_n$ multilayers on a colloid template highlights the physical and chemical stability of hollow rGO capsules upon removal of colloidal templates by organic solvent. In addition, in order to provide the potential of LbL, we have incorporated a new functionality into the hollow capsule of graphenes. For example, here, we prepared Au-NP-decorated rGO hollow capsules. The positively charged 4-(dimethylamino)pyridine (DMAP)-coated Au-NPs (diameter of 11 nm) and $rGO\text{-}COO^-$ sheets were easily coupled to form a stable nanocomposite graphene sheet decorated with a high density of nanoparticles. With a modification of the LbL process of traditional bilayer format, we have incorporated positively charged Au-NPs in an alternate tetralayer of $(rGO\text{-}NH_3^+/rGO\text{-}COO^-/Au\text{-}NPs/rGO\text{-}COO^-)_n$ multilayers, followed by PS colloid template removal to yield the free-standing hollow Au-NP-incorporated rGO capsules. Indeed, this was the case, as is depicted in the TEM images for both two and three tetralayers (Figure 3c–f), thus confirming the LbL assembly of the charged components on the particles. It is apparent that the increase of the number of tetralayers can easily enhance the amount of incorporation of Au-NPs in hollow rGO capsules.

In conclusion, we have demonstrated the formation of graphene-based capsules through LbL assembly of surface-functionalized rGO nanosheets of opposite charges onto PS colloidal particles to produce multilayer thin films of graphene nanosheets with an architecture of $(rGO\text{-}NH_3^+/rGO\text{-}COO^-)_n$. Subsequent removal of the sacrificial PS colloidal templates by THF treatment further produced the hollow graphene capsule successfully. Furthermore, incorporation of gold nanoparticles into a shell of hollow graphene capsules was carried out with $(rGO\text{-}NH_3^+/rGO\text{-}COO^-/Au\text{-}NPs/rGO\text{-}COO^-)_n$ multilayer films. The hollow capsule of rGO nanosheets exhibited superior physical and chemical stabilities against external stimuli introduced during the removal of PS colloidal particle templates by THF treatment. By taking advantage of versatile LbL assembly, we have demonstrated the successful formation of three-dimensional hollow GO capsules using suspensions of two-dimensional structure of GO nanosheets. We anticipate that the results presented in this study will provide a basis for designing hollow graphene capsules to open new possibilities in drug delivery, catalysts, and electrochemistry.

SUPPORTING INFORMATION AVAILABLE

Detailed experimental procedures of the preparation of rGO multilayers on colloidal particles. Additional SEM images of $(rGO\text{-}NH_3^+/rGO\text{-}COO^-)_n$ multilayer films on PS colloidal particles and TEM images of hollow graphene capsule films after removing the sacrificial PS colloidal particles as a function of bilayer (n). This material is available free of charge via the Internet at http://pubs.acs.org.

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