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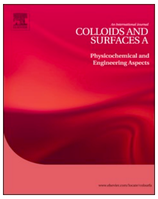

Sealing of through-holes on hollow glass bubbles with graphene oxide

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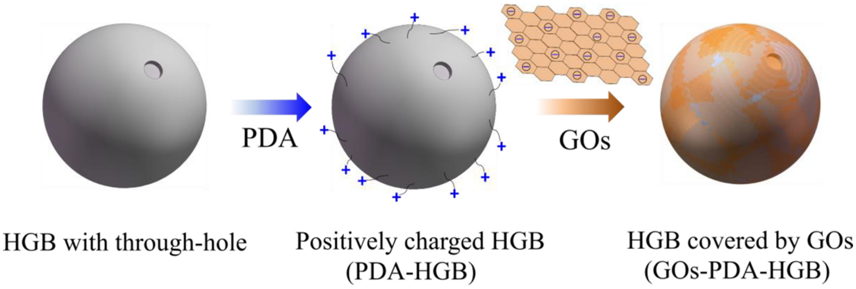
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, hollow glass bubbles (HGBs) of about 70 μm with through-holes of about 5 μm were successfully separated from a commercialized product and were used as targets to be sealed/covered by GO sheets of size about 24 μm. Firstly, these HGBs were treated with poly(ethyleneimine) (PEI) cross-linked polydopamine (PDA) to positively charge their outer surface. After treatment, the outer surface of HGBs was uniformly deposited with PDA nano-particles. During sealing/covering process, GO sheets were successfully attracted to the PDA modified HGBs by electrostatic force between the negatively charged GO sheets and positively charged HGBs introduced by the deposited PDA nano-particles, and were anchored by PDA nano-particles at the outer surface to avoid sucking of GO sheets into HGBs through the holes. While most of HGBs were tightly sealed/covered, some of them were partially sealed due to the fractured or collapsed GO sheets on the through-holes.

1. Introduction

Graphene (G) or graphene oxide (GO) is a 2-dimensional (2D) layered material with large surface area, high strength and flexibility, as well as abundant chemical and physical properties. Since its discovery in 2004 [1], investigations on it have been explosively increasing due to its unique and distinctive properties. Based on only one or the combination of those properties, G/GOs were used in various applications, including conductive films, electronic devices, energy generation and storage, sensors, catalysts, and polymeric composites [2–4].

Besides the above-mentioned applications, G/GOs can also be used to enwrap other materials to modify or improve properties of the targets. Various methods were explored to realize the enclosure process using G/GO sheets. Before the discovery of mono-layer graphene, carbon shells, recognized as G later, were produced around nano-

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particles by arc discharge method to protect the targets [5]. Later, *in-situ* chemical vapor deposition (CVD) method was explored to encapsulate catalyst nano-particles by forming high-quality G layers with controllable thickness [6,7]. According to the principle that like attracts like, i.e. materials with similar affinity are prone to gathering together, otherwise repelling, the hydrophilicity similarity between G/GO sheets [8] and targets, or hydrophilicity conversion between G and GO sheets [9], were also explored to enwrap materials. Another method is to disperse both the G/GO sheets and targeting nano-materials in solvents, and thereafter rapidly dry the dispersion for the self-assembly of G/GO sheets and targets [10,11]. The most significant way is to modify the surface to positively charge the targeting materials, so that they can attract the negatively charged GO sheets by electrostatic force. It is a versatile way to enwrap different nano-materials because various methods can be used to positively charge the targets [12].

However, in the previous studies, almost all the cases only used nano-particles as targets for encapsulation by G/GO sheets. During the encapsulation process, the whole nano-particles were enwrapped by a single G/GO sheet because the G/GO sheet is big enough for particles with size at nano scale. Big particles, like hollow glass bubble (HGB), were rarely or not reported to be encapsulated by G/GO sheets.

HGBs with dense outer shell and big inner cavity are promising carriers to reserve or store other functional materials. By etching HGBs by diluted hydrofluoric acid (HF) solution using a specially designed device, Zhang and Yang [13,14] successfully achieved HGBs with through-holes of sub-micron or several microns, and further used these HGBs to carry healants for self-healing epoxy composites. They directly incorporated the loaded HGBs into epoxy matrix without sealing the through-holes in advance [15–17], which may lead to loss of the carried liquids during storage and service of the loaded HGBs with through-holes. Considering the size of through-holes, it is difficult to seal them by traditional methods. G/GO sheets may be an alternative material to seal the through-holes on HGBs instead. However, to achieve this, G/GO sheets with size big enough should be adopted, or the through-hole is not able to be covered by a single G/GO sheet with high flexibility, and the surface of HGBs should be modified in advance.

HGBs are not able to be directly used as targets to electrostatically attract negatively charged GO sheets because they are also negatively charged due to residual hydroxyl groups at outer surface. However, their surface can be easily modified to be positively charged by several methods, like being treated with saline coupling agent having amine groups [12], or being coated with polymeric polydopamine (PDA). However, for coating with saline, the treatment condition is a little complicated, since organic solvents, relatively high temperature, and long processing time are necessary for the hydrolysis of saline coupling agent [18]. What is more, hydrophilicity is completely altered when organic solvents are used. PDA is a very promising polymer as it can self-polymerize with/without the aid of other chemicals under very ambient conditions. Since its discovery in 2007 [19], it has been extensively explored for surface modification of other materials [18,20–24] with different morphology and affinity. After modification, outer surface of the material turns to hydrophilic and coarse due to the deposited PDA nano-particles with huge amount of polar groups.

Here in this investigation, a strategy was come up with to seal/cover the through-hole on HGB shell by GO sheets, as schematically shown in Fig. 1. Firstly, outer surface of HGBs with trough-holes was modified by poly(ethyleneimine) (PEI) cross-linked PDA. And then the PDA modified HGBs were treated by big GO sheets to seal/cover the through-hole in the shell of HGBs.

2. Experiments

2.1. Materials

HGBs with bulk density of 0.37 g/ml were purchased from 3 M (USA). Expandable graphite (400 mesh) for preparation of GOs was supplied by Shandong Pingdu Pengsong Graphite Co., Ltd. All the chemicals used in this study, including potassium permanganate ($KMnO_4$), concentrated sulphuric acid (H_2SO_4, 98 wt%), hydrogen peroxide (H_2O_2, 35%), dopamine hydrochloride (DA·HCl), poly(ethyleneimine) (PEI, Mw ~ 800 Da, Mn ~ 600 Da), tris(hydroxymethyl) aminomethane (Tris), and 1 M HCl aqueous solution, were purchased from Sigma-Aldrich, and used as received. Deionized (DI) water with electric resistance of 18 MΩ was prepared in laboratory using a Millipore Milli-Q Integral System.

2.2. Separation of HGB with through-hole

HGBs with through-holes at several microns were separated from the commercialized HGBs from 3 M under vacuum. Firstly, the raw HGBs were added into excessive amount of water in a vacuum jar. After all the HGBs were wetted by water, they were subjected to high vacuum to extract out the air inside HGBs if there are through-holes in shell of the HGBs. After evacuation for about 5 min, vacuum was removed and water around was forced into the HGBs through the holes. Once HGBs with through-holes were fully filled with water after the evacuation process was repeated for 3–4 times, their density would be bigger than that of water and they separated and further precipitated to bottom when the vacuum jar was kept still for about 30 min. The precipitated HGBs were collected and dried naturally at room temperature (RT ~22–25 °C) for about 24 h. In order to remove debris and HGBs with relatively bigger through-holes, the collected HGBs were immersed into water again and shaken in an incubator at 200 rpm for about 10 min. Later the mixture was kept still for about 20 min for the precipitation of debris and HGBs with relatively bigger through-holes due to fast inflow of water through bigger holes. The floating HGBs were collected and dried naturally again at RT for 24 h as the targeting product.

2.3. Preparation of large GOs

Large GO sheets were prepared from expandable graphite using a pressurized oxidation method as described by Bao et al. [25]. Briefly, after an autoclave with capacity of 200.0 ml and all the chemicals were fully cooled down to 4 °C, the autoclave was charged with 4.0 g graphite, 14.0 g $KMnO_4$, and 100.0 ml H_2SO_4. Later, it was sealed and left at 4 °C for 1 h, heated in an oven at 80 °C for 1 h, and then cooled down to RT in order. The obtained product was diluted in 200.0 ml DI water, and charged with H_2O_2 under stirring mechanically (Caframo, Model: BDC6015) at 500 rpm until it turned to golden yellow. The product was washed with 1 M HCl aqueous solution (about 3.65 wt%) for about 8 times and then washed with DI water using dialysis tubes for 2 months. The obtained slurry was diluted in DI water and treated in an ultrasonic bath (70 W) for about 10 min. The final concentration of the obtained GO aqueous dispersion is about 1.6 wt%.

2.4. Surface treatment of HGBs with PEI cross-linked PDA

0.2 g as-prepared HGBs with through-holes was added into 100.0 ml DI water and shaken at 200 rpm in a 250 ml conical flask in an incubator for about 12 h at RT. In this process, water infiltrates into HGB through the hole in the shell, leading to density increase of the HGB and therefore more uniform suspension of HGB in water. Tris base buffer solution with Tris concentration of 10.0 mM was prepared by adjusting its pH to 8.5 with 1 M HCl. PEI-Tris solution was prepared by adding 200.0 mg PEI into 90.0 ml Tris solution, and DA-Tris solution was prepared by dissolving 200.0 mg DA·HCl in 10 mg Tris solution and hand-shaking dramatically for about 5–10 s. The DA-Tris solution was immediately poured into the PEI-Tris solution and mixed by dramatic hand-shaking for 5–10 s. In this mixture, the final concentration of DA and PEI in Tris is 2.0 mg/ml. After that, the mixture was rapidly transferred into the HGB suspension under shaken, and was allowed to react for about 4 h for deposition of PDA onto surface of HGBs. Finally,