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

He Zhang[a,b], Chenlu Bao[c], Jinglei Yang[d,*]

[a] *The National Engineering Research Center of Novel Equipment for Polymer Processing, The Key Laboratory of Polymer Processing Engineering (SCUT), Ministry of Education, South China University of Technology, Guangzhou, PR China, 510641*
[b] *School of Mechanical and Aerospace Engineering, Nanyang Technological University, 639798, Singapore*
[c] *School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin, PR China, 300387*
[d] *Department of Mechanical and Aerospace Engineering, Hong Kong University of Science and Technology, Kowloon, Hong Kong SAR, PR China*

GRAPHICAL ABSTRACT
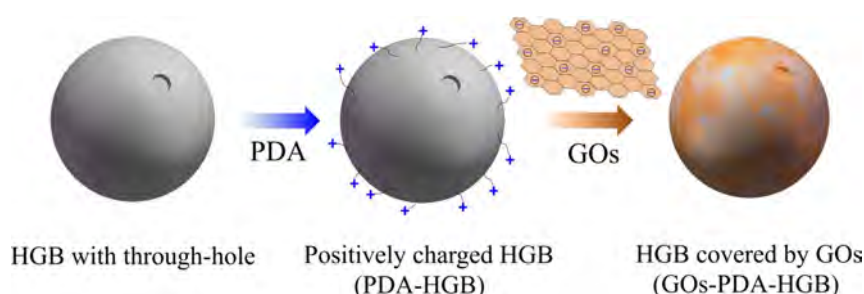
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ABSTRACT

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,

Fig. 1. Schematic procedure (not to scale) about sealing/covering of HGBs with through-holes by GOs: (a) Surface treatment with PDA to positively charge HGBs; and (b) Sealing of positively charged HGBs with GOs.

Fig. 2. FESEM images of original HGBs with small through-holes: (a) Overview; (b) An enlarged HGB with a through-hole; (c) Typical morphology of outer surface of HGB; and (d) Cross-section of a fractured HGB.

the process was ceased and the PDA modified HGBs (denoted as PDA-HGBs) was separated by rinsing the mixture with DI water and decanting supernatant for 3–4 times. The PDA-HGBs were dried at RT for 24 h for further usage.

2.5. Sealing/Covering of PDA-HGBs with GO sheets

The PDA-HGBs were re-suspended in 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. 0.1 wt% GO dispersion was prepared by diluting 1.0 ml 1.6 wt% GO dispersion with 15.0 ml DI water and sonicating for about 10 min. After the GO dispersion was dropwisely added into the PDA-HGBs suspension under shaken, the mixture was further shaken in the incubator for about 12 h for the deposition of GO sheets onto PDA-HGBs. And finally the PDA-HGBs sealed by GOs (denoted as GOs-PDA-HGBs) were separated by rinsing the GOs-PDA-HGBs with DI water and decanting supernatant for 3–4 times. The collected treated HGBs were dried naturally at RT for 24 h.

2.6. Characterization

Morphology and size of the original HGBs, PDA-HGBs, GOs-PDA-HGBs, and GOs, were characterized using field emission scanning electronic microscope (FESEM, JOEL JSM-7600 F). Before being imaged by FESEM, the samples were gold coated for 30 s for better conductivity to avoid charging during FESEM observation. Diameter and distribution of HGBs and through-hole, as well as size distribution of the adopted GOs, were measured from FESEM images using software, ImageJ, based on at least 100 individuals.

3. Results and discussion

3.1. Original HGBs with through-holes

HGBs with through-holes were separated from the original HGBs from 3 M using density difference among water (~1.0 g/ml at RT), intact empty HGBs (0.37 g/ml), and water filled HGBs with through-holes (bigger than 1.0 g/ml). When the raw HGBs were immersed into

water, all of the HGBs with/without through-holes were floating at top surface of the mixture due to density mismatch. If there are some ready channels, like through-holes, for the flowing of air or water, the air inside HGBs can be easily extracted out when vacuum was applied and water around can be easily forced into the HGBs through the hole upon removal of vacuum. The evacuation process can be applied repeatedly for several times for the better infiltration of water. Once density of HGBs with through-holes is bigger than that of water due to the infiltrated water, they will be prone to precipitating to the bottom when kept still. By this process, the HGBs with through-holes can be easily achieved by only physical process, although percentage of this kind of HGBs in the commercialized product is relatively low and intact HGBs can be etched using diluted HF solution to have through-holes [13,14].

Fig. 2 shows FESEM images of the collected HGBs with through-holes after removing debris and HGBs with relatively bigger through-holes. It demonstrates that this physical process can successfully separate these HGBs. Overview of the HGBs and a typical HGB with through-hole can be seen in Fig. 2a and b, respectively. The measured diameter based on at least 100 individuals is $69.6 \pm 9.8\,\mu m$. It is observed from Fig. 2c that outer surface of the HGBs is smooth with adhered glass nano-particles. Cross-section of the HGBs can be observed from the fractured HGBs, as shown in Fig. 2d. The shell is very dense and has a uniform thickness of $1.16 \pm 0.57\,\mu m$. Fig. 3 shows size distribution of through-holes on the collected HGBs and the related frequency. The size of through-holes was measured as the minimum circumcircle of the though-hole with irregular shape. In order to minimize the inaccuracy of this measuring method, only HGBs with through-holes right at the top or very close to the top point in the FESEM images were selected for the measurement. It is observed that most of the HGBs have through-holes with size of 4 μm and 5 um, and that more than 80% of the through-holes is less than 8 μm. The average size of the through-holes based on at least 100 individuals is $5.3 \pm 2.5\,\mu m$. This relatively small size of through-holes makes sealing of them possible by other 2D materials.

3.2. GO sheets

According to Bao et al. [25], single-layered GO sheet with big size can be achieved by the proposed pressurized oxidation method. Fig. 4 shows FESEM images of the obtained GOs. It demonstrates that the GOs are indeed relatively big, although small ones can also be observed. Fig. 5 gives the size distribution based on at least 250 individuals of GO sheet. Since shape of almost all the GO sheets is irregular, the size here means the averaged value of the longest distance and the shortest distance of a single GO sheet. It can be seen that the size has a wide distribution with majority in 10–30 μm, and the average size is $24 \pm 14\,\mu m$. It is necessary to point out that the too small GO sheets in

Fig. 3. Size distribution and frequency of through-holes on the collected HGBs after separation process.

FESEM images (smaller than 5 μm) were not counted in this distribution because they are useless for this application to seal the through-holes on HGBs. And secondly, the distribution and average size is just a rough estimation of the real size. On one hand, the shape of most GO sheets are so irregular that the longest and shortest distance sometimes cannot reflect the real size. On the other hand, since single-layered GO sheet are ultra-soft and ultra-flexible, they may fold during sample preparation for FESEM imaging, leading to decrease of the size. Nevertheless, it can be concluded that most of the GO sheets obtained by this pressurized oxidation method is far bigger than the size of though-holes in the HGB shell.

Besides the irregular contour, the GO sheets have a lot of defective areas inside the sheets, as indicated by arrows in Fig. 4b. It indicates the pressurized oxidation process destroys the integrity of graphene structure and generates a lot of carbonyl groups and hydroxyl groups as the locations for negative charges.

3.3. PDA-HGBs

Although up to now it is still unclear about the structure of PDA, it has been extensively adopted for surface modification due to the fast self-polymerization in weak alkaline solution (pH > 7.5), which can be attributed to the coexistence of reactive catechol and amine groups [26]. Fig. 6a shows oxidation of the catechol groups in DA to quinone in Tris basic buffer solution with pH of 8.5, and the further polymerization of quinone to PDA. When the PDA oligomers solution was added with PEI, it can be cross-linked by the added PEI through Michael addition or Schiff base reaction between amine groups in PEI and catechol groups in PDA [27,28], as illustrated in Fig. 6b. The PDA-HGBs can be seen from the FESEM images in Fig. 7. It is observed from Fig. 7a and b that most of the HGBs are similar to the original HGBs. However, compared with the smooth outer surface with some adhered glass nano-particles, the outer surface of PDA-HGBs is much rougher with more nano-particles, as shown in Fig. 7c, which means the HGBs are successfully coated with PDA. The PDA nano-particles, with size up to about 100 nm, were uniformly deposited on the outer surface without any agglomeration. In contrast to diameter of through-hole in the HGB shell at micron scale, these PDA nano-particles are too small to block the through-holes during surface treatment of HGBs. Because of this, through-holes can be observed for every HGB after the surface treatment process, as shown in Fig. 7b.

It is necessary to point out that the reason why separated original HGB with through-hole, rather than etched HGB with through-hole, was adopted is that the adhered glass nano-particles on the separated HGBs can be potential anchors to fix the adhered GO sheets. Given that PDA is not sensitive to the morphology and affinity of subject during surface treatment, and PDA can completely cover outer surface of the separated HGBs (Fig. 7c), it is reasonable that it can also modify the etched HGBs with through-holes. In this investigation, we also treated etched HGBs with through-holes using the same process. It verified that outer surface of the etched HGB is identical to that of the separated HGB after the treating process.

3.4. GOs-PDA-HGBs

Fig. 8 shows HGBs with through-holes after being surface treated with PDA and further covered with GO sheets (GOs-PDA-HGBs). Different from PDA-HGBs as shown in Fig. 7a, through-holes in the shell of HGBs disappeared and some dented areas were found on the outer surface after the sealing process, as illustrated by the overview FESEM image in Fig. 8a. In contrast to the HGBs without any connection to each other for the original HGBs and PDA-HGBs, some of the GOs-PDA-HGBs were connected after being dried, as indicated by the arrows in Fig. 8a. When big GO sheets with size up to several tens microns were added into the PDA-HGB suspension, they may be attracted by neighboring HGBs at the same time, leading to the connection of different
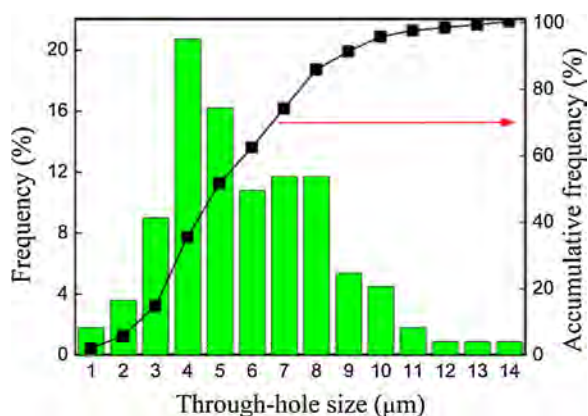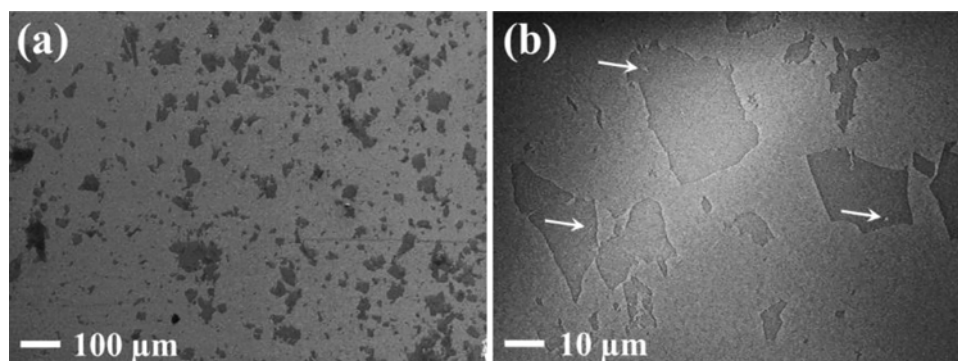
Fig. 4. Adopted GOs with big size for sealing of through-hole and coverage of outer surface of HGBs. Arrows in (b) indicate the defective areas inside GO sheets.
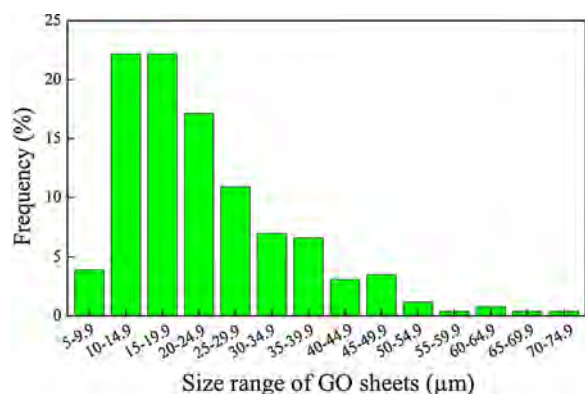

Fig. 5. Size distribution of the achieved GO sheets by pressurized oxidation.

HGBs as shown in the figure. Nevertheless, no serious agglomeration was observed during the treating process or after the drying process because of this bridging effect. The disappearing of through-holes preliminarily demonstrated the GO sheets with diameter of

$24 \pm 14 \mu m$ is large enough for the sealing/covering of HGBs with size around 70 μm. Fig. 8b gives a typical HGB with its through-hole sealed/covered by attracted GO sheets. It is observed from the enlarged through-hole in Fig. 8c that the sealing by GO sheets is very tight. The white rectangular area was further enlarged in Fig. 8d to check the structure in that area. Characteristic wrinkles of GO sheets can be found near the edge of through-hole. In both Fig. 8c and d, the deposited PDA nano-particles disappeared due to coverage of GO sheets. As can be seen from Fig. 8b, the outer surface, with grey zones and light zones inter-penetrating each other, is totally different from those of the original HGBs (Fig. 2b) and PDA-HGBs (Fig. 7b). Fig. 8e gives the enlarged outer surface of GOs-PDA-HGBs. It is found that the grey zones are covered surface by the attracted GO sheets while the light zones are naked area without any GO sheets, which means the outer surface was not completely covered by GOs. And even for the covered areas, some naked PDA nano-particles, as indicated in the white rectangles in Fig. 8f, still can be seen. This might be attributed to the defects in GO sheets introduced during the preparation process of single-layered GOs as shown in Fig. 4b, or gaps among the attracted different GO sheets.

The above observation demonstrates the successful sealing/covering of PDA-HGBs by the attracted GO sheets. Due to addition of PEI, more
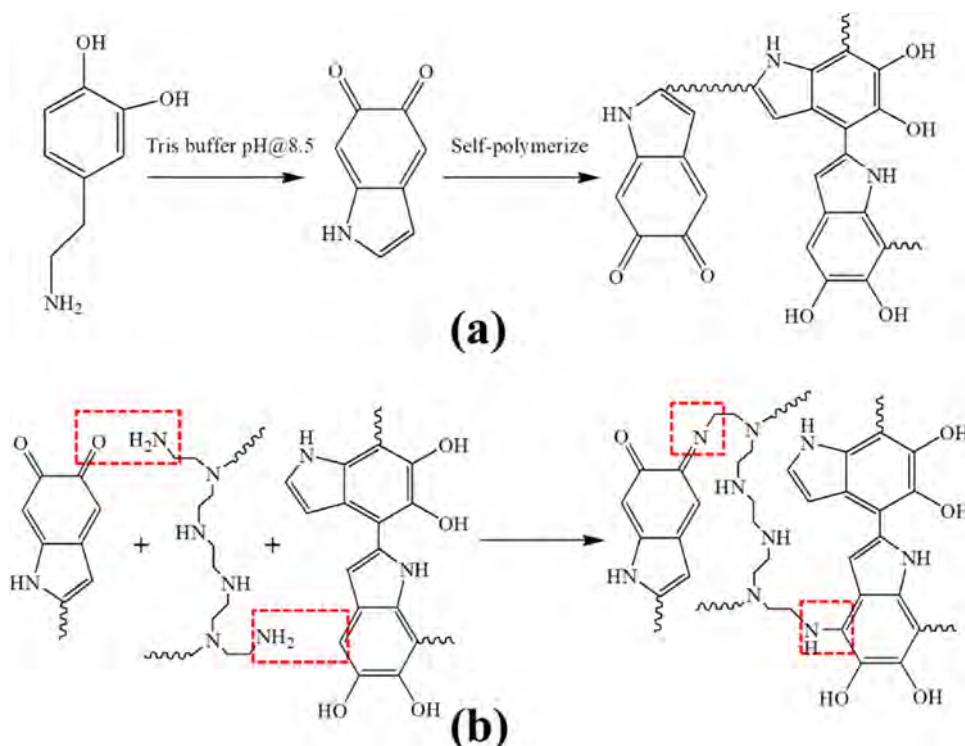

Fig. 6. Scheme of (a) Self-polymerization of DA in Tris buffer, and (b) Cross-linking of PDA by PEI.
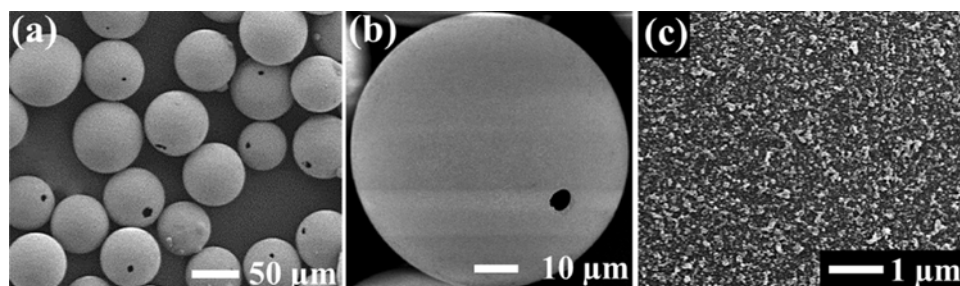
Fig. 7. HGBs with through-holes after being treated with PDA: (a) Overview; (b) An enlarged typical HGB; and (c) Morphology of the outer surface of treated HGBs.

primary, secondary, and tertiary amine groups were grafted into the molecule of PDA (Fig. 6b) [18], compared with the pure polymeric PDA (Fig. 6a). The grafted amine groups can hydrate and further ionize to become quaternary amine, leading to positive charging of the deposited

PDA nano-particles and therefore the HGBs, as illustrated in Fig. 1a. When the negatively charged GO sheets were added into the suspension of this PDA treated HGBs, the GO sheets can be attracted to cover the surface of HGBs due to electrostatic force between the negative charges
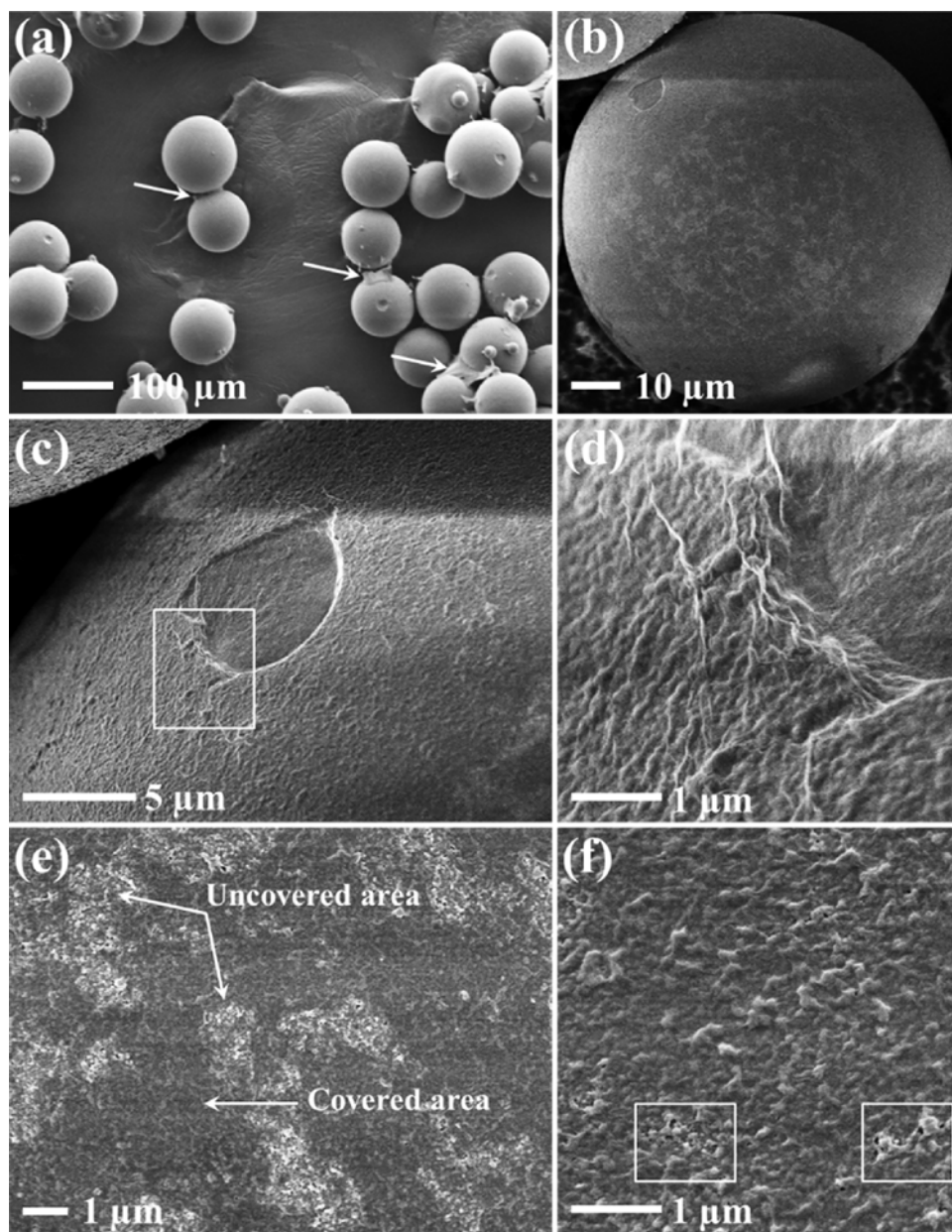
Fig. 8. FESEM images of the PDA treated HGBs after being covered by GOs (GOs-PDA-HGBs): (a) Overview of the covered HGBs by GOs; (b) An enlarged typical HGB with through-hole sealed by GOs; (c) Enlargement of the covered through-hole; (d) Enlargement of the rectangular area in (c); (e) Outer surface of the covered HGBs by GOs; and (f) Enlargement of the outer surface.
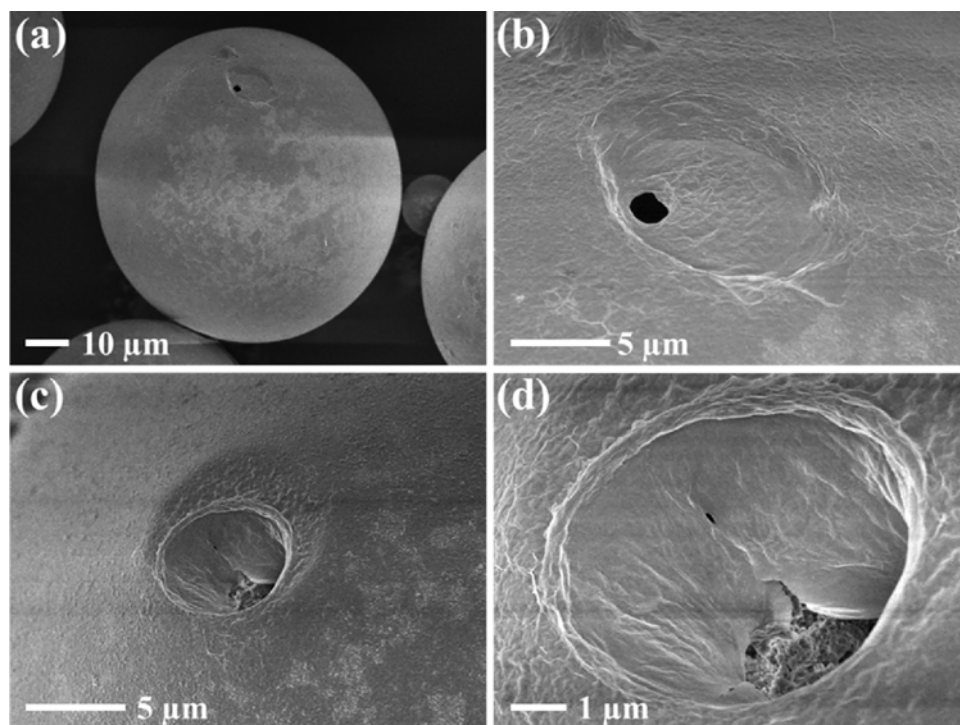
Fig. 9. Sealed HGBs by GOs with GO sheets: (a) and (b) fractured ; and (c) and (d) collapsed on the through-hole.

on GO sheets and the positive charges introduced by PDA nano-particles, as illustrated in Fig. 1b. Since charges on both GO sheets and HGBs are chemically bonded rather than physically absorbed, the attraction is permanent after the treating, separating and drying process.

Although the adhered GO sheets dent a little bit on through-holes, they were not sucked into HGBs through the holes without any support on the hole, but tightly seal and fully spread on the holes, as illustrated by Fig. 8c and d. It demonstrates that, besides providing the positive charges for the outer surface of HGBs, the deposited PDA nano-particles have another important function as anchors for the attracted ultra-soft and ultra-flexible GO sheets, as shown by Fig. 8d and f. Compared with original HGBs with smoother outer surface, the PDA treated HGBs with much rougher surface can generate much higher friction between GO sheets and HGBs.

Besides through-holes completely sealed by GO sheets as mentioned above, through-holes with other morphology can also be seen, as shown in Fig. 9. Fig. 9a and b show that there is a hole on the attracted GO sheets. Possible reasons may be that there are some existed holes on the GO sheets before the sealing process with HGBs, as indicated by the arrows in Fig. 2b. When this kind of GO sheets is attracted to the outer surface, the holes on the GO sheet will be clearly shown as the GO sheet is spread. It can also be indirectly verified by the naked nano-particles without being covered by GO sheets in Fig. 8f. In addition to the fractured GO sheets on the through-holes, collapsed GO sheets were also found, as shown in Fig. 9c and d. This might happen when the water inside HGBs evaporates to leave the flawed GO sheets without any supporting.

Covering/Sealing of through-hole in HGB by GO differs from the previous cases that used G/GO to enwrap nano-particles. Firstly, in this study, the modified structure is a big hollow object with surface defects at micron scale, rather than some small solid objects at nano scale. Since HGB with diameter at about 70 μm is much larger than size of the adopted GO sheet, it is impossible to cover/seal the whole HGB by a single GO sheet. Consequently, in order to achieve the coverage of HGB, several individual GO sheets should act at the same time as patches. While most of the surface area is covered by different GO sheets, the rest is naked, as shown in Fig. 8b. Nevertheless, the size of GO sheet

meets the purpose to cover/seal the small through-hole at micron level. Secondly, as GO sheet is ultra-soft and ultra-flexible, it is impossible to fix the GO sheet to the through-hole without any support only by the electrostatic force. If no anchors, i.e. the PDA nano-particles in this study, exist, the extracted GO sheets are very likely to be sucked into the chamber of HGBs through the holes.

And finally, etched HGBs with through-holes after being treated by PDA were also subjected to the sealing/covering process by GOs. Similar to the separated original HGBs with through-holes, the through-holes can also be successfully sealed by GO sheets. This step, i.e. sealing the through-hole, together with the etching process to controllably generate through-holes by an etching process, [13,14] complete a whole story about using this commercialized HGB.

4. Conclusion

In this investigation, a method was proposed to seal through-hole of diameter about 5 μm on HGB of around 70 μm using GO sheets of about 24 μm. The surface coating process with PEI cross-linked PDA can not only positively charge the outer surface of HGBs, but also provides a rough surface with deposited PDA nano-particle of size up to 100 nm. While the positive charge can attract the negatively charged GO sheets by electrostatic force, the nano-particles acts as anchors to fix GO sheets on the outer surface. Differs from nano-particle that can be completely enwrapped by a single G/GO sheet, the big HGB of about 70 μm needs several big GO sheets to cover it simultaneously. Although not all the surface area can be covered by the GO sheets, the through-hole on HGB can be successfully sealed by GO sheets. Together with generation of through-hole on HGB etched by diluted HF solution, sealing of the through-hole by GO sheets can make a complete loop for the applications of this commercialized HGB.

Acknowledgement

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