Graphene quantum dots and polypyrrole incorporated polyacrylic acid hydrogels with enhanced conductivity

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Abstract. Highly conductive hydrogels of functional graphene quantum dots (FGQDs) and polypyrrole (PPy) incorporated polyacrylic acid (FGQDs/PAA20/PPy) were fabricated through chemical cross-linking and in-situ polymerization. The amount of FGQDs, PPy and cross-linker affecting on the morphology, swelling ratio and electrical properties of FGQDs/PAA20/PPy composite hydrogels was investigated. FGQDs produced smaller-sized pores on the structure of PAA hydrogels, but hardly affected their porosity and swelling ratio. A high conductivity of 0.29 S/m was achieved for FGQDs/PAA20/PPy hydrogels, which promised high possibility in various fields.

1. Introduction

Hydrogels, polymer cross-linking to form three-dimensional porous materials, could absorb large amounts of water and retain their original structure after swollen.1 Through volume swelling or contraction, some hydrogels sensively respond to tiny changes in external stimuli (e.g., temperature, pH, ionic strength, solvent, light, electric field, magnetic field), alongside the swelling behavior, biocompatibility, mechanical behavior, and surface properties, hydrogels find applications in various areas including biomedical devices, wastewater treatments, electronic component, enzyme immobilization, and agriculture.2 Practically, the electrical field is the most important stimuli for functional hydrogels, because the electric field is easily realized and the intensity is controllable.3 However, hydrogels commonly have low inherent conductivity, which retard greatly their applications. In order to improve the conductivity of hydrogels, both organic and inorganic component were incorporated to form functional hydrogel nanocomposites. For example, metal nanoparticles, conducting polymers, and carbon nanomaterials were all hybrid into the hydrogels matrix to increase their electrical properties.4, 5

Poly(acrylic acid) (PAA), a negatively charged polyelectrolyte due to the presence of carboxylic groups on its polymer backbone, is preferred as a hydrogel matrix. The PAA-based hydrogels are generally mechanical strong with electrically conductivity, export stable electrical signal without dispersion problems, thus are promising candidates to be used as flexible electronics and mobile energy sources.6 To further enhance the electrical properties of PAA-based hydrogels, the most common approaches are either polymerizing conducting polymers or loading metallic conductors into the hydrogel matrix.7
Graphene quantum dots (GQDs) have been well applied as reinforcement elements to improve the conductivity of different matrix, due to the stable lattice structure and fast charge transport across the sheets. Furthermore, various heteroatoms and functional groups can be introduced into the structure of GQDs to alter their electronic characteristics, which widely broaden their applications.

Herein, to achieve high conductivity and expand the applications of PAA hydrogels, functionalized GQDs (FGQDs) and a classic conductive polymer polypyrrole (PPy) were simultaneously incorporated into PAA hydrogels to improve their physicochemical properties such as conductivity and swelling ability. FGQDs were synthesized by a facile procedure containing the N,N'-methylenebisacrylamide (MBA) participated citric acid pyrolysis, the FGQDs were then used as cross-linking agents to assist the polymerization of the three-dimensional PAA hydrogel network. After the in-situ polymerization of PPy, a new three-dimensional conductive FGQDs/PAA/PPy hydrogel network with better comprehensive properties was obtained. The influence of FGQDs and PPy ratio on the morphology, conductivity and swelling ability of FGQDs/PAA/PPy hydrogels was also characterized.

2. Experimental

2.1. Materials
Acrylic acid, citric acid, pyrrole, ammonium persulfate (APS) and N, N-methylene bisacrylamide (MBA) was obtained from Sinopharm Chemical Reagent Co., Ltd. Acrylic acid was distilled under vacuum conditions and stored in the refrigerator. Deionized water (resistivity: 18.2 MΩ·cm) was used throughout the experiment.

2.2. Characterization
Morphologies were observed by scanning electron microscope (SEM, Verios 460) and transmission electron microscope (TEM, JEM-2010). FTIR measurements were performed on a Nicolet iS50 Fourier transform infrared spectrometer (Thermo Electron, USA). Thermo gravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC2 apparatus, the samples were placed in a platinum pan and heated from room temperature to 900 °C at 15 °C/min under N2 atmosphere. Electrical properties were conducted on a Gamry Reference 3000 Potentiostat/Galvanostat/ZRA instrument.

2.3. Preparation of FGQDs
FGQD was synthesized by the pyrolysis of citric acid and MBA. Briefly, 4.2 g of citric acid and 0.62 g of MBA were dissolved in 20 mL of H2O. The mixture was heated at 200 °C for 3.5 h, filtered with a 220 μm membrane, then dialyzed in H2O for two days to get the FGQDs.

2.4. Preparation of FGQDs/PAA hydrogel
The FGQDs incorporated polyacrylic acid (PAA) hydrogels FGQDs/PAA were developed by solution polymerization of acrylic acid in the presence of FGQDs, APS and MBA in aqueous media. The reactions were taken place under 70 °C for 12 h, the proportions of raw materials were detailed in Table 1 & 2. Generally, in a 20 mL reaction system, with x mg of APS and x mg of NMB in the system, the hydrogels were labeled as FGQDs/PAAx, x=2, 5, 10, 20, 50, 100.

2.5. Preparation of FGQDs/PAA20/PPy hydrogel
FGQDs/PAA20 hydrogels were immersed in H2O for 48 h at room temperature to reach swelling equilibrium. Then the FGQDs/PAA20 hydrogels were incubated in different concentrations of pyrrole solution (0.72-21.6 mM) for 24 h, APS (mole ratio of pyrrole to APS = 1:1) was added, and HCl was also added to reach a concentration of 1 M, then the mixture was shaking at 120 rpm for 6 h to get the FGQDs/PAA20/PPy hydrogels. The hydrogels were washed and incubated in H2O for 48 h to reach swelling equilibrium.
2.6. Determining the swelling degree
Swelling ability of the FGQDs/PAAx and FGQDs/PAA_{20}/PPy hydrogels was evaluated in H_{2}O via a gravimetric method. Hydrogels were freeze dried, weighted (W_{0}), and immersed in H_{2}O for 48 h. The sample was weighed (W_{t}) after removing excess surface liquid by gently blotting with a filter paper. The swelling ratio was calculated as: Swelling Ratio = (W_{t}-W_{0})/W_{0}×100 %.

2.7. Porosity
The porosity of FGQDs/PAAx and FGQDs/PAA_{20}/PPy hydrogels was examined via a liquid displacement method using ethanol as the displacement liquid. The samples were freeze dried and immersed in ethanol (volume: V_{1}) for 24 h, then the total volume (ethanol and the ethanol-impregnated gels) was recorded as V_{2}. The gel was removed, and the residual ethanol volume was recorded as V_{3}. The porosity of the hydrogels was obtained as: Porosity (%) = (V_{1}-V_{3})/(V_{2}-V_{3})×100 %.

3. Results and Discussion
FGQDs were prepared by a one-step reaction through the pyrolysis of citric acid and MBA. The pyrolysis of citric acid was a commonly used method to synthesize graphene quantum dots with multiple oxygen-containing groups,^{12, 13} the introduction of MBA offered the as-prepared graphene quantum dots with more functional groups including amino groups and alkene, which favored the following cross-linking with acrylic acid. As shown in Fig. 1, FGQDs showed lateral dimensions of 5-15 nm, and the high resolution TEM image illustrated lattice fringes with a d-spacing of ~0.24 nm.

Fig. 1 TEM images of FGQDs with (A) low and (B) high magnification, the inset showed the photograph of GQDs suspension.

FGQDs were then utilized as an assisting cross-linker to realize the three-dimensional network crosslinking of PAA, and acquired the FGQDs functionalized ionic conductive FGQDs/PAA hydrogels. The proportions of raw materials were detailed in Table 1 & 2. Although the preparation process of FGQDs contained MBA, the FGQDs alone was not enough for cross-linking the PAA to get hydrogels, and MBA was necessary to the hydrogel formation. With increasing amount of FGQDs, the color of the FGQDs/PAA hydrogels gradually deepened (Fig. 2A), and the FGQDs/PAA hydrogels retained their yellow color after swelling (Fig. 2B), indicating that FGQDs participated in the cross-linking of hydrogels. Different content of FGQDs led to distinct porous structure. More FGQDs resulted in smaller-sized and more intensive pores, which may because that the presence of FGQDs increased the crosslinking points in hydrogels (Fig. 2C-2E).
Table 1. Amount of raw materials added in 20 mL of reaction system to synthesize FGQDs/PAA20 hydrogels with different content of FGQDs.

| No. | APS (mg) | MBA (mg) | FGQDs (mg) | PA (g) | Mass ratio of FGQDs to PA |
|-----|----------|----------|------------|--------|--------------------------|
| 1   | 20       | 20       | 0          | 4.244  | 0                        |
| 2   | 20       | 20       | 4.5        | 4.244  | 0.001                    |
| 3   | 20       | 20       | 11.25      | 4.244  | 0.003                    |
| 4   | 20       | 20       | 22.5       | 4.244  | 0.005                    |
| 5   | 20       | 20       | 112.5      | 4.244  | 0.027                    |
| 6   | 20       | 20       | 225        | 4.244  | 0.053                    |
| 7   | 20       | 20       | 450        | 4.244  | 0.106                    |

Table 2. Amount of raw materials added in 20 mL of reaction system to synthesize FGQDs/PAAx hydrogels with different content of FGQDs.

| Samples | APS (mg) | MBA (mg) | FGQDs (mg) | PA (g) | Mass ratio of FGQDs to PA |
|---------|----------|----------|------------|--------|--------------------------|
| FGQDs/PAA2 | 2        | 2        | 0          | 4.244  | 0                        |
| FGQDs/PAA2 | 2        | 2        | 22.5       | 4.244  | 0.003                    |
| FGQDs/PAA2 | 2        | 2        | 112.5      | 4.244  | 0.027                    |
| FGQDs/PAA2 | 2        | 2        | 225        | 4.244  | 0.053                    |
| FGQDs/PAA2 | 2        | 2        | 450        | 4.244  | 0.106                    |
| FGQDs/PAA40 | 2        | 2        | 0          | 4.244  | 0                        |
| FGQDs/PAA40 | 2        | 2        | 4.5        | 4.244  | 0.001                    |
| FGQDs/PAA40 | 2        | 2        | 112.5      | 4.244  | 0.003                    |
| FGQDs/PAA40 | 2        | 2        | 225        | 4.244  | 0.005                    |
| FGQDs/PAA40 | 2        | 2        | 450        | 4.244  | 0.003                    |

On the other hand, the porosity and swelling ratio of FGQDs/PAA hydrogels were hardly affected by the content of FGQDs (Fig. 3). The porosity of FGQDs/PAA20 hydrogels were all > 80 %, and showed high swelling ratio in H2O. For example, after immersing in H2O for 48 h, the volume of hydrogel significantly increased, despite the content of FGQDs (Fig. 2B). Because of the presence of pendant polar groups such as carboxyl groups, PAA is a superabsorbent polyelectrolyte, and the swelling ratio of FGQDs/PAA hydrogels was mainly influenced by the amount of cross-linker MBA and initiator APS. More cross-linker and initiator led to lower swelling ratio.
Fig. 2 (A-B) Photographs of FGQDs/PAA\textsubscript{20} hydrogels with different content of FGQDs (A) before and (B) after immersing in H\textsubscript{2}O for 48 h. (C-E) SEM images of FGQDs/PAA\textsubscript{20} hydrogels with mass ratio of GQDs to PA at (C) 0.003, (D) 0.053, and (E) 0.106.

Fig. 3 (A) Porosity of FGQDs/PAA\textsubscript{20} hydrogels. (B) Swelling ratio of FGQDs/PAA hydrogels in H\textsubscript{2}O for 48 h.

Fig. 4 Conductivity of FGQDs/PAA hydrogels with different FGQDs content.
Flexible conductive gels have gained attention and been extensively used as sensors and energy devices. The hybridization of FGQDs to PAA altered the conductivity of FGQDs/PAA hydrogels. As shown in Fig. 4, FGQDs significantly enhanced the conductivity of FGQDs/PAA hydrogels. GQDs have attractive electronic properties, and have been proved to be able to offer synergistic effect on various nanomaterials. GQDs may promote the ion transport of PAA hydrogels and thus enhance their conductivity.

Fig. 5 (A) Photograph of FGQDs/PAA\textsubscript{20}/PPy hydrogels with different content of PPy. (B-E) SEM images of FGQDs/PAA\textsubscript{20}/PPy hydrogels that synthesized with increasing concentrations of PPy.

Fig. 6 SEM images of (A) individual PPy and (B) PPy particles on the surface of FGQDs/PAA\textsubscript{20}/PPy hydrogels.
Fig. 7 (A) FTIR and (B) TGA analysis of FGQDs/PAA\textsubscript{20}/PPy composites.

Fig. 8 Conductivity of FGQDs/PAA\textsubscript{20}/PPy hydrogels that synthesized in different concentrations of Py.

FGQDs/PAA\textsubscript{20} hydrogels with mass ratio of FGQDs to PA = 0.053 were chosen to further incorporate with PPy. As shown in Fig. 5A, the hydrogel gradually turned black as the increasing of PPy amount. The pyrrole (Py) monomer was fully incorporated into the FGQDs/PAA\textsubscript{20} three-dimensional network hydrogels structure pore and adsorbed on the surface that rich in oxygen functional groups. The adding of initiator initiating the polymerization of Py monomer, completed the \textit{in-situ} polymerization both inside the pore and on the surface, realized the interpenetrating and filling of the conductive PPy in the hydrogel network. SEM images (Fig. 5B-5E) confirmed the formation of PPy nanoparticles decorated on the surface and into the pores of hydrogels. Comparing to the PPy alone (Fig. 6A), the PPy nanoparticles in the hydrogels showed smaller diameter, and tend to form cluster structures (Fig. 6B).

FT-IR spectra showed that the FGQDs/PAA\textsubscript{20}/PPy hydrogels exhibited the typical absorption peaks of FGQDs, PAA, and PPy (Fig. 7A). For example, FGQDs/PAA\textsubscript{20}/PPy hydrogels showed not only the strong peaks from pyrrole at 1552 cm\textsuperscript{-1} (C-C stretching vibration) and 1055 cm\textsuperscript{-1} (in-plane vibration of C-H),\textsuperscript{18} but also the peaks from FGQDs and PAA at 1713 cm\textsuperscript{-1} (C=O stretching vibration). TGA was performed to characterize the stability of FGQDs/PAA\textsubscript{20}/PPy composites (Fig. 7B). With more PPy incorporated, the thermal stability of FGQDs/PAA\textsubscript{20}/PPy composites enhanced. For example, the weight loss of 20 % happened at 259 °C for FGQDs/PAA\textsubscript{20}, and 286 °C for FGQDs/PAA\textsubscript{20}/PPy that synthesized in 21.6 mM of Py, while more PPy led to more weight residue at 900 °C.

The introduction of PPy further increased obviously the conductivity of the composite hydrogels. As shown in Fig. 8, FGQDs/PAA\textsubscript{20}/PPy composite hydrogels synthesized in different concentrations of Py resulted in conductivity various in 0.06-0.3 S/m. The FGQDs/PAA\textsubscript{20}/PPy composite hydrogels showed a highest conductivity of 0.29 S/m, better than or comparable to many PAA-based hydrogels\textsuperscript{19, 20}. The FGQDs/PAA\textsubscript{20}/PPy composite hydrogels combined the good mechanical properties of PAA hydrogels and the conductivity of FGQDs and PPy, indicating great promise in various applications.
4. Conclusion
In summary, a novel composite hydrogel system was produced in which PAA was crosslinked as matrixes, FGQDs as cross-linker, and polypyrrole as electroconducting component. The effects of the content of each part as well as the crosslink density on the structure of the composite hydrogels was investigated, and the swelling ratio and electrical properties were also studied. Highly conductive FGQDs/PAA_{20}/PPy hydrogels were got with a conductivity of 0.29 S/m, promising as conducting elements in various applications.

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