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Aggregation-mediated assembly of graphene oxide on amine-functionalized poly(glycidyl methacrylate) microspheres for core-shell structures with controlled electrical conductivity

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Abstract

We present a novel method for regulating the shell thickness of core-shell microspheres consisting of a polymer core and graphene oxide (GO) or reduced graphene oxide (RGO) shell. A strategy of pH-induced instability of GO and their gradual assembly with the core particles is employed. Interestingly, the thickness of the shell gradually increases from around 20 to 70 nm as the pH of the suspension decreases from 10 to 3 during the assembly process, which significantly changes the electrical properties of the core-shell microspheres. We are able to fabricate core-shell microspheres with a broad range of electrical conductivities from 1.79 to 31.43 S m⁻¹.

Introduction

Particles with core-shell structures are of great interest in various fields such as electronics, optics, catalysts and sensors, since the hybridization of different types of functional materials enables selective adjustment of the material properties and the development of unique characteristics.¹⁻⁶ Materials properties of core-shell structures are greatly affected by the size of the particles and the thickness of the shell component. Thus, to obtain particles with desired properties, the size of the core and the thickness of the shell should be precisely regulated.^{7,8}

Recently, graphene has been extensively explored as a shell material for numerous applications due to its unique electrical, mechanical, optical, and thermal properties.⁹⁻¹⁴ However, there is a big challenge in controlling the thickness of graphene shell. For two-dimensionally assembled structures, it can be typically achieved by varying the number of repetitive processes or the processing time using methods such as layer-by-layer technique, spin coating, dip coating, and electrophoretic deposition.¹⁵ Unfortunately, these techniques are not applicable to small-scale materials with even simple structures such as spheres and rods. For graphene-coated core-shell structures in nano/micrometer size, graphene oxide (GO) is usually used as a shell component, since the process is carried out in a solvent. Once the surface of the core is covered with a thin layer of GO, the GO shell starts to repel other GO sheets to be deposited due to the electrostatic repulsion.¹⁶ Thus, the growth of GO shell cannot progress further, suggesting that increasing the thickness of the shell is limited regardless of the input of GO. An ideal means to overcome this is to fabricate GO sheets with the uniform numbers of layers, but there have been no methods available so far. Thus, it is essential to develop an appropriate method to overcome this problem.

We present a pH-responsive aggregation-mediated (PRAM) self-assembly of GO onto amine-

functionalized poly(glycidyl methacrylate) microspheres, leading to core-shell particles with various shell thicknesses. By adjusting the pH of the GO suspension mixed with polymer microspheres, we were able to gradually grow the thickness of the GO shell. As the shell thickness increases, the electrical conductivity of the core-shell microspheres significantly enhances, forming highly conductive core-shell microspheres with uniform size. This technique is facile and capable of producing large volumes of GO-coated core-shell microspheres with controlled thickness. As a result, the material properties can be adjusted over a wide range. We believe that the developed PRAM method has great potential for making various types of graphene-based core-shell structures.

Results and Discussion

To obtain functional monodisperse polymer cores, dispersion polymerization of glycidyl methacrylate (PGMA) was conducted and the epoxy groups were further modified with ethylenediamine to give amine-functionalized polymer microspheres (PGMA-ed, Fig. S1a in supplementary information). The diameter of PGMA-ed is around 1.8 μm and uniform in size with a smooth surface (Fig. S1b). The zeta potential of the PGMA-ed is around -30 mV at pH 10, indicating the surface is negatively charged. It gradually increases as the pH decreases and reaches to +5 mV at pH 2. The net surface charge of the PGMA-ed is affected by both the amine functional groups and the grafted PVP stabilizers on the surface (Fig. S1c).

Graphene oxide was obtained using oxidation and mechanical exfoliation of graphite. During the process, oxygen-containing functional groups, such as hydroxyl and epoxy groups on the basal plane, and carboxyl groups at the edge, are generated. The incorporation of these functional groups broadens the G peak of graphite and forms D peak due to the amorphization of graphite (Fig. S2). The functional groups allow the GO to be well-dispersed in water or polar solvents.¹⁷ Above pH 5, the GO dispersions are very stable, but the stability

gradually decreases as the pH lowers due the protonation of the carboxylic acid groups and it finally becomes unstable below pH 3 (Fig. S2d).

The fabrication process of the GO/PGMA-ed core-shell microspheres initiated at pH 10, where the surface charges of both GO and PGMA-ed are the same. It suggests that the assembly of the GO sheets on the surface of the PGMA-ed occurs by the chemical reaction between functional groups of the GO and PGMA-ed, not by the electrostatic attraction. We presume that it is the ring-opening reaction between the epoxy groups of the GO and the amine groups of the PGMA-ed. The GO/PGMA-ed microspheres were easily isolated from the GO dispersion by centrifugation (Fig. S3). The GO/PGMA-ed core-shell particles were redispersed in water and added with hydrazine to reduce the GO shell to RGO. XPS results show that the C/O ratio of GO/PGMA-ed increases after the reduction from 5.8 to 8.8, confirming that the GO shell is partially reduced (Fig. S4). Fig. 1 displays the SEM images of the RGO/PGMA-ed core-shell microspheres produced at pH 10 (a), 7 (b), 5 (c), 3 (d), and 2 (e). The RGO/PGMA-ed core-shell particles are also uniform in size with an average diameter of 1.8 μm without aggregation between particles except for the one obtained at pH 2. The surface is slightly rough and the roughness gradually increases as the pH decreases. At pH 2, highly rough surface of the core-shell particles and irregularly aggregated GO sheets are found, indicating that GO sheets are not only assembled on the outer surface of the core particles, but also with each other to form aggregates. This result implies that the self-assembly of GO sheets onto core particles is favored in acidic conditions, but in highly acidic conditions (below pH 3), GO sheets are rather randomly aggregated because most of the carboxylic acid groups of the GO sheets are abruptly protonated, leading to significant loss of stability.

The insets of Fig. 1 (a) to (d) are digital images of the powder form of the RGO/PGMA-ed

microspheres. The color of the RGO/PGMA-ed produced at pH 10 is light gray, and it becomes darker as the pH decreases. In general, a single layer of graphene or GO is highly transparent in the visible region, and the transmittance is linearly reduced with increases in the number of layers.¹⁸ This suggests that the layers of the RGO shell increase as the pH decreases. It has been known that the reduction degree can affect the transparency of the RGO shell. Highly reduced GO contains more π -conjugated carbon networks than slightly reduced GO, which increases the absorption in the range of 280-800 nm, resulting in darkening.¹⁹ However, in our case, since the reduction conditions were carefully controlled, the reduction degrees of RGO shell are not the reason for the darkening.

To confirm the thickness of the shell, cross-sectional TEM analysis was conducted. Fig. 2 displays the cross-sectional TEM images of the RGO/PGMA-ed microspheres fabricated at pH 10 (a), 7 (b), 5 (c), 3 (d), and 2 (e). The PGMA-ed microspheres are completely covered with RGO shells without voids or delamination at the interface between the core and shell. It clearly shows that the shell gradually grows with decreasing pH. The average shell thicknesses obtained from the images of the core-shell particles produced at pH 10, 7, 5, 3, and 2 are approximately 24, 37, 55, 70, and 100 nm, respectively. Assuming that the thickness of a single layer of GO is around 1 nm, the shell is composed of up to 70 layers of GO at pH 3.²⁰ We expected that a very thin shell less than 10 nm would be formed at pH 10, but the shell is thicker than expected. We assume that this is because the synthesized GO sheets are composed of various numbers of layers of GO, from one layer to tens of layers, and also the GO sheets are randomly folded and overlapped while being assembled on the core particles.

Fig. 3 shows the electrical conductivity for the RGO/PGMA-ed core-shell microspheres as a function of the volume change. As shown in the graph, the electrical conductivity of each

sample rapidly increases at the beginning of the deformation to 15 %, and slowly reaches to its maximum at around 45 %, and then slightly declines. The conductivity of the conductive particles strongly depends on its packing density and surface contact area. We expect that the RGO/PGMA-ed microspheres are less densely packed initially. With the compression, the packing density increases as the interstitial space between the particles is packed, resulting in the rapid increases in the conductivity, and subsequently the contact area gradually increases by the deformation of the core-shell particles. We assume that the drop in the conductivity results from the partial fracture of the RGO/PGMA-ed upon large deformation. The conductivity of the core-shell microsphere linearly rises as the thickness of the RGO shell increases, since the electrical path expands. The RGO/PGMA-ed microspheres fabricated at pH 10, 7, 5 and 3 reaches the maximum conductivities of 1.79, 4.06, 19.5, and 31.43 s m^{-1} , respectively. By varying the thickness of the shell, the electrical properties of the core-shell particles can be widely adjusted up to 17 times. Compared with previous reports, the maximum conductivity is significantly enhanced by more than 7 times.^{10, 21} Unlike other carbonaceous materials, graphene and graphene derivatives can assemble to itself and forms robust structures, which enables graphene to be used as a shell component without using binders. The advantage of the graphene-coated core-shell particles is that the overall size can be readily tuned from hundreds of nanometers to tens of micrometers by selecting suitable substrates. We believe that the electrical properties can be more diversely tuned by using different sizes of core particles and controlling the reduction degree of the RGO shell.

Fig. 4 shows a schematic of the pH-responsive aggregation-mediated self-assembly of GO onto polymer microspheres. When the PGMA-ed and GO in solution are mixed together, the GO sheets are assembled on the surface of the PGMA-ed microspheres by the ring-opening reaction between epoxy groups of GO and amine groups of PGMA-ed, or both, leading to the

formation of GO/PGMA-ed core-shell structures.^{9, 10} At high pH, once a thin GO shell is formed on the polymer surface, the assembly of GO onto the PGMA-ed core does not continue, since there is no attraction between the attached and unattached GO sheets. As the pH of the suspension reduces, some portion of the unbound GO sheets is protonated and loses its stability, triggering aggregation of the unstable GO to the existing GO shell. Accordingly, lower pH results in a thicker GO shell. However, in highly acid conditions, the rate of aggregation is too fast, forming a large number of GO aggregates. For conductive microspheres, the GO shell can be chemically reduced by the addition of a reducing agent such as hydrazine or sodium borohydride, which gives core-shell particles with various electrical properties.

Conclusions

We have demonstrated the aggregation-mediated self-assembly of GO onto amine-functionalized polymer microspheres triggered by pH variation, enabling precise control of the thickness of GO shells. As the pH of the suspension of GO and PGMA-ed microspheres decreases from 10 to 3, the thickness of the GO shell gradually increases from 24 to 70 nm. However, below pH 3, the GO sheets not only tend to assemble onto the core particles, but also aggregate with themselves, resulting in a number of random aggregates. The electrical properties of the RGO/PGMA-ed core-shell particles with different shell thicknesses were measured as a function of the volume changes. The electrical conductivity can be widely adjusted from 1.79 to 31.43 S m⁻¹ as the thickness of shell changes. We expect that the properties of the GO-coated core-shell particles can be more diversely tuned for various applications by adjusting the core size, the shell thickness, and reduction level. It is highly believed that the developed method has great potential to be applied for numerous types of

core materials with various structures.

Acknowledgements

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Figure captions

Fig. 1. SEM images of RGO/PGMA-ed core-shell microspheres produced at pH 10 (a), 7 (b), 5(c), 3 (d), and 2 (e) with insets showing powder form of the core-shell particles

Fig. 2. Cross-sectional TEM images of RGO/PGMA-ed core-shell microspheres produced at pH 10 (a), 7 (b), 5 (c), 3 (d), and 2 (e)

Fig. 3. Electrical conductivity for the RGO/PGMA-ed core-shell microspheres produced at pH 10, 7, 5, and 3 as a function of the volume change.

Fig. 4. Schematic of the pH-responsive aggregation-mediated self-assembly of GO onto polymer microspheres.

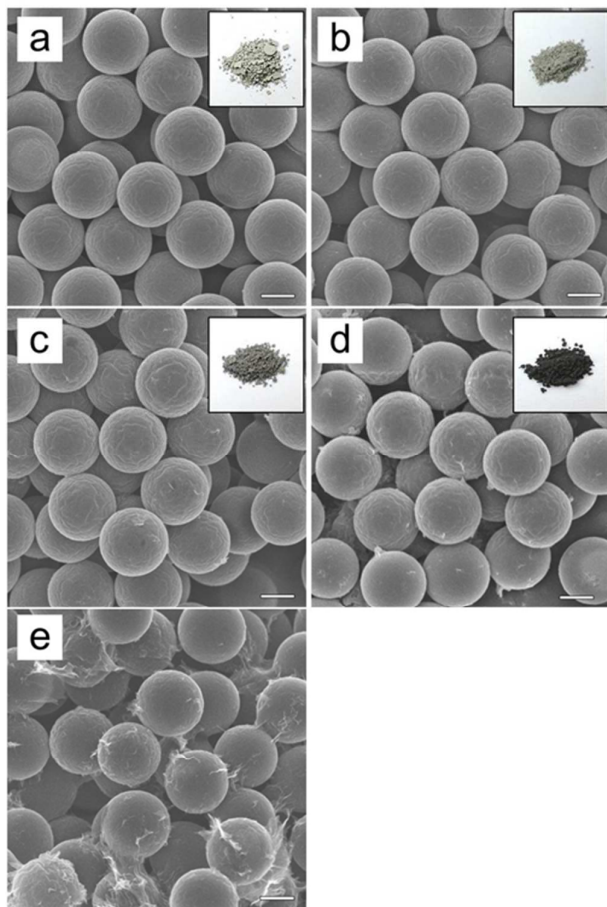


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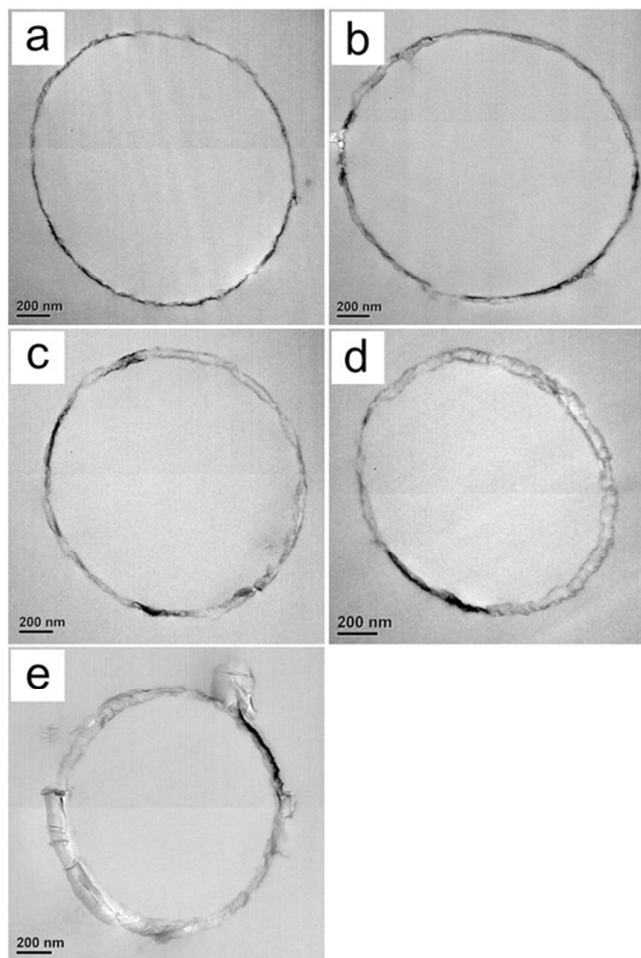


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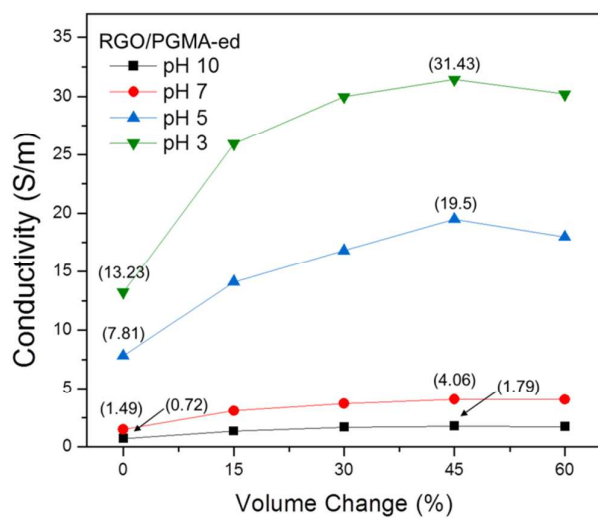


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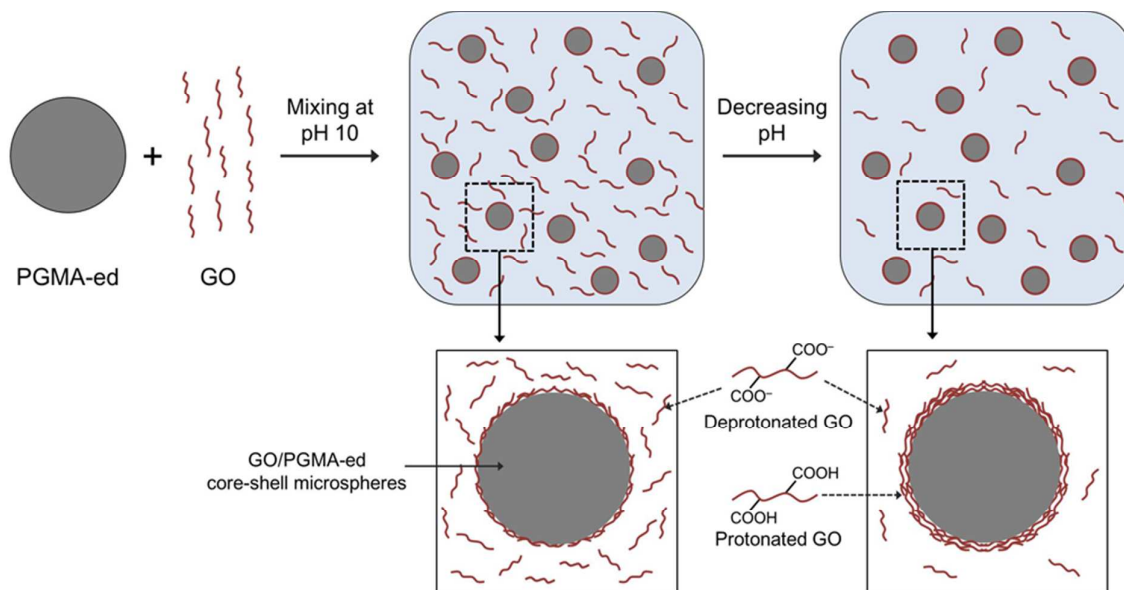


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