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Oil absorbing graphene capsules by capillary molding
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Oil absorbing graphene capsules are synthesized by capillary molding of graphene oxide (GO) sheets against a polystyrene bead template in evaporating aerosol droplets, followed by simultaneous reduction of GO and decomposition of the polymer template during ultrasonic spray pyrolysis.

Graphite oxide layers, now named graphene oxides (GOs), are an exfoliated form of mineral graphite obtained by chemical oxidation that was first discovered over 150 years ago.1,2 Since 2004,3 GO has attracted significant new interest as a solution processable precursor for making graphene-based materials.4–8 GO sheets are essentially soft, water-dispersible, single atomic layers that can easily turn into a conductive form, which make GO a very unique soft material with applications beyond its use as a graphene precursor.9 The high flexibility of GO sheets makes it possible to mold them and the strong attraction between sheet-like materials can help to fix the final shapes. In an earlier work, we developed the fluorescence quenching procedure, determination of oil adsorption and dye adsorption of GO sheets from the bulk of solution to the template surface.10 Thermodynamically, such a strategy requires specific attractive interactions for GO sheets to absorb onto the surface of the template,15 and kinetically it requires the diffusion of GO sheets from the bulk of solution to the template surface. Although such a strategy has been very successful for molecular surface assembly, applying it to GO is not as straightforward due to its large lateral dimensions. For example, the diffusion of GO sheets in solution would be much slower than that of common molecules due to their very high molecular weights. For typical GO sheets that are as large as, or even larger than the diameter of the template particles, surface absorption alone may not provide enough driving force to make a tight conformal coating. A capillary molding approach, in which the soft GO sheets can be pushed to wrap the template particles by capillary force, is more general as it eliminates the need for specific interactions required for self-assembly. Meanwhile, the capillary shock at the end of solvent evaporation can tighten the GO wrapping around the template, leading to high fidelity shape replication. Finally, high throughput fabrication can be achieved using aerosol spray pyrolysis, where the aerosol droplets containing GO and the template particles are blown through a pre-heated furnace to achieve capillary molding, GO reduction, and template decomposition in one step.

Aerosol spray pyrolysis has been widely used in industry for the production of ultrafine particles because the technique allows continuous mode of operation and can be easily scaled for mass production. Here, we chose sub-micron sized polystyrene colloids as the model sacrificial template since they can be conveniently synthesized by emulsion polymerization in large quantities. They can also be readily decomposed when flying through a hot furnace maintained at above 500 °C. The schematic drawings in Fig. 1 illustrate the process for fabricating graphene capsules. Aqueous aerosol droplets containing GO sheets and polystyrene colloids are first generated by an ultrasonic atomizer, and then blown into a preheated tube furnace by Ar carrier gas. As they fly through the heating zone, the aerosol droplets first rapidly evaporate, generating GO wrapped polystyrene beads that eventually turn into hollow graphene capsules due to thermal reduction of GO and decomposition of the polystyrene beads. If a second component such as metal or metal oxide nanoparticles is added in the initial dispersion, they can be readily incorporated into the final hollow capsules. The product can be collected on a particle filter attached to the end of the tube.

The low magnification scanning electron microscopy (SEM) image in Fig. 2a gives an overview of the sample morphology, removal step.‡ Thermodynamically, such a strategy requires specific attractive interactions for GO sheets to absorb onto the surface of the template,15 and kinetically it requires the diffusion of GO sheets from the bulk of solution to the template surface. Although such a strategy has been very successful for molecular surface assembly, applying it to GO is not as straightforward due to its large lateral dimensions. For example, the diffusion of GO sheets in solution would be much slower than that of common molecules due to their very high molecular weights. For typical GO sheets that are as large as, or even larger than the diameter of the template particles, surface absorption alone may not provide enough driving force to make a tight conformal coating. A capillary molding approach, in which the soft GO sheets can be pushed to wrap the template particles by capillary force, is more general as it eliminates the need for specific interactions required for self-assembly. Meanwhile, the capillary shock at the end of solvent evaporation can tighten the GO wrapping around the template, leading to high fidelity shape replication. Finally, high throughput fabrication can be achieved using aerosol spray pyrolysis, where the aerosol droplets containing GO and the template particles are blown through a pre-heated furnace to achieve capillary molding, GO reduction, and template decomposition in one step.

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The low magnification scanning electron microscopy (SEM) image in Fig. 2a gives an overview of the sample morphology,
This journal is the capillary molding process. For example, gold nanoparticles incorporated to create new functionalities without interfering with mold, smaller nanoparticles of metal or metal oxide can be of the resulting particles. In addition to the polystyrene particle tool for on-demand engineering of the structures and properties to serve different purposes, which makes it a very convenient/c2

\[ V_f = \frac{4}{3} \pi r^3 \]

from single polystyrene particles with a diameter of 580 nm.

\[ V_f \approx 10^6 \text{ cm}^3 \text{ per capsule} \]

For the bulk sample, monomeric capsule powders should have a free volume of 4.50 µl mg⁻¹ and a density of 0.20 g cm⁻³. Therefore, compared to solid graphite, monomeric graphene capsules would occupy at least 10 times more space. Note that this ratio will be significantly increased with oligomeric capsules due to the third power dependence of free volume on the size of the template.

One advantage of the spray pyrolysis method is that one can incorporate multiple components into the aerosol droplets to serve different purposes, which makes it a very convenient tool for on-demand engineering of the structures and properties of the resulting particles. In addition to the polystyrene particle mold, smaller nanoparticles of metal or metal oxide can be incorporated to create new functionalities without interfering with the capillary molding process. For example, gold nanoparticles (Fig. 3a) and Fe₃O₄ nanoparticles (Fig. 3b) have been added to render potential catalytic activity and magnetic response of the graphene capsules, respectively.

The graphene capsules have several structural features and properties that could make them attractive for oil absorption and recovery. For example, they are lightweight powders with large free volumes, which are spreadable over large areas to collect oils. The decomposition of the polystyrene template during the pyrolysis should generate small openings on the resulting capsules, which makes capillary absorption of oil into the hydrophobic structure possible. Magnetic particles can be added to decorate the capsules, making them responsive to magnetic manipulation. To test the maximum absorption of graphene capsules decorated with Fe₃O₄ nanoparticles, incremental amounts of vegetable oil colored with oil red dye, from 10 to 50 µl, are mixed with 1 mg of carbon powder. Next water is added to make the oil–carbon blend float, which can then be dragged by a magnet in order to see whether there is any unabsorbed oil outside capsules (Fig. S2a–e, ESI†). The maximal absorption of the capsules is reached when red oil starts to appear after magnetic separation (Fig. S2c, ESI†). Note that this method can reveal a large amount of unabsorbed oil that is just temporarily trapped in the interstitial space between the powders. Alternative methods for determining oil uptake, such as by weighing the carbon powders soaked in oil, would usually include the unabsorbed interstitial oil, leading to overestimation of the absorption capability. Using the method shown in Fig. S2 (ESI†), the maximum absorption capability of Fe₃O₄ decorated hollow r-GO spheres is qualitatively determined to be between 17.5 and 21.0 µl mg⁻¹. Even after including the Fe₃O₄ (20 wt%) nanoparticles in the base mass, the absorption capacity is still a few times higher than the free volume of the monomeric capsules. This is expected due to the contribution from the larger oligomeric capsules.

A set of control experiments were carried out to compare the oil absorption capability of graphene capsules against some high surface area carbon materials such as activated carbon (Norit Darco G60) and carbon black powders (Cabot Vulcan XC-72) (Fig. 4a). The specific surface areas of the graphene capsules, carbon black and activated carbon were measured to be 84 m² g⁻¹, 230 m² g⁻¹ and 789 m² g⁻¹, respectively, by the Brunauer–Emmett–Teller (BET) method based on nitrogen absorption. SEM images reveal that activated carbon (Fig. S3a, ESI†) and carbon black (Fig. S3b, ESI†) are made of primary particles of tens of nanometers. The high surface area of activated carbon is due to nanoporous channels.
inside the particles.\textsuperscript{18} Although the specific surface area of single layer graphene is around 2600 m\(^2\) g\(^{-1}\), the value of graphene stacks should be 2600/n m\(^2\) g\(^{-1}\), where n is the number of layers in the stack. Since the wall of the capsules has about 30 layers of graphene sheets, the measured BET surface area is in good agreement with the expected value, which also suggests that the accessible surface area is largely limited to the physical surface of the hollow spheres.

We found that high specific surface area is beneficial for molecular adsorption, but not necessarily for oil absorption. Dye adsorption tests of these carbon materials in aqueous solution were carried out using methylene blue as a marker.\textsuperscript{19} The powders were first added to an aqueous solution of methylene blue, and the characteristic optical absorption band of the dye at 664 nm was monitored by a UV/vis spectrometer over time to determine the amount of dye being adsorbed. The plot in Fig. S3d (ESI) illustrates the amount of dye being absorbed by the three types of carbon powders over time, clearly showing the correlation between specific surface area and the dye adsorption capability. However, the oil absorption experiments (Fig. 4a) show that despite having the smallest surface area, the graphene capsules have the highest oil adsorption capability. This offers a basic design principle for oil absorption materials, which is used to create as high free volume as possible. After oil uptake, the oil filled graphene capsules aggregate on the water surface, which facilitates their collection. In a demonstration shown in Fig. 4b–e, initially 100 µl of dyed vegetable oil was spread on the water surface. Then, 10 mg of magnetically decorated capsule powders were sprayed onto the oil film, which quickly shrank within a few minutes (Fig. 4c), and eventually tuned into a thick carbon–oil droplet (Fig. 4d), which can be manipulated by a magnet. When underdecorated graphene capsules were used, the resulting blend can be directly picked up and removed by a glass rod (Fig. 4f–i).

In conclusion, graphene (a.k.a., r-GO) capsules can be fabricated in one step by spray pyrolysis from a dispersion of GO and polystyrene colloids. The technique employs evaporation induced capillary force to mold GO sheets into the shape of the polymer colloids, thus eliminating the need for selective surface recognition between GO and the template. Therefore, this should be a general approach for producing hollow graphene particles of various shapes replicating the morphologies of the template, such as polyhedral particles, nanorods or nanowires and their aggregates. The resulting capsules have high free volume determined by the size of the template, and show promising oil absorption property. Moreover, an additional component can be conveniently added into the starting dispersion to modify the wall of the graphene capsules, which renders new functionalities. In our preliminary work, scaled up production can be readily achieved using commercial spray driers, which are capable of handling massive volumes of solutions. Therefore, capillary molding in evaporating aerosol droplets should become a very powerful technique for on-demand engineering of the size, shape, chemical composition and interior structures of GO or graphene capsules.

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Notes and references