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Short Communication

Template-free assembly of three-dimensional networks of graphene hollow spheres at the water/toluene interface

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ABSTRACT

Hypothesis: The Pickering emulsion system, generated by amphiphilic graphene oxide (GO) sheets trapped between water/toluene liquid interfaces, can be directly used for template-free formation of three-dimensional (3D) structure of GO hollow spheres.

Experiments: The method involves the formation of highly stable micron-sized Pickering emulsions *via* mild sonication of GO aqueous solution and toluene in the presence of polyvinyl alcohol (PVA), followed by direct freeze-drying of the mixture for preserving the unique 3D hollow spherical structures.

Findings: The 3D structure of interconnected GO hollow spheres, with a diameter in the range ~2 to 10 μm, has been prepared. Transmission and scanning electron microscopy analyses confirmed the formation of the 3D structure directly from the Pickering emulsion system. The presence of PVA is critical in supporting the GO hollow spherical structures. Raman analysis confirmed the structural integrity of the GO in the 3D products.

1. Introduction

Constructing low dimensional materials into three-dimensional (3D) structures while preserving their properties is important in realising the full potential of such material in practical applications. This is particularly critical for thermodynamically unstable two-dimensional (2D) materials such as graphene [1], which tend to restack into graphitic forms *via* van der Waals interactions, unless they are shrouded by stabilising agents or covalently derivatized [2]. 3D structures of graphene-based materials offer high specific surface area, enhanced mechanical strength, and fast mass and electron transport kinetics [3–5]. Different methods have been explored in recent years for fabricating 3D graphene architectures [6], including gelation [7,8], hydrothermal reduction [3,9], and template-directed processes [5,10–12]. Nevertheless, there are still inherent challenges in their synthesis such as controlling the microscopic morphology, structural stability, and product scalability. Indeed, there is scope for developing novel, straightforward, and low-cost protocols to prepare 3D graphene, with potential ability to manipulate the microstructures and to obtain functional nano-composites by selective loading and confinement of substances.

Herein we report a relatively straightforward and robust method to prepare a unique 3D structure of graphene oxide (GO) hollow spheres. This involves mild probe sonication of a mixture of an aqueous solution of GO and toluene in the presence of polyvinyl alcohol (PVA), followed by an immediate freeze-drying process, as summarised in Fig. 1a. GO is amphiphilic due to its hydrophilic groups (e.g. carboxyl and hydroxyl groups) at the edges and hydrophobic polyaromatic islands of unoxidized benzene rings within the basal plane [13]. Therefore, GO is capable of creating highly stable Pickering emulsions of immiscible liquids by acting as a colloidal surfactant trapped at liquid interfaces in minimizing surface energy [14–17]. GO sheets can spontaneously wrap around toluene droplets during a shaking to form an emulsion phase with long term stability at the water/toluene interface. A similar strategy has been used for readily organising one-dimensional (1D) nanostructures such as palladium nano-wires and carbon nanotubes into toroidal structures in an oil/water mixture [18]. It is reasonable to expect that the emulsion phase generated by GO sheets at the water/toluene interface can be potentially used for template-free constructing 3D GO networks, with preserved hollow spherical structures.

Abbreviations: 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; GO, graphene oxide; PVA, polyvinyl alcohol; TGA, thermal gravimetric analysis; BET, Brunauer–Emmett–Teller; TEM, transmission electron microscopy; SAED, selected area electron diffraction; SEM, scanning electron microscopy; ESI, electronic supplementary material.

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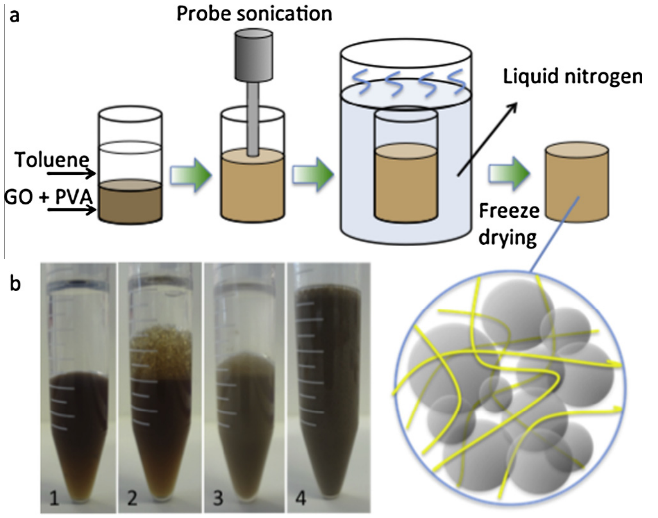

Fig. 1. (a) Synthetic procedure for fabricating 3D structures of GO hollow spheres. (b) Photographs of (1) the initial GO aqueous solution (0.2 mg mL^{-1}) and toluene mixture, (2) the emulsion phase formed upon shaking a mixture of (1), (3) the mixture in (1) after probe sonication, (4) the mixture of GO aqueous solution (2 mg mL^{-1}) with toluene after probe sonication.

2. Experimental section

2.1. Materials

The aqueous solution of GO at ~2 mg mL^{-1} was prepared from graphite powder (SP-1, Bay Carbon) following the modified Hummer's method [19,20]. Toluene from LiChrosolv, Merck Chemicals, was used directly without any pre-treatment. PVA (M.W. 14,000) was used as received from BDH Chemicals Ltd.

2.2. Sample preparation

Direct mixing of the GO aqueous solution (3 mL, 0.2 mg mL^{-1}) and toluene in 1:1 volume ratio gives two immiscible liquid phases with toluene as the upper layer, as shown in Fig. 1b(1). Shaking the mixture generates a bubble-like region at the GO solution/toluene interface, Fig. 1b(2). The bubbles are filled with toluene given that this region occupies part of the volume of the toluene rather than that of the GO aqueous solution. The volume of the emulsion phase depends on the concentration of GO in solution and the volume of toluene, which is in accordance with other findings [14]. Toluene droplets in water are formed upon shaking, typically with diameters in the hundreds of micrometres [14].

Mild sonication of the mixture of GO aqueous solution and toluene produces much smaller emulsion droplets, in the micron range [17]. This relates to the cavitation process associated with sonication and the consequential vigorous micro-mixing between the two liquid phases [21]. As shown in Fig. 1b(3), sonication of the mixture in Fig. 1b(1) generates a uniform dispersed GO solution phase, which may contain well-dispersed small GO stabilised toluene droplets. With the same volume ratio, GO solution with a higher concentration (2 mg mL^{-1}) can mix with the entire toluene to form a seemingly one-phase mixture, Fig. 1b(4). This is a relatively simple method to generate a large number of stable GO spheres of few-microns in size, without the need for a template. These GO spheres pack together forming a 3D structure. However, they tend to collapse after drying in air, as the toluene inside evaporates. In attempting to stabilise the spheres, we added PVA, a water-soluble polymer, into the mixture prior to the addition of toluene. The PVA acts as a potential physical cross-linking agent between the spheres to maintain the integrity of the 3D structure on loss of solvent. Previous results have shown that PVA is effective in preparing graphene composite hydrogels due to the strong interfacial interaction between the two components [22–24].

In a typical experiment, PVA was added directly into GO aqueous solution (2 mg mL^{-1}, 10 mL) prior to the addition of toluene (10 mL). Then the two-phase GO solution/toluene system was subjected to 5 min of mild probe sonication (40% amplitude, Vibra-Cell™ VCX130). This results in what appears as a single uniform viscous phase. Thereafter, 1 mL of the slurry was immediately transferred into a centrifuge vial (with a few holes punched on the cap), which was dipped into liquid nitrogen for 1 min, followed by 24 h of freeze-drying (Delivery: 20 L/min, Ultimate vacuum: 8 mbar). Drying the final product essentially maintained its volume, as evident in Fig. S1, ESI. The weight of the final product is ~0.9% of that of the slurry before the freeze-drying. The thermal stability of the final product was investigated using thermal gravimetric analysis (TGA), in Fig. S2, ESI. The Brunauer–Emmett–Teller (BET) test of the material, Fig. S3, showed a relatively low specific surface area of 22.3 m^2 g^{-1} due to stacking of GO sheets at the toluene/water interface which is retained in the final product. This is consistent with a number of GO sheets being required in order to stabilise the toluene Pickering emulsions.

2.3. Characterization

Transmission electron microscopy (TEM) characterizations were carried out using the JEOL 2100 instrument operating at 120 kV and Philips CM200 instrument operating at 200 kV. The TEM samples were prepared by directly dropping the GO aqueous suspension or liquid emulsion phase onto the holey carbon film coated copper grids (#2450-AB, SPI supplies), and dried under ambient conditions. Scanning electron microscopy (SEM) analysis was performed on the FEI Quanta 450, with high voltage, 10 kV, and working distance, 10 mm. Raman spectra were acquired using a Horiba XploRA confocal Raman microscope with 532 nm excitation wavelength. TGA analysis on the pure PVA powder and the resulting composite 3D GO product was carried out using a TA instrument. Samples were heated from room temperature at a rate of 10 °C min^{-1} in an atmosphere of air. BET test was carried out on a MicroMeritics Gemini VII surface area analyser.

3. Results and discussion

TEM analysis was carried out on the synthesized GO and GO spheres. The GO sheets have lateral dimensions between ~200 nm and 10 μm, Fig. 2a. The selected area electron diffraction (SAED) pattern of the GO in Fig. 2b shows a typical sixfold symmetry, with the peaks labelled by Miller-Bravais ($hkil$) indices [25]. This is a definitive identification of graphene or GO; for multilayers the intensity ratio is $I_{\{1\,1\,0\,0\}}/I_{\{2\,1\,1\,0\}} < 1$, whereas for monolayers it is $I_{\{1\,1\,0\,0\}}/I_{\{2\,1\,1\,0\}} > 1$ [26]. The inner diffraction peaks, $(0\,{-1}\,1\,0)$ and $({-1}\,0\,1\,0)$, are higher than that of the outer ones, $(1\,{-2}\,1\,0)$ and $({-2}\,1\,1\,0)$, confirming the presence of monolayer sheets. Fig. 2c and d shows the TEM images of the GO spheres prepared during sonication of GO solution/toluene without the addition of PVA. Networks comprised of spherical structures of GO are evident in Fig. 2c, although they probably have collapsed. TEM analysis reveals that the GO spheres have a relatively narrow size distribution, with a diameter in the range ~2 to10 μm.

SEM analysis of the freeze-dried product revealed an interconnected 3D structure, Fig. 3a and b. Fig. 3c and d show zoomed-in images of the 3D structure of GO hollow spheres. The dimension of the GO spheres is consistent with that observed in TEM, indicating that the integrity of the structures formed in the emulsion phase have been well preserved. During the sonication process micron-sized toluene droplets are generated and stabilised by GO sheets,