

Porous hollow carbon nanotube composite cages

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Mechanically robust, hollow carbon nanotube composite spheres that are permeable to large chemical species were prepared by a layer-by-layer assembly and templating technique.

Polyelectrolyte hollow spheres have been extensively investigated due to their potential applications as filler materials, microreactors, artificial cells and drug delivery vehicles.¹ Among the currently available fabrication methods, the one adopting the layer-by-layer (LBL) coating technique is of particular interest due to the benefits of allowing multiple layers of different functional materials (*e.g.*, functional polyelectrolytes) to be coated onto a sacrificial template particle. Subsequent template removal results in hollow spheres whose functionality and cage size can be controlled by the coated material and diameter of the template particle, respectively.^{1,2} For certain applications mentioned above, hollow spheres with a porous shell that allow the controlled transport of target species across it are required. However, for extremely large target species such as enzymes and proteins, the size of the pores present within the shell have to be made comparable to the size of those molecules, deteriorating the mechanical strength of the hollow sphere.³ The simultaneous achievement of a robust hollow architecture and improved large molecule permeability still remains a challenge.

This work reports the fabrication of composite hollow spheres, consisting of carbon nanotubes (CNTs), polyelectrolyte molecules and inorganic materials (*e.g.*, silica and titania), which are both mechanically robust and permeable to large species such as nanoparticles. CNTs, a class of nanoscale fullerene-related material, are well known for their unique and superior mechanical, optical and electrical properties.⁴ Recent progress in surface modification techniques further allow various chemical modifiers to be covalently attached onto the CNT's surface, facilitating their dispersion in various media and the synthesis of a large family of CNT-based functional nanocomposites.⁵ It has been demonstrated that CNTs can form non-woven fabrics with large interconnected pores.⁶ We hypothesize that such planar, non-woven fabrics can be constructed into hollow composite spheres that are permeable to large species. It is anticipated that the incorporated CNTs will provide the composite spheres with mechanical strength and unique properties (*e.g.*, electrical conductivity), while the polyelectrolyte will provide flexible functionality and tunable surface

charges. Meanwhile, the inorganic component may provide protection, additional mechanical strength and other functionalities (*e.g.*, titania may provide photocatalytic properties).

Our synthesis strategy is based on the LBL assembly and templating technique described by the following four steps:[†] (1) Functionalization of the CNTs with hydrophilic surface carboxylic groups, (2) repeated adsorption of the CNTs onto the polystyrene (PS) template particles, pre-coated with positively-charged polyelectrolyte poly(diallyldimethylammonium chloride (PDDA), (3) infiltration of the inorganic component (*e.g.*, SiO₂ or TiO₂) into the PDDA/CNT composite layers *via* a sol-gel process, strengthening the shell architecture, and (4) removal of the PS template, leading to the formation of hollow composite spheres that allow the transport of large species such as nanoparticles. Although the assembly of CNTs and polyelectrolytes on both planar and spherical surfaces has been previously reported,^{6–8} the formation of a robust hollow sphere has not yet been achieved due to the fragile nature of its structure. Although carbon nanotube composites containing inorganic silica or polymers have been prepared, to the best of our knowledge, this is the first example of mechanically robust hybrid hollow spheres that are permeable to extremely large species.

Fig. 1 shows representative scanning electron microscopy (SEM) images of (A) ambient-dried CNT/PDDA and (B–D) CNT/PDDA/SiO₂ composite spheres prepared by the LBL technique. In order to match the length of the CNTs,⁸ PS particles with diameters of 4–6 μm were used. The use of template particles with smaller diameters causes significant aggregation, since the relatively long CNTs may bridge the PS spheres. Due to the strong interactions between positively-charged PDDA surface and the carboxylic acid group, the CNTs were adsorbed onto the polyelectrolyte PDDA surfaces, forming CNT networks. As shown in Fig. 1A, the porous hairy surface observed originates from the dangling CNT tail ends, consistent with previous reports.⁶ However, most of the spheres were broken after the removal of the PS templates, indicating the poor mechanical stability of the hollow structure. Multiple CNT/PDDA coatings were found to improve the mechanical strength to some extent, but not enough to solve the problem. Although CNT/polyelectrolyte composites could be further strengthened by thermal treatment,⁷ we used an alternative and more effective method to stabilize the structure by incorporating inorganic materials, such as silica and titania, within the CNT/PDDA layers. The hypothesis is that the incorporated inorganic materials might “glue together” the CNT and PDDA and help solidify the overall structure. Fig. 1B shows a SEM image of the CNT/PDDA/SiO₂ nanocomposite particles before template removal. The infiltrated silica fills the interstitial voids in the CNT/PDDA shell layers, converting the hairy surface

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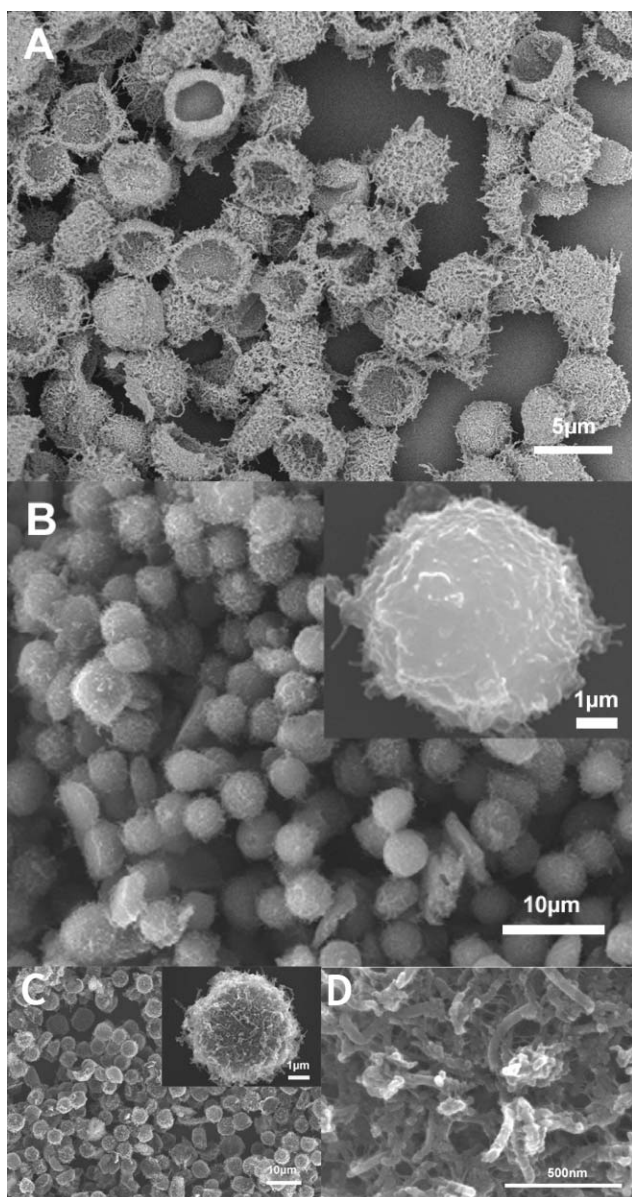


Fig. 1 SEM micrographs of (A) CNT/PDDA and (B–D) CNT/PDDA/SiO₂ composite spheres. (A) Ambient-dried CNT/PDDA hollow spheres after template removal, mostly collapsed, (B) and (C) SiO₂ strengthened composite spheres before and after template removal, respectively, (D) a zoom-in image of the sphere surface shown in Fig. 1C, showing the porous morphology.

morphology (Fig. 1A) into a smooth appearance (Fig. 1B). The silica content measured by thermogravimetric analysis (TGA) is around 6 wt% of the composite. The spherical shape is well maintained after template removal by dimethylformamide (DMF) (Fig. 1C), indicating the enhanced mechanical stability. Interestingly, template removal also restores the same hairy morphology as that shown in Fig. 1A. The magnified SEM image shown in Fig. 1D consistently reveals a porous nanotube network structure. The formation of porous channels upon removal of the PS template may be due to the osmotic pressure inducing an eruption of the dissolved polymer through the weak regions of the composite layers.

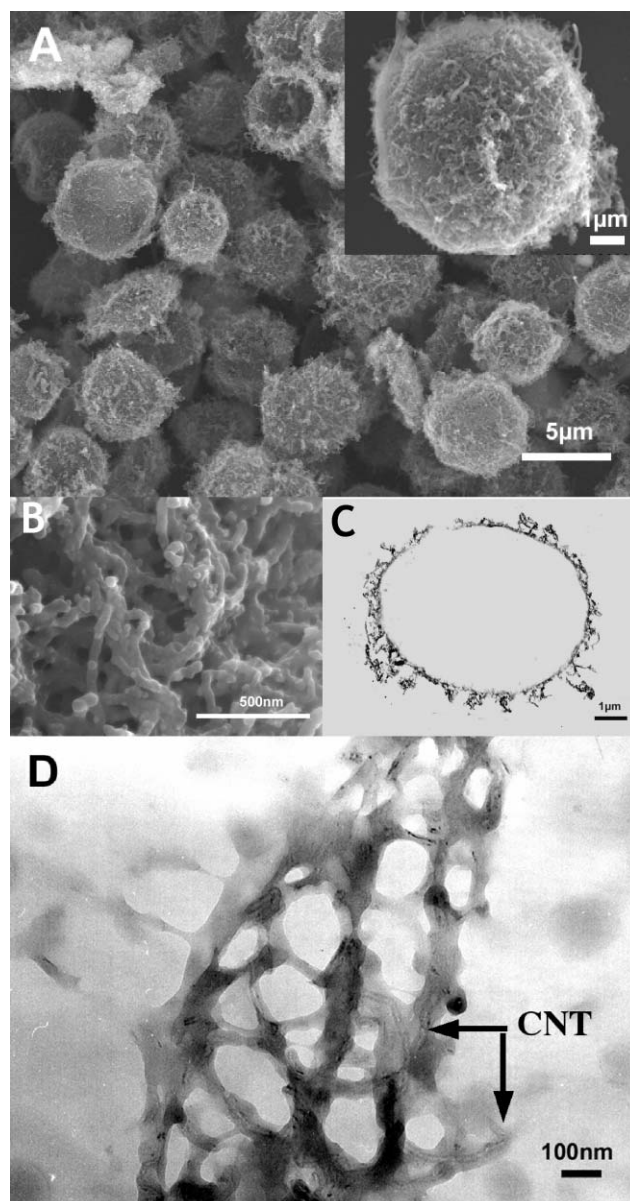


Fig. 2 SEM (A,B) and TEM (C,D) micrographs of titania-strengthened hollow spheres at low and high magnification, respectively. The TEM samples were prepared by ultramicrotoming.

Other appropriate inorganic materials can also be used to strengthen the CNT network. For example, titania-strengthened CNT/PDDA composite hollow spheres were also prepared and showed similar morphological features to those of SiO₂-strengthened samples. As shown in Fig. 2A and 2B, well-maintained hollow spheres with a porous and hairy surface morphology are obtained after template removal. Different from SiO₂, titania forms nanoparticles in the range 20 to 50 nm. Fig. 2C is a cross-sectional transmission electron microscopy (TEM) image of a hollow structure prepared by ultramicrotoming,[‡] clearly displaying the porous hollow structure. As shown in the blow-up TEM image of the shell region (Fig. 2D), the CNTs are dispersed within the composite, serving as a structural scaffold for the porous shell. The network of such composite wires builds up the porous shell and provides the spheres with robust mechanical

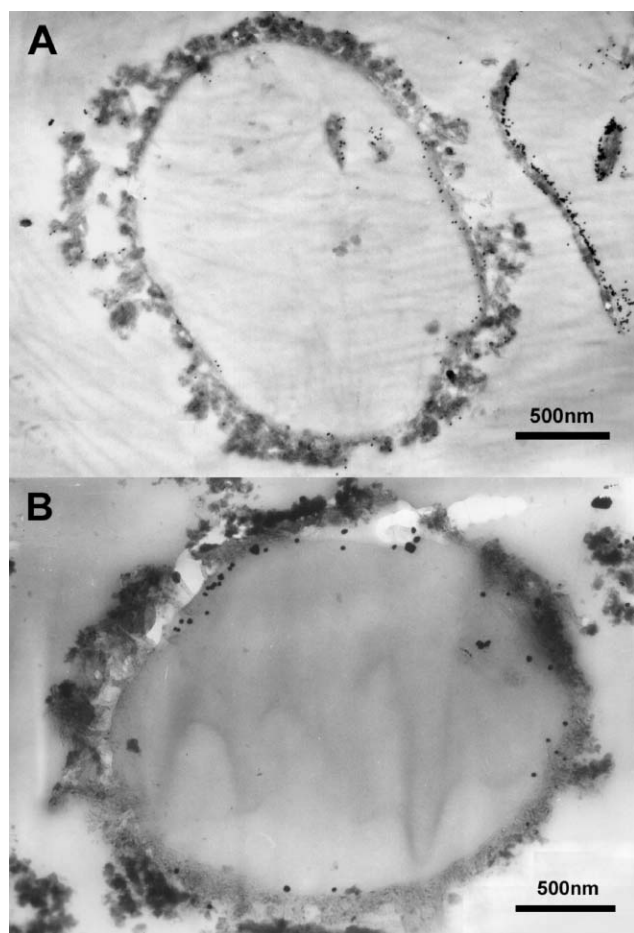


Fig. 3 TEM micrographs of an ultramicrotomed section of hollow spheres with gold nanoparticles inwardly diffused. The hollow spheres were strengthened by (A) SiO₂ and (B) TiO₂, respectively.

strength. It is anticipated that grafting responsive materials onto the porous surface can control the size of the pores, which may be an attractive way to form robust hollow spheres with controlled release capabilities.

The permeability of the porous shell was investigated using 15 nm gold nanoparticles⁹ as a model chemical species. Fig. 3 shows TEM images of the hollow spheres immersed in a solution of the gold nanoparticles.‡ The gold nanoparticles diffuse inwardly through the porous shell into the hollow cage, evidenced by their presence inside the spheres. These results indicate that the porous shell is permeable to chemical species as large as 15 nm. Note that the gold nanoparticles are predominantly distributed near the interior surface and within the surface pores, which may be due to the strong interactions between the composite surface and the citrate-stabilized gold nanoparticles.

In summary, utilizing the superior mechanical strength and tunable surface chemistry of CNTs, we have demonstrated a general fabrication method towards mechanically robust composite hollow spheres that are permeable to large chemical species. This work provides novel platforms for microreactors, artificial cells, controlled delivery and other applications. Further work is under way to synthesize CNT-based hollow spheres with controlled pore sizes, tunable functionalities, responsive properties

through tuning the coating process and conditions, tuning functionalities and charges on CNTs, introducing functional components, and other strategies.

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Notes and references

† Monodispersed PS spheres with a diameter of 4 μm were synthesized according to patent¹⁰ and kindly provided by Professor T. Su. PDDA was LBL-deposited onto the PS spheres to create a positively-charged surface.^{6,11} Multi-walled CNTs (Shenzhen Nanotech Port Co., Ltd, China; 10–20 nm in diameter) were acidically modified, rendering approximately 15 wt% carboxylic acid groups on the CNT surface, estimated by TGA and titration.¹² Modified CNTs were deposited onto PDDA-coated spheres from aqueous suspension (0.25 mg ml⁻¹) three times (LBL technique). Silica was formed within the composite layers by adding 5 μl tetraethyl orthosilicate (TEOS) into a 20 ml ethanol solution containing 0.01 g of CNT/PDDA coated PS spheres, with stirring, over a period of 1 h. The pH of the solution was kept at 9 using aqueous ammonium hydroxide. A total amount of 60 μl TEOS was used by repeating this procedure. In the case of titania, a mixture of tetrabutyl titanate (TBT)/ethanol (1 : 1 vol/vol) solution was used to soak the CNT/PDDA-coated PS spheres for 8 h. Titania was formed by reacting the centrifuged materials with a mixture of water/ethanol (1 : 1 vol/vol) for 5 h. The titania incorporation process was repeated four times. Hollow spheres were obtained by dissolving the PS templates using DMF, followed by centrifugation and rinsing with water. The structure and morphology of the hollow spheres were studied using a TEM (JEOL JEM-2010, operated at 200 kV) and SEM (Hitachi S-4300). TGA was conducted on a Perkin-Elmer TGA-7 thermogravimetric analyzer using air as the carrier gas at a heating rate of 5 °C min⁻¹.

‡ The hollow spheres with incorporated gold nanoparticles were then embedded in resins and microtomed for microscopic characterization.

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