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ChemComm
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Synthesis of peptide-nanotube platinum-nanoparticle composites†

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Received (in West Lafayette, IN, USA) 16th February 2004, Accepted 24th March 2004
First published as an Advance Article on the web 6th April 2004

Nanotubes prepared by the self-assembly of D-Phe-D-Phe molecules are investigated by electron microscopy and Monte Carlo simulations; the nanotubes appear to be porous and are capable of forming novel peptide–nanotube platinum–nanoparticle composites.

Peptide nanostructures offer numerous opportunities for chemical variation and thus provide a key direction for the controlled fabrication of novel nanoscopic materials and devices.[1–11] A breakthrough in peptide-based nanotubes was reported by Ghadiri and coworkers, who showed that a cyclic octapeptide with alternating L and D amino acids could form a nanotubular structure by self-assembly.[3–5] Recently, Reches and Gazit reported the self-assembly of a very short peptide, consisting of the Alzheimer's β-amyloid diphenylalanine structural motif, into long stiff nanotubes.[2] The authors used the nanotubes as scaffolds for producing discrete silver nanowires with a long persistence length by the reduction of silver ions inside the nanotubes. We now report a simplified method for the preparation of peptide nanotubes, an investigation of the formation and the structures of these nanomaterials, and the incorporation of platinum nanoparticles into the nanotubes to form novel peptide-nanotube platinum-nanoparticle composites.

Peptide nanotubes synthesized by the Reches and Gazit method,[2] which involves the use of a fluorinated alcohol for solubilizing the peptide, are several micrometers in length and 50 to 300 nm in diameter. We found that it was possible to simplify the synthesis of the nanotubes and make it more enviromentally benign by omitting the fluoropropanol. In a typical synthesis, 10 mg of lyophilized peptide (D-Phe-D-Phe) was dissolved in 5 mL of Nanopure water at 65 °C, and the sample equilibrated for 30 min and then gradually cooled to room temperature. Scanning electron microscopy (SEM) images show that the nanotubes obtained using this procedure are 100 nm to 2 μm in diameter (Fig. 1a) and can exceed 100 μm in length. Interestingly, when 0.1 mL of the nanotube mixture was diluted by adding 0.1 mL of water, vesicles were observed in addition to the nanotubes (Fig. 1b). Similar vesicles have been observed when linear surfactant-like hepta- or octapeptides are allowed to self-assemble into a network of nanotubes.[12,13] These results indicate that the concentration of the peptide is a key factor in the formation of the nanotubes and that the fluoropropanol is not critical for the self-assembly process.

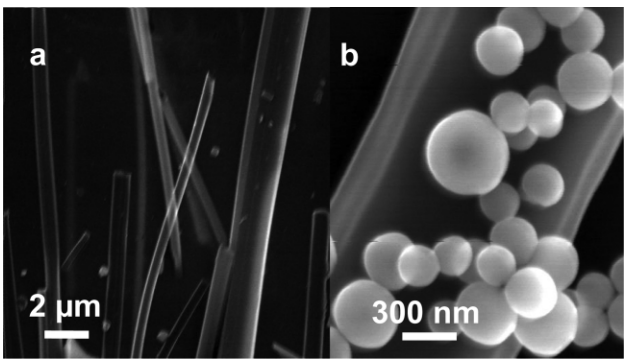

Fig. 1 SEM images of (a) peptide nanotubes and (b) a mixture of nanotubes and vesicles.

To gather more insight into the self-assembly of the diphenylalanine in water, NVT Monte Carlo simulations were performed using a lattice model (32 × 32 × 32) with periodic boundary conditions (Fig. 2).[14–16] The simplified structure in Fig. 2b incorporates the salient features of the diphenylalanine molecule (Fig. 2a). The interactions of the diphenylalanine and water molecules modelled in the simulations are shown in Fig. 2c. The isoelectric point for the amino acid (5.8) is close to the pH used in the nanotube preparation (6.2), so the system was modelled using $-NH_3^+$ (grey) and $-COO^-$ (dark blue) groups and a polar –CONH– group (orange). The hydrophobic phenyl side-chains (red) were modelled using two lattice sites each to represent the bulkiness of the phenyl group. The hydrophobic groups interact *via* the van der Waals potential only, whereas the hydrophilic groups include electrostatic interactions and hydrogen bonding (which is treated isotropically).

At the lowest concentration of peptide (0.083 by volume), the calculations give spherical unilamellar vesicles; Fig. 2d illustrates the bilayer membrane cut away to show the inner aqueous region.

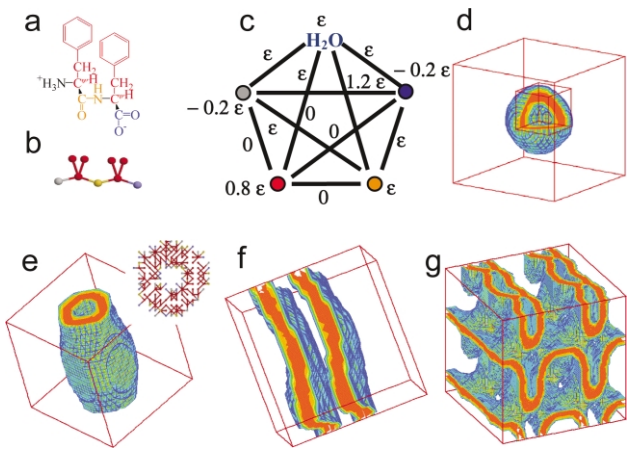

Fig. 2 (a) Chemical structure of D-Phe-D-Phe; (b) lattice model of D-Phe-D-Phe in which colored spheres correspond to identical colored parts in (a); (c) interaction parameters expressed in terms of ε (the negative of the attractive potential between two neighboring water molecules); (d–g) structures at selected concentrations; (d) cut-away portion of spherical vesicle at 0.083 chain concentration; (e) complete nanotube and rasmol rendition of two slices of nanotube at 0.218 chain concentration; (f) close-spaced curved double lamellae at 0.365 chain concentration; (g) porous structure with continuously connected hydrophilic, mainly water, channels at 0.471 chain concentration.

† Electronic supplementary information (ESI) available: EDX spectrum and SAED patterns of the platinum-peptide composites. See http://www.rsc.org/suppdata/cc/b4/b402126f/

DOI: 10.1039/b402126f

At a higher peptide concentration (0.218), the peptide assembly gives unilamellar nanotubes also with an inner aqueous region (Fig. 2e). The packing of molecules in the tubes (Fig. 2e, inset) is similar to that seen in the crystal structure of L-Phe-L-Phe.[17] Porous and nonporous multilamellar structures with water trapped between the layers are observed at concentrations of 0.292 (structure not shown) and 0.365 (Fig. 2f). Finally, porous bi-continuous phases are predicted at concentrations of 0.471 (Fig. 2g) and 0.551 (structure not shown). The simulations indicate that the peptide behaves somewhat like a surfactant; the polar groups segregate from the hydrophobic phenyl groups to form bilayers, and some of the structures and continuous phases formed are similar to surfactant assemblies.

The large nanotubes and vesicles observed in the SEM images have thick walls that must be composed of multilamellar or bicontinuous phases. We used a procedure previously employed to grow Pt nanostructures on surfactant templates[18] to investigate whether the walls are porous and if metal nanocomposites can be made. A solution of nanotubes and vesicles (0.3 mL) was mixed with aged aqueous K_2PtCl_4 (0.1 mL, 20 mM). Ascorbic acid solution (0.1 mL, 0.15 M) was added as a reductant and to minimize oxidation of the peptide. After several hours at room temperature, the mixture changed color from a light yellow solution (the color of the Pt complex) containing a white mass of nanotubes to a clear solution with a brownish-black mass at the bottom of the glass reaction vessel. The reaction mixture was then centrifuged for 1 minute at 3000 *g*, the supernatant liquid removed and replaced with 0.5 mL of Nanopure water, and the sample sonicated for one minute to re-suspend the black mass. This procedure was repeated three times to remove salts and unattached Pt particles; most of the Pt was found to be associated with the black mass.

SEM and transmission electron microscopy (TEM) were used to characterize the black material (Figs. 3 and 4). The nanotubes seen in the images were typically 5 to 60 μm in length, with an outer diameter of 400 to 2000 nm, an inner diameter of 300 to 1800 nm, and a wall thickness between 50 to 200 nm. Energy-dispersive X-ray (EDX) spectroscopy confirms the presence of platinum in the nanotubes and vesicles (Fig. S1†). High-resolution TEM images (Fig. 3b) show that 2–3 nm Pt nanoparticles are embedded in the walls of the peptide nanostructures. Selected-area electron diffraction (SAED) patterns (Fig. S2†) exhibit diffuse diffraction rings, which are also consistent with the presence of small Pt nanoparticles. Few of the Pt nanoparticles are found on the inner or outer surfaces of the tubes. High-angle annular dark-field (HAADF)[19,20] scanning TEM images like that shown in Fig. 4 give the density profiles of platinum in the nanotubes and vesicles. The profiles of the tubes (*e.g.*, Fig. 4a) are consistent with a uniform density of Pt nanoparticles throughout the walls of the tubes. This supports the idea that nanoparticles are formed in pores within the tube walls and suggests a porous lamellar or bicontinuous phase that would allow free diffusion of Pt ions and reductant to all regions within the walls.

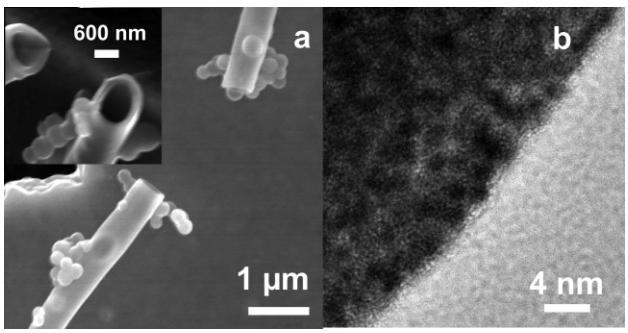

Fig. 3 SEM images of (a) peptide nanotubes and nanovesicles containing Pt particles (inset: tilted image showing the tubes are hollow) and (b) a high-resolution TEM image showing the 2 nm Pt nanoparticles embedded in the wall of a platinum nanotube.

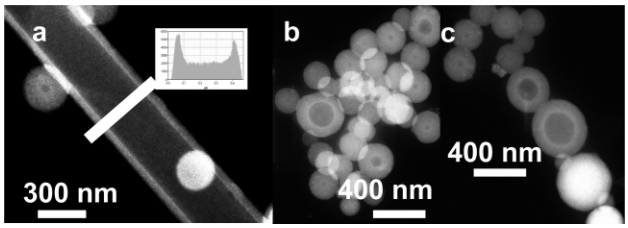

Fig. 4 HAADF scanning TEM images of (a) tubes (inset: density profile along the white band crossing the tube) and (b, c) vesicles.

The vesicles containing Pt nanoparticles (Figs. 3a, 4b,c) range in diameter from about 200 to 600 nm; both solid vesicles and vesicles with aqueous cores are observed. The TEM images show that some vesicles are continuously connected but have separated aqueous cores, while others are simply overlapping (as shown by light areas in the overlap regions of Fig. 4b). The joined vesicles frequently form necklace-like structures (Fig. 4c), which may be precursors to the nanotubes. (Joined unilamellar vesicles with isolated aqueous cores are given by the lattice simulations at concentrations intermediate between those of unilamellar vesicles and unilamellar tubes.)

The present work suggests that the walls of peptide nanostructures can be porous. The porosity allows the formation of novel nanocomposites without the disruption of the original nanostructure morphology. The Pt–nanoparticle peptide–nanostructure composites prepared in this study have many potential applications, *e.g.*, catalysis. They may also serve as useful scaffolds for the synthesis of other nanomaterials.

This work was partially supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy (DE-FG02-02ER15369). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DEAC04-94AL85000.

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