Assembling carbon nanotubosomes using an emulsion-inversion technique

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Novel micro-capsules (carbon nanotubosomes) have been fabricated by cross-linking shells of amine-functionalised multi-walled carbon nanotubes (MWNTs) produced by their adsorption on water-in-oil emulsion drops followed by an emulsion-inversion.

Functionalisation of carbon nanotubes has been receiving an increasing amount of attention in the last couple of years for applications ranging from sensing to nano-electronics. For example, covalent functionalisation schemes through amide linkages have been explored for nanotube interconnects,[1] proteins[2] and nanocrystals.[3] Colloidosomes are hollow-shell microstructures of shells produced from coagulated, cross-linked or partially swollen monolayers of colloid particles. Recently it has been recognised that colloidosome membranes offer great potential in controlling the permeability of entrapped species. Various methods for fabrication of colloidosomes (hollow-shell micro-structures) based on templating sacrificial solid particles (cores)[4] or emulsions[5–9] have been reported. These methods involve dissolution of the core (solid or liquid)[5,7,9] or transfer of the produced shells from the oil to the water phase by centrifugation.[6,8] Fabrication of colloidosomes with shells of spherical particles[5–8] and polymeric microrods[9] have been recently reported.

Here we report the fabrication of carbon nanotubosomes or micro-capsules consisting of covalently cross-linked carbon nanotubes, based on assembling MWNTs into shells around water-in-oil droplets. Our method is illustrated in Fig. 1. and involves the following three steps: (i) a water-in-oil emulsion is prepared by ultra-sonication of amine-functionalised multi-walled carbon nanotubes (NH_2–MWNT) in tricaprylin. (ii) Water and isopropanol (IPA) are added and the system is emulsified using a microsyringe with 25 passes, resulting in water drops coated with NH_2–MWNT which are subsequently cross-linked (covalently) with glutaraldehyde. (iii) The produced carbon nanotube shells (nanotubosomes) were washed with ethanol to dissolve the oil (continuous phase). This allowed us to prepare carbon nanotubosomes ranging in size up to 20 μm depending on the emulsion droplet size. Details of the method are given below.

Ten milligrams of catalytic chemical vapour deposition produced NH_2–MWNT[1] (obtained from Nanocyl S.A., Belgium, see Fig. 2(A) and ref. 1 for more details) were suspended in 2 mL tricaprylin (Sigma) using high-power sonication for 3 min. 5% (weight per volume) Milli-Q water and 5% (w/v) IPA were added. The system was emulsified by 25 passes through the needle of a microsyringe. Fig. 2(B) shows an optical image of a typical emulsion sample in tricaprylin, with the nanotube shell clearly visual on the surface of the bigger water droplets. Pristine carbon nanotubes are extremely hydrophobic in nature. The addition of amine groups to the surface of nanotube results in their partial hydrophilisation. Therefore, the nanotubes adsorb and self-assemble at the oil/water interface, as this is energetically more favourable. The assembled nanotubes are also stabilising the emulsion droplets, with IPA providing additional fine tuning of their contact angle.

It is well known that aldehydes react with primary amines resulting in imines, also known as Schiff bases. This reaction was used to bind the self-assembled nanotube shell by cross-linking the nanotubes' primary amines with glutaraldehyde. For this purpose, glutaraldehyde solution (70% in water, Sigma) was added to 1 mL of tricaprylin and homogenised by 10 passes with a syringe. The solution was centrifuged to separate water and oil phases. 200 μL of the oil phase was added to the MWNT-stabilised emulsion, followed by incubation for 1 h. The solution was washed multiple times with ethanol. Samples were visualised by scanning electron microscopy (SEM).

Fig. 2(C) shows a scanning electron microscopy (SEM) image of a typical carbon nanotubosome (diameter $\approx$ 10 μm). Various nanotubosomes were imaged (diameter range 1–20 μm) and it is evident that the surface is densely coated with nanotube material. Entangled and cross-linked carbon nanotubes can be seen in a close-range view of the nanotubosome surface (Fig. 2(D)). Thus,

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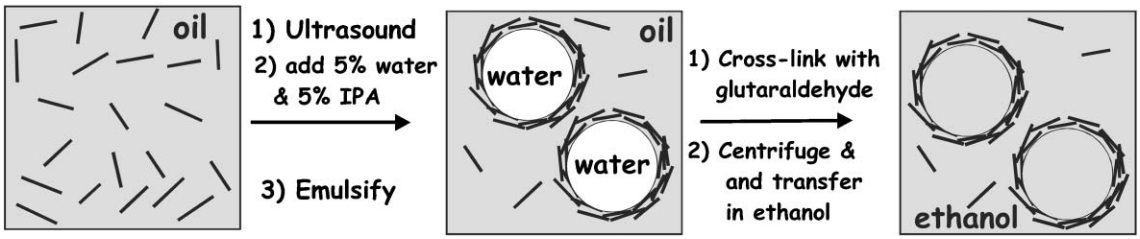

Fig. 1 Schematics of the preparation of the carbon nanotubosomes by an emulsion-inversion technique.

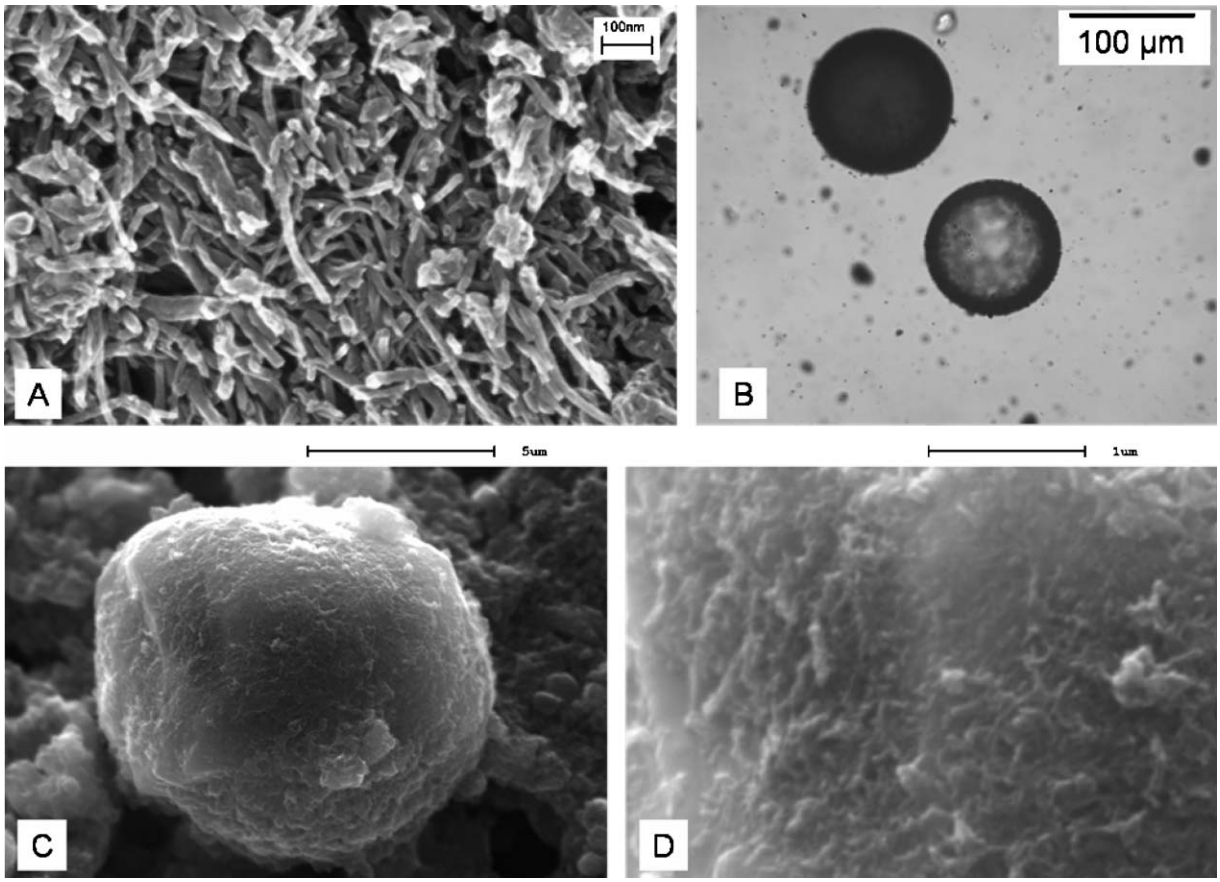

Fig. 2 (A) Scanning electron microscopy image of starting material, amine-functionalised multi-walled carbon nanotubes. (B) Optical microscopy image of water-in-oil emulsion with NH_2–MWNT self-assembled on the surface of the water droplets. (C) Scanning electron microscopy (SEM) image of the obtained carbon nanotubosomes after covalent cross-linking with glutaraldehyde and transferring to ethanol. (D). Close-range view of the carbon nanotubosome surface showing entangled and cross-linked MWNTs.

the assembled nanotube layer has been succesfully cross-linked into a nanotube membrane.

To investigate the composition of nanotubosomes, the sample was frozen in liquid nitrogen and mechanically treated (scratched with a metal blade), resulting in crack-opening of a very small portion of the nanotubosomes. Fig. 3 shows the remnants of a broken capsule clearly showing the shell (white arrows) and its hollow interior (ellipse). It is evident from the SEM image that a tubosome shell consists of entangled and cross-linked MWNTs.

In summary, we report the fabrication of carbon nanotubosomes by an emulsion-inversion technique. Self-assembled MWNTs at the interface of water and oil are covalently

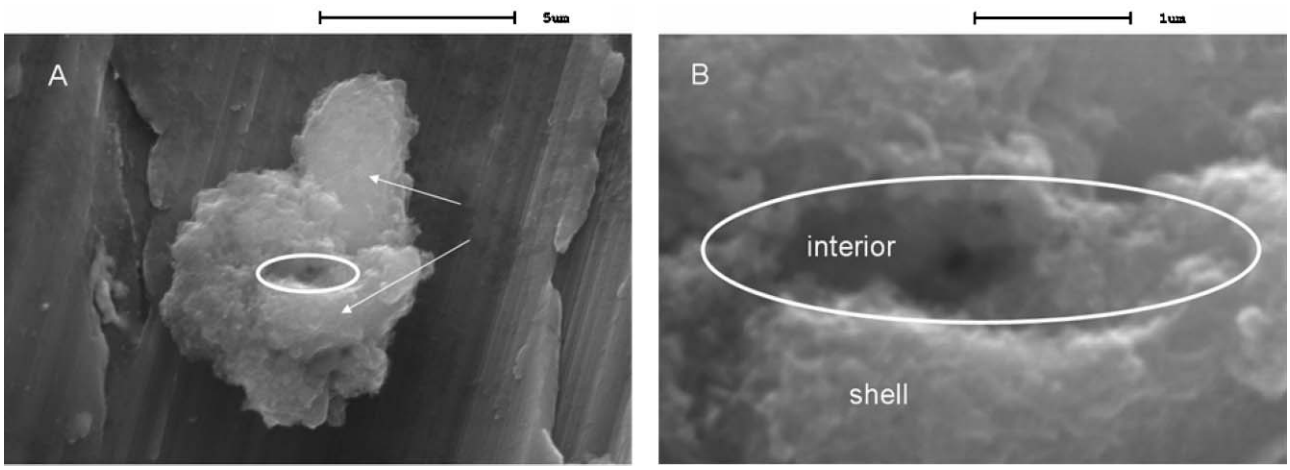

Fig. 3 (A) Scanning electron microscopy (SEM) image of a cracked-open carbon nanotubosome obtained by mechanical treatment after freezing in liquid nitrogen. Arrows indicate remnants of shell, ellipse indicates interior. (B) Close-up showing parts of shell and interior.

cross-linked to produce hollow micro-capsules consisting of MWNT shells. It is expected that these micro-capsules could aid the development of encapsulation of catalysts. Further research involving studies of the carbon nanotubosomes permeability with respect to entrapped species and potential applications will be reported in a follow up publication.

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