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Confined organization of Au nanocrystals in glycolipid nanotube hollow cylinders†

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Mild fabrication of anisotropic metal–lipid nanotube (LNT) nanocomposites, in which Au nanoparticles of 3–10 nm wide are organized in a glycolipid nanotube hollow cylinder, has been achieved by filling the internal channel of the LNT with $HAuCl_4$ aqueous solution by capillary force and subsequent photochemical reduction of $[AuCl_4]^-$.

Isolated hollow cylinder architectures, made of diverse inorganic or organic substances, with nanometer-sized inner diameters have been of great interest in nanomaterials science due to their potent applications and the continuing interest in nano-space-specific fundamental phenomena.[1] During the last decade, there have been many attempts to fabricate metallic nanowires and one-dimensional nanocomposites using a hollow cylinder of carbon nanotubes, mesoporous materials and lipid tubules as templates.[2–6] However, filling the inner core of lipid nanotubes (LNTs) with high axial ratios with a foreign constituent has never been addressed although we can refer to one example of the metal deposition inside tobacco mosaic virus.[7] The most characteristic advantage of synthetic LNTs,[8] which clearly differs from that of well-known carbon nanotubes, is the possession of neutral and hydrophilic surfaces covering the molecular assemblies. This situation enables them to provide unique hollow cylinders suitable for the encapsulation of relatively larger guest substances like biological macromolecules. In particular, glycolipid LNTs[9] are promising for biological use since the sugar headgroup should have high biocompatibility and specificity to a certain protein. Furthermore, the size distribution of their inner diameters is generally in the range 10–200 nm, which well compensates with that of carbon nanotubes. Here we describe for the first time the confined organization of Au nanocrystals in an aqueous LNT hollow cylinder at room temperature, achieved by filling a vacant glycolipid nanotube hollow cylinder with $HAuCl_4$ solution and subsequent photochemical reduction in a "ship-in-bottle" fashion.

In order to search for potential molecular building blocks self-assembling into LNTs with 100% efficiency, we have so far focused on synthetic glycolipids and examined in detail the incorporation effect of a *cis*-double bond into the lipophilic part on tubular morphologies.[9] In consequence we have recently found that a newly optimised glycolipid, *N*-(11-*cis*-octadecenoyl)-β-D-glucopyranosylamine **1** self-assembles in water to produce monodispersed and well-defined LNTs in approximately 100% yields.‡ The typical transmission electron microscopic (TEM) and field-emission scanning electron microscopic (FE-SEM) images of the glucose-derived LNTs clearly show the tubular structure, an homogeneous hollow cylinder with two completely opened ends (Figs. 1a and 1b). The inner and outer diameter distributions of the nanotubes are very narrow, giving approximately 80 and 200 nm average diameters, respectively.

Fig. 2 shows a schematic illustration of the present experimental procedure, in which we can organize Au nanocrystals in the LNT core under mild conditions. The glycolipid **1** self-assembles in pure water to form LNTs (step 1). To get a one-dimensional vacant LNT hollow, we then removed the water from inside the LNT hollow cylinder (step 2). The LNT hollow cylinder was filled by capillary force with an aqueous solution of hydrogen tetrachloroaurate(III) ($HAuCl_4$) (step 3) and the $[Au^{III}Cl_4]^-$ ion was photochemically reduced to Au^0 by UV irradiation (λ = 254 nm) in the confined internal volume of the LNT (step 4). To empty the nanotube hollow cylinder, we lyophilized the LNTs.§ As a result, we successfully obtained a cotton-like solid mass of the LNT. Fig. 3a displays the structure of a LNT, observed using TEM, after the lyophilization treatment. The picture clearly shows that the hollow interior of this open-ended LNT remains almost intact as compared with those before the treatment. Thus we confirmed that the present LNTs can keep their tubular structures without any destruction even after the lyophilization process.

In the next step, we added the lyophilized LNT powders directly into 20% ethanolic aqueous solutions containing 10 mM $HAuCl_4$ and then stirred the mixture gently to fill the LNT hollow cylinder with the $HAuCl_4$ aqueous solution by capillary suction. The reaction mixture was allowed to stand for 12 h to allow complete

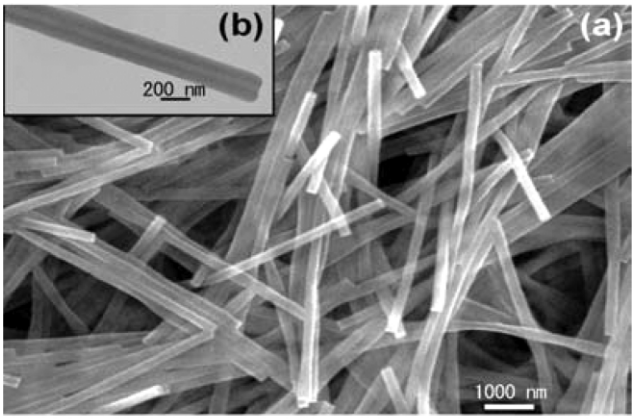

Fig. 1 (a) FE-SEM and (b) TEM images of monodispersed and well-defined LNTs self-assembled from the glycolipid **1**.

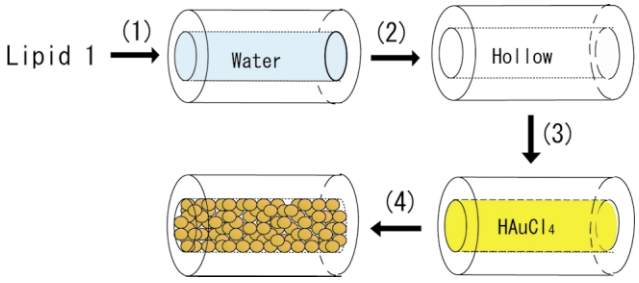

Fig. 2 Schematic diagram for the fabrication of a glucose-derived LNT hollow cylinder filled with Au nanocrystals. Each step is detailed in the text.

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filling with $HAuCl_4$ solution. The filled LNTs were separated by filtration using MILLIPORE membrane with a 200 nm pore size and were washed 5 times with Milli-Q water to completely remove the $HAuCl_4$ species existing outside of the LNTs. We re-dispersed the washed LNTs again in water and irradiated them using a UV light [a 135 W low pressure mercury lamp (λ = 254 nm), UVB-110 (Sen Tokushu Kogen)] for 2 h in argon atmosphere at room temperature. Upon UV irradiation, we employed ethanol as a radical generator, which proved to increase the reduction reaction rate of the $[AuCl_4]^-$ ions. Photoreaction was thus actually carried out using the LNT hollow cylinder as a nanometer-scale reaction flask.

The TEM images for the obtained product revealed that the hollow space of the LNT clearly displays dark contrast compared with that before filling with $HAuCl_4$ aqueous solution (Figs. 3a and 3b), indicating that Au nanocrystals are confined to organize in the LNT hollow cylinder. A high magnification TEM image revealed that Au nanocrystals of 3–10 nm were produced in the one-dimensional nano-space of the LNT (Fig. 3c). To prove the successful reduction of $[AuCl_4]^-$ in the LNT hollow cylinder, we carried out energy-dispersive X-ray analysis (EDX) for the area shown in Fig. 3b. The EDX spectrum in Fig. 3d displayed two signals at E = 2.12 and 9.17 keV ascribable to Au M_α and L_α, respectively, indicating the exact presence of Au element in the LNT. The absence of Cl signals at E = 2.62 (K_α) and 2.81 keV (K_β) also supports the view that the Au ions have been completely reduced to Au crystals. Fig. 3d also shows signals of copper, carbon and oxygen originated from the copper grid and LNTs. We have also taken the electron diffraction (SAED) pattern for the selected area shown in Fig. 3b (Fig. 3e). The characteristic rings of the polycrystalline diffraction pattern can be indexed to [111], [200], [220], and [311] ascribable to the reflecting planes expected from *fcc* Au. This diffraction feature of the rings is certainly manifesting the presence of Au nanocrystals.

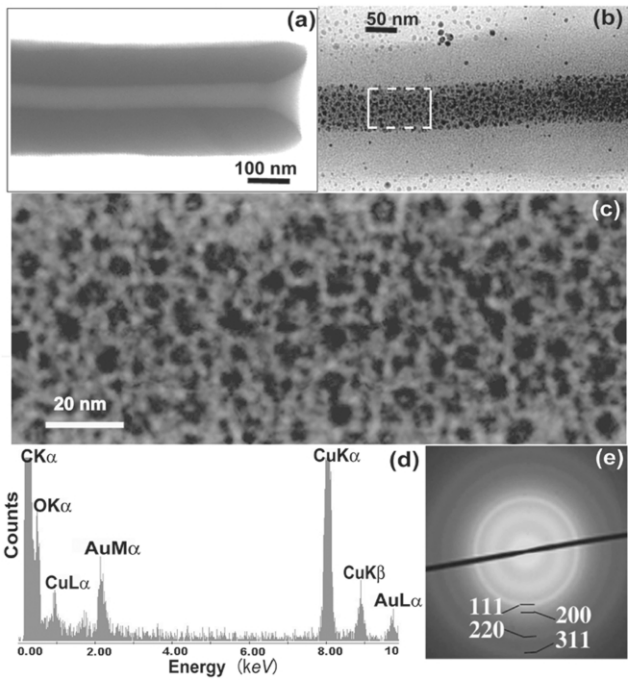

Fig. 3 TEM images of (a) a lyophilized LNT, (b) a LNT filled with Au nanocrystals (low magnification) and (c) the magnified core part of Fig. 3(b). (d) EDX spectrum and (e) SAED pattern for the area shown in Fig. 3(b).

The crucial key step for the present methodology is in the drawing of the $HAuCl_4$ aqueous solution into the LNT hollow cylinder through capillary force. When using non-lyophilized LNTs for the process, we found that very low percentage of the LNTs (< 3%) encapsulate Au nanoparticles. However, if we used the lyophilized LNTs, the percentage increased to approximately 30%. In our work, the contact angle (θ) of the $HAuCl_4$ aqueous solutions on the present LNT surface was estimated to be 8°. This means that the $HAuCl_4$ aqueous solution can be smoothly drawn into the hydrophilic inside of the LNTs, according to Dujardin's report.[5] Thus, the nanometer-scale hollow cylinder of the LNT provides an effective, one-dimensional nanospace for the confined organization of Au nanocrystals. The obtained product can be defined as a novel one-dimensional nanocomposite, in which the Au nanocrystals are stably encapsulated in the LNT.

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Notes and references

‡ Preparation of the LNTs: A solution of 1 mg lipid **1** in 1 mL methanol was evaporated in a round-bottomed flask. To the residue in the flask was added 20 mL Milli-Q water and the aqueous dispersion was then sonicated for 1 h. The dispersion was heated at 110 °C for 1 h to give a transparent solution. The solution was allowed to gradually cool to room temperature overnight. Eventually we obtained a white suspension of the LNTs.

§ Lyophilization of the LNTs: A glass test tube containing a 20 mL aqueous dispersion of the glucose-derived LNTs was put in liquid nitrogen for 10 min. The sample was then transferred into a freeze dryer and dried in high vacuum (9.0 Pa) for 72 h.

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