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Selective Hybridization of Dendron-Cyclodextrin Nanotubes with Metal Nanoparticles

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The controlled organization of organic moieties with inorganic elements provides not only unique complex hybrid nanostructures but also synergistic functional properties.¹⁻³ For this purpose, several synthetic approaches have been developed by using organic supramolecules as a template for the construction of organized organic-inorganic hybrid architectures.⁴⁻¹² In addition, the electronic or chemical communication between organic and inorganic moieties would provide an opportunity to produce unique functional hybrids.^{13,14} In particular, organic nanotubes have attracted considerable attention as a template for nanohybrids,^{3,15,16} for examples, lipid nanotubes for the template of silica^{3,15} and peptide nanofibers for the template of biomineralization.^{5,9,11} In particular, fabrication of linear assemblies of inorganic elements is of great interest for the development of nano-devices due to their anisotropic properties in 1-dimensional state.¹⁶ For that purpose, carbon nanotubes are excellent template for the fabrication of linear assembly of inorganic elements.^{17,18} In addition, biomolecules such as DNA,¹⁹ peptides,¹⁶ and viruses²⁰ were used as a template for the organization of nanoparticles. Self-assembled organic nanotubes are particularly advantageous as a template for the linear organization of nanoparticles because the surface anchoring functionality can be efficiently tailored.

Recently, we reported on the cyclodextrin-covered organic nanotubes (Den-CD-NTs) constructed by the self-assembly of the amide dendrons with the focal pyrene unit which is included into the cavity of β - or γ -cyclodextrin (CD).^{21,22} The narrow rim of CDs is exposed to the surface of the tube. Therefore, the surface functionality of the tube can be controlled in a facile manner during the self-assembly process *via* the host-guest interaction between the amide dendron and CDs. Therefore, we reasoned that the tunable well-defined surface of Den-CD-NTs would be an effective template for growing inorganic nanoparticles which can electronically communicate with the pyrene moiety included in the cavity of CDs on the surface of the tube. This approach would provide a facile route to unique nanotube-nanoparticle hybrid systems for nanoelectronics or biosensor applications. Herein we present a unique approach to produce the hybrid of organic nanotube and metal nanoparticle by using Den-CD-NTs as a template.

We have demonstrated that the amphiphilic amide dendrons can self-organize not only in organic phase but also in aqueous

phase.²³⁻²⁸ In particular, amide dendron **1** with the focal pyrene moiety in Figure 1 self-organizes into a vesicular structure in an aqueous phase. Addition of β -CD into the vesicular solution of dendron **1** induces formation of Den-CD-NT of which the surface is covered with β -CD.²¹ The C-6 functionality of on the narrow of CDs is then exposed to the surface of Den-CD-NTs. This methodology provides a facile synthetic route to diverse Den-CD-NTs with a variety of surface functional groups. In order to introduce the anchoring sites for metal nanoparticles on the surface of Den-CD-NT, the control of the surface functionality of the tube is critical. Therefore, the unique self-assembly characteristics of the dendron nanotube system can be effectively utilized to introduce diverse surface anchoring groups by addition of C-6 functionalized CDs into the vesicular solution of dendron **1**.²²

In order to decorate metal nanoparticles on the surface of the tubes, we prepared Den-CD-NTs with amine or carboxyl surface functionality, as the template for hybrids, by utilizing self-assembly of amide dendron **1** with CD **2** or **3** following the strategy described in Figure 2. Dendron **1** and CDs **2-3** were synthesized by the reference procedure.^{21,22} Addition of mono(6-amino-6-deoxy)- β -CD, **2**, into the vesicular solution of dendron **1** resulted in change of the pyrene fluorescence from the excimer emission at 420 - 550 nm with an excitation at 345 nm to the monomeric emission at 370 - 420 nm, as shown in Figure 3, by the formation of pyrene-CD inclusion complex, which then induced transformation of vesicle to the nanotube with the amine functionality on the surface (Den-NH₂-CD-NT). The outer diameter and wall thickness of Den-NH₂-

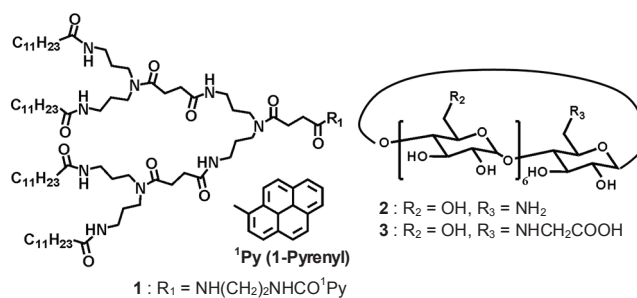


Figure 1. Chemical structures of amide dendron and cyclodextrins.

CD-NT are approximately 40 nm and 10.5 nm, respectively.²² In addition, the carboxyl-functionalized nanotube, Den-COOH-CD-NT, also was prepared by addition of CD 3, mono(6-carboxymethylamino-6-deoxy)- β -CD, into the vesicular solution of dendron 1.²² It should be noted that the surface functionality on Den-CD-NTs can be precisely controlled by our method.

The anionic or cationic precursor of metal nanoparticles then can be adsorbed on the surface of Den-NH₂-CD-NT and Den-COOH-CD-NT templates *via* electrostatic interactions under appropriate conditions as shown in Figure 2. Subsequent reduction would give rise to formation of the nanoparticle on the surface of Den-CD-NT. The tubes with different surface functional groups exhibited selective adsorption behaviour towards different metal nanoparticle precursors, as described here for Pt and Ag nanoparticles.

The nanotube with cationic surface (zeta potential 0.96 mV), Den-NH₂-CD-NT, can accommodate anionic metal precursors. Den-NH₂-CD-NT covered with Pt nanoparticulate clusters (Pt/Den-NH₂-CD-NT) was efficiently prepared with high specificity. Briefly, an aqueous solution of 0.4 mM K₂PtCl₄ was added into the aqueous solution of Den-NH₂-CD-NT, and then the metal precursor was reduced by addition of the aqueous solution of NaBH₄ (0.6 mM, 20 μ L). The Pt/Den-NH₂-CD-NT hybrid could be visualized with TEM (Figure 3a). The EDX

analysis indicates the presence of Pt, C, N, and O on the Pt/Den-NH₂-CD-NT hybrid (Figure 3b). The electron diffraction pattern in Figure 2a revealed the crystalline nature of the Pt/Den-NH₂-CD-NT hybrid. As shown in Figure 3c, the formation of Pt nanoparticle on Den-NH₂-CD-NT gave rise to fluorescence quenching of the pyrene emission from Pt/Den-NH₂-CD-NT.

Metal cations can be adsorbed on the anionic surface of Den-COOH-CD-NT (zeta potential -14.36 mV) to form nanotube-nanoparticle hybrid by subsequent reduction. For this purpose, cationic silver precursor, AgNO₃ (0.1 mM, 25 μ L), was added into the Den-COOH-CD-NT solution, and then the mixture was reduced by NaBH₄ (0.2 mM, 10 μ L). As shown in the TEM image in Figure 4a, Ag nanoparticles were attached on the surface of Den-COOH-CD-NT (Ag/Den-COOH-CD-NT). The mean diameter of Ag nanoparticle was 8.8 ± 2.4 nm (Figure 4b). The EDX analysis confirmed the presence of Ag,

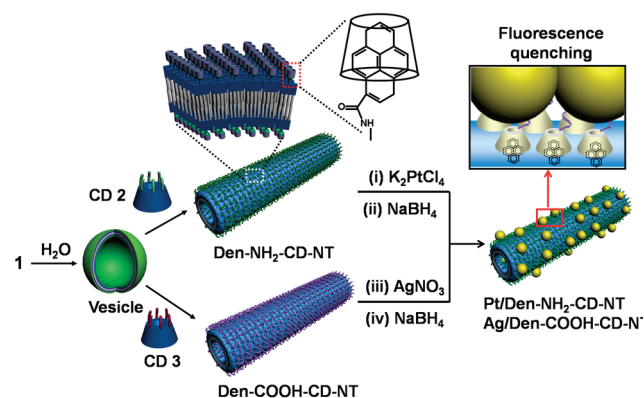


Figure 2. Schematic description for the preparation of organic-inorganic nanohybrids.

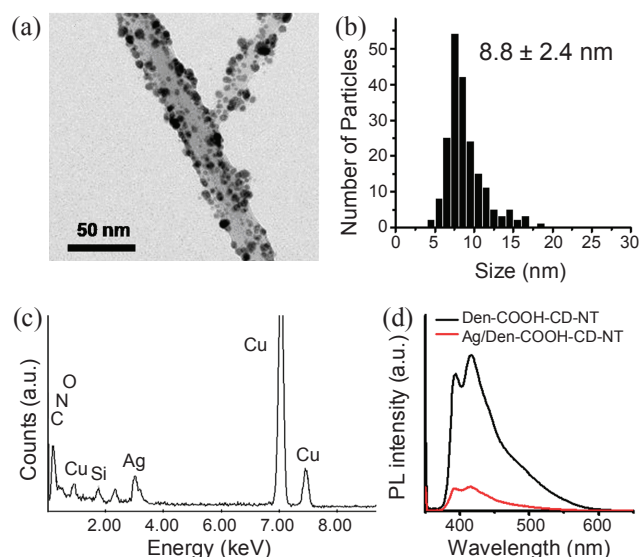


Figure 4. (a) TEM image of Ag/Den-COOH-CD-NT. (b) Size distribution of Ag nanoparticles on Ag/Den-COOH-CD-NT. (c) EDX spectrum of Ag/Den-COOH-CD-NT. (d) Fluorescence spectra of Den-COOH-CD-NT and Ag/Den-COOH-CD-NT. The Ag precursor was reduced by addition of the aqueous solution of NaBH₄ (0.2 mM, 10 μ L).

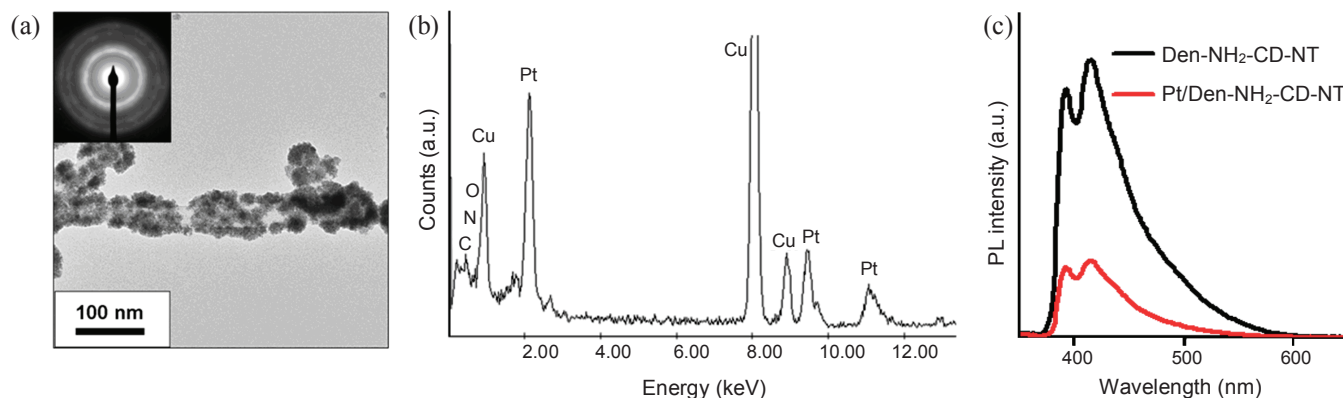


Figure 3. (a) TEM image of Pt/Den-NH₂-CD-NT. (b) EDX spectrum of Pt/Den-NH₂-CD-NT. (c) Fluorescence spectra of Den-NH₂-CD-NT and Pt/Den-NH₂-CD-NT.

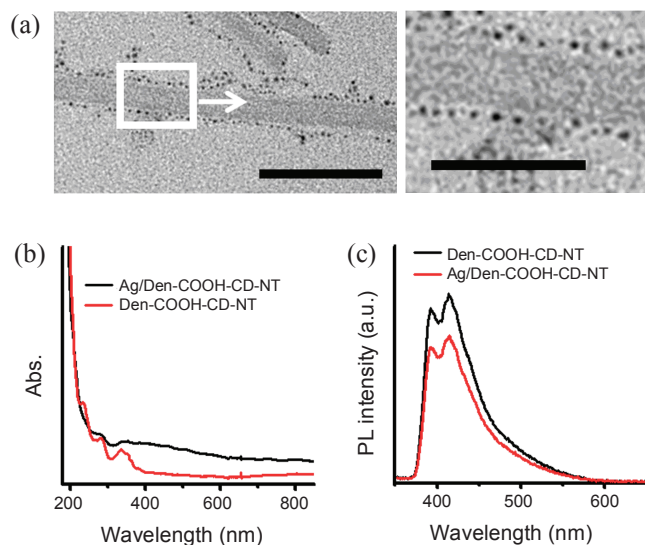


Figure 5. (a) TEM images of Ag/Den-COOH-CD-NT (scale bar; 100 nm and 50 nm, respectively). (b) Absorption spectra of Den-COOH-CD-NT and Ag/Den-COOH-CD-NT. (c) Fluorescence spectra of Den-COOH-CD-NT and Ag/Den-COOH-CD-NT. The Ag precursor was reduced by addition of the aqueous solution of NaBH₄ (0.1 mM, 2 μ L).

C, N, and O on Ag/Den-COOH-CD-NT (Figure 4c). As shown in Figure 4d, we observed fluorescence quenching of pyrene emission in Ag/Den-COOH-CD-NT.

Interestingly, the size of the Ag nanoparticle could be controlled depending on the amount of reducing agent. In case of adding smaller amount of NaBH₄ aqueous solution (0.1 mM, 2 μ L), Ag nanoparticles with average diameter of about 2–3 nm were adsorbed on the Den-COOH-CD-NT surface (Figure 5a).

The enlarged image in Figure 5a revealed that Ag nanoparticles were arranged into an ordered one-dimensional array on the nanotube surface. The lateral distance between the silver nanoparticles was approximately 3 nm. The UV-vis spectrum showed a broad surface plasmon band around 400–550 nm, characteristics of metallic silver nanoparticle (Figure 5b). The fluorescence spectra in Figure 5c showed that the pyrene emission was slightly quenched in Ag/Den-COOH-CD-NT. The control experiment with cationic silver precursor, AgNO₃, by using Den-NH₂-CD-NT with cationic surface as a template did not produce silver nanoparticles on the surface of the tube. This result indicates that the carboxyl moiety of Den-COOH-CD-NT was the anchoring site for the cationic precursor of silver nanoparticles.

In conclusion, the self-assembled Den-CD-NTs are effective templates for constructing the nanotube-nanoparticle hybrid by control of the surface functionality of the tube. The ionic metal precursors are adsorbed selectively on the cationic or anionic surface of Den-CD-NTs through electrostatic interaction, and then metal nanoparticles are formed on the nanotubes by subsequent reduction. The unique surface engineering approach for self-assembled Den-CD-NTs realized that the Den-CD-NTs with different surface functional groups exhibited selective adsorption behaviour towards different metal nanoparticles. The hybridization of Den-CD-NTs with metal nanoparticles brought about not only unique self-assembled

structure but also electronic communication between them. The fluorescence emission from the pyrene moiety of the nanotube was quenched due to the proximity between the pyrene moiety included in CDs and the metal nanoparticles on the surface. This approach would provide a unique route to multi-functional nanotube platforms. We are currently investigating the biosensory function of the nanoparticle-nanotube hybrids.

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