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Controlled Gold Nanoparticle Diffusion in Nanotubes: Platfom of Partial Functionalization and Gold Capping

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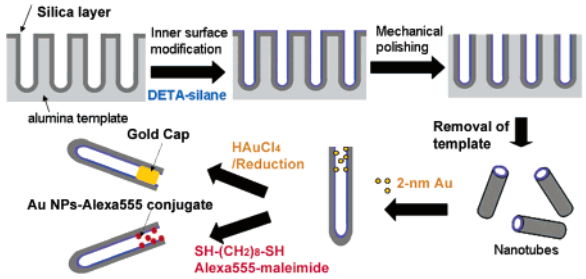
Having multifunctionality is fundamentally advantageous for nanomaterials and is highly required for the modern biomedical and biotechnological applications.[1] For example, multifunctional nanomaterials are considered to be ideal units for the cancer-specific therapeutic and imaging agents that can avoid biobarriers, target biomarkers, and report therapeutic efficacies.[1c] Unlike spherical nanoparticles, nanotubes have two different surfaces which can be independently modified with desired functional groups using the template synthesis method.[2] Our research and that of others led us to develop smart multifunctionalized nanotubes (NTs) for single-molecule sensing, bioseparation, and drug/gene delivery carriers.[3] The use of NTs as potential universal drug delivery vehicles was recently exploited.[3b,4] In addition, NTs provide straight cylindrical nanochannels or nanopores required in the nanofluidic sensors for a single-molecule detection.[5]

In order to fabricate multifunctional nanodevices based on NTs or nanochannels and to enhance their performance, selective partial functionalization of NTs is essential. Each functionality should be located at optimal positions, depending on their roles such as targeting, tracking, and transporting. This enables avoidance of possible malfunction or interference caused by having randomly distributed multiple groups (e.g., hydrophobic and hydrophilic) in the same space. Recently, asymmetric functionalization has been demonstrated between two tips, the tip/side wall, and the inner/outer surfaces of NTs.[2,6] In the aspect of multifunctionality, however, a general selective partial functionalization method of NT inner surfaces still remains a challenge. For this reason, we describe a selective partial functionalization method of NTs using controlled gold nanoparticle (Au NP) diffusion in nanotubes and the preparation method of Au-capped silica nanotubes.

The methodology is outlined in Scheme 1. First, silica nanotubes (SNTs) were prepared according to the surface sol−gel (SSG) template synthesis.[3b,7] The inner surface of SNTs was selectively modified with (3-trimethoxysilylpropyl)diethylenetriamine (DETA−silane), while SNTs were still embedded in the pores of template. After the dissolution of the template, free-standing SNTs were obtained by filtration and stored in water. To a solution of 500 μL of 2-nm gold nanoparticle (obtained from BBInternational), ca. 10^9 SNTs were added and incubated at 27 °C for 20 h. Excess Au NPs remaining in solution were removed by filtration and washed with water four times. These SNTs partially modified with 2-nm Au NPs were then used for the synthesis of Au-capped SNTs by seed-mediated gold growth[8] or for further selective functionalization using Au-thiol interaction.[9]

Figure 1A shows the transmission electron microscopy (TEM) image of SNTs which have a positively-charged amine layer only on their inner surface after incubation with 2-nm Au NPs. Surprisingly, all of the Au NPs were found exclusively on the inner surfaces of SNTs, localized near the open end of SNT. However, Au NPs were not found on the outer surface or the deep inner surface of SNTs. Since Au NPs are covered with negatively charged

Scheme 1. Method for Partial Modification of SNT with Au NPs



thiocyanate anions, their spontaneous diffusion from bulk into the positively charged nanochannels of SNTs leads to Au NPs trapped on the inner surface of SNTs. Due to its low isoelectric point (pI), silica bears a net negative charge above pH 2.[10] As a result, this prevents Au NPs from being trapped by a nonfunctionalized outer surface of SNTs because of electrostatic repulsion. As anticipated, in the two control experiments, SNTs with an amine layer on both surfaces (Figure 1B) and SNTs without any modification (Figure 1C), Au NPs were found on both surfaces or almost nowhere, respectively.

As seen in Figure 2A, the degree of inner surface functionalization with Au NPs shows strong correlation with the channel diameters of SNTs, suggesting channel diameter-dependent diffusion. In addition, the Au NP number density profile along the channel of a SNT (Figure 2B) demonstrates the number of Au NPs per unit area is maintained at a constant level for a certain range and then decreases gradually, which is expected to be a result of diffusion. Diffusion into the channel is explained by one or more of following three mechanisms: Knudsen diffusion, surface diffusion, and hindered diffusion.[11] However, we can exclude Knudsen diffusion and surface diffusion mechanisms because solute−solvent interaction (Au NPs and water) is major factor rather than solute−pore wall interaction, and surface transport was not observed.[11d] Further experiments revealed that, although less than 2% of original Au NPs were consumed during the diffusion process, neither the total diffusion length nor the number density was significantly changed over time (up to 1 week) even after replacing the Au NP solution with a fresh solution. Hindered diffusion also cannot explain this phenomenon. At present, the exact mechanism is unclear, but we may be able to explain this phenomenon as being due to the repulsive forces between negatively charged Au NPs becoming a dominant factor after a portion of inner surface is occupied by Au NPs. As a result the occupation begins to affect the diffusion of nother Au NPs and begins to block further diffusion, which may be considered as nanoparticle Donnan exclusion. This effect is more prominent in smaller channel diameters and causes an early blockage that leads to short diffusion distance.

In attempts to control the functionalization length regardless of channel diameters of SNTs, we explored the effects of Au NP concentration and the type of mixing solvent on the Au NP

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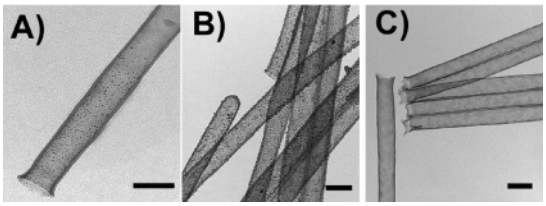

Figure 1. TEM images of various silica nanotubes (SNTs) after incubation with 2-nm Au NPs (1.5×10^{15} mL^{-1}); (A) SNTs with DETA-modified inner surfaces and bare silica outer surfaces; (B) SNTs with DETA−silane on both surfaces; (C) bare SNTs without any modification. Inner diameter (ID) of SNT was 63 nm, and scale bars are 100 nm. See Supporting Information.

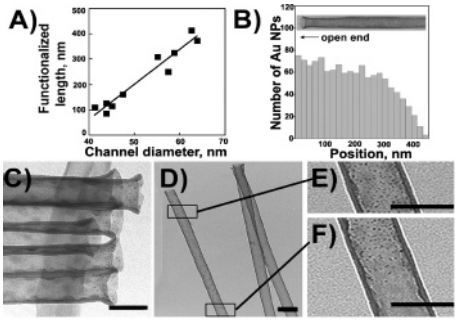

Figure 2. (A) Plot of total functionalized length of SNT with Au NPs vs the channel diameter of SNTs. (B) Number density of Au NPs along SNTs inner channel (63 nm ID). (C) TEM images of SNTs incubated with 1.5×10^{14} mL^{-1} of Au NPs (1/10 of Figure 1A). (D,E) TEM images of ethanol-filled SNTs (63-nm ID) after incubation with Au NPs. Scale bars are 100 nm.

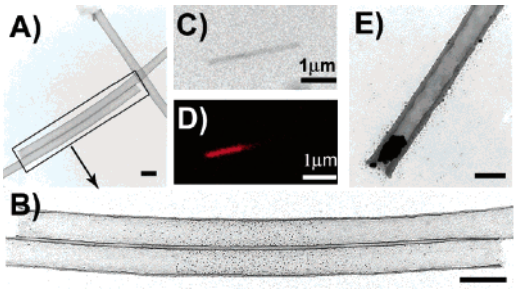

Figure 3. TEM images of SNTs (65 nm ID) partially functionalized with Au NPs in the middle of their nanochannels (A, B); Bright-field optical microscopy (C) and fluorescence microscopy (D) of SNTs with Au NPs inside (63-nm ID, prepared from ethanol-filled SNTs) after selective modification of Au NPs with 1,8-octanedithiol and Alexa555-maleimide. (E) Au-capped SNTs (58-nm ID) after seed-mediated gold growth. Scale bars are 100 nm, if not specified.

diffusion. Shorter functionalization was achieved with the use of a lower concentration of Au NPs (Figure 2C), whereas deeper functionalization was achieved by solvent exchange using SNTs initially filled with ethanol. Panels D−F of Figure 2 show that the inner surface of SNTs was functionalized with Au NPs up to ca. 1.5 μm from the open end. It is likely that entropy-driven diffusion is major contribution to this enhanced functionalization by overcoming electrostatic repulsive forces generated by pretrapped Au NPs.

Not only is the degree of functionalization adjustable but so also is the location of functionalization. This was accomplished by partially removing the DETA layer of the SNT inner surface using Ar plasma in order not to functionalize the inner open end area with Au NPs (Supporting Information). As seen in Figure 3A,B, Au NPs were found only in the middle of the SNT channel because the DETA layer near the open end was selectively discarded due to limited accessibility of Ar plasma into the pores.

Au NPs trapped inside of SNTs can serve as an anchoring point for further selective chemical functionalization. First, Au NPs trapped inside of SNTs were selectively modified with 1,8-octanedithiol via the Au/thiol bond, and then the remaining thiol group was reacted with Alexa555-maleimide (Supporting Information). Bright-field optical microscopy (Figure 3C) and fluorescence microscopy (Figure 3D) show that the red fluorescent dye Alexa555 was selectively functionalized onto the Au NPs. In contrast, in the control experiment performed with SNTs without Au NPs, no detectable fluorescence was observed.

Pretrapped Au NPs can also serve as seeds for Au growth that cap the open end of SNTs. $HAuCl_4$ was exclusively deposited onto the pretrapped Au NPs after reduction with ascorbic acid.[8]

Figure 3E shows a TEM image of Au-capped SNTs. It is notable that this approach to the preparation of capped NTs can be performed with NTs that are free of their template supporter under biocompatible conditions.[4] We believe that our capping procedure can be potentially adopted for a general in situ encapsulation of biomaterials (e.g., DNA or enzyme) and organic/inorganic materials.

In conclusion, selective functionalization of the inside of NTs was successfully demonstrated using the diffusion of Au NPs into the channel of NTs. The degree of functionalization was controlled by the channel diameter, Au NP concentration, and solvent type. Au NPs exclusively entrapped near the open end of NTs provide a route to the preparation of Au-capped nanotubes.

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Supporting Information Available: Experimental details and detailed analysis of TEM and SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Martin, C. R.; Kohli, P. *Nat. Rev. Drug Discovery* **2003**, *2*, 29−37. (b) Whitesides, G. M. *Nat. Biotechnol.* **2003**, *21*, 1161−1165. (c) Ferrari, M. *Nat. Rev. Cancer* **2005**, *5*, 161−171.

(2) Mitchell, D. T.; Lee, S. B.; Trofin, L.; Li, N.; Nevanen, T. K.; Soderlund, H.; Martin, C. R. *J. Am. Chem. Soc.* **2002**, *124*, 11864.

(3) (a) Goldberger, J.; Fan, R.; Yang, P. *Acc. Chem. Res.* **2006**, *39*, 239−248. (b) Son, S. J.; Reichel, J.; He, B.; Schuchman, M.; Lee, S. B. *J. Am. Chem. Soc.* **2005**, *127*, 7316−7317. (c) Chen, C. C.; Liu, Y. C.; Wu, C. H.; Yeh, C. C.; Su, M. T.; Wu, Y. C. *Adv. Mater.* **2005**, *17*, 404−407. (d) Kam, N. W.; O'Connell, M.; Wisdom, J. A.; Dai, H. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 11600−11605.

(4) Hillebrenner, H.; Buyukserin, F.; Kang, M.; Mota, M. O.; Stewart, J. D.; Martin, C. R. *J. Am. Chem. Soc.* **2006**, *128*, 4236−4237.

(5) Fan, R.; Karnik, R.; Yue, M.; Le, D. Y.; Majumdar, A.; Yang, P. D. *Nano Lett.* **2005**, *5*, 1633−1642.

(6) (a) Lee, K. M.; Li, L.; Dai, L. *J. Am. Chem. Soc.* **2005**, *127*, 4122−4123. (b) Bahr, J. L.; Tour, J. M. *J. Mater. Chem.* **2002**, *12*, 1952−1958. (c) Banerjee, I. A.; Yu, L.; Matsui, H. *Nano Lett.* **2003**, *3*, 283−287.

(7) Kovtyukhova, N. I.; Mallouk, T. E.; Mayer, T. S. *Adv. Mater.* **2003**, *15*, 780−785.

(8) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389−1393.

(9) Ciszek, J. W.; Stewart, M. P.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 13172−13173.

(10) Moul, C.-Y.; Lin, H.-P. *Pure Appl. Chem.* **2000**, *72*, 137−146.

(11) (a) Coppens, M.-O.; Dammers, A. J. *Fluid Phase Equilib.* **2006**, *241*, 308−316. (b) Rieley, H.; Kendall, G. K.; Zemicael, F. W.; Smith, T. L.; Yang, S. *Langmuir* **1998**, *14*, 5147−5153. (c) Johnson, K. A.; Westermann-Clark, G. B.; Shah, D. O. *Langmuir* **1989**, *5*, 932−938. (d) Cussler, E. L. *Diffusion: Mass Transfer in Fluid Systems*; Cambridge University Press: New York, 1984; pp 187−189.

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