

Substrate-Enhanced Electroless Deposition of Metal Nanoparticles on Carbon Nanotubes

Liangti Qu and Liming Dai*

Department of Chemical and Materials Engineering, School of Engineering, The University of Dayton,
300 College Park, Dayton, Ohio 45469-0240

Received May 27, 2005; E-mail: ldai@udayton.edu

Carbon nanotubes have been demonstrated to possess excellent electronic properties, a good chemical stability, and a large surface area.¹ These unique properties make carbon nanotubes very useful for supporting metal nanoparticles in many potential applications, ranging from advanced catalytic systems through very sensitive electrochemical sensors to highly efficient fuel cells.² Consequently, functionalization of carbon nanotubes with metal nanoparticles has received ever-increasing interest in recent years, and a few interesting routes have now been devised for either covalently or noncovalently attaching certain metal nanoparticles onto carbon nanotubes.^{3–7} Examples include chemical binding through DNA double-helix linkages,³ electrochemical deposition,⁴ electroless deposition with and without the aid of reducing agents,^{5,6} and physical/chemical deposition on carbon nanotubes with and without surface activation.^{2a,7} Among them, the electroless deposition is of particular interest because its simplicity could facilitate a large-scale production of the nanotube–nanoparticle hybrids. General applications of the electroless deposition, however, are limited by the fact that only metal ions of a redox potential higher than that of a reducing agent or carbon nanotube can be reduced into nanoparticles on the nanotube support. Given that a single-walled carbon nanotube (SWNT) has a redox potential of +0.5 V vs SHE (standard hydrogen electrode),⁶ it is impossible to reduce Cu^{2+} ($\text{Cu}(\text{NO}_3)_2/\text{Cu}$, +0.340 V vs SHE) or Ag^+ ($\text{Ag}(\text{NH}_3)_2^+/\text{Ag}$, +0.373 V vs SHE)⁸ into metal nanoparticles by SWNTs via a galvanic displacement reaction without the aid of a reducing agent,⁶ though Au ($\text{AuCl}_4^-/\text{Au}$, +1.002 V vs SHE) and Pt ($\text{PtCl}_4^{2-}/\text{Pt}$, +0.775 vs SHE) nanoparticles have been successfully deposited on nanotubes through spontaneous reduction of the metal ions by SWNTs.⁶ By simply supporting carbon nanotubes with a metal substrate of a redox potential lower than that of the metal ions to be reduced into nanoparticles, we demonstrated for the first time that metal ions even with a redox potential lower than that of a carbon nanotube can be readily reduced into metal nanoparticles onto the nanotube support—a process that we designated as Substrate-Enhanced Electroless Deposition (SEED). Here, we report this facile yet versatile and effective SEED method for electroless deposition of a large variety of metal nanoparticles, including Cu and Ag nanoparticles, on both SWNTs and multiwalled carbon nanotubes (MWNTs) in the absence of any additional reducing agent.

Figure 1 schematically shows the galvanic displacement reaction governing the SEED process. As can be seen, the deposition of metal nanoparticles is achieved via the redox reaction of a galvanic cell, in which the nanotube acts as a cathode for metal deposition (M) from the reduction of metal ions (M^{m+}) in solution, while the metal substrate serves as an anode where metal atoms (Sub^0) are oxidized into (Sub^{n+}) followed by dissolution.⁹ Therefore, the SEED process should allow electroless deposition of any metal nanoparticles (M) on conducting carbon nanotubes as long as the redox potential of the substrate metal ($\text{Sub}^{n+}/\text{Sub}^0$) is lower than that of

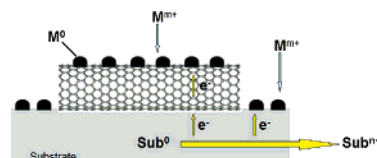


Figure 1. Schematic illustration of metal nanoparticle deposition on carbon nanotubes via the SEED process.

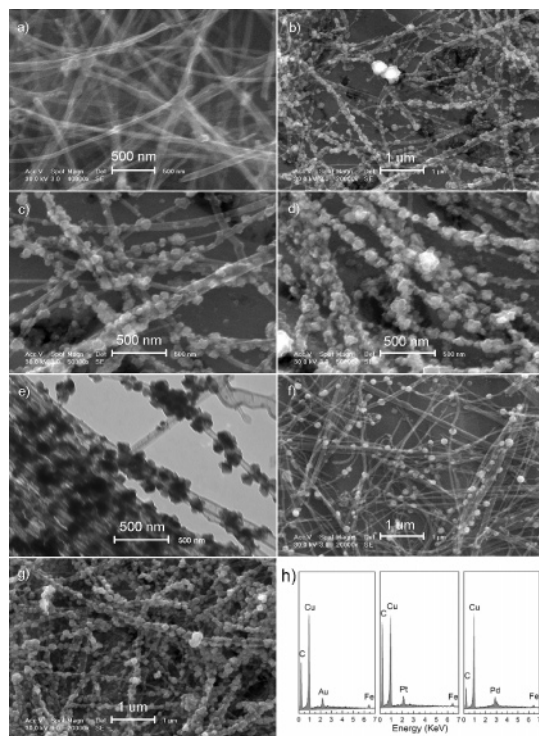


Figure 2. SEM images of MWNTs supported by a copper foil after being immersed into an aqueous solution of HAuCl_4 (3.8 mM) for different periods of time: (a) 0 s, (b) 10 s, (c) same as for (b) under a higher magnification, (d) 30 s. (e) A transmission electron microscopic (TEM) image of Au nanoparticle-coated MWNTs, (f) the Cu-supported MWNTs after being immersed into an aqueous solution of K_2PtCl_4 (4.8 mM) for 10 s, and (g) the Cu-supported MWNTs after being immersed into an aqueous solution of $(\text{NH}_4)_2\text{PdCl}_4$ (7.0 mM) for 10 s. (h) EDX spectra for the Au, Pt, and Pd nanoparticle-coated MWNTs on Cu foils.

the metal ions (M^{m+}/M) in solution, indicating a great potential for functionalization of carbon nanotubes with various metal nanoparticles by the SEED process that is as yet almost unrecognized.

To demonstrate the SEED process, we started with MWNTs prepared by pyrolysis of iron(II) phthalocyanine (FePc).¹⁰ Figure 2a represents a typical scanning electron microscopic (SEM, Philips XL30 FEG) image of the FePc -generated MWNTs randomly

dispersed on a copper foil (EMS US), showing that the pristine nanotubes possess a smooth surface and almost free from pyrolytic impurities on the nanotube surface (e.g., amorphous carbon and residual catalyst nanoparticles). Upon immersion of the Cu-supported MWNTs into an aqueous solution of HAuCl_4 (3.8 mM), we found that Au nanoparticles spontaneously formed on the nanotube sidewalls. The SEM images taken at different stages during the SEED process reveal that the nucleation of Au nanoparticles started within seconds. Au clusters with a diameter around 100 nm are clearly evident along the nanotube sidewalls after about 10 s of exposure to the HAuCl_4 solution (Figure 2b,c). Longer reaction times caused no obvious change in the particle size but a significant increase in the density of particles along the nanotube length (Figure 2d). These observations indicate that particle nucleation on nanotubes is fast (<10 s) and not correlated with any defect site of the nanotube structure, as, at least, partially evidenced by the rather homogeneous distribution of nanoparticles along the high quality nanotubes shown in Figure 2e (TEM image, Hitachi H-7600). Furthermore, the nanoparticle growth process is most likely controlled by diffusion of the AuCl_4^- from the bulk solution to the nanotube/solution interface. Under the diffusion control, smaller particles often gain a faster growth than larger particles due to relatively more surface-receiving sites for the metal ions intrinsically associated with their higher surface-to-volume ratios. This could eventually lead to the formation of nanoparticles with a rather uniform size and effectively avoid the formation of abnormally large particles. Similar galvanic displacement reactions were observed for the carbon nanotubes with aqueous solutions of K_2PtCl_4 (4.8 mM, Figure 2f) and $(\text{NH}_4)_2\text{PdCl}_4$ (7.0 mM, Figure 2g). Energy-dispersive X-ray analyses (EDX) on the Au, Pt, and Pd nanoparticle-coated carbon nanotubes corresponding to Figure 2b,f,g clearly show peaks of Au, Pt, and Pd, respectively (Figure 2h), along with peaks for Cu, C, and Fe arising from the copper substrate and traces of Fe catalyst possibly end-encapsulated within the nanotube structure.^{10b} As expected, no similar particle deposition occurred when a metal substrate (e.g., Au) with a higher redox potential than that of metal ions (e.g., $\text{Cu}(\text{NO}_3)_2$, $\text{Ag}(\text{NH}_3)_2^+$) was used.

In our further investigation on the functionalization of carbon nanotubes, we found that a large variety of metal nanoparticles could also be electrolessly deposited onto Cu-supported SWNTs (Figure 3a) by the SEED process, as exemplified by Figure 3b–d for the Au, Pt, and Pd nanoparticle-coated SWNTs, respectively. By simply changing the copper foil (Cu^{2+}/Cu , 0.34 V vs SHE)⁸ to metal substrates of a lower redox potential (e.g., Zn^{2+}/Zn , -0.76 V vs SHE),⁸ we can further extend the capacity of the SEED process for electroless deposition of those metal nanoparticles even with a lower redox potential than that of carbon nanotubes. Figure 3e–h shows typical SEM images for Zn-supported SWNTs and MWNTs coated with Cu and Ag nanoparticles by the SEED process in the absence of any additional reducing agent, which otherwise are impossible with more conventional electroless depositions. These results clearly indicate, once again, that the newly developed SEED process is a very simple and highly versatile method useful for an effective electroless deposition of various metal nanoparticles on carbon nanotubes. In addition, our preliminary results reveal that the SEED process can also be used to deposit metal nanoparticles on the inner-wall of carbon nanotubes, and that the nanotube-supported metal nanoparticles (both on the inner- and outer-walls) are electrochemically active (Supporting Information).

In summary, we have developed a facile yet versatile and effective substrate-enhanced electroless deposition (SEED) method for functionalization of carbon nanotubes with a large variety of

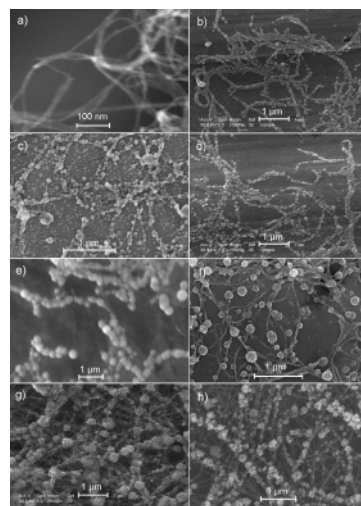


Figure 3. SEM images of (a) the pristine SWNTs and the Cu-supported SWNTs after being immersed in an aqueous solution of (b) HAuCl_4 (3.8 mM), (c) K_2PtCl_4 (4.8 mM), and (d) $(\text{NH}_4)_2\text{PdCl}_4$ (7.0 mM) for 5 s. SEM images of (e, f) SWNTs and (g, h) MWNTs supported by a zinc foil after being immersed in an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ (3.8 mM) and $\text{Ag}(\text{NH}_3)_2^+$ (3.8 mM), respectively, for 5 s.

metal nanoparticles, in the absence of any additional reducing agent, by simply supporting the nanotubes with a metal substrate of a redox potential lower than that of the metal ions to be reduced into nanoparticles. Judicious selection of the metal substrates allowed the SEED process for electroless deposition of various metal nanoparticles, including those otherwise impossible by more conventional electroless deposition methods, on both the outer- and inner-walls of carbon nanotubes. These nanotube-supported metal nanoparticles are electrochemically active. Therefore, the SEED process can be regarded as a general approach to effective functionalization of carbon nanotubes with various metal nanoparticles for a wide range of potential applications, including in advanced sensing and catalytic systems.

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Supporting Information Available: A TEM image and cyclic voltammograms of MWNTs with their inner- and outer-walls coated by Au and Pt nanoparticles, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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