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Spontaneous Reduction of Metal Ions on the Sidewalls of Carbon Nanotubes

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There has been much interest lately in the covalent and noncovalent sidewall chemistry of single-walled carbon nanotubes (SWNTs).[1a−i] The research activities are motivated by modifying the inert nanotube sidewalls to impart solubility in solvents or to immobilize various organic, inorganic, or biological species to afford nanotube "macromolecules" with chemical functionality. Covalent modification of nanotube sidewalls includes oxidation, fluorination, and formation of amide bonds.[1a,b,g] Noncovalent approaches utilize π-stacking or van der Waals interactions between aromatic molecules or polymers and nanotubes.[1d−f,2]

Attaching metal nanoparticles to nanotube sidewalls is of interest for obtaining nanotube/nanoparticle hybrid materials with useful properties,[1c] and for forming metal nanowires on nanotube templates.[3,4] It has been shown, for instance, that functionalization of SWNTs by Pd nanoparticles imparts sensitivity to molecular hydrogen for nanotube electrical detectors.[1c] Previous approaches to metal nanoparticle functionalization of nanotubes include physical evaporation,[1c,3,4] attachment after oxidation of nanotubes,[5] solid-state reaction with metal salts at elevated temperatures,[6] and electroless deposition from salt solutions with the aid of reducing agents or catalyst.[7]

This Communication reports spontaneous metal nanoparticle formation on SWNT sidewalls when nanotubes are immersed in corresponding metal salt solutions. The work is motivated by a recent observation by Buriak et al. that metal particles form spontaneously on semiconductor and metal surfaces in solutions containing certain redox-active species.[8] The deposition process differs from traditional electroless deposition in that no reducing agents or catalysts are required. In a related work, Yang et al. have elegantly shown the spontaneous formation of one type of metal nanowire on semiconductor nanowire templates by redox chemistry.[9] A more recent work is the formation of core-sheath nanowires obtained by electroless redox deposition of Au on Cu_2S nanowires.[10] Here, we present the observation of highly selective electroless metal nanoparticle deposition on SWNTs as a result of direct redox reactions between metal ions and nanotubes. Charge transfer during the reaction is probed electrically, as it causes significant changes in the electrical conductance of nanotubes by hole doping. Further, we show that this phenomenon can be exploited to form line-like metal structures with width <10 nm on removable nanotube templates.

The nanotube samples used here are as-grown SWNTs on SiO_2 substrates. The growth of nanotubes has been described previously, involving deposition of discrete catalytic Fe nanoparticles on SiO_2 followed by chemical vapor deposition.[11] The samples comprise pure SWNTs on SiO_2 substrates, with each nanotube encasing an Fe nanoparticle at one of the ends.[11] Various salt solutions are prepared at 5 mM concentration in doubly distilled water and an equal volume of ethanol, intended for better wetting of the nanotube surfaces. The samples are immersed in a salt solution for varying periods of time, after which the samples are rinsed with copious amounts of water and ethanol, dried in a N_2 stream, and characterized by atomic force microscopy (AFM).

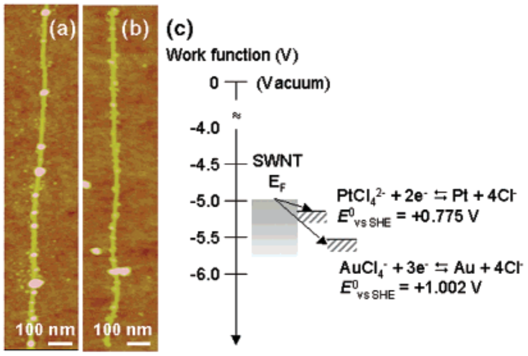

Figure 1. AFM images of metal nanoparticles formed on SWNT sidewalls. (a) Au nanoparticles spontaneously and selectively formed on an individual SWNT after immersion in a Au^{3+} solution for 3 min. (b) Pt nanoparticles formed on a SWNT after 3 min exposure to a Pt^{2+} solution. (c) Diagram showing the Fermi energy (E_F) of a SWNT, and the reduction potentials of Au^{3+} and Pt^{2+} vs SHE, respectively. The reduction potentials of most other metal ions lie above E_F, except for Ag^+.

After immersion of SWNTs in $HAuCl_4$ (Au^{3+}) and Na_2PtCl_4 (Pt^{2+}) solutions, we find that Au and Pt nanoparticles, respectively, have spontaneously formed on the sidewalls of SWNTs in a selective manner. Figure 1a shows an AFM image of Au nanoparticles decorating a SWNT after immersion in the $HAuCl_4$ solution for 3 min. Notice that particles formation is selective to the nanotube sidewall and not to the surrounding SiO_2 substrate. The average size of Au particles is estimated at 7 nm from topography measurements. When varying the reaction time, we find that small Au clusters on SWNTs can start to be resolved by AFM after ~30 s of exposure to the $HAuCl_4$ solution. Longer reaction times (≥3 min) cause the formation of larger particles (up to 16 nm) but do not lead to any apparent increase in the density of particles along the nanotubes. These results indicate that particle nucleation on nanotubes is fast and ceases in the initial ~30 s, after which particle growth, rather than further nucleation, dominates. In a similar manner, we observe that Pt nanoparticles spontaneously form selectively on the sidewalls of SWNTs in ethanolic aqueous solution of 5 mM Na_2PtCl_4. The density of Pt particles on SWNTs appears higher than that of Au (Figure 1b). Similar results are obtained in the dark, under room light, halogen lamp and UV light for Au and Pt, suggesting no significant light effect to the electroless deposition process. Thus far, the selective electroless metal deposition on SWNTs is found to be unique for Au and Pt. Treatment of our samples by other metal ion solutions such as Ag^+, Ni^{2+} and Cu^{2+} finds nonspecific particle deposition over the substrate.

The formation of Au and Pt particles on SWNT sidewalls is attributed to direct redox reaction between nanotubes and metal

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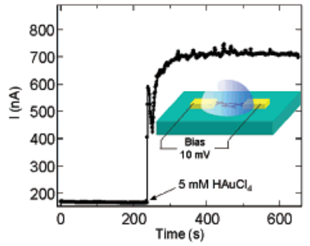

Figure 2. Monitoring the change in current across a SWNT mat during exposure to a 5 mM HAuCl$_4$ solution. The period before the exposure corresponds to the nanotube mat in 1:1 ethanol and water. (Inset) Schematic for the experiment setup. Spacing between points: 1 s.

ions. It is well known that certain metal/metal-ion pairs exhibit spontaneous oxidation and reduction in solution. For instance, when Zn is exposed to a Cu^{2+} solution, spontaneous oxidation of Zn to Zn^{2+} and reduction of Cu^{2+} to Cu occurs, leading to the familiar galvanic cell. The nanotube/Au^{3+} and nanotube/Pt^{2+} systems can be categorized as such redox pairs. The work function of SWNTs has been determined to be $\sim$5 eV.[12] The Fermi level of a SWNT is therefore about $+0.5$ V above the potential of a standard hydrogen electrode (SHE),[13] and it is well above the reduction potentials of AuCl$_4^-$ and PtCl$_4^{2-}$, which are $+1.002$ and $+0.775$ V vs SHE, respectively[14] (Figure 1c). The relative potential levels rationalize the spontaneous electron transfer from the nanotube (oxidation) to the metal ions and their reduction.

The metal ion reduction and SWNTs oxidation during electroless metal deposition can be probed by measuring the electrical conductance of SWNTs immersed in solutions. When SWNTs act as electron donors, hole injection into SWNTs is expected to cause an increase in the electrical conductance[15] to the already p-type nanotubes due to O_2 doping under ambient conditions.[16] This is indeed as observed in Figure 2, in which addition of a 5 mM solution of HAuCl$_4$ to a "mat" of SWNTs leads to a sharp increase in the conductance across the mat (monitored at 10 mV bias voltage). The nanotube conductance rapidly rises to a plateau in 40 s after exposure to HAuCl$_4$, and the $\sim$40 s time is attributed to the nucleation stage of metal nanoparticles on SWNTs, in accordance with the finding by AFM described above. Note that control experiments reveal 2 nA current at 10 mV bias through the 5 mM salt solution itself without the presence of a nanotube mat. Thus, the 600 nA current rise upon the addition of salt solution in Figure 2 is due to hole injection into nanotubes. The high-density deposited metal nanoparticles may have contributed to the overall large conductance enhancement. The initial rise, however (in $\sim$2 s), when the metal deposition is far from continuous should be largely due to the redox process described above. We have also observed similar hole injection into SWNT during Pt electroless reaction with nanotubes.

Spontaneous metal deposition on SWNTs by the electroless process allows for facile, efficient, and selective immobilization of metal species on nanotubes, which could be useful for sensor and catalysis applications. It also provides a useful approach to metal wire-like structures using nanotubes as removable templates.

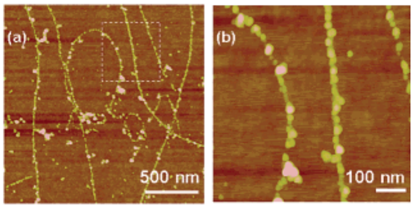

Figure 3. Pt wire-like structures formed by electroless deposition of Pt nanoparticles. The AFM images are recorded after removal of the nanotube templates. (b) Details of boxed area in (a).

After Pt deposition on SWNTs, we heat the sample to 600 °C in air for 10 min. This leads to Pt nanoparticles forming chain-like structures, as seen by AFM (Figure 3), with the underlying nanotube completely oxidized away. The Pt particle chains are as narrow as 2 nm, with continuous wire sections up to 500 nm in length. The gaps between the nanoparticles vary and are as small as 1−2 nm. We are currently exploring ways to increase the nucleation sites on nanotubes, aimed at obtaining metal nanowires that are truly uniform and continuous. Such structures can find applications as narrow metal electrodes for molecular electronics.

In summary, we have observed formation of Au and Pt nanoparticles on single-walled carbon nanotubes due to spontaneous reduction of metal ions in solutions. This process differs from typical electroless deposition that requires reducing agents or catalyst, as a result of direct redox reactions between ions and nanotubes. We have probed this phenomenon by microscopy and investigated the redox process by directly using nanotubes as analytical tools. Further, we have shown that the phenomenon of selective metal formation on nanotubes can be exploited to obtain metal nanowire structures by templating chemistry

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References

(1) (a) Chen, J.; Hammon, M. A.; Hu, H.; Chen, Y. S.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95. (b) Boul, P.; Liu, J.; Mickelson, E.; Huffman, C.; Ericson, L.; Chiang, I.; Smith, K.; Colbert, D.; Hauge, R.; Margrave, J.; Smalley, R. *Chem. Phys. Lett.* **1999**, *310*, 367. (c) Kong, J.; Chapline, M.; Dai, H. *Adv. Mater.* **2001**, *13*, 1384. (d) Chen, R.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001**, *123*, 3838. (e) Star, A.; Stoddart, J.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E.; Yang, X.; Chung, S.; Choi, S.; Heath, J. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1721. (f) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265. (g) Bahr, J.; Yang, J.; Kosynkin, D.; Bronikowski, M.; Smalley, R.; Tour, J. *J. Am. Chem. Soc.* **2001**, *123*, 6536. (h) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; R, R. W.; Jellen F *Angew. Chem., Int. Ed.* **2001**, *40*, 4002. (i) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760.
(2) Shim, M.; Kam, N.; Chen, R.; Li, Y.; Dai, H. *Nano Lett.* **2002**, *2*, 285.
(3) Bezryadin, A.; Lau, C. N.; Tinkham, M. *Nature* **2000**, *404*, 971.
(4) Zhang, Y.; Dai, H. *Appl. Phys. Lett.* **2000**, *77*, 3015.
(5) Azamian, R.; Coleman, K.; Davis, J.; Hanson, N.; Green, M. *Chem. Commun.* **2002**, 366.
(6) (a) Lago, R.; Tsang, S.; Lu, K.; Chen, Y.; Green, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1355. (b) Xue, B.; Chen, P.; Hong, Q.; Lin, J.; Tan, K. *J. Mater. Chem.* **2001**, *11*, 2378.
(7) Li, J.; Moskovits, M.; Haslett, T. *Chem. Mater.* **1998**, *10*, 1963.
(8) Choi, H. C.; Lon A. Porter, J.; Schmeltzer, J. M.; Ribbe, A. E.; Buriak, J. M., manuscript in preparation.
(9) Song, J.; Wu, Y.; Messer, B.; Kind, H.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 10397.
(10) Wen, X.; Yang, S. *Nano Lett.* **2002**, *2*, 451
(11) (a) Li, Y.; Kim, W.; Zhang, Y.; Rolandi, M.; Wang, D.; Dai, H. *J. Phys. Chem. B* **2001**, *105*, 11424. (b) Zhang, Y.; Li, Y.; Kim, W.; Wang, D.; Dai, H. *Appl. Phys. A* **2002**, *74*, 325.
(12) (a) Suzuki, S.; Bower, C.; Watanabe, Y.; Zhou, O. *Appl. Phys. Lett.* **2000**, *76*, 4007. (b) Kazaoui, S.; Minami, N.; Matsuda, N.; H, H. K.; Achiba, Y. *Appl. Phys. Lett.* **2001**, *78*, 3433.
(13) Memmingm, R. *Top. Curr. Chem.* **1994**, *169*, 105.
(14) *Handbook of Chemistry and Physics*, 73th ed.; CRC Press: Cleveland OH, 1992; pp 8-17 to 8-22.
(15) Kong, J.; Franklin, N.; Zhou, C.; Chapline, M.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.
(16) (a) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science* **2000**, *287*, 1801. (b) Chen, R.; Franklin, N.; Kong, J.; Cao, J.; Tombler, T.; Zhang, Y.; Dai, H. *Appl. Phys. Lett.* **2001**, *79*, 6951.

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