One Step Synthesis of Multiwalled Carbon Nanotube/Gold Nanocomposites for Enhancing Electrochemical Response

Renyun Zhang and Xuemei Wang*

State Key Lab of Bioelectronics (Chie-Shiung Wu Laboratory), Southeast University, No. 2 Sipailou, Nanjing 210096, People's Republic of China

Received November 22, 2006
Revised Manuscript Received January 26, 2007

Carbon nanotubes attract continuing interest in various areas since their discovery because of their unique structure and electrical/mechanical properties.[1,2] Many potential applications of carbon nanotubes in electronic devices, biosensors, and catalyst supports have been explored in the past years.[3−5] Specifically, metal/carbon-nanotube hybrid materials have attracted attention because of their promising applications in nanoelectronics as well as highly sensitive biosensors.[6−11] The "bottom-up" routes toward nanometer-scale electronics as functional building blocks for electronic devices based on the respective carbon nanotubes have been focused in the related research areas.[12−14]

With the aim of "bottom-up" constructions, different metal nanoparticles have been coated or deposited (covalently or noncovalently) on the side wall of both single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs).[15,16] By adding some salts to the reaction system which may increase the barrier toward homogeneous metal nucleation, Pt nanoparticles could be deposited on the exterior walls of carbon nanotubes.[17] Besides, ZnO nanorods and nanoparticles could be coated on carbon nanotubes as hybrid structures through chemical vapor deposition.[18−20] Among those nanoparticles that have been commonly deposited or coated on carbon nanotubes, gold nanoparticles have been paid much interest, where several methods including electrochemical and other chemical/physical methods have been utilized to deposit gold nanoparticles on carbon nanotubes.[21,22] Recently, it is reported that through direct redox reactions by the immersion of SWCNTs in a Au^{3+} ions containing solution, gold nanoparticles could be readily deposited on SWCNTs.[23] Moreover, by using the reduction reaction of gold salts with surfactant-suspended carbon nanotubes in water, a carbon nanotube/gold nanoparticle hybrid could be prepared in a homogeneous phase.[24] Meanwhile, some reports demonstrate that microwaves could efficiently assist the binding of gold nanoparticles to MWCNTs.[25,26]

On the basis of these obervations, in this study we have explored a new strategy to deposit gold nanoparticles on the side wall of MWCNTs by one step reaction in aqueous solution, where the gold nanoparticles could be self-coated on the carbon nanotubes during their synthesis process.

It is well-known that there exist different methods for the synthesis of gold nanoparticles,[27,28] and the citrate reduction is one of the most commonly used ways, where the stable and dispersed gold nanoparticles could be readily obtained and the size of the gold nanoparticles could be easily controlled.[29,30] In view of this observation, in this work we adopt the citrate reduction method for the synthesis of the gold nanoparticles coated on the carbon nanotubes as multiwalled carbon nanotube/gold (MWCNT−Au) nanocomposites.

Initially, MWCNTs were purified by using acid treatment. Then, the respective carbon nanotubes (1 mg) were suspended in 1 wt % $HAuCl_4$ solution (1 mL) by sonication for 5 min to make nanotubes dispersed equably. The suspended solution was then diluted to 100 mL with doubly distilled water and heated to boiling while stirring. Afterward, sodium citrate was subsequently added to the boiling solution. To control the size of the gold nanoparticles,

(1) Iijima, S. *Nature* **1991**, *354*, 56−58.
(2) Collins, P. G.; Zettle, A.; Bando, H.; Thess, A.; Smalley, R. E. *Science* **1997**, *278*, 100−103.
(3) Dekker, C. *Phys. Today* **1999**, *52*, 22−28.
(4) Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K. J.; Dai, H. J. *Science* **2000**, *287*, 622−625.
(5) Planeix, J. M.; Coustel, N.; Coq, B.; Brotons, V.; Kumbhar, P. S.; Dutartre, R.; Geneste, P.; Bemier, P.; Ajayan, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 7935−7936.
(6) Van Bommel, K. J. C.; Friiggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980−999.
(7) Bexryadin, A.; Lau, C. N.; Tinkham, M. *Nature* **2000**, *404*, 971−974.
(8) Hrapovic, S.; Liu, Y.; Male, K. B.; Luong, J. H. T. *Anal. Chem.* **2004**, *76*, 1083−1088.
(9) Wang, D.; Li, Z. C.; Chen, L. W. *J. Am. Chem. Soc.* **2006**, *128*, 15078−15079.
(10) Cha, S. I.; Kim, K. T.; Arshad, S. N.; Mo, C. B.; Hong, S. H. *Adv. Mater.* **2005**, *11*, 1377−1381.
(11) Lee, Y.; Song, H. J.; Shin, H. S.; Shin, H. J.; Choi, H. C. *Small* **2005**, *1*, 975−979.
(12) Duan, X. F.; Niu, C. M.; Sahi, V.; Chen, J.; Parce, J. W.; Empedocles, S.; Goldman, J. L. *Nature* **2003**, *425*, 274−278.
(13) Zhong, Z. H.; Wang, D. L.; Cui, Y.; Bockrath, M. W.; Lieber, C. M. *Science* **2003**, *302*, 1377−1379.
(14) Fu, L.; Liu, Z. M.; Liu, Y. Q.; Han, B. X.; Hu, P. G.; Cao, L. C.; Zhu, D. B. *Adv. Mater.* **2005**, *17*, 217−221.
(15) Li, W. Z.; Liang, C. H.; Zhou, W. J.; Qiu, J. S.; Zhou, Z. H.; Sun, G. O.; Xin, Q. *J. Phys. Chem. B* **2003**, *107*, 6292−6299.
(16) Ye, X. R.; Lin, Y. H.; Wang, C. M.; Wai, C. M. *Adv. Mater.* **2003**, *15*, 316−319.
(17) Wang, Y.; Xu, X.; Tian, Z. Q.; Zong, Y.; Cheng, H. M.; Lin, C. J. *Chem. Eur. J.* **2006**, *12*, 2542−2549.
(18) Kim, H.; Sigmund, W. *Appl. Phys. Lett.* **2002**, *81*, 2085−2087.
(19) Sun, J.; Gao, L.; Iwasa, M. *Chem. Commun.* **2004**, 832−833.
(20) Zhu, Y. W.; Elim, H. I.; Foo, Y. L.; Yu, T.; Liu, Y. J.; Ji, W.; Lee, J. Y.; Shen, Z. X.; Wee, A. T.-S.; Thong, J. T.-L.; Sow, C. H. *Adv. Mater.* **2006**, *18*, 587−592.
(21) Day, T. M.; Unwin, P. R.; Wilson, N. R.; Macpherson, J. V. *J. Am. Chem. Soc.* **2005**, *127*, 10639−10647.
(22) Kim, K.; Lee, S. H.; Yi, W.; Kim, J.; Choi, J. W.; Park, Y.; Jin, J. I. *Adv. Mater.* **2003**, *15*, 1618−1622.
(23) Choi, H. C.; Shim, M.; Bangsaruntip, S.; Dai, H. *J. Am. Chem. Soc.* **2004**, *124*, 9058−9059.
(24) Kim, D. S.; Lee, T.; Geckeler, K. E. *Angew. Chem.* **2006**, *118*, 110−113.
(25) Li, J. X.; Grennberg, H. H. *Chem.*−*Eur. J.* **2006**, *12*, 3869−3875.
(26) Raghuveer, M. S.; Agrawal, S.; Bishop, N.; Ramanath, G. *Chem. Mater.* **2006**, *18*, 1390−1393.
(27) Love, C. S.; Chechik, V.; Smith, D. K.; Wilson, K.; Ashworth, I.; Brennan, C. *Chem. Commun.* **2005**, *15*, 1971−1973.
(28) Walker, C. H.; John, J. V. St.; Wisian-Neilson, P. *J. Am. Chem. Soc.* **2001**, *123*, 3486−3487.
(29) Frens, G. *Nature* **1973**, *241*, 20−23.
(30) Gearheart, L. A.; Ploehn, H. J.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 12609−12615.

10.1021/cm062791v CCC: $37.00
Published on Web 02/10/2007

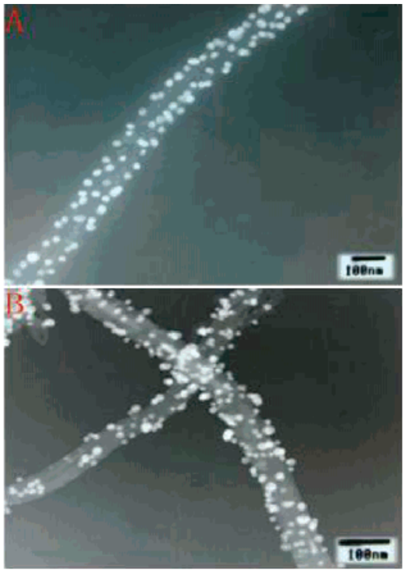

Figure 1. TEM images of synthesized MWCNT−Au nanocomposites. (A) MWCNT−Au nanocomposites obtained upon addition of 1.5 mL of sodium citrate in $HAuCl_4$ solution suspended with carbon nanotubes (100 mL), (B) MWCNT−Au nanocomposites obtained upon addition of 4.0 mL of sodium citrate in $HAuCl_4$ solution suspended with carbon nanotubes (100 mL). The scale bars represent 100 nm.

different amounts of sodium citrate were added to the boiling solution which was kept heating for 5−10 min until the color of the solutions did not change.

Figure 1 shows the typical TEM images of the synthesized MWCNT−Au nanocomposites, which demonstrate that the carbon nanotubes could be nicely coated with gold nanoparticles. It is noted that a well assembled nanocomposite could be obtained when 1.5 mL of sodium citrate was added to 100 mL of $HAuCl_4$ solution suspended with carbon nanotubes, where transmission electron microscopy (TEM) micrographs demonstrate that the gold nanoparticles could be equiaxed and decorated on the MWCNTs uniformly along its length. Moreover, our observations indicate that the size of gold nanoparticles coated on carbon nanotubes is in the range of 20 to 24 nm with the average of 22 nm when 1.5 mL of sodium citrate was applied for the respective preparation, while the range is 9 to 13 nm with the average of 12 nm when 4 mL of sodium citrate was added to the relative reaction. In comparison, the typical TEM images of gold nanoparticles synthesized in the absence of MWCNTs illustrate that the average diameter of gold nanoparticles is about 21 and 12 nm for the application of 1.5 mL and 4 mL of sodium citrate, respectively, for the related preparation (as shown in Supporting Information).

Additionally, to find the best conditions for the synthesis of the new nanocomposites, we have explored the different procedures for the preparation of the MWCNT−Au hybrid materials. Our observations indicate that the premixing of carbon nanotubes with $HAuCl_4$ solution could efficiently induce the adsorption of $HAuCl_4$ molecules on the nanotubes, while it will readily lead to the growth of gold nanoparticles on the side wall of the carbon nanotubes when the sodium citrate was subsequently added. Thus, it appears that almost all of the synthesized gold nanoparticles were observed on the wall of carbon nanotubes and little free gold nanoparticles could be observed in solution, as illustrated in TEM images

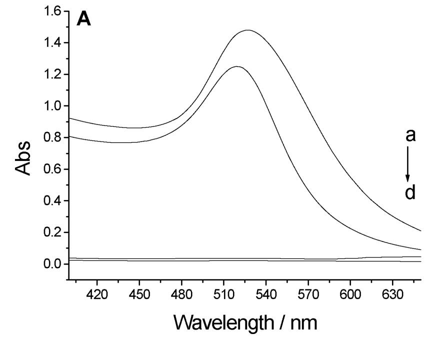

Figure 2. UV−vis absorption spectra of colloid gold solution synthesized in the absence of MWCNTs (a, b) and suspension centrifuged from synthesized MWCNT−Au nanocomposites (c, d). (a) Colloid gold solution synthesized by adding 1.5 mL of sodium citrate in $HAuCl_4$ solution (100 mL), (b) colloid gold solution synthesized by adding 4.0 mL of sodium citrate in $HAuCl_4$ solution (100 mL), (c) suspension centrifugal from MWCNT−Au nanocomposites synthesized by adding 1.5 mL of sodium citrate in $HAuCl_4$ solution suspended with carbon nanotubes (100 mL), and (d) suspension centrifuged from MWCNT−Au nanocomposites synthesized by adding 4.0 mL of sodium citrate in $HAuCl_4$ solution suspended with carbon nanotubes (100 mL).

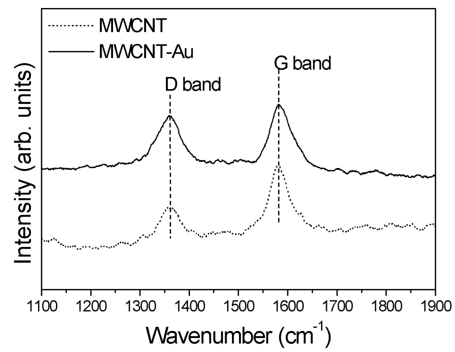

Figure 3. Raman spectra of MWCNTs and MWCNT−Au nanocomposites.

and UV−vis absorption studies (see Figures 1 and 2). In comparison, the relevant control experiments were performed without the premixing of the MWCNTs with the $HAuCl_4$ solution, where the MWCNTs were added together with sodium citrate into the $HAuCl_4$ solution (i.e., without the premixing of carbon nanotubes with $HAuCl_4$ solution). Our TEM observations indicate that the deposited ratio of the respective gold nanoparticles on the carbon nanotubes is much lower than that with the premixing of carbon nanotubes with $HAuCl_4$ solution, and the diameters of the nanoparticles at the side wall of carbon nanotubes are incoordinate (as shown in Supporting Information).

On the basis of these observations, we have further investigated the amount of the synthesized gold nanoparticles on the MWCNTs by using UV−vis absorption spectroscopy to explore the efficiency of the respective synthesis. As shown in Figure 2, the results of our UV−vis absorption spectroscopic studies of gold nanoparticles synthesized in the absence of MWCNTs and the respective centrifugal suspensions in the presence of MWCNTs indicate that more than 99% of the synthesized gold nanoparticles have been coated on the carbon nanotubes.

Figure 3 shows the Raman spectra of MWCNTs and the MWCNT−Au nanocomposites. As illustrated in Figure 3, the important features such as a tangential G-band and D-band[31] of carbon nanotubes were observed in the MWCNT−Au nanocomposites. Our observations illustrate

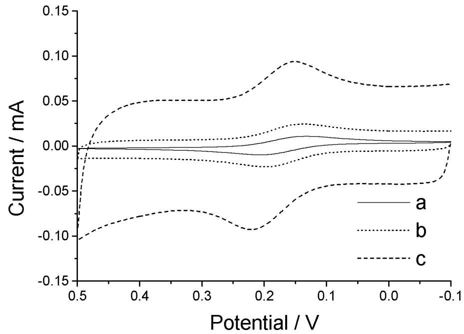

Figure 4. Cyclic voltammogram of 5 mM $K_3(FeCN)_6$ at the bare GCE (a), pure MWCNT modified GCE (b), and MWCNT−Au nanocomposite modifed GCE (c). During the modification of the respective GCE electrodes, a 10 μL droplet of MWCNT−Au or MWCNT solution (1.0 mg/mL) was pipetted onto the GCE surface and dried with nitrogen.

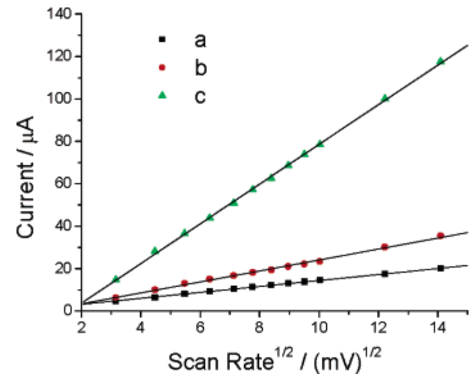

Figure 5. Calibration plots of the $K_3(FeCN)_6$ reduction peak current vs square root of scan rate at different electrodes. (a) Bare GCE, (b) pure MWCNT modified GCE, and (c) MWCNT−Au nanocomposite modifed GCE.

a significantly higher D-band intensity (normalized to the G-band) for the MWCNT−Au nanocomposites than that of the pure MWCNTs. Since the D-bands correspond to disordered structures in carbon nanotubes, the increasing intensity reflects the rise in the defect density in the respective nanotubes upon the deposition of gold nanoparticles onto the side wall of MWCNTs. Besides, the D and G bands have up-shifting, which indicates the forces associated with gold nanoparticles and MWCNTs.[32−35]

Since MWCNT−Au nanocomposites prepared by combining gold nanoparticles and carbon nanotubes are conductive nanomaterial, they could be incorporated into the electrochemical system to facilitate the electron exchange between the electrode and the electrochemical probe due to the enhanced conductivity of the matrices. It is already known that gold nanoparticles and carbon nanotubes have been usually utilized to modify the electrodes to enhance the relevant detection sensitivity as well as catalytic properties. Thus, based on these considerations, electrochemical studies have been carried out to investigate the enhancement effect of MWCNT−Au nanocomposites at glassy carbon electrodes (GCE). Figure 4 shows the enhanced electrochemical response of 5 mM $K_3(FeCN)_6$ at the respective modified glassy carbon electrodes. The results indicate that the electrochemical response of 5 mM $K_3(FeCN)_6$ at the MWCNT−Au nanocomposites modified electrode is much stronger than that of simply carbon naotubes modified GCE as well as the bare GCE. Figure 5 shows the calibrated plots of reduction peak current of $K_3(FeCN)_6$ versus square root of scan rate at different electrodes. The results demonstrated that there is an excellent linear relationship ($R = 0.9997$) between peak current and square root of scan rate for $K_3(FeCN)_6$ at the MWCNT−Au nanocomposites modified GCE. Moreover, it is evident that the MWCNT−Au nanocomposites at the electrode surface could efficiently accelerate the electron transfer at the GCE and enhance the respective electrochemical performance.

In summary, we have reported novel one step synthesized MWCNT−Au nanocomposites to obtain a well-defined nanomaterial in this paper. Our results indicate that the premixing of MWCNTs with $HAuCl_4$ solution could contribute to the $HAuCl_4$ molecule distribution at the carbon nanotube surface and further induce the good deposition of gold nanoparticles on the carbon nanotubes. Besides, the synthesized conductive nanocomposites could efficiently enhance the respective electrochemical response, suggesting that the MWCNT−Au nanocomposites could afford a novel strategy to prepare the promising nanomaterial for the highly sensitive electrochemical sensors.

Acknowledgment. This work is supported by National Natural Science Foundation of China (20675014, 20535010, and 60121101) and the program (050462) for New Century Excellent Talents in University, the Chinese Ministry of Education.

Supporting Information Available: TEM images of gold nanoparticles synthesized in the absence of carbon nanotubes and TEM images of synthesized multiwalled carbon nanotube/gold nanoparticle composites without previous mixing of carbon nanotubes with $HAuCl_4$ solution (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM062791V

(31) Cui, J. B.; Daghlian, C. P.; Gibson, U. J. *J. Phys. Chem. B* **2005**, *109*, 11456−11460.
(32) Raghuveer, M. S.; Agrawal, S.; Bishop, N.; Ramanath, G. *Chem. Mater.* **2006**, *18*, 1390−1393.
(33) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza Filho, A. G.; Saitio, R. *Carbon* **2002**, *40*, 2043−2061.
(34) McNally, T.; Potschke, P.; Halley, P.; Murphy, M.; Martin, D.; Bell, S. E. J.; Brennan, G. P.; Bein, D.; Lemoine, P.; Quinn, J. P. *Polymer* **2005**, *46*, 8222−8232.
(35) Kim, U. J.; Furtado, C. A.; Liu, X.; Chen, G.; Eklund, P. C. *J. Am. Chem. Soc.* **2005**, *127*, 15437−15445.