Homogeneous coating of Au and SnO_2 nanocrystals on carbon nanotubes *via* layer-by-layer assembly: a new ternary hybrid for a room-temperature CO gas sensor†

Ning Du, Hui Zhang, Xiangyang Ma and Deren Yang*

Received (in Cambridge, UK) 23rd July 2008, Accepted 12th September 2008
First published as an Advance Article on the web 20th October 2008
DOI: 10.1039/b812695j

CNT/Au/SnO_2 nanotubes have been synthesized through homogeneous coating of Au and SnO_2 nanocrystals on carbon nanotubes (CNTs) and applied in a room-temperature CO gas sensor.

Carbon nanotubes (CNTs) have spurred numerous research interests, because of their extraordinary physical, chemical and mechanical properties, since their discovery in 1991.[1] Recently, great efforts have been paid to the design of hybrids of CNTs and nanocrystals in order to extend their applications to various fields such as energy conversion,[2] sensors,[3] hydrogen storage[4] and catalysts.[5] For examples, the highly efficient generation of photocurrent *via* the interaction between the excited nanocrystals (CdS, CdSe and CdTe) and conductive CNTs confirm their importance as building blocks for light-harvesting assemblies;[6] noble-metal nanocrystal/CNT hybrids have acted as excellent biosensors for glucose over a wide range of concentration.[7] It is also expected that those hybrids can be applied as effective catalysts for hydrogen, ethanol, or methanol oxidation.[8] Moreover, improved gas sensor performances can be achieved by using metal (metal-oxide) nanocrystal/CNT hybrids owing to their nanostructures and the interaction between gas, CNTs and nanocrystals.[9]

At present, most efforts have been devoted to the synthesis of binary CNT-based hybrids.[2–9] However, from the fundamental viewpoint, the ternary or even more complex CNT-based hybrids may exhibit particular properties compared with the binary CNT-based hybrids because of their complexity, multifunctional composition and the interaction between them.[10] Up to now, few reports have been cited on the synthesis of ternary CNT-based hybrids. More recently, Li *et al*. have employed a step-by-step self-assembly approach to prepare CNT/Au/TiO_2 and CNT/Co_3O_4/TiO_2 nanocomposites using pre-synthesized nanocrystals as primary building units.[10] However, the nanocrystals must be pre-synthesized and treated with expensive and toxic reagents, such as toluene and oleic acid. Overall, it is still a challenge to synthesize ternary or more complex CNT-based hybrids *via in situ* deposition of nanocrystals onto the CNTs. In this Communication, we have attempted to synthesize a ternary CNT-based hybrid of CNT/Au/SnO_2 nanotubes.

The Au–SnO_2 composite has been proved to selectively detect CO,[11] which is different from pure SnO_2 that is sensitive to a broad spectrum of gases.[12] The addition of Au to the SnO_2 can enhance the catalytic reactions between CO and the active area of the device. Moreover, Au is also known to generate an important surface state band on the SnO_2 valence band edge and an important crystallographic distortion localized at the grain surface.[11] However, the most frequently investigated Au-doped SnO_2 bulk films have a limited maximum sensitivity and need high working temperatures in the CO gas sensor.[11] More recently, nanostructured materials, which possess higher surface-to-volume ratio compared with the bulk materials, have been proved to be desirable for chemical sensors.[13] Among the nanostructures, nanotubes are believed to be one of the most promising structures for chemical sensors because of their higher surface-to-volume ratios and, moreover, they do not aggregate as easily as nanoparticles.[13d,e] Therefore, the CNT/Au/SnO_2 nanotubes are believed to possess merits both from the Au/SnO_2 composite and from the CNTs, showing higher sensitivity than the pure Au/SnO_2 composite and better selectivity than the CNT/SnO_2 nanotubes when applied in a CO gas sensor (see Fig. 3b and S5†)

Herein, we report the synthesis of CNT/Au/SnO_2 nanotubes through *in situ* homogeneous coating of Au and SnO_2 nanocrystals on carbon nanotubes *via* layer-by-layer assembly. The layer-by-layer assembly method has been widely used to synthesize hybrid materials.[14] Herein, this method is first used to prepare CNT-based ternary materials. As an example of their application, the CNT/Au/SnO_2 nanotubes have been applied in a room-temperature CO gas sensor, which definitely exhibits better performance than that based on the hybrid Au/SnO_2 nanocrystals and CNT/SnO_2 nanotubes.

As schematically illustrated in Fig. 1a, a layer of polyelectrolyte, *e.g*. sodium poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA), was first coated on to the surface of the pristine CNT by layer-by-layer assembly, thus enabling the CNTs to be positively charged.[15] Secondly, a mixed aqueous solution of $HAuCl_4$ and trisodium citrate dihydrate was added into the polyelectrolyte-modified CNT solution. The negatively charged $AuCl_4^-$ was adsorbed on to the surface of the positively charged CNTs due to electrostatic attraction between the charged species. Thirdly, an excess of $NaBH_4$ solution was gradually dropped into the above-mentioned solution, and consequently, the $AuCl_4^-$ was reduced to Au and then deposited on the surface of the CNTs.

State Key Lab of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, People's Republic of China. E-mail: mseyang@zju.edu.cn; Fax: +86-571-87952322; Tel: +86-571-87951667

† Electronic supplementary information (ESI) available: Experimental details; TEM images of the CNT/Au hybrids; XPS spectra of the CNT/Au/SnO_2 nanotubes; sensitivity response to CO, CH_4 and ethanol of the nanocrystal hybrids. See DOI: 10.1039/b812695j

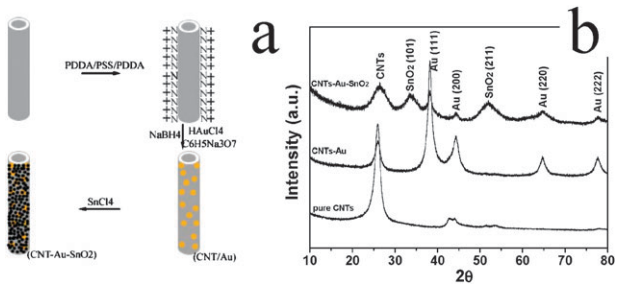

Fig. 1 (a) Schematic diagram for the growth process of CNT/Au/SnO_2 nanotubes. (b) The evolution of X-ray diffraction patterns (XRD) along with the layer-by-layer coating of Au and SnO_2 nanocrystals on CNTs.

For comparison, carbon nanotubes without polyelectrolyte modification or with negatively charged polyelectrolyte were also applied to adsorb Au nanocrystals. There are many Au nanocrystals existing in solution besides those on the surface of the carbon nanotubes and the distribution of Au nanocrystals is irregular (Fig. S1†). Therefore, positively charged carbon nanotubes are prerequisite for the homogenous deposition of Au nanocrystals. Finally, a $SnCl_4$ solution was dropped into the above-mentioned solution, leading to a SnO_2 layer deposited onto the CNT/Au nanotubes.

Fig. 1b shows the evolution of X-ray diffraction patterns (XRD) along with the layer-by-layer assembly of Au and SnO_2 on CNTs. As can be seen, all peaks can be assigned to CNTs before the coating of Au and SnO_2. After the coating of Au on CNTs the peaks ascribed to Au appear, indicative of the formation of a CNT/Au hybrid. For the final product, another two peaks appear, which can be assigned to tetragonal SnO_2 (03 −11 14), indicating that a ternary hybrid of CNT/Au/SnO_2 has formed by the layer-by-layer assembly. Note that the XRD peaks are considerably broadened, indicating that Au and SnO_2 exist in the form of nanocrystals, which will be verified by TEM observation.

In our strategy, controllable deposition of Au nanocrystals on CNTs is prerequisite for the synthesis of hybrid CNT/Au/SnO_2 nanotubes. Fig. S2† shows the TEM images of the CNT/Au hybrids generated by addition of 0.5 and 2 ml $HAuCl_4$ (0.025 M) solution as the reactant, respectively. As can be seen, in both cases, the resulting Au nanocrystals deposited onto the CNTs homogeneously. Moreover, in comparison with the case of adding 2 ml $HAuCl_4$ (0.025 M) solution, the addition of 0.5 ml $HAuCl_4$ (0.025 M) solution led to Au nanocrystals that were smaller and more sparsely deposited onto the CNTs. It should be stated that the use of trisodium citrate dehydrate as the complexing agent is critical for the homogenous deposition of Au nanocrystals on the CNTs. In the control CNT/Au hybrids prepared in absence of trisodium citrate dehydrate, as shown in Fig. S3,† the Au nanocrystals are relatively larger and deposit inhomogeneously onto the CNTs. For the further deposition of SnO_2 nanocrystals onto the CNT/Au hybrid, in the following, we chose the CNT/Au hybrid prepared with the addition of 0.5 ml $HAuCl_4$ (0.025 M) solution as the template. This choice takes the following two aspects into account: (1) the sparser deposition of Au nanocrystals onto the CNTs leaves much more CNT surface to be positively charged, which facilitates the deposition of SnO_2 nanocrystals; (2) the relative ratio of Au to SnO_2 is more desirable in terms of sensing CO gas.

As mentioned above, for the deposition of SnO_2 nanocrystals, a $SnCl_4$ solution was further dropped into the solution containing CNT/Au hybrids and $NaBH_4$. Most of the surface of the carbon nanotubes remained blank and positively charged which can attract negatively charged BH_4^-.[16] Due to the strongly reductive effect of $NaBH_4$, the Sn nanocrystals were first formed and then deposited onto the surface of the CNTs. When $NaBH_4$ was exhausted, the Sn nanocrystals on the surface of the CNTs were quickly oxidized into SnO_2 nanocrystals under the oxygen atmosphere in solution. Fig. 2 shows the morphological, structural and compositional characterizations of CNT/Au/SnO_2 nanotubes. As can be seen from the comparison of Fig. S2a† and 2a, a SnO_2 layer assembled by the SnO_2 nanocrystals (of several nanometers in size) was further coated on the surface of the CNT/Au nanotubes. Fig. 2b shows the TEM image of an individual CNT/Au/SnO_2 nanotube, which further confirms the coating of a SnO_2 layer with a thickness of about 10 nm. The HRTEM image (Fig. 2c) indicates that there are three kinds of lattice fringes with lattice spacings of about 0.34, 0.33 and 0.23 nm, corresponding to the {111} plane of the CNTs, {110} plane of SnO_2 and {111} plane of Au, respectively. This further confirms the deposition of Au and SnO_2 nanocrystals onto the CNTs. The energy dispersive X-ray (EDX) analysis of the CNT/Au/SnO_2 nanotubes is shown in Fig. 2d. The peaks for Sn, O, Au and C, originated from SnO_2, Au and the CNTs, are found in the spectrum, while, the Cu peaks come from the Cu grid used for TEM measurements. From the EDX analysis, it is roughly estimated that the molar ratio of Au to SnO_2 is 2%.

As mentioned above, the CNT/Au/SnO_2 nanotubes possibly exhibit a high performance in sensing CO gas. Fig. 3a shows a room-temperature sensitive (defined as I_g/I_a) response of the CNT/Au/SnO_2 nanotube based gas sensor *versus* time in an example of sensing CO at a concentration of 2500 ppm. As revealed, this gas sensor exhibits a high sensitivity of about 70 and a superior response with a recovery time of less than 20 s; moreover, it displays good reproducibility with minor

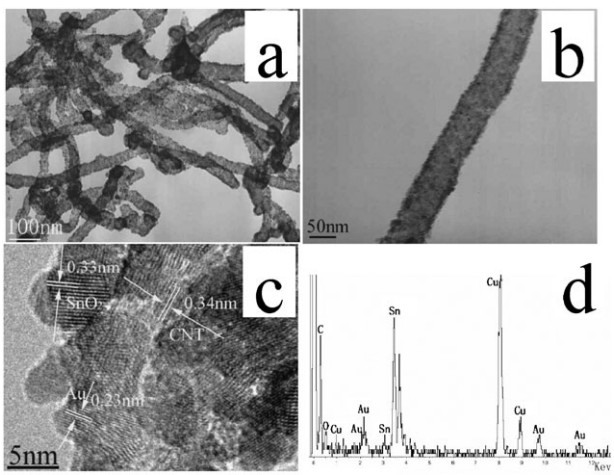

Fig. 2 Morphological and structural characterization of CNT/Au/SnO_2 nanotubes: (a), (b) TEM images; (c) HRTEM image; (d) EDX pattern.

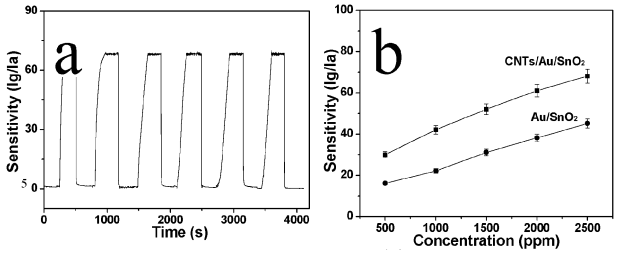

Fig. 3 (a) Sensitivity response of the gas sensor based on CNT/Au/SnO_2 nanotubes *versus* time for a CO concentration of 2500 ppm at room temperature. (b) Sensitivity response *versus* CO concentration (500–2500) ppm at room temperature based on CNT/Au/SnO_2 nanotubes and Au/SnO_2 nanocrystal hybrids.

deviations for six replicates. For illustrating the advantage offered by the CNT template, the gas sensor based on the hybrid Au/SnO_2 nanocrystals is compared with that based on CNT/Au/SnO_2 nanotubes, in terms of the sensitivity towards CO gas. Fig. 3b shows the sensitivity response *versus* CO concentration (500–2500 ppm) at room temperature for the above-mentioned two kinds of gas sensors. As can be seen, the sensitivities of both gas sensors increase with CO concentration. Moreover, the gas sensor based on the CNT/Au/SnO_2 nanotubes exhibits a higher sensitivity to each concentration of CO gas than that based on the hybrid Au/SnO_2 nanocrystals. In order to identify the selectivity, the CNT/Au/SnO_2 nanotubes and CNT/SnO_2 nanotubes were applied in CO, CH_4 and ethanol gas sensors with the same concentration of 500 ppm (Fig. S5†). As can be seen, CNT/Au/SnO_2 nanotubes show much higher sensitivity to CO than CH_4 and ethanol (more than double). On the contrary, the difference in the sensitivity to CO, CH_4 and ethanol based on the CNT/SnO_2 nanotube gas sensor is small and the sensitivity is relatively low. Therefore, the gas sensor based on CNT/Au/SnO_2 nanotubes shows better selectivity to CO than that based on CNT/SnO_2 nanotubes. The better selectivity and enhanced sensitivity are believed to be due to the doping of the Au nanocrystals, higher surface-to-volume ratio and nanotubular structure pertaining to the CNT/Au/SnO_2 nanotubes.

In summary, CNT/Au/SnO_2 nanotubes have been synthesized through homogeneous deposition of Au and SnO_2 nanocrystals on carbon nanotubes *via* layer-by-layer assembly. Such a strategy could be extended to prepare other CNT-based ternary hybrids. Moreover, the as-prepared CNT/Au/SnO_2 nanotubes have been applied in a room-temperature CO gas sensor, which exhibits better performance compared with Au/SnO_2 nanocrystals and CNT/SnO_2 hybrids because of the doping of Au nanocrystals, the higher surface-to-volume ratio and nanotubular structure.

The authors appreciate financial support from the Program for Changjiang Scholars and Innovative Research Team in University, Program 973 (No. 2007CB613403), ZiJin Project, Zhejiang Provincial Natural Science Foundation of China (Y407138) and the Doctoral Program of the Ministry of Education of China (No. 20070335014).

Notes and references

1 S. Iijima, *Nature*, 1991, **345**, 56.
2 H. Lee, S. W. Yoon, E. J. Kim and J. Park, *Nano Lett.*, 2007, **7**, 778.
3 G. G. Wildgoose, C. E. Banks and R. G. Compton, *Small*, 2006, **2**, 182.
4 (*a*) H. S. Kim, H. Lee, K. S. Han, J. H. Kim, M. S. Song, M. S. Park, J. Y. Lee and J. K. Kang, *J. Phys. Chem. B*, 2005, **109**, 8983; (*b*) J. Y. Lee, H. Lee and H. S. Kim, *Mater. Sci. Forum*, 2005, **475**, 2463; (*c*) X. P. Gao, Y. Lan, G. L. Pan, F. Wu, J. Q. Qu, D. Y. Song and P. W. Shen, *Eletrochem. Solid-State Lett.*, 2001, **4**, A173.
5 H. Zhang, J. Qiu, C. Liang, Z. Li, X. Wang, Y. Wang, Z. Feng and C. Li, *Catal. Lett.*, 2005, **101**, 211.
6 (*a*) L. Sheeney-Haj-Ichia, B. Basnar and I. Willner, *Angew. Chem., Int. Ed.*, 2005, **44**, 78; (*b*) I. Robel, B. A. Bunker and P. V. Kamat, *Adv. Mater.*, 2005, **17**, 2458; (*c*) B. J. Landi, S. L. Castro, H. J. Ruf, C. M. Evans, S. G. Bailey and R. P. Raffaelle, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 733; (*d*) D. M. Guldi, G. M. Aminur Rahman, V. Sgobba, V. Kotov, N. A. Bonifazi and M. Prato, *J. Am. Chem. Soc.*, 2006, **128**, 2315.
7 (*a*) S. Hrapovic, Y. Liu, K. B. Male and J. H. T. Luong, *Anal. Chem.*, 2004, **76**, 1083; (*b*) M. Yang, Y. Yang, Y. Liu, G. Shen and R. Yu, *Biosens. Bioelectron.*, 2006, **21**, 1125; (*c*) S. H. Lim, J. Wei, J. Lin, Q. Li and J. K. You, *Biosens. Bioelectron.*, 2005, **20**, 2341.
8 (*a*) J. P. Tessonnier, L. Pesant, G. Ehret, M. J. Ledoux and C. Pham-Huu, *Appl. Catal., A*, 2005, **288**, 203; (*b*) X. R. Ye, Y. Lin and C. M. Wai, *Chem. Commun.*, 2003, **9**, 642; (*c*) X. R. Ye, Y. Lin, C. Wang, M. H. Engelhard, Y. Wang and C. M. Wai, *J. Mater. Chem.*, 2004, **14**, 908.
9 (*a*) J. Kong, G. C. Michael and H. J. Dai, *Adv. Mater.*, 2001, **13**, 1384; (*b*) Y. G. Sun and H. H. Wang, *Adv. Mater.*, 2007, **19**, 2818; (*c*) Y. J. Chen, C. L. Zhu and T. H. Wang, *Nanotechnology*, 2006, **17**, 3012.
10 J. Li, S. B. Tang, L. Lu and H. C. Zeng, *J. Am. Chem. Soc.*, 2007, **129**, 9401.
11 (*a*) N. S. Ramgir, Y. K. Hwang, S. H. Jhung, H. Kim, J. Hwang, I. S. Mulla and J. Chang, *Appl. Surf. Sci.*, 2006, **252**, 4298; (*b*) P. Nelli, G. Faglia, G. Sberveglieri, E. Cereda, G. Gabetta, A. Dieguez, A. Romano-Rodriguez and J. R. Morante, *Thin Solid Films*, 2000, **371**, 249; (*c*) S. R. Wang, Y. Q. Zhao, J. Huang, Y. Wang, S. H. Wu, S. M. Zhang and W. P. Huang, *Solid-State Electon.*, 2006, **50**, 1728; (*d*) G. Behr and W. Fliegel, *Sens. Actuators, B*, 1995, **26**, 33; (*e*) A. Cabot, J. Arbiol, J. R. Morante, U. Weimar, N. Bârsan and W. Göpel, *Sens. Actuators, B*, 2000, **70**, 87.
12 G. Sberveglieri, *Sens. Actuators, B*, 1995, **23**, 103.
13 (*a*) Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, 2001, **291**, 1947; (*b*) P. D. Yang, H. Q. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. R. He and H. J. Choi, *Adv. Funct. Mater.*, 2002, **12**, 323; (*c*) J. F. Liu, X. Wang, Q. Peng and Y. D. Li, *Adv. Mater.*, 2005, **17**, 764; (*d*) Z. Y. Sun, H. Q. Yuan, Z. M. Liu, B. X. Han and X. R. Zhang, *Adv. Mater.*, 2005, **17**, 2993; (*e*) N. Du, H. Zhang, B. D. Chen, X. Y. Ma, Z. H. Liu, J. B. Wu and D. R. Yang, *Adv. Mater.*, 2007, **19**, 1641.
14 (*a*) G. Decher, *Science*, 1997, **277**, 1232; (*b*) J. Park, L. D. Fouche and P. T. Hammond, *Adv. Mater.*, 2005, **17**, 2575; (*c*) Z. Y. Tang, N. A. Kotov, S. Magonov and B. Ozturk, *Nat. Mater.*, 2003, **2**, 413; (*d*) F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 1998, **282**, 1111; (*e*) F. Caruso, R. A. Caruso and H. Mohwald, *Chem. Mater.*, 1999, **11**, 3309; (*f*) M. A. Correa-Duarte, N. Sobal, L. M. Liz-Marzan and M. Giersig, *Adv. Mater.*, 2004, **16**, 2179.
15 S.-S. J. Huang, A. B. Artyunhin, Y. M. Wang, J. -W. Ju, P. Stroeve and A. Noy, *J. Am. Chem. Soc.*, 2005, **127**, 14176.
16 N. Du, H. Zhang, B. D. Chen, X. Y. Ma and D. R. Yang, *Chem. Commun.*, 2008, 3028.

