J Mater Sci (2007) 42:6972–6976
DOI 10.1007/s10853-006-1307-x

Synthesis and electrocatalytic activity of multi-walled carbon nanotubes/Cu–Ag nanocomposites

**Jing Xu · Xian-Wen Wei · Xiao-Jie Song ·
Xiao-Jing Lu · Chang-Chun Ji · Yong-Hong Ni ·
Guang-Chao Zhao**

Received: 7 July 2006 / Accepted: 21 November 2006 / Published online: 26 April 2007

Abstract Cu–Ag bimetallic nanoparticles with atomic ratio of 2.1:1 and diameter in the range of 15–30 nm were decorated on acid-treated multi-walled carbon nanotubes by a chemical reduction method, which was characterized by transmission electron microscope (TEM), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). The Cu–Ag/MWNTs nanocomposites were used to construct a modified electrode toward biosensing of H_2O_2 with a high sensitivity. The catalytic ability of MWNTs/Cu–Ag toward H_2O_2 was much better than that of MWNTs/Cu and MWNTs/Ag, which indicated that there is a cooperation effect between Cu and Ag.

Introduction

Carbon nanotubes (CNTs) discovered by Iijima [1] have attracted considerable interests for their unique structures and exceptional properties, and have many potential applications in various fields of materials research [2, 3]. In recent years, deposition of some functional materials on carbon nanotubes has become one of the important fields, because these composites exhibit better physical and chemical properties and will lead to an even more diverse range of applications [4–6] in catalysis, nanoelectronic devices, polymer or ceramic reinforcement and biosensors [7]. There have been various approaches to deposit metal such as Ni [8, 9], Cu [9], Pd [10–12], Pt [11, 13], Ag [11, 13] and Au [11, 13] nanoparticles on the surface of carbon nanotubes by electrochemical deposition [8], electroless plating [9], chemical vaporation deposition [10], solid-state reaction [11], supercritical carbon dioxide deposition [12] and chemical decoration [13]. It is still a challenge to coat CNTs with bimetallic systems or alloys although Pt–Ru [14], Co–B amorphous alloy [15], Fe–Ni alloys [16] and cluster-derived bimetallic nanoparticles [17] have been deposited onto CNTs.

The subtle electronic properties suggest that CNTs can be used as modified electrodes to catalyze the electrochemical reaction of some biomolecules, such as dopamine, NADH, cytochrome c [18–20], etc. In this paper, Cu–Ag bimetallic nanoparticles were firstly deposited successfully on multi-walled carbon nanotubes (MWNTs) by hydrazine hydrate reduction, and MWNTs/Cu–Ag-modified electrode had been constructed as an unmediated H_2O_2 biosensor, which shows a strong electrocatalytic activity for the reduction of H_2O_2. This may open the way to construct MWNTs composites in a wide range of sensing applications.

Experimental

MWNTs with an average outer diameter between 20 and 50 nm and length up to a dozen micrometers were prepared by the thermal catalytic decomposition of hydrocarbon [21] and the purity is more than 95%, which were further purified with refluxing nitric acids for 24 h before used. In a typical synthesis, 100 mg of acid-treated MWNTs were put in the mixture of 40 cm^3 of 0.5 mol dm^{-3} $Cu(NO_3)_2$ and 20 cm^3 of 0.5 mol dm^{-3} $AgNO_3$ (molar ratio of $Cu^{2+}:Ag^+ = 2:1$) aqueous solution, and stirred for 8 h. Then the suspension was centrifuged for 3 min at

J. Xu · X.-W. Wei (✉) · X.-J. Song · X.-J. Lu ·
C.-C. Ji · Y.-H. Ni · G.-C. Zhao
College of Chemistry and Materials Science, Anhui Key
Laboratory of Functional Molecular Solids, Anhui Normal
University, Wuhu 241000, P.R. China
e-mail: xwwei@mail.ahnu.edu.cn

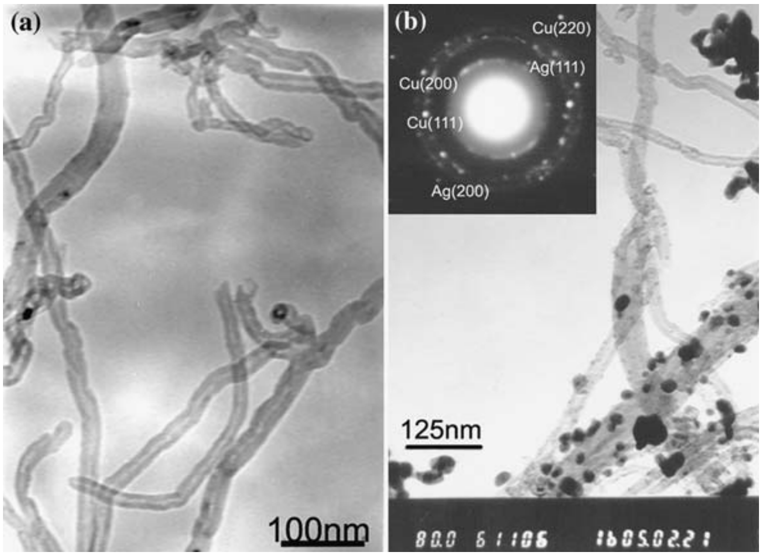

Fig. 1 TEM images of (**a**) acid-treated MWNTs and (**b**) MWNTs coated with Cu–Ag

2000 rpm and the solid was dried at 100 °C until the solvent was evaporated completely. The dried solids obtained were mixed with 10 cm^3 of hydrazine hydrate (50%), and vigorously stirred for 2 h under an argon atmosphere, then filtered. The black solids were washed with distilled water for several times, and vacuum dried at room temperature overnight. MWNTs/Ag and MWNTs/Cu were synthesized, respectively, by the same procedures.

The glassy carbon (GC) electrode ($\Phi = 3$ mm) was firstly polished with a $1700^{\#}$ diamond paper and washed successively with double distilled water and acetone in an ultrasonic bath. About 25 μL of MWNTs/Cu–Ag suspension (0.25 mg/mL) in acetone was cast on the surface of GC electrode and dried in air to form an MWNTs/Cu–Ag modified electrode. Similarly the MWNTs/Cu and MWNTs/Ag modified electrodes were obtained.

TEM micrographs were taken using a Hitachi Model H-800 transmission electron microscope, with an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) was performed using JEOL 2010 microscope operated at optimum defocus with accelerating voltages of 200 kV. X-ray powder diffraction (XRD) was carried out on a Shimadzu (Japan) XRD-6000 X-ray diffractometer with Cu Kα radiation (λ=0.15406 nm, U=40 kV, I=30 mA) at a scanning rate of 0.02° s^{-1} in the 2θ range from 10° to 80°. Cyclic voltammograms were recorded on CHI 660A electrochemistry workstation.

Results and discussion

Characterization

In order to obtain well-decorated Cu–Ag nanoparticles on MWNTs, acid-treated MWNTs were used. It is known that refluxing carbon nanotubes with nitric acid not only opens the closed tips of the tubes, but also creates acid sites on the surface [22]. The TEM image shows that the MWNTs are almost open and shorten after being treated with nitric acids (Fig. 1a). Figure 1b shows the TEM image of MWNTs/Cu–Ag nanocomposites, which indicated that the MWNTs have been coated with Cu–Ag particles, and the larger diameter nanotube has, the more particles coated on it. The size of the Cu–Ag particles is in the range of 15–30 nm, and some aggregations were obviously seen. The selected-area electron diffraction (SAED) patterns of the Cu and Ag on MWNTs are shown in Fig. 1b (inset), which can be indexed to the reflection of cubic Ag and cubic Cu structure.

The well-resolved lattice fringes can be observed with HRTEM image shown as in Fig. 2, the interplanar spacing of Cu is about 0.18 nm, which corresponds to the (200) plane of the cubic Cu. And the interplanar spacing of Ag is about 0.23 nm, which corresponds to the (111) plane of the cubic Ag. These indicated that the Cu–Ag nanoparticles formed are bimetallic systems.

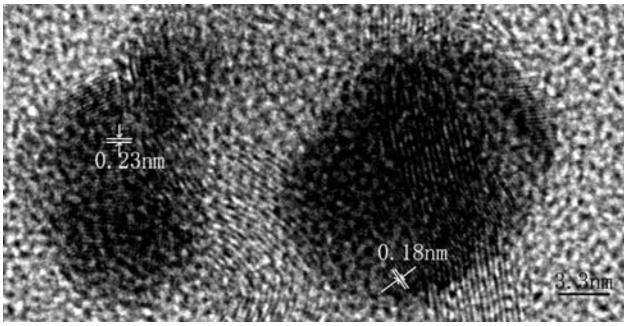

Fig. 2 HRTEM image of MWNTs coated with Cu and Ag

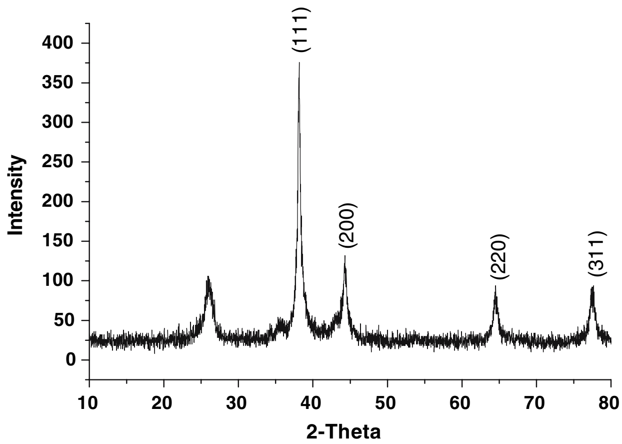

Fig. 3 XRD pattern of MWNTs/Cu–Ag composites

The XRD pattern of the products obtained is shown in Fig. 3, which also indicates that crystalline Cu–Ag nanoparticles were decorated on the MWNTs. The peak at 2θ values of 25.96° is the characteristic peak of MWNTs. The diffraction peaks at 2θ values of 38.08°, 44.27°, 66.48° and 77.51°, correspond to (111), (200), (220), (311) planes of the cubic structure of Ag (JCPDS 04-0783), respectively. The peak at 43.32° that is the strongest peak of Cu is overlapped with the peak of Ag, can be assigned to (111) plane of the cubic structure of Cu (JCPDS 85-1326). The mean size of Cu–Ag nanocrystal particles obtained from the half-width of the (111) diffraction peak using the Scherrer equation is *ca.* 18 nm, which accords with the result of TEM image for the particle sizes.

In Fig. 4, the XPS spectrum showed clearly the presence of Cu and Ag on the surface of MWNTs. The Auger lines of Cu and Ag were also obtained. XPS indicates a predominance of Cu (30.5 at%) and Ag (14.3 at%), means the ratio of Cu to Ag is 2.1:1. It was noted that the composition of the Cu–Ag nanoparticles attached on the surface of carbon nanotubes formed from their mixed nitrate solution was close to but different to the original composition of nitrates.

Electrochemical activity

Because carbon nanotubes have ability of promoting electron transport and have stable chemical properties, they can connect with another electrode surface as modifier [23]. It has been reported that myoglobin on the MWNTs (MWNTs/Myb) modified electrode can act as an effective catalyst to catalyze the reduction of H_2O_2 [24]. Herein, the MWNTs/Cu–Ag nanocomposites modified electrode was applied to catalyze the reduction of H_2O_2.

The MWNTs/Cu–Ag-modified GC electrode was put into 5 mmol dm^{-3} $[Fe(CN)_6]^{3-/4-}$ to perform the EIS experiments. Figure 5 shows the complex plane diagram (–Z″ vs. Z′) of EIS obtained at the MWNTs-modified and MWNTs/Cu–Ag-modified GC electrode. In a Nyquist plot, the semicircle part corresponds to the electron-transfer limited process. Compared with the MWNTs-modified GC electrode (Fig. 5a), the curve b is nearly linear. It shows that the electron-transfer resistance of the ferri/ferro cyanide redox couple decreased at a MWNTs/Cu–Ag-modified GC electrode and the conductivity of this composite is increased. It also proves the Cu–Ag nanoparticles are decorated on the MWNTs.

Figures 6–8 displayed cyclic voltammograms of MWNTs/Cu-modified, MWNTs/Ag-modified and MWNTs/Cu–Ag-modified GC electrodes, respectively, in 0.05 mol dm^{-3} phosphate buffer solution containing (a) 0.5 mmol dm^{-3}, (b) 1.0 mmol dm^{-3}, (c) 2.0 mmol dm^{-3}, (d) 5.0 mmol dm^{-3} of H_2O_2. An obvious reduction peak of H_2O_2 at ca. –0.25 V was obtained at all three modified electrodes. From the distinctive peak current difference among Figs. 6, 7 and 8, it could be concluded that the catalytic ability of MWNTs/Cu–Ag toward H_2O_2 was much better than that of MWNTs/Cu and MWNTs/Ag. It is

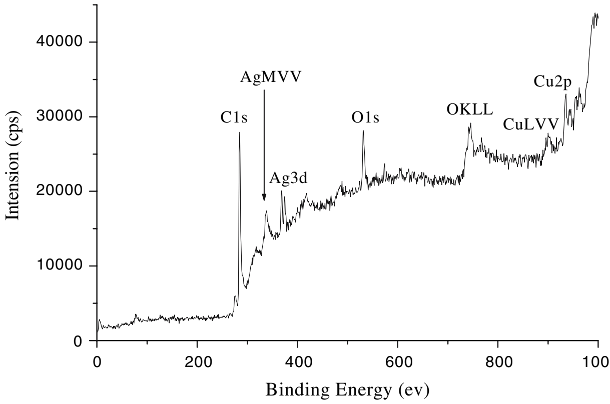

Fig. 4 XPS spectrum of MWNTs/Cu–Ag composites

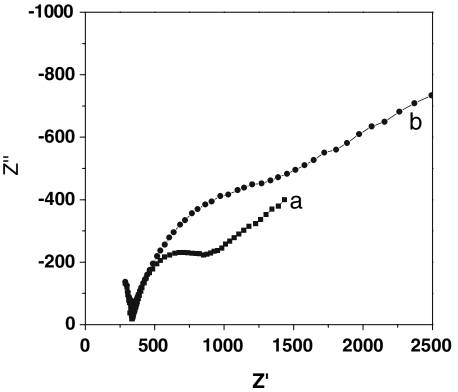

Fig. 5 Nyquist diagram (–Z′ vs. Z′) for the EIS measurements in the presence of 5 mmol dm^{-3} $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ at (a) MWNTs-modified and (b) MWNTs/Cu–Ag-modified glassy carbon electrodes

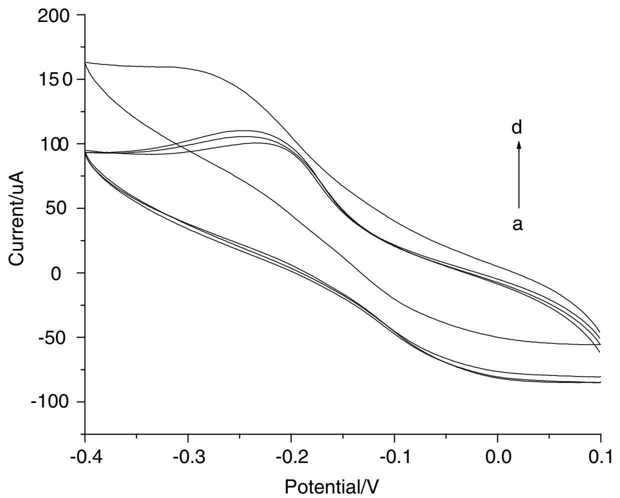

Fig. 6 Cyclic voltammograms of MWNTs/Cu-modified glassy carbon electrode in 0.05 mol dm^{-3} phosphate buffer solution (pH = 7.0) containing 0.5 mmol dm^{-3} H_2O_2 (a), 1.0 mmol dm^{-3} H_2O_2 (b), 2.0 mmol dm^{-3} H_2O_2 (c), 5.0 mmol dm^{-3} H_2O_2 (d) at scan rate of 50 mV/s

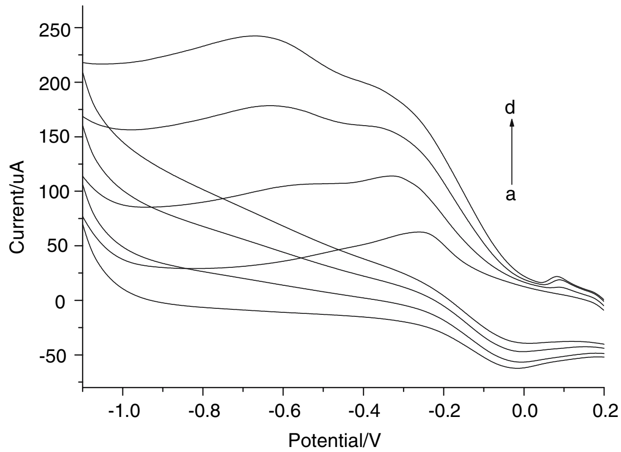

Fig. 7 Cyclic voltammograms of MWNTs/Ag-modified glassy carbon electrode in 0.05 mol dm^{-3} phosphate buffer solution (pH = 7.0) containing 0.5 mmol dm^{-3} H_2O_2 (a), 1.0 mmol dm^{-3} H_2O_2 (b), 2.0 mmol dm^{-3} H_2O_2 (c), 5.0 mmol dm^{-3} H_2O_2 (d) at scan rate of 50 mV/s

proposed that there is conspiracy between Cu and Ag. It is shown that the absolute value of the reduction current of H_2O_2 was increased significantly on MWNTs/Cu–Ag when the concentration of H_2O_2 was increased, as shown in Fig. 8.

The mechanism of H_2O_2 reduction can be assumed that the electrons remove from Cu–Ag to H_2O_2. In order to examine the response character of MWNTs/Cu–Ag-modified electrode to H_2O_2, we have undertaken the detection of H_2O_2 in phosphate buffer solution with a constant potential voltammetry. Figure 9 displays typical constant potential

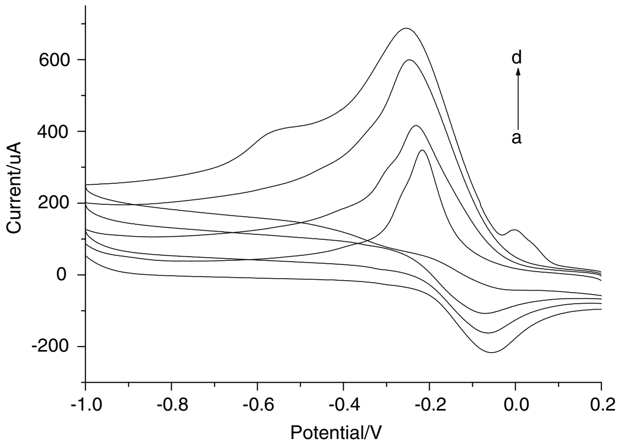

Fig. 8 Cyclic voltammograms of MWNTs/Cu–Ag-modified glassy carbon electrode in 0.05 mol dm^{-3} phosphate buffer solution (pH = 7.0) containing 0.5 mmol dm^{-3} H_2O_2 (a), 1.0 mmol dm^{-3} H_2O_2 (b), 2.0 mmol dm^{-3} H_2O_2 (c), 5.0 mmol dm^{-3} H_2O_2 (d) at scan rate of 50 mV/s

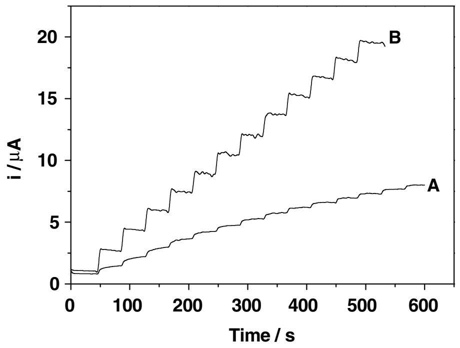

Fig. 9 Amperometric responses for H_2O_2 concentration in steps at (A) MWNTs-modified and (B) MWNTs/Cu–Ag-modified glassy carbon electrodes in 0.05 mol dm^{-3} phosphate buffer solution; each addition was 2.5 μmol dm^{-3} H_2O_2. Alternating current was measured at constant potential of –0.25 V

amperometric response at –0.25 V of the (A) MWNTs-modified and (B) MWNTs/Cu–Ag-modified GC electrodes to successive addition of H_2O_2. When an aliquot of H_2O_2 is added into the buffer solution, the reductive current rises steeply to reach a stable value. The cathodic peak current increases linearly with the concentration of H_2O_2. Figure 9 indicated that the MWNTs/Cu–Ag-modified electrode has higher electrocatalytic sensitivity toward H_2O_2 than MWNTs-modified electrode has. These results demonstrated that the MWNTs/Cu–Ag-modified electrode could be used as a sensor for the detection of H_2O_2.

The further experimental results showed that the catalytic currents increased linearly with the H_2O_2 concentration in the range of 2–420 μM with a correlation coefficient of 0.9968. The relative standard deviation is 4.0% for seven successive determinations at 360 μM H_2O_2 and the limit of detection is 2.82 μM at a signal-to-noise ration of three.

Conclusions

In summary, MWNTs/$Cu_{2.1}Ag$ bimetallic nanocomposite was fabricated firstly by a chemical reduction route; it exhibited an electrocatalytic activity for the reduction of H_2O_2 and can be used as an amplified biosensor toward H_2O_2 with a detection limit of 2.82 μM. This may open the way to construct MWNTs composites in a wide range of sensor applications.

Acknowledgements We thank Science and Technological Fund of Anhui Province for Outstanding Youth (No. 04046065), the Education Department (Nos. 2001KJ115ZD, 2006KJ006TD) of Anhui Province, the State Education Ministry (EYTP, SRF for ROCS) and National Natural Science Foundation (Nos. 20271002, 20490217, 20671002) of P.R. China for financial support.

References

1. Iijima S (1991) Nature 354:56
2. Dai HJ, Hafner JH, Rinzler AG, Colbert DT, Smalley RE (1996) Nature 384:147
3. Deheer WA, Chatelain A, Ugarte D (1996) Science 270:1179
4. Ebbesen TW, Lezec HJ, Hiura H, Bennett JW, Ghaemi HF, Thio T (1996) Nature 382:54
5. Treacy MMJ, Ebbesen TW, Gibson JM (1996) Nature 381:678
6. Chen GZ, Shaffer MSP, Coleby D, Dixon G, Zhou W, Fray DJ, Windle AH (2000) Adv Mater 12:522
7. Wang J, Musameh M, Lin Y (2003) J Am Chem Soc 125:2408
8. Xu Q, Zhang L, Zhu J (2003) J Phys Chem B 107:8294
9. Ang LM, Hor TSA, Xu GQ, Tung CH, Zhao SP, Wang JLS (2000) Carbon 38:363
10. Kong J, Chapline MG, Dai H (2001) Adv Mater 13:1384
11. Xue B, Chen P, Hong Q, Lin JY, Tan KL (2001) J Mater Chem 11:2378
12. Ye XR, Lin YH, Wai CM (2003) Chem Commun 642
13. Satishkumar BC, Vogl EM, Govindaraj A, Rao CNR (1996) Appl Phys 29:3173
14. Rajesh B, Thampi KR, Bonard JM, Viswanathan B (2000) J Mater Chem 10:1757
15. Liu ZJ, Xu ZD, Yuan ZY, Chen WX, Zhou WZ, Peng LM (2003) Mater Lett 57:1339
16. Wu HQ, Cao YJ, Yuan PS, Xu HY, Wei XW (2005) Chem Phys Lett 406:148
17. Hermans S, Sloan J, Shephard DS, Johnson BFG, Green MLH (2002) Chem Commun 276
18. Musameh M, Wang J, Merkoci A, Lin Y (2002) Electrochem Commun 4:743
19. Wang G, Xu JJ, Chen HY (2002) Electrochem Commun 4:506
20. Wang J, Li M, Shi ZJ, Li NQ, Gu ZN (2002) Anal Chem 74:1993
21. Liu BC, Tang SH, Liang Q, Gao LZ, Zhang BL, Qu MZ, Yu ZL (2001) Chin J Chem 19:983
22. Tsang SC, Harris PJF, Green MLH (1993) Nature 362:520
23. Ajayan PM (1999) Chem Rev 99:1787
24. Zhao GC, Zhang L, Wei XW (2004) Anal Biochem 329:160