

Construction of a carbon nanotube/diamond hybrid functionalized electrode surface

Xili Tong · Meichuan Liu · Guohua Zhao

Received: 29 December 2008 / Revised: 19 March 2009 / Accepted: 20 March 2009 / Published online: 5 May 2009
© Springer-Verlag 2009

Abstract Multiwalled carbon nanotubes were attached to the surface of boron-doped diamond by electropolymerization using a bridge of polyaniline. A carbon nanotube/diamond hybrid functionalized surface was obtained and testified by field emission scanning electron microscopy. The electrochemical impedance spectroscopy and cyclic voltammetry measurements revealed that this carbon hybrid surface possessed low electron-transfer resistance, large double-capacitance value, and high electrocatalytic ability. This indicated that this functionalized surface had a variety of potential sustainable technology applications such as in supercapacitors, biomolecule-sensing devices.

Keywords Carbon nanotube · Boron-doped diamond · Polyaniline · Electropolymerization

Introduction

Carbon nanotubes (CNTs) have attracted much attention for wide electrochemical applications such as energy storage system, electrocatalysis, and biosensing device [1] because of their extraordinary electrical and mechanical properties [2]. To achieve the aforesaid applications of CNTs, the electrode substrate for loading CNTs must have good chemical stability and electronic conduction. As compared to commonly used glassy carbon, graphite, and other materials, boron-doped diamond [3] thin film has its unique nature, such as broad potential window, high resistance to

deactivation by impurities, long-term response stability, and low and stable voltammetric background current. Therefore, boron-doped diamond would surely be an excellent substrate for CNTs. Polyaniline (PANI) [4] has also attracted considerable attention due to its high conductivity, stability in atmospheric environments, and ease of preparation. Tremendous efforts have been made over the past decade to obtain CNT/PANI hybrid [5] for its excellent synergistic merit. We propose to deposit pristine multiwalled carbon nanotubes (MWCNTs) on the surface of boron-doped diamond substrate using a bridge of PANI by electropolymerization aimed to obtain an excellent Sp^3 - Sp^3 carbon hybrid functionalized surface. The traditional method for the load of CNT onto the substrate is mechanical coating with CNT suspension, which results in inhomogeneity of the electrode surface. However, in our reaction system, CNTs can be loaded onto the substrate with uniform morphology and smooth surface by electropolymerization due to the formation of CNT-aniline complex [6] which can be dissolved in H_2SO_4 solution.

Experimental

CNTs were fabricated by catalytic pyrolysis of the propylene-hydrogen ($C_3H_8/H_2=2:1$) mixture at $750^\circ C$ in a ceramic tube furnace using Ni particles as catalysts. Dilute nitric acid treatment was employed to remove the catalyst particles before use [7]. Boron-doped diamond film was deposited on a p-Si(100) substrate (area 15×15 mm) that had been pretreated by polishing with hydrogen for 20 min at low pressure using a microwave assisted chemical vapor deposition system [8]. The boron-doped diamond surface area was limited to 0.09 cm² using O-ring. Aniline was purified by distillation under common pressure and stored

X. Tong · M. Liu · G. Zhao (✉)
Department of Chemistry, Tongji University,
Siping Road 1239,
Shanghai 200092, China
e-mail: g.zhao@mail.tongji.edu.cn

in the sealed state at 4°C. MWCNTs were added to 10 mL of aniline with content of 0.2 wt.%(weight percent with respect to aniline monomer). The mixture was heated at reflux for 3 h in the dark [6]. Electrochemical experiments were performed with a CHI-660C electrochemical workstation with a three-electrode system, consisting of a boron-doped diamond, a bright platinum wire, and saturated calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively. The temperature was maintained at room temperature.

Results and discussion

Figure 1 shows electropolymerization images of MWCNTs/PANI (A) and PANI (B) in the range between -0.2 and

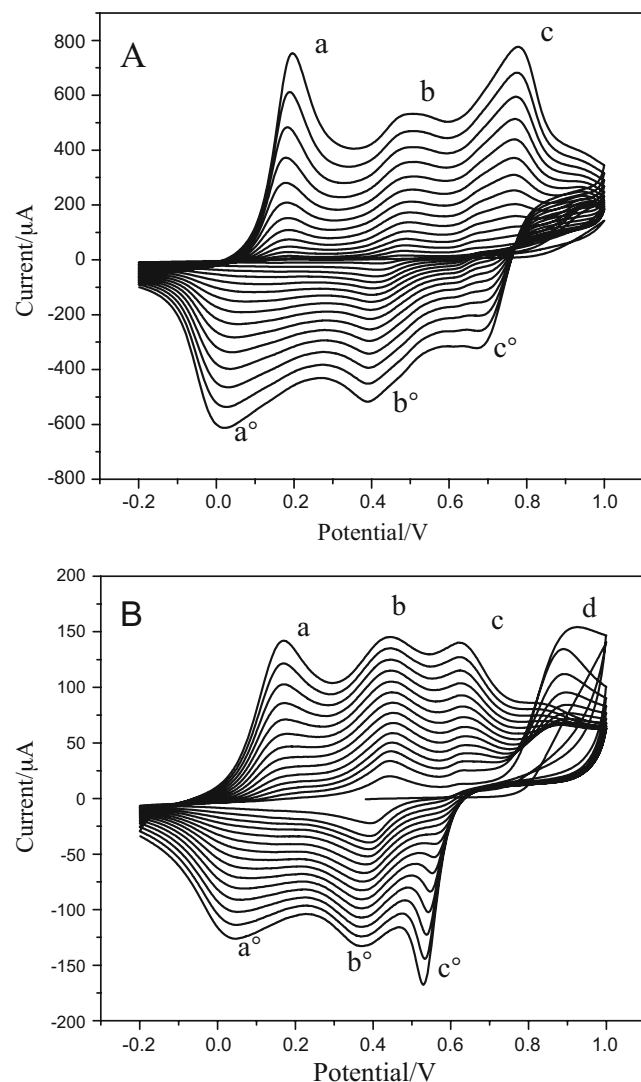


Fig. 1 Cyclic voltammograms of **a** 1 mL MWCNT/ PANI and **b** 1 mL PANI in 100 mL 0.1 M H₂SO₄ solution (scan rate 50 mV·s⁻¹, cyclic number 15)

1.0 V (vs. SCE). In both cases, the formation of PANI was evident from three identifiable anodic peaks at around 200, 460, and 700 mV with cathodic counter parts at around 35, 380, and 630 mV, respectively. It was similar to that

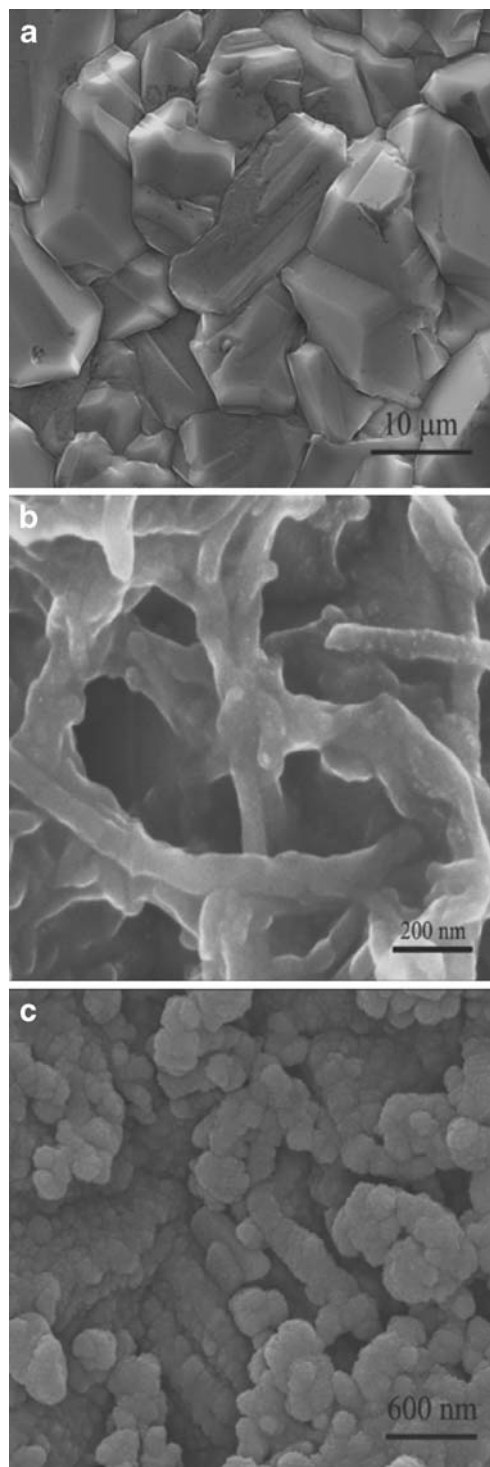


Fig. 2 Surface morphologies of the boron-doped diamond electrode after cyclic voltammogram in 1 mL WCNT/PANI + 100 mL 0.1 M H₂SO₄ solution and cyclic number is **a** 0, **b** 5, and **c** 15, respectively

reported in the literature [9]. In Fig. 1a, the peak currents of redox couples of a/a°, b/b° and c/c° were much larger, and the peak shapes were more distinct. This phenomenon was related to MWCNTs which had large surface and excellent electron transfer ability. The d peak in Fig. 1b was attributed to the nucleation of aniline on boron-doped diamond electrode, which was similar to the previous report [10]. However, there was no obvious d peak in Fig. 1a, which indicated that interaction between MWCNTs and aniline had a visible effect on the nucleation of aniline, further suggesting the successful load of MWCNTs to boron-doped diamond surface owing to the formation of MWCNT and aniline donor-accepted complex [6].

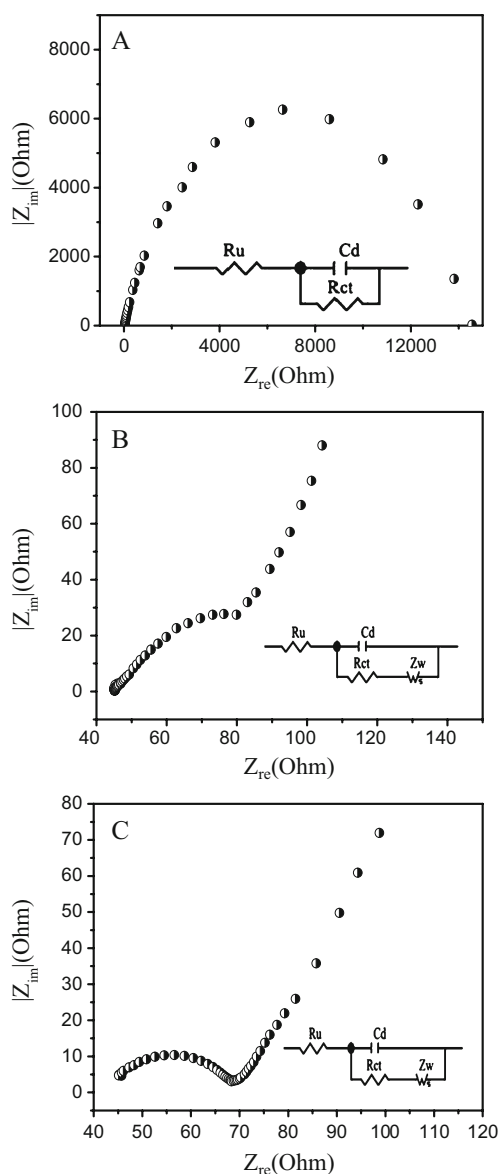


Fig. 3 Electrochemical impedance spectroscopy of **a** unmodified boron-doped diamond, **b** PANI-modified boron-doped diamond, and **c** WCNT/PANI-modified boron-doped diamond

Figure 2 shows the field emission scanning electron microscope (FESEM) images of carbon hybrid surface. In Fig. 2a, the FESEM image revealed that the diamond surface was composed of well-faceted randomly oriented microcrystallites of approximately 5–15 μm. After electropolymerization for 5 cycles, MWCNT/PANI hybrids were found to be deposited at the electrode (Fig. 2b). The MWCNT/PANI hybrid fibers entangled to form a relatively uniform web and made hybrid film more highly porous, and the surface of diamond could still be approximately distinguished. The fiber shape became illegible when 15 cycles were performed (Fig. 2c). It is important to note that the reunion of hybrids with a nanoscale component will take place spontaneously during the process of electropolymerization, which could be helpful to explain the changes between the morphology in Fig. 2b, c.

Figure 3 shows the electrochemical impedance spectroscopy of different electrode surfaces in 0.1 M H₂SO₄ solution. Figure 3a revealed that electrochemical testing for unmodified boron-doped diamond was under electrochemical control and the resistance for electron transfer was 14.5 KΩ. The effect of surface modification, which reduced the electron-transfer resistance on the electrode, was clearly manifested as a much smaller diameter of the semicircle in the Nyquist plot (in Fig. 3b, c). Insert plots in Fig. 3 were equivalent circuits for impedance data evaluation of Fig. 3a–c, where the respective components correspond to (1) Ru, the ohmic resistance of the electrolyte solution; (2) a combination of resistor Rct, Warburg impedance Zw, and capacitor Cd, reflecting the properties of the carbon hybrid surface. Rct and Cd in Fig. 4b, c were 50 Ω and 2.5 μF and 20 Ω and 6.25 μF, respectively. The decrease in Rct and the increase in Cd indicated that there was an increased density of ionic charges at the interface after MWCNTs dissolved into PANI matrix. The surface resistance value of unmodified boron-doped diamond, PANI-modified boron-doped diamond, PANI-modified and MWCNT/PANI-modified

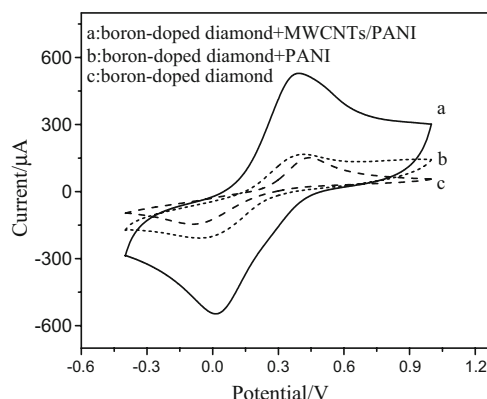


Fig. 4 Cyclic voltammograms of different electrode surfaces in 1 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ +0.1 M KCl solution (scan rate 100 mV·s⁻¹)

boron-doped diamond were 67.5, 52.2, and 30.5 K Ω /cm in 60 Hz, respectively (Precision Impedance Analyzer 4294A). Changing trend of surface resistance of the three electrodes was accordant with that of their electron-transfer impedance. More attractively, MWCNT/PANI hybrids could be easily stripped at 3.6 V for 20 s with constant-potential electrolysis, while pure PANI would completely decompose under this condition.

Figure 4 shows cyclic voltammetry response of the different unmodified electrodes in the solution containing $\text{Fe}(\text{CN})_6^{3-/4-}$ (the other experimental condition was uniform). Increase in both anodic and cathodic peak current response, decrease in peak-to-peak separation were found when boron-doped diamond was modified with pure PANI or MWCNT/PANI hybrid by electropolymerization for five circles due to the large surface and fine electroactive character of PANI or MWCNT/PANI hybrid. For MWCNT/PANI-modified hybrid electrode, both anodic and cathodic peak currents were the highest, and peak-to-peak separation was the smallest, which could be ascribed to excellent synergistic effect of MWCNTs and PANI.

Conclusion

It has been demonstrated that using a simple electropolymerization to construct a highly electroactive Sp^2 – Sp^3 carbon hybrid functionalized electrode surface. Compared to

mechanical coating, electropolymerization is a feasible and controllable method to construct uniform and stable hybrid electrode surface. And this surface is helpful to a variety of potential sustainable technology application fields such as in supercapacitor and biomolecule sensing devices.

Acknowledgements This work was supported by National Nature Science Foundation People's Republic of China (No. 20877058), 863 Program (No. 2008AA06Z329) from the Ministry of Science, Nanometer Science Foundation of Shanghai (No. 0852nm01200), and Shanghai Educational Development Foundation (No. 2007CG24)

References

1. Tasis D, Tagmatarchis N, Bianco A, Prato M (2006) *Chem Rev* 106:1105
2. Zhang M, Fang S, Zakhidov AA, Lee SB, Aliev AE, Williams CD, Atkinson KR, Baughman RH (2005) *Science* 309:1215
3. Honda K, Noda T, Yoshimura M, Nakagawa K, Fujishima A (2004) *J Phys Chem B* 108:16117
4. Huang J, Moore JA, Henry Acquaye J, Kaner RB (2005) *Macromolecules* 38:317
5. Baibarac M, Baltog I, Godon C, Lefrant S, Chauvet O (2004) *Carbon* 42:3143
6. Sun Y, Wilson SR, Schuster DI (2001) *J Am Chem Soc* 123:5348
7. Lia C, Wang D, Liang T, Wang X, Jia L (2004) *Mater Lett* 58:3774
8. Einaga Y, Sato R, Olivia H, Shin D, Ivandini TA, Fujishima A (2004) *Electrochim Acta* 49:3989
9. Orata D, Buttry DA (1987) *J Am Chem Soc* 109:3574
10. Ou Yang LY, Chang C, Liu S, Wu C, Yau SL (2007) *J Am Chem Soc* 129:8076