Microchim Acta 155, 379–386 (2006)
DOI 10.1007/s00604-006-0570-5

Microchimica Acta
Printed in Austria

Original Paper

Assemble-Electrodeposited Ultrathin Conducting Poly(Azure A) at a Carbon Nanotube-Modified Glassy Carbon Electrode, and its Electrocatalytic Properties to the Reduction of Nitrite

Jinxiang Zeng[1], **Wanzhi Wei**[1,*], **Xiurong Zhai**[1], **Pinghua Yang**[1,2], **Jian Yin**[1], **Ling Wu**[1], **Xiaoyin Liu**[1], **Kai Liu**[1], and **Shuguo Gong**[1]

[1] State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Hunan, Changsha 410082, P.R. China
[2] College of Chemistry and Chemical Engineering, Jiujiang University, Jiujiang 332005, P.R. China

Received November 27, 2005; accepted February 22, 2006; published online May 17, 2006

Abstract. A new type of ultrathin conducting polymer/carbon nanotubes (UCP/CNTs) nanomaterials with high catalytic surface area was proposed in this work. The electrode covered with an ultrathin layer of poly(azure A)/carbon nanotubes nanomaterials was fabricated by two steps: firstly, the single-wall carbon nanotubes (SCNTs) modified glassy carbon (GC) electrode was immersed in an azure A solution to assemble a thin azure A monomer film. Secondly, the assembled AA was electropolymerized in a phosphate buffer solution by cyclic voltammetry (CV). The electrocatalytic activity of the obtained ultrathin conducting poly(azure A)/carbon nanotubes (UCPAA/CNTs) nanomaterials was tested using sodium nitrite. The results showed thus prepared electrode exhibited excellent electrocatalytic behavior to the reduction of nitrite and facilitates the detection of nitrite at an applied reduction peak potential of 0.1 V. A linear range from 3.0 μM to 4.5 mM for the detection of sodium nitrite has been observed with fast response (within 3 s) and a detection limit of 1.0 μM based on a signal-to-noise ratio of 3.

Key words: Assemble-electrodeposit; carbon nanotubes; azure A; nitrite; UCPAA/CNTs; nanomaterials.

Since their discovery in 1991 [1], carbon nanotubes (CNTs), as one of the most interesting carbon materials, have attracted enormous interest over the past years due to their exceptional electrical, chemical, and mechanical properties which make them an attractive candidate for diverse applications such as in nanoelectronics, biosensors, and so on [2–10]. Recently, the fabrication of CNTs/conducting polymer (CNTs/CP) composites has gained great interest as the CNTs can improve the electrical and mechanical properties of polymers [11, 12] and it has been demonstrated that the obtained CNTs/CP possess properties of the individual components with a synergistic effect [13–18]. Different CP have been used, such as polypyrrole (PPy) [13, 14], poly(phenylene vinylene) (PPV) [15, 16], and polythiophene (PTh) and its derivatives [17,18]. Polyaniline (PAn)/CNTs composites were also prepared [19]. Among the CP nanocomposite materials, high surface-to-volume ratio CP such as nanowires are extremely attractive for a wide range of nanoelectronic and sensing applications owing to their novel electron transport properties [20–22]. At present, the combination of CP and CNTs composite with high surface-to-volume ratio are mainly focused on polypyrrole (PPy) [23],

---

* Author for correspondence. E-mail: weiwz2003@126.com

polyaniline (PAn) [24, 25] and polythiophene (PTh) [26]. For examples, PPy/CNTs were prepared by template-directed electropolymerization of PPy in the presence of a CNTs dopant [23], PAn/CNTs were prepared by self-assembly [24] or in situ polymerization [25], PTh/CNTs were fabricated through van der Waals and electrostatic interactions between polythiophene and CNTs [26]. However, according to our knowledge, there are no reports on the fabrication of poly(phenothiazine)/CNTs nanocomposite with high surface-to-volume ratio although the phenothiazine and poly(phenothiazine) compounds are widely applied for construction of electrochemical sensors and biosensors.

On the other hand, determination of nitrite is of great significance due to its important role in environmental processes and its toxicity and suspected carcinogenicity in human body. Among the various nitrite sensors, electrochemical ones have attracted much attention because of quick response, high sensitivity, as well as abilities to be miniaturized. At present, one way for electrocatalytic reduction of nitrite is to use carbon nanotubes modified electrode [27] and carbon nanotube powder microelectrode [28]. The other way is to use conducting polymers [29, 30]. However, when carbon nanotubes and polymers used alone, the sensitivity is relatively low [27, 28, 30]. Cupric ions added in the solution has the ability to improve the sensitivity of carbon nanotubes modified electrode [27], but compared with solution-phase materials, immobilization of materials together with carbon nanotubes on the electrode surface to improve the detection sensitivity may be preferable for multiple and practical use.

In this work, ultrathin conducting poly(azure A)/carbon nanotubes (UCPAA/CNTs) nanomaterials with high catalytic surface area was prepared by assembling-electrodepositing azure A onto the surface of SCNTs modified glassy carbon electrode. As the UCPAA/CNTs nanomaterials was in the form of small bundles and single nanotube and distributed very homogeneously on the surface of GC electrode exhibiting a special three-dimensional structure with huge catalytic surface area, it exhibits excellent electrocatalytic activity toward the reduction of nitrite. The new method for immoblization of ultrathin conducting polymer together with CNTs to improve the detection sensitivity is expected to be practically used for the construction of electrochemical sensors.

Experimentals

Chemicals and Instrumentation

Single-walled carbon nanotubes (SCNTs) were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China) and purified by refluxing the as-received SCNTs in 2.6 M HNO_3 for 10 h. Azure A (dye content >70%) was obtained from Amresco (USA). An azure A (AA) solution of 5.0 mM was prepared by dissolving 146 mg AA in 100 mL phosphate buffer ($pH = 6.5$). Other chemicals were analytical grade. Double-distilled water was used throughout.

Cyclic voltammetric and amperometric measurements were carried out in a conventional three-electrode cell controlled by CHI 660A Electrochemical Work Station (Chenhua Instrument Co. of Shanghai, China). A glassy carbon electrode (diameter 3 mm) was used as working electrode; a platinum foil was applied as the counter electrode and a saturated calomel electrode (SCE) served as reference electrode. All potential values given below refer to SCE. Amperometric measurements were carried out under stirred conditions and the response current was marked with the change value between the steady state current and the background current. All experiments were performed at room temperature. UV-vis spectroscopic measurements were performed with a LabTech UV2000/2100 UV-vis spectrophotometer (LabTech Inc., USA). Scanning electron microscopy (SEM) images were obtained by using a JEOL JSM-6700F microscope (Japan).

Preparation of AA/CNTs Nanomaterials

The AA/CNTs nanomaterials were prepared by sonicating 25 mg SCNTs in 100 mL 5 mM AA aqueous solution for 2 h at room temperature. The resulting suspension was filtered with a Millipore filter (0.45 μm, Millipore). The obtained sample was first thoroughly rinsed with distilled water to remove the nonadsorbed AA and then dried at 75 °C for 5 h to obtain AA/CNTs nanomaterials. The nanomaterials were dispersed in distilled water for UV-vis spectroscopic measurement.

Methods for Preparation of the Modified Electrodes

The GC electrodes were carefully polished with emery paper and aqueous slurries of fine alumina powders (0.3 and 0.05 μm) on a polishing cloth until a mirror finish was obtained. After 10 min sonication, the electrodes were immersed in phosphate buffer ($pH = 7.0$) and firstly oxidized at 2.0 V for 100 s followed by reduction at -1.1 V for 50 s. Then the electrodes were cleaned by cyclic voltammetry between -1.1 V and $+0.9$ V at 50 mV s^{-1} until a stable profile was obtained. The prepared electrodes were dried under a nitrogen stream and used for modification immediately. SCNTs (1 mg) were dispersed in 1.0 mL of double-distilled water with the aid of sonication. The CNTs layer modified electrode was prepared by casting 5 μL of the dispersion on the surface of a GC electrode, which was air-dried at room temperature. When the water was volatilized, a CNTs film was formed. The AA-CNTs modified electrode was obtained by immersing the CNTs modified electrode in an AA solution of 5 mM for 2 h. The AA modified GC electrode was obtained by immersing the bare GC electrode in an AA solution for 2 h. The electrodes modified with AA/CNTs and AA were electropolymerized by cyclic voltammetry between -0.5 V and $+0.9$ V at 50 mV s^{-1} in phosphate solution (pH 6.5) for 40 cycles and rinsed with water. The prepared electrodes were denoted as PAA/CNTs/GC, PAA/GC electrode hereafter, respectively. The resulted electrodes were then transferred to the electrochemical cell for cyclic voltammetry between -0.2 V and $+0.5$ V at 50 mV s^{-1} in

$0.2\,M\ H_2SO_4$ solution until a stable profile was obtained. The prepared electrodes were used as working electrode for determination of sodium nitrite in $0.2\,M\ H_2SO_4$ solution.

Results and Discussion

AA Assembled onto the Surface of CNTs and its Spectroscopic Evidence

The CNTs consists of seamlessly rolled-up graphene sheets of carbon, exhibiting a special sidewall curvature and possessing a π–π conjugative structure with a highly hydrophobic surface. These unique properties of the CNTs essentially allow them to interact with some organic compounds, (polynuclear) aromatic compounds, in particular, through π–π electronic and hydrophobic interactions and thus form new nanostructures as demonstrated previously [31–33]. As AA is a typical polynuclear aromatic compound, it can also be assembled onto the hydrophobic surface of CNTs through π–π electronic and hydrophobic interactions to form a new kind of stable nanomaterials. The purification of carbon nanotubes is mainly to remove metal catalyst and amorphous carbon although yielded small amount oxygen-containing functional groups such as carboxylic groups [34]. But those groups mainly located at the open ends of the CNTs, so the hydrophobic surface of CNTs is still remained and won't affect the interaction of AA and CNTs. As the AA modified CNTs was through assemble, the film of AA is maybe a single molecules or several molecules layers, thus ultrathin film of AA could be obtained.

A typical UV-vis spectrum of AA/CNTs nanomaterials (curve 2) and AA (curve 1) in water was displayed in Fig. 1. The UV-vis spectra of CNTs dispersed in aqueous solution exhibits a featureless adsorption (not shown), whereas the spectrum of free AA in aqueous solution displays a strong absorbance at 633 nm (curve 1). The chemisorption of AA onto the CNTs was evident from the spectrum of AA/CNTs nanomaterials (curve 2), which is similar to that of free AA. Moreover, a close inspection of the spectrum of free AA and the AA/CNTs nanomaterials reveals that there is a change in the spectrum of AA after its adsorption onto the CNTs. For example, the adsorption peak of free AA in solution at 633 nm and 289 nm was shift to 621 nm and 275 nm, respectively, after its adsorption onto CNTs, which was due to the aggregation of AA molecules onto CNTs [35].

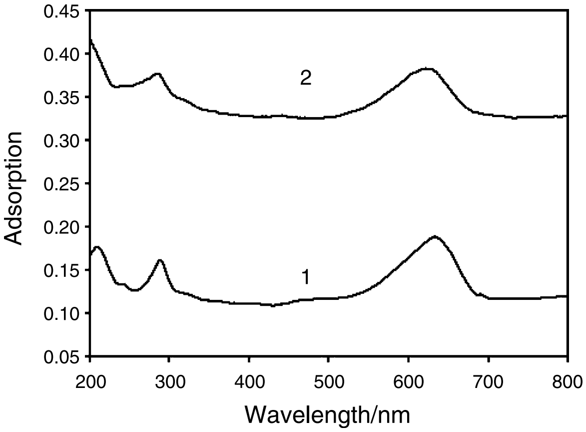

Fig. 1. UV-vis spectra of AA/CNTs nanostructure (*curve 2*) and AA (*curve 1*) in water

Electropolymerization of Assembled AA and Electrochemical Response of the PAA-CNTs/GC and PAA/GC and Characterization of the Prepared Electrodes

The electropolymerization of assembled AA was performed in phosphate buffer (pH = 6.5) by cyclic voltammetry between −0.5 V to 0.9 V. The scan rate of cyclic voltammetry is $50\,mV\,s^{-1}$. Figure 2A and B is the typical set of cyclic voltammogram obtained from the electropolymerization of AA assembled on the GC and CNTs/GC, respectively. The cyclic voltammograms shows that the current of the monomer of AA at about −0.26 V decreased while the current of PAA at about −0.05 V increased step by step, which means both of the assembled AA could be electropolymerized and form conducting polymer successfully. The two cyclic voltammograms are very similar, which shows that the structure of PAA didn't change on the surface of CNTs. The difference of the two electropolymerization procedures is the current response of electropolymerization. From the Fig. 2A and B, one can see that the current of AA on the CNTs/GC is far bigger than that of AA on bare GC. Figure 2C is the typical CV of the CNTs/GC (trace 2) and GC (trace 1) modified with PAA in $0.2\,M\ H_2SO_4$ solution, respectively. The current of PAA/CNTs/GC at about 0.2 V is about 120 µA, which is about 5 times higher than that of PAA/GC (about 25 µA). This phenomenon may ascribe to four aspects: firstly, CNTs have larger hydrophobic surface area and interacts strongly with AA, which contributed to larger adsorption amount of AA. Secondly, the adsorption strength of AA of the bare GC is relatively low. Thirdly, the CNTs can facilitate the electron transfer of PAA. Lastly, there may be

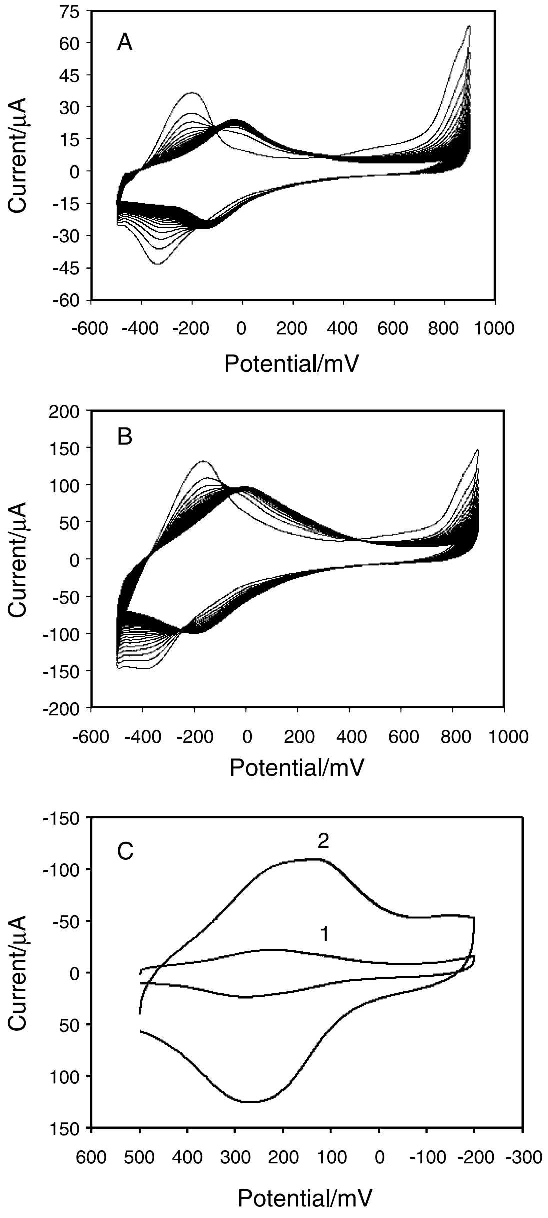

Fig. 2. CVs obtained at glassy carbon electrode (A) and CNTs/GC (B) assembled AA in pH 6.5 phosphate solutions. Sweep rate: 50 mV s^{-1}. C represents the CVs of PAA/GC (*trace 1*) and PAA/CNTs/GC electrodes (trace 2) in a 0.2 M H_2SO_4 solution. Sweep rate: 50 mV s^{-1}

positive synergistic effect between AA and CNTs. As a result, the current of PAA/CNTs/GC was greatly increased. Figure 3 shows the cyclic voltammograms of the PAA/ CNTs/GC electrode in 0.2 M H_2SO_4 solution at various scan rates in a range from 20 to 120 mV s^{-1}. As shown, the peak currents are linear with potential scan rates in a range from 20 to 120 mV s^{-1} (inset) at the peak potentials 0.2 and 0.1 V, while the peak potential only slightly changed. This demonstrates the redox process of the PAA-CNTs nanostructure on the GC electrode is a fast and surface-confined process.

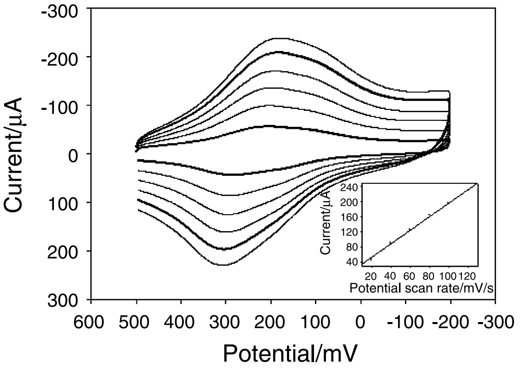

Fig. 3. CVs of the PAA/CNTs/GC electrode in 0.2 M H_2SO_4 at different scan rate, scan rate (from inner to outer), 20, 40, 60, 80, 100, 120 mV s^{-1}. (Inset) Plots of peak currents vs. potential scan rate

Figure 4 displays the typical morphology of the CNTs/GC (A) and PAA/CNTs/GC (B) characterized by scanning electron microscopy (SEM). From Fig. 3, it can be seen that the CNTs was in the form of small

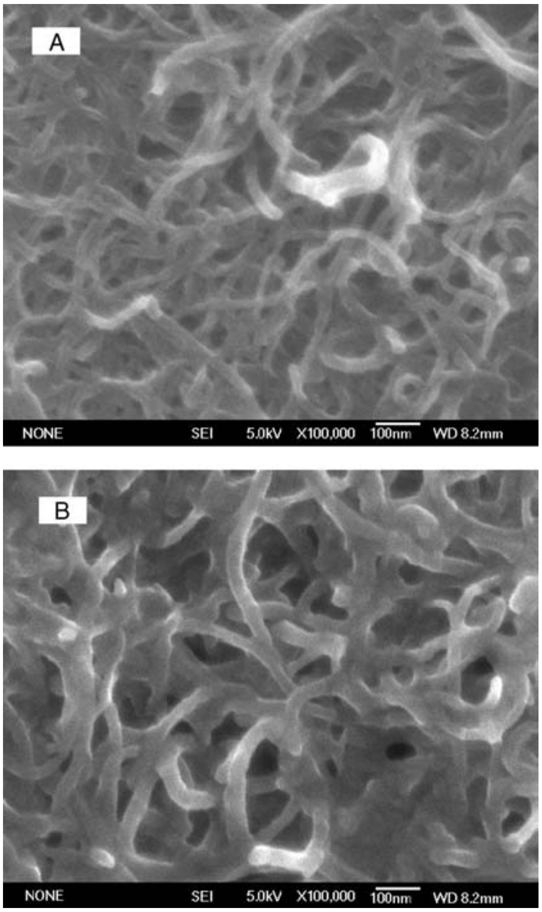

Fig. 4. SEM images of CNTs (A) and PAA/CNTs (B)

bundles and single nanotube and distributed very homogeneously on the surface of GC electrode exhibiting a special three-dimensional structure. The electroplolymerized AA on the surface of CNTs (B) didn't change the morphology of CNTs. While the diameters of PAA/CNTs were slightly thicker than that of CNTs, which means the PAA layer is very thin. Such small bundles and single nanotubes of PAA/CNTs catalyst homogeneously distributed on GC electrode were expected to be very attractive for the construction of electrochemical sensors as the catalyst with huge surface area is fully and easily accessible to the analytes, and consequently can be readily and totally used as electrochemical sensing unit, yielding a high ratio of signal-to-noise for electrochemical determination of analytes.

CNTs Concentration, Acidity Effect and Stability of PAA Response

The effect of CNTs concentration was studied. With the increment of CNTs concentration, the current response of PAA increased accordingly, which indicates the AA could be actually adsorpted onto the surface of CNTs. Although higher PAA results in higher sensitivity, the background and noise level is also increased. Therefore 5 μL 1.0 mg mL^{-1} CNTs was selected for fabrication of PAA/CNTs/GC electrode in this experimental. The acidity effect on PAA/CNTs is investigated by CV. The peak current was increased and the differential of peak potential became smaller with the increased acidity, which means the CV of PAA became more reversible. When the H_2SO_4 concentration is higher than 0.2 M, the peak current and potential changed only slightly. The stability is also dependant on the acidity. When the concentration of H_2SO_4 is below 0.2 M, the PAA film is quite stable while higher than 0.2 M, the PAA film is not very stable. So the H_2SO_4 concentration of 0.2 M was used for further studies.

Electrochemical Reduction of Nitrite at a PAA/CNTs/GC Electrode

One of the objectives of the study was the development a modified electrode capable of the electrocatalytic reduction of nitrite. As the PAA/CNTs nanomaterials were in the form of small nanotubes with high surface area, it was expected that the modified electrode could exhibit excellent electrocatalytic activity. Figure 5 compares the cyclic voltammograms for 2 mM nitrite

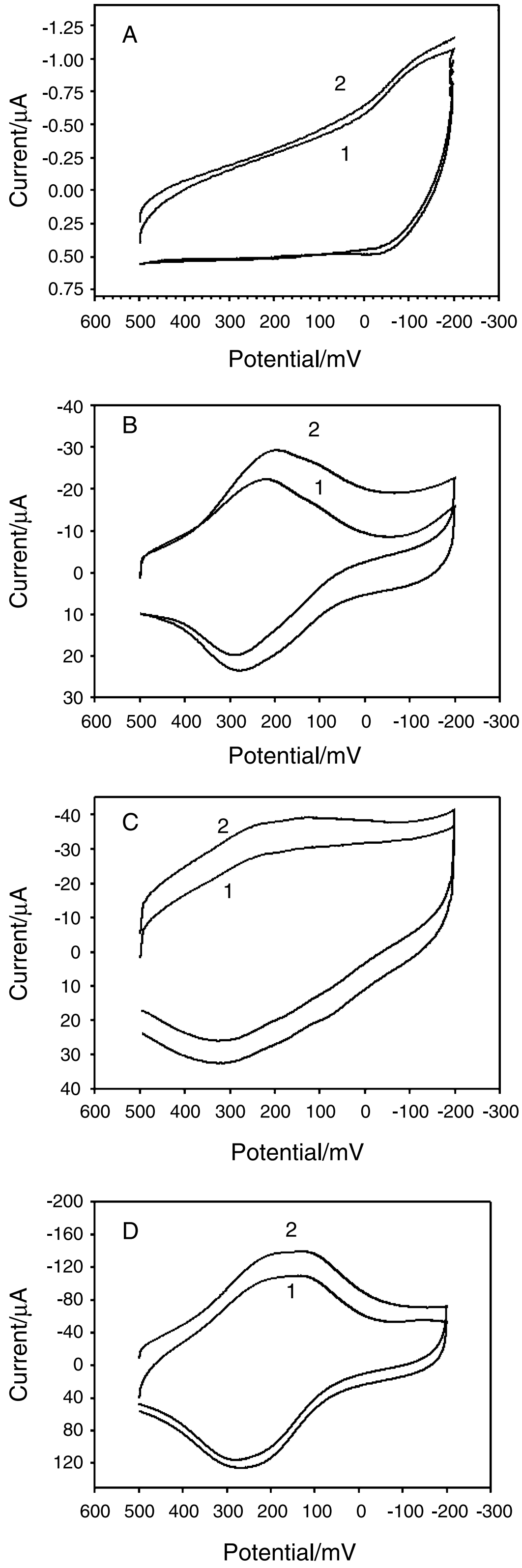

Fig. 5. The CVs of bare GC electrode (A) in the presence (*trace 2*) and absence (*trace 1*), the PAA/GC electrode (B) in the presence (*trace 2*) and absence (*trace 1*), the PAA/CNTs/GC electrode (5) in the presence (*trace 2*) and in the absence of (*trace 1*) 2.0 mM nitrite

in 0.2 M H_2SO_4 recorded at 50 mV s^{-1} of bare GC (A), PAA/GC (B), CNTs/GC (C) and PAA/CNTs/GC (D) electrodes. As shown in Fig. 5A, the bare GC shows no response toward the reduction of nitrite. In the absence of nitrite (Fig. 5B, trace 1), a couple of well-behaved redox reaction for PAA on the CNTs modified GC electrode can be observed. Upon the addition of 2 mM sodium nitrite (Fig. 5B, trace 2), the cathodic current is enhanced and the anodic current is decreased, which indicates the PAA modified GC electrode could electrocatalyze the reduction of nitrite. The CNTs/GC electrode (Fig. 5C, trace 2 and 1 represent in the presence and absence of 2 mM nitrite, respectively) also exhibits good electrocatalytic effect toward the reduction of nitrite. But the current response value of PAA and CNTs modified electrode is much less than that of PAA/CNTs/GC, which means CNTs could effectively enhance the electrocatalytic activity of PAA. This may contribute to three facts: first, the CNTs could increase the assembled AA amounts; second, the PAA/CNTs nanomaterials are in the form of nanotubes, which could provide a huge catalytic surface; third, the CNTs could facility the electron translation. As a result, the response current of nitrite increased greatly.

The electrocatalytic activity of the PAA/CNTs/GC, PAA/GC, CNTs/GC and bare GC electrodes were further investigated by current response curves to the successively addition of 1.0 mM sodium nitrite and the applied potential is the cathodic peak potential (0.1 V) of nitrite in 0.2 M H_2SO_4 solution. The results were displayed in Fig. 6. The current response of bare GC (Fig. 6, trace 1) is about 0.32 μA. And the response current of the CNTs/GC (Fig. 6, trace 2) and PAA/GC (Fig. 6, trace 3) is about −6.8 μA and −7.3 μA respectively. While the response current of PAA/CNTs/GC (Fig. 6, trace 4) is about −14.3 μA. The response current is almost the sum of the response currents of the CNTs/GC and PAA/GC electrode, which means higher sensitivity than that of carbon nanotubes and PAA modified electrodes. Furthermore, the response time is very fast (within 3 s) as the film is very thin.

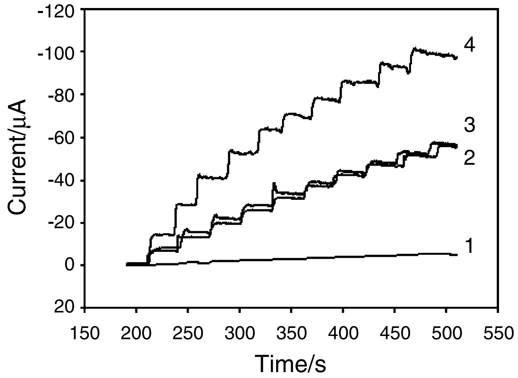

Fig. 6. The steady amperometric response of the successively added 1.0 mM nitrite at 0.1 V of bare GC (*trace 1*), CNTs/GC (*trace 2*), PAA modified GC (*trace 3*), PAA/CNTs modified GC (4) electrodes

Calibration Curve of Standard Nitrite Solution

The corresponding of calibration curve is shown in Fig. 7. Linear range from 3.0μM to 4.5 mM has been observed for the PAA/CNTs/GC with a detection limit of 1.0 μM based on a signal-to-noise ratio of 3. Table 1 compares the electrocatalytic characteristics of the PAA/CNTs/GC electrode with other carbon nanotubes and polymer modified electrodes. From Table 1, it could be observed that the detection limit of the PAA/CNTs/GC electrode is lower than the reports of carbon nanotube powders microelectrode [28] and poly(pyrrole) nanowires [30] modified electrode. The linear range is wider than the reports of poly(methylene violet) [29] and carbon nanotubes in the presence cupric ions [27]. Compared with the report of [27], although the detection limit is slightly higher, the immobilization PAA together with CNTs onto the electrode surface may be facilitate for multiple and practical use.

Accuracy, Precision and Reproducibility of the PAA/CNTs/GC Electrodes

Accuracy, precision and reproducibility of the PAA/CNTs/GC electrodes were investigated. The relative

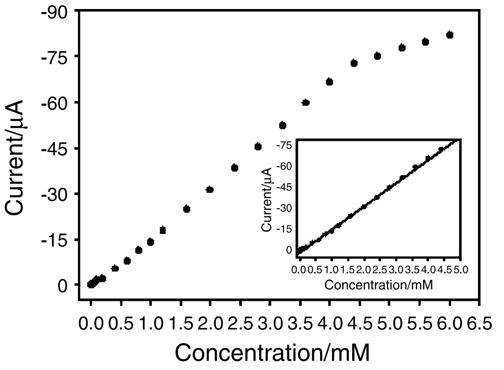

Fig. 7. Calibration curve of the response of the sensor to nitrite in 0.2 M H_2SO_4 (Inset) The linear part of the calibration curve of PAA/CNTs/GC

Table 1. Comparable methods for electrochemical determination of nitrite

Method	Limit of detection	Linear range	Reference
Reduction nitrite at 100 mV at a carbon nanotube/poly(azure A) nanomaterials modified electrode	1.0 μM	3 μM to 4.5 mM	this method
Reduction nitrite at −550 mV at a carbon nanotube electrode in the presence of cupric ions added in solution	0.5 μM	2 μM to 10 μM and 20 μM to 1 mM	[27]
Reduction nitrite at 300 mV at carbon nanotube powder microelectrode	8 μM	16 μM to 150 mM	[28]
Reduction nitrite at −15 mV at a poly(methylene violet) modified electrode	be absent	10 μM to 3 mM	[29]
Reduction nitrite at 180 mV at a poly(pyrrole) nanowires modified electrode	22.8 μM	22.8 μM to 20 mM	[30]

standard deviation (RSD) of 10 measurements of 1.0 mM NADH at the same PAA/CNTs/GC electrode was 4.8%, and the mean accuracy of 4 different nitrite concentration of 0.05 mM, 0.5 mM, 1.0 mM, 2.0 mM measurements is −3.5%. The reproducibility was studied using 5 different PAA/CNTs/GC electrodes. The RSD of the 5 electrodes to 1.0 mM nitrite measurements is 4.3%.

Interference Study

Possible interference for the detection of nitrite at PAA/CNTs/GC electrode was investigated by addition of various ions to 0.2 M H_2SO_4 aqueous solution in the presence of 1.0 mM sodium nitrite. The common ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cl^-, NO_3^-, ClO_3^-, $H_2PO_4^-$, HPO_4^{2-}, CO_3^{2-}, and SO_4^{2-} in a 40-fold concentration and Zn^{2+}, Cd^{2+}, Ba^{2+}, and Br^- in a 10-fold concentration did not show interference to nitrite detection, while Fe^{3+}, Cu^{2+}, I^-, BrO_3^-, and IO_3^- have been found to exhibit serious interference. As for the common interferents in biological samples for the determination of nitrite, uric acid and acetaminophen in the same concentration of nitrite had slightly effect on the detection, but ascorbic acid did show interference to the current response.

Conclusion

Uultrathin conducting poly(azure A)/carbon nanotubes (UCPAA/CNTs) nanomaterials with high catalytic surface area was prepared by assembleing-electrodepositing. The UCPAA/CNTs nanomaterials exhibited excellent electrocatalytic activity toward the reduction of nitrite. This new method for fabrication of UCPAA/CNTs nanomaterials is expected to be practically used for the construction of electrochemical sensors.

Acknowledgements. This work was supported by National Natural Science Foundation of China (No. 20077006), Doctorate Fund (No. 20020532007) and Key Sci./Tech. Res. (No. 03123) of Education Department, China.

References

[1] Lijima S (1991) Nature 354: 56

[2] Ebbesen T W (1997) Carbon nanotubes: preparation and properties, CRC Press, Boca Raton, FL

[3] Kaiser A B (2001) Adv Mater 13: 927

[4] Baughman R H, Zakhidov A A, Heer W A D (2002) Science 297: 787

[5] Zhao Q, Gan Z, Zhuang Q (2002) Electroanalysis 14: 1609

[6] Terrones M (2003) Annu Rev Mater Res 33: 419

[7] Ajayan P M (1999) Chem Rev 99: 1787

[8] Wohlstadter J N, Wilbur J L, Sigal G B, Biebuyck H A (2003) Adv Mater 15: 1184

[9] Wang J, Musameh M, Lin Y (2003) J Am Chem Soc 125: 2408

[10] Wang J, Liu G, Jan M R (2004) J Am Chem Soc 126: 3010

[11] Sandler J, Schaffer M, Prasse T, Bauhofer W, Schulte K, Windle A H (1999) Polymer 40: 5967

[12] Wei C Y, Srivastava D, Cho K J (2002) Nano Lett 2: 647

[13] Hughes M G, Chen Z, Schaffer M S P, Fray D J, Windle A H (2002) Chem Mater 14: 1610

[14] An K H, Jeong S Y, Hwang H R, Lee Y H (2004) Adv Mater 16: 1005

[15] Kymakis E, Amaratunga G A J (2002) Appl Phys Lett 80: 112

[16] Woo H S, Czerw R, Webster S, Carroll D L, Park J W, Lee J H (2001) Synth Met 116: 369

[17] Musa I, Baxendale M, Amaratunga G A J, Eccleston W (1999) Synth Met 102: 1250

[18] Coleman J N, Curran S, Dalton A B, Davey A P, McCarthy B, Blau W, Barklie R C (1999) Synth Met 102: 1174

[19] Zengin H, Zhou W, Jin J, Czerw R, Smith D W, Echegoyen L Jr, Carroll D L, Foulger S H, Ballato J (2002) Adv Mater 14: 1480

[20] Zhang F, Nyberg T, Inganas O (2002) Nano Lett 2: 1373

[21] Ramanathan K, Banger M A, Yun M, Chen W, Mulchandani A, Myung N V (2004) Nano Lett 4: 1237

[22] Martin C R (1995) Acc Chem Res 28: 61

[23] Wang J, Dai J, Yarlagadda T (2005) Langmuir 21: 9

[24] Wei Z, Wan M, Lin T, Dai L (2003) Adv Mater 15: 136
[25] Wei Z, Zhang Z, Wan M (2002) Lamgmuir 18: 917
[26] Aminur Rahman G M, Guldi D M, Cagnoli R, Mucci A, Schenetti L, Vaccari L, Prato M (2005) J Am Chem Soc 127: 10051
[27] Zhao G, Liu K, Lin S, Liang J, Guo X, Zhang Z (2004) Microchim Acta 144: 75
[28] Zhao Y D, Zhang W D, Luo Q M, Li S F Y (2003) Microchem J 75: 189
[29] Wang Y, Zhou D, Chen G, Chen H (1997) Chem J Chin Univ 18: 864
[30] Tian Y, Wang Y, Wang Z, Wang S (2004) Synthetic Metals 143: 309
[31] Chen R J, Zhang Y, Wang D, Dai H J (2001) J Am Chem Soc 123: 3838
[32] Dai H J (2002) Acc Chem Res 35: 1035
[33] Star A, Stoddart J, Steuerman D, Diehl M, Boukai A et al. (2001) Angew Chem Int Ed 40: 1721
[34] Kuznetsova A, Popova I, John T, Yates Jr et al. (2001) J Am Chem Soc 123: 10699
[35] Yan Y M, Zhang M N, Gong K P, Su L et al. (2005) Chem Mater 17: 3457