Int. J. Electrochem. Sci., 8 **(2013)** 12296 - 12307

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Nano-Copper-MWCNT-Modified Glassy Carbon Electrode for Selective Detection of Dopamine

Shiying Zheng[1,2], *Yiyin Huang*[1], *Jindi Cai*[1], *Yonglang Guo*[1,*]

[1] College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, 350108, P. R.China
[2] School of life science, Fujian Agriculture and Forestry University, Fuzhou, 350002, P.R. China
[*]E-mail: yguo@fzu.edu.cn

Received: 25 July 2013 / *Accepted:* 19 August 2013 / *Published:* 25 September 2013

This paper reports the electrochemical deposit and characterization of copper nanoparticles on the multi-walled carbon nano-tubes (MWCNTs) and the application of nano-copper-MWCNT-modified glassy carbon electrode (GCE) in the electrochemical determination of dopamine (DA). Cyclic voltammetric experiments indicated that the nano-copper-MWCNT-modified GCE displayed very high electrochemical catalytic activity compared to the MWCNT-modified GCE in 0.06 M H_2SO_4. The nano-copper-MWCNT-modified GCE was found to be suitable for the selective determination of DA. The presence of uric acid (UA) and high concentration ascorbic acid (AA) did not interfere in the detection of DA on this electrode. The observed linear range of the glassy carbon electrode modified by nano-copper-MWCNT composite membrane was from 0.1 to 156.0 μM for DA and its detection limit was 0.05 μM. It was demonstrated that this electrode can be used for the determination of DA in real samples such as DA injectable formulations and human urine.

Keywords: Nanoparticle copper; multi-walled carbon nano-tubes; Glass carbon electrode; Dopamine; Cyclic voltammetry

1. INTRODUCTION

Because of the good mass transport and large effective surface area which accelerate the electron exchange rate between the electrode surface and solution, the metal nanoparticles exhibit excellent electro-catalytic properties [1-5]. Copper is much cheaper compared to other noble metals. Therefore, the application of copper nanoparticle-modified electrodes is very promising in the catalysis of organic small molecules.

The attractive features of the multi-walled carbon nano-tubes (MWCNTs) including their unique mechanical and electrical properties are significant advantages in the design and development of the electrochemical sensors [6-8]. Furthermore, MWCNTs modified by the adsorption of small organic molecules or metal nanoparticles via redox or electro-deposition can be used to determine H_2O_2, iodate, dopamine (DA), organic small molecules, inorganic ion and even widely used as catalytic electrodes of fuel cells [9-15].

Dopamine (DA), as an important neurotransmitter, plays a key role in mammalian central nervous system [16]. The study on DA has attracted much attention in the past years [17-21]. Since DA is electrochemically active, the electrochemical methods can be applied to the determination of this compound. However, the electrochemical detection of DA in physiological samples is challenging because of the effect of ascorbic acid (AA) with high concentration [22]. The main problem is that the oxidation potentials of DA and AA are nearly the same on most of the material electrodes. So it is important to develop new sensors to detect DA selectively in the presence of AA.

Copper nanocluster/multi-wall carbon nano-tubes (MWCNTs) modified glassy carbon electrode was used to detect glucose in alkaline media [23]. However, its electrochemical preparation and its application in detecting DA were rarely reported. In this work, the glassy carbon electrode modified by the nano-copper-MWCNT composite membrane was prepared by the electrochemical method and used for DA sensing in the presence of UA and AA with high concentration in acidic media. It is found that the nanoparticle copper can obviously improve the properties of the modified electrode. The voltammetric response of DA on the proposed sensor was greatly increased compared with that on the MWCNT modified glassy carbon electrode. Therefore, the sensitive and selective determination for DA can be achieved on this proposed sensor.

2. EXPERIMENTAL

2.1. Reagents and materials

Multi-walled carbon nano-tubes (MWCNTs) was purchased from Alpha Nano Technology Co., Ltd. (diameter 10–20 nm, length 5~15 μm, purity ≥ 95%), uric acid (UA) and dopamine (DA) from SIGMA-ALDRI, ascorbic acid (AA) from Tianjing Fuchen chemical reagent Co. (China), $CuSO_4 \cdot 5H_2O$ from Sinopharm chemical reagent Co. (China). Other chemicals were of analytical grade purity and used as received. Double distilled water was used in all experiments.

2.2. Apparatus and measurements

Cyclic voltammetric (CV) experiments were performed on a CHI 1140A electrochemical workstation (Shanghai, China). A conventional three electrode system was used in all electrochemical experiments. The system consisted of a platinum wire as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and the MWCNT-modified GCE or nano-copper-MWCNT-modified GCE as working electrode. Prior to electrochemical experiments, the solution was bubbled with high purity nitrogen for 5 min to remove dissolved oxygen. All experiments were carried out at room temperature.

2.3. Preparation of MWCNT/GCE and nano-copper -MWCNT/GCE

To prepare electrode, the glassy carbon electrode with a diameter of 4 mm was polished with 0.05 μm aluminum oxide slurry to obtain a mirror surface, rinsed and sonicated in double distilled water, and dried in the air. 5.0 mg of MWCNTs were dispersed in 5 mL isopropyl and 50 μL 15 wt.% nafion as binder with ultrasonic agitation to get a stable suspension, and then 12.0 μL of the MWCNT suspension was dropped on the pretreated GCE and dried at room temperature, to obtain MWCNT-modified GCE.

To prepare the copper nanoparticle-modified MWCNT membrane by the electrochemical deposition method, the MWCNT-modified GCE was performed by the cyclic voltammetry in the potential range of -0.6 ~ 0.8 V in 0.06 M H_2SO_4 + 10.7 μM $CuSO_4$ at a scan rate of 100 mV s^{-1} for 50 cycles. The obtained electrode was ready for use after a final wash with double distilled water and denoted as the nano-copper-MWCNT/GCE.

2.4. Cyclic voltammetry

To increase the peak current response in DA oxidation and prevent nanoparticle copper from dissolving, the nano-copper-MWCNT/GCE was immersed in 0.06 M H_2SO_4 + 10.7 μM $CuSO_4$ solution containing DA. The accumulation time on open circuit was 60 s. Then the cyclic voltammograms were obtained between -0.6 and +0.8 V (*vs.* SCE), and the initial sweep potential was -0.6 V.

3. RESULTS AND DISCUSSION

3.1. Electrochemical deposition of Cu nanoparticles on MWCNT/GCE

In order to deposit Cu nanoparticles on MWCNT/GCE, the MWCNT/GCE electrode was cycled in 0.06 M H_2SO_4 containing 10.7 μM $CuSO_4$ for 50 cycles in the potential range from -0.6 to 0.8 V at 100 mV s^{-1} and their voltammograms (CVs) were displayed in Fig. 1. It is clear that there are cathodic and anodic peaks at about -0.15 and -0.05 V corresponding to the reduction of Cu^{2+} ions and the oxidation of Cu nanoparticles, respectively. And a couple of small redox peaks appear in the range of 0.35 - 0.4 V and they are attributed to the oxidation and reduction of the oxygen-containing species adsorbed on the electrode surface, which can promote the catalytic oxidation of organic molecules [24]. In the continuous cycles, the redox peaks of the cupper nanoparticles become higher and higher and tend to be stable after 50 cycles. It is interesting to find that both oxidation and reduction peak potentials of the Cu nanoparticles shift in the positive direction with cycling, suggesting that the reduction of Cu^{2+} ions into the Cu nanoparticles becomes easier and easier while its oxidation becomes increasingly more difficult in the cycles [25]. That is the irreversible oxidation of the Cu occurs on the electrode. Therefore, the Cu nanoparticles deposits and accumulates on the MWCNT/GCE surface in the continuous cycles.

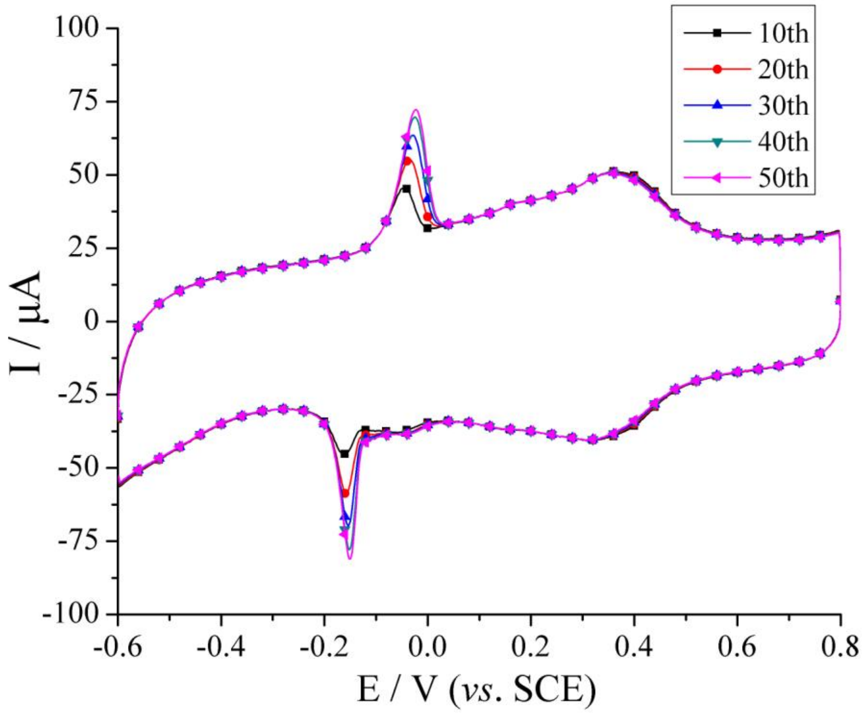

Figure 1. CVs of MWCNT/GCE in 0.06 M H_2SO_4 containing 10.7 μM $CuSO_4$. Scan rate: 100 mV s^{-1}.

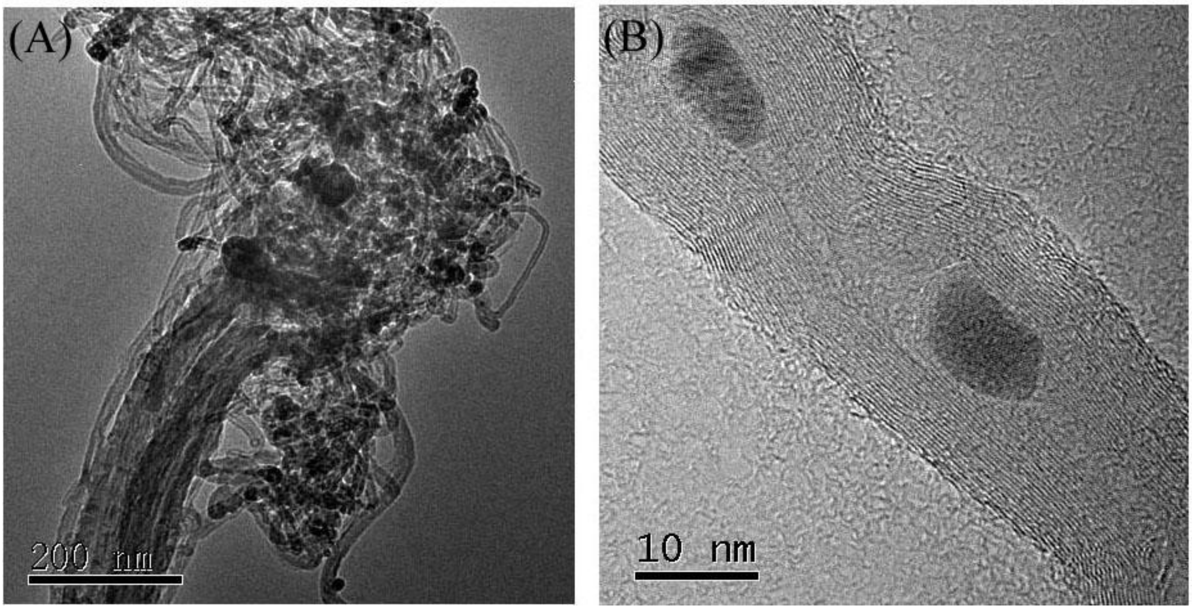

Figure 2. TEM images of nano-copper-MWCNT

The typical TEM images of MWCNT decorated by the Cu nanoparticles is shown in Fig. 2. It shows that Cu nanoparticles were dispersed on the external and inner walls of MWCNTs. The Cu nanoparticles inside MWCNTs also have a response in DA oxidation because the solution can penetrate into the interior of MWCNTs. And the oxidation dissolution of the Cu nanoparticles inside MWCNTs is difficult during cycling because the diffusion of internal Cu^{2+} ions to the outside needs a long distance compared to external Cu^{2+} ions and they will be reduced again in the subsequent negative-going sweep. This phenomenon is beneficial for the steady response to DA oxidation. The average diameter of Cu nanoparticles is about 8–10 nm in MWCNTs.

3.2. Electrocatalytic oxidation of DA

The cyclic voltammograms of nano-copper-MWCNT-modified glassy carbon electrodes in the $CuSO_4 + H_2SO_4$ solution with and without 39 μM DA are shown in Fig. 3. In the presence of DA, a well defined reversible redox peaks are obtained and its anodic and cathodic peak potentials appear at 485 and 453 mV, respectively. There is a cathodic peak at about -0.14 V corresponding to the reduction of Cu^{2+} ions and the re-oxidation peak of Cu nanoparticles appears at 0.02 V. It is interesting to find that the anodic and cathodic peaks of Cu are greatly enhanced when DA exists compared to those in Fig. 1. Obviously, there is an obvious interaction between Cu nanoparticles and DA.

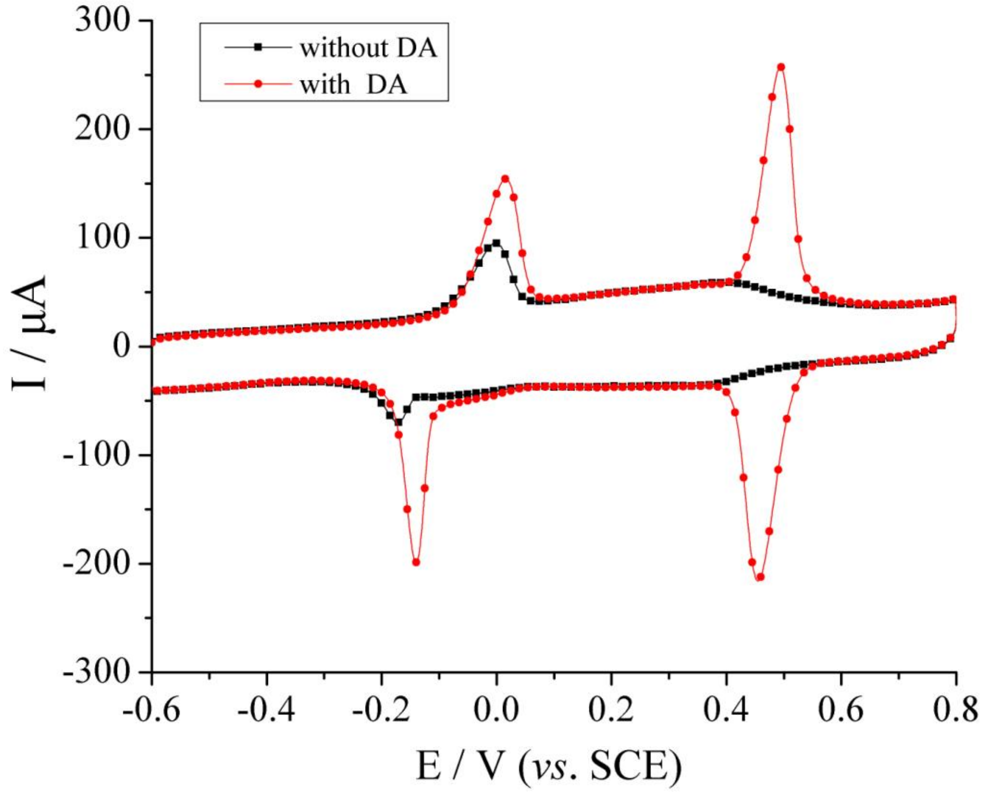

Figure 3. CVs of nano-copper-MWCNT/GCE in 0.06 M H_2SO_4 containing 10.7 μM $CuSO_4$ (black) and 10.7 μM $CuSO_4$ +39 μM DA (red). Scan rate: 100 mV s^{-1}.

The 5th of cyclic voltammograms of nano-copper-MWCNT-modified glassy carbon electrodes in DA solutions with and without containing Cu^{2+} ions are shown in Fig. 4. A well-defined reversible redox pair for DA appears in both solutions. The anodic and cathodic peak currents of DA in the solutions with and without Cu^{2+} are almost the same. It indicates that the Cu^{2+} ions in the solution does not affect the determination of DA. The redox peak currents of Cu nanoparticles in the solution without Cu^{2+} are obviously lower compared to those in the solution with Cu^{2+} ions. It can be concluded from the results above that the Cu nanoparticles deposited on the electrode play a major catalytic role in the electro-catalytic oxidation of DA. The redox peak currents of Cu nanoparticles in the solution without Cu^{2+} ions in Fig. 4 are only a little lower compare to those in the solution with Cu^{2+} ions in Fig. 3. This result indicates that part of copper nanoparticles suffer dissolving in the solution without Cu^{2+} ions. However, it is greatly mitigated because of some Cu nanoparticles located inside MWCNTs. Therefore, in order to prevent the Cu nanoparticles from dissolving, the nano-copper-MWCNT/GCE was immersed in 0.06 M H_2SO_4 + 10.7 μM $CuSO_4$ solution containing DA for determination next.

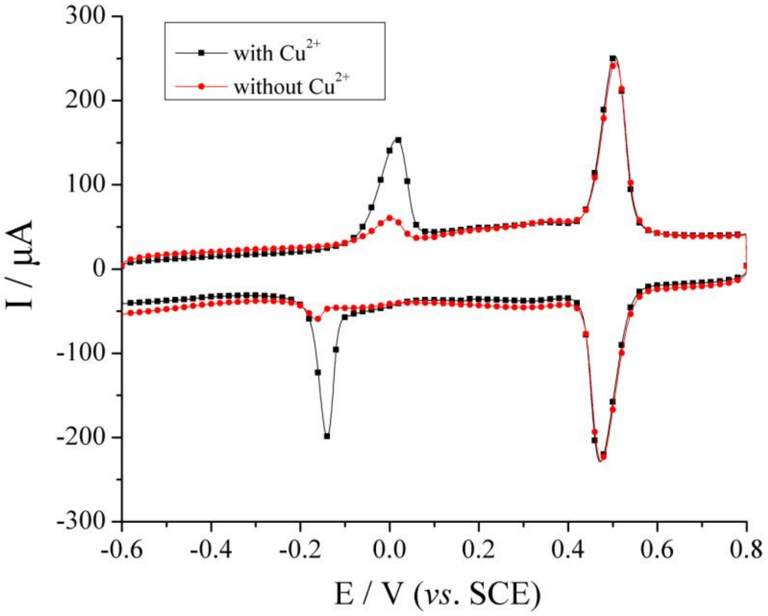

Figure 4. CVs of nano-copper-MWCNT/GCE in 0.06 M H_2SO_4 containing 39 μM DA (red) and 10.7 μM $CuSO_4$ +39 μM DA (black). Scan rate: 100 mV s^{-1}.

Cyclic voltammograms of MWCNT/GCE with and without Cu nanoparticle decoration are used to determine DA, as shown in Fig. 5. A well-defined reversible redox pair for DA is obtained on both MWCNT/GCE and nano-copper-modified MWCNT/GCE, while the redox pair of Cu disappears on the MWCNT/GCE because no Cu exists in the solution and on the electrode. In contrast to the MWCNT/GCE in Fig. 5, the anodic and cathodic peak currents of DA on nano-copper-modified MWCNT/GCE are nearly doubled. This result indicates that the detection sensitivity towards DA on nano-copper-modified MWCNT/GCE is greatly improved. The enhanced sensitivity in the presence of Cu on MWCNT/GCE is due to the fact that the copper nanoparticles can provide the oxygen-containing species to promote the catalytic oxidation of DA and the presence of DA is in turn beneficial to the deposition of Cu nanoparticles shown in Fig. 3. Both are enhanced by their interaction.

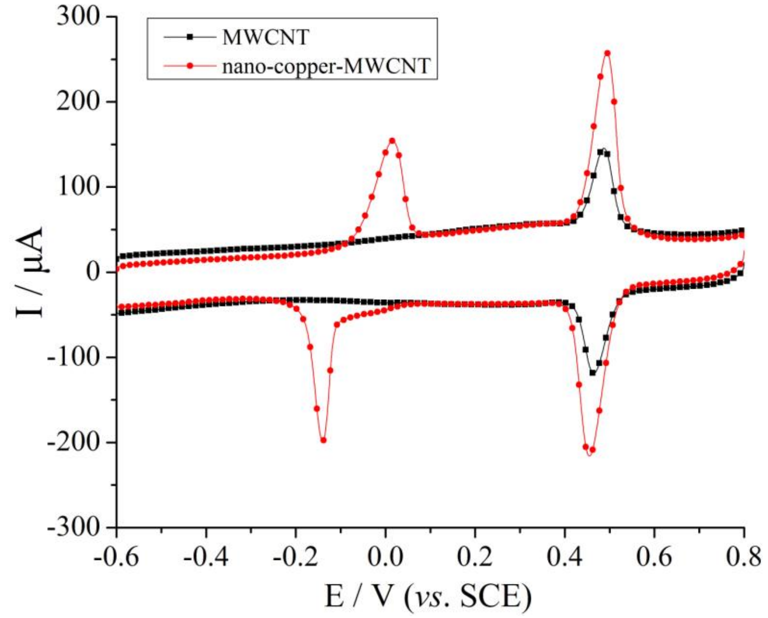

Figure 5. CVs of MWCNT/GCE (black) and nano-copper-MWCNT/GCE (red) in 39 μM DA + 0.1 M 0.06 M H_2SO_4. Scan rate: 100 mV s^{-1}.

3.3. Effects of scan rate on electrochemical response of DA

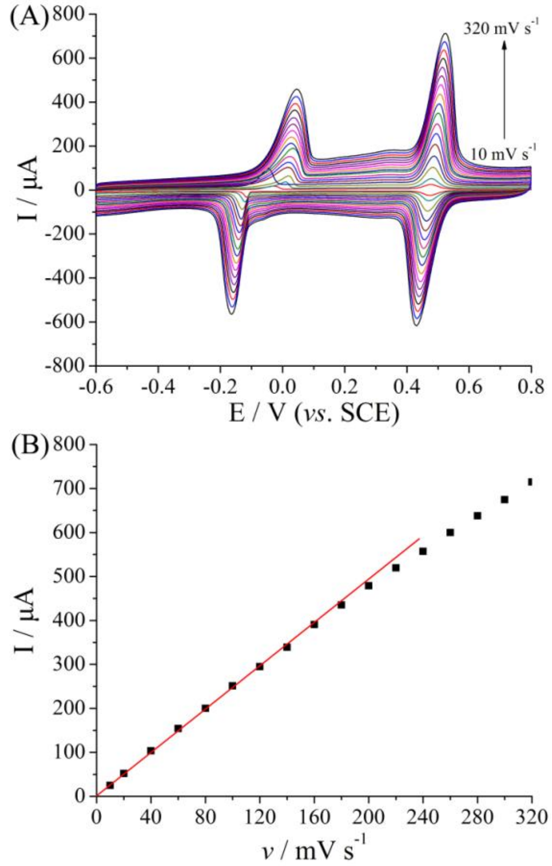

Figure 6. (A) CVs of nano-copper-MWCNT/GCE in 0.06 M H_2SO_4 containing 39 μM DA + 10.7 μM Cu^{2+}. (B) Plots of anodic peak current of DA *vs*. scan rate. Scan rate range: 10~320 mV s^{-1}.

The influence of the scan rate on the oxidation peak current of DA on the nano-copper-MWCNT-modified GCE is shown in Fig. 6A. The potential scan rates are between 10 and 320 mV s^{-1}. It is noticed that there is a good linear relationship between the peak current and the scan rate in the range of 10 – 220 mV s^{-1}, with a linear regression equation of I (μA) = 11.2744 + 2.36046 *v* (mV s^{-1}) (R = 0.99911) (Fig. 6B). This result indicates that the system presents the feature of an adsorption controlled process for DA oxidation [26].

3.4. The influence of AA and UA as interfering compounds

Cyclic voltammograms of the nano-copper-MWCNT/GCE in 0.06 M H_2SO_4 solution respectively containing AA, DA, UA or the mixture of AA, DA and UA are shown in Fig. 7. No new peak related to AA is found in the red line in Fig. 7, indicating that AA can not be oxidized or reduced on the electrode. A small oxidation peak appears at about 654 mV in the presence of UA (blue line) and it is isolated from the oxidation peak of DA (green line). For the cyclic voltammograms of the nano-copper-MWCNT/GCE in 0.06 M H_2SO_4 solution containing a mixture of 390 μM AA, 39 μM DA and 39 μM UA (black line), a small UA oxidition peak is also found at about 654 mV and at the same time no new peak related to AA is observed. The anodic and cathodic peak potentials of DA and their peak currents in the mixture (black line) are the same as those of DA in H_2SO_4 solution (green line). It shows once again that detection of DA was realized, eliminating AA interference completely [27], different from the previous reports based on the potential separations [28]. Therefore, the presence of AA and UA can not cause an interference to the determination of DA even if the concentration of AA is 10 times higher than that of DA. These results indicate that the selective and sensitive determination of DA can be achieved on the nano-copper-MWCNT/GCE.

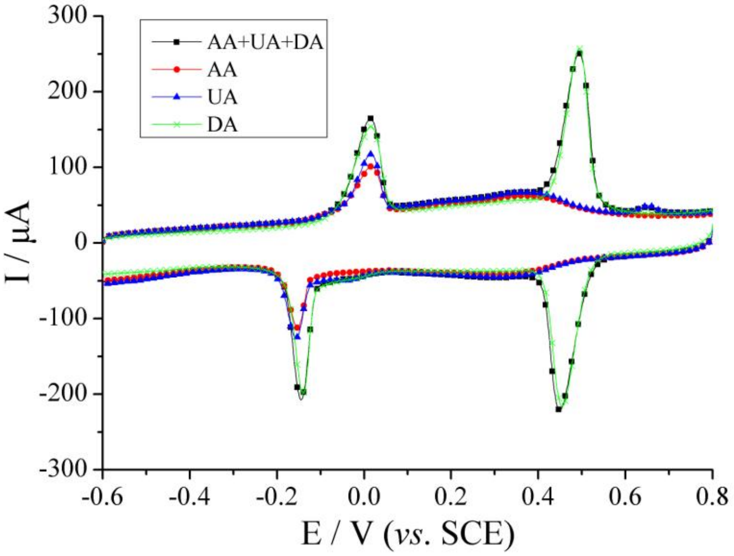

Figure 7. CVs of the nano-copper-MWCNT/GCE in 0.06 M H_2SO_4 including 390 μM AA+39 μM UA+39 μM DA (black), 39 μM DA (green), 390 μM AA (red) and 39 μM UA (blue), respectively. Scan rate: 100 mV s^{-1}

3.5. Determination of DA in nano-copper-MWCNT/GCE

Fig. 8A shows that the oxidation peak current of DA increases linearly with the increase of DA concentration. Good linear relationship was observed from 0.1 to 156.0 μM ($R^2 = 0.9982$) in Fig. 8B. The linear equation was I_{DA} (μA) = 2.1827 + 3.7866C_{DA} (μM). The detection limit of DA was 0.05 μM. To characterize the reproducibility of the nano-copper-MWCNT/GCE, several measurements were carried out in the solution containing 39 μM DA. It was found that the relative standard deviation (RSD) of voltammetric responses was only 1.5% when repeating this determination of DA for 5 times on the nano-copper-MWCNT/GCE. The result shows that the modified electrode has the excellent reproducibility of the sensor for determination of DA.

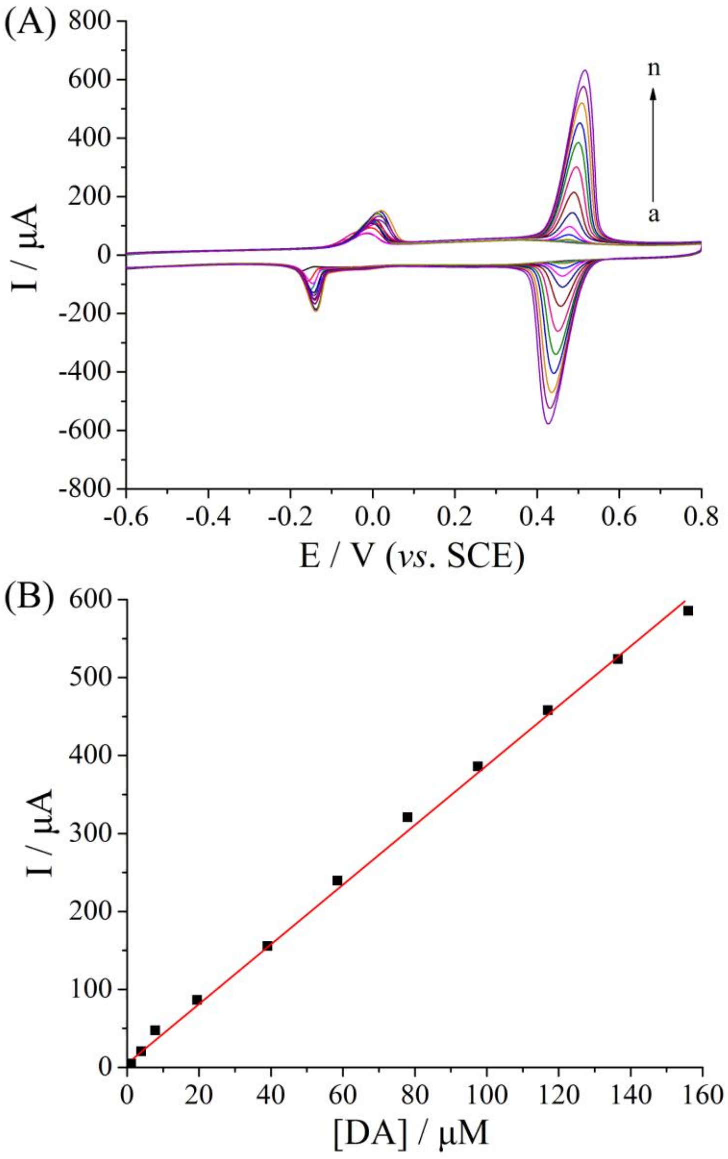

Figure 8. (A) CVs of nano-copper-MWCNT/GCE in 0.06 M H_2SO_4 with different DA concentrations: (a) 0; (b) 0.05; (c) 0.10; (d) 1.17;(e) 3.9; (f) 7.8; (g) 19.5, (h) 39; (i) 58.5; (j) 78; (k) 97.5; (l) 117; (m) 136.5; (n) 156 μM. (B) The plots of the oxidation peak currents of DA *vs* DA concentrations. Scan rate: 100 mV s^{-1}

3.6. Sample Analysis

3.6.1. Determination of DA in medical samples

The accuracy of the proposed cyclic voltammetry was evaluated by the analysis of two samples of dopamine injectable formulations on the nano-copper-MWCNT/GCE. 5 μL of dopamine hydrochloride injection was added into 30 mL H_2SO_4 (0.06 M) solution, and a standard addition method was applied to measure the accuracy. The test values of the DA concentration and the reported DA amounts in the injections are shown in Table 1. Therefore, DA of the real samples can be accurately detected by the proposed method.

Table 1. Results of the determination of DA in the injection using nano-copper-MWCNT/GCE.

Samples	Amount Claimed (mg)	Amount obtained (mg)	Added DA (μM)	Obtained DA (μM)	Recovery (%)
1	20.0 mg DA	20.3	22.00	22.2	100.9
2		20.7	22.00	22.1	100.5

3.6.2. Determination of DA in biological samples

The practical analytical utility of the nano-copper-MWCNT/GCE is illustrated by the quantitative determination of DA in biological fluids without any pretreatment. The sample to be detected was prepared as follows, a little different from the literature [26]: the supporting electrolyte of fresh urine sample from the healthy volunteer was diluted for 50 fold by 0.06 M H_2SO_4. When DA was detected in the real biological sample, AA and UA with the same concentration of 100 μM were dissolved in the supporting electrolyte to gain the synthesized biology sample. The nano-copper-MWCNT composite electrode was successfully applied for the determination of DA in human urine. The acceptable recovery date is shown in Table 2. The good recoveries of the synthesized biology samples indicate the successful applicability of the proposed method to determination of DA and the presence of AA and UA does not interfere in its detection.

Table 2. Results of the determination of DA in synthesized biological samples using nano-copper -MWCNT/GCE.

Samples	Added DA (μM)	Obtained DA (μM)	Recovery (%)
1	22.0	21.80	99.1
2	22.0	22.12	100.5

4. CONCLUSIONS

In this study, the Cu nanoparticle-modified MWCNT glassy carbon electrode was prepared by the electro-deposition method. The TEM shows that Cu nanoparticles were dispersed inside and outside MWCNTs. The deposition of Cu nanoparticles inside MWCNTs obviously inhibits the oxidation dissolution of Cu nanoparticles so that its accumulation occurs in the cycles. The copper nanoparticles on MWCNTs can greatly promote the catalytic oxidation of dopamine through providing the oxygen-containing species and the presence of dopamine is in turn beneficial to the deposition of Cu nanoparticles, indicating that there is an obvious mutual catalytic action between Cu nanoparticles and DA. Therefore, the nano-copper-MWCNT-modified glassy carbon electrode has high electrochemical activity and selectivity towards dopamine oxidation compared to MWCNT-modified glassy carbon electrode in 0.06 M H_2SO_4. The linear range of DA determination is from 0.1 to 156.0 μM and the sensitivity is 3.786 μA μM^{-1}. It was demonstrated that the accurate determination of dopamine can be achieved in the presence of ascorbic acid and uric acid even if the concentration of ascorbic acid exceeded that of dopamine by 10 times.

ACKNOWLEDGMENTS
We are grateful to NSFC (No. 51072037) in China and Natural Science Foundation of Fujian Province (No. 2013J01039) for financial support for this work.

References

1. C.M. Welch, R.G. Compton, *Anal. Bioanal. Chem*. 384 (2006) 601.
2. D.D. La, C.K. Kim, T.S. Jun, Y.J. Jung, G.H. Seong, J. Choo, Y.S. Kim, *Sens. Actuators*, B 155 (2011) 191.
3. S.F. Li, X.Y. Zhu, W. Zhang, G.M. Xie, W.L. Feng, *Appl. Surf. Sci*. 258 (2012) 2802.
4. J.Q. Yang, J.W. Chen, Y.K. Zhou, K.B. Wu, *Sens. Actuators,* B 153 (2011) 78.
5. Y. Oztekin, M. Tok, E. Bilici, L. Mikoliunaite, Z. Yazicigil, A. Ramanaviciene, A. Ramanavicius, *Electrochim. Acta* 76 (2012) 201.
6. B. Habibi, M.H. Pournaghi-Azar, *Electrochim. Acta* 55 (2010) 5492.
7. M. Arvand, A. Niazi, R. Motaghed Mazhabi, P. Biparva, *J. Mol. Liq*. 173 (2012) 1.
8. S.J. Richard Prabakar, C. Sakthivel, S. Sriman Narayanan, *Talanta* 85 (2011) 290.
9. A. Esmaeilifar, M. Yazdanpour, S.R. zamir, M.H. Eikani, *Int. J. Hydrogen Energy* 36 (2011) 5500.
10. Y. Zhao, Y.F. E, L.Z. Fan, Y.F. Qiu, S.H. Yang, *Electrochim. Acta* 52 (2007) 5873.
11. A. P. Periasamy, Y.H. Ho, S.M. Chen, *Biosens. Bioelectron*. 29 (2011) 151.
12. A. S. Kumar, P. Swetha, *Colloids Surf., A* 384 (2011) 597.
13. S.A. Kumar, S.F. Wang, Y.T. Chang, H.C. Lu, C.T. Yeh, *Colloids Surf*., B 82 (2011) 526.
14. J. Zhang, L. Gao, *J. Alloys Compd*. 505 (2010) 604.
15. Z. Dursun, B. Gelmez, *Electroanalysis* 22 (2009) 1106.
16. A.H. Liu, I. Honma, H.S. Zhou, *Biosens. Bioelectron*. 21 (2005) 809.
17. H.Y Wang, Y. Sun, B. Tang, *Talanta* 57 (2002) 899.
18. D.J. Yu, Y.B. Zeng, Y.X. Qi, T.S. Zhou, G.Y. Shi, *Biosens. Bioelectron*. 38 (2012) 270.
19. G.S. Liu, J.N. Chen, Y.F. Ma, *J. Chromatogr*. B 805 (2004) 281.
20. Z.H. Su, Y. Liu, Q.J. Xie, L. Chen, Y. Zhang, Y. Meng, Y. Li, Y.C. Fu, M. Ma, S.Z. Yao, *Biosens. Bioelectron*. 36 (2012) 154.
21. S.L. Yang, G. Li, Y.L. Yin, R. Yang, J.J. Li, L.B. Qu, *J. Electroanal.Chem*. 703 (2013) 45.
22. M. Ghita, D.W.M. Arrigan, *Electrochim. Acta* 49 (2004) 4743.
23. X.H. Kang, Z.B. Mai, X.Y. Zou, P.X. Cai, J.Y. Mo, *Anal. Biochem*. 363 (2007) 143.
24. Y.Y. Huang, J.D. Cai, S.Y. Zheng, Y.L. Guo, *J. Power Sources* 210 (2012) 81.

25. L.M. Abrantes, L.V. Araujo, M.D. Levli, *Miner. Eng.* 8 (1995) 1467.
26. D. Zheng, J.S. Ye, L. Zhou, Y. Zhang, C.Z. Yu, J. *Electroanal.Chem.* 625 (2009) 82.
27. Y.Wang, Y.M. Li, L.H. Tang, J. Lu, J.H. Li, *Electrochem. Commun.* 11 (2009) 889.
28. S. Shahrokhian, H. R. Zare-Mehrjardi, Electrochim. Acta 52 (2007) 6310.