An electrochemical ascorbic acid sensor based on palladium nanoparticles supported on graphene oxide

Geng-huang Wu[a], Yan-fang Wu[a], Xi-wei Liu[a], Ming-cong Rong[a], Xiao-mei Chen[b], Xi Chen[a,*]

[a] Department of Chemistry and Key Laboratory of Analytical Sciences of Xiamen University, College of Chemistry and Chemical Engineering and State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China
[b] College of Biological Engineering, Jimei University, Jimei, Xiamen, Fujian 361021, China

HIGHLIGHTS

- PdNPs with a mean diameter of 2.6 nm were homogeneously deposited on GO.
- The proposed sensor exhibited a rapid amperometric response to AA within 5 s.
- Good selectivity, wide linear range, low detection limit for AA.

GRAPHICAL ABSTRACT
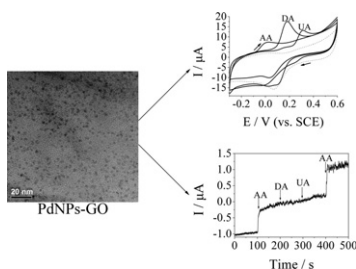
ARTICLE INFO

ABSTRACT

In this study, an electrochemical ascorbic acid (AA) sensor was constructed based on a glassy carbon electrode modified with palladium nanoparticles supported on graphene oxide (PdNPs-GO). PdNPs with a mean diameter of 2.6 nm were homogeneously deposited on GO sheets by the redox reaction between $PdCl_4^{2-}$ and GO. Cyclic voltammetry and amperometric methods were used to evaluate the electrocatalytic activity towards the oxidation of AA in neutral media. Compared to a bare GC or a Pd electrode, the anodic peak potential of AA (0.006 V) at PdNPs-GO modified electrode was shifted negatively, and the large anodic peak potential separation (0.172 V) of AA and dopamine (DA), which could contribute to the synergistic effect of GO and PdNPs, was investigated. A further amperometric experiment proved that the proposed sensor was capable of sensitive and selective sensing of AA even in the presence of DA and uric acid. The modified electrode exhibited a rapid response to AA within 5 s and the amperometric signal showed a good linear correlation to AA concentration in a broad range from 20 μM to 2.28 mM with a correlation coefficient of $R = 0.9991$. Moreover, the proposed sensor was applied to the determination of AA in vitamin C tablet samples. The satisfactory results obtained indicated that the proposed sensor was promising for the development of novel electrochemical sensing for AA determination.

1. Introduction

Ascorbic acid (AA, vitamin C), which is present in both the animal and plant kingdoms, is an essential nutrient for humans and plays a key role in biological metabolism. It helps in cell development, the healing of injuries and burns, and the synthesis of collagen, blood vessels, cartilage, bones and tendons [1,2]. Besides its importance for therapeutic purposes such as its use for the prevention and treatment of the common cold, mental illness, infertility, cancer and AIDS [3], it is also consumed on a wide scale as an antioxidant agent in foods, fruits, vegetables and soft drinks. Thus, the development of a simple and rapid method for the determination of AA with high selectivity and sensitivity is desirable for diagnostic and food safety applications. Several methods such as electrophoresis [4],

* Corresponding author. Tel.: +86 592 2184530; fax: +86 592 2184530.
E-mail address: xichen@xmu.edu.cn (X. Chen).

fluorescence [5], chemiluminescence [6], liquid chromatography [7] and electrochemical methods [8–12] have been reported for the determination of AA. Among them, electrochemical methods are considered to be one of the most potential approaches because of their high sensitivity and simplicity, and low cost. However, direct oxidation of AA at bare electrodes is irreversible and the product, 2,3-diketogluconic acid, is readily adsorbed onto the electrode surface and thus results in the electrode fouling [13,14] and a high overpotential for AA oxidation. In addition, electrochemical oxidation of AA and co-existing electroactive components such as uric acid (UA) and dopamine (DA) results in highly overlapping peaks, leading to poor reproducibility and low selectivity. Therefore, the selective detection of AA in the presence of the other two species or their simultaneous determination has been a major goal of much research [10,11]. In all cases, modifications of bare electrodes with nanomaterials as the redox active site have been used in the design and development of electrochemical sensors. Thus, the design of new nanomaterials is most necessary and has become a challenging research topic.

Recently, noble metal nanoparticles (NMNPs, such as Au, Ag, Pt, Pd, Ru and their alloys) have emerged as a new class of compounds and received increasing attention [15] owing to their unique electrical, magnetic, optical, and catalytic properties. Among them, Pd-based catalysts have become a hot topic of interest because of their lower cost and greater resistance to CO in comparison with Pt catalysts [16]. Pd nanomaterials have also been used for making various types of electrochemical sensors. For example, there are reports of electrospining PdNPs loaded carbon nonofiber modified electrode for simultaneous electrochemical determination of DA, UA and AA [17]; Pd incorporated poly(3,4-ethylenedioxythiophene) films for simultaneous determination of DA and UA [18]; and an utrathin Pd nanowire modified electrode for selective detection of AA [11]. Importantly, these electrocatalytic activities differ from those of the bulk materials mainly depending on the particle size and morphology. On the other hand, the emergence of graphene nanosheet has recently opened up an exciting new field in the science and technology of two-dimensional nanomaterials with continuously growing academic and technological impetus [19]. Graphene can be used as an excellent electrocatalytic material towards the determination of a variety of electroactive species including AA, DA and UA [20,21].

Composite nanomaterials that consist of nanocarbons in combination with nanometals are of considerable interest due to their novel optical, electronic and catalytic properties [22]. Many methods are reported involving the modification of graphene or graphene oxide (GO) with NMNPs in order to combine the unique properties of graphene with the high electrocatalytic activity of NMNPs. However, the usage of reducing agents such as sodium borohydride [23] and hydrazine hydrate [24] is hazardous. In addition, surfactants are always needed to prevent potential agglomeration, which may influence the physicochemical properties and limit the further applications of the nanocomposites [25]. Recently, we note that GO can act as a reductant and dispersant in the synthesis of PdNPs doped GO, and "clean" and well-dispersive PdNPs doped GO can be obtained without the additional reductant and surfactants [26]. The as-made PdNPs-GO express high electrocatalytic ability in formic acid and ethanol oxidation relative to a commercial Pd/C catalyst. Based on these result, in our work, a PdNPs-GO modified glassy carbon electrode (GCE) was developed and applied in the detection of AA. Cyclic voltammetric results showed that the PdNPs-GO modified GCE presented obvious electrocatalytic activity towards AA, and the amperometric i–t curves indicated that the modified electrode was highly sensitive and had stable sensing characteristics for AA.

2. Experimental

2.1. Reagents

Graphite powder was purchased from the Lvyin Co. (Xiamen, China); potassium permanganate, concentrated sulfuric acid and sodium nitrate were obtained from the Chemical Reagent Company of Shanghai (China); K_2PdCl_4 was purchased from the Wake Pure Chemicals, Co. Ltd. (Osaka, Japan); DA and UA from Alfa Aesar (Ward Hill, MA); AA from the Chemical Reagent Company of Guangzhou (China); and 0.05 M phosphate buffer solution (PBS, pH 7.4) was employed as a supporting electrolyte. Rod GCEs were from the BAS Co. Ltd. (Tokyo, Japan). All other reagents were of analytical grade and used without further purification. The pure water for solution preparation was from a Millipore Autopure WR600A system (Millipore Ltd., USA).

2.2. Instruments

The morphology of PdNPs-GO was examined using a high resolution transmission electron microscope (HRTEM, FEI Tecnai-F30 FEG). Electrochemical measurements were performed using a CHI 660B Electrochemical Analyzer (CHI Co., Shanghai, China). A conventional three-electrode system was used comprising a GCE coated with PdNPs-GO film, a platinum auxiliary electrode and a saturated calomel reference electrode.

2.3. Preparation of GO and PdNPs-GO

GO was prepared from natural graphite using the modified Hummers' method [27,28]. 50 mg as-synthesized GO was dispersed in 100 mL water to obtain a yellow-brown aqueous solution with the aid of ultrasonication. The resulting GO solution was heated in an oil bath at 100 °C for 24 h to obtain thermal reduction [29].

Decoration of PdNPs onto GO was achieved using the auto redox method based on our previous studies with little modified [26]. In a typical experiment, a homogeneous GO suspension (5 mL 0.5 mg mL^{-1}) and K_2PdCl_4 (0.5 mL 10 mM) aqueous solution were kept in a vial under vigorous stirring for 30 min at 30 °C. Then, the reaction mixture was washed with pure water and centrifuged to remove the remaining reagents.

2.4. Preparation of PdNPs-GO modified GCE

Before the modification, a GCE was polished with 1, 0.3, and 0.05 μm α-Al$_2$O$_3$, sequentially. After ultrasonic concussion, the polished GCE was dried at room temperature. 4 μL PdNPs-GO suspensions were then dropped onto the GCE surface. The electrode was subsequently dried at room temperature to finish the modification.

3. Results and discussion

3.1. Characterization of PdNPs-GO

The TEM and HRTEM images depicted in Fig. 1 show the direct morphological observations of the as-prepared PdNPs-GO. In Fig. 1A, it can be seen that the PdNPs are well distributed, with a high density on the GO surfaces, which could be confirmed by the characteristic wrinkles on the sheets [30]. A higher magnification TEM image, as shown in Fig. 1B, indicated that PdNPs appeared spherical in shape, and gave a narrow particle size distribution with a mean diameter at 2.6 nm. The HRTEM image (Fig. 1C) of the PdNPs shows that the interplanar spacing of the particle lattice was 0.229 nm, which agreed with the (1 1 1) lattice spacing of facecentered cubic Pd (0.224 nm).
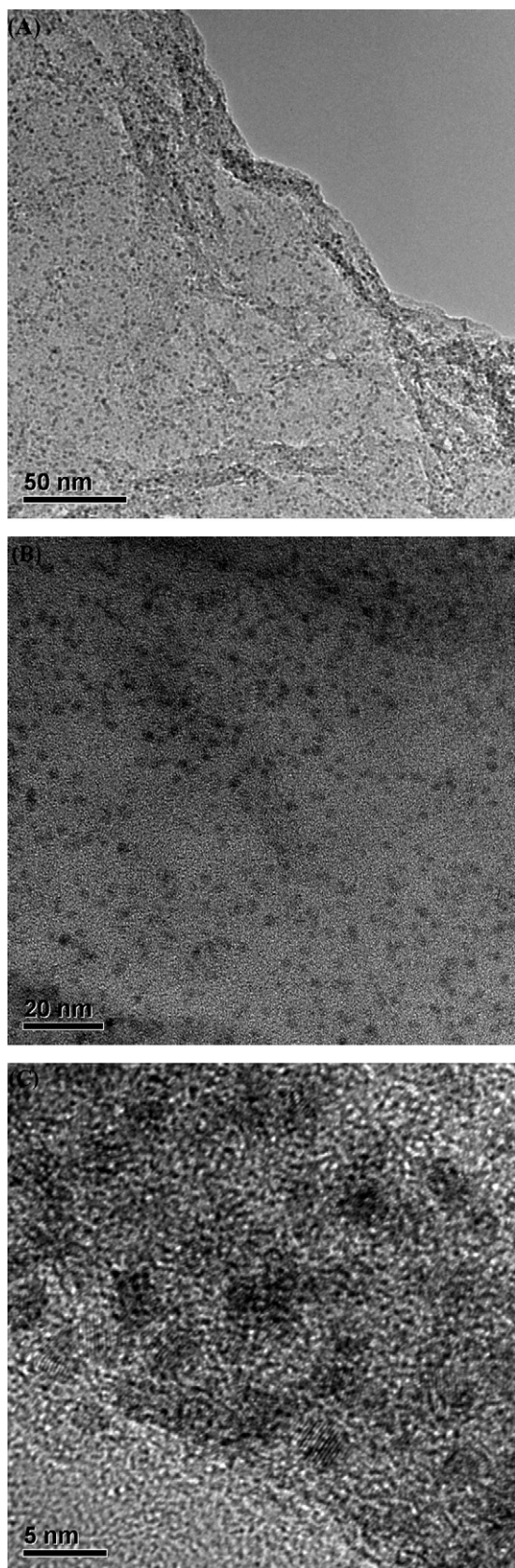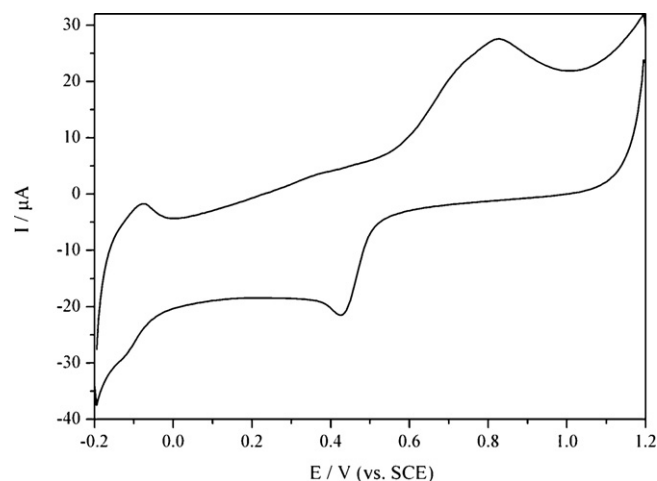
Fig. 2. Cyclic voltammograms of PdNPs-GO modified GCE in a 0.5 M H_2SO_4 solution at a potential scan rate of 50 mV s^{-1}.

Cyclic voltammetry (CV) was used to characterize the PdNPs-GO modified GCE in a solution of 0.5 M H_2SO_4 (Fig. 2). Hydrogen adsorption and absorption started at around −0.003 V. A single peak of surface oxide formation could be observed at 0.825 V during the first voltammetric scan. Oxide reduction occurred at 0.429 V. Both peaks showed the typical features of a Pd electrode [31], indicating that the nanocomposite maintained the electrochemical performance of the PdNPs.

3.2. Electrocatalytic oxidation of AA, DA and UA

Fig. 3 shows the individual CV results of 2 mM AA, 0.5 mM DA and 1 mM UA using a bare GC, a Pd electrode and a PdNPs-GO modified electrode, respectively. All of the electrodes exhibited an electrocatalytical oxidation response towards AA, DA and UA, but the difference of their oxidation potentials was small at the bare GCE (Fig. 3A) and the Pd electrode (Fig. 3C). The anodic peak potential difference (ΔE) of AA and DA at the GCE was 0.050 V and at the Pd electrode 0.095 V. Moreover, the oxidation peak of AA was broader and highly overlapped with those of UA and DA. Using the PdNPs-GO modified electrode, a narrow oxidation peak of AA could be obtained at 0.006 V, and the ΔE between AA and DA was 0.172 V, almost three fold that from the bare GCE. Another notable difference between the three electrodes was that the anodic peak potential of AA at the PdNPs-GO modified electrode was shifted negatively. It is known that AA oxidation is an inner-sphere reaction and the electron transfer kinetics are sensitive to the electrode's surface properties [32]. Thus, such an improvement in electron transfer kinetics can partially be ascribed to the catalytic activity of PdNPs [33]. In addition, the high density of edge plane-like defective sites on thermal reduction GO sheets offers some favorable sites for transferring the electron to bimolecular, which would facilitate/accelerate the electron transfer between electrode surface and electroactive species in solution [34]. In general, "clean" and well-dispersive PdNPs doped GO integrated the unique properties of graphene and the high electrocatalytic activity of PdNPs as proposed. Moreover, the larger ΔE between AA and DA or UA indicated the possibility of amperometric sensing of AA with high selectivity by selecting an appropriate potential.

3.3. Amperometric sensing of AA

The amperometric response of the PdNPs-GO modified GCE to successive additions of AA was further evaluated under optimized experimental conditions. Fig. 4 shows the amperometric

Fig. 1. (A and B) TEM and (C) HRTEM images of the synthesized PdNPs-GO.

Table 1

Comparison of the working potential, linear range, correlation coefficient, and actual applications of PdNPs-GO modified GCE with some other chemical modified electrodes from the previous methods.

| Sensing surface	E (mV)	Linear range (mM)	R^2	Applications	Ref.
Poly(eriochrome black T)/GCE	150	0.15–1	0.9913	–	[35]
Pt/Au/GCE	200	0.103–0.165	0.9906	Vitamin C tablet	[36]
PAN nano-network-ABSA/GCE	150	0.035–0.175	0.998	Vitamin C tablet and Urine	[37]
Ag/CNT–CPE	200	0.03–2	0.9983	–	[38]
MWNT–SiNW–AuNPs/GCE	200	1–5	0.9992	Pharmaceutical and fruit juices	[10]
PdNPs-GO/GCE	100	0.02–2.28	0.9991	Vitamin C tablet	This work
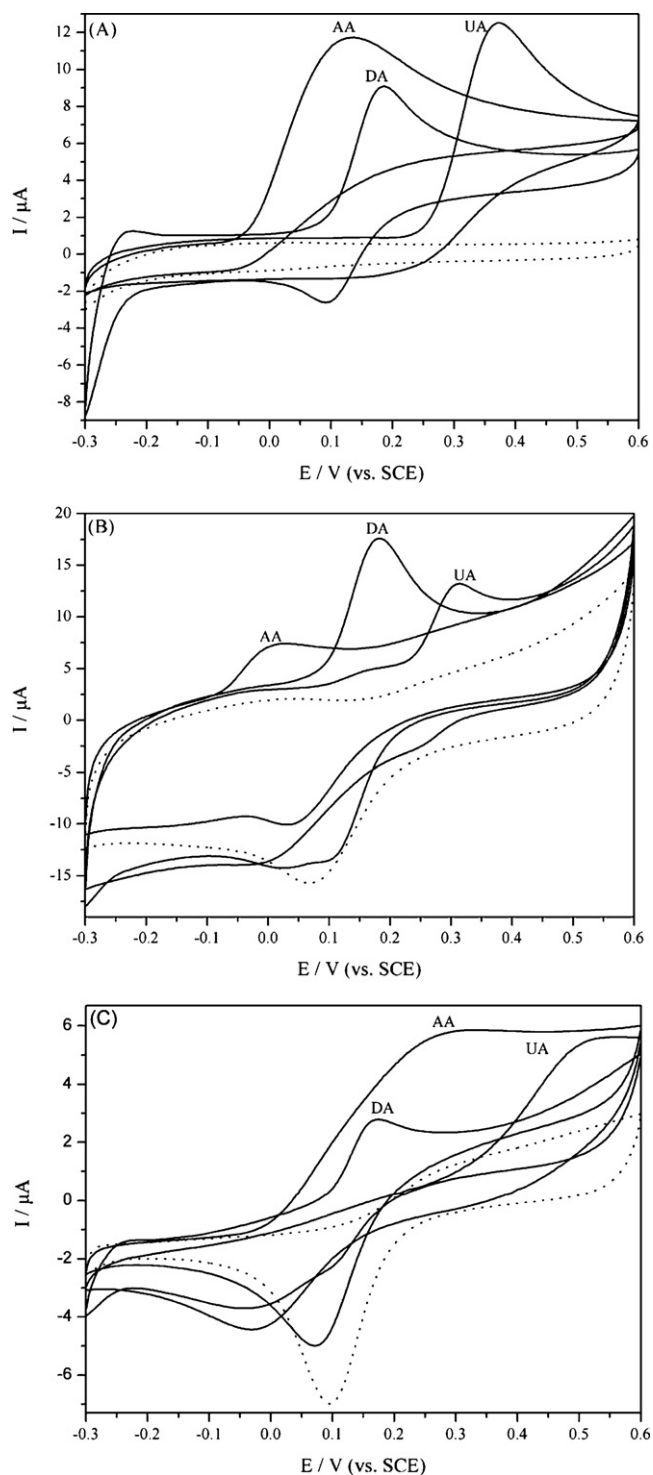
Fig. 3. (A) CVs of 0.05 M PBS (dotted line) with AA (2 mM), DA (0.5 mM) and UA (1 mM) at the surface of (A) bare GC; (B) PdNPs-GO modified; and (C) bare Pd electrodes. Scan rate: 50 mV s^{-1}.

current–time response of AA at 0.1 V. As illustrated, upon addition of an aliquot of AA to the stirred PBS, the oxidation current increased steeply and reached a steady-state current within 5 s. The amperometric signal showed a good linear correlation to AA concentration in the range from 20 µM to 2.28 mM. The linear regression equation was expressed as I_{pa} (µA) = −1.805 + 6.148 C_{AA} (mM) with a correlation coefficient of R = 0.9991 (n = 26). Table 1 illustrated the comparison of some response characteristics of the proposed modified electrode with those previously reported. The proposed approach exhibited lower overvoltage and broader linear range.

3.4. Selectivity and stability

Generally, co-existing electroactive components such as UA and DA show serious interference in the electrochemical detection of AA. Therefore, the amperometric responses of DA and UA were also tested. The normal physiological level of AA and UA is generally much higher than that of DA (100–1000 times) [39]. Thus, the interfering effects of successive additions of 1 µM DA and 100 µM UA were examined with reference to 100 µM AA and presented in Fig. 5. If the amperometric response of AA was set as 1, the responses of DA and UA were only 3.47 and 8.82%.

Stability of the PdNPs-GO modified GCE in the measurements was investigated in the presence of 2 mM of AA. After 30 successive measurements, only 1.6% decrease of the original response could be found for the modified GCE. The storage stability of the modified GCEs was also tested by keeping these electrodes at room temperature in a dark place. After 2 weeks storage, these modified electrodes still maintained 86% of their original activity, and displayed good response towards the concentration change of AA.
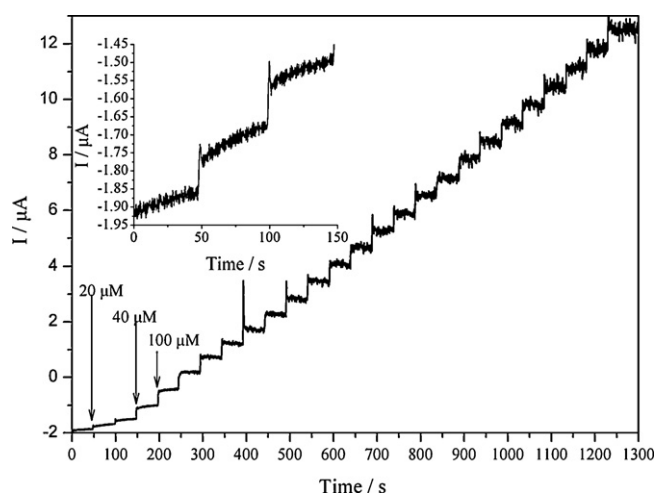

Fig. 4. Typical amperometric responses of the PdNPs-GO modified GCE to successive additions of AA at 0.02, 0.04 and 0.1 mM with stirring in 0.05 M PBS (pH 7.4) at a potential of 0.10 V. The inset shows the amperometric responses of two sensors to AA in 150 s.
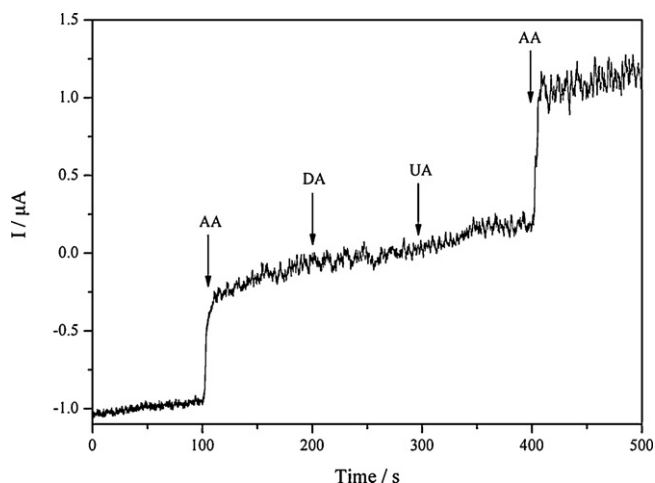
Fig. 5. Amperometric response of the PdNPs-GO modified GCE to successive additions of 100 μM AA, 1 μM DA, 100 μM UA and 100 μM AA with stirring in 0.05 M PBS (pH 7.4) at a potential of 0.10 V.

Table 2
Determination of AA in vitamin C tablets ($n = 3$).

Sample	Content (μM)	Add (μM)	Found (μM)	Recovery	RSD%
1	22.7	40	63.5	103.4	9.61
2	45.4	40	81.5	91.4	7.07
3	68.1	40	107.5	99.1	4.32

3.5. Sample analysis

In order to study the applicability of the PdNPs-GO modified electrode, the content of AA in vitamin C tablets was analyzed. Vitamin C tablets were firstly dissolved in PBS (pH 7.4). In the analysis, the standard addition method was applied, by which a known amount of AA in PBS (pH 7.4) was added into the test solution. The recovery for the determination of AA was in the range of 91.4–103.4% for three samples were illustrated in Table 2, indicating the potential usefulness of the PdNPs-GO modified GCE for the practical determination of AA in real samples.

4. Conclusions

In summary, we successfully constructed a PdNPs-GO modified GCE for AA electrochemical sensing. In comparison to GC and Pd electrodes, the modified electrode provided superior electrocatalytic activity towards the oxidation of AA. The low oxidation potential and larger peak difference between AA and DA on the PdNPs-GO modified GCE could be contributed by the synergistic effect of GO and PdNPs. In amperometric current–time measurements, the modified electrode showed excellent selectivity and high sensitivity towards AA in the presence of DA and UA. Moreover, the proposed method was applied to the determination of AA

in real samples with satisfactory results. Thus, it is believed that this new nanocomposite, PdNPs-GO, can provide a novel platform for the construction of sensitive and selective biosensors.

References

[1] S. Klebanoff, D. Dziewiatkowski, G. Okinaka, J. Gen. Physiol. 42 (1958) 303–318.
[2] B.A. Eipper, R.E. Mains, C.C. Glembotski, Proc. Natl. Acad. Sci. U.S.A. 80 (1983) 5144–5148.
[3] M.B. Davies, J. Austin, D.A. Partridge, Vitamin C: Its Chemistry and Biochemistry, The Royal Society of Chemistry, Cambridge, 1991.
[4] T. Wu, Y. Guan, J. Ye, Food Chem. 100 (2007) 1573–1579.
[5] X. Wu, Y. Diao, C. Sun, J. Yang, Y. Wang, S. Sun, Talanta 59 (2003) 95–99.
[6] N. Anastos, N.W. Barnett, B.J. Hindson, C.E. Lenehan, S.W. Lewis, Talanta 64 (2004) 130–134.
[7] L. Nováková, D. Solichová, P. Solich, J. Chromatogr. A 1216 (2009) 4574–4581.
[8] J. Kulys, E.J. D'Costa, Anal. Chim. Acta 243 (1991) 173–178.
[9] S.A. Kumar, P.H. Lo, S.M. Chen, Biosens. Bioelectron. 24 (2008) 518–523.
[10] D. Ragupathy, A.I. Gopalan, K.P. Lee, Sens. Actuators B 143 (2010) 696–703.
[11] D. Wen, S. Guo, S. Dong, E. Wang, Biosens. Bioelectron. 26 (2010) 1056–1061.
[12] S. Qiu, S. Gao, Q. Liu, Z. Lin, B. Qiu, G. Chen, Biosens. Bioelectron. 26 (2011) 4326–4330.
[13] F. Prieto, B.A. Coles, G. Richard, J. Phys. Chem. B 102 (1998) 7442–7447.
[14] C.R. Raj, K. Tokuda, T. Ohsaka, Bioelectrochemistry 53 (2001) 183–191.
[15] B. Wu, Y. Kuang, X. Zhang, J. Chen, Nano Today (2011) 75–90.
[16] Z. Zhang, J. Ge, L. Ma, J. Liao, T. Lu, W. Xing, Fuel Cells 9 (2009) 114–120.
[17] J. Huang, Y. Liu, H. Hou, T. You, Biosens. Bioelectron. 24 (2008) 632–637.
[18] S. Harish, J. Mathiyarasu, K.L.N. Phani, V. Yegnaraman, J. Appl. Electrochem. 38 (2008) 1583–1588.
[19] S. Guo, S. Dong, Chem. Soc. Rev. 40 (2011) 2644–2672.
[20] F. Li, J. Li, Y. Feng, L. Yang, Z. Du, Sens. Actuators B 20 (2011) 110–114.
[21] J. Ping, J. Wu, Y. Wang, Y. Ying, Biosens. Bioelectron. 34 (2012) 70–76.
[22] C.L. Sun, H.H. Lee, J.M. Yang, C.C. Wu, Biosens. Bioelectron. 26 (2011) 3450–3455.
[23] R. Muszynski, B. Seger, P.V. Kamat, J. Phys. Chem. C 112 (2008) 5263–5266.
[24] L.M. Lu, H.B. Li, F. Qu, X.B. Zhang, G.L. Shen, R.Q. Yu, Biosens. Bioelectron. 26 (2011) 3500–3504.
[25] Y. Chen, X. Zheng, H. Wang, W. Zheng, Thin Solid Films 520 (2011) 179–185.
[26] X. Chen, G. Wu, J. Chen, Z. Xie, X. Wang, J. Am. Chem. Soc. 133 (2011) 3693–3695.
[27] S. William, J. Hummers, R. Offeman, J. Am. Chem. Soc. 80 (1958) 1339–1341.
[28] L.J. Cote, F. Kim, J. Huang, J. Am. Chem. Soc. 131 (2008) 1043–1049.
[29] Z. Lin, Y. Yao, Z. Li, Y. Liu, C.P. Wong, J. Phys. Chem. C 114 (2010) 14819–14825.
[30] A. Gil, S. Adhikari, F. Scarpa, J. Bonet, J. Phys.: Condens. Matter 22 (2010) 145302.
[31] M. Hara, U. Linke, T. Wandlowski, Electrochim. Acta 52 (2007) 5733–5748.
[32] N. Maleki, A. Safavi, F. Tajabadi, Anal. Chem. 78 (2006) 3820–3826.
[33] P.R. Roy, M.S. Saha, T. Okajima, T. Ohsaka, Electroanalysis 16 (2004) 289–297.
[34] Z.H. Sheng, X.Q. Zheng, J.Y. Xu, W.J. Bao, F.B. Wang, X.H. Xia, Biosens. Bioelectron. 34 (2012) 125–131.
[35] H. Yao, Y. Sun, X. Lin, Y. Tang, L. Huang, Electrochim. Acta 52 (2007) 6165–6171.
[36] S. Thiagarajan, S.M. Chen, Talanta 74 (2007) 212–222.
[37] L. Zhang, C. Zhang, J. Lian, Biosens. Bioelectron. 24 (2008) 690–695.
[38] J. Tashkhourian, M. Nezhad, J. Khodavesi, S. Javadi, J. Electroanal. Chem. 633 (2009) 85–91.
[39] R.M. Wightman, L.J. May, A.C. Michael, Anal. Chem. 60 (1988) 769–779.