

Carbon nanotubes/alizarin red S–poly(vinylferrocene) modified glassy carbon electrode for selective determination of dopamine in the presence of ascorbic acid

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Abstract A modified electrode was fabricated by electrochemical formation of poly(vinylferrocene) on the multi-wall carbon nanotube-alizarin red S matrix covered glassy carbon electrode. A higher electrochemical activity was obtained to the electrocatalytic oxidation of dopamine. The electrode surface was characterized electrochemically and spectroscopically. Poly(vinylferrocene) (PVF) in electrode was used as an electron transfer mediator in the electrochemical oxidation of compounds due to its perfect reversible redox properties. Multi-wall carbon nanotubes (MWCNTs) / alizarin red S (ARS)–PVF electrode was used to the determination of dopamine in the presence of ascorbic acid in 0.1 M sulphate buffer solution at pH 7. The performance of the MWCNTs/ARS–PVF electrode was evaluated by DPV and amperometry.

Keywords Poly(vinylferrocene) · Multi-walled carbon nanotubes · Alizarin red S · Dopamine

Introduction

Composite electrodes are widely used in analytical application as sensors [1]. Preparation of composite electrodes by incorporation of carbon nanotubes (CNTs) and polymers on the electrode surface can enhance the catalytic activity of the electrodes [2]. An important ability of CNTs is promoting electron transfer in electrochemical reactions for electroanalytical applications [3]. CNT has also mechanical properties with high effective surface area. The modification of electrode surfaces with redox active polymers has also found significant interest in electrochemistry. One of the most common polymers to be studied is poly(vinylferrocene) (PVF). Analytical applications of PVF layers include the deployment in biosensors [4–7].

Dopamine (DA), belonging to the class of catecholamines, has an important role in the function of central nervous, renal, hormonal, and cardiovascular systems [8, 9]. Changes in its concentration results in several disorders like Parkinson's disease and schizophrenia due to decrease in DA levels [8]. Therefore, selective and sensitive quantification of DA is fully required. The development of methods for the quantification of DA in blood and biological fluids has found the wide research area [10, 11]. DA is easily oxidized so that it is very suitable for electrochemical analysis. However, electrochemical oxidation of DA at conventional electrodes is difficult because of fouling of the electrode surface due to the adsorption of oxidation products and interference of ascorbic acid (AA) in biological fluids, which also undergoes oxidation more or less at the same potential. Therefore, development of a DA sensor using voltammetric method for the detection of DA in the presence of AA is a difficult subject. An electrochemical sensor for DA and serotonin prepared by

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covalent modification of 5-hydroxy tryptophan on glassy carbon (GC) has been proposed [12]. Another report has been the selective nanomolar detection of DA in the presence of 3,4-dihydroxyphenylalanine (L-dopa), AA, uric acid (UA), and other DA metabolites by using a boron-doped diamond modified by successive polymerization of tyramine and pyrrole-1-propionic acid [13]. Simultaneous determination of DA, AA, and UA at a GC electrode modified by polymerization of acid chrome blue has been described [14].

In this work, we report a new method for the deposition of a thin composite film of multi-wall carbon nanotubes (MWCNTs) / alizarin red S (ARS) with poly(vinylferrocene) (PVF) on a glassy carbon electrode. The MWCNTs–ARS film was fabricated on the surface of a glassy carbon electrode by the electropolymerization of ARS in the MWCNTs–ARS solution [15]. Then vinylferrocene was electropolymerized on the MWCNTs–ARS film. The thin MWCNTs/ARS–PVF film was characterized by surface enhanced Raman spectroscopy (SERS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and UV-Vis methods. The strong electrocatalytic activity of the modified electrode toward DA was observed and used in the selective and sensitive determination of DA in the presence of AA.

Experimental

Reagents and apparatus

Vinylferrocene, L-ascorbic acid (AA), dopamine HCl (DA), and MWCNTs were obtained from Sigma-Aldrich (Taufkirchen, Germany). Phosphate (0.1 M) buffer solution of pH 7 was employed as the electrolytic medium. The sulphate buffer solution (SBS) was prepared from NaHSO₄ and Na₂SO₄. Alizarin red S and tetrabutylammoniumtetrafluoroborate (TBABF₄) were obtained from Aldrich and used without further purification. All aqueous solutions were prepared using deionized water (18.2 MΩ cm) free from organic matter, obtained from a millipore purification system, deaerated with argon to remove the oxygen present.

Electrochemical experiments were performed with a Gamry Potentiostat (model reference 600), CH instruments (Model 660). A conventional three-electrode system consisting of a glassy carbon working electrode (GC) (3 mm, BAS, Inc.), a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE), was employed. All data points reported in this work represent the average of three replicates. All experiments were run at room temperature. UV-Vis and SERS spectra were obtained by Perkin Elmer Lambda 750 spectrometer and DeltaNu, respectively. SEM images were taken by Nova NanoSEM 600.

Preparation of MWCNTs/ARS–PVF-modified GC

Reproducible modified electrode is possible if GC electrode is activated with pretreatment. Activation of electrode is performed firstly by mechanical polishing over a micro-cloth with 0.05-mM alumina slurry after rinsed and ultrasonicated in ethanol and double distilled deionized water. In our experiment, the open-ended and cut 1 mg MWCNTs and 1 mg mL⁻¹ ARS aqueous solution was mixed. Due to their special molecular structure, ARS molecules interacted with MWCNTs by non-covalent interactions to dissolve the MWCNTs into aqueous solution [15]. The resulting mixture solution was stirred for 30 min with a magnetic stirring bar. This solution was quite stable as even after 3 months the MWCNTs did not precipitate from the ARS solution. Electrodeposition of MWCNTs–ARS on GC electrode carried at 2.2 V and 0.0 V at a scan rate of 100 mV s⁻¹ for 30 scans in aqueous solution. The resulting coated electrode was briefly left to dry in the air before use. Then, the MWCNTs/ARS–GC electrode was coated with poly(vinylferrocene) by electrochemical polymerization. The procedure involved scanning between 1.0 and -1.2 V (vs. Ag wire) in a 0.025-mM vinylferrocene solution in acetonitrile, with 0.1-M TBABF₄ as supporting electrolyte, at a scan rate of 100 mV s⁻¹ for 15 scans. For comparative amperometric study, MWCNTs-coated GC electrode was also prepared. The cleaned GC electrode was coated by casting 50 μL of the black suspension of MWCNTs and dried in air.

Result and discussion

Electrodeposition of MWCNTs/ARS–PVF film

Deposition of MWCNTs was achieved electrochemically on GC electrode scanning between 0.0 and 2.2 V vs. SCE in an aqueous solution containing 1 mg mL⁻¹ MWCNTs and 1 mg mL⁻¹ ARS. Typical cyclic voltammogram was shown in Fig. 1. The oxidation current after about 1.5 V decreased with increasing cycle number. This denoted that the surface of GC electrode changed in each cycle, in other words, MWCNTs deposited on the electrode surface in the presence of ARS. On this modified electrode, polyvinylferrocene was electropolymerized by scanning between 1.0 and -1.2 V vs. Ag/AgCl in an acetonitrile solution containing 0.025 mM vinylferrocene monomer. It is clear that the oxidation and reduction peak currents observed at 0.6 V and 0.2 V increased with increasing cycle number as shown in Fig. 2. Figure 3c shows the cyclic voltammogram of this electrode (MWCNTs/ARS–PVF) in acetonitrile solution containing 0.1 M TBABF₄ (blank solution). The oxidation and reduction peaks about 0.5 V and 0.4 V

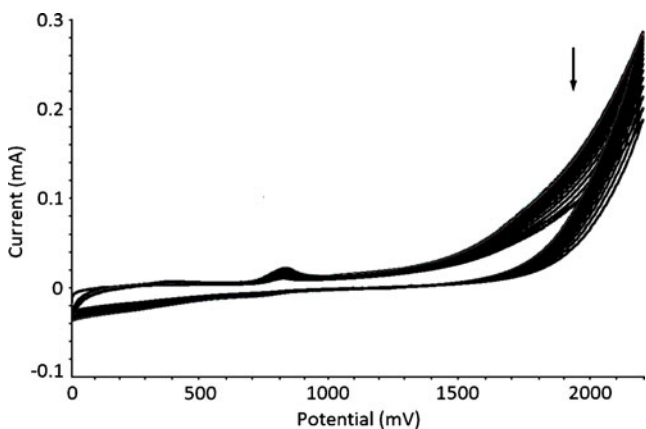


Fig. 1 Electrochemical deposition of MWCNTs with ARS scanning between 0.0 and 2.2 V on GC electrode, $\nu=100 \text{ mV s}^{-1}$

should belong to ferrocene moiety on the electrode surface. Besides, electrodeposition of vinylferrocene was examined on the bare GC electrode electrochemically under the same condition as shown in Fig. 3b and the peaks of ferrocene moiety which was taken from blank solution was not observed. This observation indicates that vinylferrocene was not deposited on GC electrode without MWCNTs/ARS.

For optimum coating of MWCNTs/ARS on electrode surface, various numbers of cycles were examined. From these voltammograms, the maximum oxidation current of ferrocene moiety was observed when the cycle number was 30. After this point, the current is decreased. According to this result, optimum cycle number for coating with MWCNTs/ARS was determined as 30. Also optimum cycle number for electrodeposition of ferrocene moiety was examined and ferrocene moiety was found to be 15 cycles on these modified electrodes in vinylferrocene monomer solution.

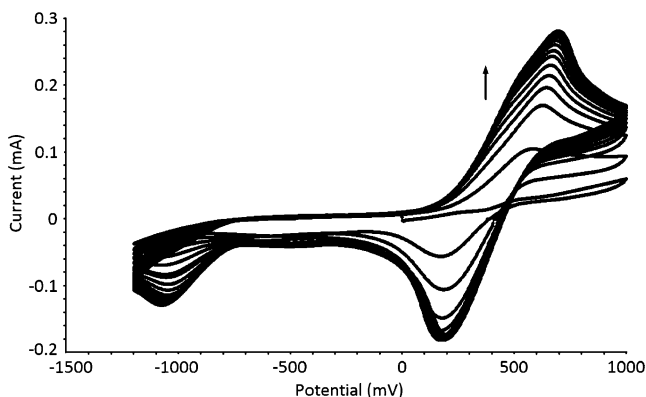


Fig. 2 Electrochemical deposition of poly(vinylferrocene) scanning between -1.2 and 1.0 V on MWCNTs–ARS-coated GC electrode, $\nu=100 \text{ mV s}^{-1}$

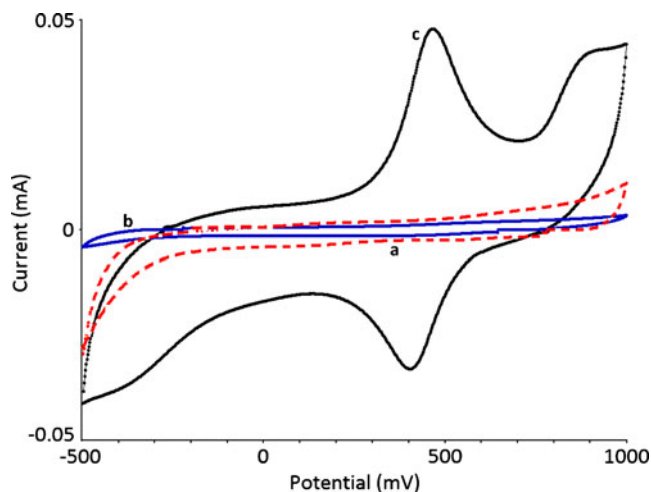


Fig. 3 Electrochemical behaviour of modified electrodes in acetonitrile (blank solution), (a) MWCNT/ARS (b) PVF (c) MWCNTs/ARS–PVF-coated GC electrodes $\nu=100 \text{ mV s}^{-1}$

Characterization of MWCNTs/ARS–PVF-modified electrode

To investigate how the vinyl ferrocene was deposited on MWCNTs/ARS modified electrode, characterization of surface was performed by SERS, FTIR, and SEM measurements. SERS of MWCNTs/ARS–PVF-modified electrode surface was taken and compared with those of solid ferrocene, vinyl ferrocene, and also chemically synthesized PVF polymer as shown in Fig. 4. The spectrum of vinyl ferrocene

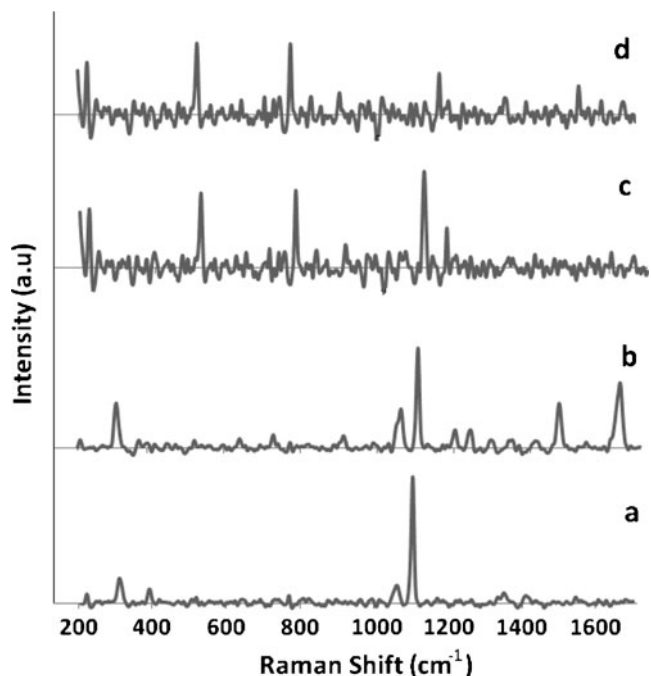
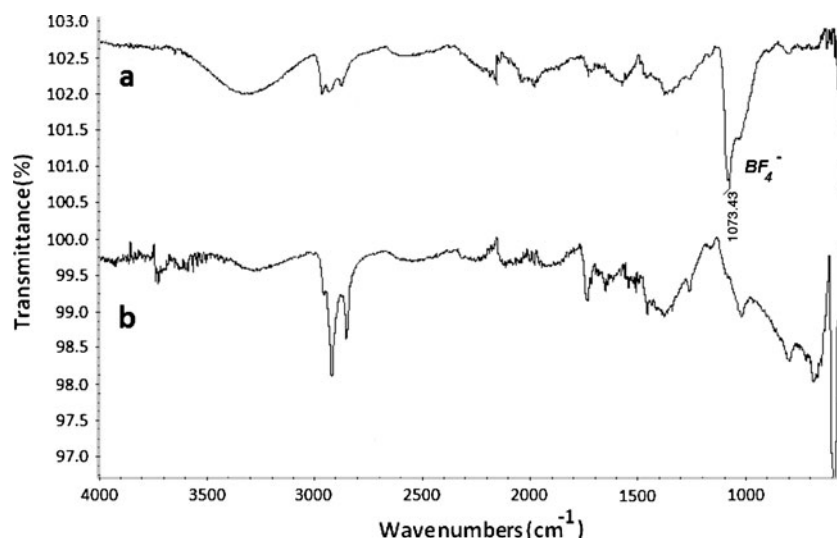


Fig. 4 SERS spectra of solid (a) ferrocene, (b) vinylferrocene, (c) PVF synthesized chemically, (d) MWCNTs/ARS–PVF-modified electrode

Fig. 5 FTIR spectra of
(a) MWCNTs/ARS and
(b) MWCNTs/ARS–PVF-coated
GC electrode



(Fig. 4b), the bands at 317, 1,057, and 1,105 cm^{-1} are assigned to ring-metal stretch, C–H bending and ring breathing in ferrocene moiety, respectively [16]. The peaks at 1,469 (CH_2 scissoring deformation) and 1,628 cm^{-1} [17]. (–C=C–stretching) are assigned to vinyl groups in vinyl ferrocene monomer when compared (Fig. 4a, b). Due to the absence of the band at 1,628 and 1,469 cm^{-1} , we also confirmed that the bands regarding vinyl groups disappeared in the spectrum of PVF synthesized chemically as shown in Fig. 4c. The new peaks at 224, 520, 771, and 1,109 cm^{-1} were observed. Similarly, the same peaks appeared in the spectrum of MWCNTs/ARS–PVF-modified electrode as displayed in Fig. 4d. Besides, the ring breathing band at 1,169 cm^{-1} in ferrocene moiety disappeared. One possible explanation is the interaction of ferrocene ring with the electrode surface. We focused our analysis on the spectral region around the strongest peak of PVF. In this region, the strongest peak of MWCNTs at 1,543 cm^{-1} assign to G band of related to E_{2g} graphite mode and indicating that C–C stretching vibrations [18].

FTIR spectrum of MWCNTs/ARS–PVF-modified electrode was taken and compared with that of MWCNTs/ARS as shown in Fig. 5. In the spectrum of MWCNTs/ARS (Fig. 5b), the bands in the 1,750–1,550 cm^{-1} range can be assigned to C=O groups in different structures (carboxylic acid, ketone/quinone) and to C=C in aromatic rings, whereas the bands in the range of 1,300–950 cm^{-1} prove the presence of C–O bonds in various chemical surroundings. A band of 1,550 cm^{-1} most probably due to aromatic and unsaturated of C=C bands near, 1,410 cm^{-1} due to sorbed water are present. In the spectrum of MWCNTs/ARS–PVF, the additional absorption band at 1,073 cm^{-1} was observed (Fig. 5a). This peak showed the presence of BF_4^- anion on the surface of modified film [19]. This means that PVF- BF_4 could be deposited on MWCNTs/ARS-coated electrode. The results of SERS and FT-IR spectra prove that the compound deposited electrochemically on MWCNTs/ARS-coated electrode in vinylferrocene/acetonitrile solution was PVF- BF_4 polymer.

Fig. 6 SEM image of
(a) MWCNTs/ARS and
(b) MWCNTs/ARS–PVF film
modified electrode

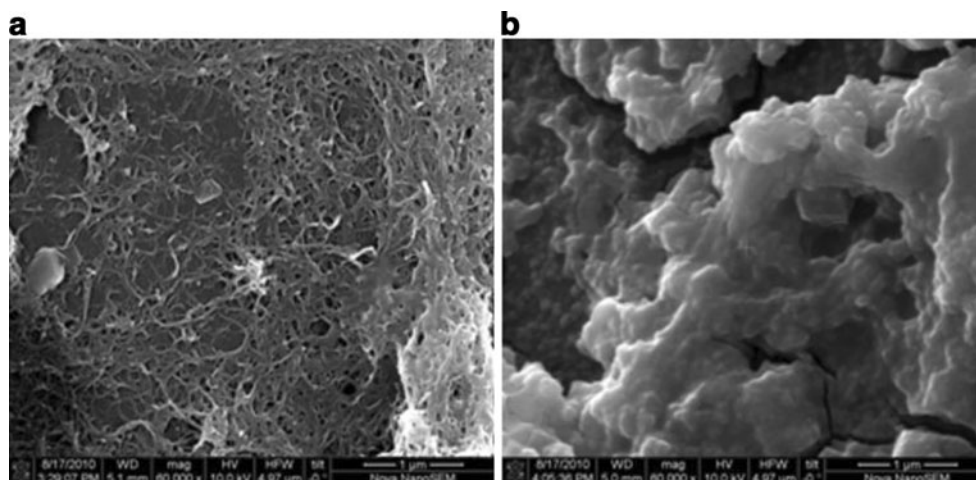


Figure 6 shows the typical SEM images of the MWCNTs/ARS and MWCNTs/ARS–PVF film deposited electrochemically on glassy carbon electrode. Figure 6a shows that MWCNTs was homogeneously dispersed on the electrode surface. As shown in Fig. 6b, the surface of the MWCNTs was covered by PVF film during electrochemical procedure. Finally, it can be claimed that a uniformly covered layer of PVF film modified MWCNT on the GC electrode could be prepared with electrochemical technique applied here according to SEM images. Energy dispersive X-ray spectroscopy study confirmed the presence of iron in the film structure (data not shown).

Dopamine selectivity of MWCNTs/ARS–PVF film

It is well-known that DA generally coexists with AA in real matrix and they indicate similar electrochemical behaviors at untreated carbon-based electrodes. Therefore, it is crucial and important to develop a method for the selective determination of DA in the presence of other interferences. Here, we examined the electrochemical behavior of MWCNTs/ARS–PVF film electrodes. The performance of MWCNTs/ARS–PVF film electrode was tested by taking differential pulse voltammetry in 0.06 mM DA and 0.06 mM AA as shown in Fig. 7. Two peaks were observed by MWCNTs/ARS–PVF film electrode at the potential values of +0.12 V and +0.55 V, corresponding to the oxidation of dopamine and PVF film, respectively. While the oxidation peak current value of AA at +0.35 V was much lower in the case of MWCNTs/ARS–PVF film electrode as shown in Fig. 7b. On the other hand, the oxidation peak current value of PVF was much lower when the MWCNTs/ARS–PVF film electrode was treated with AA.

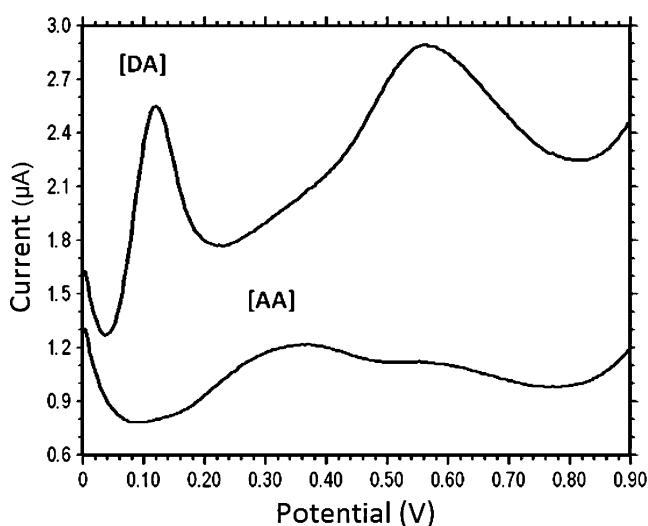


Fig. 7 DPV voltammograms obtained from same concentrations of AA and DA, $6.0 \times 10^{-5} \text{ mol L}^{-1}$

To verify the facility of MWCNTs/ARS–PVF-modified electrode for the selective determination of DA in the presence of AA, differential pulse voltammograms were recorded for varying concentrations of DA in the presence of fixed amount of AA. Figure 8 shows the differential pulse voltammetry (DPV) curves of the different DA concentrations on MWCNTs/ARS–PVF film electrode coexisting 0.6 M of AA. As shown in Fig. 8, the electrooxidation peak current of DA was selectively determined at 0.12 V on the surface of MWCNTs/ARS–PVF-modified electrode in the presence of AA. This may arise from the complexation between diol group in dopamine and iron ion in ferrocene moiety [20].

Interactions of DA with PVF/PVF⁺ polymer were also investigated by UV-Vis spectroscopy. Firstly, PVF⁺BF₄⁻ film was deposited potentiostatically at 0.70 V on indium tin oxide (ITO) electrode. Next, the coated electrodes were immersed in $5.0 \times 10^2 \text{ mM}$ DA solutions for 10 min and then immersed in water to remove these compounds adsorbed on electrode surface. Figure 9 shows UV-Vis spectra of the electrodes before and after these treatments. For comparison, the spectrum of PVF-coated electrode was recorded and given in the same figure. PVF-coated electrode was prepared by immersing the ITO electrode into the solution of 1.0 mg mL^{-1} PVF in methylene chloride and following solvent evaporation [21]. One can speak of two major absorption bands that can be singled out in the spectra of PVF/PVF⁺. The first band with a pronounced maximum about 450 nm that corresponds to π - π^* electronic transitions in the case of a PVF film (reduced state) and other absorption band corresponding to the oxidized film fragments in deposited film as PVF⁺BF₄⁻ about 650 nm. As seen from this figure, the ratio peak

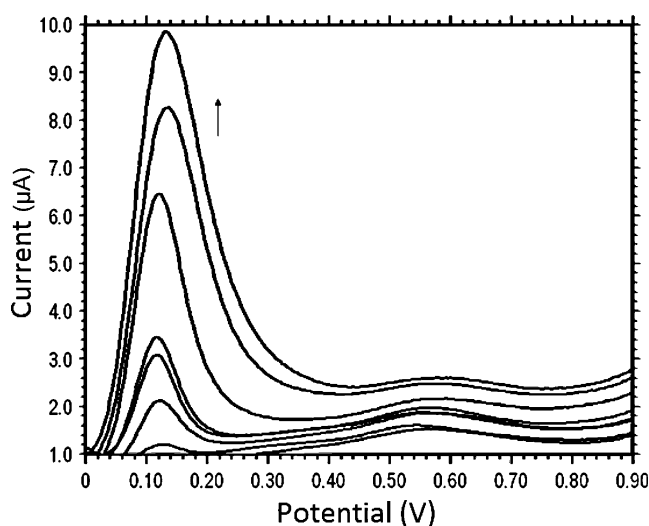


Fig. 8 DPV voltammograms of the MWCNTs/ARS–PVF electrode in pH 7 SBS with a mixture of AA 0.6 mM and various concentrations of DA between $1.0 \times 10^{-5} \text{ mol L}^{-1}$ and $6.0 \times 10^{-5} \text{ mol L}^{-1}$

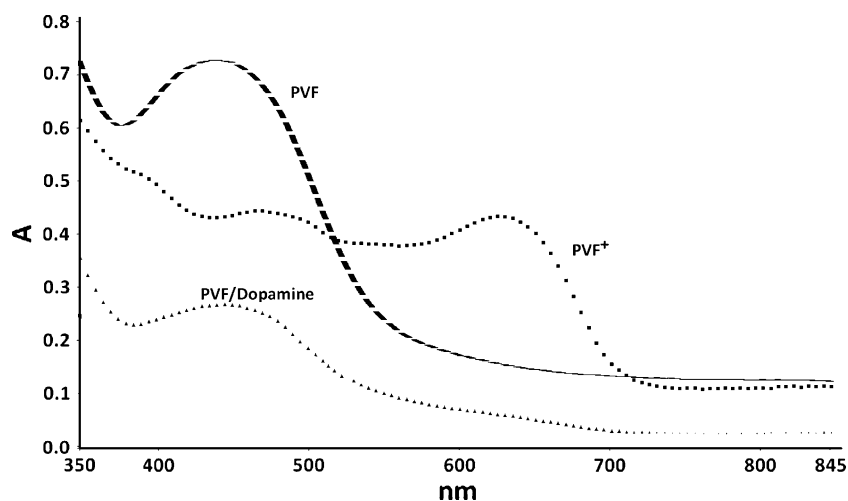


Fig. 9 UV-Vis spectra of PVF, PVF⁺-coated electrodes and also PVF⁺ electrode after interaction with 5.0×10^{-2} mM DA solution

intensity observed at 650 to 450 nm decrease after interaction of DA. It can be concluded from UV-Vis spectra that PVF⁺ on the MWCNTs/ARS–PVF film electrode reduces to PVF after interaction of dopamine.

DPV determination of DA

The determination of DA concentration was performed using DPV method. The DPV curves of the different DA concentrations were recorded in SBS buffer at pH 7. The optimum pH was determined as 7 and used in the subsequent experiments. Figure 10 shows the DPV curves of the different DA concentrations on the MWCNTs/ARS–PVF film electrode. The results show that the measured peak current is proportional to DA concentration in the range of 2×10^{-6} to 3×10^{-4} mol L⁻¹. The linear equation is obtained through I_{DA} (10^{-6} A) = $-2.47 + 0.21 c_{DA}$ (10^{-6} mol L⁻¹) with a linear relative coefficient of $r^2 = 0.9924$ and a detection limit of $2 \times$

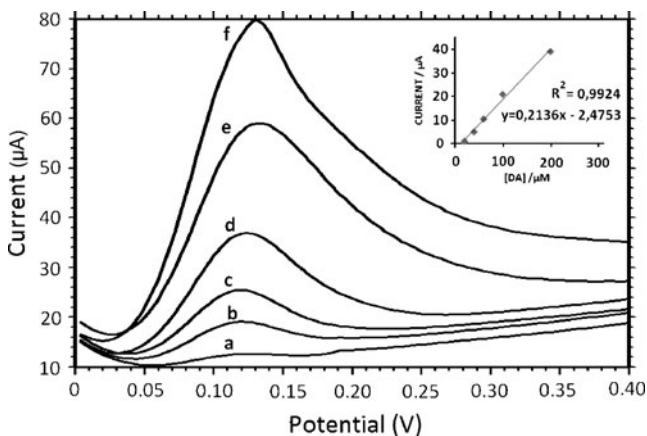


Fig. 10 DPV voltammograms obtained from different concentrations of DA in pH 7 SBS (a) 1.0×10^{-5} , (b) 2.0×10^{-5} , (c) 3.0×10^{-5} , (d) 4.0×10^{-5} , (e) 6.0×10^{-5} , (f) 8.0×10^{-5} mol L⁻¹. The inset shows a plot of i_{pa} vs. DA

10^{-7} mol L⁻¹ ($S/N=3$). The relative standard deviation of the five successive scans was 5% for 2×10^{-5} mol L⁻¹ for DA. The MWCNTs/ARS–PVF film electrode shows good reproducibility and sensitivity and has been used for the determination of DA in the presence of AA in samples with satisfactory results.

Amperometric sensing of DA

We also attempted to investigate the amperometric response of DA at MWCNTs/ARS–PVF film electrode. The amperometric response to DA of the MWCNTs/ARS–PVF-modified electrode under optimized conditions was carried out in pH 7 SBS as shown in Fig. 11. The amperometric response of the MWCNTs/ARS–PVF electrode was obtained at a potential of +0.1 V on the successive additions of various concentration of DA in a stirred solution. The nearly equal current steps for each addition of DA indicated the stable and efficient catalytic properties of the

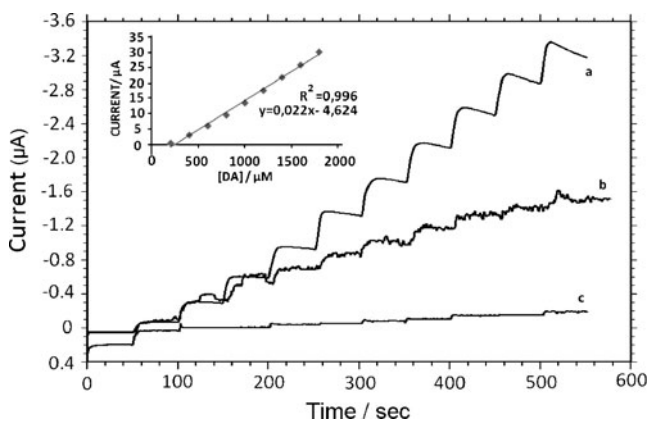


Fig. 11 Amperometric i - t curve of (a) MWCNTs/ARS–PVF (b) MWCNTs/ARS (c) MWCNTs film electrode obtained from different concentrations of dopamine in pH 7. The inset shows a plot of i_{pa} vs. DA obtained from MWCNTs/ARS–PVF film

MWCNTs/ARS–PVF electrode. To demonstrate the role of the PVF, we also performed the experiments to show the amperometric response of MWCNTs and MWCNTs/ARS film electrode. The comparison of the amperometric responses of MWCNTs, MWCNTs/ARS and MWCNTs/ARS–PVF film electrode were shown in Fig. 11. As can be seen in Fig. 11, MWCNTs and MWCNTs/ARS film were found to be less sensitive towards DA amperometric response. The MWCNTs/ARS–PVF electrode displays a rapid response to the change in DA concentration and steady-state signals obtained in less than 3 s. From amperometric curves, linear relationships between peak current and concentration of DA was investigated in the concentration range of 2.5×10^{-5} mol L⁻¹ to 2.6×10^{-3} mol L⁻¹. The linear regression equation is given by for I_{DA} (10⁻⁶ A) = $-4.62 + 0.02 c_{DA}$ (10⁻⁶ mol L⁻¹) and correlation coefficient $r^2 = 0.996$. The detection limit of dopamine was found 2.5×10^{-6} mol L⁻¹. It can be concluded that MWCNTs/ARS–PVF electrode could be also used as amperometric sensor of DA.

Conclusion

A MWCNTs/ARS–PVF electrode was used to investigate the electrochemical behavior of DA. The catalytic activity of bare glassy carbon electrode towards DA oxidation was improved by the formation of stable MWCNTs/ARS–PVF film due to the large surface area as well as the higher electroactivity. The prepared MWCNTs/ARS–PVF electrode showed high selectivity and sensitivity towards DA in the presence of AA. The performance of the MWCNTs/ARS–PVF electrode was evaluated by DPV and amperometry.

References

- Dursun Z, Gelmez B (2010) Simultaneous determination of ascorbic acid, dopamine and uric acid at Pt nanoparticles decorated multiwall carbon nanotubes modified GCE. *Electroanal Chem* 22(10):1106–1114
- Hickman JJ, Ofer D, Laibinis PE, Whitesides GM, Wrighton MS (1991) Molecular self-assembly of 2-terminal, voltammetric microsensors with internal references. *Science* 252(5006):688–691
- Liu GD, Riechers SL, Mellen MC, Lin YH (2005) Sensitive electrochemical detection of enzymatically generated thiocholine at carbon nanotube modified glassy carbon electrode. *Electrochem Commun* 7(11):1163–1169
- Gulce H, Ozyoruk H, Celebi SS, Yildiz A (1995) Amperometric enzyme electrode for aerobic glucose monitoring prepared by glucose-oxidase immobilized in poly(vinylferrocenium). *J Electroanal Chem* 394(1–2):63–70
- Leddy J, Bard AJ (1985) Polymer-films on electrodes.18. Determination of heterogeneous electron-transfer kinetics at poly(vinylferrocene) and nafion ru(bpy)32+ polymer-modified electrodes by convolution voltammetry. *J Electroanal Chem* 189(2):203–219
- Hillman AR, Loveday DC, Bruckenstein S (1991) Electrochemical quartz microbalance monitoring of poly(vinylferrocene) electrodeposition. *Langmuir* 7(1):191–194
- Peerce PJ, Bard AJ (1980) Polymer-films on electrodes.3. Digital-simulation model for cyclic voltammetry of electroactive polymer film and electrochemistry of poly(vinylferrocene) on platinum. *J Electroanal Chem* 114(1):89–115
- Pihel K, Walker QD, Wightman RM (1996) Overoxidized polypyrrole-coated carbon fiber microelectrodes for dopamine measurements with fast-scan cyclic voltammetry. *Anal Chem* 68(13):2084–2089
- Venton BJ, Wightman RM (2003) Psychoanalytical electrochemistry: dopamine and behavior. *Anal Chem* 75(19):414a–421a
- Pandey PC, Chauhan DS, Singh V (2009) Poly(indole-6-carboxylic acid) and tetracyanoquinodimethane-modified electrode for selective oxidation of dopamine. *Electrochim Acta* 54(8):2266–2270
- Kumar SS, Mathiyarasu J, Phani KLN, Yegnaman V (2006) Simultaneous determination of dopamine and ascorbic acid on poly (3,4-ethylenedioxythiophene) modified glassy carbon electrode. *J Solid State Electr* 10(11):905–913
- Li YX, Huang X, Chen YL, Wang L, Lin XQ (2009) Simultaneous determination of dopamine and serotonin by use of covalent modification of 5-hydroxytryptophan on glassy carbon electrode. *Microchim Acta* 164(1–2):107–112
- Shang FJ, Liu YL, Hrapovic S, Glennon JD, Luong JHT (2009) Selective detection of dopamine using a combined permselective film of electropolymerized (poly-tyramine and poly-pyrrole-1-propionic acid) on a boron-doped diamond electrode. *Analyst* 134(3):519–527
- Zhang R, Jin GD, Chen D, Hu XY (2009) Simultaneous electrochemical determination of dopamine, ascorbic acid and uric acid using poly(acid chrome blue K) modified glassy carbon electrode. *Sensor Actuat B-Chem* 138(1):174–181
- Wu KB, Hu SS (2004) Deposition of a thin film of carbon nanotubes onto a glassy carbon electrode by electropolymerization. *Carbon* 42(15):3237–3242
- Bodenheimer J, Loewenthal E, Low W (1969) The Raman spectra of ferrocene. *Chem Phys Lett* 3(9):715–716
- Machado NFL, Calheiros R, Gaspar A, Garrido J, Borges F, Marques MPM (2009) Antioxidant phenolic esters with potential anticancer activity: solution equilibria studied by Raman spectroscopy. *J Raman Spectrosc* 40(1):80–85
- Costa S, Borowiak-Palen E, Kruszynska M, Bachmatiuk A, Kalenczuk RJ (2008) Characterization of carbon nanotubes by Raman spectroscopy. *Mater Sci-Poland* 26(2):433–441
- Latonen RM, Kvarnstrom C, Ivaska A (2001) In situ UV-vis and FTIR attenuated total reflectance studies on the electrochemically synthesized copolymer from biphenyl and 3-octylthiophene. *J Electroanal Chem* 512(1–2):36–48
- Lin G, Reid G, Bugg TDH (2001) Extradial oxidative cleavage of catechols by ferrous and ferric complexes of 1,4,7-triazacyclononane: insight into the mechanism of the extradial catechol dioxygenases. *J Am Chem Soc* 123(21):5030–5039
- Bard AJ, Faulkner LR (2001) *Electrochemical methods: fundamentals and applications*, 2nd edn. Wiley, New York, p 5