Electronic Supplementary Data

A multi-walled carbon nanotubes/poly-2, 6 – Dichlorophenolindophenol film modified

carbon paste electrode for the amperometric determination of L-Tyrosine

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Fig. S1: Cyclic voltammograms of electropolymerization of DCPIP on CPE (a) and MCPE/MWCNTs (b).





Scheme S1: Proposed mechanism of electropolymerization of DCPIP.

Fig. S2: Nyquist plots of 2.0 mM K_3 [Fe(CN)₆]/ K_4 [Fe(CN)₆] (1:1) in 0.1 M KCl. Inset: equivalent circuit.



Fig. S3: Cyclic voltammograms of various concentrations of Tyr (in mM): 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 (a \rightarrow f) at MCPE/MWCNTs/p-DCPIP in 0.1 M PBS of pH 7.0 containing 0.1 M KCl at a scan rate of 50 mV s⁻¹. The inset shows plot of the variation of I_{pa} with concentration of Tyr.



Fig. S4: Cyclic voltammograms of 5×10^{-4} M of Tyr at various scan rates (in mV s⁻¹): 150, 125, 100, 75, 50, 25 and 10 (a \rightarrow g) at MCPE/MWCNTs/p-DCPIP in 0.1 M PBS of pH 7.0 containing 0.1 M KCl. Inset represents the plot of the variation of I_{pa} with scan rate.



Fig. S5: Calibration plot of E_{pa} with log υ



Fig. S6: Plot of variation of (a) I_{pa} and (b) E_{pa} of 5.0×10^{-4} M Tyr in 0.1 M PBS of different pH at MCPE/MWNCTs/p-DCPIP at a scan rate 50 mV s⁻¹.



Fig. S7:Cyclic voltammogramsof 5.0×10^{-4} M Tyr in 0.1 M PBS of different pH of 3, 4, 5, 6, 7 and 8 (f \leftarrow a) containing 0.1 M KCl at MCPE/MWCNTs/p-DCPIP at a scan rate of 50 mVs⁻¹.



Fig. S8: Effect of volume of MWCNTs suspension on CPE (a) Concentration of DCPIP for the electropolymerisation (b) Scan rate variation on electropolymerisation (c) and number of electropolymerisation cycles (d) on I_{pa} of 5.0×10^{-4} M Tyr in 0.1 M PBS of pH 7.0 containing 0.1 M KCl at a scan rate of 50 mV s⁻¹.



Volume of MWCNTs suspension / µl

Fig. S9: Plots showing change in absorbance of Tyr measured at (a) 229 nm and (b) 274 nm with time at a constant applied potential. Cottrell treatment of the plots of variation in absorbance with time at (c) 229 nm and (d) 274 nm.



Fig. S10: Chronoamperograms obtained at MCPE/MWCNTs/p-DCPIP in 0.1M PBS of pH 7.0 containing 0.1 M KCl for different concentrations of Tyr (in mM): 0.1, 0.3, 0.5, 0.7 and 1.0 $(a\rightarrow e)$ by setting the potential of working electrode at 620 mV (a). Insets: Plots of I vs. t^{-1/2} (b) and plot of the straight lines against the Tyr concentrations (c).



Fig. S11: Cyclic voltammograms various concentrations (in mM) of AA ranging from 0.5 to 2.0, DA, UA and Tyr ranging from 0.2 to 1.0 obtained at MCPE/MWCNTs/p-DCPIP in 0.1 M PBS of pH 7.0 containing 0.1 M KCl at a scan rate of 50 mV s⁻¹.



Fig. S12: Amperometric response for the addition of Tyr in the presence of various interferents at MCPE/MWNCTs/p-DCPIP in 0.1 M PBS of pH 7.0 containing 0.1 M KCl. Applied potential: 635.0 mV.



Fig. S13: Amperometric response of 5.0×10^{-4} M Tyr at MCPE/MWCNTs/p-DCPIPfor 30.0 minutes in 0.1 M PBS of pH 7.0 containing 0.1 M KCl. Applied potential: 635.0 mV.



S 1.0. Generation of oxygen functionalities on MWCNTs

Pretreatment of CNTs prevent them from aggregating thereby increases their biocompatibility. Since the oxygen functionalities on the surface of MWCNTs improve their electrochemical properties, they were generated by treating MWCNTs with a mixture of concentrated H₂SO₄ and HNO₃ (molar ratio 3:1). In a typical experiment, 75.0 mL of conc. H₂SO₄ (97%) and 25.0 mL of conc. HNO₃ (65%) were mixed and added to 1.0 g of MWCNTs in a round-bottomed flask and heated under constant agitation at 50.0 °C for 8.0 h. It was allowed to cool down to room temperature after which an equal quantity of deionized water was added. It was filtered and the residue was washed several times with deionized water until neutral pH was attained. The residue was then filtered and freeze-dried [1].

[1] P. Martis, B.R. Venugopal, J.-F. Seffer, J. Delhalle, Z. Mekhalif, Infrared irradiation controlled decoration of multiwalled carbon nanotubes with copper/copper oxide nanocrystals Acta Mater. 59 (2011) 5040–5047.