Electronic Supplementary Information

Fluid interface-mediated nanoparticle membrane as electrochemical sensor

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ESI 1. Modification of the gold electrode with nanoparticle-decorated membrane

Modification of gold electrode surface

The bare gold electrode was polished with 0.05 μm alumina powder and then, thoroughly, rinsed with distilled water. This, mechanically, cleaned gold electrode was, again, uncontaminated by repetitive cycling between potential -0.2 to +1.5 V *vs.* Ag/AgCl in 1.0 M H_2SO_4 solution until a stable characteristic cyclic voltammogram was obtained. The electrode was, then, rinsed with distilled water and clamped in such a manner that the gold surface is in contact with the Fe_3O_4 nanoparticle-decorated membrane formed at the water/chloroform interface. After 20 h keeping the solution undisturbed for overnight, the membrane modified gold electrode was formed and washed, thoroughly, with distilled water for further use.

Electrochemical characterisation of membrane-modified electrode

The characterisation of membrane-modified gold electrode was conducted using the redox probe $[Fe(CN)_6]^{3-/4-}$ as shown in Fig. SI 1. Panel a shows the cyclic voltammogram of the bare electrode (black curve) and membrane-modified electrode (red curve) in 1.0 mM $[Fe(CN)_6]^{3-/4-}$ in PBS at pH 7.0. For a bare gold electrode, the signature of a well-defined redox couple of $[Fe(CN)_6]^{3-/4-}$ was appeared with a peak-to-peak separation, ΔE_p = 74 mV. However, after modification with membrane, the peak current increased and peak-to-peak separation decreased, (ΔE_p = 63 mV) indicating successful modification of the electrode with the membrane.

The Nyquist plot presented in panel b shows that after modification of the gold electrode, the charge transfer resistance (R_{CT}) decreased compared to bare gold electrode [R_{CT} (bare): 19056 Ω and R_{CT} (modified): 11004 Ω] which is due to monolayer formation over gold electrode surface. The surface coverage θ = 0.73, was obtained using, $\theta = [1 - (R_{ct}^0 / R_{ct})]$, where, R_{ct}^0 and R_{ct} are

the charge transfer resistances of the redox probe at bare and membrane-modified gold electrodes, respectively, under similar conditions.

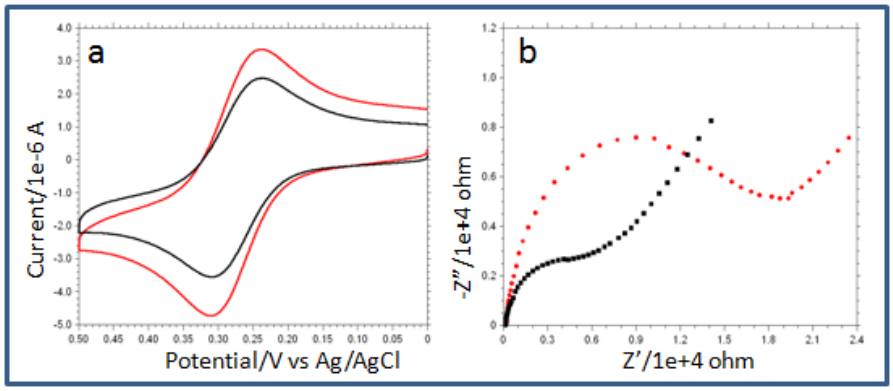

Fig. SI 1. (a) Cyclic voltammogram and (b) electrochemical impedance spectroscopy of 1.0 mM $K_4[Fe(CN)_6]$ at bare (black curve) and Fe_3O_4 membrane-modified electrode (red curve) at pH=7.0.

ESI 2. Electrocatalytic oxidation of L-Dopa at different pH

L-Dopa has been detected by membrane-modified electrode at different pH to investigate the effect of pH on sensing (Fig. SI 2). At pH 7.0, the interaction between membrane-modified gold electrode and L-Dopa (exists as negatively charged at this pH) is maximum as shown by the profile showing the variation of peak current as a function of pH. Below or above pH 7.0, the interaction is less because L-Dopa exists in zwitterionic form at pH 5.0 (isoelectric point, pI = 5.2) and doubly negatively charged at pH >>7.0. Therefore, it is evident that, the electrostatic interaction between L-Dopa and membrane-modified electrode surface is less as apparent from the low anodic current height in the cyclic voltammogram.

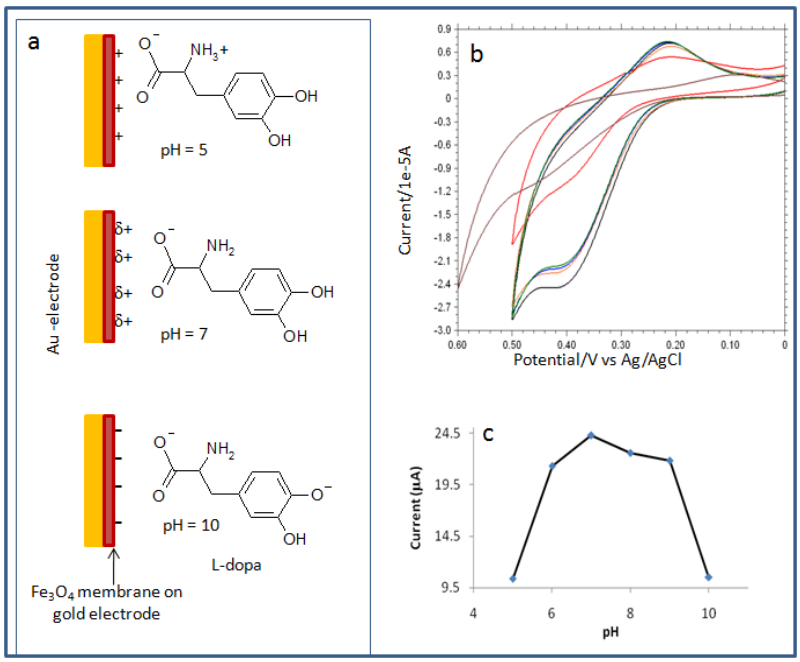

Fig. SI 2. (a) Schematic presentation of L-Dopa and its interaction with membrane-modified gold electrode (b) cyclic voltammogram of L-Dopa at membrane modified gold electrode at different pH. [pH= 5.0 (violet); 6.0 (green); 7.0 (black); 8.0 (pink); 9.0 (blue); 10.0 (red)] (c) plot of pH *vs.* peak current of L-Dopa at membrane-modified gold electrode.

ESI 3. Sensing capabilities of different materials and methods for L-Dopa determination

Table SI 1. Comparative account of the sensing capabilities for the determination of L-Dopa in the presence of different materials and methods

Materials	Method	Concentration range (μM)	LOD (μM)	Reference
Oxovanadium-salen complex	flow injection method	1-100	0.80	Teixeira et al. [Ref. 11]
Phenylboronic acid derivative of lucifer yellow	fluorescence spectroscopy	0-5000	–	Coskun et al. [Ref. 12]
Chloro(pyridine) bis(dimethylglyoximato) cobalt(III)/multi-walled carbon nanotube	cyclic voltammetry	3-100	0.86	Leite et al. [Ref. 13]

Cobalt hexacyanoferrate/ large mesopore carbon composite modified electrode	cyclic voltammetry	0.1-1900	0.02	Yan et al. [Ref. 14]
Fe_3O_4 membrane	cyclic voltammetry	0.05-10	0.01	Present work

ESI 4. Simultaneous determination of L-Dopa and ascorbic acid in binary mixtures

Simultaneous detection of L-Dopa and ascorbic acid (AA) in binary mixtures was studied at membrane-modified gold electrode. Fig. SI 3 shows the overlaid differential pulse voltametry obtained for a L-Dopa and AA mixture at membrane-modified electrode in PBS (pH = 7.0) by changing the concentration of both L-Dopa and AA (1, 2, 3, 4, 5, 6 uM). The oxidation peaks of L-Dopa (0.38 V) and AA (0.24 V) with a peak separation of 140 mV was observed with increasing the concentration of both compounds. The regression equation for L-Dopa and AA was found to be, I_p (μA) = 0.2217 C (μM) + 6.1231 and I_p (μA) = 0.2254 C (μM) + 1.8549, respectively in the range of (1- 6 μM). The current responses of both L-Dopa and AA, linearly, increase with a correlation coefficient of 0.998 and 0.999, respectively. Therefore, it could be inferred that, the nanoparticle-decorated membrane could be employed as an electrochemical sensor for simultaneous determination of L-Dopa and ascorbic acid in a binary mixture of the compounds.

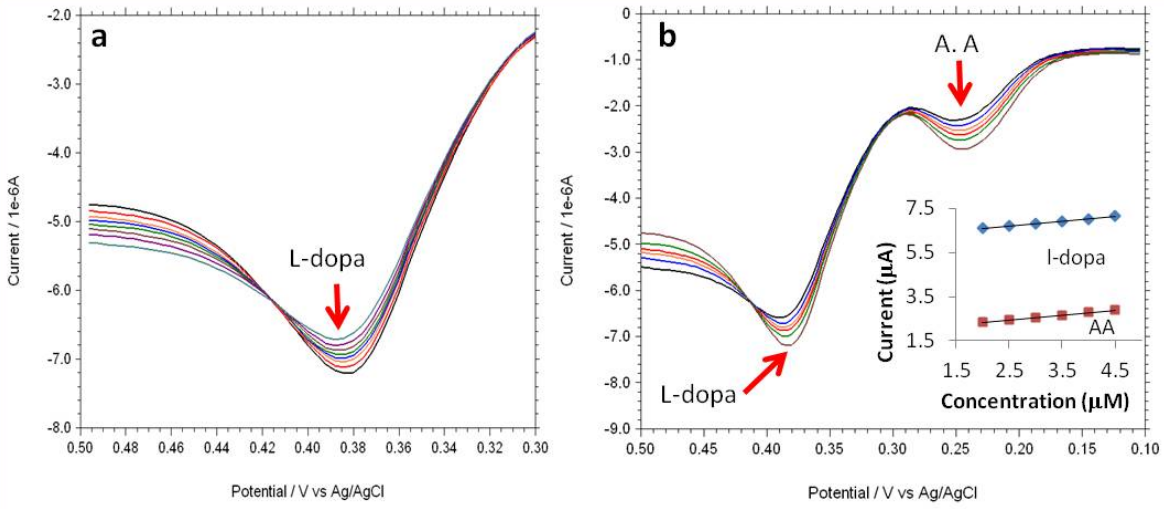

Fig. SI 3. (a) Differential pulse voltametry of L-Dopa in different concentrations: (a) 1.0, (b) 1.5, (c) 2.0, (d) 2.5, (e) 3.0, (f) 3.5, (g) 4.0 and (h) 4.5 μM; and (b) overlaid differential pulse voltametry of L-Dopa and ascorbic acid in different concentrations. Inset shows the plots of current (μA) *vs.* concentration (μM) of L-Dopa and ascorbic acid.