

RSC Advances

Electronic supplementary Information

Simultaneous electrochemical detection of dopamine and epinephrine in presence of ascorbic acid and uric acid using AgNPs-penicillamine-Au electrode

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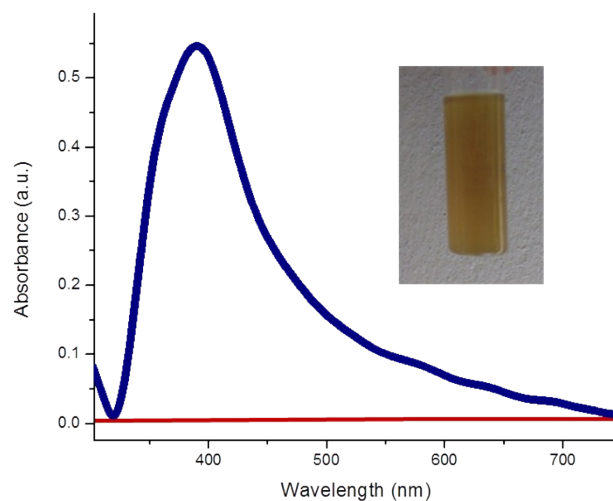


Figure S1 UV-Vis spectra of PVP stabilized AgNPs. [Blue line: AgNO_3 + PVP + Ascorbic acid + EtOH; Red line: AgNO_3 + PVP + EtOH]

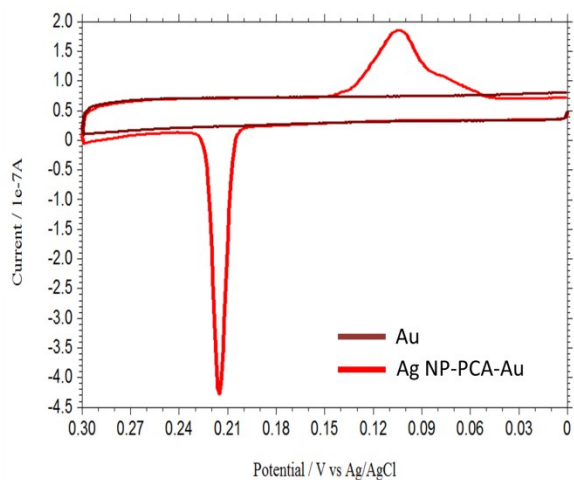


Figure S2 Cyclic voltammograms obtained at bare and AgNPs-PCA modified gold electrode in 0.1 M PBS (pH 7.0)

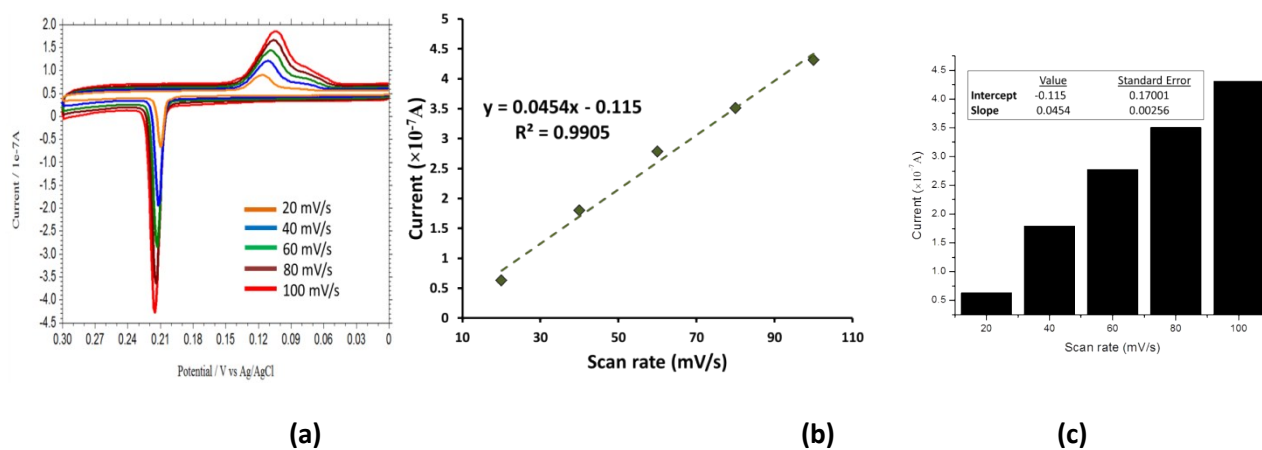


Figure S3 Overlaid cyclic voltammograms obtained with increasing scan rate at AgNPs-PCA-Au electrode in 0.1 M PBS (pH 7.0) (a). Plot of current as a function of scan rate with a linear trend line ($R^2 > 0.99$) (b), Bar diagram of current versus scan rate (c).

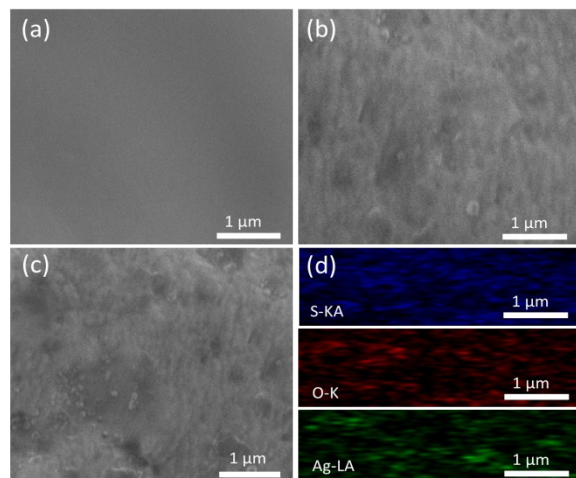


Figure S4 SEM images of bare (a), PCA modified (b) AgNP-PCA modified gold electrode (c) and elemental mapping of AgNPs-PCA modified gold electrode

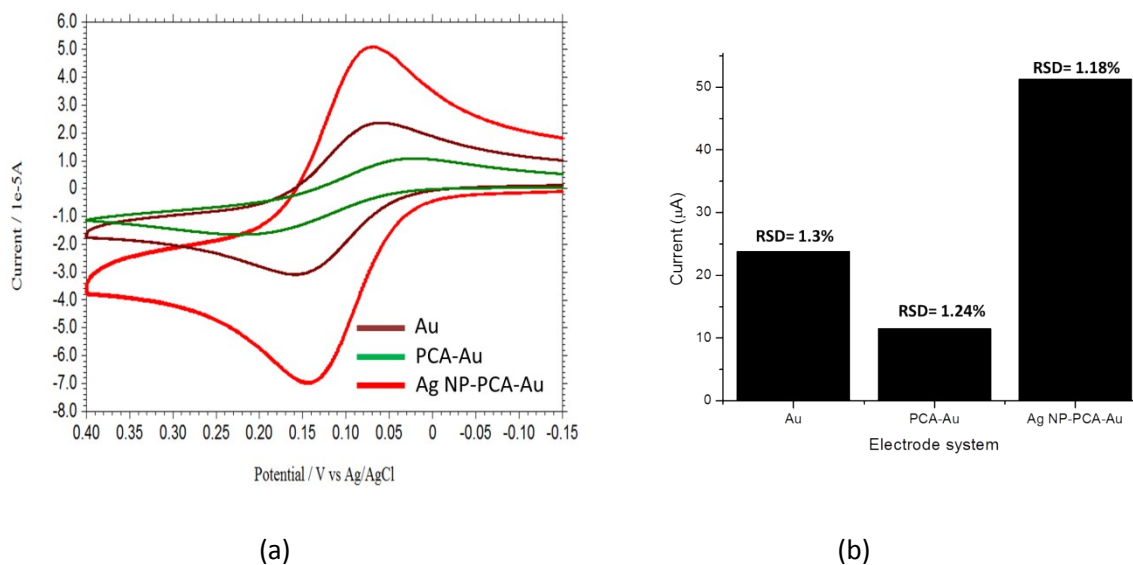


Figure S5 Cyclic voltammograms of 0.5 mM $K_4[Fe(CN)_6]$ in 0.1 M PBS at pH 7.0 using different working electrode (bare Au, PCA-Au and AgNPs-PCA-Au electrode)(a). Bar diagram of cathodic peak current at different electrode system, (b) Five times measurement ($n = 5$) were taken.

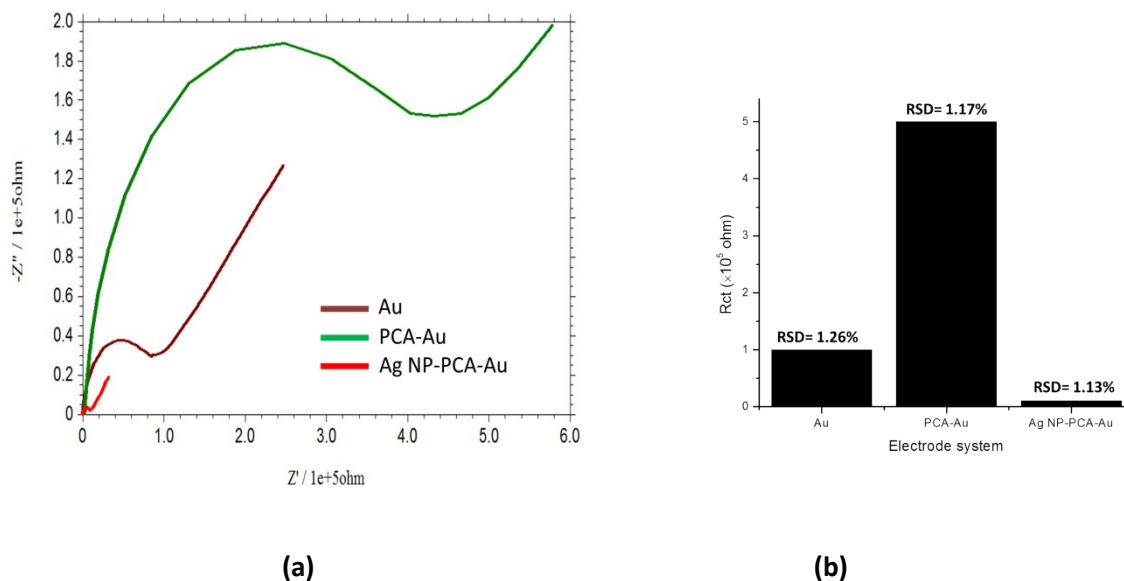


Figure S6 Nyquist plot ($-Z''$ versus Z') of 0.5 mM $K_4[Fe(CN)_6]$ in 0.1 M PBS at pH 7.0 using different working electrode (bare Au, PCA-Au and AgNPs-PCA-Au electrode) (a). Bar diagram of R_{ct} values at different electrode system, (b) Five times measurement ($n = 5$) were taken.

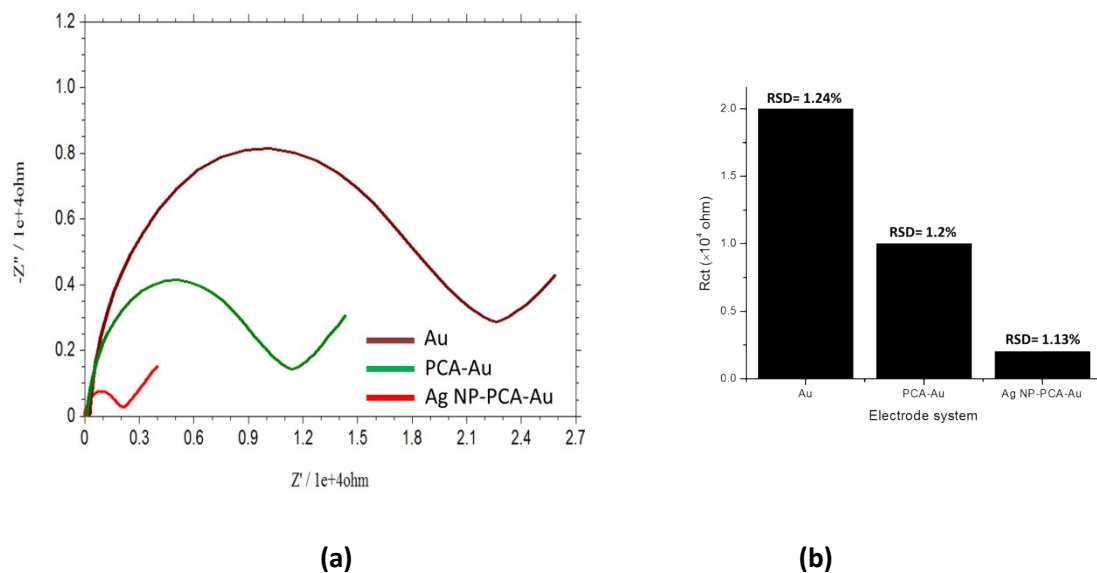


Figure S7 Nyquist plot of 10 μ M DA in 0.1 M PBS at pH 7.0 using bare Au, PCA-Au and AgNPs-PCA-Au electrode (a). Bar diagram of R_{ct} values at different electrode system (b), Five times measurement ($n = 5$) were taken.

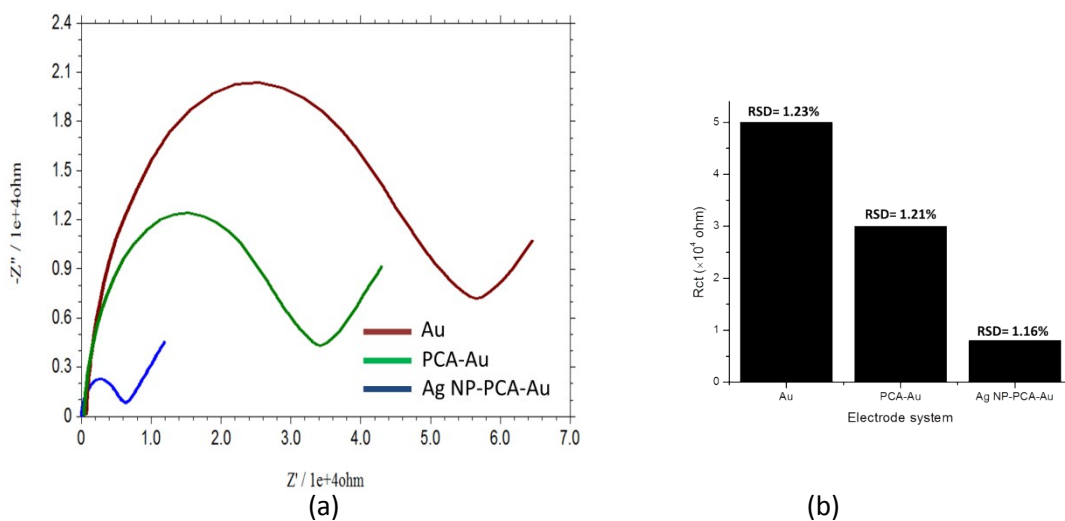


Figure S8 Nyquist plot of 10 μ M EP in 0.1 M PBS at pH 7.0 using bare Au, PCA-Au and AgNPs-PCA-Au electrode (a). Bar diagram of R_{ct} values at different electrode system (b), Five times measurement ($n = 5$) were taken.

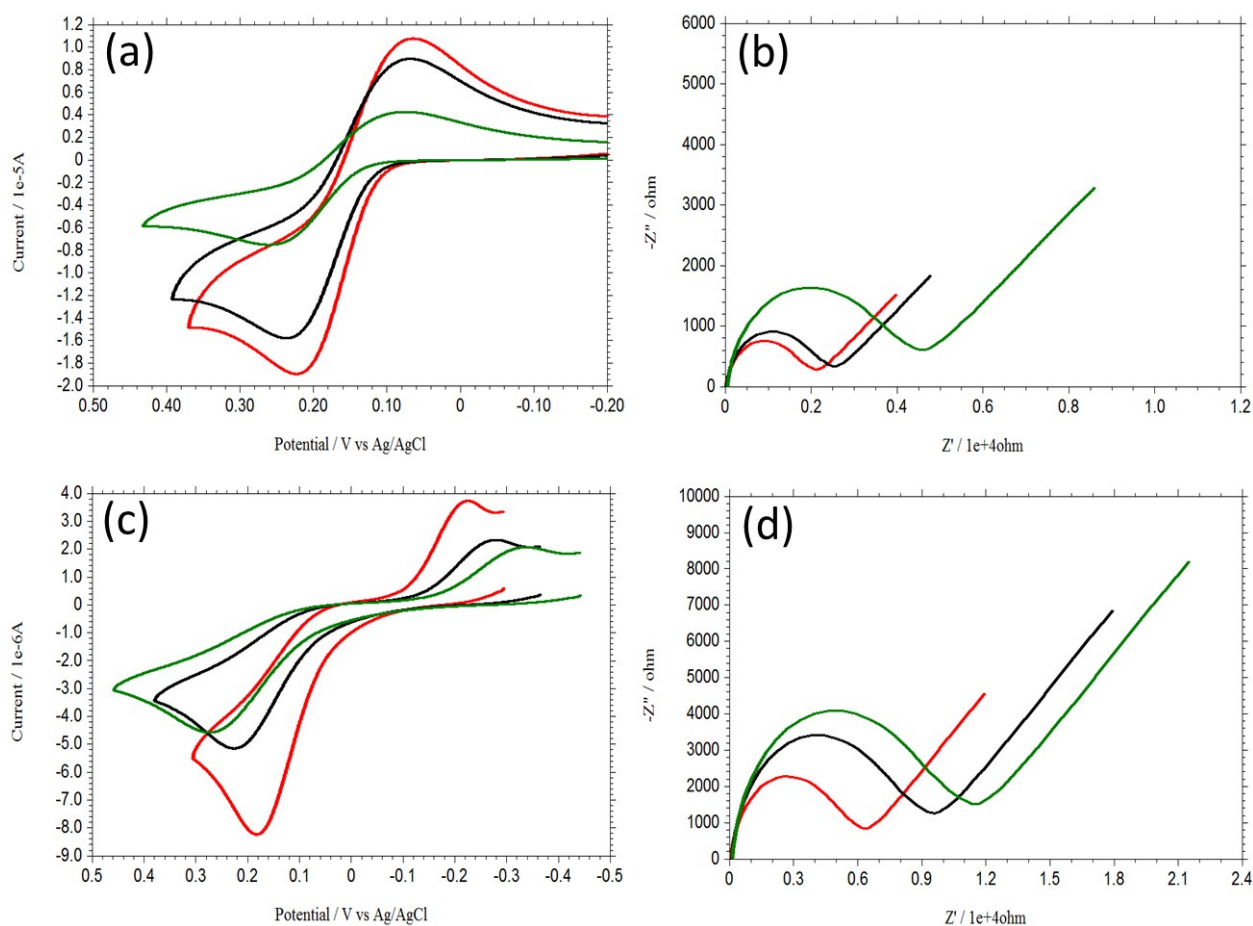


Figure S9 Cyclic voltammogram of 10 μM DA (a) and 10 μM EP (c) in 0.1 M PBS (pH 7.0) at AgNPs (4 nm)-PCA (red curve), AgNPs (10 nm)-PCA (black curve) and AgNPs (20 nm)-PCA (green curve) modified gold electrodes.

Nyquist plot of 10 μM DA (b) in 0.1 M PBS (pH 7.0) using different sized AgNPs modified gold electrodes. $E_{ac} = 10$ mV, frequency range: 0.01 – 100000 Hz [AgNPs (4 nm)-PCA-Au (red curve), $R_{ct} = 0.20 \times 10^4 \Omega$; AgNPs (10 nm)-PCA-Au (black curve), $R_{ct} = 0.25 \times 10^4 \Omega$; and AgNPs (20 nm)-PCA-Au (green curve), $R_{ct} = 0.45 \times 10^4 \Omega$].

Nyquist plot of 10 μM EP (d) in 0.1 M PBS (pH 7.0) using different sized AgNPs modified gold electrodes. $E_{ac} = 10$ mV, frequency range: 0.01 – 100000 Hz [AgNPs (4 nm)-PCA-Au (red curve), $R_{ct} = 0.6 \times 10^4 \Omega$; AgNPs (10 nm)-PCA-Au (black curve), $R_{ct} = 0.9 \times 10^4 \Omega$; and AgNPs (20 nm)-PCA-Au (green curve), $R_{ct} = 1.2 \times 10^4 \Omega$].

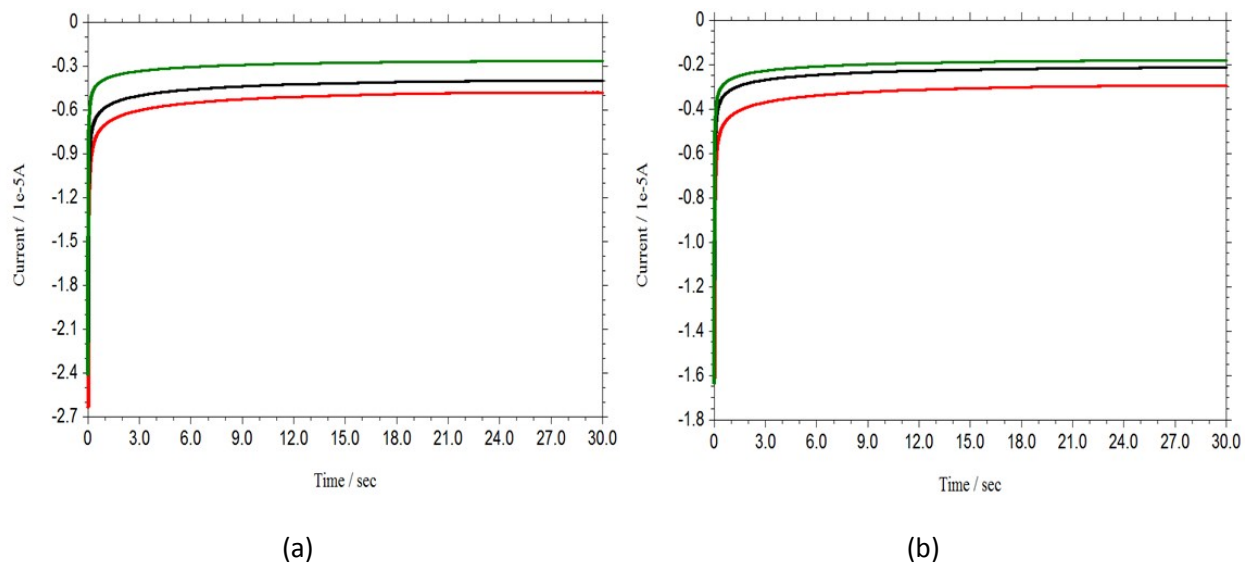
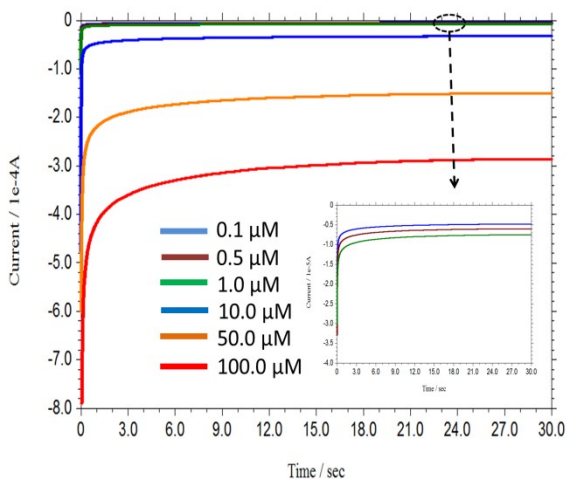
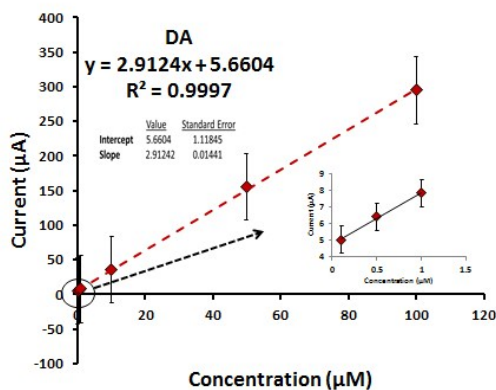


Figure S10 Chronoamperograms of 10 μM DA (a) and 10 μM EP (b) in 0.1 M PBS (pH 7.0) at +0.22 V and +0.18 V versus Ag/AgCl, respectively using AgNPs (4 nm)-PCA (red curve), AgNPs (10 nm) -PCA (black curve) and AgNPs (20 nm) -PCA (green curve) modified gold electrodes. In both cases (DA and EP) resulting current decreases with increasing size of the AgNPs, $I = 0.5$ to 0.3×10^{-5} A for DA and $I = 0.3$ to 0.15×10^{-5} A for EP at 30 seconds and the results supports that the electrochemical sensing behavior decreases with increasing size of the silver nanoparticles.

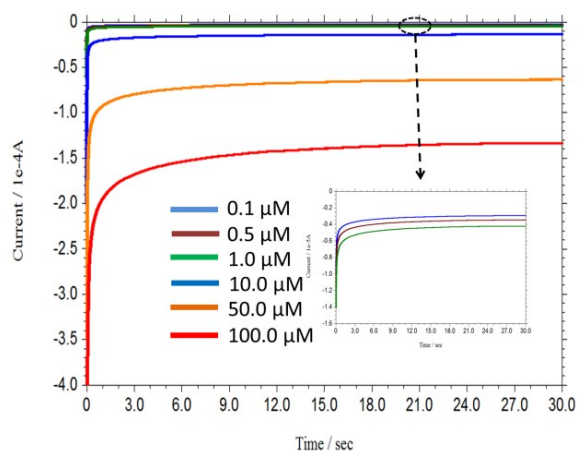




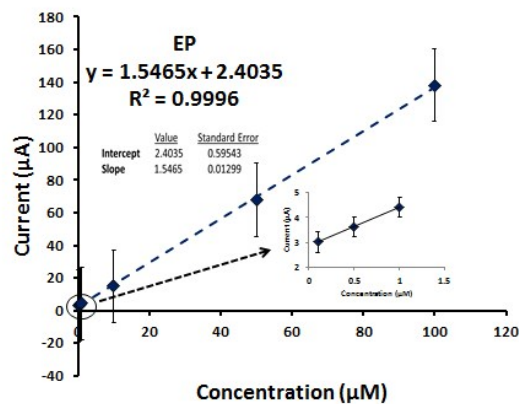
(a)

(b)

Figure S11 Chronoamperograms with increasing concentration of DA (0.1 to 100.0 mM) in 0.1 M PBS (pH 7.0) using AgNPs-PCA-Au electrode at +0.22 V versus Ag/AgCl, LOD = 0.2 nM (S/N = 3) (a). Plot of resulting current in chronoamperometry at 30 seconds versus concentration of DA (b), Five times measurement were taken (n = 5).

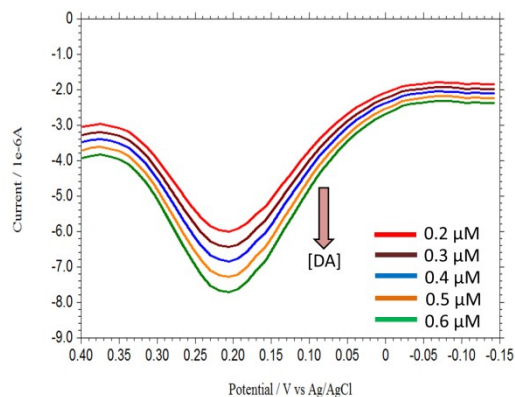


(a)

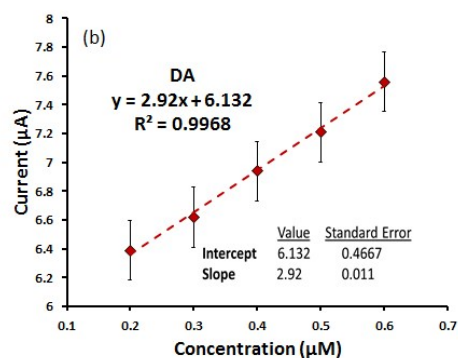


(b)

Figure S12 Chronoamperograms with increasing concentration of EP (0.1 to 100.0 mM) in 0.1 M PBS (pH 7.0) using AgNPs-PCA-Au electrode at +0.18 V versus Ag/AgCl, LOD = 0.5 nM (S/N = 3) (a). Plot of resulting current in chronoamperometry at 30 seconds versus concentration of EP (b), Five times measurement were taken (n = 5).

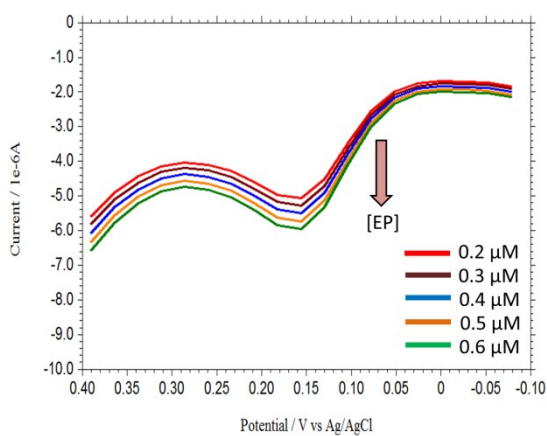


(a)

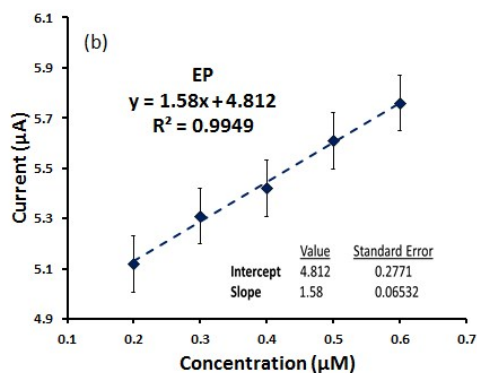


(b)

Figure S13 Overlaid DPVs for each increment of 0.1 μM DA at AgNPs-PCA-Au electrode in 0.1 M PBS solution at pH 7.0 (a). A plot of oxidation peak current *versus* increasing concentration of DA (b), Five times measurement were taken ($n = 5$).

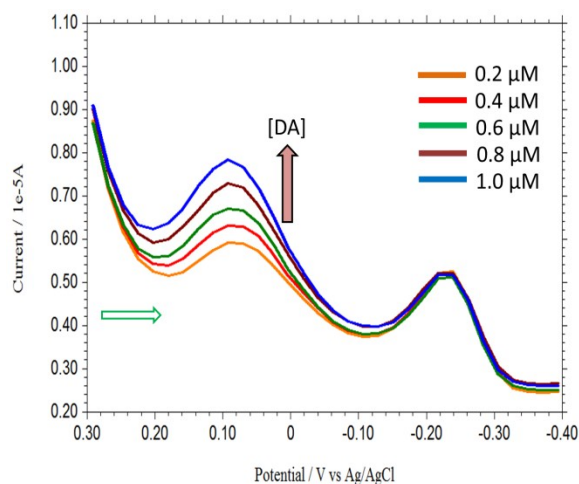


(a)

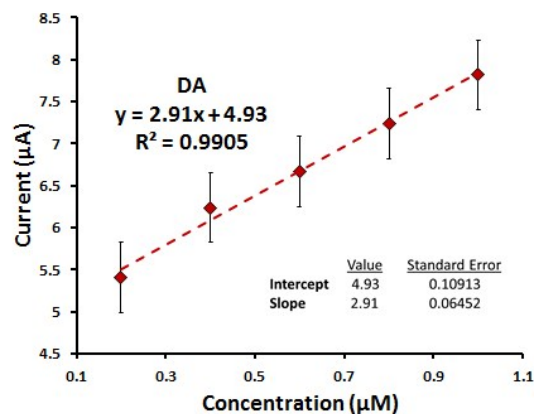


(b)

Figure S14 Overlaid DPVs for each increment of 0.1 μM EP at AgNPs-PCA-Au electrode in 0.1 M PBS solution at pH 7.0 (a). A plot of oxidation peak current *versus* increasing concentration of EP (b), Five times measurement were taken ($n = 5$).

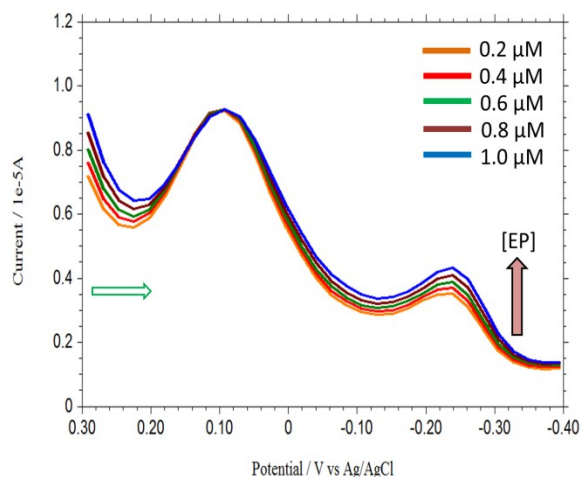


(a)

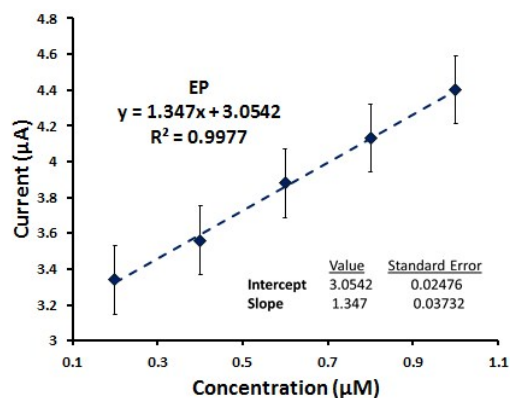


(b)

Figure S15 Overlaid differential pulse voltammogram for each increment of 0.2 μM DA to 0.2 μM EP at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). A plot of reduction peak current versus increasing concentration of DA (b), Five times measurement were taken ($n = 5$).

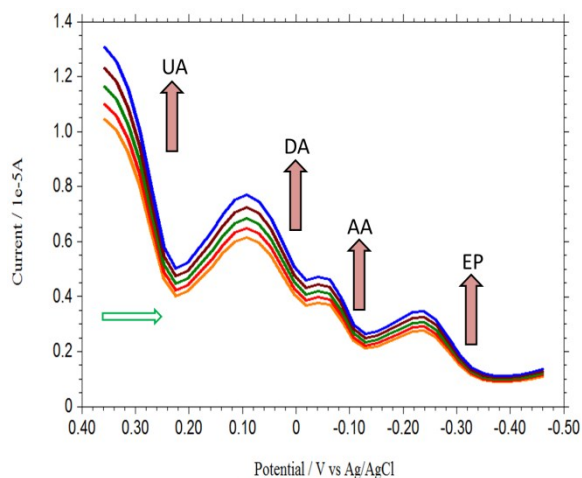


(a)

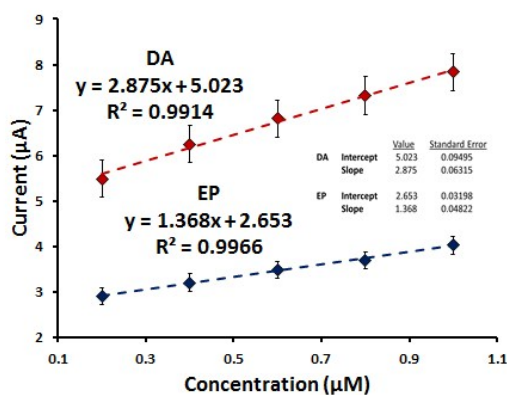


(b)

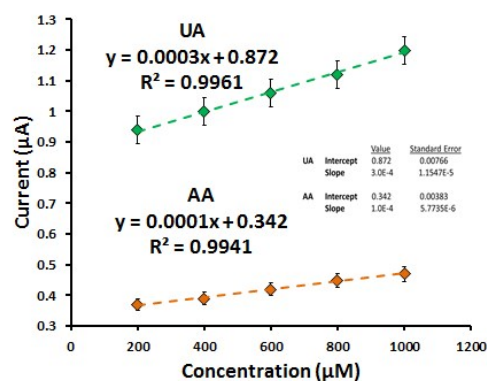
Figure S16 Overlaid differential pulse voltammogram for each increment of 0.2 μM EP to 0.2 μM DA at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). A plot of reduction peak current versus increasing concentration of EP (b), Five times measurement were taken ($n = 5$).



(a)

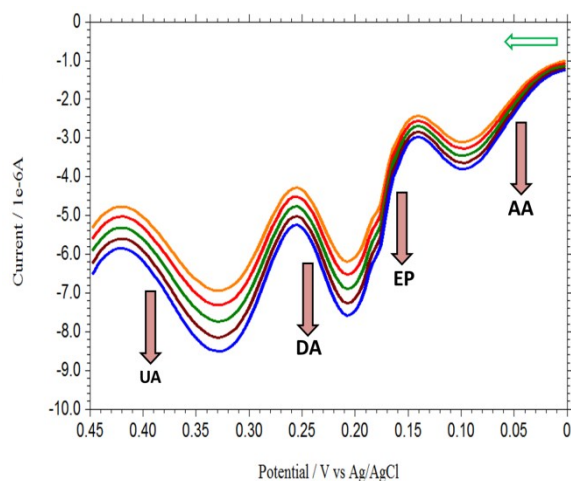


(b)

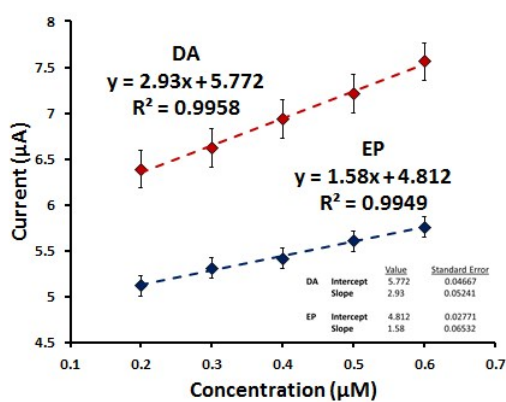


(c)

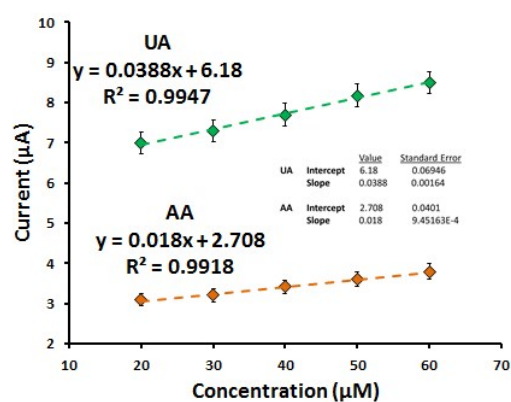
Figure S17 Overlaid differential pulse voltammogram for simultaneous increment of DA, EP, AA and UA at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). Plot of reduction peak current *versus* increasing concentration of DA, EP, AA and UA (b and c), Five times measurement were taken in each case ($n = 5$).



(a)



(b)



(c)

Figure S18 Overlaid DPV for simultaneous increment of DA, EP, AA and UA at AgNPs-PCA-Au electrode in 0.1 M PBS buffer solution at pH 7.0 (a). Plot of oxidation peak current *versus* increasing concentration of DA, EP, AA and UA (b and c), Five times measurement were taken in each case ($n = 5$).

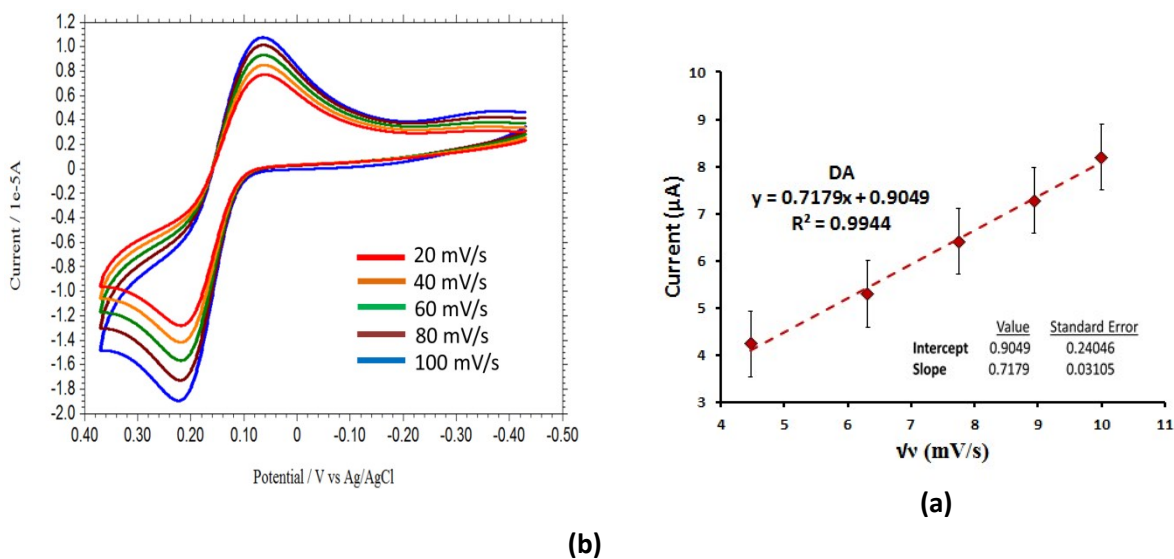


Figure S19 Cyclic voltammograms of 10 μM DA in 0.1 M PBS (pH 7.0) at different scan rate using AgNPs-PCA modified gold electrode (a). Plot of oxidation peak current *versus* square root of scan rate (b), Five times measurement were taken ($n = 5$).

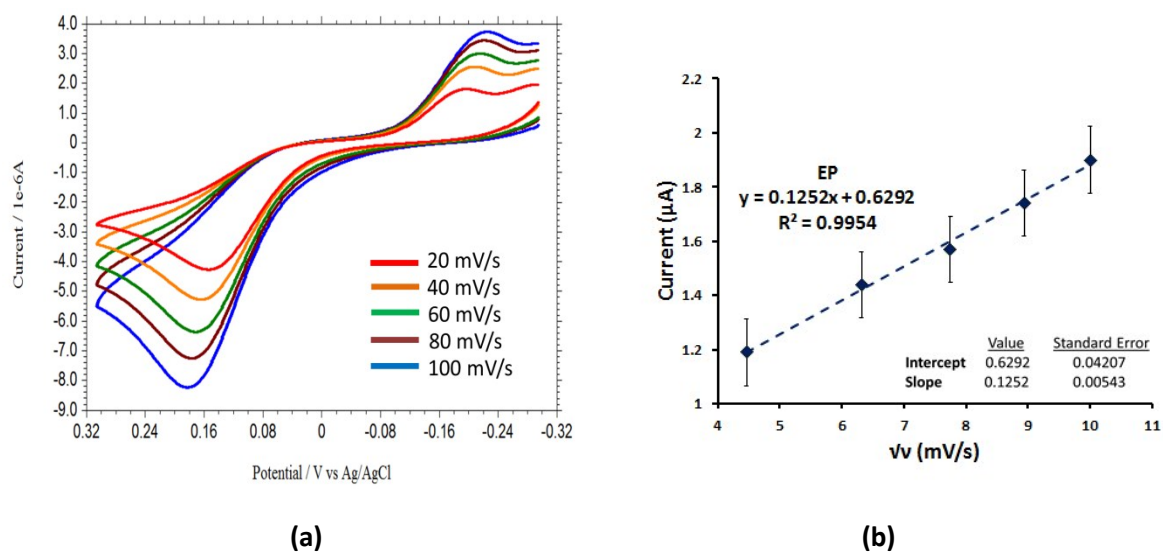
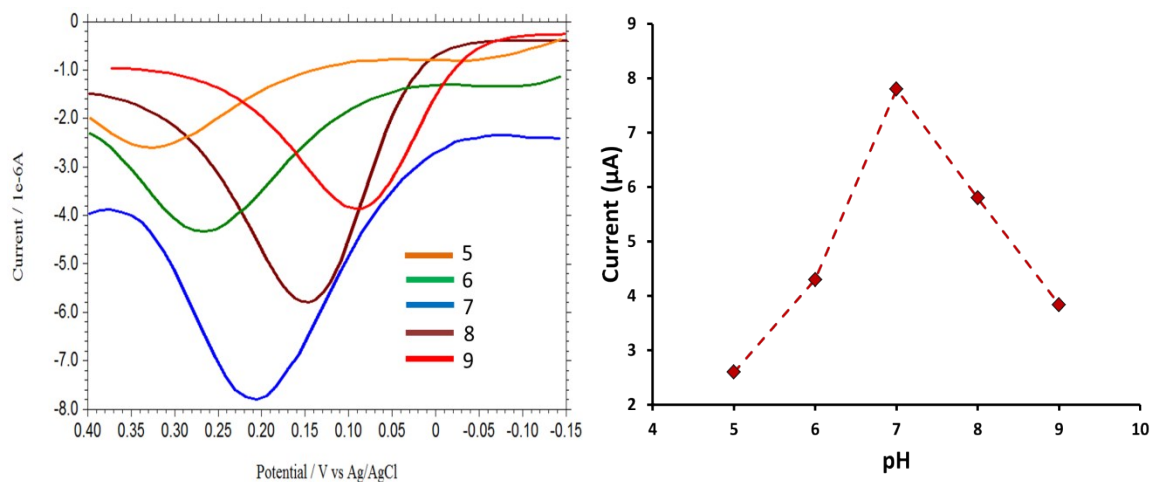
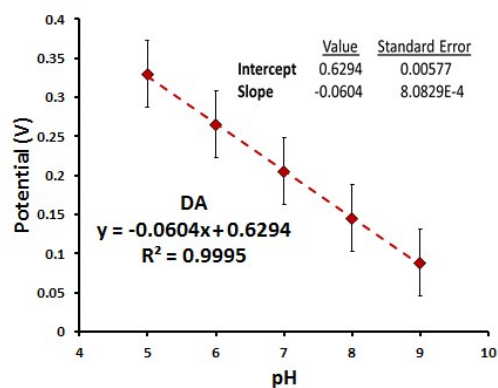


Figure S20 Cyclic voltammograms of 10 μM EP in 0.1 M PBS (pH 7.0) at different scan rate using AgNPs-PCA-Au electrode (a). Plot of oxidation peak current *versus* square root of scan rate (b), Five times measurement were taken ($n = 5$).



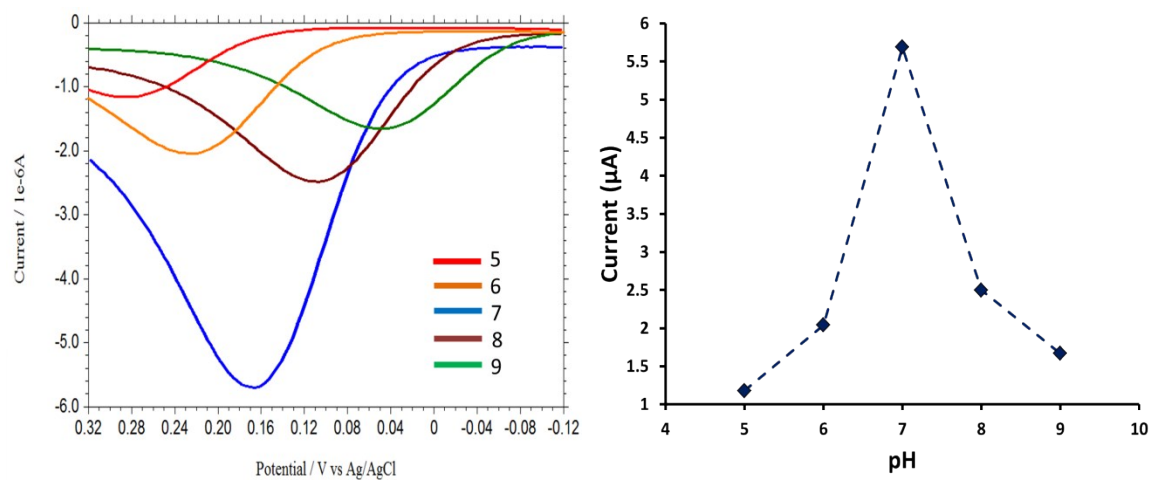
(a)

(b)



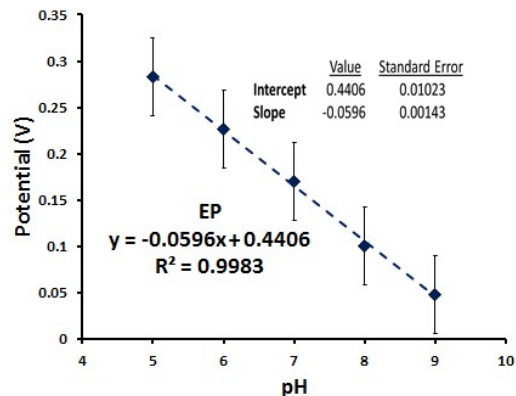
(c)

Figure S21 DPVs of 0.6 μM DA in 0.1 M PBS at different pH using AgNPs-PCA modified gold electrode (a), Plot of anodic peak current of 0.6 μM DA versus pH(b), Plot of oxidation peak potential of 0.6 μM DA versus pH(c), Five times measurement were taken($n = 5$).



(a)

(b)



(c)

Figure S22 DPVs of 0.6 μM EP in 0.1 M PBS at different pH (5.0 - 9.0) using AgNPs-PCA modified gold electrode (a), Plot of anodic peak current of 0.6 μM EP versus pH(b), Plot of oxidation peak potential of 0.6 μM EP versus pH(c), Five times measurement were taken ($n = 5$).

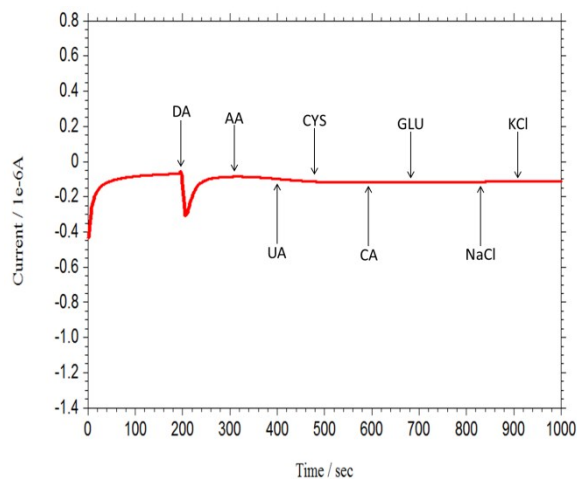


Figure S23 Amperometric response at AgNPs-PCA-Au with an applied potential of + 0.22 V on subsequent addition of 0.01 μM DA, 1.0 μM AA, 1.0 μM UA, 1.0 μM Cys, 1.0 μM CA, 1.0 μM Glu, 1.0 μM NaCl, 1.0 μM KCl under stirring condition (Supporting electrolyte: 0.1 M PBS, pH 7.0).

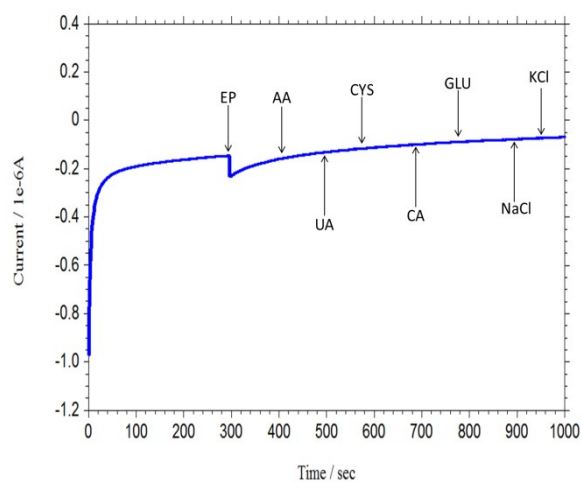


Figure S24 Amperometric response at AgNPs-PCA-Au electrode with an applied potential of + 0.18 V on subsequent addition of 0.01 μM EP, 1.0 μM AA, 1.0 μM UA, 1.0 μM Cys, 1.0 μM CA, 1.0 μM Glu, 1.0 μM NaCl, 1.0 μM KCl under stirring condition (Supporting electrolyte: 0.1 M PBS, pH 7.0).

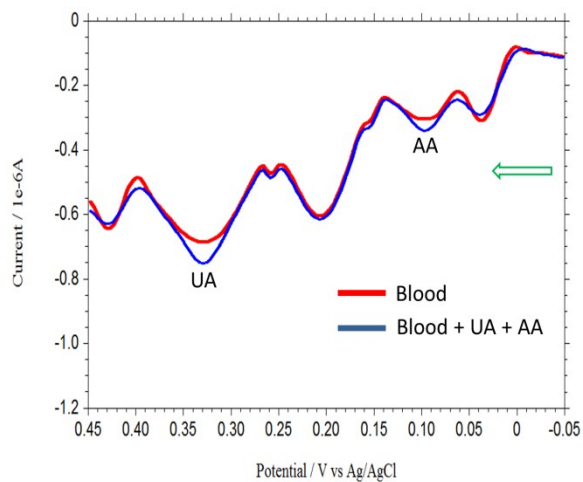


Figure S25 Overlaid DPVs of human blood sample solution and after addition of standard UA and AA solution in blood sample solution.

Table S1 Analytical data for the simultaneous determination of EP, DA, UA and AA at AgNPs-PCA-Au electrode

Species	Linear regression equation	Linear range (μM)	Correlation coefficient (R^2)	Detection limit
DA	$I_{pa} = 2.93 C + 5.772$	0.2-0.5	0.9958	0.2 nM
EP	$I_{pa} = 1.58 C + 4.812$		0.9949	0.5 nM
UA	$I_{pa} = 0.038 C + 6.180$	20-60	0.9947	
AA	$I_{pa} = 0.018 C + 2.708$		0.9918	
DA	$I_{pc} = 2.875 C + 5.023$	0.2-1.0	0.9914	0.2 nM
EP	$I_{pc} = 1.368 C + 2.653$		0.9966	0.5 nM
UA	$I_{pc} = 0.0003 C + 0.872$	200-1000	0.9961	
AA	$I_{pc} = 0.0001 C + 0.342$		0.9941	

Table S2 Comparative account of different electrochemical sensors for DA and EP sensing

Sensor	DA	EP	Reference
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	Linear range (μM)	Detection limit (μM)	Linear range (μM)	Detection limit (μM)	
DNA-Ppyox-CPE	0.3 – 10.0	0.08	0.5– 20	0.06	[1]
α -CD-CNT-GCE	2.0-1000.0	1.0	1.0-1000	0.5	[2]
L-methionine-GCE	1.0 -500.0	0.42	0.5– 100	0.36	[3]
Poly(caffeic)acid-GCE	1.0 – 35.0	0.1	1.0 -35.0	0.2	[4]
PLG-Ag-GCE	5.0-100.0	0.5	10.0-100.0	0.8	[5]
Au/AuO-CMC-Pt	-	0.078	-	0.35	[6]
Polydopamine-nanogold composite-GCE	1.0 – 80.0	0.1	1.0 – 80.0	0.08	[7]
NiONPs-MWCNT-DPH-GCE	0.07– 4.8	0.05	0.37– 9.5	0.082	[8]
AgNPs-SiO ₂ -GO-GCE	-	0.26	-	0.27	[9]
PCA-Au	20 – 800.0	4.0	-	-	[10]
PCA-Au	-	-	5.0– 200	0.13	[11]
AgNPs-PCA-Au	0.1-100.0	0.0002	0.1-100	0.0005	Present work

Ppyox: overoxidized polypyrrole; α -CD: α -cyclodextrin; PLG-Ag: Silver doped poly(L-glutamic acid); CMC: carboxylated multi-walled carbon nanotubes; GO: graphene oxide; DPH: dihexadecylphosphate; PCA: Penicillamine

References

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