Electronic Supplementary Material (ESI) for New Journal of Chemistry.

An electrochemical sensor based on reduced graphene oxide decorated with polypyrrole nanofiber and Zinc oxide-copper oxide p-n junction heterostructures for the simultaneous voltammetric determination of Ascorbic acid, Dopamine, Paracetamol, and Tryptophan

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The effect of pH on the electrochemistry of 500 μM AA, DA, PAR, and TRP at Cu_xO-ZnO /PPy/RGO/GCE was also performed by CV from pH 4.0 to 9.0 in PBS. As shown in Fig

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S1, the oxidation peak potential of the CV curves with increasing the pH shifts negatively. The linear relationship between the pH and the oxidation peak potentials of AA, DA, PAR, and TRP vary linearly with pH as follows:

E_{pa} versus Ag/AgCl (V) =0.3633-0.0524 pH (R^2 = 0.9901) (AA)

E_{pa} versus Ag/AgCl (V) =0.5308-0.0576 pH (R^2 = 0.9902) (DA)

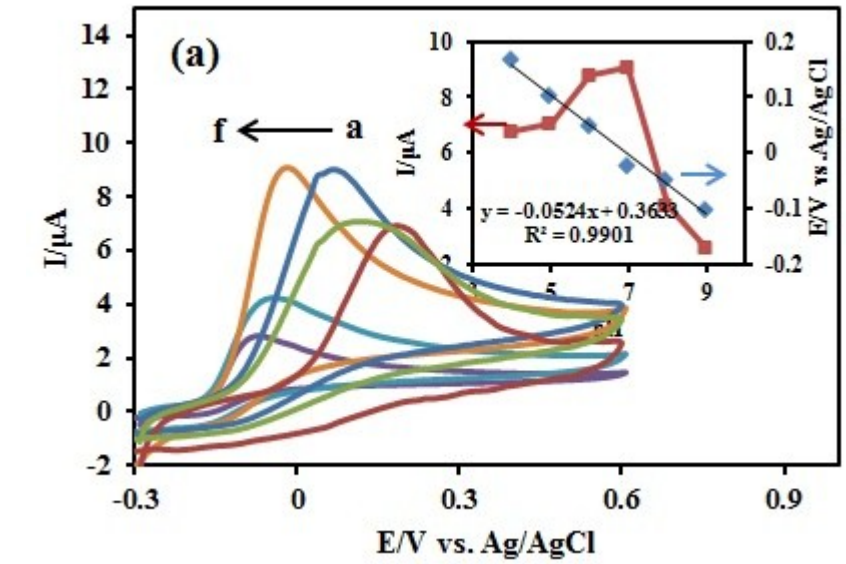
E_{pa} versus Ag/AgCl (V) =0.8786-0.0599 pH (R^2 = 0.9937) (PAR)

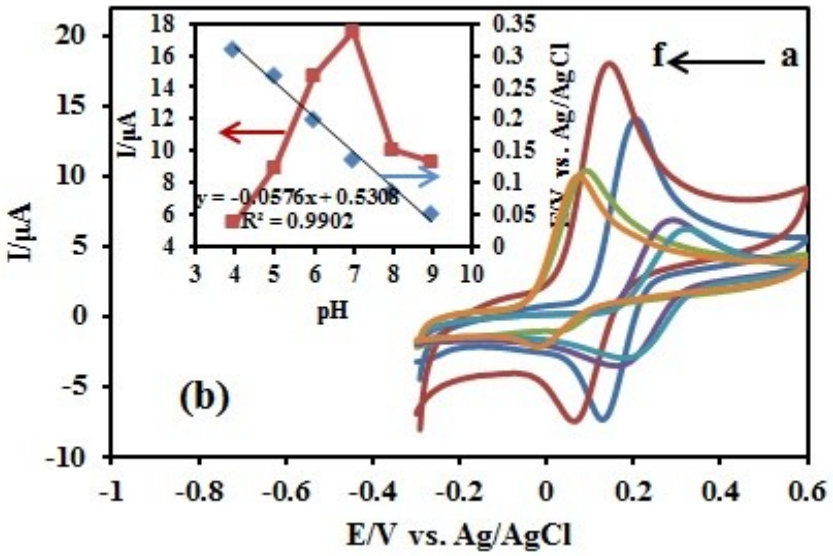
E_{pa} versus Ag/AgCl (V) =1.0635-0.0527 pH (R^2 = 0.9961) (TRP)

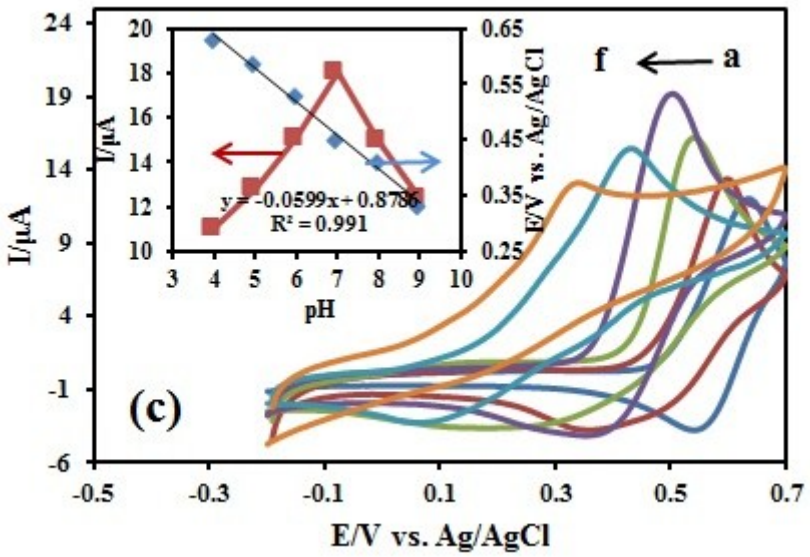
By considering the Nernst equation,

dE_p=dpH = -2.303 mRT/nF

The parameters of m and n are the number of protons and electrons involved in the reaction, respectively. The values of m/n are 0.89, 0.97, 1.01, and 0.89, for AA, DA, PAR, and TRP, respectively, which are approximately equal to 1, indicating that equal numbers of protons and electrons are involved during the electrochemical oxidation process. Based on the m/n values and Nernstian values for the oxidation of AA, DA, PAR, and TRP, one can conclude that two electrons and two protons are involved during the electrochemical oxidation of AA, DA, PAR, and TRP. Also, the peaks current of AA, DA, PAR, and TRP increases as the pH changes from 4.0 to 7.0 and decreases in the alkaline environment of pH 8.0 and 9.0 (Fig. S1). Finally, the pH 7.0 was chosen as the optimized pH value in the present work. In addition, the pH of human blood is about this pH, suggesting that the proposed Cu_xO-ZnO /PPy/RGO/GCE is quite suitable for the practical measurements.


(a)
f ← a
I/μA
E/V vs. Ag/AgCl
y = -0.0524x + 0.3633
R² = 0.9901
E/V vs.Ag/AgCl


(b)
f ← a
I/μA
E/V vs. Ag/AgCl
y = -0.0576x + 0.5308
R² = 0.9902
pH
E/V vs. Ag/AgCl


(c)
f ← a
I/μA
E/V vs. Ag/AgCl
y = -0.0599x + 0.8786
R² = 0.991
pH
E/V vs. Ag/AgCl

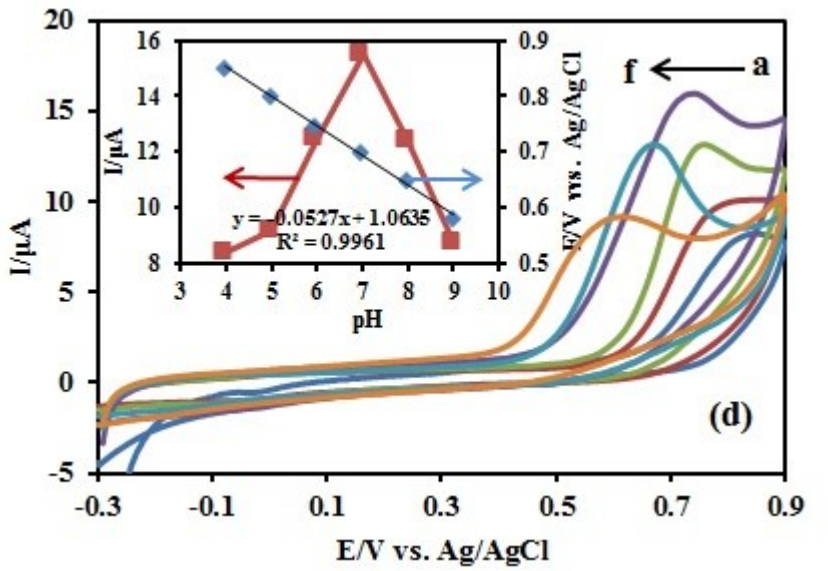
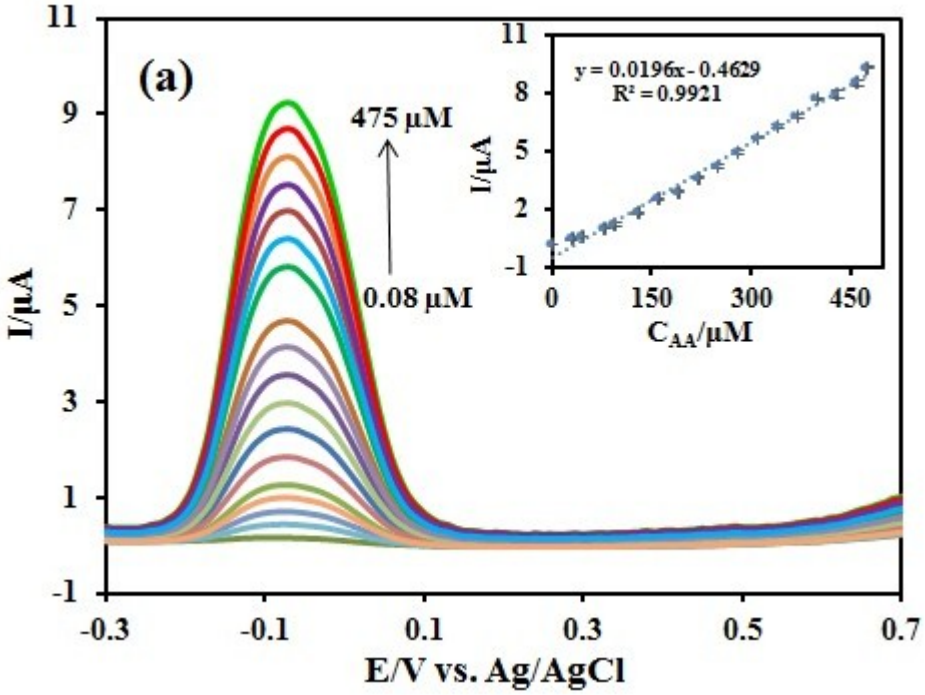
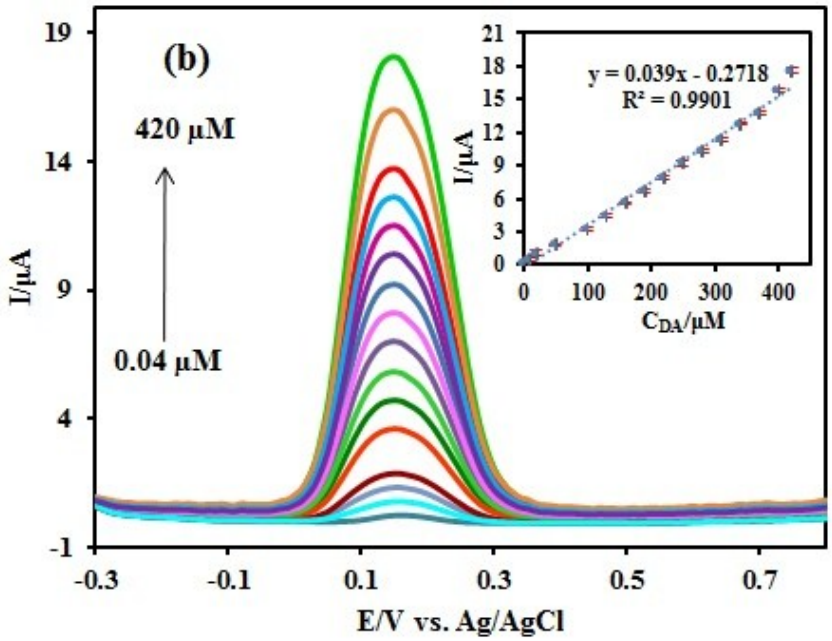


Fig. S1. Cyclic voltammograms of the 500 µM AA (a), DA (b), PAR (c), and TRP (d) at the 3DCuxO-ZnO/PPy/RGO/GCE in the range of pH 4.0-9.0 (a to f) respectively, at a scan rate of 100 mV s^{-1}. Inset: Dependence of peak current and peak potential on pH.

Differential pulse voltammetry (DPV), because of its good resolution and higher sensitivity, was employed for individual determination of AA (a), DA (b), PAR (c), and TRP (d) and PB (b) on the modified electrode (Fig. S2). The linear relationship exhibited between the peak currents and the concentrations of AA, DA, PAR, and TRP in the ranges of 0.08–475, 0.04–420, 0.033-400, and 0.053–480 µM, with the detection limits of 0.024, 0.012, 0.010, and 0.016 µM (S/N = 3), respectively. The linear relation could be expressed by regression equation of $Ip_{AA} = 0.0196\ C_{AA} - 0.4629$ ($R^2 = 0.9921$), $Ip_{DA} = 0.039\ C_{DA} - 0.2718$ ($R^2 =$

0.9901), Ip $_{PAR}$= 0.0444 C_{PAR} + 0.4663 (R^2= 0.9955), and Ip $_{TRP}$= 0.0306 C_{TRP} + 1.7269 (R^2= 0.9904), respectively.





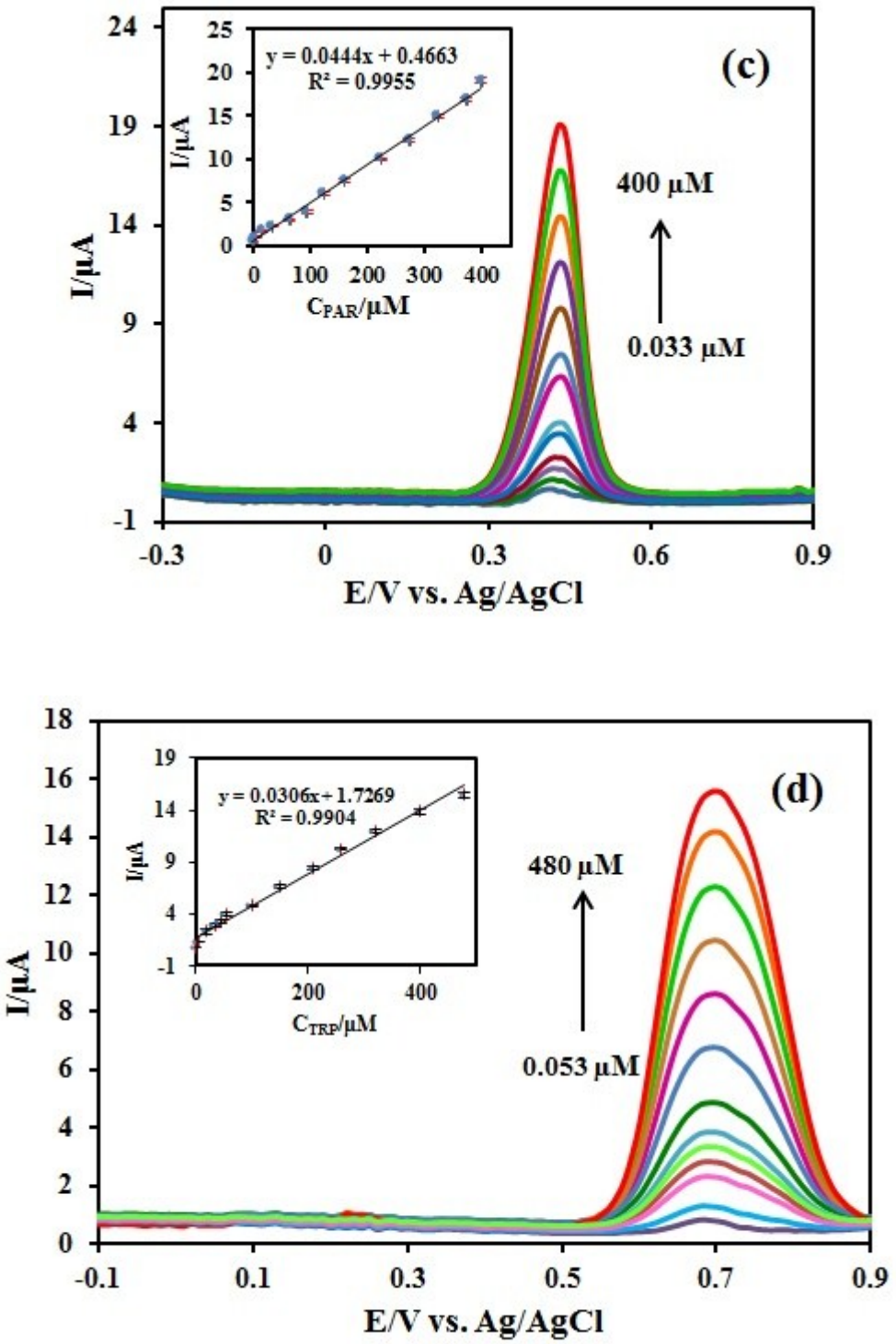
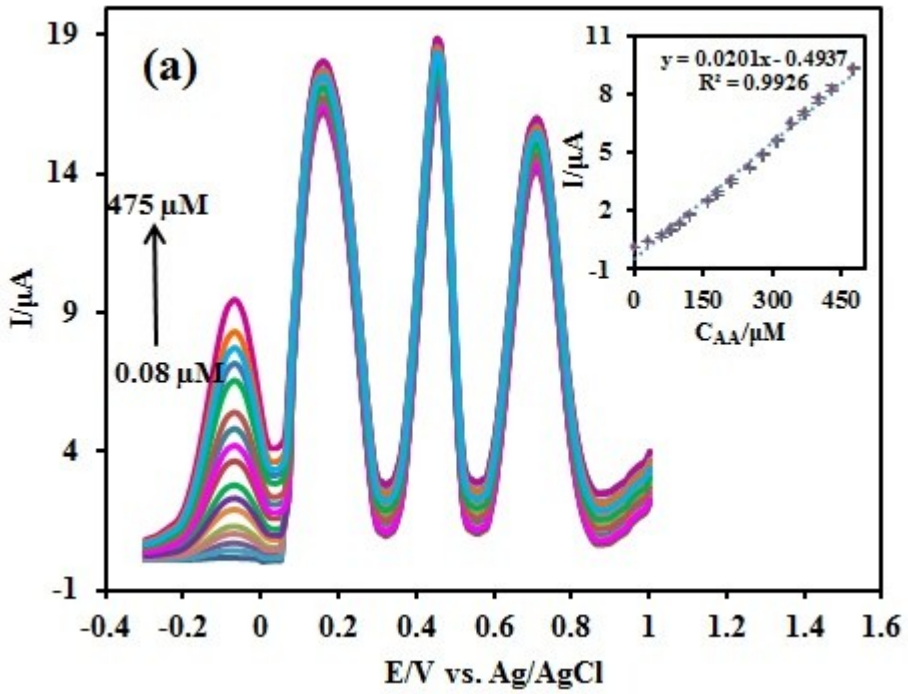
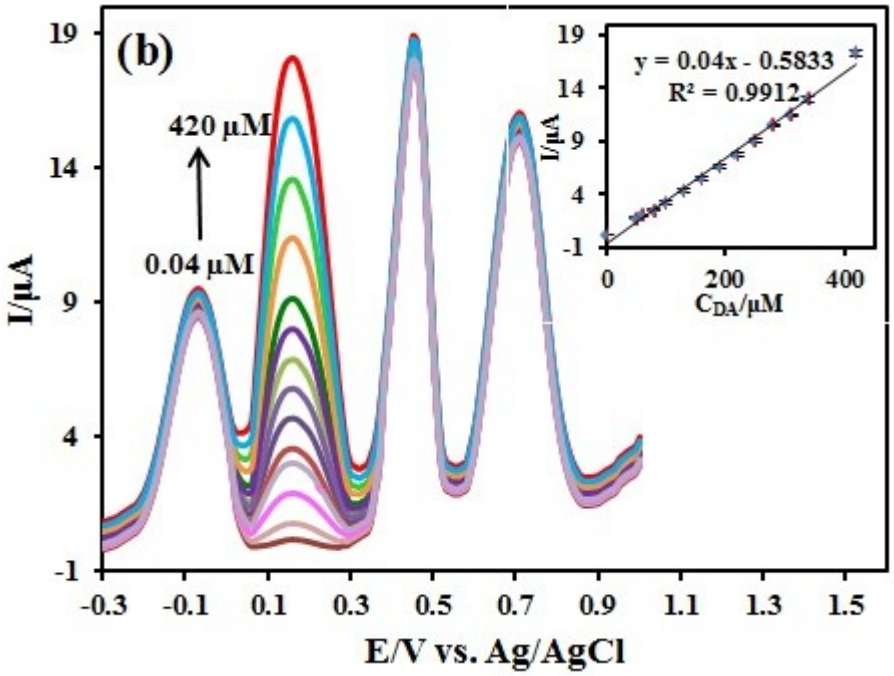


Fig. S2. DPVs of (a) different concentrations of AA (0.08–475.0 μM); (b) different concentrations of DA (0.04–420.0 μM); (c) different concentrations of PAR (0.033-400 μM); (d) different concentrations of TRP (0.053–480.0 μM). DPV experimental conditions: pulse amplitude of 50 mV, pulse time of 100 ms, sweep rate of 50 mV s^{-1};

in 0.1 M PBS solution (pH 7.0). Error bars indicate the standard deviations of three repeated measurements.

DPV was used to investigate the possibility of using the 3DCu$_x$O-ZnO/PPy/RGO nanocomposite for simultaneous determination of AA, DA, PAR, and TRP. The DPVs in Fig. S3 (a-d) show the non-interfered change in the peak current response to oxidation of each individual species as its concentration changed in the presence of fixed amounts of the other three species. The insets show the current responses of all four species increasing linearly with their corresponding concentration. The linear regression equations were Ipa = $0.0201C_{AA}$-0.4937 ($R^2 = 0.9926$), Ipa = $0.04C_{DA} – 0.5833$ ($R^2 = 0.9912$), Ipa = $0.0489C_{PAR} – 0.4823$ ($R^2 = 0.9956$) and Ipa = $0.0297C_{TRP} + 2.1325$ ($R^2 = 0.9911$), and the linear concentration ranges were 0.08-475 μM, 0.04–420 μM, 0.033-400 μM, and 0.053-480 μM with detection limits (S/N = 3) of 0.024 μM, 0.012 μM, 0.010 μM, and 0.016 μM, for AA, DA, PAR, and TRP, respectively. These results indicate that the proposed method can be used for selective determination of the three species.


(a)
475 µM
0.08 µM
I/µA
E/V vs. Ag/AgCl
y = 0.0201x - 0.4937
R² = 0.9926
I/µA
C_AA/µM


(b)
420 µM
0.04 µM
I/µA
E/V vs. Ag/AgCl
y = 0.04x - 0.5833
R² = 0.9912
I/µA
C_DA/µM

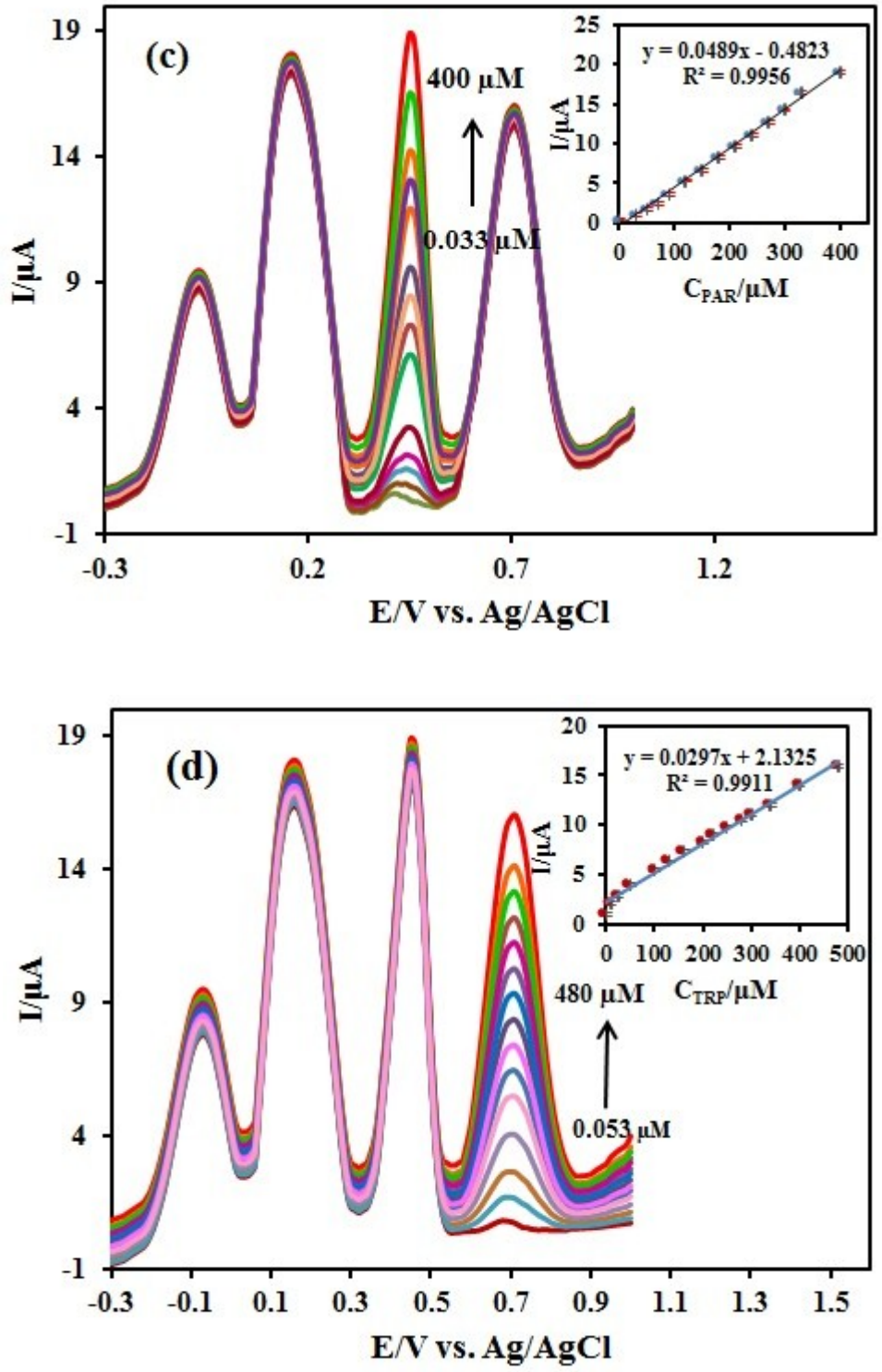


Fig. S3. . DPVs of (a) different concentrations of AA (0.08–475.0 µM) in the presence of 500.0 µM of DA, PAR, and TRP; (b) different concentrations of DA (0.04–420.0 µM) in the presence of 500 µM of AA, PAR, and TRP; (c) different concentrations of PAR (0.033–400.0 µM) in the presence of 500.0 Mm of AA, DA, and TRP; (d) different concentrations of TRP (0.053–

480.0 μM) in the presence of 500.0 Mm of AA, DA, and PAR. DPV experimental conditions: pulse amplitude of 50 mV, pulse time of 100 ms, sweep rate of 50 mV s^{-1}; in 0.1 M PBS solution (pH 7.0). Error bars indicate the standard deviations of three repeated measurements.

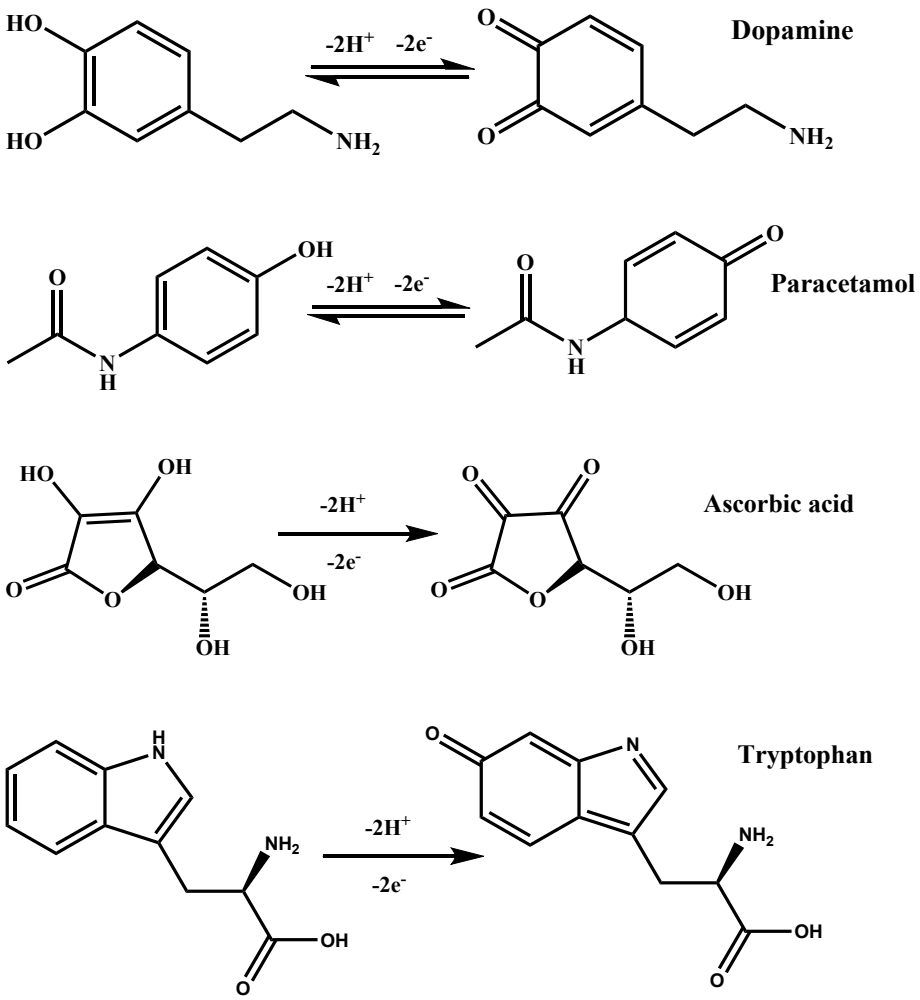


Fig.S4: Electrochemical Oxidation of AA, DA, PAR, and TRP.

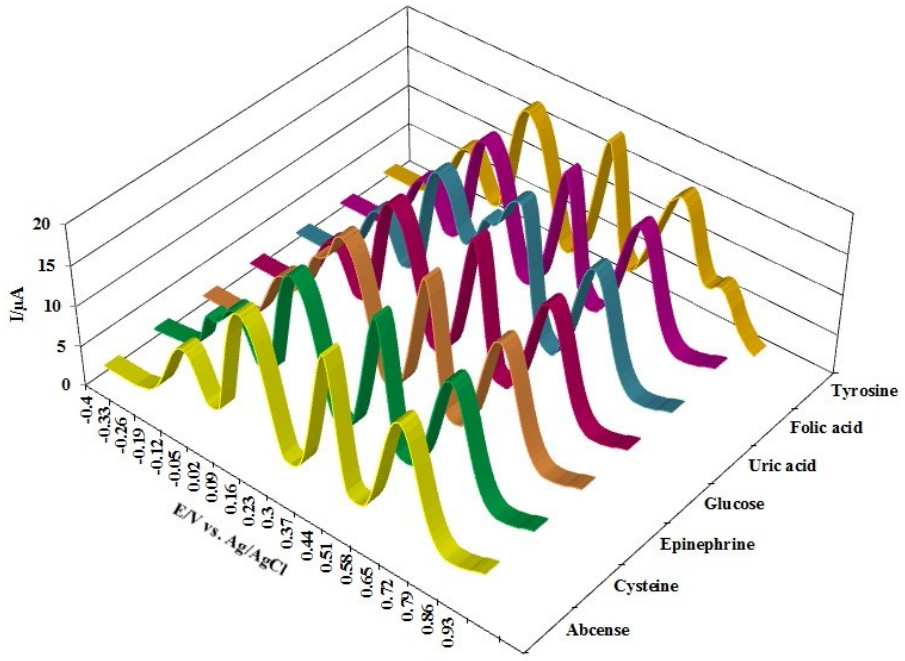


Fig. S5: Interference test of the 3DCu$_x$O-ZnO/PPy/RGO/GCE in 0.1 M phosphate buffer solution (pH 7.0) containing 500 µM of AA, DA, PAR, and TRP, and other interferents as indicated.

Table S1: Effect of various interferents on the AA, DA, PAR, and TRP sensing response of 3DCu$_x$O-ZnO/PPy/RGO/GCE.

Interferences	Average of I_p(µA)				%E(±)				%RSD			
	AA	DA	PAR	TRP	AA	DA	PAR	TRP	AA	DA	PAR	TRP
Cysteine (500)	9.60	18.12	19.07	16.13	1.91	0.78	0.37	0.50	1.06	0.16	0.80	0.95
Epinephrine (500)	9.50	18.48	19.12	16.29	0.84	2.78	0.63	1.49	1.06	0.42	0.66	1.14
Glucose (500)	9.47	18.28	19.40	16.27	0.53	1.67	2.11	1.37	1.62	0.42	0.18	0.68
Uric acid (500)	9.39	18.08	19.33	16.18	0.32	0.56	1.74	0.81	0.84	0.42	1.32	0.47
Folic acid (500)	9.36	17.98	19.10	17.17	0.64	0	0.53	6.96	0.96	0.42	0.53	0.95
Tyrosine (500)	9.41	17.88	19.15	16.37	0.11	0.56	0.79	1.99	0.96	0.42	0.79	0.95
Interference free Average	9.42	17.98	19.00	16.05								