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SUPPORTING INFORMATION

3D reduced graphene oxide and flower-like ZnO crystal composites for electrochemical detection of reducing small biomolecules

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TEXT:

2.2 Preparation of electrode modification materials

A mixture containing 0.5 g graphite powder, 0.5 g $NaNO_3$ and 23 mL concentrated H_2SO_4 was put into an ice bath for 30 min under mild agitation. Then 3.0 g $KMnO_4$ was added slowly and the mixed suspension was heated to 35℃ and kept for 1 h. After adding 40 mL of double deionized water (DDW), the heating temperature of the mixed solution was raised to 90℃ and kept for another 30 min. Then, 100 mL DDW was added to dilute the above mixture. With the slow addition of H_2O_2 (30%, 30mL), the mixture turned from dark brown to bright yellow. After that, the resulting mixture was centrifuged and washed with anhydrous ethanol and DDW. Finally, the obtained GO sample was dried in vacuum at 60℃ for 24 h. The as-prepared GO was sonicated for 1.0 h in water to obtain a homogeneous suspension at 2.0 mg/mL, which was ready for the preparation of 3DrGO.

30 mL of GO dispersion was well mixed with 100 mg of *L*-cysteine. The mixture was then poured into a 75 mL Teflon-lined stainless-steel autoclave and kept at 200℃ for 12 h. After the autoclave was naturally cooled to room temperature, the precipitate was gathered by centrifugation, washed with anhydrous ethanol and DDW for several times. Finally, the product named as 3DrGO was dried overnight for further use.

0.48 g $Zn(CH_3COOH)_2H_2O$ were dissolved in 25 mL DDW, followed by addition of 1.0 mol/L NaOH to the formation of a transparent $[Zn(OH)_4]^{2-}$ solution. Then, 2.0 mL anhydrous ethanol and 0.1 g of citric acid were added under stirring. The mixture was transferred to a 75 mL Teflon-lined stainless-steel autoclave and kept in an oven at 200℃ for a period of 12 h. After cooling, the flower-like ZnO crystal was separated by centrifuge, washed several times with anhydrous ethanol and DDW, and then dried in vacuum at 60℃ for 24 h.

FIGURES:

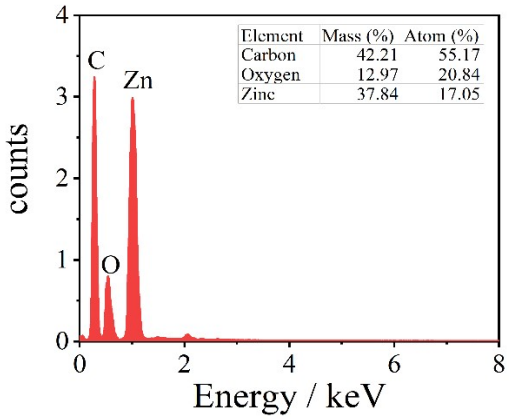

Fig. S1 EDX spectrum of 3DG-ZnO.

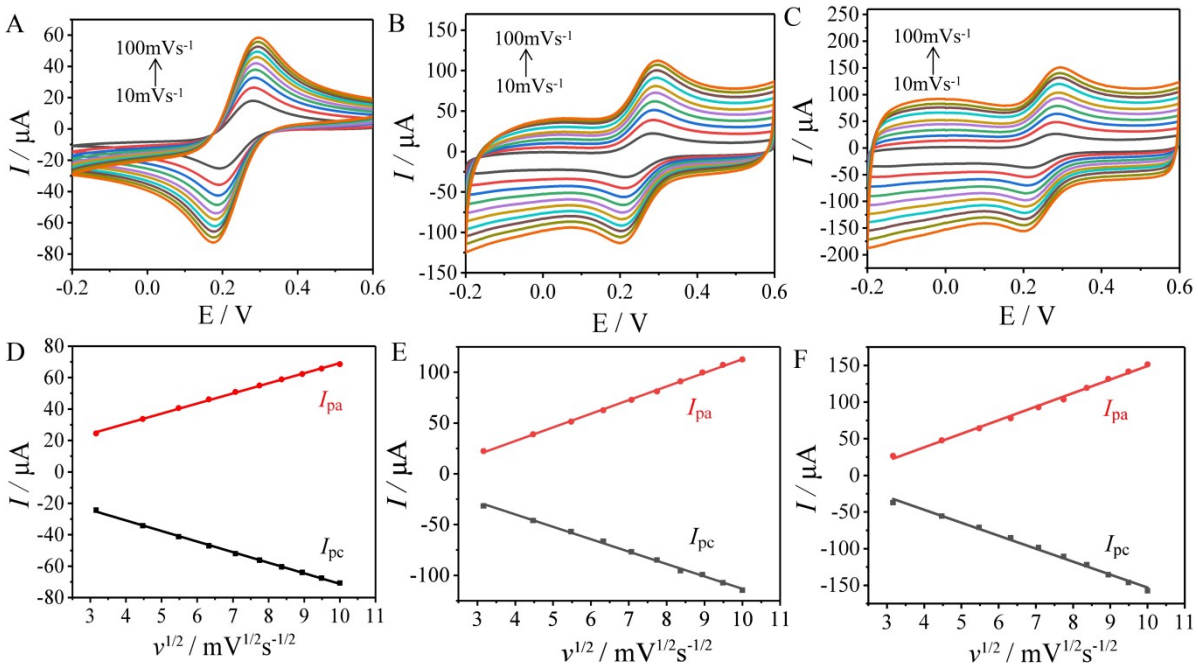

Fig. S2 CV curves of (A) bare GCE, (B) 3DrGO /GCE, and (C) 3DrGO-ZnO/GCE in 5 mmol/L $[Fe(CN)_6]^{3-/4-}$ at different scan rates. (D)-(F) The corresponding plots of peak current versus square root scan rate. The measurement was implemented in PBS containing 0.1 moL L^{-1} KCl medium.

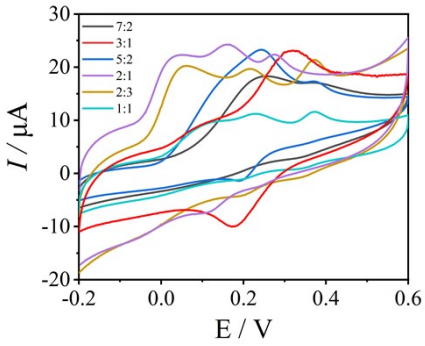

Fig. S3 CVs of 3DrGO-ZnO/GCE in mixture of AA (1 mmol/L), DA (50 μmol/L) and UA (200 μmol/L) at different volume ratios.

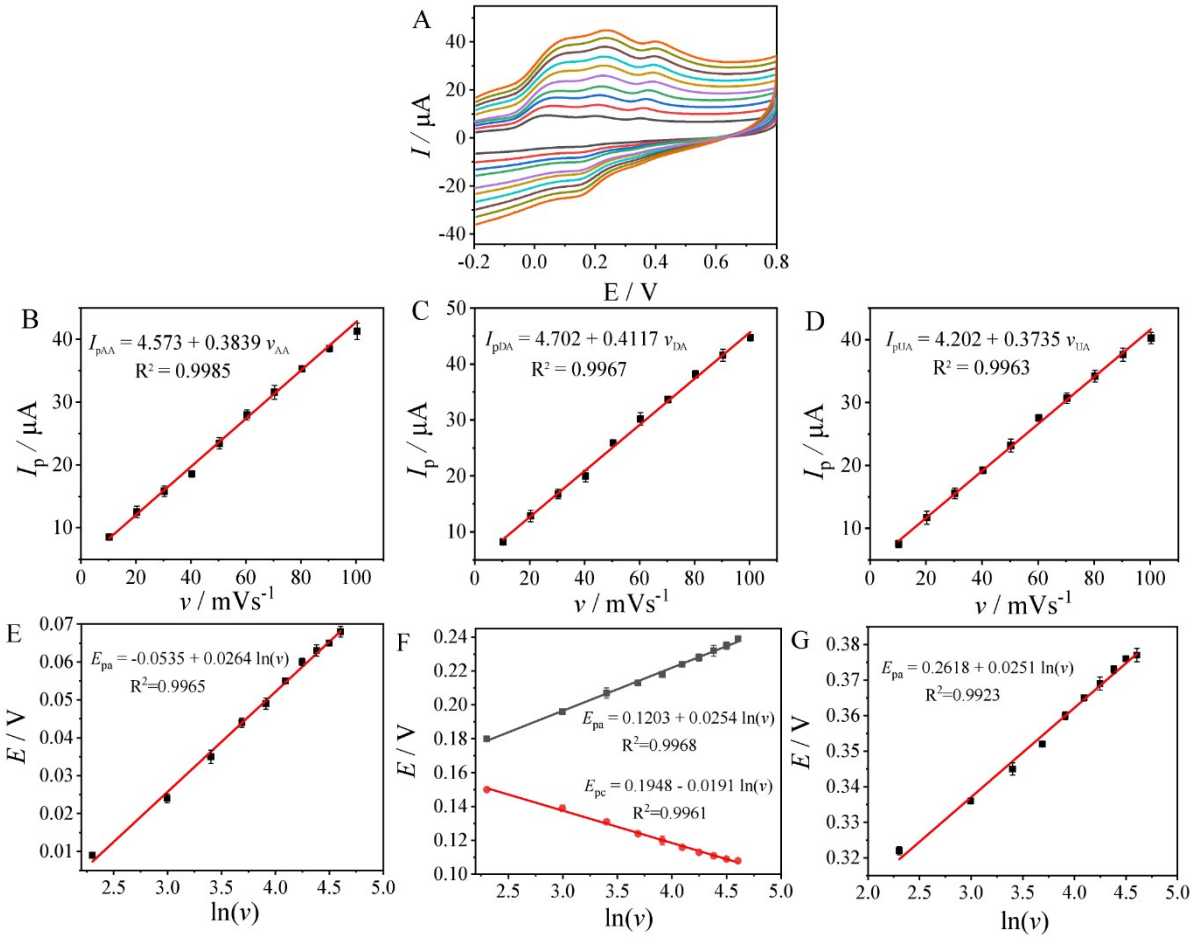

Fig. S4 (A) CV curves of 3DrGO-ZnO/GCE in mixture of AA (1 mmol/L), DA (50 μmol/L) and UA (200 μmol/L) at different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s). (B)-(D) The plots of peak current versus scan rate. (E)- (G)The plots of peak potential versus ln(v). The measurement was implemented in PBS (pH 7.5) medium.

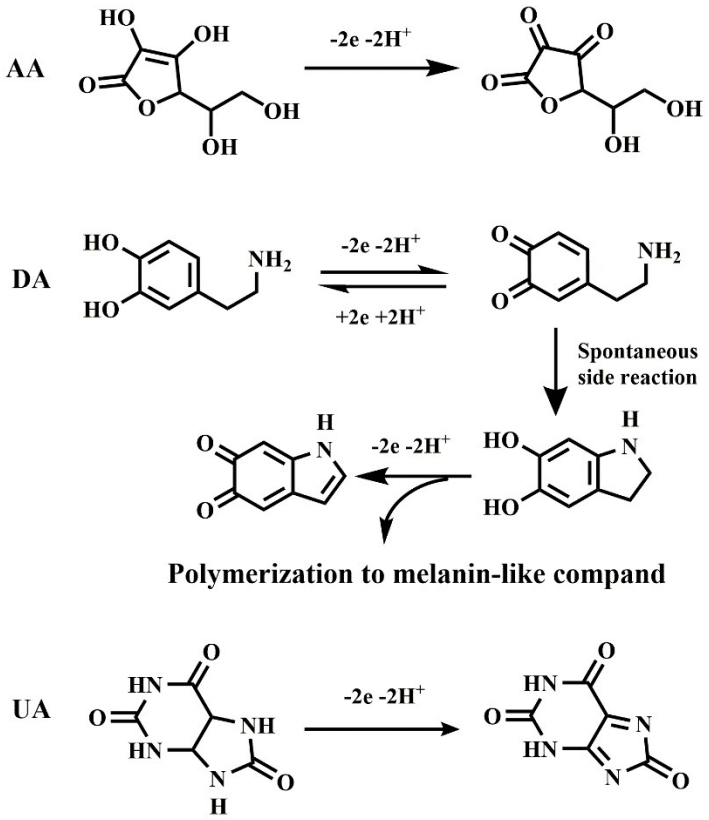

Fig. S5 Reaction mechanism of AA,DA and UA on 3DrGO-ZnO/GCE

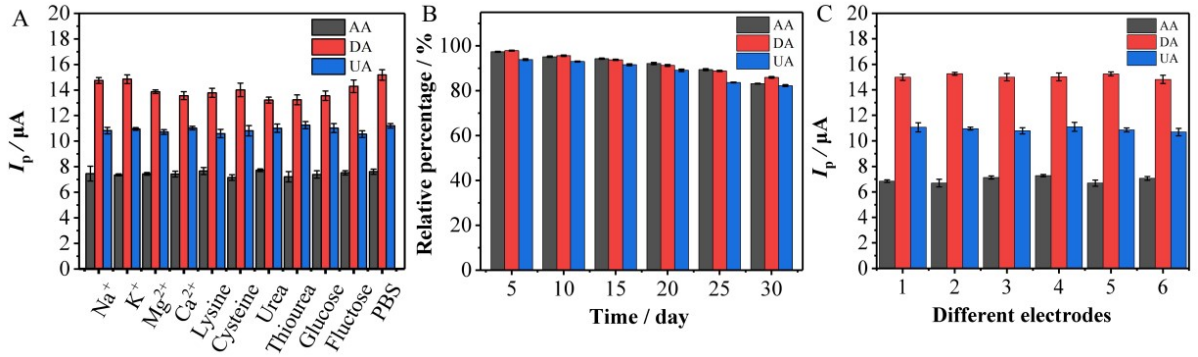

Fig. S6 (A) Effects of different interfering substances on the simultaneous determination of AA, DA and UA in PBS (pH = 7.5) by DPV technology at 3DG-ZnO NFs/GCE; (B) The oxidation peak currents of AA, DA and UA at different storage times; (C) the oxidation currents of AA, DA and UA at different electrodes.

TABLE:

Table S1 Comparison of analytical performance of 3DrGO-ZnO/GCE with other modifed electrodes

Electrode	Detection method	Linear range (μmol/L)			Detection limit (μmol/L)			References
		AA	DA	UA	AA	DA	UA	
3D-KSC/C_{CSBP}	DPV	1980─6000	14.1-100	450-1200	660	4.6	150	[14]
ZnO-CuO/PCS/GCE	DPV	100-3000	13-400	6-800	18.94	1.03	0.42	[16]
ERGO/GCE	DPV	500-2000	0.5-60	0.5-60	300	0.5	0.5	[42]
PdPt-PDDA-RGO/GCE	DPV	40-1200	4-200	4-400	0.61	0.04	0.10	[43]
Au-RGO/GCE	DPV	240-1500	6.8-41	8.8-53	51	1.4	1.8	[44]
GS/GCE	DPV	100-1000	1-20	3-21	100	1	3	[45]
Au/HG	DPV	4-600	0.4-20	0.6-60	1.76	0.02	0.57	[46]
BN	DPV	30-1000	0.5-150	1-300	3.77	0.02	0.15	[47]
CB-CNT/PI/GCE	DPV	1000-24000	3-300	5-500	154	1.86	3.0	[48]
N-rGO/GCE	DPV	100-4000	1-60	1-30	9.6	0.1	0.2	[49]
PEDOT-GO/GCE	DPV	100-1000	6.0-200	40-240	20	2.0	10	[50]
3DG-ZnO NFs/GCE	DPV	100-2500	2.0-35	1.0-150	39	0.67	0.34	This work