A Simultaneous determination of dihydroxybenzene isomers using a three-dimensional over-oxidized polypyrrole-reduced graphene oxide composite film electrode prepared by electrochemical method

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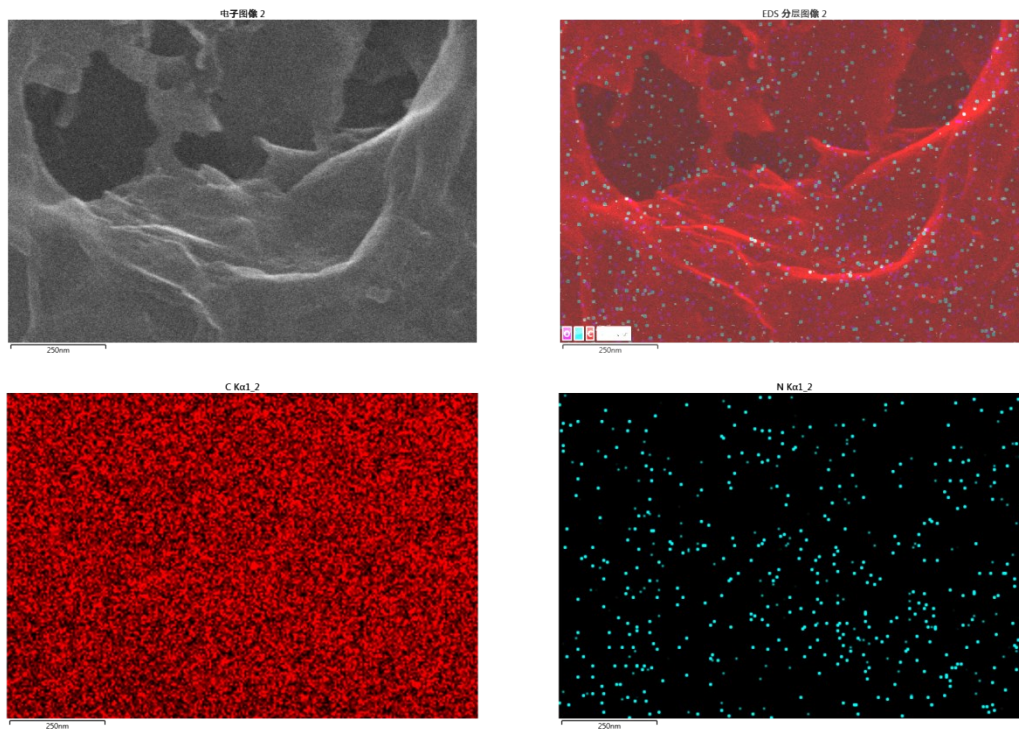Tel.: + 86 911 2332037, fax: + 86 911 2332317

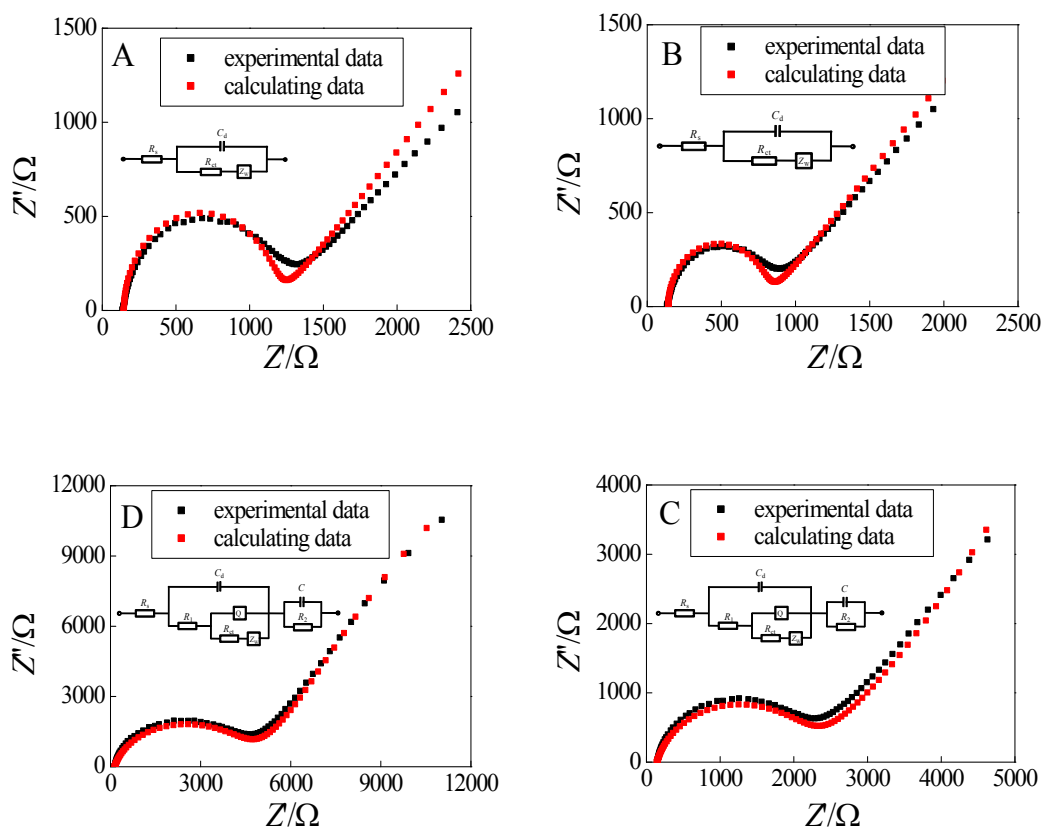**Figure S1** the surface element mapping diagrams of OPPy/ERGO/CCE (E-H)

Figure S2 Nyquist plots of bare CCE (A), ERGO/CCE (B), OPPy/CCE (C) and 3D-OPPy/ERGO/CCE (D). the black dots represented the measured data, and the red dots were the data fitted by ZSimpWin software.

The ZSimpWin software was used to fit the EIS data, the results were showed in Fig.S2 (in this section). For bare CCE (A) and ERGO/CCE (B), the equivalent circuit were R(C(RW)). For OPPy/CCE (C) and OPPy/ERGO/CCE (D), the equivalent circuit were R(C(R(Q(RW))))(CR). It can be seen that the fitting effect were good. From fig. S2, the charge transfer resistance (R_{ct}) of the above electrodes was 1013 (bare CCE), 649 (ERGO/CCE), 4388 (OPPy/CCE), and 2067 (OPPy/ERGO/CCE), respectively. The error was 2.1% (Bare CCE), 2.1% (ERGO/CCE), 2.8% (OPPy/CCE), and 2.4% (OPPy/ERGO/CCE), respectively.
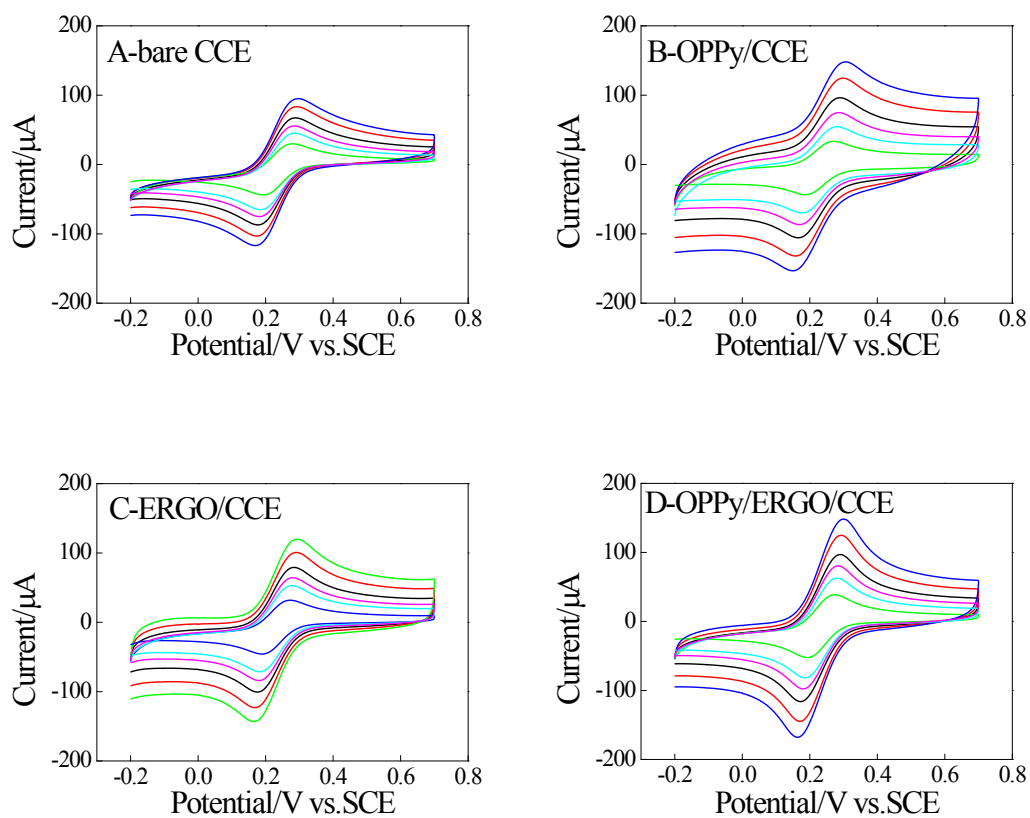
Figure S3 CV graphs of various modified electrodes of CCE (A), OPPy/CCE (B), ERGO/CCE (C) and OPPy/ERGO/CCE (D) in 0.1 mol L^{-1} KCl containing 5.0 mM K$_3$Fe(CN)$_6$ at various scan rates (20, 50, 70, 100, 150, and 200 mV s^{-1}).
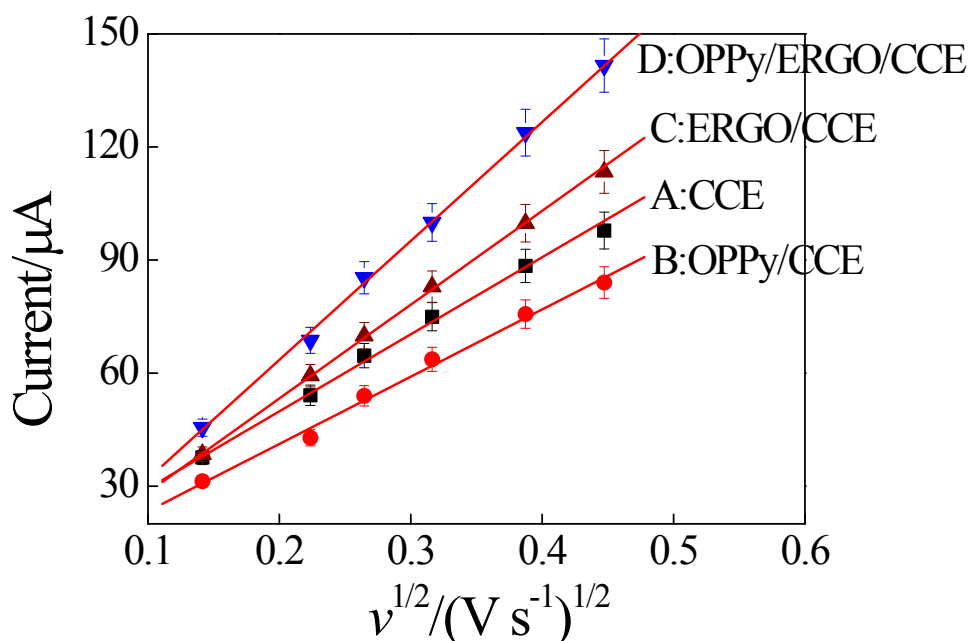
Figure S4 linear relationship between the anodic peak currents to the square root of potential scan rates, (A). CCE, (B). OPPy/CCE, (C). ERGO/CCE, (D). OPPy/ERGO/CCE. According to this diagram, the effective electrode area of different electrodes can be calculated as 0.055 (bare CCE), 0.048 (OPPy/CCE), 0.067 (ERGO/CCE) and 0.085 (OPPy/ERGO/CCE) cm^2, respectively.

[1] N. Sabbaghi, M. Noroozifar, *Anal. Chim. Acta*, 2019, **1056**, 16−25.

The effective area of different electrodes was determined by CV. Fig. S3 exhibited the CV graphs of bare CCE (A), OPPy/CCE (B), ERGO/CCE (C) and OPPy/ERGO/CCE (D) in 0.1 mol L^{-1} KCl containing 5.0×10^{-3} mol L^{-1} K$_3$Fe(CN)$_6$ at various scan rates (20, 50, 70, 100, 150, and 200 mV s^{-1}). Based on the Randles-Sevcik equation, the peak current on CV can be expressed as equation (1):

$$I_p = 2.69 \times 10^5 \; n^{3/2} \; A \; D^{1/2} \; c \; v^{1/2} \tag{1}$$

where I_p was the anode peak current on CV (A), n was the electron transfer number ($n = 1$), c was the concentration of K$_3$[Fe(CN)$_6$] (5.0×10^{-6} mol cm^{-3}), v was the potential scan rate, D was the diffusion coefficient of K$_3$[Fe(CN)$_6$] (7.6×10^{-6} cm^2 s^{-1}) [1], and A was the effective area of the electrode (cm^2). According to the linear

relationship between I_p and $v^{1/2}$, the effective electrode area A can be calculated. Fig. S4 was the linear relationship between I_p and $v^{1/2}$ of CCE (A), OPPy/CCE (B), ERGO/CCE (C) and OPPy/ERGO/CCE (D), respectively. Based on this, the effective electrode areas of these electrodes can be calculated as 0.055 (bare CCE), 0.048 (OPPy/CCE), 0.067 (ERGO/CCE) and 0.085 (OPPy/ERGO/CCE) cm², respectively.
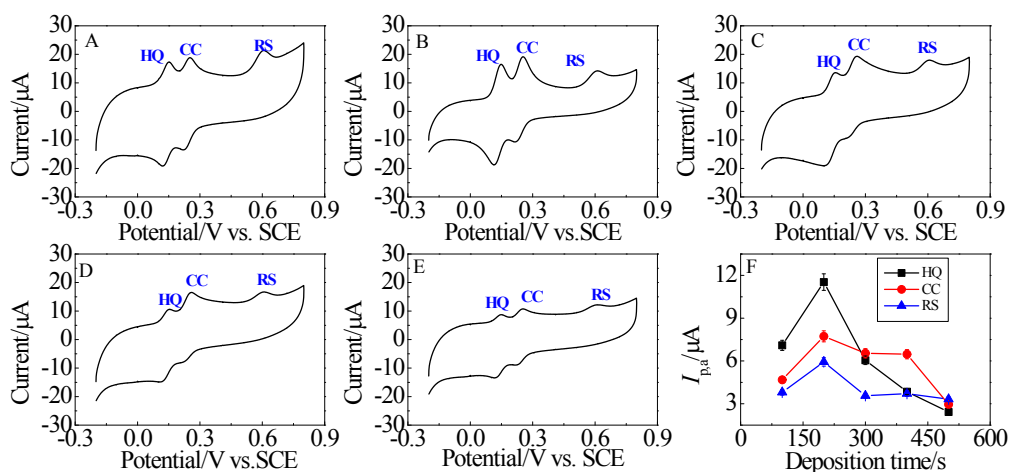

Figure S5 CV graphs of 0.1 mM (HQ), (CC) and (RS) on 3D-OPPy/ERGO/CCE prepared at various deposition times of 100 s (A), 200 s (B), 300 s(C), 400 s (D) and 500 s (E), and the curves between peak currents versus deposition time (F), the other experimental conditions are the same as those in figure 4.
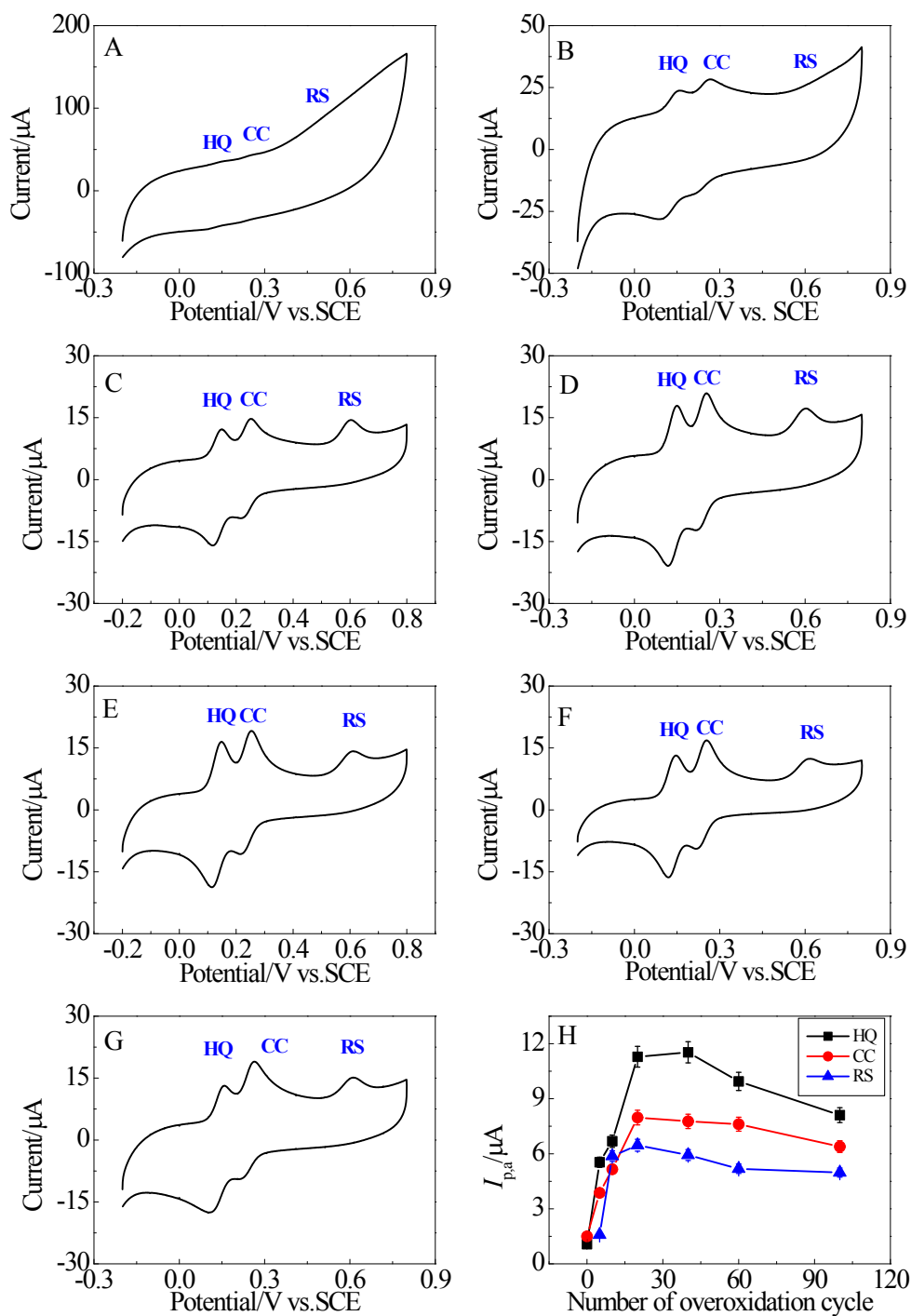
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Figure S6 CV graphs of 0.1 mM HQ, CC and RS on 3D-OPPy/ERGO/CCE prepared with different overoxidation cycles of 0 (A), 5 (B), 10 (C), 20 (D), 40 (E), 60 (F) and 100 cycle (G), and the curves between peak currents versus overoxidation cycle (H), the other experimental conditions are the same as in fig. 4.
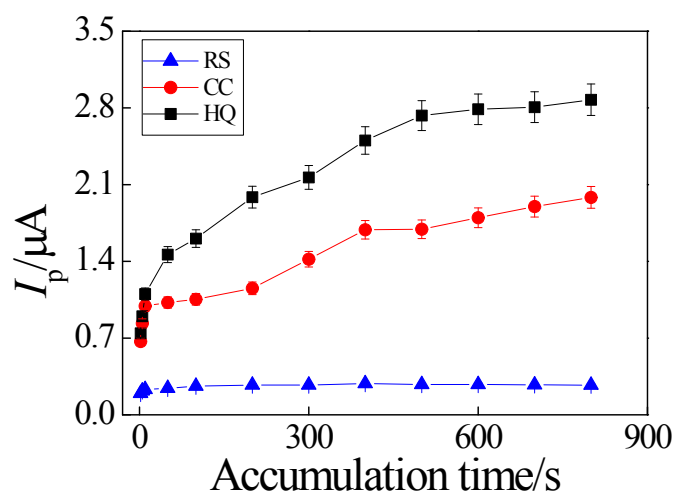
Figure S7 Effect of accumulation time on the oxidation peak currents of 5.0 μM HQ, CC and RS, the parameters of DPV were as follows, sweep potential range, − 0.2 − 0.8 V, potential increment, 4 mV, pulse amplitude, 50 mV, pulse period, 0.05 s, sampling width, 0.0167 s, the supporting electrolyte, 0.10 M phosphate buffer (pH 6.0).
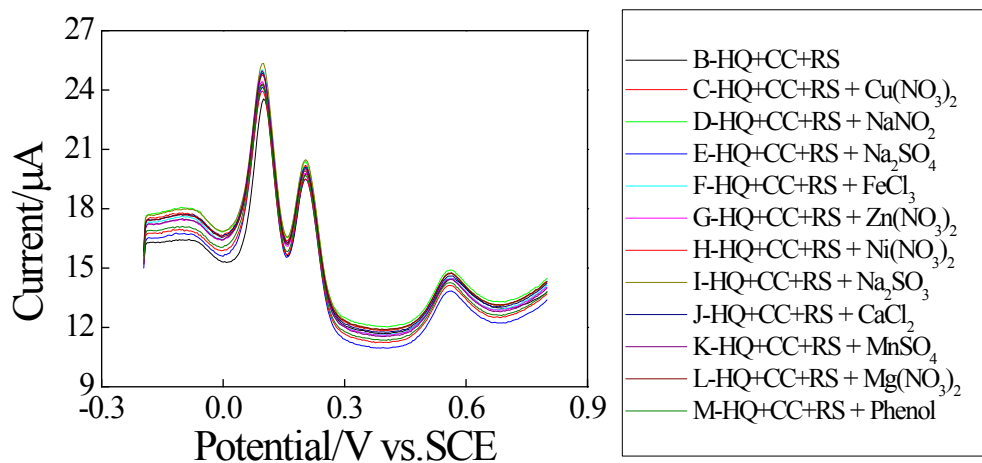

Figure S8 DPV curves of 30.0 μM HQ + CC + RS with the addition of some common interfering substances in water.

Table S1 Peak current changes caused by some common interfering substances for HQ, CC and RS.

| Substances	Peak current (μA)			Peak current changes r (%)		
	HQ	CC	RS	HQ	CC	RS
0.03 mM (HQ + CC + RS)	8.348	5.387	2.177	-	-	-
0.3 mM Cu(NO$_3$)$_2$ + 0.03 mM (HQ + CC + RS)	8.054	5.387	2.143	-3.5	2.0	-1.6
0.3 mM NaNO$_2$ + 0.03 mM (HQ + CC + RS)	8.697	5.501	2.238	4.2	2.1	2.8
6.0 mM Na$_2$SO$_4$ + 0.03 mM (HQ + CC + RS)	8.291	5.249	2.231	-0.7	-0.6	2.5
0.3 mM FeCl$_3$ + 0.03 mM (HQ + CC + RS)	8.592	5.434	2.211	2.9	2.9	-1.5
3.0 mM Zn(NO$_3$)$_2$ + 0.03 mM (HQ + CC + RS)	8.710	5.327	2.187	4.3	0.8	-0.5
3.0 mM Ni(NO$_3$)$_2$ + 0.03 mM (HQ + CC + RS)	8.222	5.153	2.209	-1.5	-2.5	1.5
1.5 mM Na$_2$SO$_3$ + 0.03 mM (HQ + CC + RS)	8.183	5.263	2.302	-2.0	-0.4	5.7
6.0 mM CaCl$_2$ + 0.03 mM (HQ + CC + RS)	8.271	5.284	2.069	-0.9	-2.0	-4.9
3.0 mM MnSO$_4$ + 0.03 mM (HQ + CC + RS)	8.426	5.248	2.112	0.9	-0.7	-3.0
6.0 mM Mg(NO$_3$)$_2$+ 0.03 mM (HQ + CC + RS)	8.702	5.303	2.228	4.2	0.4	2.3
0.03 mM Phenol + 0.03 mM (HQ + CC + RS)	7.943	5.046	2.318	-4.9	-4.5	4.5
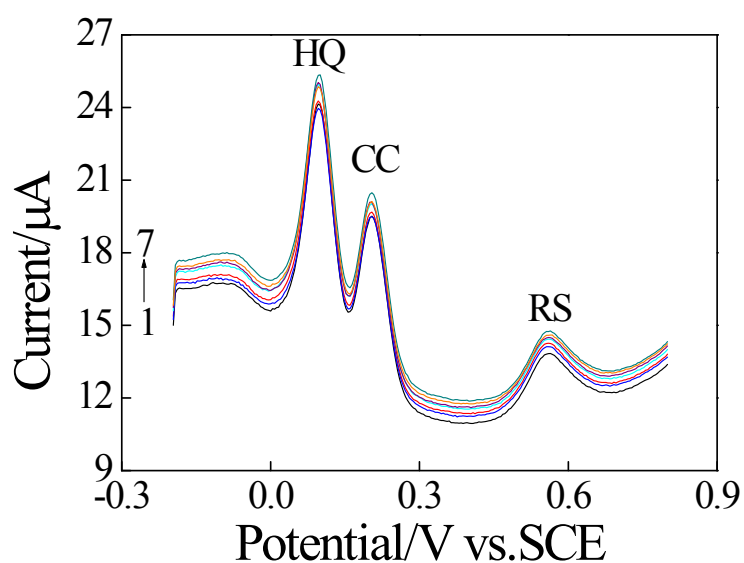
Figure S9 DPV curves for 7 times parallel determination of 30.0 μM HQ, CC and RS mixture using a same modified electrode.

Table S2 The peak currents and its RSD for 7 times parallel determination of 30.0 µM HQ, CC and RS mixture using a same modified electrode.

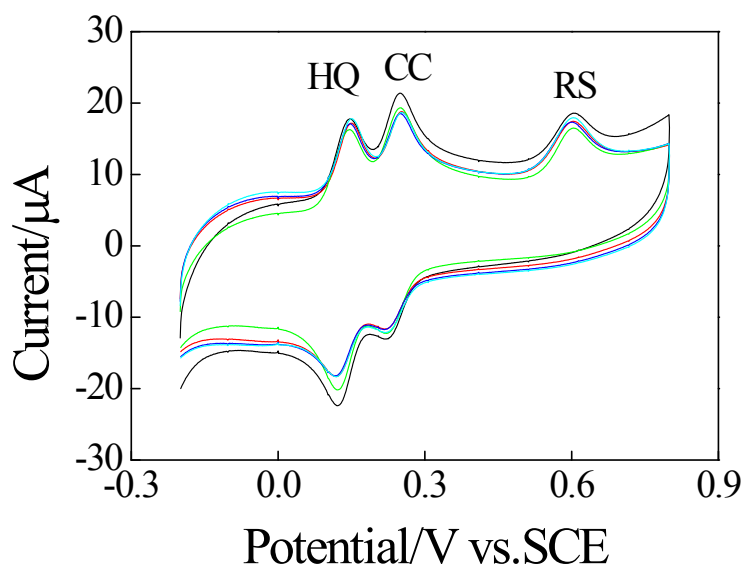| Number	Peak current (µA)			RSD (%)		
	HQ	CC	RS	HQ	CC	RS
1	8.442	5.211	2.240			
2	8.340	5.315	2.226			
3	8.121	5.199	2.248			
4	8.003	5.162	2.210	2.2	1.1	2.0
5	8.461	5.249	2.177			
6	8.430	5.293	2.221			
7	8.216	5.165	2.120			

Figure S10 CV graphs of 0.1 mM HQ, CC and RS on five modified electrodes prepared by the same procedure.

Table S3 Peak currents and RSD of 0.1 mM HQ, CC and RS on five modified electrodes prepared by the same procedure.

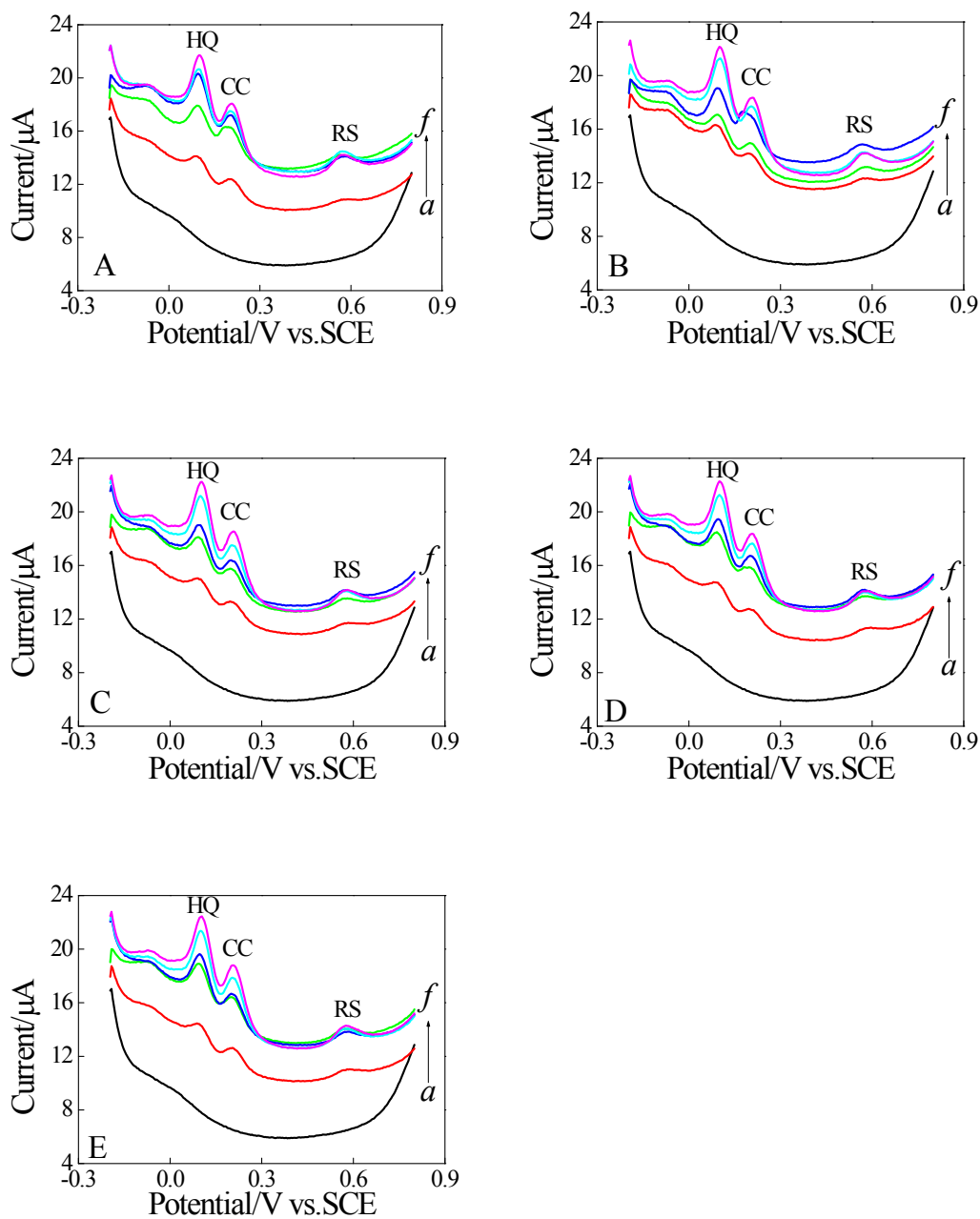| Number	Anode peak current (µA)			RSD (%)		
	HQ	CC	RS	HQ	CC	RS
1	10.48	7.118	6.901			
2	10.31	6.483	7.349			
3	10.81	7.303	7.142	2.3	7.5	4.8
4	10.20	6.276	7.248			
5	10.32	6.217	7.861			

Figure S11 DPV curves for 5 times parallel determination (A-E) of water sample and the spiked samples, curve a. water sample, b-f. the spiked samples with addition of 3.00, 6.00, 9.00, 12.0, and 15.0 μM HQ + CC + RS standard solution.