Simultaneous determination of hydroquinone, catechol, resorcinol and nitrite using gold nanoparticles-loaded poly-3-amino-5-mercapto-1,2,4-triazole-MWNTs modified electrode

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## 1. Reagents and chemicals

Carboxylic Multiwall carbon nanotubes (MWNTs >95% purity) were purchased from Chengdu Organic Chemicals Co. Ltd. of the Chinese Academy of Science. Catechol (CC), hydroquinone (HQ) and resorcinol (RC) were obtained from aladdin reagent Co. (Shanghai, China). Sodium nitrite (NaNO<sub>2</sub>) was purchased from Chemical Reagent Co. (Chongqing, China). Phosphate buffer solutions (PBS) (0.1 M) at various pH values were prepared using 0.1 M Na<sub>2</sub>HPO<sub>4</sub>, 0.1 M KH<sub>2</sub>PO<sub>4</sub> and 0.1 M KCl. Double-distilled water was used throughout the experiments.

2. Apparatus

All electrochemical experiments were performed with a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China). The

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three-compartment electrochemical cell contained a modified electrode as the working electrode, a saturated calomel reference electrode (SCE), and a platinum wire auxiliary electrode. Scanning electron micrographs were studied with a scanning electron microscope (SEM, S-4800, Hitachi, Japan). All measurements were taken out at room temperature.

The glassy carbon electrode (GCE, diameter 4.0 mm) was successively polished with 0.3 and 0.05  $\mu$ m alumina slurry to obtain mirror-like surface, and then rinsed thoroughly with ethanol and water. Finally, it was allowed to dry at room temperature. 3. The effect of pH on the electrochemical oxidation of HQ, CC, RC and NO<sub>2</sub><sup>-</sup> at Au/pAMTa-MWNTs/GCE.

The effect of pH value on the electrochemical response of the Au/pAMTa-MWNTs/GCE toward the simultaneous determination of HQ, CC, RC and  $NO_2^-$  in their mixed solution was carefully investigated by CVs in a wider pH range (pH 5.0-9.0). As can be seen from Fig. 3S, with the increasing of pH value, all the oxidation potentials for HQ, CC and RC shift negatively. Moreover, the oxidation peak current increase with increasing pH value until it reaches 7.0, and then the oxidation peak currents decrease when the pH increases further. Considering the high sensitivity and selectivity, a pH value of 7.0 was selected for further experiments.

4. Simultaneous voltammetric determination of HQ, CC, RC and NO<sub>2</sub><sup>-</sup>

The overall facility of the Au/pAMTa-MWNTs/GCE for simultaneous determination of HQ, CC, RC and  $NO_2^-$  was demonstrated by changing their concentrations simultaneously. As can be seen in Fig. 4S, in the quaternary mixture,

the Au/pAMTa-MWNTs/GCE resolved the mixed voltammetric responses into four clear and well-defined voltammetric peaks, which corresponded to HQ, CC, RC and  $NO_2^-$ , respectively. In addition, the current intensity corresponding to the oxidation of HQ, CC, RC and  $NO_2^-$  increased linearly with their concentrations. Finally, from these CV results, it can be concluded that the Au/pAMTa-MWNTs/GCE is a suitable mediator for the simultaneous determination of HQ, CC, RC and  $NO_2^-$ .

5. In order to obtain the effective surface areas of the pAMTa-MWNTs and Au/pAMTa-MWNTs,  $K_3[Fe(CN)_6]$  is used as a probe. CV experiments have been performed at pAMTa-MWNTs/GCE (Fig 5S) and Au/pAMTa-MWNTs/GCE (Fig 6S) in 5 mM  $[Fe(CN)_6]^{3^-}/[Fe(CN)_6]^{4^-}$  solution at various scan rates. For a reversible process <sup>1</sup>:

$$I_P = 2.69 \times 10^5 \times (D_0) \cdot A \cdot v^{1/2} \cdot n^{3/2} \cdot C_0$$

For  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  (5 mM), n= 1, C<sub>0</sub>= 5×10<sup>-6</sup> moL cm<sup>-3</sup> D<sub>0</sub>= 1×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>. Then the effective surface area of the pAMTa-MWNTs and Au/pAMTa-MWNTs are estimated to be 0.3832 cm<sup>2</sup> and 0.3997 cm<sup>2</sup>.

6. The effect of scan rate on the redox peak potential was also investigated (Fig 7S). With the increase of scan rate, the oxidation peak potential shifted positively and the reduction peak potential shifted negatively. The charge transfer coefficient, can be calculated based on the slopes of the two straight lines of Ep versus logv using the following equation<sup>2</sup>:

$$Log \frac{k_a}{K_c} = Log \frac{\alpha}{1-\alpha}$$
 Or  $\frac{k_a}{K_c} = \frac{\alpha}{1-\alpha}$ 

Where  $k_a$  and  $k_c$  is the slope of the straight lines for  $E_{pa}$  versus logv and  $E_{pc}$  versus

logv, respectively. Thus,  $\alpha$  was calculated to be 0.389 and 0.430 for HQ and CC, respectively.

The apparent heterogeneous electron transfer rate constant ( $k_s$ ) can be calculated according to the model of Laviron for a surface-controlled electrode process. The equation is as follows <sup>3</sup>:

$$Logk_s = \alpha Log(1-\alpha) + (1-\alpha)Log\alpha - Log\frac{RT}{nFv} - \frac{\alpha(1-\alpha)nF \cdot \Delta E_p}{2.3RT}$$
.

Where *R* is an ideal gas constant, *T* is the temperature in Kelvin degree; *F* is Faraday constant; *v* is the scan rate and  $\Delta E_p$  is the separation of anodic to cathodic peak potentials. When *v* is taken as 200 mV s<sup>-1</sup>,  $\Delta E_p$  is calculated to be 70 Mv and 67 mV for HQ and CC,  $k_s$  are determined as 1.97 s<sup>-1</sup> and 2.10 s<sup>-1</sup> for HQ and CC.

The relationship between the anodic peak potential  $(E_{pa})$  and the natural logarithm of the scan rate for RC was also studied. For a totally irreversible electrode process, the relationship between  $E_{pa}$  and lnv is expressed as follows by Laviron<sup>2</sup>

$$E_{pa} = E_0 + \frac{RT}{\alpha nF} Ln \left(\frac{RTK^0}{\partial nF}\right) + \frac{RT}{\alpha nF} LnV$$

Where  $\alpha$  is charge transfer coefficient, n is transfer electron number, R, T and F have their usual meanings. Because the electron number involved in the oxidation process is 2,  $\alpha$  was calculated to be 0.362 for RC.

## **Figure captions**

**Table 1S.** Comparison of the fabricated electrode with other electrodes.

**Table 2S.** Determination of HQ, CC, RC and  $NO_2^-$  in river water samples using DPV. **Fig. 1S.** DPVs recorded at Au/pAMTa-MWNTs/GCE in 0.1 M PBS (pH 7.0) with no analyte. DPVs recorded at Au/pAMTa-MWNTs/GCE of (a) 9 circles, (b) 12 circles, (c) 15 circles, (d) 18 circles and (e) 21 circles electropolymerization of AMTa on the GCE (the electrodeposition time of Au is 60 s) in 0.1 M PBS (pH 7.0) containing 0.06 mM HQ, 0.06 mM CC, 0.12 mM RC and 1.00 mM  $NO_2^-$ . DPV conditions: scan rate, 20 mVs<sup>-1</sup>; amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms.

**Fig. 2S**. DPVs at the Au/pAMTa-MWNTs/GCE in 0.1 M PBS (pH 7.0) with different electrodeposition time of Au (a) 40 s, (b) 60 s, (c) 80 s, (d) 100 s and (e) 120 s on the polymer film (15 circles) in 0.1 M PBS (pH 7.0) containing 0.06 mM HQ, 0.06 mM CC, 0.12 mM RC and 1.00 mM  $NO_2^{-1}$ . DPV conditions: scan rate, 20 mVs<sup>-1</sup>; amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms.

**Fig. 3S.** CVs of the Au/pAMTa-MWNTs/GCE in a mixture of 0.06 mM HQ, 0.06 mM CC, 0.12 mM RC and 1.00 mM NO<sub>2</sub><sup>-</sup> with different pH values. Scan rate: 50 mV s<sup>-1</sup>. **Fig. 4S.** CVs at the Au/pAMTa-MWNTs/GCE in 0.1 M PBS (pH 7.0) Scan rate: 50 mV s<sup>-1</sup>. (A) containing 0.06 mM CC, 0.12 mM RC and 1.00 mM NO<sub>2</sub><sup>-</sup> and different concentrations of HQ (from inner to outer): 0.009, 0.024, 0.054, 0.084, 0.114, 0.174, 0.234, 0.294, 0.354, 0.414, 0.504, 0.594 and 0.684 mM; (B) containing 0.06 mM HQ, 0.12 mM RC and 1.00 mM NO<sub>2</sub><sup>-</sup> and different concentrations of CC (from inner to outer): 0.009, 0.024, 0.354, 0.444 and 0.534

mM; (C) containing 0.06 mM HQ, 0.06 mM CC and 1.00 mM  $NO_2^-$  and different concentrations of RC (from inner to outer): 0.009, 0.024, 0.054, 0.084, 0.114, 0.144, 0.174, 0.234, 0.294 and 0.354; and (D) containing 0.06 mM HQ, 0.06 mM CC, and 0.12 mM RC and different concentrations of  $NO_2^-$  (from inner to outer): 0.300, 0.800, 1.300, 1.800, 2.300, 2.800, 3.050, 3.300, 3.550, 3.800, 4.050, 4.550, 5.050, 6.050, 7.050 and 8.050 mM.

**Fig. 5S.** CVs of pAMTa-MWNTs/GCE in 5 mM  $K_3[Fe(CN)_6]$  with 0.1 M KCl as the supporting electrolyte at scan rates of (from inner to outer): 0.01, 0.03, 0.05, 0.08, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 and 0.55 V s<sup>-1</sup>. Inset shows: Ipa is plot of anodic peak current vs. square root of scan rate.

**Fig. 6S.** CVs of Au/pAMTa-MWNTs/GCE in 5 mM  $K_3$ [Fe(CN)<sub>6</sub>] with 0.1 M KCl as the supporting electrolyte at scan rates of (from inner to outer): 0.01, 0.03, 0.05, 0.08, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 and 0.55 V s<sup>-1</sup>. Inset shows: Ipa is plot of anodic peak current vs. square root of scan rate.

Fig. 7S. Effect of scan rate on the redox behavior of 0.06 mM HQ, 0.06 mM CC, 0.12 mM RC and 0.30 mM  $NO_2^-$  at scan rates of (from inner to outer): 0.01, 0.03, 0.05, 0.07, 0.08, 0.10, 0.14, 0.16, 0.18, 0.20 and 0.25 V s<sup>-1</sup>.

Fig. 8S. SEM image of MWNTs

Electrode materials	pН	Linear range (µM)			Detection limit (µM)			Reference		
		HQ	CC	RC	$NO_2^-$	HQ	CC	RC	$NO_2^-$	
Grapheme-chitosan	7.0	1.0-300.0	1.0-400.0	1.0-550.0		0.75	0.75	0.75		4
MWCNT-NF-PMG	1.5	400-1000	400-1300			3.5	2.5			5
PEDOP/MWCNTs-Pd	7.4	0.1-5000	0.01-6000			0.029	0.026			6
GS/BMIMPF6	5.0	0.5-50	0.5-50			0.01	0.02			7
GR	4.5	1.0-50.0	1.0-50.0			0.015	0.01			8
Au/pAMTa-MWNTs	7.0	7.2-391.2	3.6-183.6	8.4-398.4	30.0-4190.0	0.30	0.24	0.60	10.00	This work

**Table 1S.** Comparison of the fabricated electrode with other electrodes.

Sample		Added (µM)	Found (µM)	Recovery (%)
Sample 1	Hydroquinone	30.0	30.1	100.3
	Catechol	30.0	29.4	98.0
	Resorcinol	30.0	29.8	99.3
	Nitrite	500.0	494.4	98.9
Sample 2	Hydroquinone	15.0	14.8	98.7
	Catechol	15.0	15.4	102.7
	Resorcinol	42.0	42.8	101.9
	Nitrite	300.0	292.2	97.4
Sample 3	Hydroquinone	24.8	24.5	98.8
	Catechol	88.1	87.9	99.8
	Resorcinol	30.0	30.0	100.0
	Nitrite	200.0	205.6	102.8

**Table 2S.** Determination of HQ, CC, RC and  $NO_2^-$  in river water samples using DPV.





Fig. 2S









Fig. 4S





Fig. 6S







## Fig. 8S



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