

## Electronic Supplementary Information

for

Discrimination of dopamine from ascorbic acid and uric acid on thioglycolic  
acid modified gold electrode

**Guangming Liu,\*<sup>a</sup> Jingjing Li,<sup>b</sup> Li Wang<sup>b</sup>, Nana Zong<sup>b</sup>, Shipeng Yu<sup>a</sup> and Feng Li\*<sup>b</sup>**

<sup>a</sup> *Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, People's Republic of China*

<sup>b</sup> *College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology,  
Qingdao 266042, People's Republic of China*

*E-mail: [lifeng@qust.edu.cn](mailto:lifeng@qust.edu.cn), Fax: +86-532-84023927; [gmliu@issas.ac.cn](mailto:gmliu@issas.ac.cn), Fax: +86-25-86881223*

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## 1. Materials and Methods

Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), N-hydroxysuccinimide (NHS), HAuCl<sub>4</sub> (Aldrich), potassium ferricyanide and dopamine hydrochloride were purchased from sigma-aldrich and used as received. Potassium hexacyanoferrate (III), dopamine (DA), ascorbic acid (AA) and uric acid (UA) were all purchased from Tianjing Chemical Reagent Factory (China). The 0.1 M phosphate buffer solutions (PBS) at various pH values were prepared by mixing the stock solutions of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>, and adjusting the pH with 0.1 M NaOH or H<sub>3</sub>PO<sub>4</sub>. All other chemicals were of analytical grade and doubly-distilled water (DDW) was used throughout this work.

The electrode modification was operated according to the following procedures. Firstly, gold nanoparticle modified electrode was obtained by electrodeposition in 3 mM HAuCl<sub>4</sub> solution including 0.1 M KNO<sub>3</sub> under a negative potential of -0.2 V for 110 s.<sup>1</sup> Then, the self-assembly monolayer of thioglycolic acid (TGA) was formed with the immersion of electrode into 2 mM TGA solution for 4 h. After activation of carboxyl groups of TGA by 2 mM EDC and 5 mM NHS in solution (0.1 M PBS pH 5.3) for 3 h,<sup>2</sup> the electrode could be used to capture DA molecule from the sample for further electrochemical determination.

## 2. Apparatus and instruments

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were performed on a CHI 832B electrochemical analyzer (Shanghai CH Instrument Company, China). Electrochemical impedance spectroscopy (EIS) was performed on a CHI 660D electrochemical analyzer (Shanghai CH Instrument Company, China). A conventional three-electrode system was used with bare Au or modified Au as the working electrode, Ag/AgCl electrode (saturated with

KCl) as the reference electrode, and platinum wire as the auxiliary electrode, respectively.

### 3. The schematic of the mechanism of attachment of DA

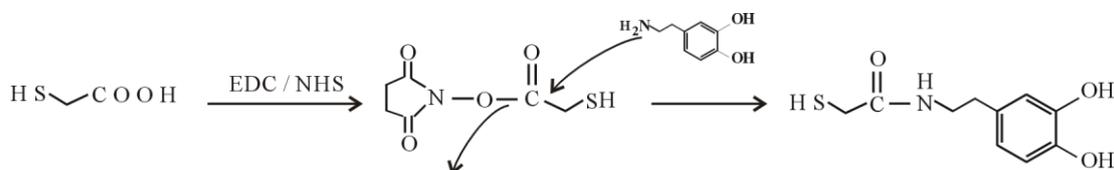


Fig. S1. Schematic mechanism of attachment of DA.

After TGA being self-assembled on the gold electrode surface, the carboxyl groups of TGA are activated with EDC and NHS, changing of the carboxylic group of TGA into a reactive intermediate which in turn is converted to a more stable reactive intermediate by NHS. This intermediate active ester is susceptible to an attack by amino groups. Subsequently, the nucleophilic attack of the nitrogen in the amine of DA, yielding the elimination of succinimide of activated TGA (Fig. S1).

### 4. Electrochemical impedance spectroscopy (EIS)

EIS was employed to characterize the interface properties of the modified electrodes. Fig. S2 shows the typical results of AC impedance spectra of the bare Au (a), AuNPs/Au (b), TGA/AuNPs/Au (c), activated TGA/AuNPs/Au (d), and DA-TGA/AuNPs/Au (e) obtained in 0.1 M KCl containing 1.0 mM  $\text{Fe}(\text{CN})_6^{3-}$  and 1.0 mM  $\text{Fe}(\text{CN})_6^{4-}$  with the frequency ranging from  $10^4$  to  $10^{-1}$  Hz. As can be seen, significant differences in the electron transfer resistance ( $R_{\text{et}}$ ) were observed upon the stepwise modification of the electrode.  $R_{\text{et}}$  value of the bare Au (Fig. S2 a) was estimated to be 1023  $\Omega$ . After electrodeposition of AuNPs onto the surface of bare Au, the value of  $R_{\text{et}}$  was decreased noticeably (Fig. S2 b), indicating an improvement of electron transfer ability of  $[\text{Fe}(\text{CN})_6^{3-/4-}]$  by the modified AuNPs. The coating of TGA film on the surface of AuNPs/Au induced the  $R_{\text{et}}$  to be 3256  $\Omega$  (Fig. S2 c). The  $R_{\text{et}}$  increase after TGA immobilization could be

well ascribed to the repulsion of redox probe from approaching electrode surface by negatively charged carboxyl groups. The activation of  $-\text{COOH}$  led to a decreased  $R_{\text{et}}$  value (Fig. S2 d), which is attributed to the negative charge of  $\text{COO}^-$  ions neutralised by activation of  $-\text{COOH}$ . After DA was covalently assembled on the modified electrode (Fig. S2 e), the  $R_{\text{et}}$  value was similar to that of the activated TGA/AuNPs/Au electrode (Fig. S2 d), which indicated that, as a small molecular monomer, DA could not lead to a large increase of  $R_{\text{et}}$  value and therefore proved that DA did not self-polymerize onto the modified electrode.

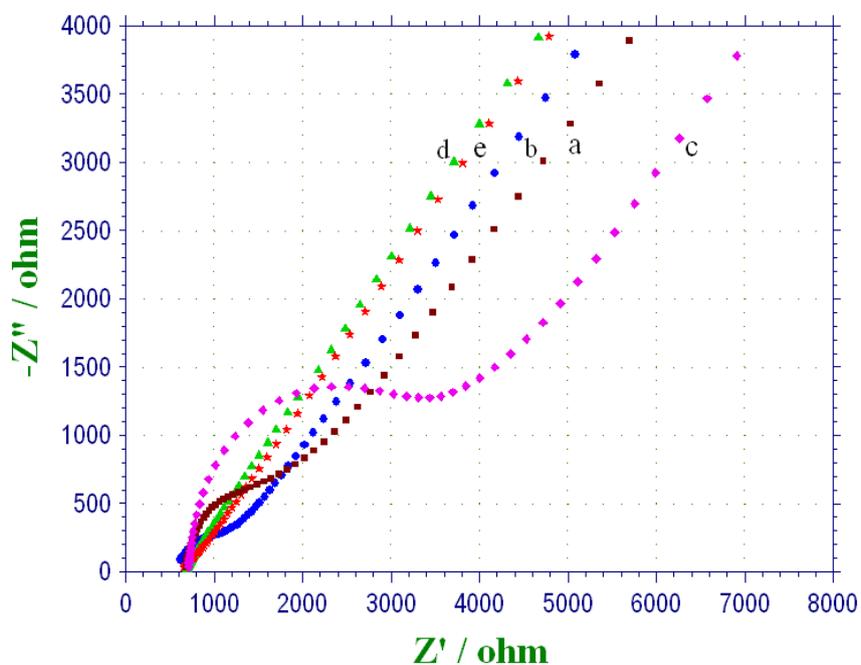


Fig. S2. EIS for (a) bare Au, (b) AuNPs/Au, (c) TGA/AuNPs/Au, (d) activated TGA/AuNPs/Au, and (e) DA-TGA/AuNPs/Au in 0.1 M KCl containing 1.0 mM  $\text{Fe}(\text{CN})_6^{3-}$  and 1.0 mM  $\text{Fe}(\text{CN})_6^{4-}$ .

## 5. pH plot

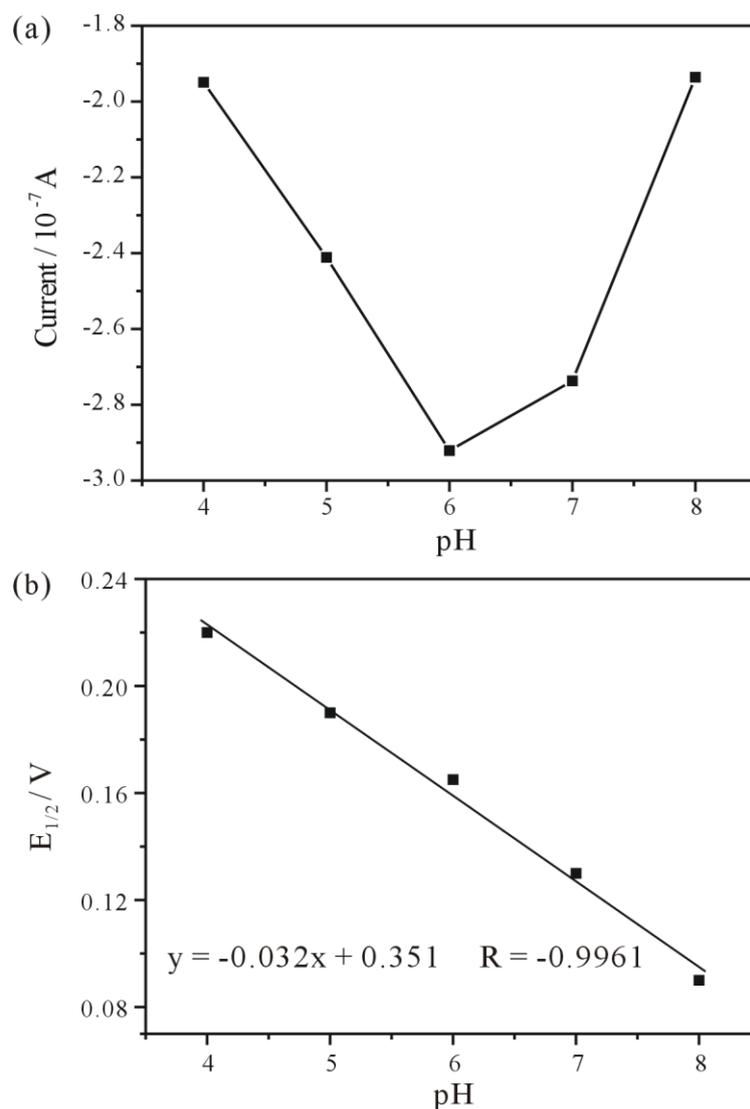


Fig. S3. pH dependence of the oxidation currents (a) and  $E_{1/2}$  potential (b) of the

DA-TGA/AuNPs/Au modified electrode in the presence of 5  $\mu\text{M}$  DA.

### Notes and References:

1 B.W. Park, D.S. Kim and D.Y. Yoon, *Korean J. Chem. Eng.*, 2011, 28, 64.

2 A. Salmanipour and M. A. Taher, *Analyst*, 2011, 136, 545.