Electronic Supplementary Information

for

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

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1. Materials and Methods

Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), N-hydroxysuccinimide (NHS), HAuCl₄ (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 NaH₂PO₄ and Na₂HPO₄, and adjusting the pH with 0.1 M NaOH or H₃PO₄. 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 HAuCl₄ solution including 0.1 M KNO₃ under a negative potential of –0.2 V for 110 s.¹ 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,² 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.](image)

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 Fe(CN)_6^{3−} and 1.0 mM Fe(CN)_6^{4−} with the frequency ranging from 10^5 to 10^1 Hz. As can be seen, significant differences in the electron transfer resistance (Ret) were observed upon the stepwise modification of the electrode. Ret value of the bare Au (Fig. S2 a) was estimated to be 1023 Ω. After electrodeposition of AuNPs onto the surface of bare Au, the value of Ret was decreased noticeably (Fig. S2 b), indicating an improvement of electron transfer ability of [Fe(CN)_6^{3−/4−}] by the modified AuNPs. The coating of TGA film on the surface of AuNPs/Au induced the Ret to be 3256 Ω (Fig. S2 c). The Ret increase after TGA immobilization could be
well ascribed to the repellence of redox probe from approaching electrode surface by negative charged carboxyl group. The activation of –COOH led to a decreased Ret valve (Fig. S2 d), which is attributed to negative charged of COO⁻ ion neutralised by activation of –COOH. After DA was covalently assembled on the modified electrode (Fig. S2 e), Ret value was similar to that of activated TGA/AuNPs/Au electrode (Fig. S2d), which indicated that, as a small molecular monomer, DA could not lead to the large increase of Ret value and therefore proved that DA was not self–polymerized onto the modified electrode.

![Graph showing complex plane impedance plots](image)

**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 Fe(CN)₆³⁻ and 1.0 mM Fe(CN)₆⁴⁻.
5. pH plot

![Graph showing 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 μM DA.](image)

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 μM DA.

**Notes and References:**
