Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

An Electrochemical Strategy for Fast Monitoring of ·OH Released from Live Cells at Electroactive FcHT-Functional Surface Amplified by Au Nanoparticles

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1. Experimental Section

Chemicals and Reagents. Indium tin oxide (ITO) coated glass plates with a square resistance of 10–15 Ω cm^{-2} were purechased from Nanbo (Shenzhen, China). Hydrogentetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99%), 1-Octadecanethiol (ODT), 6-(ferrocenyl) hexanethiol (FcHT), lipopolysaccharide (LPS) from Salmonella enterica serotype typhimurium were obtained from Sigma Aldrich. 3-aminopropanesilicane (APTMS) were purchased from Alfa Aesar, 2,2'-Azobis (2-methylpropionamidine) dihydrochloride (AAPH), sodium hypochlorite solution (7.5%) were bought from Aladdin Chemistry Co. Ltd (China). 30% Hydrogen peroxide, Trisodium citrate dehydrate (97%), potassium superoxide, and sodium hydroxide (KOH) were bought from Sinopharm Chemical Reagent Co. Ltd. All other regents were of analytical grade and used as received. All aqueous solutions were prepared with pure water. In the selectivity experiments, Superoxide anion (O_2^-) derived from dissolved KO_2 (20 μM) in the dimethyl sulphoxide (DMSO) solution. The concentration of O_2^- was estimated to be the half concentration of KO_2. Alkyl peroxyl radical (ROO·) was generated by thermolysis of AAPH (10 μM) in air-saturated aqueous solution at 310 K. and has the same concentration of AAPH. Singlet oxygen ($^1O_2$) was generated as a product of H_2O_2 (10 μM) and NaClO (10 μM) in ethanol solution, and the concentration of $^1O_2$ is also same as that of H_2O_2. Both H_2O_2 (10 μM) and ClO^- (10 μM) came from diluted commercial H_2O_2 and NaClO, and the concentration of ClO^- is considered to be the same as NaClO. ·OH was generated by the Fenton reaction (0.1 μM H_2O_2 and 0.1 μM Fe^{2+}). The influences of ROS on the decrease of peak current with SWV at the FcHT-ODT functionalized electrode were obtained within 15 min reaction time.

Apparatus and Instruments. UV-Vis (Agilent 8453) was used to measure colloidal Au. Scanning electron microscopy (SEM) (model S-4800, Hitachi, Japan) measurement was carried out to evaluate the modification of AuNPs modified ITO substrate. X-ray photoelectron spectroscopy (XPS) (model PHI 5000 ESCA, Perkin Elmer, USA) equipped with Al Kα source (1486.6 eV photons) was used to track the modification processes and decomposition of FcHT on the ITO substrate. And the binding energy of the

spectra was corrected with respect to the C 1s peak at 284.6 eV. All electrochemistry measurements were accomplished by a computer controlled CHI 660D electrochemical working station (shanghai, China). Three electrode electrochemical cell of home- made was used with KCl-saturated Ag|AgCl electrode as reference electrode and a platinum wire as counter electrode. All cyclic voltammogram (CV) and square wave voltammogram (SWV) experiments were conducted in 0.1 M PBS.

Modification Processes. After sequential sonication in soap water, ethanol, 0.1 M KOH and Milli-Q water, ITO substrates was dried with nitrogen gas and immersed in an absolute ethanol solution containing 5% APTMS at 301 K for 24 h. This substrate was denoted as APTMS/ITO electrode. Then APTMS/ITO substrates were rinsed with ethanol and Milli-Q water, dried and treated in an oven at 313 K for 1 h. Afterwards, These substrates were immersed in gold colloid solution at 277 K for 24 h, and the colloidal gold nanoparticles (AuNPs) were prepared with the reduction of $HAuCl_4$ in the presence of Trisodium citrate.[1] The characterization of AuNPs was demonstrated in Figure S1. After the attachment of AuNPs onto APTMS/ITO substrate, the electrode was denoted as AuNPs/APTMS/ITO thereafter. Finally, The AuNPs/APTMS/ITO electrodes were immersed in an absolute solution including 1 mM ODT and 1 mM FcHT at 277 K for 14 h. Before the electrochemistry experiments, they were rinsed with ethanol and Milli-Q water, dried with nitrogen gas, and denoted as FcHT-ODT/AuNPs/APTMS/ITO electrode. The preparation process stepwise was illustrated in Scheme 1.

References:

1 G. Frens, *Nature*, 1973, **241**, 20.

2. UV-Vis spectra of AuNPs and Scanning electron spectroscopic (SEM) image of AuNPs after attaching on the APTMS/ITO surface

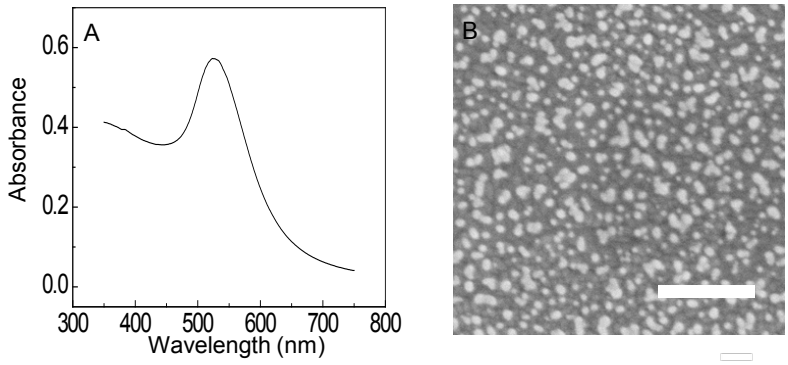

Figure S1. (A) UV-Vis absorbance spectrum of AuNPs; (B) SEM image of AuNPs after attaching on the APTMS/ITO substrate, scale bar: 100 nm.

3. Cyclic voltammograms (CVs) obtained at different surfaces

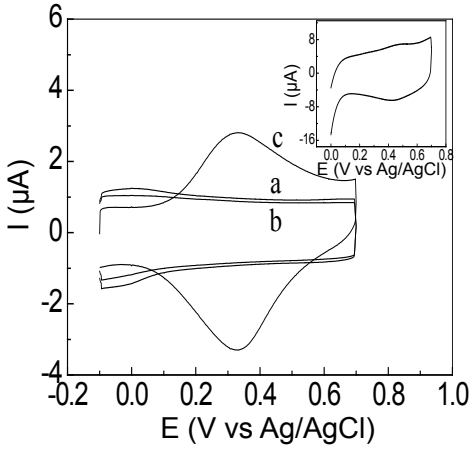

Figure S2. Cyclic voltammograms (CVs) obtained at (a) bare ITO, (b) APTMS/ITO, (c) FcHT-ODT/AuNPs/APTMS/ITO electrodes in 0.1 M PBS (pH=7.4). Insert: CV obtained at AuNPs/APTMS/ITO, Potential scan rate: 100 mV s^{-1}.

4. Relationship between peak current obtained at FcHT-ODT/AuNPs/APTMS/ITO electrode and different scan rates

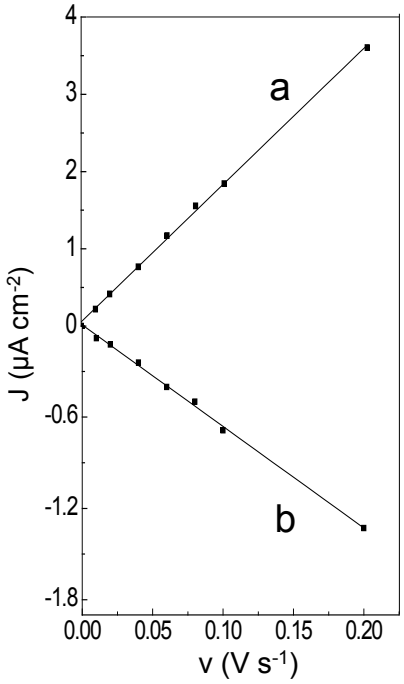

Figure S3. Relationship between anodic (a) and cathodic (b) peak currents obtained at FcHT-ODT/AuNPs/APTMS/ITO electrode and different scan rates.

5. Stability test for FcHT-ODT/AuNPs/APTMS/ITO electrode

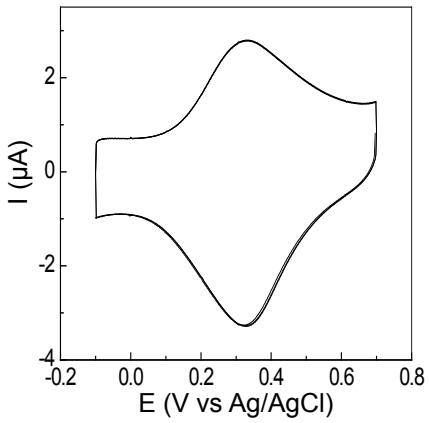

Figure S4. CVs obtained at the FcHT-ODT/AuNPs/APTMS/ITO surface in 0.1 M PBS after 100 cycles. Potential scan rate: 100 mV s^{-1}.

6. XPS spectra for FcHT-ODT/AuNPs/APTMS/ITO electrode attacked by ·OH

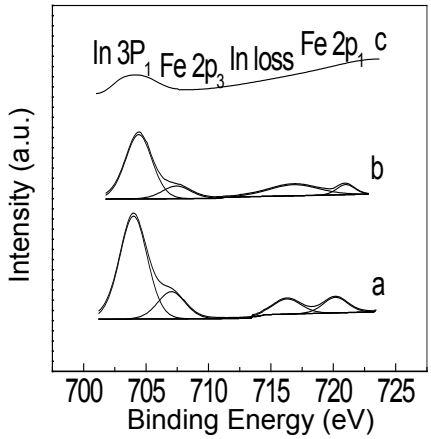

Figure S5. XPS spectra for In $3P_1$, Fe $2p_3$, In loss, Fe $2p_1$ obtained at FcHT-ODT/AuNPs/APTMS/ITO substrate (a) before and (b, c) after being attacking by (b) 0.01 M ·OH and (c) 0.1 M ·OH.

As shown in Figure S5, the part decomposition of FcHT were verified by obviously reduction of both the Fe 2p3 and Fe 2p1 peak area from 3742.9, 1889.3 to 1813.7, 913.0 respectively, after attacking by 0.01 M ·OH. When adding more ·OH up to 0. 1 M, Fe $2p_3$ and Fe $2p_1$ peak disappeared, demonstrating complete destruction of FcHT.

7. Sensitivity of FcHT-ODT/AuNPs/APTMS/ITO electrode and FcHT-ODT functionalized gold electrode towards ·OH.

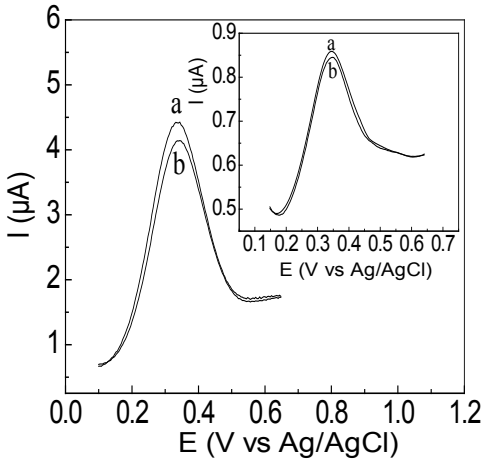

Figure S6. Square wave voltammograms (SWVs) obtained at FcHT-ODT/AuNPs/APTMS/ITO electrodes in 0.1 M PBS (pH=7.4) after adding (a) 0 nM, (b) 5 nM Fenton regents (Fe^{2+} : H_2O_2 = 1 : 1). Insert: SWVs obtained at FcHT-ODT functionalized gold electrode after adding (a) 0 nM, (b) 5 nM Fenton regents.