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SUPPLEMENTARY INFORMATION

Single Particle Electrochemistry of *p*-Hydroxythiophenol-labeled Gold Nanoparticles **†**

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The fabrication of Carbon Fiber Microdisk electrode (CFMDE)

Carbon Fiber Microdisk Electrodes (CFMDEs) were fabricated as following method. As shown in Scheme 1, briefly, A glass capillary (i.d. 0.3 mm, length 100 mm) was heated on the alcohol lamp and pulled it carefully. The fine tip of pulled capillary was 15-20 μ m in inner diameter. The pulled capillary was used as the sheath of CFMDE. A carbon fiber (7 μ m in diameter) was carefully inserted into the pulled capillary. The carbon fiber exposed to the fine end of the capillary with 1 mm and to the other with 1 cm. The fine end of the capillary was heated again with alcohol lamp carefully. The capillary melted slightly and shrunk to smaller size in diameter. Finally, there are no bubbles between carbon fiber and capillary. The tip of well-sealed capillary surface was polished mechanically with graded alumina powder on a polishing cloth. The exposed carbon fiber on the other end was attached to a copper wire with copper conducting adhesive, and kept it under 80 °C for two hours. After the copper conducting epoxy dried, this area was protected by the heat shrink tube. The fabricated Carbon Fiber Microdisk Electrode should be sonicated orderly in acetone, 3 M HNO₃, 1.0 M KOH, and distilled water each for 5 min before using.

Preparations of gold nanoparticles (AuNPs)

The colloidal AuNPs and *p*-HTP-functionalized AuNPs were prepared by the following method. Briefly, 31.7 mL of 0.01 % HAuCl₄·4H₂O (Sigma-Aldrich) solution was boiled with vigorous stirring. And the 1.7 mL of 1.00 % trisodium citrate (Sinopharm Chemical Reagent Co., Ltd) solution was quickly added to the boiling solution. All solutions were prepared using ultrapure water of resistivity $\geq 18.2 \text{ M}\Omega$ cm at 298 K (Millipore). Formation of AuNPs was indicated by the color change of

the resulting solution from pale yellow to deep red. Followed by continuous stirring and cooling down, the excess trisodium citrate was removed by centrifuging and washing with ultrapure water three times. The resulting AuNPs colloidal solution was stored in dark place at 4 °C before use. The obtained citrate modified AuNPs was denoted as C-AuNPs in the following text. Ligand exchanging was performed by adding 2 mL of 5.0 mM *p*-HTP into 2 mL of 1.4×10^{-9} M C-AuNPs dropwisely under stirring. Then the resulting solution was stirred for 24 h at room temperature. Excessive free ligands was removed by centrifugation at 8000 rpm against water until no *p*-HTP was detected in the leacheate. The purified product was redispersed in ultrapure water and stored at 4 °C, denoted as *p*-HTP-AuNPs.

The number of *p*-HTP molecular on the AuNPs (N_t)

According to the research by Rees et al. the N_t can be represented as equation (1)

$$N_t = \frac{f \times S}{S_t} \tag{1}$$

With *f* being the fractional filling efficiency assuming optimal close-packing of tag moleculars (0.91 for spheres on a plane), *S* being the surface area of the bare AuNP, S_t being the two-dimensional area occupied by a tag molecular. And the S_t can be estimated by the atomic size and the bond length in the *p*-HTP molecular. Finally, basing on the above hypothesis, the N_t is equal to 8824 approximately when the size of AuNP is about 16 nm.

Characterization of AuNPs

TEM: TEM images were obtained using a Tecnai G2F20S-TWIN transmission electron microscope (FEI company, U.S.). Samples were prepared by depositing a drop of the particles' suspension onto a Cu grid (3 mm diameter) and dried in air at room temperature. Fig. S1 shows two representative TEM micrographs of C-AuNPs

and *p*-HTP-AuNPs. The size distribution is shown in the insets. It can be seen that both of the AuNPs are quite uniform in shape and size. More importantly, the size and morphology of AuNPs after surface passivation ligand exchange remain unchanged. The average diameter of AuNPs is between 14~18 nm. The geometric shape of the particles is a truncated decahedron or truncated octahedron.

FT-IR: The presence of *p*-HTP on AuNPs was demonstrated by FT-IR measurements (Fig. S2). The Fourier transform infrared spectra were obtained on a TENSOR 27 FT-IR spectrophotometer (Bruker, Germany). The broad peak centered at about 3500 cm⁻¹ appeared in all three samples may be attributed to the O-H vibrational stretch. The S-H vibration at 2600 cm⁻¹ in *p*-HTP molecule vanished when *p*-HTP was modified onto gold core. This is because S-H bond was replaced by S-Au bond when modification was completed. The *p*-HTP-AuNPs share common feature with *p*-HTP molecules in the range of 2000-500 cm⁻¹, whereas being quite distinct from C-AuNPs. The peaks at 1430 and 1240 cm⁻¹ were from C-O in-plane bending and stretching. =C-H stretching is observed at 3250 cm⁻¹ in *p*-HTP and *p*-HTP-AuNPs, whereas not appeared in C-AuNPs. Peaks at 1600 cm⁻¹ most likely arises from C = C stretching. In addition, peak at 1275-1000 cm⁻¹ and 900-690 cm⁻¹ can be ascribed to in-plane and out-of-plane bending of C-H bending.

UV-Vis: UV-Vis spectroscopic study was performed on UV-2550 а spectrophotometer (Shimazu company, Japan) at room temperature from 300 to 800 nm. The typical absorption feature of the two AuNPs include an exponential decay of the absorption spectra with increasing wavelength (Mie scattering) onto which a surface plasmon band at 520 nm due to the interband transition of the gold core 5d electrons is superimposed (seen in Fig. S3). It is well known that specific surface plasma resonance energy of nanoparticles has been found to be extremely sensitive to the particle size and shape as well as to the optical and electronic properties of the immediate surrounding media. One can easily see that the surface plasma resonance band doesn't shift after exchange of the surface passivation ligand. This indicates that

size of the AuNPs before and after surface ligands exchange remained unchanged.

Electrochemistry: The cyclic voltammetry (CV) experiments were performed in a Faraday cage with a CHI 660D electrochemical workstation (Chenhua, Shanghai, China) in an electrolyte containing 50 mM sodium dihydrogen citrate (Sinopharm Chemical Reagent Co., Ltd) and 90 mM potassium chloride (Tianjin Regent Chemicals Co., Ltd) unless stated. A glassy carbon electrode loaded with certain amount of C-AuNPs or *p*-HTP-AuNPs was used as the working electrode, which was prepared by drop casting 5 μ L C-AuNPs or *p*-HTP-AuNPs suspensions (ca. 10¹⁴ particles dm⁻³) on the electrode. The Ag/AgCl (filled with 1 M KCl in agar) and 0.5 mm Pt electrode were applied as the reference and counter electrode respectively. As shown in Fig. S4, there are no featured electrochemical response appeared on both the naked GCE (black curve) and C-AuNPs modified GCE (red curve). However in the case of GC electrode modified with *p*-HTP-AuNPs, a pair of distinct redox peaks can be observed (magenta curve) at about 0.4 V and 1.0 V.

The electrochemical impedance thus was measured with CHI 660D electrochemical workstation (Chenhua, Shanghai, China) in the electrolyte of 5 mM Fe(CN)₆^{3-/4-} and 0.1 mM KCl. The results were showed in Fig. S5. The capacitances of double layer (C_{dl}) were fitting by the Zview, with 0.95 μ F, 0.85 μ F, 2.15 μ F for C-AuNPs, 1-pentanethiol-AuNPs, *p*-HTP-AuNPs modified GCE respectively.

APC experiments of various AuNPs

In APC experiments, two electrode system (prepared carbon fiber microdisk electrode as a working electrode and a Ag/AgCl electrode as reference) was employed and the measurements for the oxidative transient were perfomed with Picoammeter (Keithley, Keithley Instruments, Inc.) in a Faraday Cage. 1.59 x 10⁻⁹ M of C-AuNPs, *p*-HTP-AuNPs or 1-pentanethiol-AuNPs were well-dispersed separately in 8 mL supporting electrolyte containing 50 mM sodium dihydrogen citrate and 90 mM potassium chloride, and then the oxidative anode transient currents were recorded under the constant potential of 1.4 V.



Scheme 1 Carbon Fiber Microdisk Electrode



Fig. S1 TEM images of a: C-AuNPs, and b: *p*-HTP-AuNPs.



Fig. S2 FT-IR spectra of C-AuNPs (black curve), *p*-HTP(red curve) and *p*-HTP-AuNPs (blue curve).



Fig. S3 UV-Vis spectra of C-AuNPs (red curve) and p-HTP-AuNPs (black curve).



Fig. S4 Cyclic voltammetry performed using a naked GCE (black curve), C-AuNPs modified GC electrode (red curve) and p-HTP-AuNPs modified GC electrode (magenta curve) in a solution of 50 mM citrate and 90 mM KCl with scan rate of 50 mV s-1. The blue curve was obtained with a naked GCE in the citrate solution containing a certain amount of p-HTP.



Fig. S5 The electrochemical impedance spectroscopy of the working electrode are C-AuNPs, 1-

pentanethiol-AuNPs, p-HTP-AuNPs modified GCE respectively.



Fig. S6 Correlation between average charge passed per spike during single NP collisions and the square of average radius of NP determined by TEM.