

# Supporting Information

## Single-Nanoparticle Electrochemical Collision for Monitoring Self-Assembly of Thiol Molecules on Au Nanoparticles

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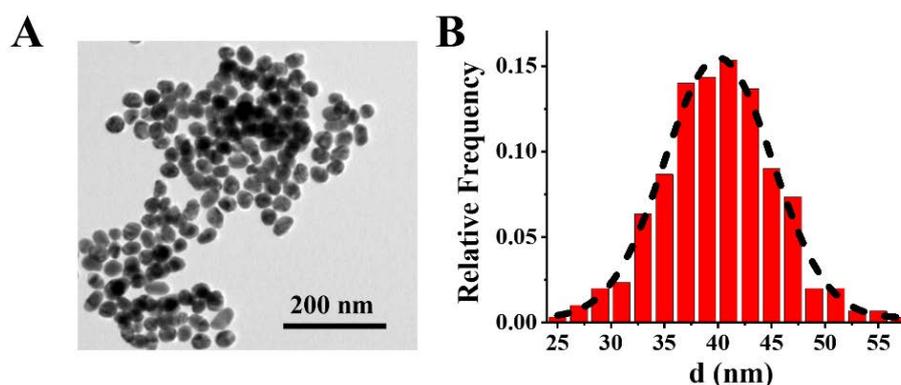
### S1. Reagents and instruments.

All chemicals were of analytical grade and used as received. 6-Mercapto-1-hexanol (6-MCH, 97%) and 1-Hexanethiol (MCH, 96%) were purchased from Aladdin and Sigma-Aldrich respectively. Sodium citrate, perchloric acid ( $\text{HClO}_4$ , 70%), chloroauric acid ( $\text{HAuCl}_4$ , 1%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Carbon fiber ( $d=7\ \mu\text{m}$ ) was purchased from Goodfellow Co. (Oxford, U.K.). Scanning electron microscope (SEM) measurements were performed on a S-4800 instrument (Hitachi, Japan).

The collision experiments were performed in a Faraday cage within 30 min to minimize agglomerate effects[1], and the chronoamperometry spikes were recorded and magnified by an EPC-10 patch-clamp amplifier (HEKA Electronics, Germany). The potential was held at -0.6 V vs  $\text{Ag}/\text{AgCl}$  (3 M  $\text{KCl}$ ), and the signals were sampled at 10 kHz, *bessel* and *I\_bessel* filtered at 10 KHz and 0.1 KHz respectively. The cyclic voltammogram (CV) tests were performed on a CHI 660E electrochemical workstation and a CHI 200B Faraday cage (CH Instruments, Inc. Shanghai, China).

### S2. Characterizations of gold nanoparticles (Au NPs).

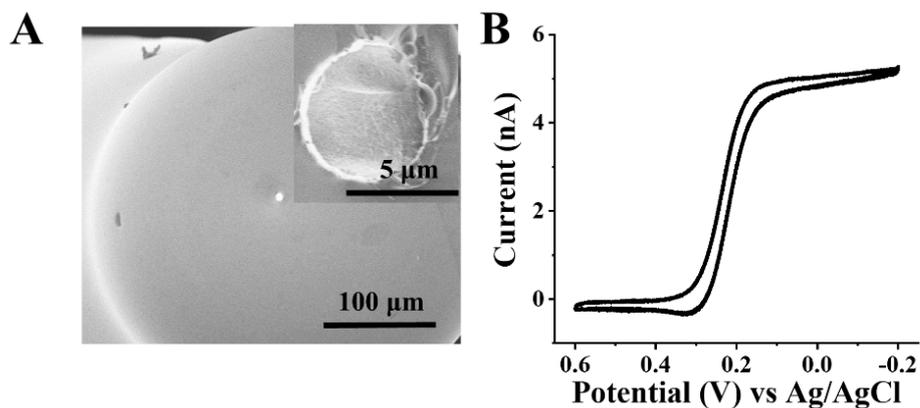
Au NPs were synthesized following a modifying sodium citrate reduction method[2]. Specifically, 0.5 mL of 1% (w/v)  $\text{HAuCl}_4$  was added to 50 mL ultrapure water and heated to 95 °C under stirring. After 5 min, 0.3 mL 1% sodium citrate was added and continued reaction for 15 min. The stocked Au NPs solution were washed with ultrapure water three times by ultrafiltration (4,000 rpm, 2 min) for later use, and the average diameters were found to be 40 nm (Figure S1).



**Figure S1.** TEM images for the synthesized Au NPs, and corresponding histograms showing statistical size distributions determined from TEM images ( $n=300$ ).

### S3. Characterizations of carbon fiber microelectrode (CFME).

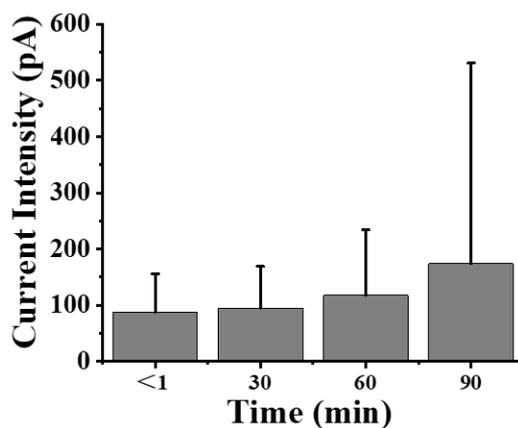
As shown in Figure S2A, CFMEs were fabricated by heat-sealing carbon fiber ( $d=7\ \mu\text{m}$ ) in borosilicate glass capillaries (1.15 mm OD; 1.0 mm ID)[3]. The prepared CFMEs were soaked in a piranha solution for about 20 s, then rinsed with ultrapure water for later use. With 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/0.1\ \text{M}\ \text{KCl}$  ( $D=7.6\times 10^{-6}\ \text{cm}^2/\text{s}$ ) afforded limiting current plateaus of approximately 5 nA (Figure S2B)[4], the real area of CFME was determined to be  $34\ \mu\text{m}^2$ .



**Figure S2.** (A) SEM images of disk CFME ( $d=7 \mu\text{m}$ ), the insert was the high-magnification SEM image of CFME. (B) Cyclic voltammograms of 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/0.1 \text{ M KCl}$  with a 50 mV/s scan rate for CFME.

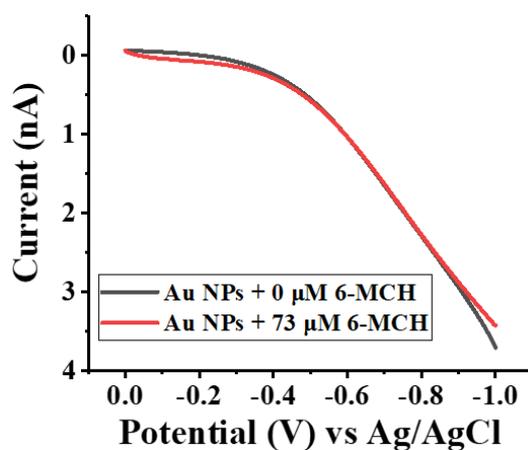
#### S4. Characterizations of the stability of Au NPs in 0.8 mM $\text{HClO}_4$ solution.

Considering that the monodispersion of NPs in collision experiments is vital for the self-assembly detection of thiol molecules on Au NPs based on SNEC, the stability of Au NPs in 0.8 mM  $\text{HClO}_4$  solution was investigated. As shown in Figure S3, current intensity measured before and after Au NPs dispersing in 0.8 mM  $\text{HClO}_4$  for 30 min had essentially the same distributions, indicating that Au NPs can basically exist stably in 0.8 mM  $\text{HClO}_4$  for 30 min. Hence, all collision experiments were performed in 0.8 mM  $\text{HClO}_4$  within 30 min to avoid agglomerate effects.



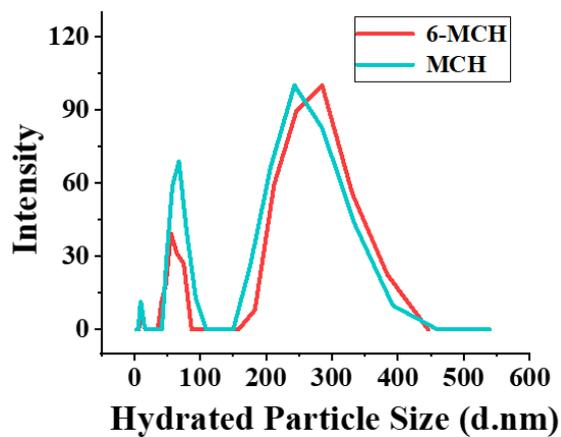
**Figure S3.** Current intensity of Au NPs ( $d=40 \text{ nm}$ ) after added in 0.8 mM  $\text{HClO}_4$  solution for different time.

**S5. Study on the interaction between CFME and 6-MCH.**



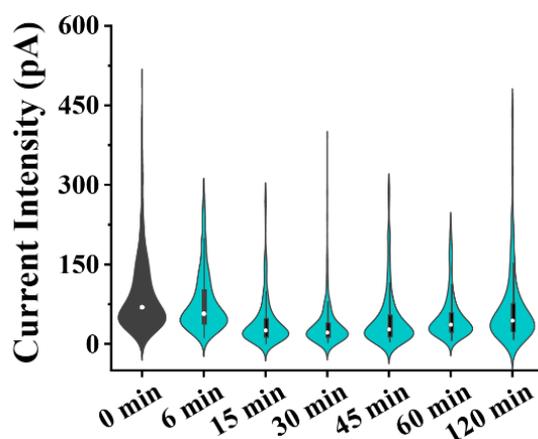
**Figure S4.** Cyclic voltammetry scans of CFME in 0.8 mM HClO<sub>4</sub> before and after 6-MCH added into Au NPs solutions.

**S6. Comparisons of hydrated particle size of 6-MCH-functionalized Au NPs and MCH-functionalized Au NPs.**



**Figure S5.** Hydrated particle size of 6-MCH-functionalized Au NPs and MCH-functionalized Au NPs.

**S7. Comparison of current intensity of Au NPs assemblies with MCH ( $C_{\text{MCH}}/C_{\text{Au NPs}} \approx 1.2 \times 10^3$ ) at different time.**



**Figure S6.** Violin plots of current intensity of Au NPs assemblies with MCH ( $C_{\text{MCH}}/C_{\text{Au NPs}} \approx 1.2 \times 10^3$ ) at different time.

**Reference**

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