

Electronic Supplementary Information

Charge State-Dependent Catalytic Activity of $[\text{Au}_{25}(\text{SC}_{12}\text{H}_{25})_{18}]$ Nanoclusters for the Two-Electron Reduction of Dioxygen to Hydrogen Peroxide

Yizhong Lu,^{a, b} Yuanyuan Jiang,^{a, b} Xiaohui Gao,^{a, b} and Wei Chen*^a

^a*State Key Laboratory of Electroanalytical Chemistry, Changchun institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China, and*

^b*University of Chinese Academy of Sciences, Beijing 100039, China*

E-mail: weichen@ciac.ac.cn

Experimental Details

1. Chemicals. All of the chemicals were commercially available and used without further purification. Hydrogen tetrachloroaurate tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, Shanghai Chemical Reagent Co. Ltd), tetraoctylammonium bromide (TOAB, 98%, Aldrich), sodium tetrahydroborate (NaBH_4 , 98%, powder, ACROS), 1-dodecanthiol (98%, Alfa Aesar), cerium (IV) sulfate tetrahydrate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, AR, Aladdin), sodium perchlorate (NaClO_4 , 98.0%, Aladdin), tetrabutylammonium perchlorate (Bu_4NClO_4 , >98%, TCL). Methanol (AR), acetone (AR), dichloromethane (AR), and THF (AR) were purchased from Beijing Chemical Works. Nanopure water with a resistivity of >18 $\text{M}\Omega \text{ cm}$ was used in the present study.

2. Synthesis of anionic Au_{25} nanoclusters (Au_{25}^-). Au_{25}^- was firstly synthesized by a modified one-phase procedure reported previously.¹ All the experiments were conducted at room temperature and under air atmosphere. Typically, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (20.59 mg, 0.05 mmol) and TOAB (32.82 mg, 0.06 mmol) were combined in a 25 mL round bottom flask, to which 5 mL THF solvent was added. After vigorously stirred for 15 min, the solution color changed from yellow to red. The $[\text{TOA}][\text{AuX}_4]$ was produced with a

mix of Cl^- and Br^- ions. Then, $\text{C}_{12}\text{H}_{25}\text{SH}$ (62 μL , 0.25 mmol) was slowly added to the flask at room temperature without changing the stirring speed. The solution color gradually changed from red to yellow and then to colorless within ~ 30 min. After that, an aqueous solution of NaBH_4 (18.92 mg, 0.5 mmol, freshly dissolved in 1.0 mL of ice-cold nanopure water) was added to (rapidly poured into) the flask all at once. The reaction generated some bubbles and the solution turned black immediately, indicating the formation of Au nanoclusters. The reaction was allowed to proceed under constant stirring for ca. 3 h (the extension of the reaction time would decrease the yield the yield of Au_{25}^- nanoclusters due to the excessive bromide attacking to the nanoclusters), during which size focusing occurred and eventually obtained pure Au_{25}^- nanoclusters exclusively. It should be noted that some white Au(I)-SR precipitates were also formed, which are insoluble in most solvents (e.g. toluene, THF, CH_2Cl_2 , etc.). After removal of the water layer, a large amount of ice-cold water was added, the precipitates were collected and thoroughly washed with water and methanol (to remove excess thiol), then dried under reduced pressure at room temperature, and acetone was added to extract Au_{25}^- nanoclusters (to remove insoluble Au(I)-SR). And then, the product was dried in a vacuum rotary evaporator at room temperature. Finally, the product was dissolved in CH_2Cl_2 for further use. Note that this solution was bubbled with N_2 to remove dissolved O_2 in solution and blanketed with N_2 , and then sealed in a cuvette.

3. Synthesis of charge neutral Au_{25}^0 nanoclusters (Au_{25}^0). The Au_{25}^0 nanoclusters were obtained according to a procedure developed by Jin's group.² Briefly, the synthesized Au_{25}^- nanoclusters dissolved in CH_2Cl_2 was bubbled with O_2 for about 15 min for the conversion of anionic Au_{25}^- to charge neutral Au_{25}^0 nanoclusters.

4. Synthesis of cationic Au_{25}^+ nanoclusters (Au_{25}^+). The synthesis of Au_{25}^+ nanoclusters was conducted with the oxidant Ce(IV).³ In a typical synthesis, 5 mL aqueous solution of $\text{Ce}(\text{SO}_4)_2$ (2.5 mM) and NaClO_4

(50 mM) was vigorously stirred with 5 mL CH₂Cl₂ solution of Au₂₅⁻ (0.05 mM) and Bu₄NClO₄ (25 mM). After stirring for 30 min, the organic phase was separated and washed three times with water and then subsequently washed three times with methanol to remove Bu₄NClO₄.

5. Synthesis of Au nanoparticles. The synthesis process of Au nanoparticles is similar to that of the Au₂₅⁻ nanoclusters but in the absence of TOAB.

6. Material Characterization. UV-Vis spectra were recorded on a VARIAN CARY 50 UV/Vis spectrophotometer at room temperature. Matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained on a linear-mode time-of-flight (TOF) mass spectrometer (AutoflexIII, Bruker, Germany) and *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene] malononitrile (DCTB) was used as the matrix. The laser intensity was kept low enough (just above the threshold intensity) and the cluster-to-matrix ration was optimized to 1:1000. The loading of Au₂₅⁹ nanoclusters were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, X Series 2, Thermo Scientific USA). X-ray photoelectron spectroscopy (XPS) measurements were performed by using a VG Thermo ESCALAB 250 spectrometer (VG Scientific) operated at 120 W. The binding energy was calibrated against the carbon 1s line.

7. Electrochemical Measurements. All experiments were carried out with a CHI 750D electrochemical workstation. The rotating ring-disk voltammetry (RRDE) assembly was provided by Pine Instruments Corporation. To prepare a catalyst-coated working electrode, catalyst was dispersed in a mixture of solvents containing water, isopropanol and Nafion (5%) (v/v/v = 4/1/0.025) to form a 1 mg/mL suspension. A calculated amount of the catalyst ink was then dropcast onto a polished GC electrode (0.196 cm² area) and dried at room temperature under a gentle flow of nitrogen. The catalyst loading is 20 μg/cm² for each case. A saturated calomel electrode (SCE) combination isolated in a double junction chamber and a Pt coil

were used as the reference and counter electrodes, respectively. All electrode potentials in the present study were referred to this SCE reference. 0.1 M KOH aqueous solution saturated with N₂/O₂ by bubbling N₂/O₂ for 30 min and then blanketed with N₂/O₂ during the experiment served as the supporting electrolyte. The H₂O₂ production was evaluated by RRDE at 10 mV/s scan rate and 1600 rpm rotation rate. Note that this scan rate is slow enough to ensure steady-state behavior at the electrode surface, and the rotation rate is sufficiently fast to aid in product removal and limit bubble formation from evolved O₂ at the electrode surface.

References

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- (2) Zhu, M. Z.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. C. *J. Phys. Chem. C* **2008**, *112*, 14221.
- (3) (a) Choi, J. P.; Murray, R. W. *J. Am. Chem. Soc.* **2006**, *128*, 10496; (b) Negishi, Y.; Chaki, N. K.; Shichibu, Y.; Whetten, R. L.; Tsukuda, T. *J. Am. Chem. Soc.* **2007**, *129*, 11322.

Supplementary Results

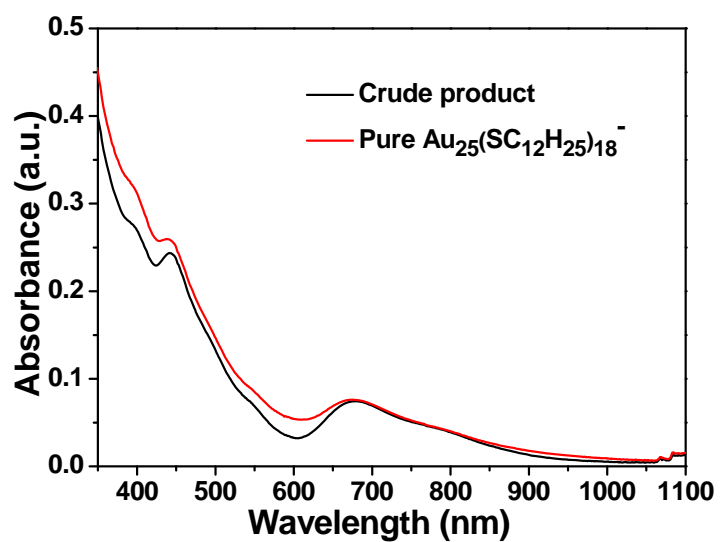


Fig. S1 UV-Vis spectra of the crude product (black curve) and the purified nanoclusters extracted into CH₂Cl₂ (red curve). The UV-Vis spectrum of the crude product is almost superimposable with that of the purified Au₂₅ nanoclusters, indicating an extraordinarily high purity of the as-synthesized Au₂₅ nanoclusters by the present revised method.

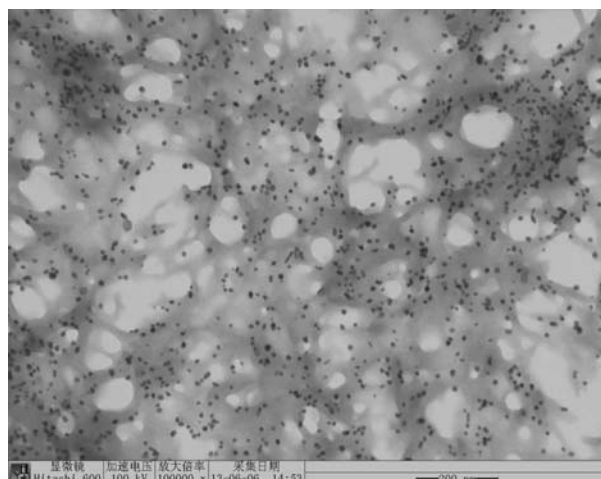


Fig. S2 TEM image of the gold nanoparticles (Au NPs).

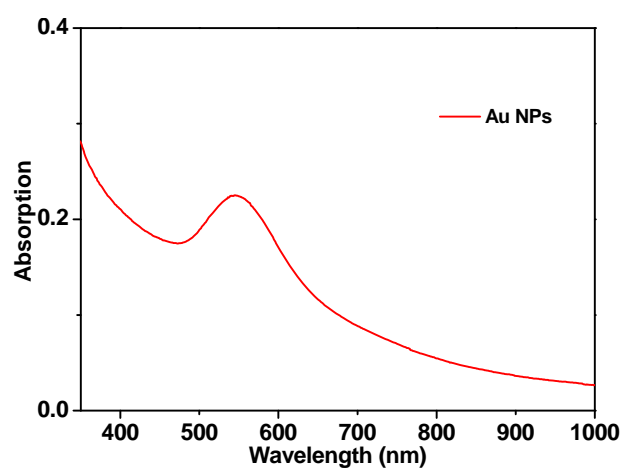


Fig. S3 UV-Vis absorption spectrum of the gold nanoparticles (Au NPs).

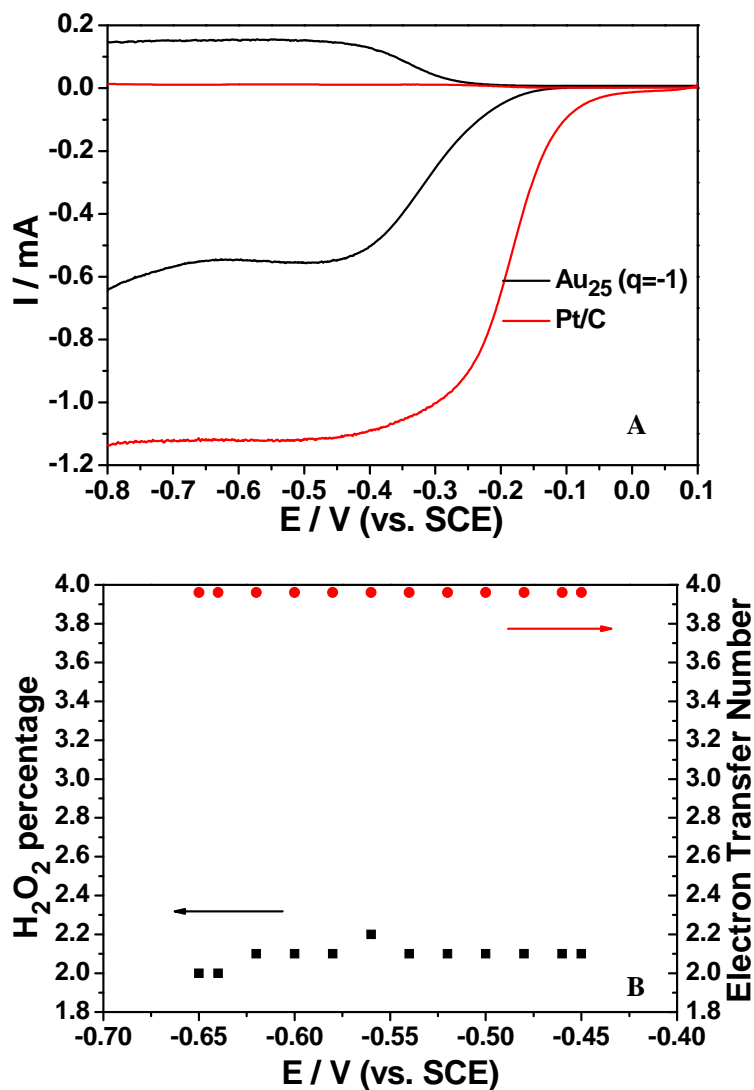


Fig. S4 (A) Comparison of the RRDE results of Au₂₅⁻ and commercial Pt/C catalysts. (B) The calculated H₂O₂ production percentage (black curve) and the electron transfer number (red curve) for oxygen reduction on the commercial Pt/C.

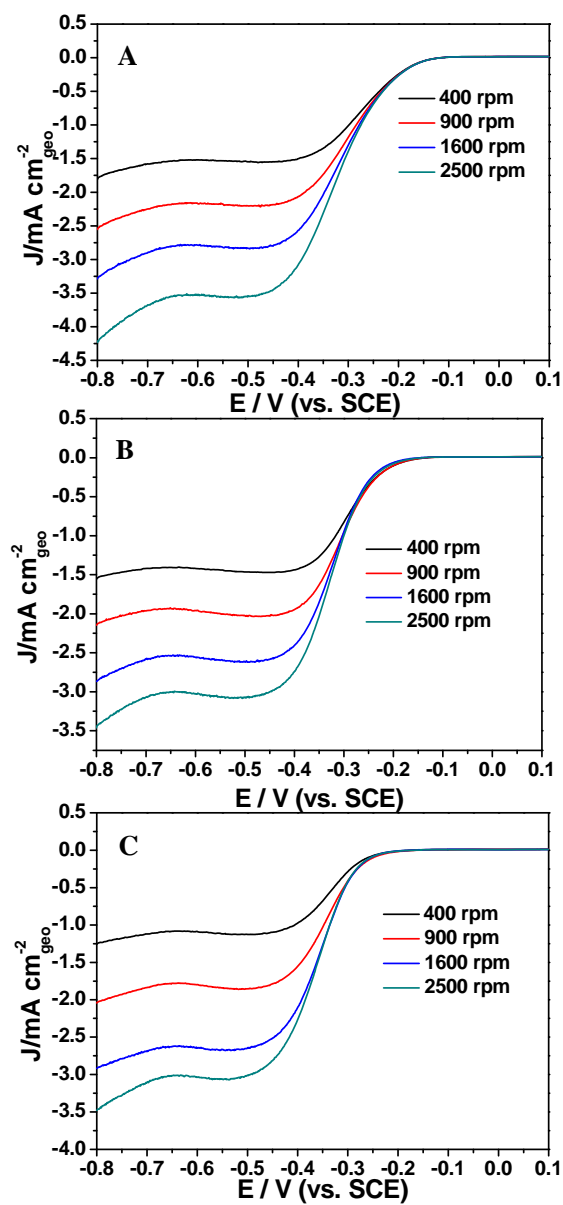


Fig. S5 ORR polarization curves recorded on the Au₂₅ nanoclusters at different rotation speeds. (A) Au₂₅⁻; (B) Au₂₅⁰; and (C) Au₂₅⁺. The potential scan rate is 10 mV/s.

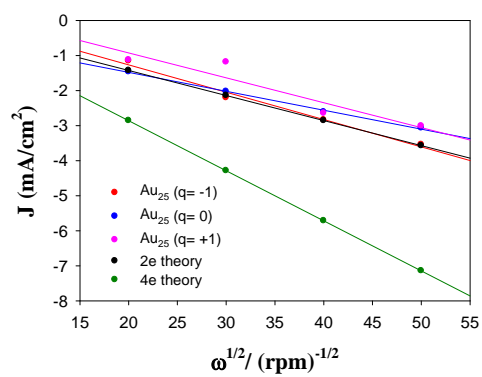


Fig. S6 Levich plots of Au₂₅ nanoclusters with different charge states. For comparison, theoretical 2e and 4e pathways are also presented.