Electronic Supplementary Information

The reactivity of phenylethanethiolated gold nanoparticles with acetic acid

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1. Experimental Section

Chemicals.

All chemicals are commercially available and used as received. Tetrachloroauric(III) acid (HAuCl₄·4H₂O, 99.7%), Tetraoctylammonium bromide (TOAB, 98.0%), 2-Phenylethanethiol (PhC₂H₄SH, 99.0%), Sodium borohydride (NaBH₄, 99.0%) were purchased from Sigma-Aldrich. Tetrahydrofuran (99.0%), acetonitrile (99.0%), methanol (99.5%), dichloromethane (AR), petroleum ether (AR), toluene (99.5%), acetic acid (99.5%) were purchased from Sinopharm chemical reagent co., ltd.

Syntheses of Au nanoparticles.

HAuCl₄·4H₂O (412 mg, 1.0 mmol) and TOAB (613 mg, 1.10 mmol) were added to toluene (25 mL). After stirring for 15 min, the mixture turned dark red, and the resulting solution was cooled to 0°C in an ice bath for another 15 min. PhC₂H₄SH (71 μ L, 0.5 mmol) was added, and the solution was stirred at 200 rpm for ca. 1.5 h. Then, the stirring speed was changed to ~1000 rpm, and an aqueous solution of NaBH₄ (424 mg, 11.2 mmol, freshly dissolved in 12.5 mL of ice-cold water) was added. After constant stirring for 15 h, the reaction was stopped. The toluene layer was transferred into a separatory funnel and washed three times with cold water. The crude product was precipitated using an adequate amount of MeOH, washed with MeOH and then dried. TEM confirmed a narrow distribution, and the average size was ca. 2 nm. PhC₂H₄SH (50 μ L) was used instead of 71 μ L of PhC₂H₄SH in the synthesis of ca. 4 nm AuNP. All the other conditions were unchanged.

Acid etching of Au nanoparticles.

The five nanoparticles were etched by acetic acid under the same conditions. Taking the etching of Au₂₅ as an example, ca. 20 mg Au₂₅ was first dissolved in 2 mL of toluene after stirring for 10 min; then, 400 μ L of acetic acid was added. The mixture was immersed in an 80°C oil bath with stirring. For the kinetics measurements, 10 μ L aliquots were taken from the reaction mixture at different time intervals and mixed with 700 μ L of toluene in a 12.4 mm quartz cuvette for optical absorption measurements. The reaction was stopped after 18 h for the synthesis of Au₃₈(PET)₂₆. The products were precipitated from the cooled toluene solution with a large amount of petroleum ether. Then, the solid was

washed with MeOH three times. The crude products were separated using PTLC (dichloromethane: petroleum ether = 1:1.5).

Characterization.

Optical absorption spectra were acquired in the range of 190-1100 nm using a Shimadzu UV-2600 spectrophotometer. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was performed on an Autoflex Speed TOF/TOF mass spectrometer (Bruker) in negative ionization mode. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Waters Q-TOF mass spectrometer equipped with a Z-spray source, and the source temperature was kept at 70°C. All samples were dissolved in toluene ($\sim 0.5 \text{ mg/mL}$), diluted (1:1 v/v) with an ethanol solution containing 0.5 mM CsOAc, and then directly infused into the chamber at 5 $\mu L/\text{min}.$ The spray voltage was 2.20 kV, and the cone voltage was kept at 60 V. Thermal gravimetric analysis (TGA) was conducted in a N₂ atmosphere (flow rate ~50 mL/min) on a TG/DTA 6300 analyzer (Seiko Instruments, Inc), and the heating rate was 10°C/min. X-ray Photoelectron Spectroscopy (XPS) measurements were taken on an ESCALAB 250Xi XPS spectrometer (ThermoScientific, America) using a monochromatized Al K α source and equipped with an Ar^+ ion sputtering gun. Fluorescence spectra were recorded on a Fluoromax-4 spectrofluorometer (HORIBA Jobin Yvon), and the

excitation wavelength was 514 nm with a slit of 10 nm. A Pt disk electrode (r = 0.25 mm) was used as the working electrode (WE). A saturated calomel electrode (dipped in KCl saturated solution) and a carbon rod were used as the reference (RE) and counter (CE) electrodes, respectively. The electrode potentials were controlled by a potentiostat (Zahner, Germany). The nanoparticles were dissolved in a solution of 0.1 M Bu₄NPF₆ that was constantly purged by N₂ during the experiments. All electrochemical experiments were conducted at room temperature.

2. Supporting figures



Fig. S1. Time evolution of optical absorption spectra of (A) Au_{25} , (B) Au_{38} , (C) Au_{144} , (D) $AuNP \sim 2$ nm and (E) $AuNP \sim 4$ nm after treated with acetic acid. Insets show the zoomed spectra in the marked regions.



Fig. S2. TEM images and size statistics of \sim 2 nm AuNPs before and after acetic acid treatment (scale bar is 20 nm). The scale bar in insets is 5 nm.



Fig. S3. TEM images and size statistics of ~4 nm AuNPs before and after acetic acid treatment (scale bar is 20 nm). The scale bar in insets is 10 nm.



Fig. S4. The plots of normalized absorption of feature peaks for $Au_{28}(TBBT)_{20}$ (365 nm), $Au_{44}(TBBT)_{28}$ (385 nm) and ~4 nm AuNP (510 nm) as a function of time.



Fig. S5. The ESI mass spectrum of $Au_{38}(PET)_{24}$ (acquired in positive mode).



Fig. S6. The long-term stability of $Au_{38}(PET)_{26}$ in dichloromethane.



Fig. S7. TEM images of $Au_{38}SR_{26}$ after staying in dichloromethane for 10 months (scale bar is 20 nm). The scale bar in inset is 5 nm.



Fig. S8. Structural anatomy of selected gold nanoclusters: $Au_{24}(SR)_{20}^{1}$, $Au_{25}(SR)_{18}^{2}$, $Au_{38}(SR)_{24}^{3}$ and $Au_{44}(SR)_{28}^{4}$. Green and pink = Au; orange = S. These nanoclusters can be viewed as one kernel protected by certain staples.



Fig. S9. XRD patterns of Au₂₄(PET)₂₀, Au₂₅(PET)₁₈, Au₃₈(PET)₂₄, and Au₄₄(TBBT)₂₈. (PET: phenylethanethiol, TBBT: 4-tert-butylbenzenethiolate)

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