

Electronic Supplementary Information (ESI) for Nanoscale

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Gold Nanocluster-Catalyzed Selective Oxidation of Sulfide to Sulfoxide

Gao Li, Huifeng Qian, and Rongchao Jin*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave, Pittsburgh, PA 15213, United

States. Email: rongchao@andrew.cmu.edu

1. Experimental

Chemicals: Tetrachloroauric(III) acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99% metal basis, Aldrich), tetraoctylammonium bromide (TOAB, 98%, Fluka), sodium borohydride (99.99% metals basis, Aldrich), 2-phenylethanethiol (99%, Acros Organics), (99%, Aldrich), toluene (HPLC grade, 99.9%, Aldrich), ethanol (absolute, 200 proof, Pharmco), methylene chloride (HPLC grade, 99.9%, Aldrich), methylphenyl sulfide (99%, Sigma–Aldrich), iodosobenzene diacetate (98%, Aldrich). All chemicals were used as received.

Synthesis of $\text{Au}_{25}(\text{SR})_{18}$ ($\text{R}=\text{CH}_2\text{CH}_2\text{Ph}$) nanoclusters: Typically, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.2 mmol, dissolved in 5 ml nanopure water) and tetraoctylammonium bromide (TOAB, 0.24 mmol, dissolved in 10 ml toluene) were combined in a 25 ml tri-neck round bottom flask. The solution was vigorously stirred for 15 min, and the aqueous was then removed. Thiol (0.6 mmol) was added to the flask, and stirring was reduced to a very low speed (50 rpm). After the solution turned to clear (2 h), NaBH_4 (2 mmol, 5 ml cold aqueous solution) was rapidly added all at once. After aging overnight, methanol was added to separate AuNCs from TOAB and other side-products. The $\text{Au}_{25}(\text{SR})_{18}$ clusters were collected after removing the supernatant.

Synthesis of Iodosobenzene (PhIO) oxidant:^[S1] A 2M NaOH aqueous solution (6 mL, 12.0 mmol) was added dropwise to solid iodosobenzene diacetate (1.0g, 3.0 mmol) over a 10 min period at 0 °C. The resulting suspension was stirred for a further 4 h at room temperature. And then 20 mL water was added, the crude product was collected on a sinter funnel, washed with water (10 mL×3). The pale yellow solid was triturated with chloroform (20 mL), filtered and dried to afford iodosobenzene (3.13 g, 92%), which did not need further purification for the oxidation of sulfide.

Preparation of Au₂₅(SR)₁₈/oxide catalysts (oxide=TiO₂, MgO, CeO₂ and Fe₂O₃):

Typically, 1 mg Au₂₅(SR)₁₈ clusters were dissolved in 5 ml DCM, and 100 mg oxide were added. After stirred for 24h at r.t., the supernatant became essentially colorless. The Au₂₅(SR)₁₈/oxides catalysts were collected by centrifugation and dry in vacuum. No thermal calcination was done prior to catalytic reactions.

Catalytic oxidation of sulfides: In a typical reaction, PhIO (0.05 mmol), sulfide (0.05 mmol) and Au₂₅(SR)₁₈/oxide catalyst (100 mg unless otherwise noted, 1%wt loading of Au₂₅(SR)₁₈) were mixed in 1 mL DCM. The mixture was stirred under N₂ atmosphere at 40 °C for 12h as indicated in Table 2. In the case of unsupported Au₂₅(SR)₁₈ as catalyst, 0.5 mg nanoclusters were used. For the recyclability test, the Au₂₅(SR)₁₈/oxide catalyst was separated by centrifugation, washed with DCM, and dry in vacuum prior to its reuse in the next cycle. The product was obtained after removal of the solvent of the supernatant. The conversion of sulfide and yields of sulfoxide and sulfone were determined by NMR (300 MHz) spectroscopic analysis.

Ref [S1] P. Dauban, L. Sanière, A. Tarrade, R. H. Dodd, *J. Am. Chem. Soc.* **2001**, 123, 7707.

2. Supporting Figures:

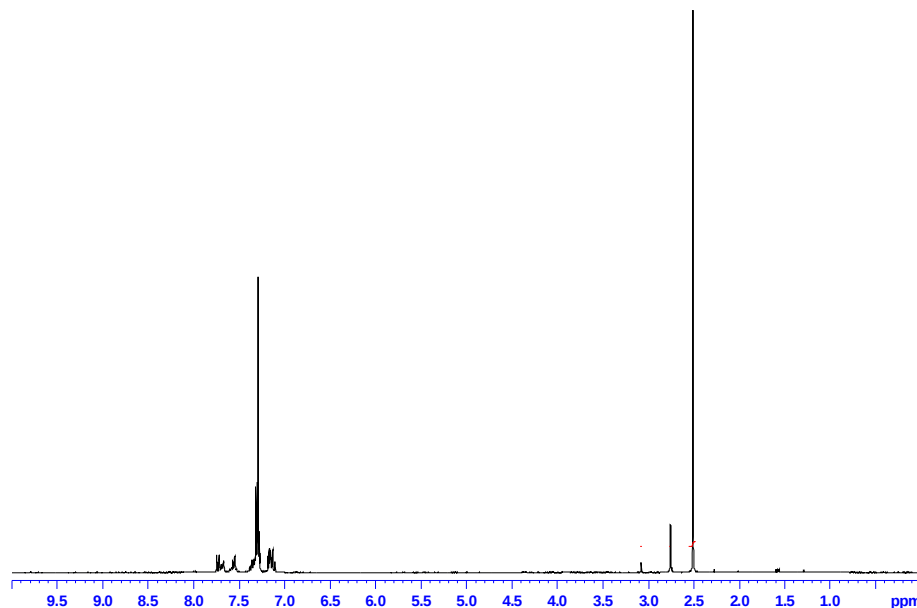


Figure S1. ¹H NMR of sulfide, sulfoxide and sulfone (-CH₃ of sulfide at 2.52, sulfoxide at 2.76 and sulfone at 3.08 ppm) (reaction product of the blank reaction).