Supplementary Information

Atomically precise Au_{25} superatoms immobilized on CeO_2 nanorods for styrene oxidation

Ping Huang,[a] Guoxiang Chen,[a] Zhi Jiang,[a] Rongchao Jin,[b] Yan Zhu*[a] and Yuhan Sun*[a,c]

[a] Low-Carbon Conversion Center, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China.
[b] Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA.
[c] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, China.

E-mail: zhuy@sari.ac.cn; sunyh@sari.ac.cn

Experimental:

Au_{25} superatoms: 0.4 mmol $HAuCl_4 \cdot 3H_2O$ dissolved in 5 mL nanopure water, and 0.47 mmol TOAB (tetraoctylammonium bromide) dissolved in 10 mL toluene, were combined in a 25 mL tri-neck round bottom flask. After 15 min stirring, the aqueous was removed using a 10 mL syringe. The toluene solution of gold(III) cooled down to 0°C in an ice bath over a period of 30 min. 0.17 mL $PhCH_2CH_2SH$ was added. After the solution turns to clear, an aqueous solution of 4 mmol $NaBH_4$ was quickly added. After 12 hours reaction, 20 mL ethanol was added to separate Au_{25} clusters from TOAB. Au_{25} superatoms were obtained after removing the supernatant.

CeO_2 nanorods: 0.002 mol $Ce(NO_3)_3 \cdot 6H_2O$ and 0.24 mol NaOH were dissolved in 40 mL nanopure water. Then, the solution was added in a 50 mL Teflon bottle with stainless steel vessel autoclave and the autoclave was transferred into an oven at 100°C. After 24 hr, the precipitates were separated by centrifugation, washed with nanopure water and ethanol several times, followed by drying at 60°C in air overnight. Yellow CeO_2 powders were obtained.

Au_{25} supported on CeO_2 nanorods: 100 mg CeO_2 were added in a dichloromethane solution with 1%wt Au_{25} superatoms, and the mixture was stirred for one day and then the solution was removed in flowing nitrogen.

Catalytic test: TBHP as an oxidant: Supported gold catalysts (100 mg powder, 1%wt loading of Au_{25}) were mixed with styrene (12 mmol), TBHP (36 mmol) and acetonitrile (15 mL) in a 50 mL sealed glass reactor with vigorous stirring. Then the mixture was heated to 353 K for 24 h.

O_2 as an oxidant: A 50 mL sealed glass reactor loaded with supported gold catalyst (100 mg powder, 1%wt loading of Au), styrene (12 mmol), and acetonitrile (15 mL) was filled with dioxygen stream (99.995%). After purging to remove air the mixture was vigorous stirred and heated to 353 K for 24 h.

Characterization: TEM images were recorded with JEOL JEM-2100 Electron Microscope (JEOL). Powder XRD measurements were performed with a Rigaku D/Max-RB X-ray diffractometer with Cu Kα radiation. The Brunauer−Emmett−Teller (BET) surface areas were determined by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010). UV-vis spectra of the Au_{25} (dissolved in CH_2Cl_2) were acquired on SHIMADZU UV-2700 diode array spectrophotometer at room temperature. All Au L_3-edge X-ray absorption measurements were conducted in fluorescence mode at the hard X-ray microanalysis (HXMA) beamline. The catalytic products were analyzed by a gas chromatograph (Agilent Technologies: 6890N).

Supporting Figures

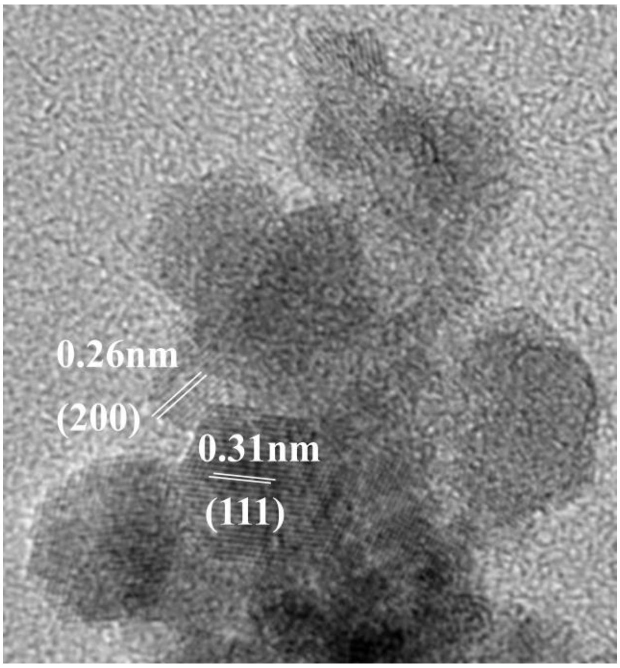

Fig. S1. HRTEM image of CeO_2 nanoparticles.

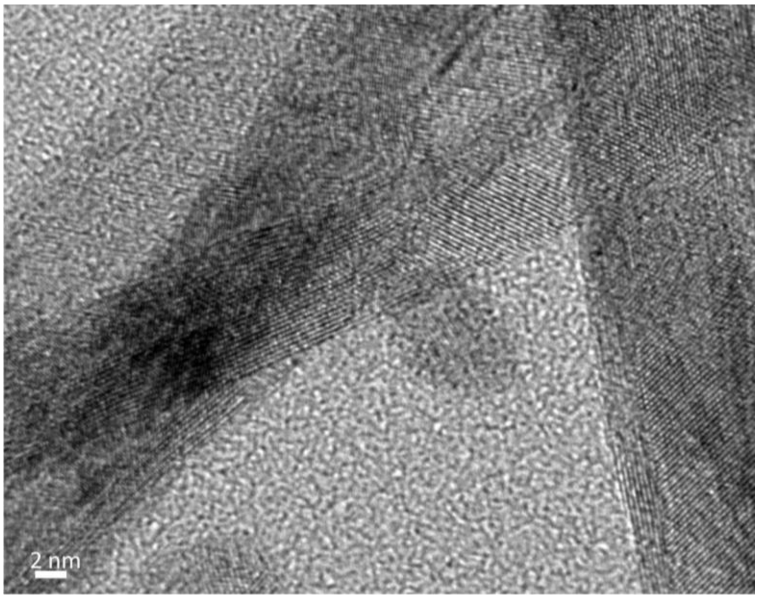

Fig. S2. HRTEM image of Au_{25}/CeO_2 nanorods.

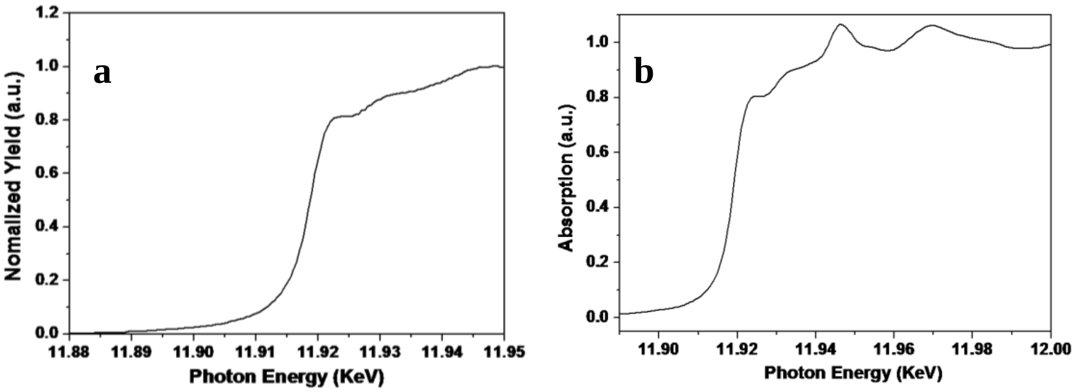

Fig. S3. Au L_3 edge XANES spectra of (a) Au_{25}/CeO_2 catalyst after reaction and (b) metallic gold nanocrystals.