

## *Supporting Information*

### **Manipulating the organic-inorganic interface of atomically precise**

### **Au<sub>36</sub>(SR)<sub>24</sub> catalysts for CO oxidation**

#### **Experimental section**

**Synthesis of Au<sub>36</sub>-I(DMBT)<sub>24</sub> and Au<sub>36</sub>-II(DMBT)<sub>24</sub>:**<sup>S1</sup> 2 mL H<sub>2</sub>O solution containing 196 mg HAuCl<sub>4</sub> was subsequently added to a solution of 310 mg tetraoctylammonium bromide (TOAB) in 30 mL CH<sub>2</sub>Cl<sub>2</sub> under stirring. After the water phase and the organic phase separated, the water layer was removed. Then, 220 μL 3,5-dimethylbenzenethiol (DMBT) was added to the above mixture and the stirring was continued for 2~3 h until the color of the solution changed from deep red to colorless. After that, an ice water solution of NaBH<sub>4</sub> (100 mg in 5 mL) was added at once, and the reaction was allowed for ~8 h. The crude products were evaporated and washed by CH<sub>3</sub>OH. The obtained black solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> and evaporated. Then, the precursor was dissolved in the mixture of 1 mL toluene and 0.8 mL 3,5-dimethylbenzenethiol in a 10 mL vial, and the vial was stirred at room temperature for 36 h. The obtained products were washed by excess CH<sub>3</sub>OH for three times and extracted by CH<sub>2</sub>Cl<sub>2</sub>. The products were further separated by thin-layer chromatography. Au<sub>36</sub>-I(DMBT)<sub>24</sub> and Au<sub>36</sub>-II(DMBT)<sub>24</sub> were both crystallized in toluene/acetonitrile solution for two weeks.

**Synthesis of Au<sub>36</sub>-I(TBBT)<sub>24</sub>:**<sup>S2</sup> 15 mL CH<sub>2</sub>Cl<sub>2</sub> was added to a 50 mL round-bottomed flask charged with 154 mg TOAB, and followed by addition of 1 mL water solution containing 98 mg of HAuCl<sub>4</sub>·4H<sub>2</sub>O. After 30 min, the water phase was removed, and 110 μL 4-tert-butylthiophenol was added dropwise. After the color of the mixed solution changed to clear, a freshly cold water solution of NaBH<sub>4</sub> (54 mg in 3 mL) was added to the solution and the reaction was allowed for 6~8 h. The obtained solution was evaporated and washed several times with CH<sub>3</sub>OH. Then, the precursor was dissolved

in 3 mL toluene and was divided into three vials, and 100  $\mu\text{L}$  4-tert-butylthiophenol was added in the three vials respectively. The three vials were etched at 80  $^{\circ}\text{C}$  for 12 h, and then the crude product was washed with excess  $\text{CH}_3\text{OH}$  for three times and extracted with  $\text{CH}_2\text{Cl}_2$ . The extracted products were evaporated and then separated using thin-layer chromatography. The single crystal of the  $\text{Au}_{36}\text{-I}(\text{TBBT})_{24}$  cluster was obtained in dichloromethane/ethanol solution for one week.

**Synthesis of  $\text{Au}_{36}\text{-I}(\text{CPT})_{24}$ :**<sup>S3</sup> The synthesis for  $\text{Au}_{36}\text{-I}(\text{CPT})_{24}$  was almost same as that for  $\text{Au}_{36}\text{-I}(\text{TBBT})_{24}$ , except that 110  $\mu\text{L}$  4-tert-butylthiophenol was used instead of 100  $\mu\text{L}$  cyclopentanethiol. The single crystal of the  $\text{Au}_{36}\text{-I}(\text{CPT})_{24}$  cluster was obtained in dichloromethane/pentane solution for 10 days.

**Synthesis of  $\text{CeO}_2$ :** A prepared solution of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (4.34 g in 20 mL  $\text{H}_2\text{O}$ ) was added in a 250 mL flask under oil bath of 65  $^{\circ}\text{C}$ , followed by 30 mL  $\text{H}_2\text{O}$  solution containing 1.41 g  $\text{Na}_2\text{CO}_3$  and 1.86 g  $\text{NaOH}$  was dropwise added. The reaction was kept for 24 h. The crude product was washed by excess water for several times. Finally, the obtained product was dried at 65  $^{\circ}\text{C}$  for 12 h.

**Synthesis of  $\text{Au}_{36}(\text{SR})_{24}/\text{CeO}_2$ :** 2 mg  $\text{Au}_{36}(\text{SR})_{24}$  clusters were dissolved with 1 mL  $\text{CH}_2\text{Cl}_2$  in a 10 mL vial, and 100 mg  $\text{CeO}_2$  was added and stirred for 10 h. Finally, the solution was dried under  $\text{N}_2$  atmosphere.

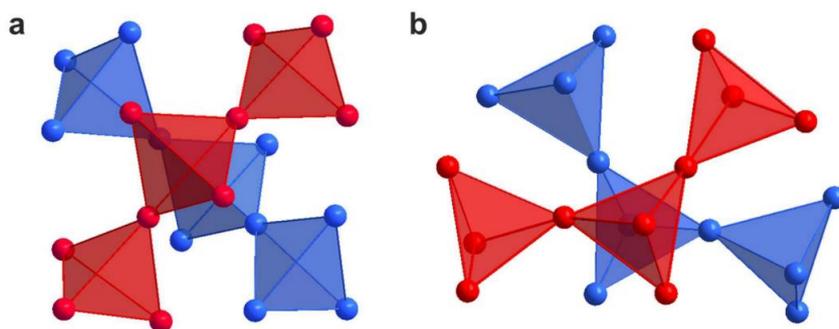
### **Characterizations**

UV-1800 spectrophotometer (Shimadzu, Japan) was used to record the UV-vis absorption spectra of catalysts. Diffuse reflectance UV-vis spectra with a range of 200-800 nm were obtained using SHIMADZU UV-3600. Thermal gravimetric analyse (TGA) was carried out by a NETZSCH Instruments (TGA STA-449C) in nitrogen atmosphere. The data of TGA were collected from 25 to 800  $^{\circ}\text{C}$  and the heating rate was 10  $^{\circ}\text{C}/\text{min}$ . The transmission electron micrographs (JEM 2800 microscope) operated at 100 kV were carried out to analyze the dispersion of catalysts before and after reactions. X-ray diffractometer characterization was carried out with Rigaku Mini Flex 600 using  $\text{Cu K}\alpha$  target as the radiation source. The tube voltage was of 50 kV and the Bragg angle  $2\theta$  scanning range was  $5^{\circ}\sim 90^{\circ}$  with a scanning speed of  $10^{\circ}/\text{min}$ . Thermo Scientific K-Alpha with an excitation source of  $\text{Al K}\alpha$  was used to perform X-

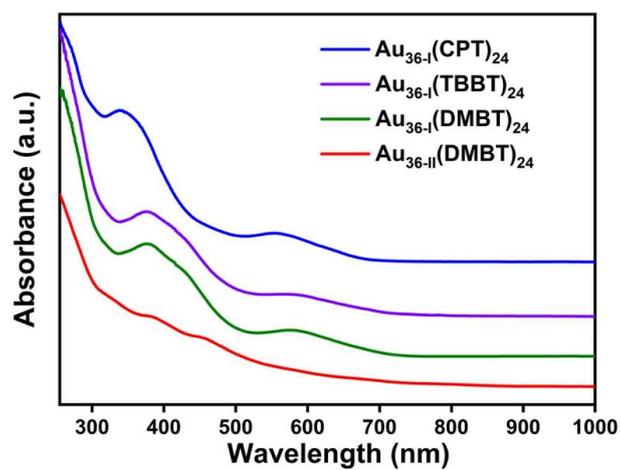
ray photoelectron spectroscopy (XPS) which can detect the binding energies of the surface species of catalysts. The detection of catalysts of Fourier-transformed infrared spectroscopy was depended on an FT-IR 660 Plus spectrometer (Jasco Co.) equipped with a MCT detector cooling by liquid nitrogen and a cell (Praying Mantis, Harrick). The KBr blank sample was purged with Ar at 150 °C for 2 h to remove impurities and water. Catalyst dissolved in DCM was dropped on KBr disk, and then disk was treated under O<sub>2</sub> atmosphere at different temperatures for 1 h. FT-IR spectra were collected continuously. For CO infrared adsorption, CeO<sub>2</sub>-supported catalyst was dropped into a handled disk and CO was continuously purged for 30 min. Subsequently, CO desorption was performed by argon purging and the FT-IR spectra were obtained.

### **Catalytic tests**

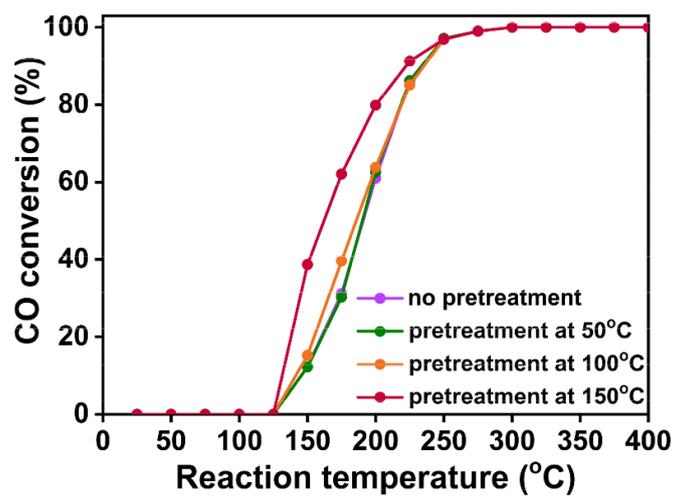
The CO oxidation activity was evaluated in a fixed bed quartz tubular reactor in at atmospheric pressure. The catalysts were processed to 30-60 mesh. The quartz wool was placed in the bottom of one side of the U-shaped tube with a diameter of 4 mm followed which 100 mg catalyst was loaded on the quartz wool. Before the reaction of CO oxidation, the catalysts were pretreated in O<sub>2</sub> atmosphere with 30 cm<sup>3</sup>/min flow rate at different temperatures for 1 h. When the feed temperature dropped to room temperature, the reactant gas of 1.0 % CO, 7.8 % O<sub>2</sub> and 91.2 % Ar was introduced into fixed bed reactor with a space velocity of 12000 cm<sup>3</sup>/h/g<sub>cat</sub>. Gas chromatograph (GC 9860) equipped with TCD detector, Plot Q and TDX-1 columns was used to analyze the CO conversion.



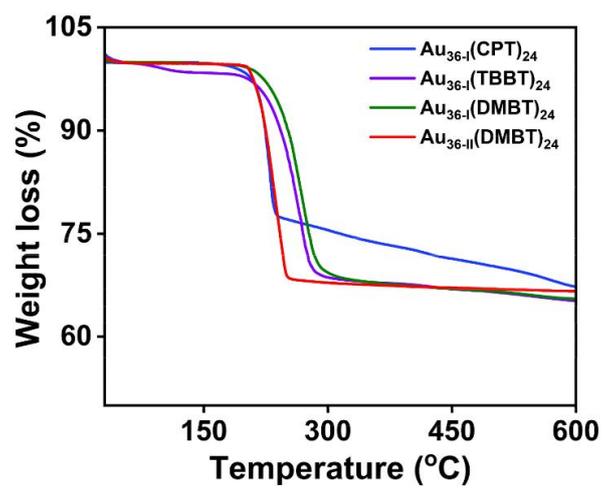
**Fig. S1** The core structures of (a) Au<sub>36-I</sub>(DMBT)<sub>24</sub> and (b) Au<sub>36-II</sub>(DMBT)<sub>24</sub> shown in tetrahedral Au<sub>4</sub> networks.



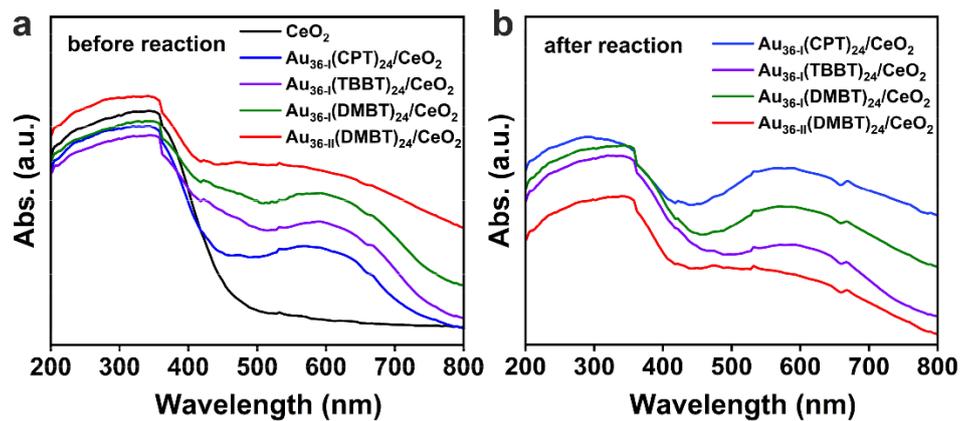
**Fig. S2** UV-vis spectra of the Au<sub>36-I</sub>(CPT)<sub>24</sub>, Au<sub>36-I</sub>(TBBT)<sub>24</sub>, Au<sub>36-I</sub>(DMBT)<sub>24</sub> and Au<sub>36-II</sub>(DMBT)<sub>24</sub> nanoclusters.



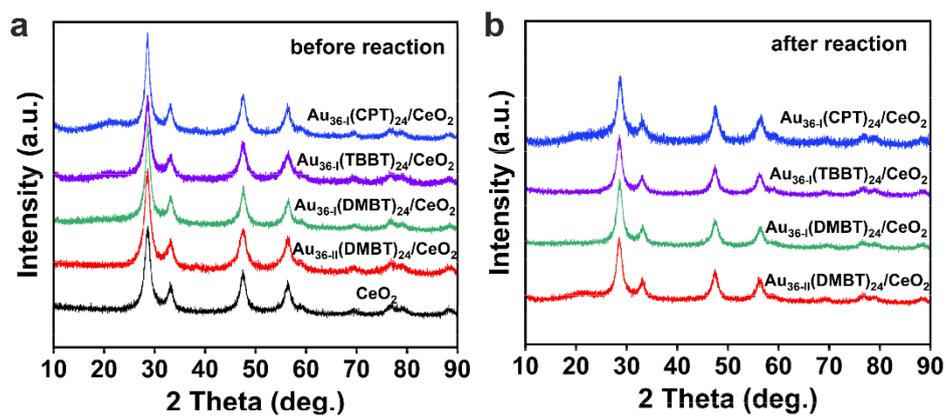
**Fig. S3** Catalytic performances of CO oxidation on CeO<sub>2</sub>.



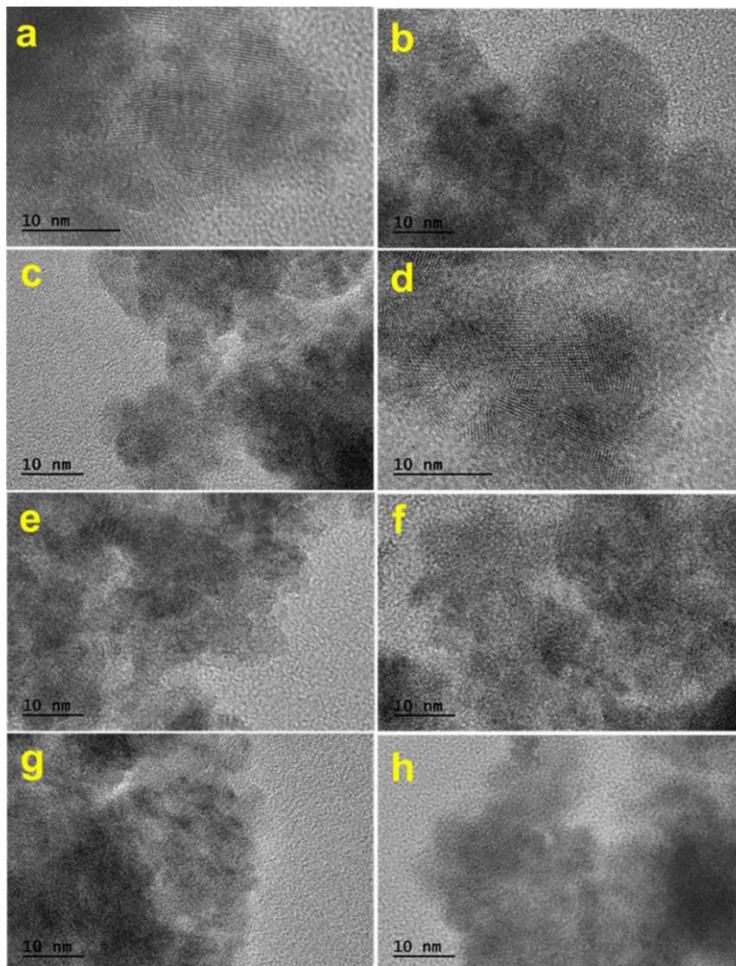
**Fig. S4** TGA data of the fresh Au<sub>36</sub>(SR)<sub>24</sub> nanoclusters.



**Fig. S5** (a) Diffuse reflectance UV-vis spectra of the  $\text{Au}_{36}(\text{SR})_{24}/\text{CeO}_2$  catalysts before reactions. (b) Diffuse reflectance UV-vis spectra of the  $\text{Au}_{36}(\text{SR})_{24}/\text{CeO}_2$  catalysts after reactions (note that the cluster catalysts were related to the pretreated cases at 150 °C).



**Fig. S6** (a) XRD patterns of the  $\text{Au}_{36}(\text{SR})_{24}/\text{CeO}_2$  catalysts before reactions. (b) XRD patterns of the  $\text{Au}_{36}(\text{SR})_{24}/\text{CeO}_2$  catalysts after reactions (note that the cluster catalysts were related to the pretreated cases at 150 °C).



**Fig. S7** TEM images of the  $\text{Au}_{36}(\text{SR})_{24}/\text{CeO}_2$  catalysts before reactions: (a)  $\text{Au}_{36}\text{-I}(\text{CPT})_{24}/\text{CeO}_2$ , (b)  $\text{Au}_{36}\text{-I}(\text{TBBT})_{24}/\text{CeO}_2$ , (c)  $\text{Au}_{36}\text{-I}(\text{DMBT})_{24}/\text{CeO}_2$  and (d)  $\text{Au}_{36}\text{-II}(\text{DMBT})_{24}/\text{CeO}_2$ . TEM images of the  $\text{Au}_{36}(\text{SR})_{24}/\text{CeO}_2$  catalysts after reactions (note that the catalysts were related to the pretreated cases at 150 °C): (e)  $\text{Au}_{36}\text{-I}(\text{CPT})_{24}/\text{CeO}_2$ , (f)  $\text{Au}_{36}\text{-I}(\text{TBBT})_{24}/\text{CeO}_2$ , (g)  $\text{Au}_{36}\text{-I}(\text{DMBT})_{24}/\text{CeO}_2$  and (h)  $\text{Au}_{36}\text{-II}(\text{DMBT})_{24}/\text{CeO}_2$ .

### Supporting references

S1. X. Liu, W. Xu, X. Huang, E. Wang, X. Cai, Y. Zhao, J. Li, M. Xiao, C. Zhang, Y. Gao, W. Ding and Y. Zhu, *Nat. Commun.*, 2020, **11**, 3349.

S2. C. Zeng, H. Qian, T. Li, G. Li, N. L. Rosi, B. Yoon, R. N. Barnett, R. L. Whetten, U. Landman and R. Jin, *Angew. Chem. Int. Ed.*, 2012, **51**, 13114-13118.

S3. A. Das, C. Liu, C. Zeng, G. Li, T. Li, N. L. Rosi and R. Jin, *J. Phys. Chem. A*, 2014, **118**, 8264-8269.