Supporting Information

Stabilizing Gold Clusters by Heterostructured Transition-Metal Oxide-Mesoporous Silica Supports for Enhanced Catalytic Activities for CO Oxidation

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Material synthesis

Synthesis of $Au_{144}(PhC_2H_4S)_{60}$: The synthesis procedure is according to the former reported by Qian et al.[1] Typically, $HAuCl_4$ $3H_2O$ (0.3 mmol, 118 mg) and TOABr (0.348 mmol, 190 mg) are added to a 50 mL trineck round-bottom flask and mixed with 15 mL of methanol. After being vigorously stirred for 15 min, the solution color changes from yellow to dark red. Then, PhC_2H_4SH (1.59 mmol, thiol/Au = 5.3/1) are added to the solution at room temperature and the color of reaction mixture rapidly turns white. After 15 min, a fresh $NaBH_4$ solution (3 mmol, dissolved in 6 mL of cold nanopure water) is rapidly added to the solution under vigorous stirring. The color of solution immediately turns black and produces Au clusters, which are then precipitated out of the methanol solution. The reaction is stopped after 5 h, and the black precipitates are collected by centrifugation (5 min at 5000 rpm). The black precipitates are washed with excess methanol and collected by centrifugation again. This step is repeated at least 3 times to completely remove the free thiol residue. Then, toluene is used to separate the Au clusters from Au(I)-SR polymers (poorly soluble in almost all solvents). The as-obtained Au clusters only contain Au_{144} $(SR)_{60}$(major product). Then, acetone is used to separate the $Au_{144}(SR)_{60}$ and $Au_{25}(SR)_{18}$ clusters.

Synthesis of Au_{25} clusters: The synthesis procedure reported by Zhu et al.[2] $HAuCl_4·3H_2O$ (0.1576 g, 0.4 mmol) dissolved in 5 mL nanopure water, and TOABr (0.2558 g, 0.47 mmol) dissolved in 10 mL toluene, were combined in a 25 mL tri-neck round bottom flask. The solution was vigorously stirred (~1100 rpm) with a magnetic stir bar to facilitate phase transfer of Au(III) salt into the toluene phase. After ~15 min, phase transfer was completed, leaving a clear aqueous phase at the bottom of the flask; the aqueous was then removed using a 10 mL syringe. The toluene solution of Au(III) was purged with N_2 and cooled down to 0^oC in an ice bath over a period of 30 min under magnetic stirring. $PhCH_2CH_2SH$ (0.17 mL, ~3 equivalents of the moles of gold) was added and stirring was reduced to a very low speed (~30 rpm). The deep red solution turned to faint yellow over a period of ~5 min, and finally to clear over ~1 hr. After the solution turns to clear (~ 1 hr), the stirring speed was changed to fast stirring (~1100 rpm), and immediately, an aqueous solution of $NaBH_4$

(0.1550 g, 4 mmol, 10 equivalents versus the moles of gold, freshly made in 7 mL ice-cold nanopure water) was quickly added all at once. The reaction was allowed to proceed overnight under N_2 atmosphere. After overnight, the aqueous layer at the bottom of the flask was removed using a syringe, and the toluene solution was dried. Ethanol (~20 mL) was added to separate Au_{25} clusters from TOABr and side products (e.g. disulfide), etc. The Au_{25} clusters were collected after removing the supernatant.

13.5%, 9%, 4.5% CuO/EP-FDU-12 support: 60mg, 40mg, 20mg $Cu(NO3)_2 \cdot 3H_2O$ was dissolved into 15mL pure water and 150mg EP-FDU-12 (Surface area 395.2 m^2/g, pore size 30nm) was added into the solution under stirring for 2h. After removing water, the powder is dried and calcined at 350^{o}C for 5h.

Co_3O_4/EP-FDU-12 support: 80mg $Co(CH_2COO)_2 \cdot 4H_2O$ was dissolved into 15mL pure water and 200mg EP-FDU-12 was added into the solution under stirring for 2h. After removing water, the powder is dried and calcined at 500^{o}C for 5h.

CuO/ Cab-O-Sil support: 80mg $Cu(NO3)_2 \cdot 3H_2O$ was dissolved into 15mL pure water and 200mg Cab-O-Sil (Surface area 373.3 m^2/g) was added into the solution under stirring for 2h. After removing water, the powder is dried and calcined at 350^{o}C for 5h.

Gold cluster loading on Co_3O_4 or CuO/EP-FDU-12: A certain amount of gold clusters dispersed into toluene under stirring and amount of support was added into this toluene solvent for another 2h. Then the product was obtained after centrifuged, dried and calcined at 300^{o}C in air for 3h.

Material Characterization:

X-ray diffraction patterns were obtained on a PANalytical Empyrean diffractometer using CuKα radiation. Scanning Transmission electron microscopy (STEM) images were acquired on a HD2000 microscope (200 kV). ICP data were acquired on Perkin Elmer Optima 2100 DV. Nitrogen adsorption isotherms were obtained on a Micrometritics Gemini BET system.

Catalytic Test: 30 mg of catalyst was packed into a quartz tube (i.d. = 4 mm) sealed by quartz wool, a gas stream of 1% CO (balance air,) flowed through the catalyst at a rate of 10 mL/min, and the exiting stream was analyzed by a gas chromatograph equipped with a dual molecular sieve/porous polymer column and a thermal conductivity detector. The reaction temperature was varied using a furnace.

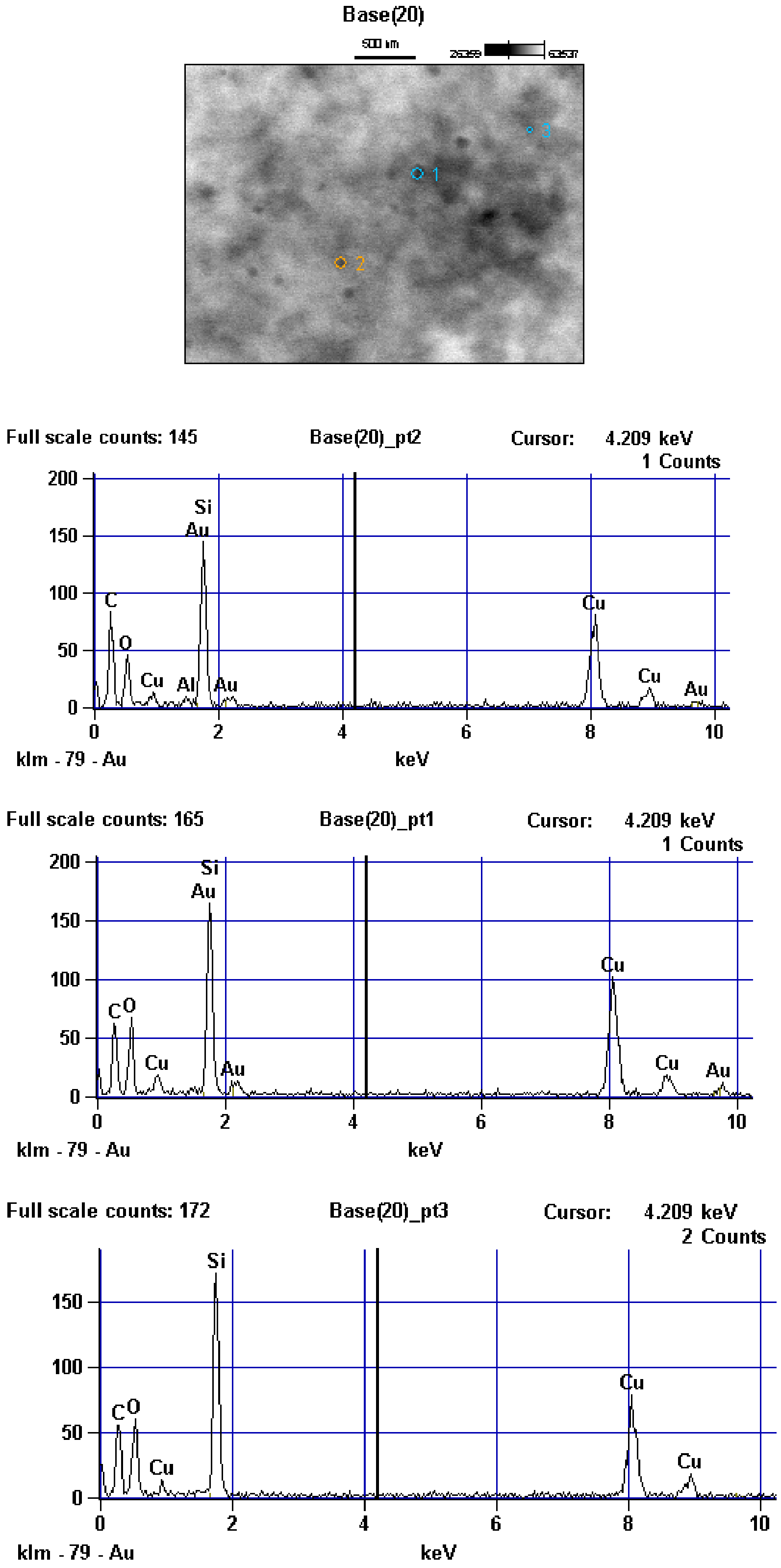

Fig. S1 EDX analysis of Au_{144} clusters supported on 9%CuO-EP-FDU-12 after calcination at 300^{o}C

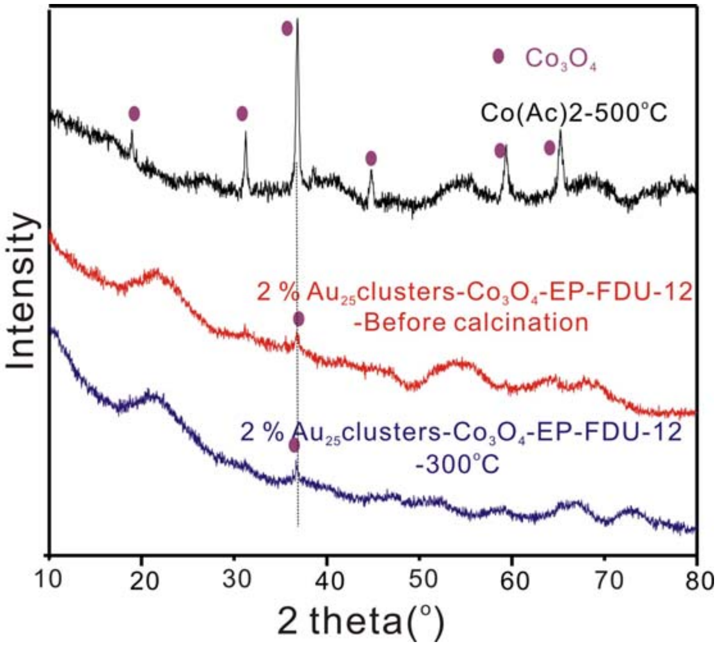

Fig. S2 XRD patterns of 2% Au_{25} clusters supported on Co_3O_4-EP-FDU-12 before and after calcination.

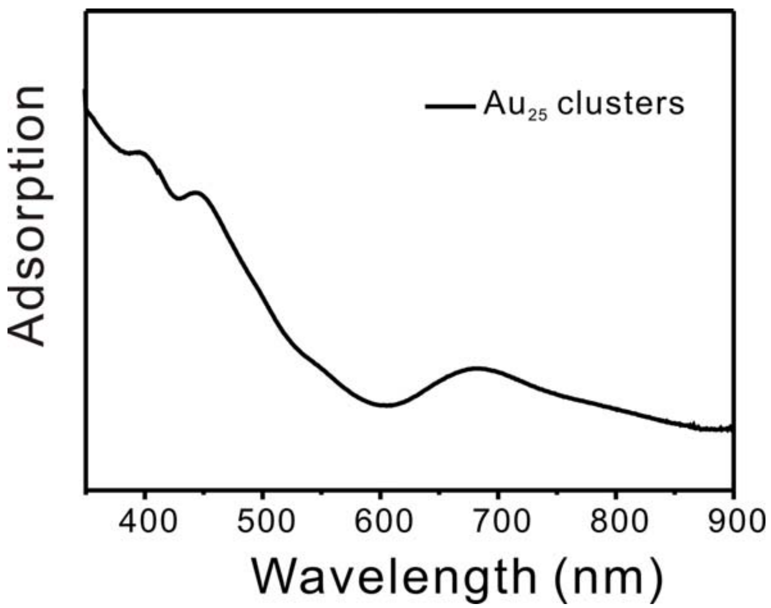

Fig.S3 UV-vis spectrum of Au_{25} clusters.

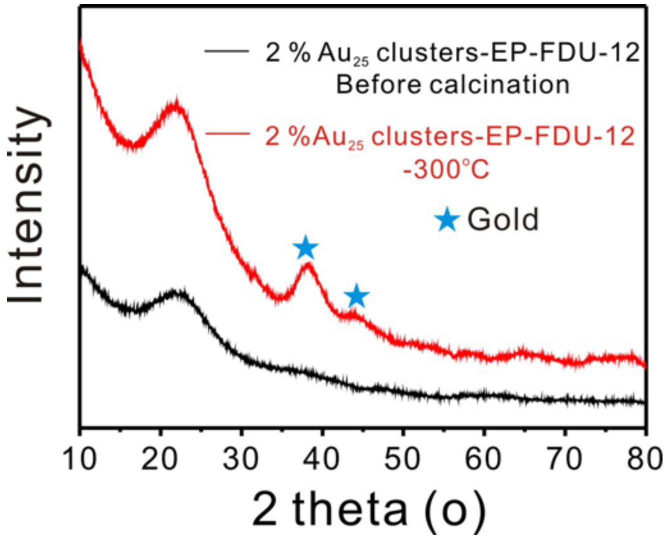

Fig.S4 XRD patterns of 2 % Au_{25} clusters supported on mesoporous silica EP-FDU-12 before and after calcination.

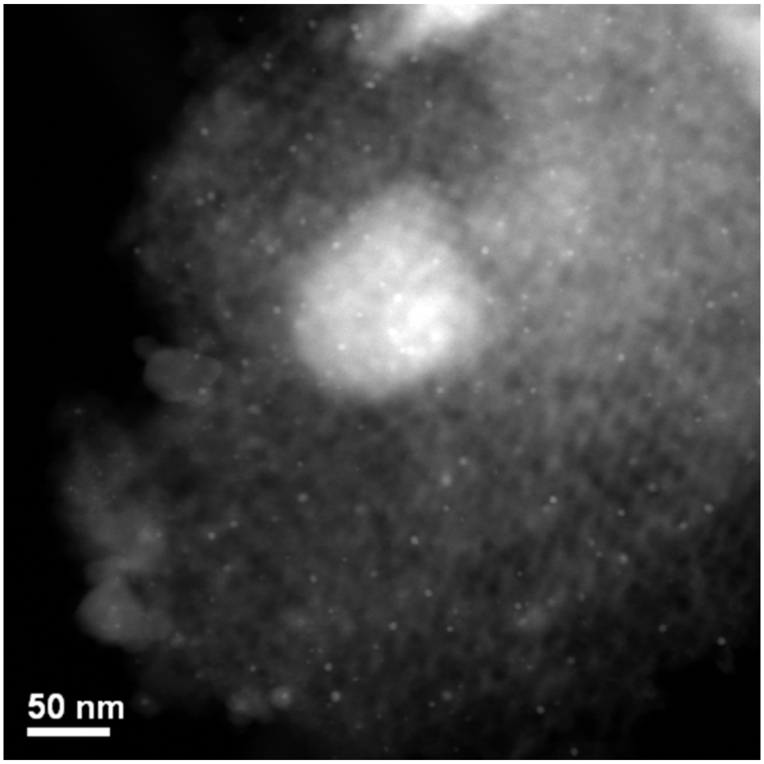

Fig. S5 STEM image of Au_{25} clusters supported on Co_3O_4-EP-FDU-12 after calcination at 300°C.

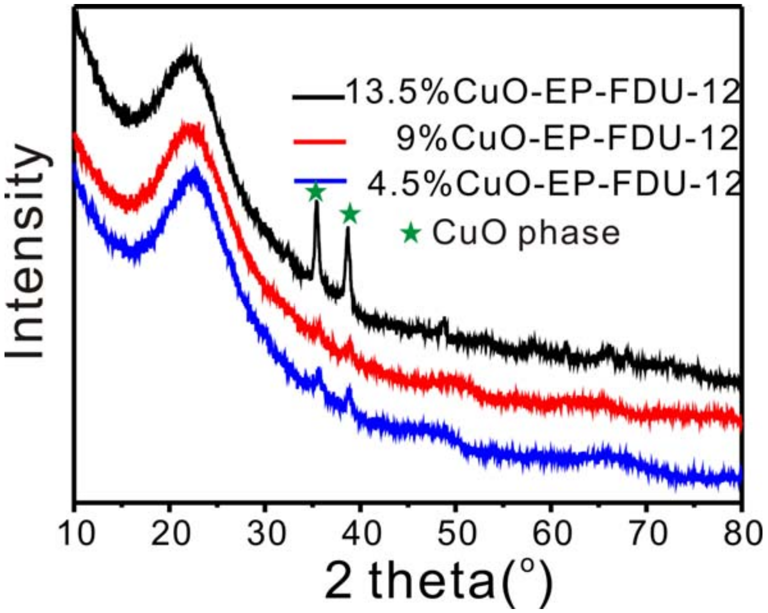

Fig. S6 XRD patterns of different copper loading amount on EP-FDU-12.

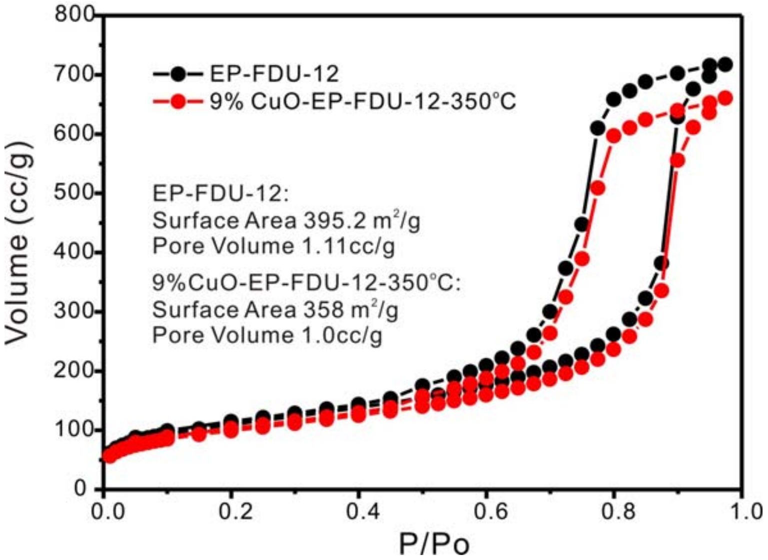

Fig. S7 Nitrogen sorption isothermals of pure EP-FDU-12 and 9% CuO-EP-FDU-12.

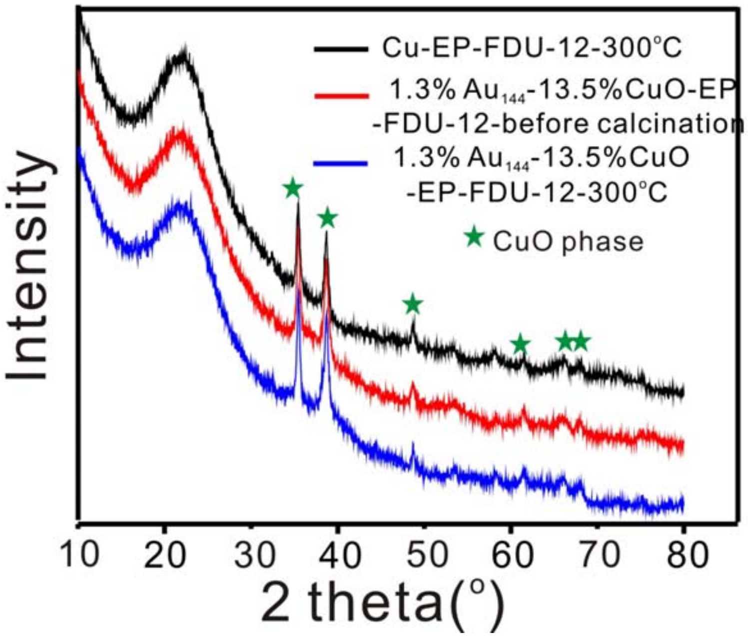

Fig. S8 XRD patterns of Au_{144} clusters supported on 13.5%CuO-EP-FDU-12 before and after calcination.

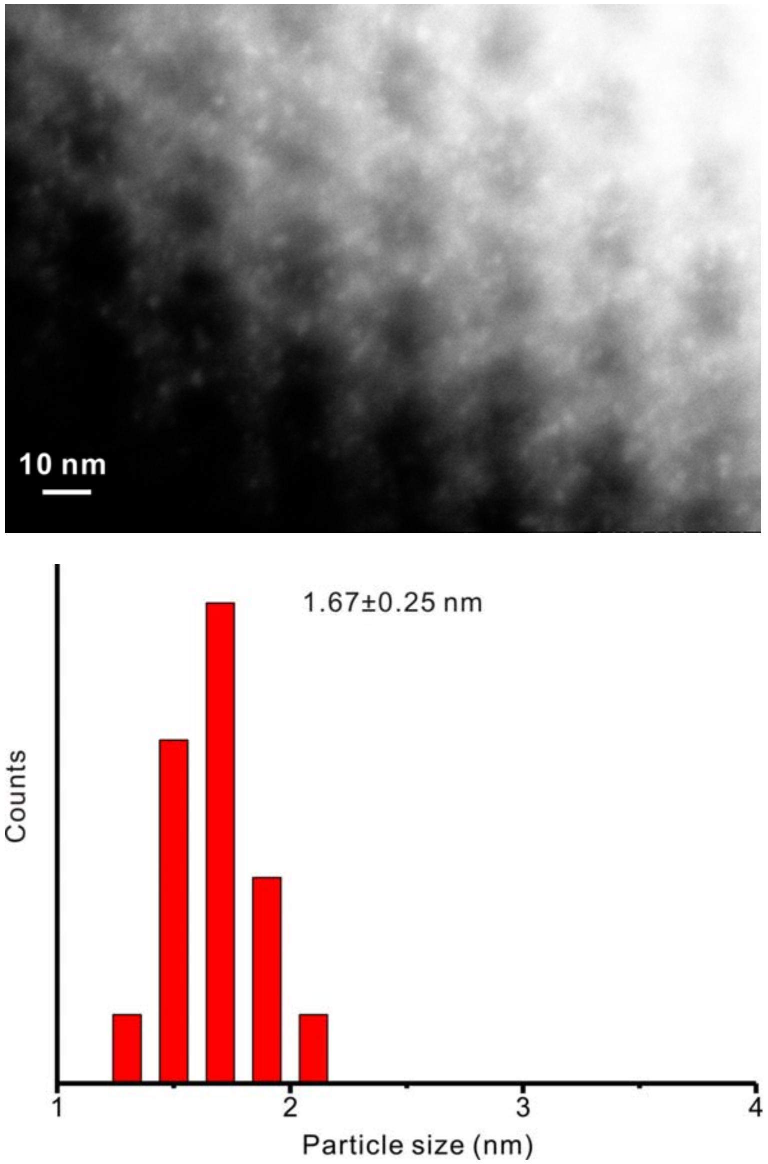

Fig. S9 STEM image of Au_{144} clusters supported on 13.5%CuO-EP-FDU-12 after calcination at 300^{o}C and size distribution of gold nanoparticles.

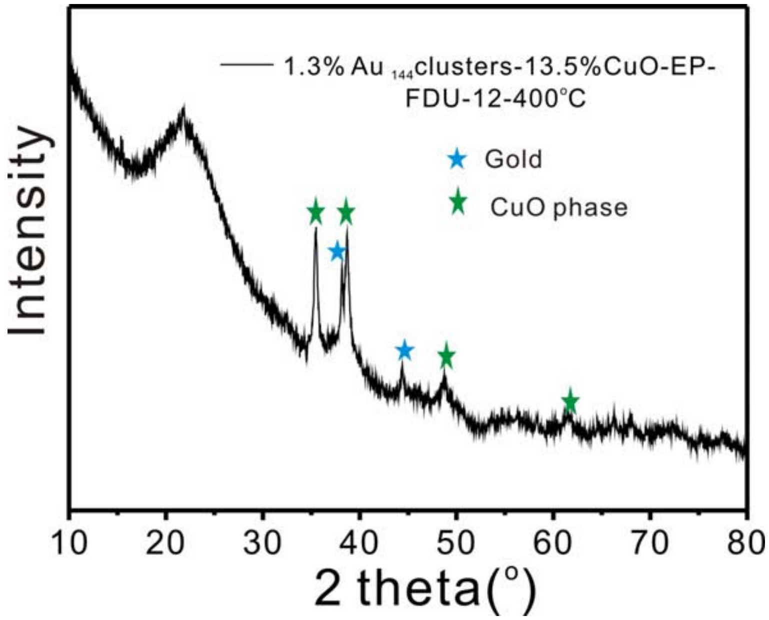

Fig. S10 XRD pattern of Au_{144} clusters supported on 13.5% CuO-EP-FDU-12 after calcination at 400°C.

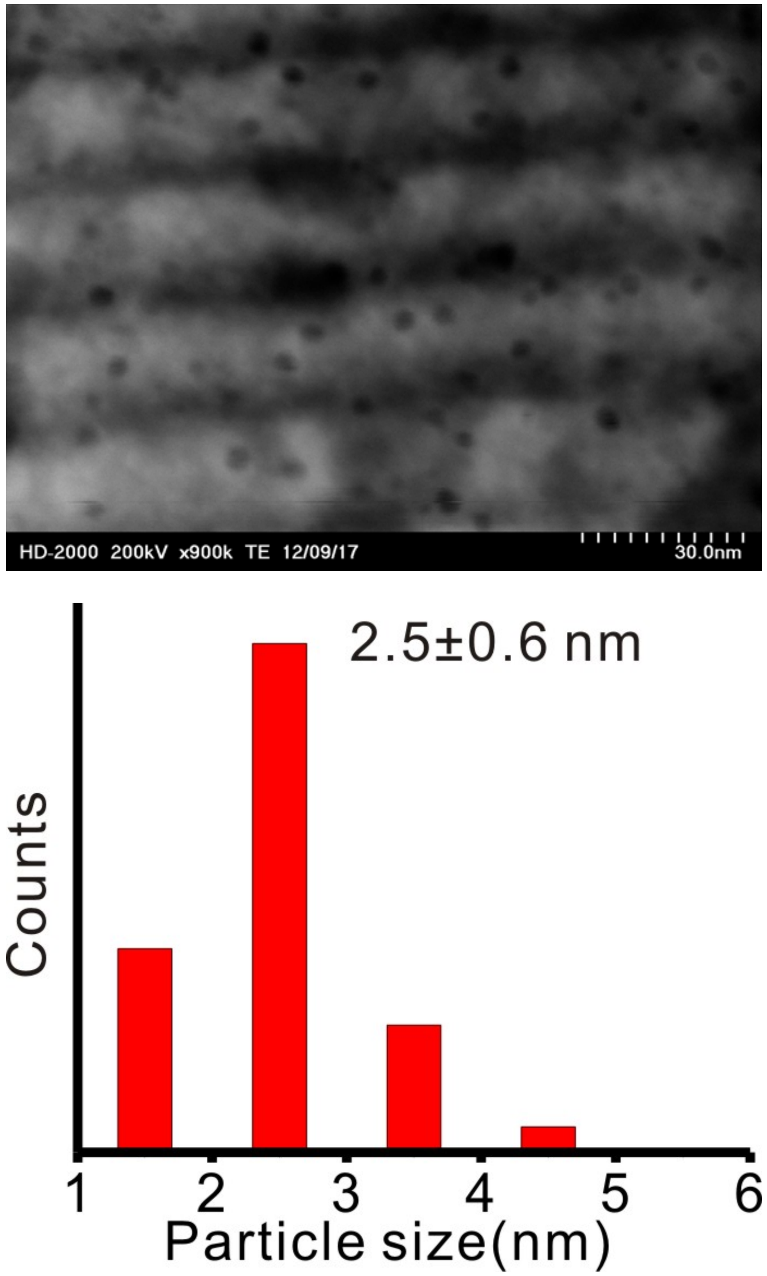

Fig. S11 TEM image of Au_{144} clusters supported on 13.5%CuO-EP-FDU-12 after calcination at 400^{o}C and size distribution of gold nanoparticles.

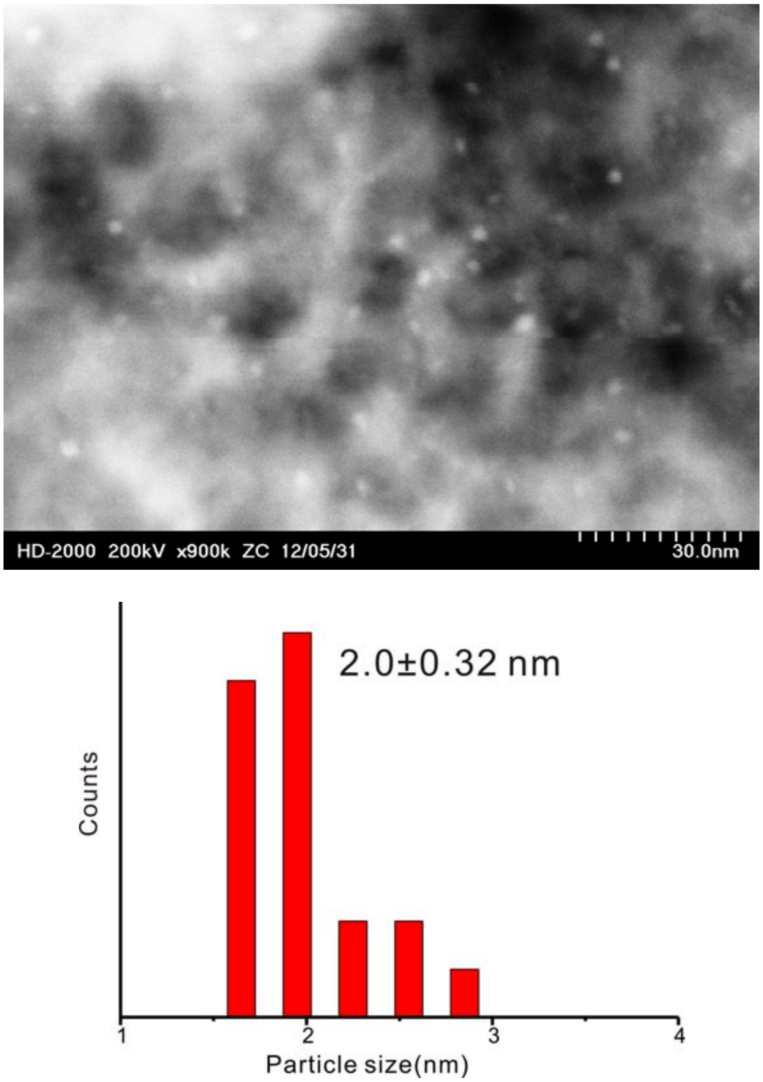

Fig. S12 STEM image of Au_{144} clusters supported on 9%CuO-EP-FDU-12 after calcination at 500^{o}C in air for 3h and size distribution of gold particles.

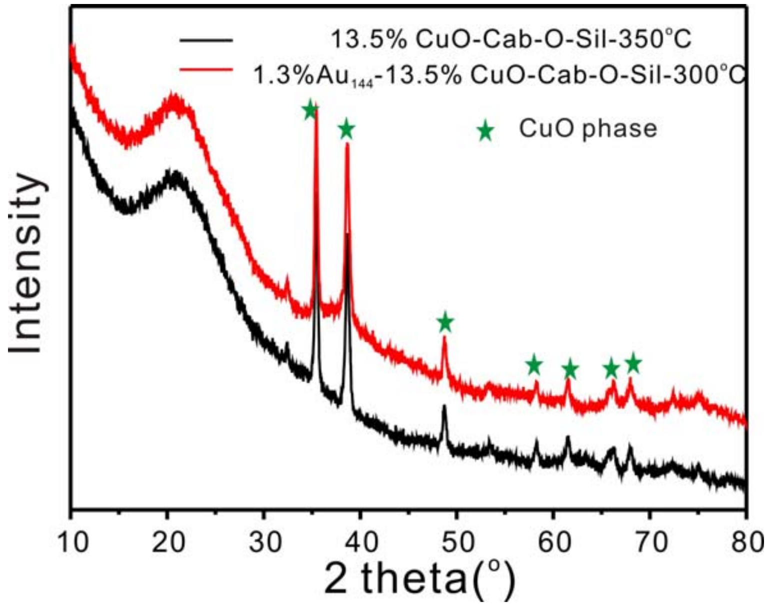

Fig. S13 XRD patterns of 1.3% Au_{144} clusters supported on 13.5%CuO-Cab-O-Sil silica after calcination.

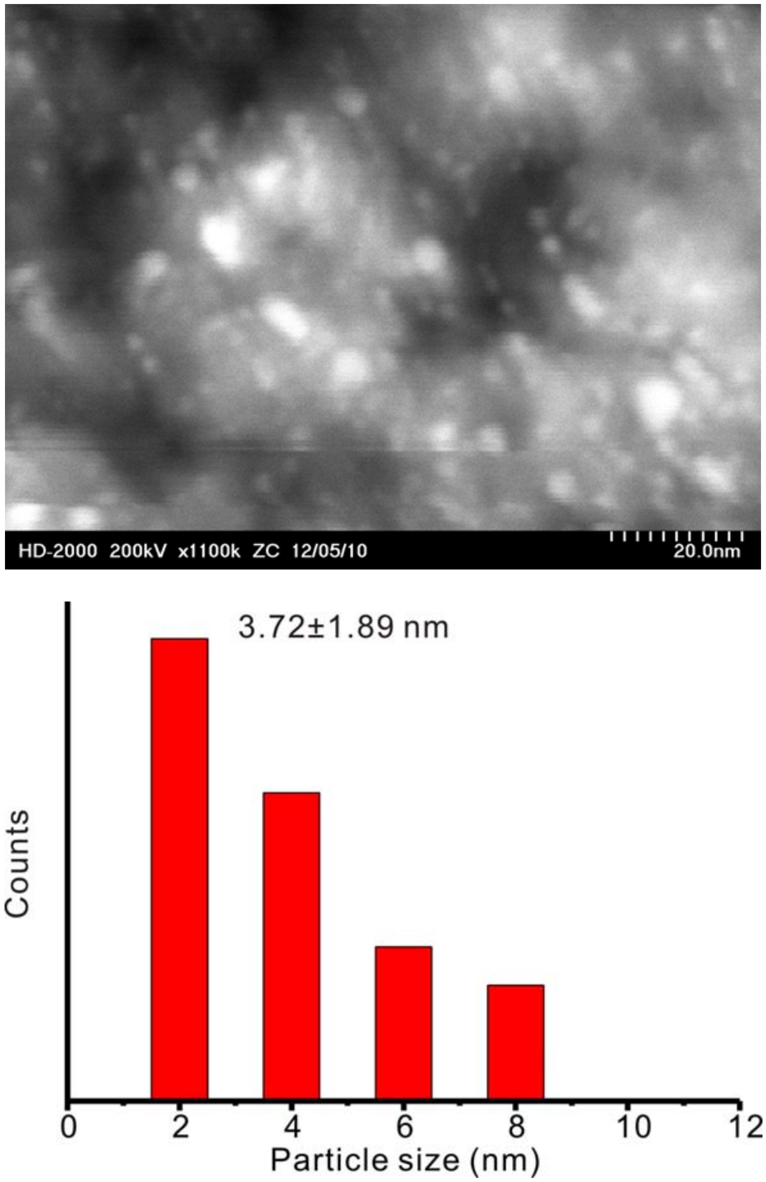

Fig. S14 STEM image of 1.3% Au_{144} clusters supported on 13.5% CuO-Cab-O-Sil after calcination at 300°C in air for 3h and size distribution of gold nanoparticles..

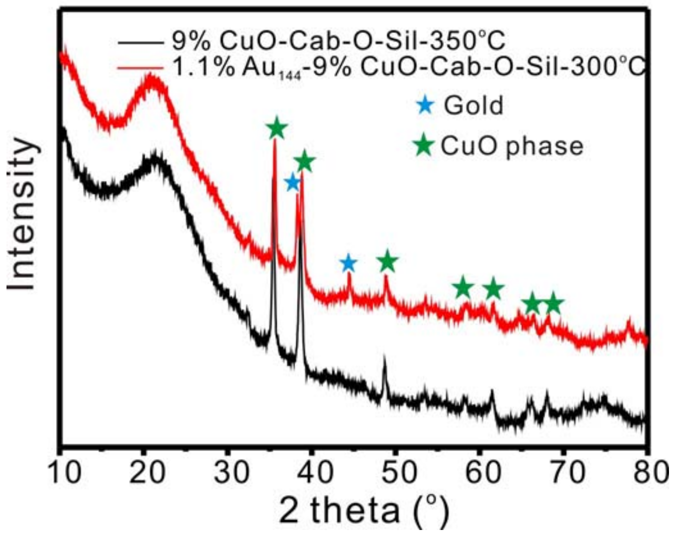

Fig. S15 XRD patterns of 1.1% Au_{144} clusters supported on 9%CuO-Cab-O-Sil silica after calcination.

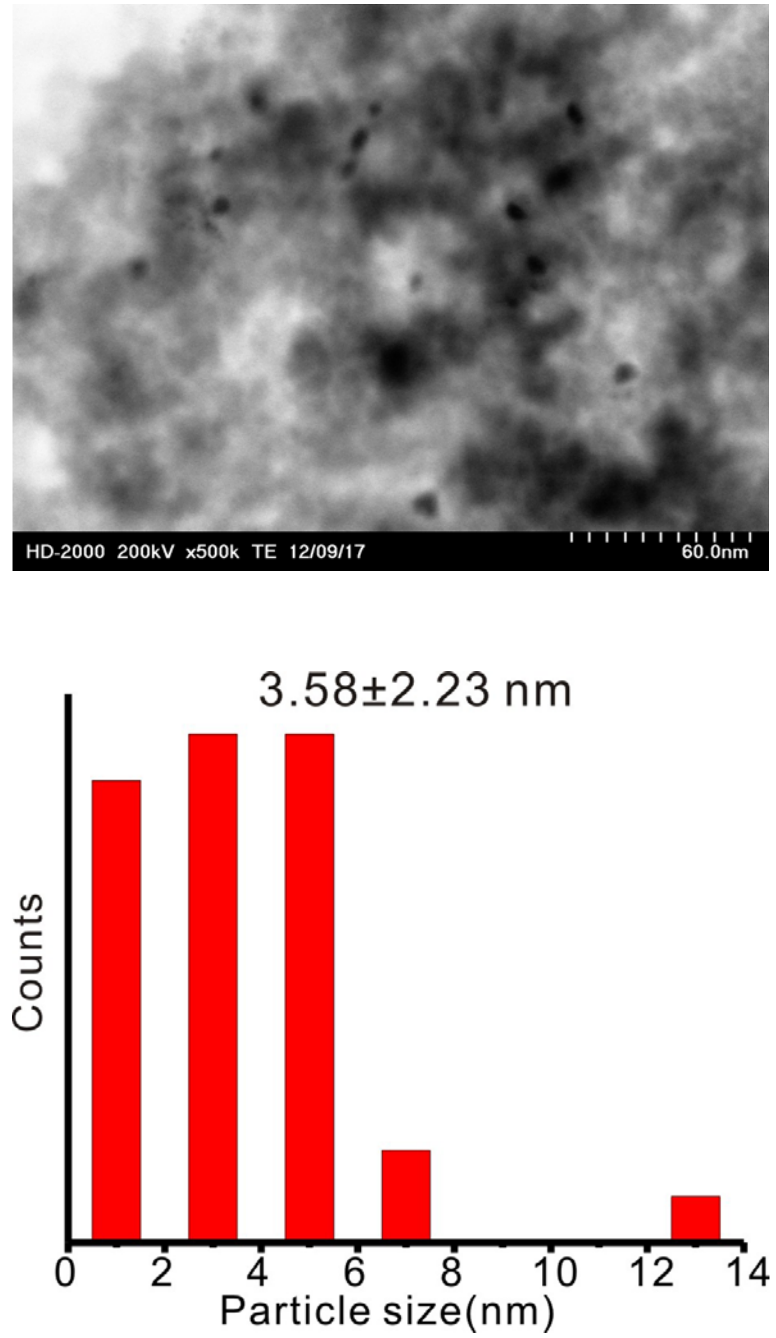

Fig. S16 TEM image of 1.3% Au_{144} clusters supported on 13.5% CuO-Cab-O-Sil after calcination at 300^{o}C in air for 3h and size distribution of gold nanoparticles..

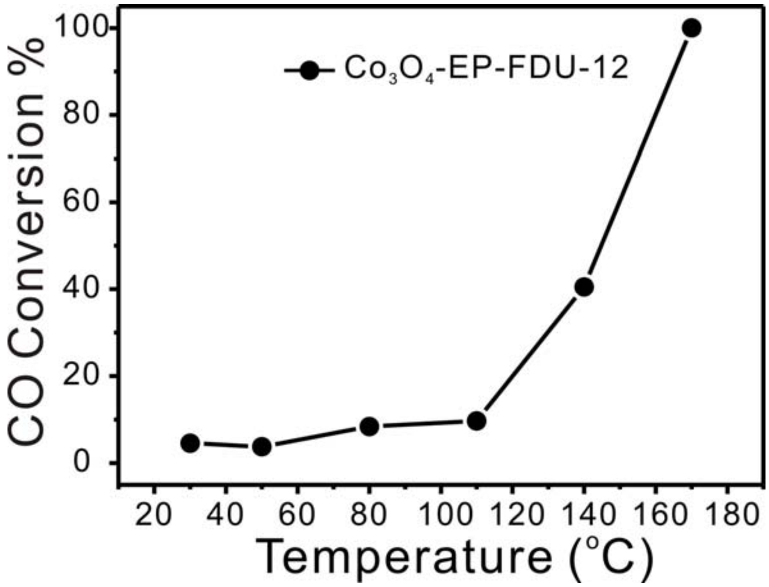

Fig. S17 The light-off curve of CO oxidation of Co_3O_4-EP-FDU-12.

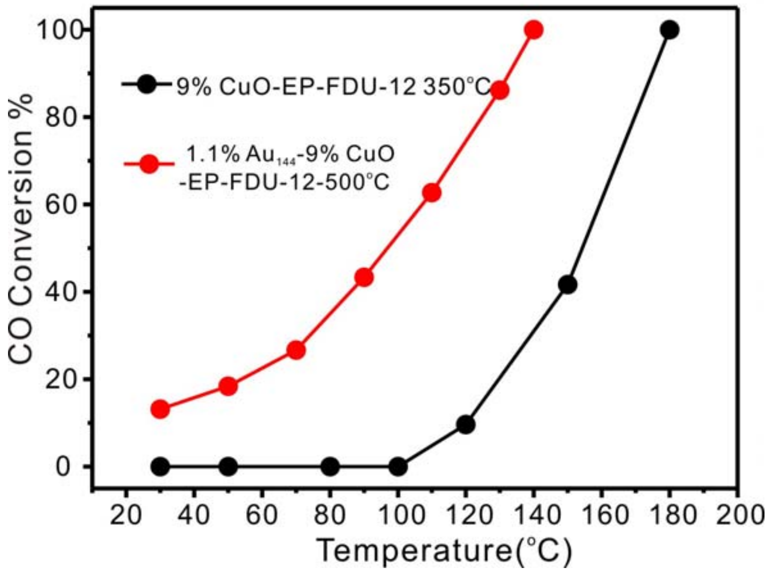

Fig.S18 The light-off curves of CO oxidation of 9%CuO-EP-FDU-12 and 1.1% Au_{144}-9%CuO-EP-FDU-12-500°C.

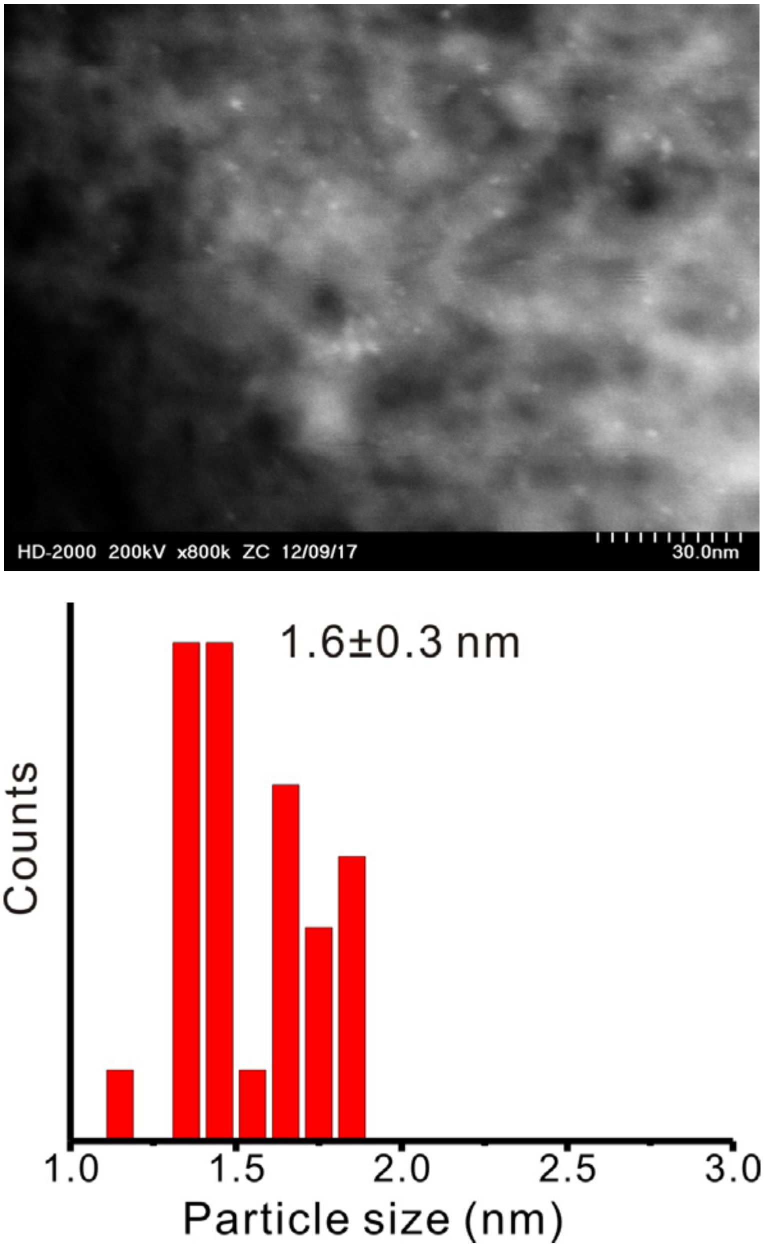

Fig. S19 TEM image of 1.1% Au_{144} clusters supported on 9% CuO-EP-FDU-12 after CO oxidation and size distribution of gold nanoparticles..

REFERENCES

1 Qian, H.and Jin, R., *Chem. Mater.*, 2011, **23,** 2209-2217.

2 Zhu, M., Lanni, E., Garg, N., Bier, M. E.and Jin, R., *J. Am. Chem. Soc.*, 2008, **130,** 1138-1139.