

Mesoporous Metal Oxide-Encapsulated Gold Nanocatalysts: Enhanced Activity for Solvent-Free Aerobic Oxidation of Hydrocarbons Catalyst Application

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Materials

Cetyltrimethylammonium bromide (CTAB) were obtained from Sigma-Aldrich. Methanol (>99.9%), ethanol (>99.5%), chloroform (99.9%), citric acid (CA) were purchased from Beijing Chemical Works. Hexamethylenetetramine (HMT), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), tert-butylamine-borane complex (TBAB, 97%), oleylamine (OAm) (C18 content: 80% - 90%), sodium borohydride (NaBH_4 , 99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Benzene (99.0%), chloro(triphenylphosphine)gold(I) (AuPPh_3Cl , 98%), dodecanethiol (98%), ascorbic acid (AA, 99.99%), tetrachloroauric acid

($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, >99.99%) were received from Aladdin. All of the chemicals were used without further purification.

Preparation of Au NPs

Au NPs were synthesized using previously reported methods.^{38,39}

Preparation of dodecanethiol-capped 3.0 nm Au NPs

0.25 mmol ClAuPPh_3 was mixed together with 0.125 ml of dodecanethiol in 10 ml of CHCl_3 to form a clear solution to which 2.5 mmol of tert-butylamine-borane complex were added in the form of powder. The mixture was then heated with stirring at 65 °C for 5 hours before it was cooled down.

Preparation of dodecanethiol-capped 2.5 nm Au NPs

1.000 g of ClAuPPh_3 and 1.000 g of dodecanethiol were mixed in 50 mL of CHCl_3 to form a clear solution. Another solution, containing 1.689 g of tert-butylamine-borane, 50 mL CHCl_3 and 20 mL ethanol, was then added to the gold precursor solution. The mixture was kept stirring at room temperature for one day to complete the reaction.

Preparation of dodecanethiol-capped 2.0 nm Au NPs

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.3150 g) dissolved in 25 mL deionized water, and tert-butylamine-borane (1.500 g) dissolved in 80 mL toluene were combined under vigorously stirred (~1100 rpm). 40 mg dodecanethiol was then added to the solution, the mixture was kept stirring at room temperature. After 10 min, an aqueous solution

of NaBH₄ (0.3600 g, freshly made in 25 mL ice-cold deionized water) was quickly added all at once. The mixture was reacted at room temperature for 3 h.

Catalytic reactions

In a typical reaction, 5 mL of organic substrate was placed into a two neck round bottom flask (25 mL capacity) together with 5 mg of the catalyst. These mixtures were stirred under molecular oxygen atmosphere (1 bar) for a required time. The reusability of the catalyst was tested for the oxidation of indane analyzed by GC-MS. When the first oxidation finished, the reaction mixture was centrifuged at 7,000 r.p.m. for 10 min and then the liquid layer was siphoned out. The solid was washed with ethanol and then centrifuged twice. The catalyst was dried in a vacuum oven at 70 °C for 24 h. Finally, the recovered catalyst was used in the subsequent reaction.

Characterization

TEM (Field Emission Transmission Electron Microscopy) analysis was conducted on FEI Tecnai G2 F20 s-twin D573 field emission transmission electron microscope operated at 200 KV. Powder X-ray diffraction (XRD) patterns were obtained by using an Ultima IV diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). N₂ adsorption-desorption isotherms were obtained at -196 °C on a NOVA 4200e. Samples were degassed at 100 °C for a minimum of 8 h prior to analysis. UV-vis spectra were recorded with a Shimadzu UV-2450 spectrometer. The thermal gravimetric analyses (TG) were performed on TGA Q500 thermogravimetric analyzer

used in air with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The X-ray photoelectron spectra were obtained with an ESCALAB 250 spherical. The XPS spectrum was shifted according to C1s peak being at 288.2 eV, so as to correct the charging effect. The element concentrations of Au were determined by inductively coupled plasma mission spectroscopy (ICP-OES, Perkin Elmer OPTIMA 3300DV, U.S.). The structure of products and by-products was identified using GCMS-QP 2010 Plus spectrometer by comparing retention times and fragmentation patterns with authentic samples.

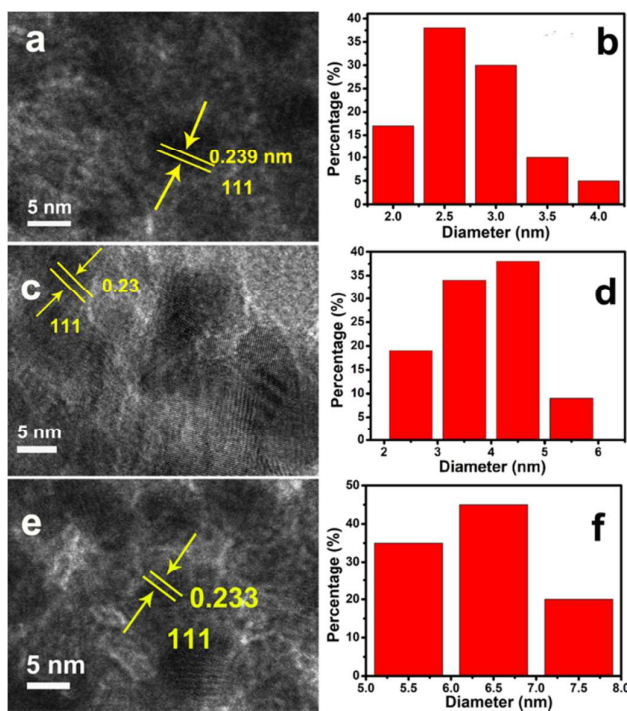


Figure S1. HRTEM images and corresponding Au NPs size distribution of 2.0Au@mZnO after calcination at 300 °C (a, b), 400 °C (c, d) and 500 °C (e, f).

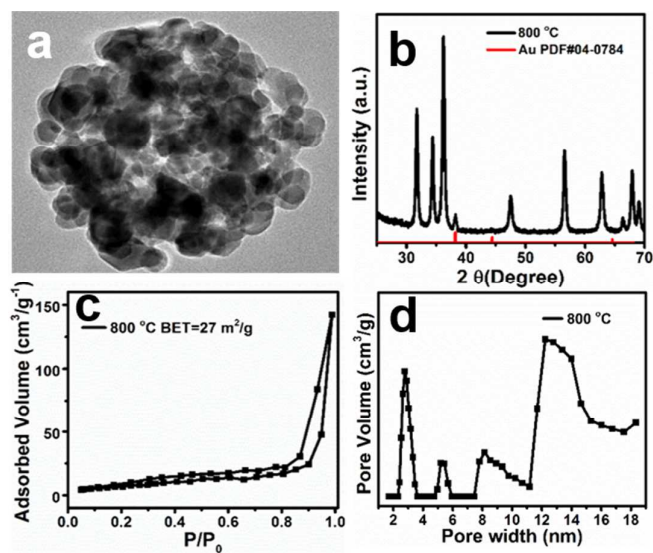


Figure S2. The TEM image (a), XRD patterns (b), N₂ adsorption-desorption isotherms (c) and pore size distribution (d) of 2.0Au@mZnO sample after calcination at 800 °C.

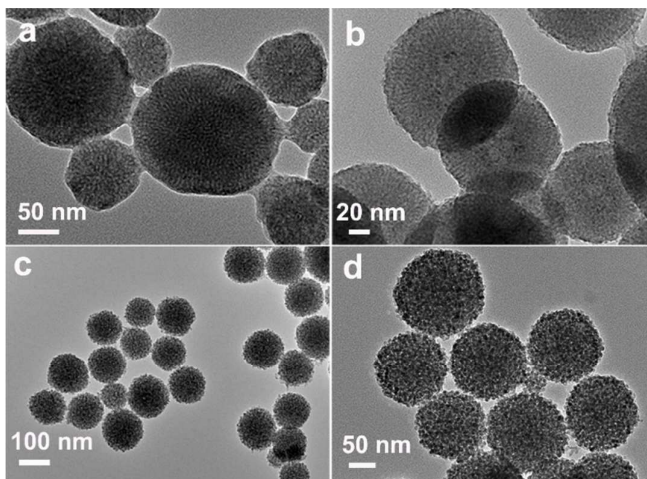


Figure S3. TEM images of 2.5Au@mZnO (a, c) and 3.0Au@mZnO (b, d) before calcined and after calcination at 300 °C.

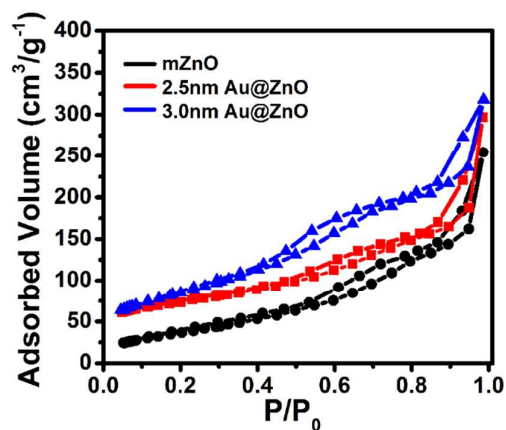


Figure S4. N₂ adsorption-desorption isotherms of mZnO, 2.5Au@mZnO and 3.0Au@mZnO after calcination at 300 °C. The red line and blue line have been offset by 10 and 20 cm³ g⁻¹, respectively, along the vertical axis for clarity.

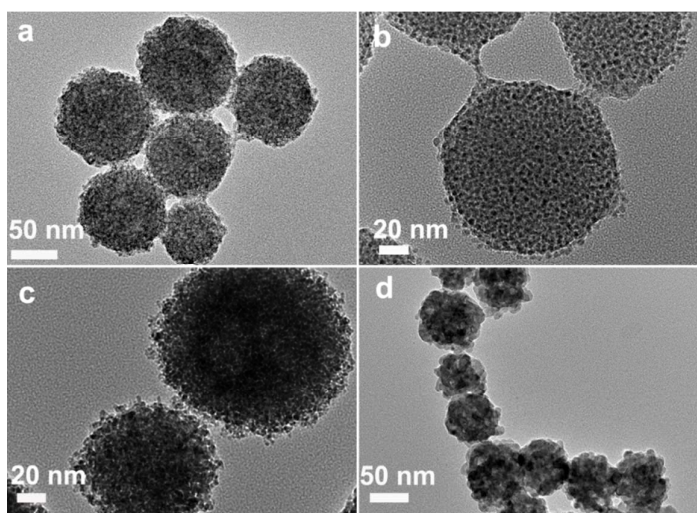


Figure S5. TEM images of 2.0Au@mCeO₂ (a, c), 2.0Au@mCuO (b, d) before calcined and after calcination at 300 °C.

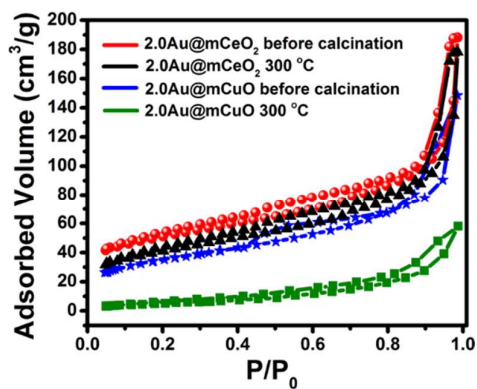


Figure S6. N₂ adsorption-desorption isotherms of 2.0Au@mCuO and 2.0Au@mCeO₂ before calcined and after calcination at 300 °C.

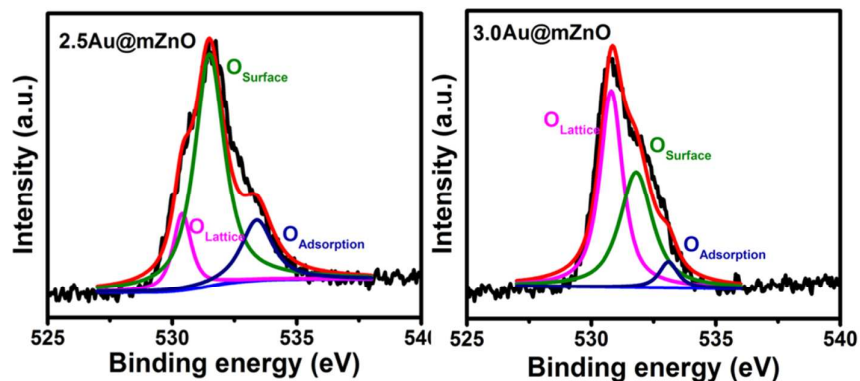


Figure S7. XPS spectra of the O 1s of 2.5Au@mZnO sample (a) and 3.0Au@mZnO sample (b) (0.3 wt % loading rate of Au NPs).

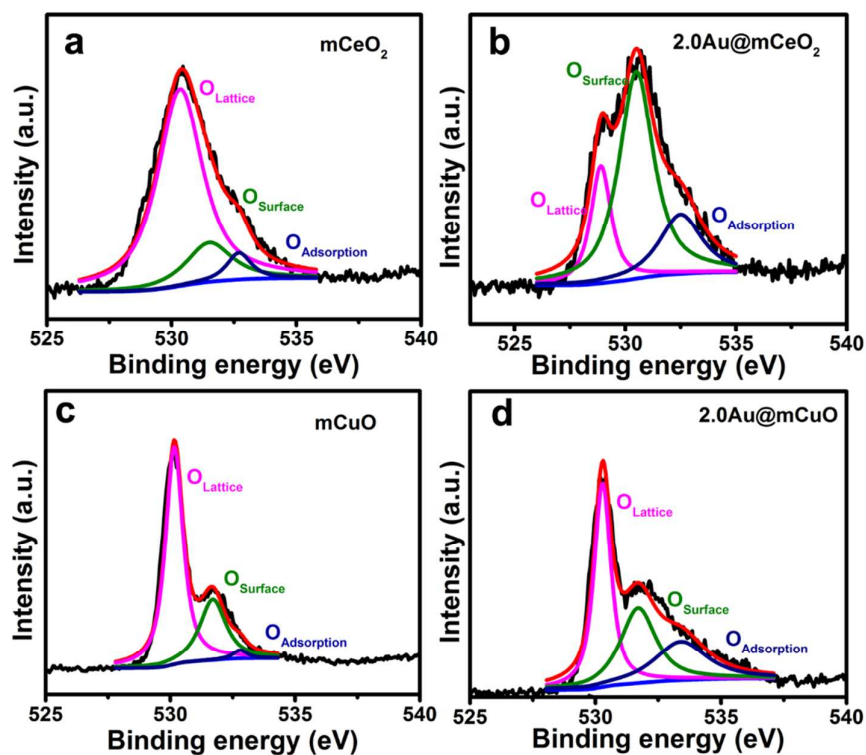


Figure S8. XPS spectra of the O 1s of mCeO₂ sample (a), 2.0Au@mCeO₂ sample (b), mCuO sample (c) and 2.0Au@mCuO sample (d) (0.3 wt % loading rate of Au NPs).

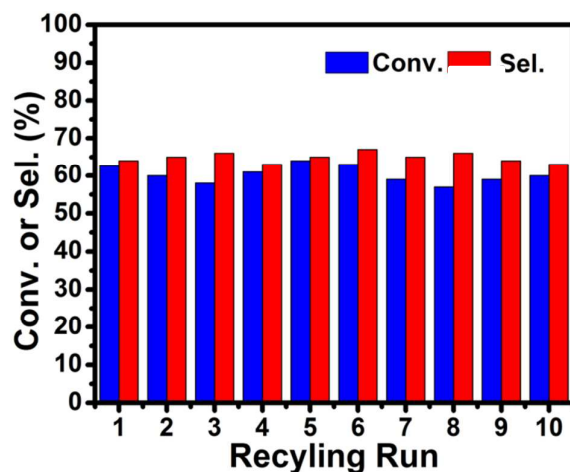


Figure S9. Recycling runs for the indane aerobic oxidations. Reaction conditions: indane 5 mL, 2.0Au@mZnO 0.01 g, 100 °C, O₂ 10 mL/min, stirring speed: 1000 rpm; Conv., conversion; Sel., selectivity. (0.3 wt % loading rate of Au NPs).

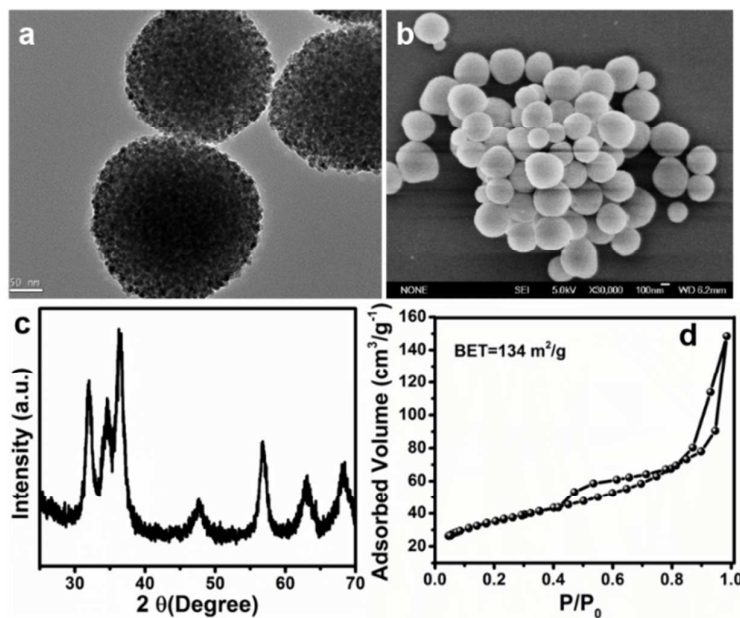


Figure S10. TEM image (a), SEM image (b), XRD pattern (c) and N₂ adsorption/desorption isotherms (d) of 2.0Au@mZnO (0.3 wt % loading rate of gold nanoparticles) after cyclic catalysis experiment.

Table S1. Comparison of indane oxidation activity of the 2.0Au@mZnO catalysts with other reported catalytic systems.

Catalyst	T/P	Solvent	Oxidant	Conversion (%)	TOF (h ⁻¹)	references
Ce _{0.5} Mn _{0.5} O _x @500	110°C	CH ₃ CN	O ₂	75.4	n.d.	33

	/1MPa					
Pd @ N-doped	120°C /0.1MPa	free	air	14.8	452	2
PW ₁₁ Fe	CH ₃ CN reflux /0.1MPa	CH ₃ CN	H ₂ O ₂	50	333 (TON)	43
CrMCM-41	80°C /0.1MPa	free	O ₂	69	n.d.	44
2.0Au@mCeO ₂	120°C /1atm	free	O ₂	88.5	9,521	this work

Table S2. The concentration of oxygen species atoms and the surface area of all catalysts.

Catalyst	O _{Lattice} (%)	O _{Surface} (%)	O _{Adsorption} (%)	BET (m ² g ⁻¹)
mZnO	66.8	30.2	3	161
2.0Au@mZnO	10	69	16	159
2.5Au@mZnO	16	64.5	19.5	152
3.0Au@mZnO	49.2	43.1	7.7	158
mCeO ₂	78	16.3	5.7	112
2.0Au@mCeO ₂	19	59	21	110
mCuO	68.9	24	7.1	119
2.0Au@mCuO	42	34	24	20