

Supporting Information

Structure Engineering of CeO₂ for Boosting Au/CeO₂ Nano-catalyst in Green and Selective Hydrogenation of Nitrobenzene

Junqing Ye,^{a,b} Meizan Jing,^c Yu Liang,^a Wenjin Li,^a Wanting Zhao,^a Jianying

Huang,^{d,e} Yuekun Lai,^{d,e,*} Weiyu Song,^c Jian Liu,^c and Jian Sun^{a,f,*}

^a School of Life Science, Beijing Institute of Technology, Beijing 100081, P.R. China

^b Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, P.R. China

^c State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum-Beijing, Beijing 102249, P.R. China

^d College of Chemical Engineering, Fuzhou University, Fuzhou 350116, P.R. China

^e Qingyuan Innovation Laboratory, Quanzhou 362801, P.R. China

^f Advanced Research Institute of Multidisciplinary Science, Beijing Institute of Technology, Beijing 100081, P.R. China

*Corresponding E-mail: yklai@fzu.edu.cn (Y. Lai), jiansun@bit.edu.cn (J. Sun)

Supporting Tables and Figures

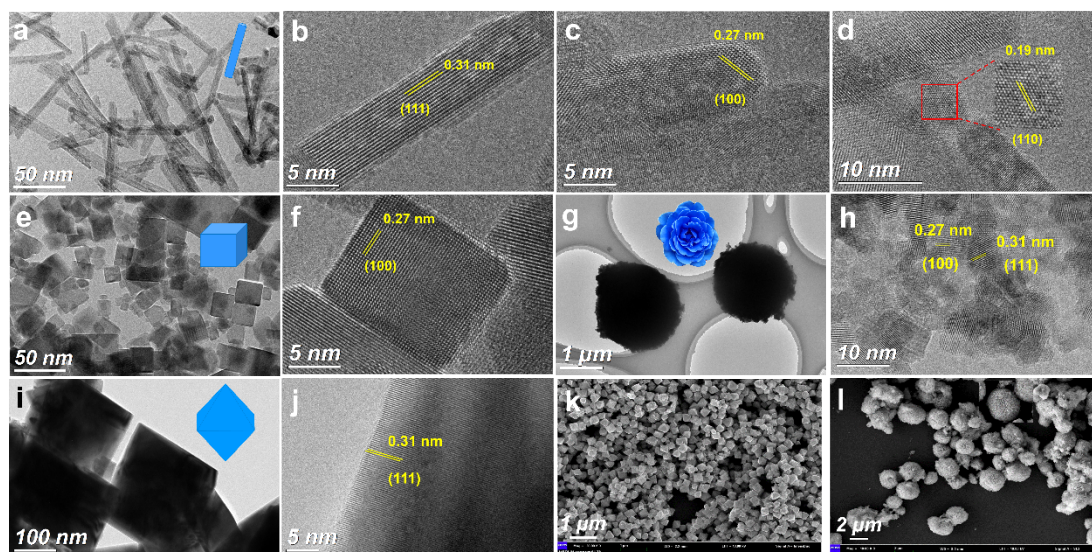


Figure S1. TEM and HRTEM images of CeO₂-rod (a, b, c, and d) and CeO₂-cube (e, f). TEM, HRTEM, and SEM images of CeO₂-flower (g, h, and l) and CeO₂-octa (i, j, and k).

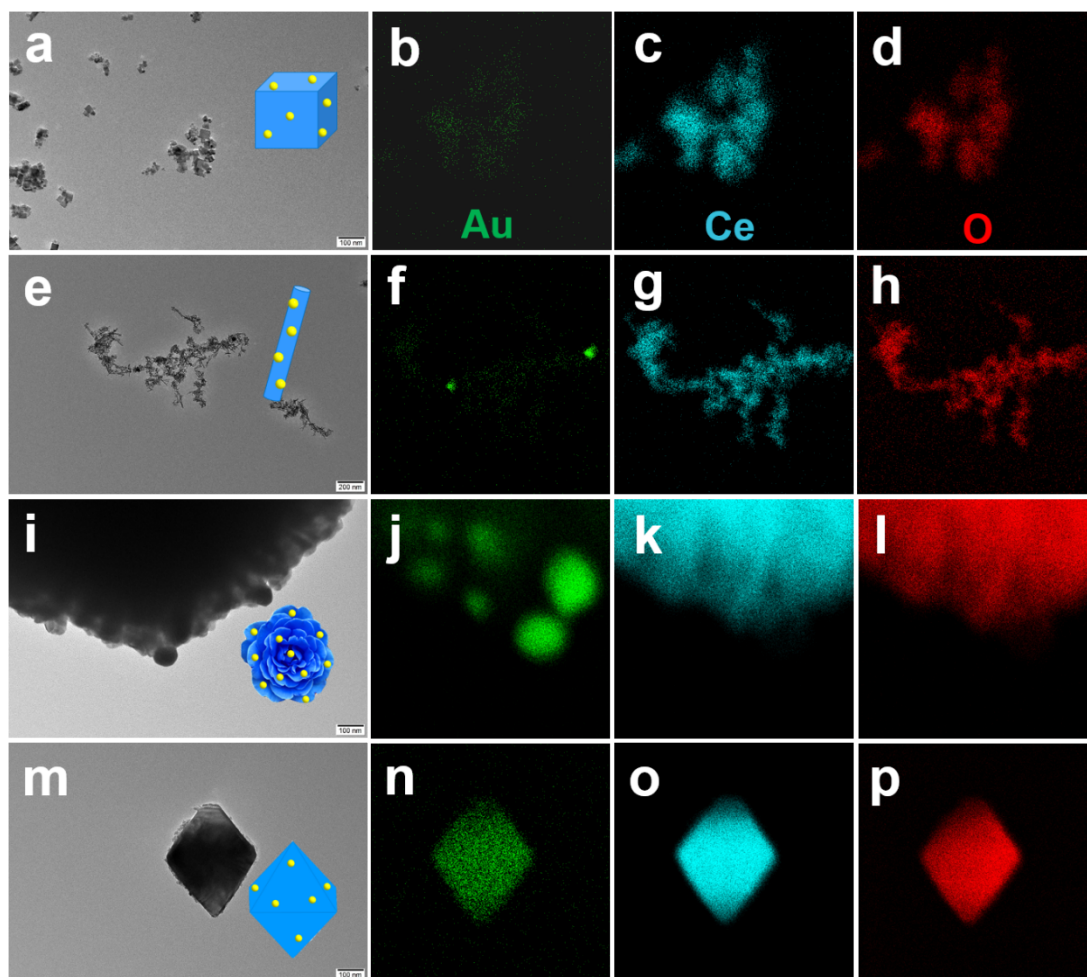


Figure S2. TEM images and EDS mapping results of Au/CeO₂ catalysts. Au/CeO₂-cube (a, b, c, and d), Au/CeO₂-rod (e, f, g, and h), Au/CeO₂-flower (i, j, k, and l), and Au/CeO₂-octa (m, n, o, and p).

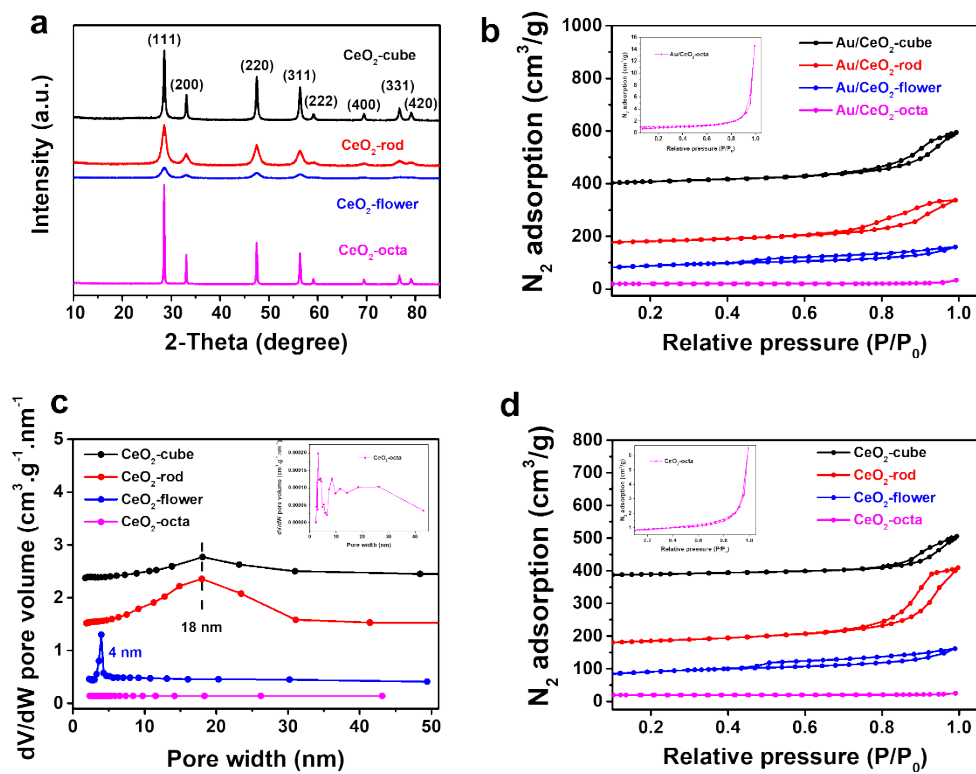


Figure S3. XRD patterns of various CeO₂ (a), N₂ adsorption and desorption isotherms of various Au/CeO₂ (b), BJH pore size distribution curves (c) and N₂ adsorption and desorption isotherms (d) of CeO₂ with different shapes.

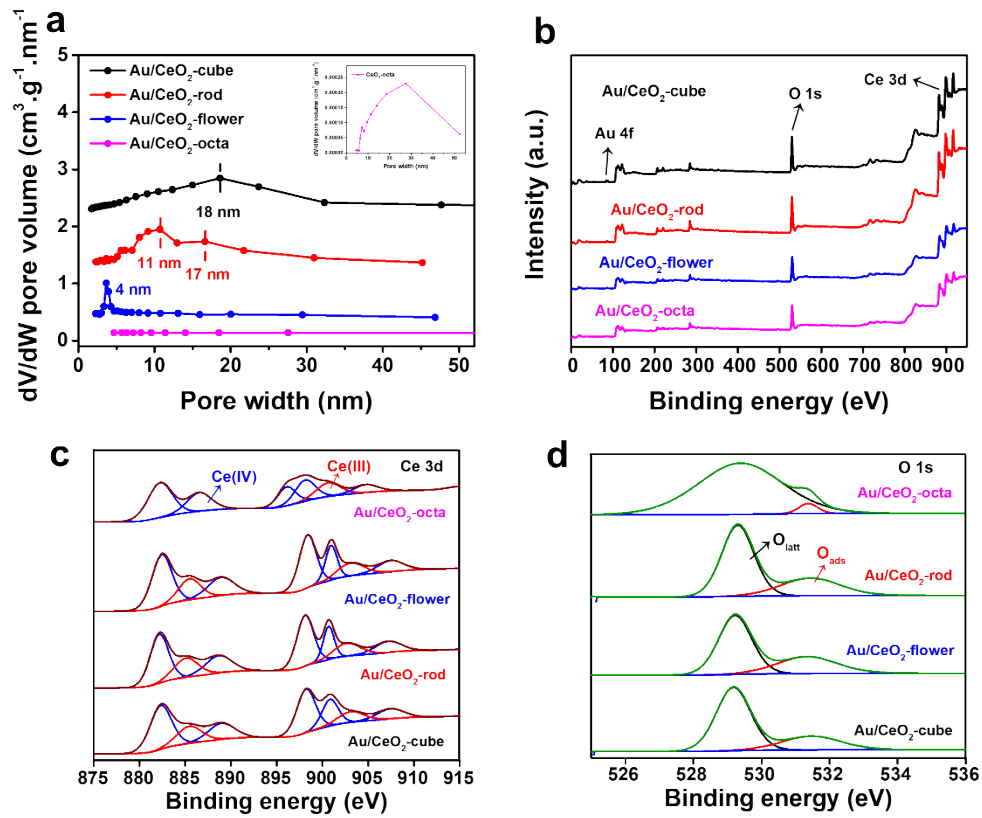


Figure S4. BJH pore size distribution curves (a) and full XPS spectra of various Au/CeO₂ samples

(b), XPS results of various Au/CeO₂ samples: Ce 3d (c), O 1s (d).

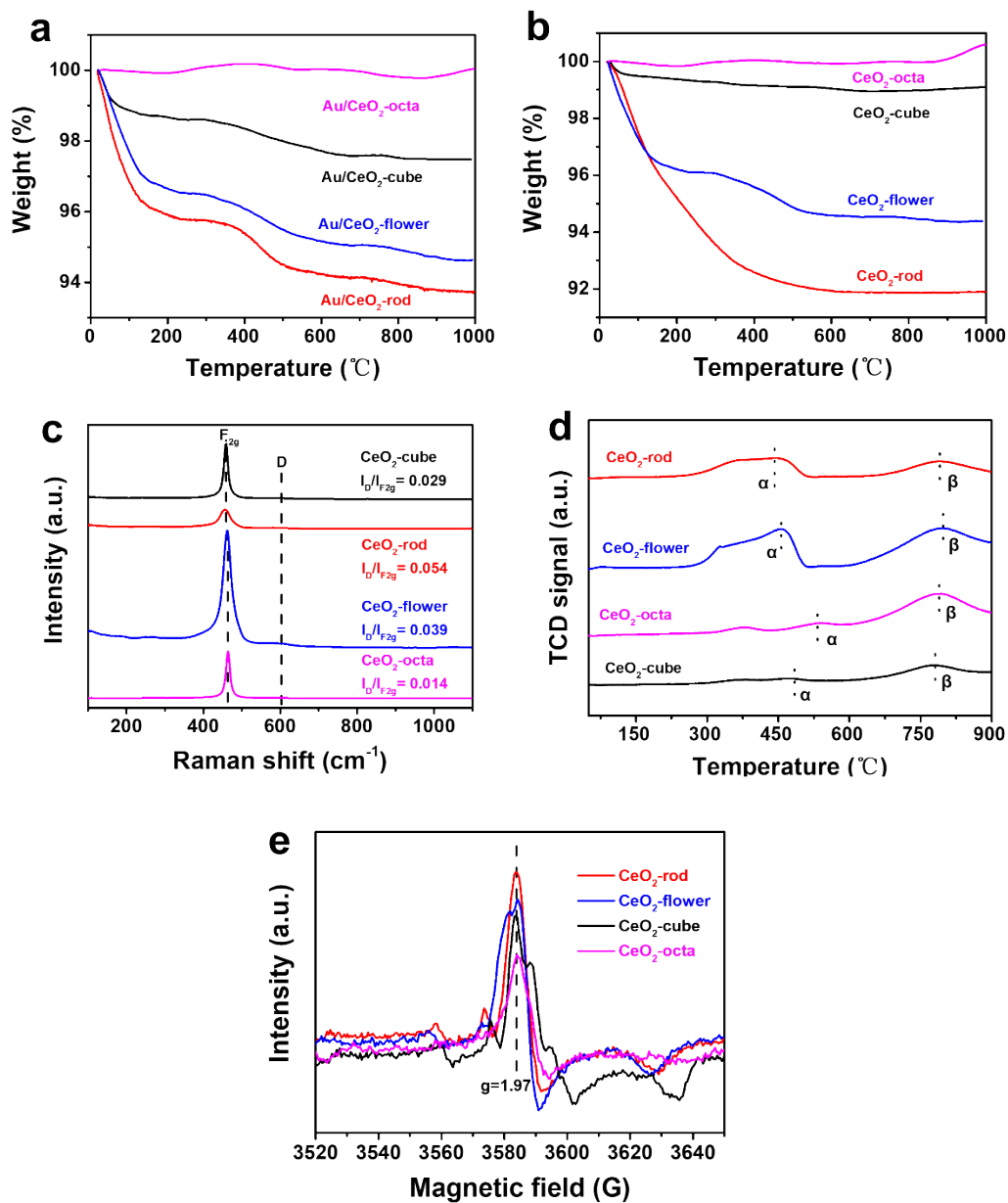


Figure S5. TGA curves of various Au/CeO₂ (a), TGA curves (b), Raman spectra (c), and H₂-TPR results (d), ESR spectra (e) of CeO₂ with different shapes.

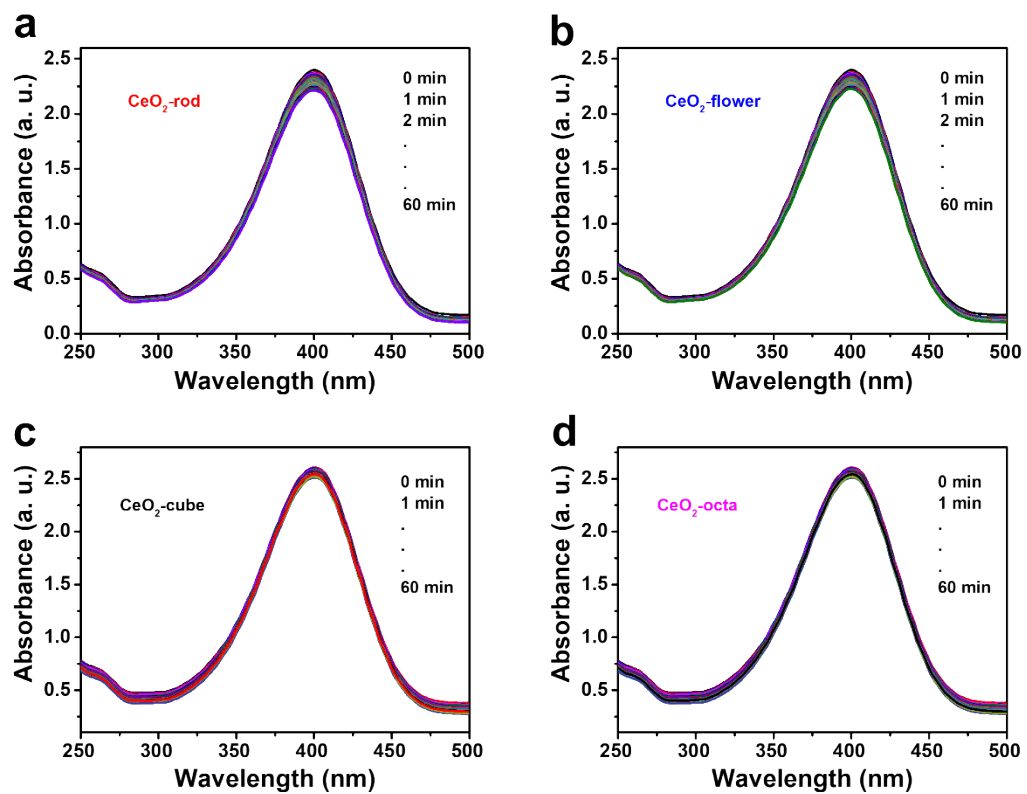


Figure S6. UV-Vis spectra obtained from 4-NP reduction with NaBH₄ at the time interval of 1 min in the presence of CeO₂-cube (a), CeO₂-rod (b), CeO₂-flower (c), CeO₂-octa (d).



Figure S7. Experimental device for catalytic transfer hydrogenation of nitrobenzene.

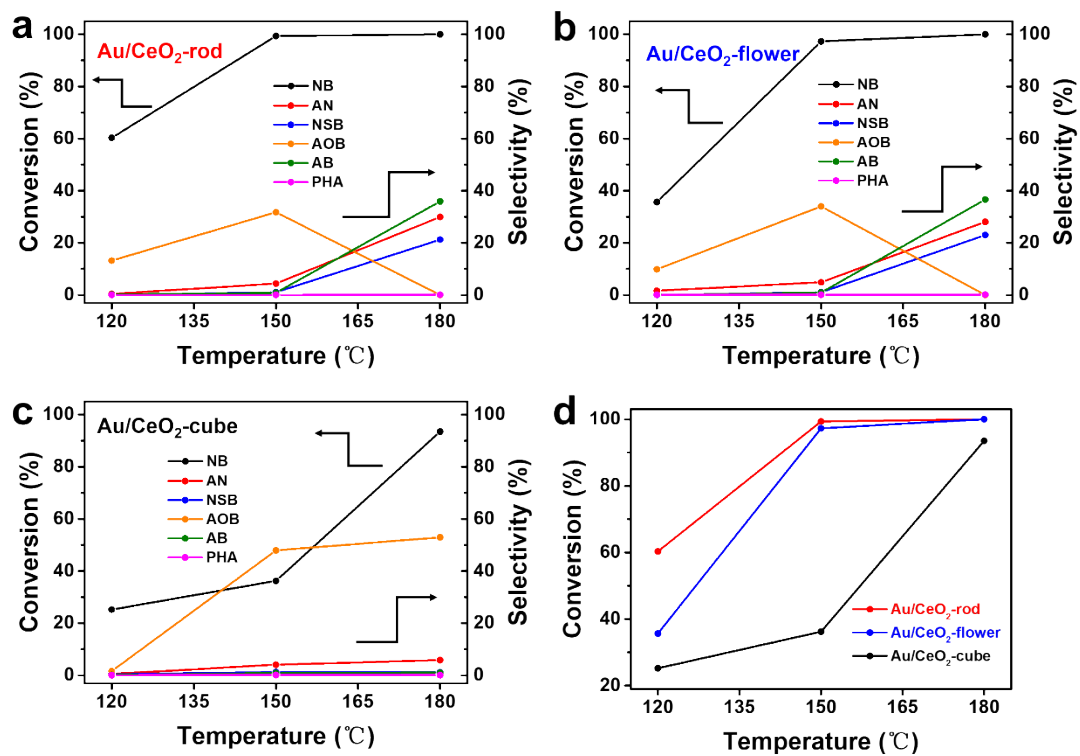


Figure S8. Effect of reaction temperature on the catalytic transfer hydrogenation of nitrobenzene over Au/CeO₂-rod (a), Au/CeO₂-flower (b), Au/CeO₂-cube (c), and the comparison of conversion of nitrobenzene over various Au/CeO₂ (d). Reaction conditions: 0.06 mL of NB, 5 mL of isopropanol, 50 mg of Au/CeO₂ catalyst, 6 h.

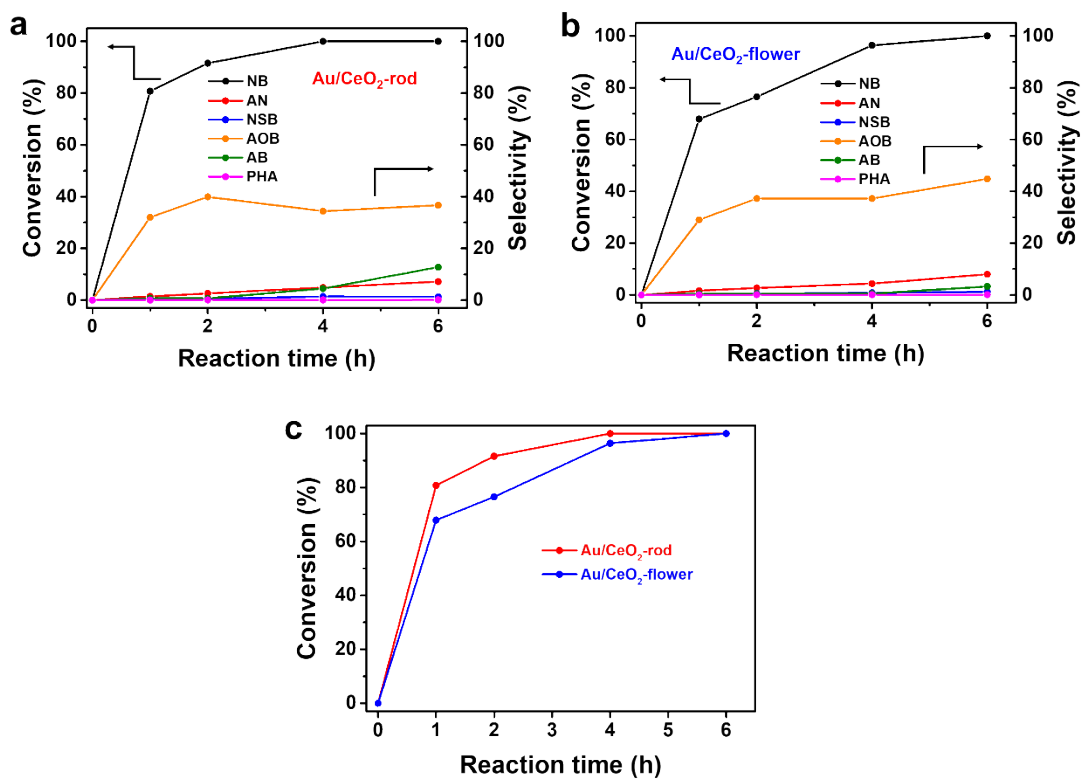


Figure S9. Effect of reaction time on the catalytic transfer hydrogenation of nitrobenzene over Au/CeO₂-rod (a), Au/CeO₂-flower (b), and the comparison of conversion of nitrobenzene over different Au/CeO₂ (c). Reaction conditions: 0.06 mL of NB, 5 mL of isopropanol, 30 mg of Au/CeO₂ catalyst, 180 °C.

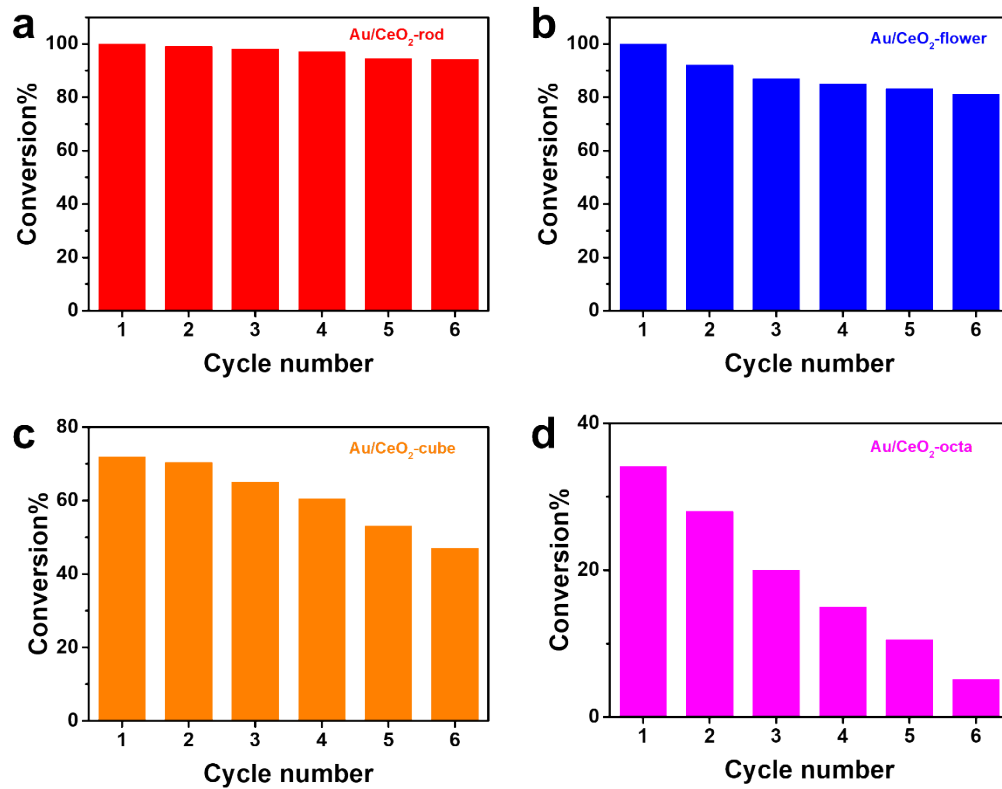


Figure S10. Recycling of various Au/CeO₂ for catalytic transfer hydrogenation of NB. Reaction conditions: 0.06 mL of NB, 30 mg of Au/CeO₂, 5 mL of isopropanol, 180 °C, and 6 h.

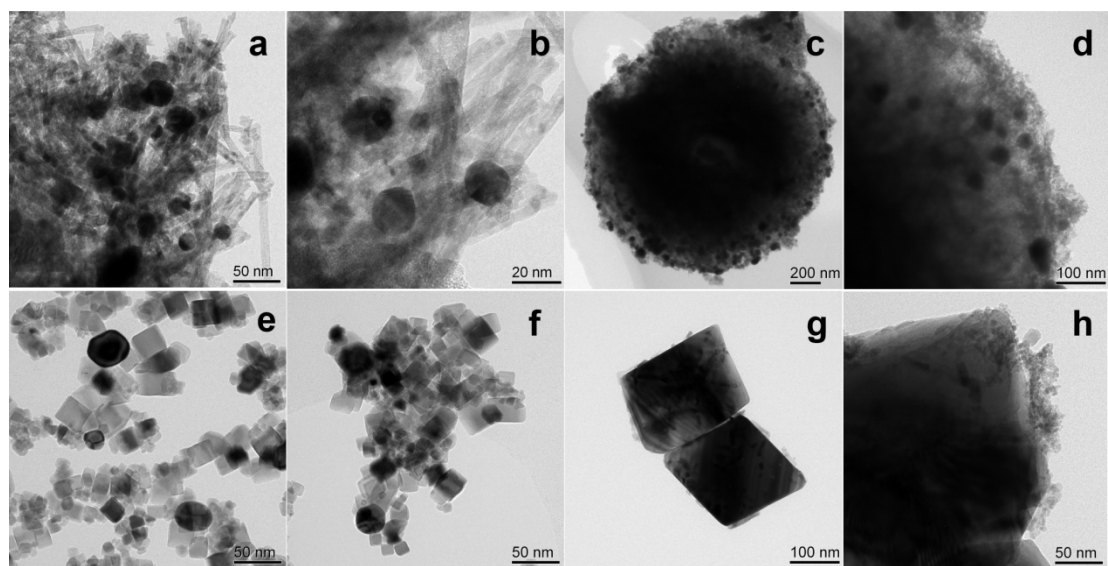


Figure S11. TEM images of spent Au/CeO₂ catalysts. Au/CeO₂-rod (a, b), Au/CeO₂-flower (c, d), Au/CeO₂-cube (e, f), Au/CeO₂-octa (g, h).

Table S1. Effect of reaction temperature on the catalytic transfer hydrogenation of nitrobenzene over various Au/CeO₂ catalysts.

Catalyst	Temperature °C	NB Conv.%	PHA Sel.%	AN Sel.%	NSB Sel.%	AOB Sel.%	AB Sel.%
Au/CeO ₂ -rod	120	60.30	0.029	0.41	0	13.23	0.15
Au/CeO ₂ -rod	150	99.33	0.044	4.41	1.05	31.72	0.85
Au/CeO ₂ -rod	180	100	0.111	29.94	21.23	0.03	35.91
Au/CeO ₂ -flower	120	35.65	0.059	1.65	0	9.85	0.08
Au/CeO ₂ -flower	150	97.28	0.054	4.87	1.04	33.99	0.96
Au/CeO ₂ -flower	180	100	0.115	28.06	23.00	0	36.62
Au/CeO ₂ -cube	120	25.22	0.043	0.55	0.36	1.61	0.09
Au/CeO ₂ -cube	150	36.22	0.10	4.09	1.23	47.91	0.89
Au/CeO ₂ -cube	180	93.5	0.071	5.85	1.18	52.95	1.06

Reaction conditions: 0.06 mL of NB, 5 mL of isopropanol, 50 mg of Au/CeO₂ catalyst, 6 h.

Table S2. Effect of catalyst dosage on the catalytic transfer hydrogenation of nitrobenzene over various CeO₂-based materials.

Catalyst	Catalyst dosage (mg)	NB Conv.%	PHA Sel.%	AN Sel.%	NSB Sel.%	AOB Sel.%	AB Sel.%
Au/CeO ₂ -rod	100	100	0.150	90.5	2.01	0.08	0.31
Au/CeO ₂ -flower	100	100	0.151	87.1	5.5	0	4.0
Au/CeO ₂ -cube	100	99.95	0.091	11.03	4.82	29.12	24.58
CeO ₂ -rod	100	99.6	0.014	15.36	1.83	44.41	5.84
CeO ₂ -flower	100	99.65	0.021	15.59	2.36	38.1	5.95
CeO ₂ -cube	100	97.8	0.032	7.02	1.57	52.52	1.31
Au/CeO ₂ -rod	50	100	0.111	29.94	21.23	0.03	35.91
Au/CeO ₂ -flower	50	100	0.115	28.06	23.00	0	36.62
Au/CeO ₂ -cube	50	93.5	0.071	5.85	1.18	52.95	1.06
Au/CeO ₂ -rod	30	100	0.102	7.16	1.30	36.67	12.75
Au/CeO ₂ -flower	30	100	0.081	7.97	1.16	44.8	3.28
Au/CeO ₂ -cube	30	72.0	0.076	4.35	0.91	54.69	0.59
Au/CeO ₂ -octa	30	34.1	0.01	0.36	0.00	1.62	0.12
CeO ₂ -rod	30	100	0.024	2.10	1.52	20.79	0.39
CeO ₂ -flower	30	98.05	0.036	2.31	1.37	32.69	0
CeO ₂ -cube	30	38.13	0.049	1.49	0.37	24.90	0.08
CeO ₂ -octa	30	20.65	0.008	0.19	0.00	1.13	0.10
Au/CeO ₂ -rod	10	78.30	0.055	2.03	0.26	36.84	0.15
Au/CeO ₂ -flower	10	68.37	0.046	1.99	0.30	28.18	0.19
Without cat.	0	2.08	trace	trace	trace	trace	trace

Reaction conditions: 0.06 mL of NB, 5 mL of isopropanol, CeO₂-based materials, 180 °C, and 6 h.

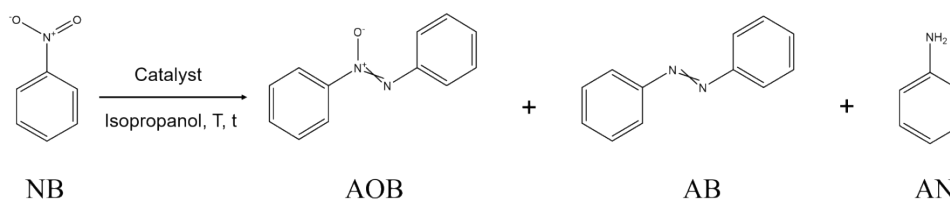
Table S3. Effect of reaction time on the catalytic transfer hydrogenation of nitrobenzene over

Au/CeO₂-rod and Au/CeO₂-flower.

Catalyst	Time (h)	NB Conv.%	PHA Sel.%	AN Sel.%	NSB Sel.%	AOB Sel.%	AB Sel.%
Au/CeO ₂ -rod	1	80.77±0.87	0.045±0.02	1.47±0.08	0.44±0.04	31.99±1.94	0.72±0.05
Au/CeO ₂ -rod	2	91.57±0.16	0.059±0.03	2.59±0.04	0.49±0.01	39.92±0.64	0.71±0.00
Au/CeO ₂ -rod	4	100±0.00	0.067±0.04	4.88±0.08	1.40±0.04	34.40±0.51	4.46±0.08
Au/CeO ₂ -rod	6	100±0.00	0.102±0.04	7.16±0.12	1.30±0.05	36.67±0.49	12.75±0.05
Au/CeO ₂ -flower	1	67.88±0.41	0.038±0.02	1.63±0.05	0.40±0.02	29.03±0.57	0.46±0.01
Au/CeO ₂ -flower	2	76.53±1.15	0.063±0.03	2.72±0.17	0.53±0.04	37.24±2.46	0.46±0.03
Au/CeO ₂ -flower	4	96.38±0.13	0.053±0.02	4.37±0.15	0.82±0.01	37.22±1.39	0.51±0.01
Au/CeO ₂ -flower	6	100±0.00	0.081±0.00	7.97±0.08	1.16±0.02	44.8±1.10	3.28±0.03

Reaction conditions: 0.06 mL of NB, 5 mL of isopropanol, 30 mg of Au/CeO₂ catalyst, 180 °C.

Table S4. The comparison of catalytic activity of transfer hydrogenation NB over various CeO₂-based materials.



Catalyst	NB Conv.%	PHA Sel.%	AN Sel.%	NSB Sel.%	AOB Sel.%	AB Sel.%
CeO ₂ -rod	100	0.024	2.10	1.52	20.79	0.39
CeO ₂ -flower	98.05	0.036	2.31	1.37	32.69	0
CeO ₂ -cube	38.13	0.049	1.49	0.37	24.90	0.08
CeO ₂ -octa	20.65	0.008	0.19	0.00	1.13	0.10
Au/CeO ₂ -rod	100	0.07	4.88	1.40	34.40	4.46
Au/CeO ₂ -flower	96.38	0.05	4.37	0.82	37.22	0.51
Au/CeO ₂ -cube	55.10	0.08	2.44	0.97	37.71	0.35
Au/CeO ₂ -octa	18.21	0.02	0.48	0	3.15	0.08

Reaction conditions: 0.06 mL of NB, 5 mL of isopropanol, 30 mg of CeO₂-based materials, 180 °C,

and 4 h.

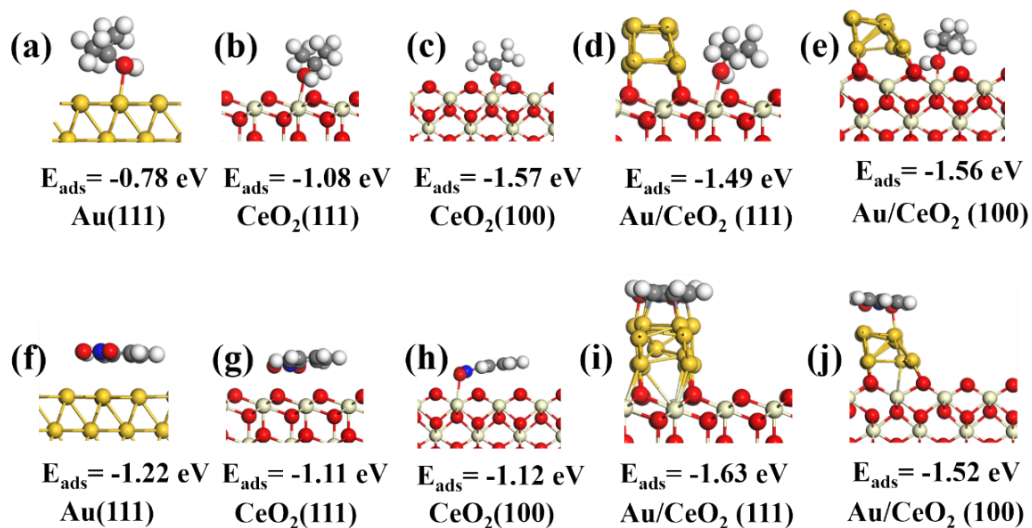


Figure S12. The optimized adsorption structures and calculated adsorption energies (E_{ads}) of isopropanol on Au (111) (a), CeO₂(111) (b), CeO₂ (100) (c), Au/CeO₂ (111) (d), Au/CeO₂ (100) (e) surfaces. The optimized adsorption structures and calculated adsorption energies (E_{ads}) of nitrobenzene on Au (111) (f), CeO₂ (111) (g), CeO₂ (100) (h), Au/CeO₂ (111) (i), and Au/CeO₂ (100) (j) surfaces.

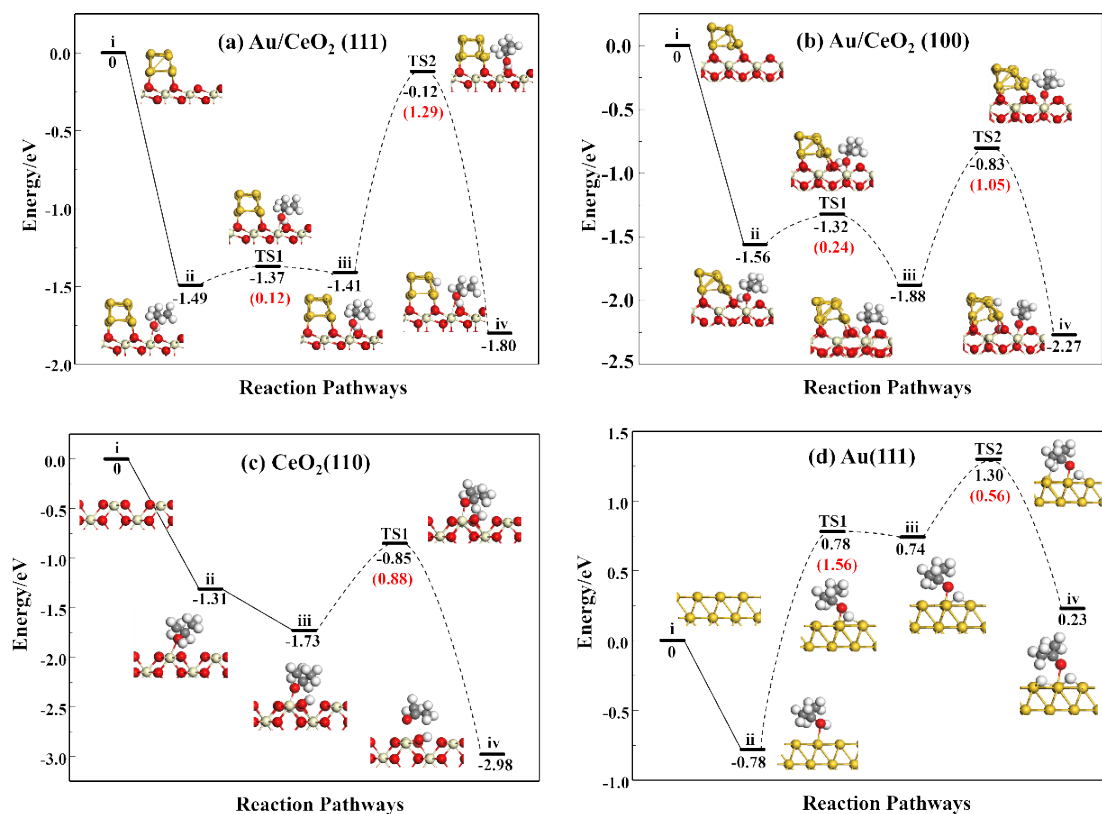
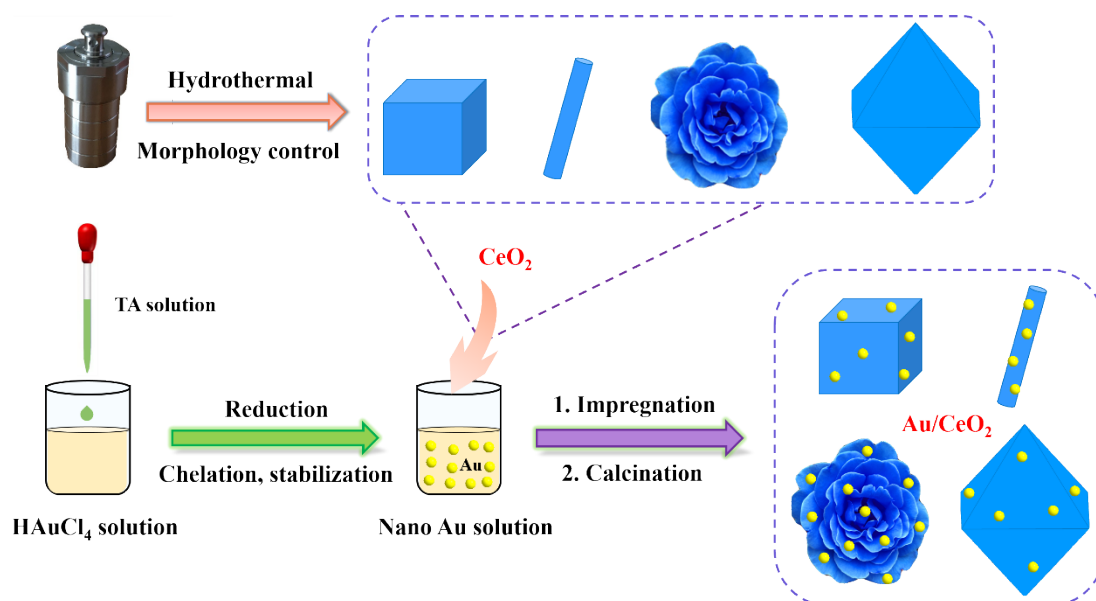


Figure S13. The reaction pathways for the dehydrogenation of isopropanol on Au/CeO₂ (111) (a), Au/CeO₂ (100) (b), CeO₂ (110) (c), and Au (111) (d) surfaces.



Scheme 1. Schematic diagram of synthesis route of Au/CeO₂ catalysts.

Preparation of CeO₂ supports

For the typical synthesis of CeO₂-rod and CeO₂-cube, first, 14.18 g KOH and 0.87 g Ce(NO₃)₃·6H₂O were dissolved in 35 mL and 5 mL of ultrapure water, respectively. Subsequently, the two solutions were mixed and stirred at 25 °C for 40 min to form a milky slurry. Next, the mixture was transferred into a Teflon bottle (100 mL), and treated at 373 K for 24 h to prepare CeO₂-rod, at 453 K for 24 h to synthesis CeO₂-cube. After cooling down to room temperature naturally, the precipitates were separated via centrifugation and washed with ultrapure water for 5 times, followed by drying at 60 °C in air overnight. The final powder was obtained and donated as CeO₂-rod and CeO₂-cube, respectively.

For the preparation of CeO₂-flower, glucose (0.01 mol) was dissolved into H₂O (80 mL) with stirring, which was followed by addition of acrylamide (0.015 mol) and Ce(NO₃)₃·6H₂O (0.005 mol) to form uniform mixture. Thereafter, NH₃·H₂O (3.2 mL, 25wt%) was added into the mixture drop by drop with continuous stirring for 5 h, and then transferred into a 100 mL autoclave. The autoclave was heated at 180 °C for 72 h and then cooled to room temperature. Subsequently, the precipitate product was centrifuged, washed with deionized water 6 times, and dried in air at 80 °C for 12 h. Finally, the dried solid was calcined at 400 °C for 4 h in air.

For CeO₂-octa, the 0.0038 g Na₃PO₄·12H₂O was dissolved in 35 mL of deionized water under stirring, followed by mixing with 5 mL of Ce(NO₃)₃·6H₂O (0.434g) by stirring for 1 h. The mixed solution was transferred into autoclave and kept at 200 °C for 20 h. After cooled to room temperature, the precipitate was collected by

centrifugation and subsequently washed by deionized water and ethanol several times.

The resulting powders were dried at 80 °C for 12 h and then calcined at 600 °C for 6 h in a muffle oven at a heating rate of 5 °C/min.