Electronic Supplementary Information

Hydrogenated Cu_2O\Au@CeO_2 Z-Scheme catalyst for Photocatalytic Oxidation of Amines to Imines

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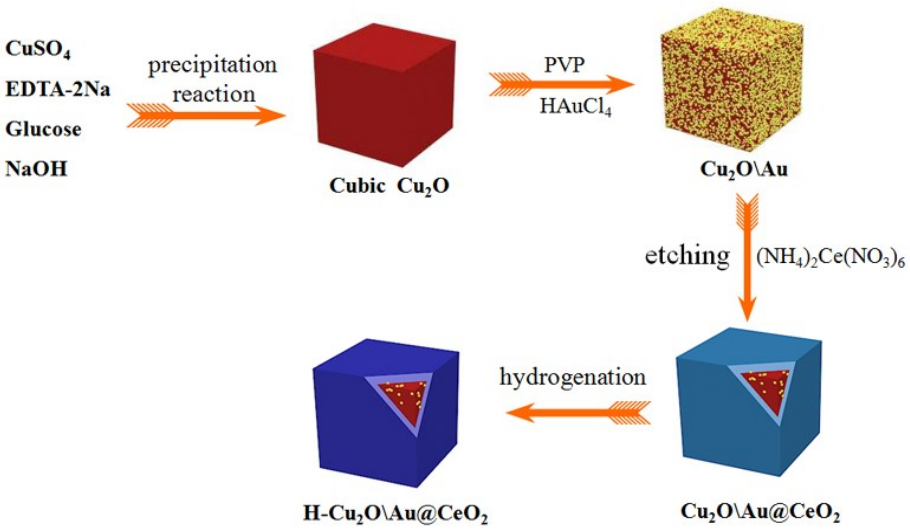
Total pages: 13

Total number of Fig.S: 17

Total number of Tables: 4



Scheme S1. Schematic illustration of the preparation of the hydrogenated Cu_2O\Au@CeO_2 (H-Cu_2O\Au@CeO_2).

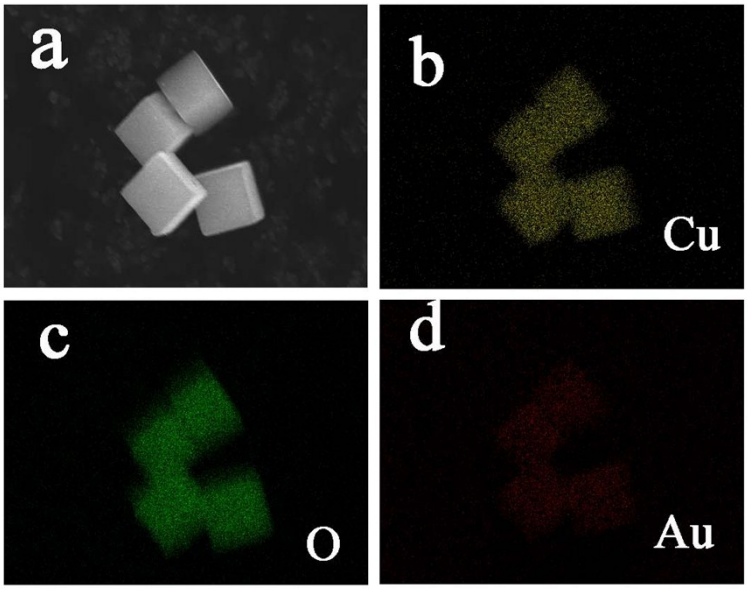


Fig. S1. SEM image (a) and the corresponding EDS element mapping images of the Cu_2O\Au (b-d).

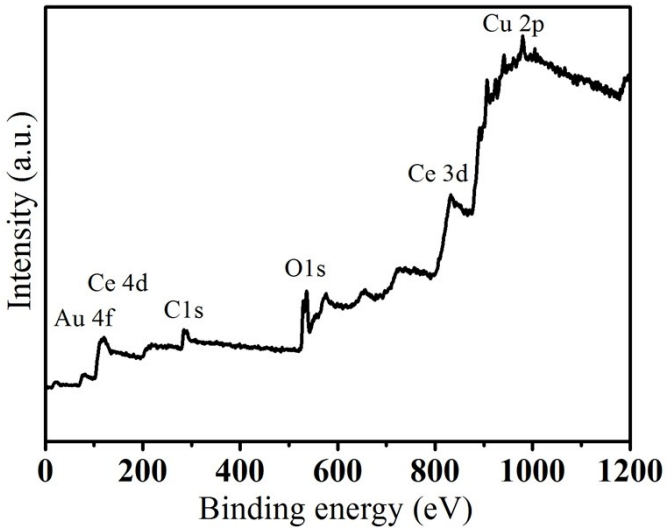


Fig. S2. The survey XPS spectrum of the H-Cu_2O\Au@CeO_2 composite.

$$Ce^{3+}(\%) = [A(Ce^{3+})]/[A(Ce^{3+}) + A(Ce^{4+})] \times 100\% \quad (1)$$

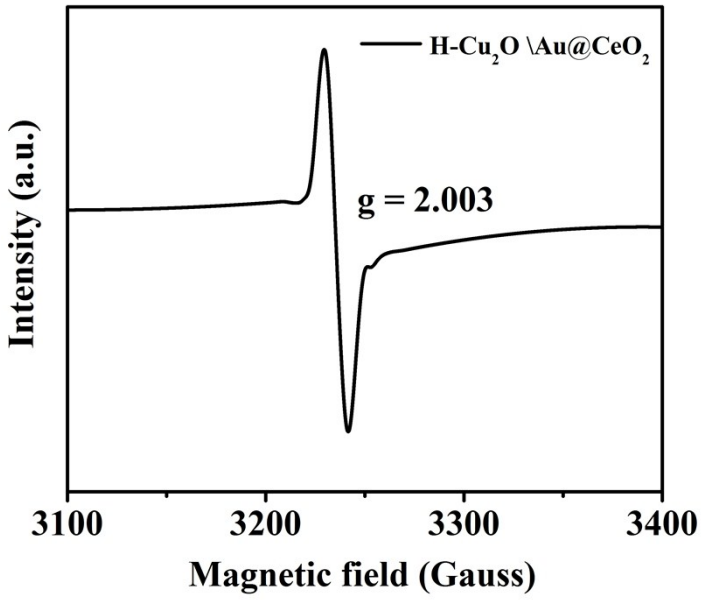


Fig. S3. Electron Paramagnetic Resonance Spectroscopy (ESR) of H-Cu_2O\Au@CeO_2.

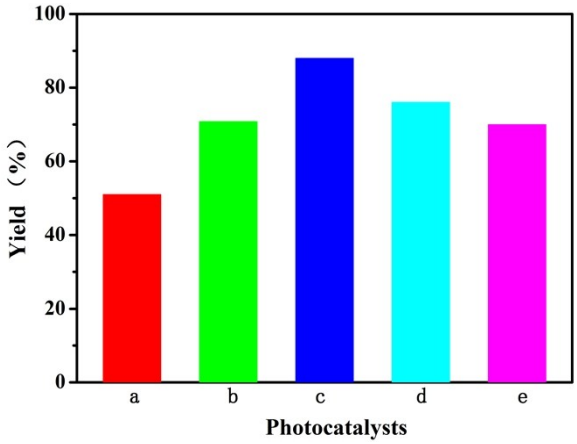


Fig. S4. Benzylamine yield over various H-Cu_2O\Au@CeO_2 with the different Au contents. a) H-Cu_2O@CeO_2, b) H-Cu_2O\Au-35@CeO_2, c) H-Cu_2O\Au-70@CeO_2 (H-Cu_2O\Au@CeO_2), d) H-Cu_2O\Au-105@CeO_2, e) H-Cu_2O\Au-140@CeO_2. Reaction conditions: 15 mg photocatalysts, 1.5 mL H_2O, 15 uL substrates, visible light ($\lambda > 400$ nm), illumination time is 5 h, O_2 atmosphere, room temperature (20-23 ^oC).

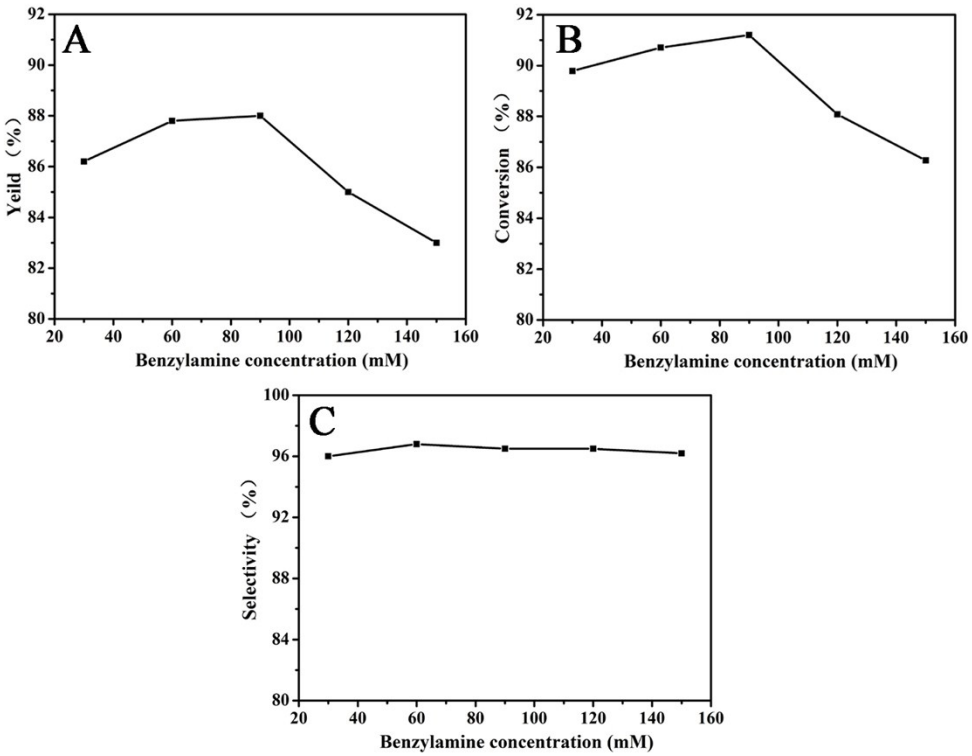


Fig. S5. The influence of benzylamine concentration on the yield (A), conversion (B), and selectivity (C) of H-Cu_2O\Au@CeO_2 in the photocatalytic oxidation of benzylamine.

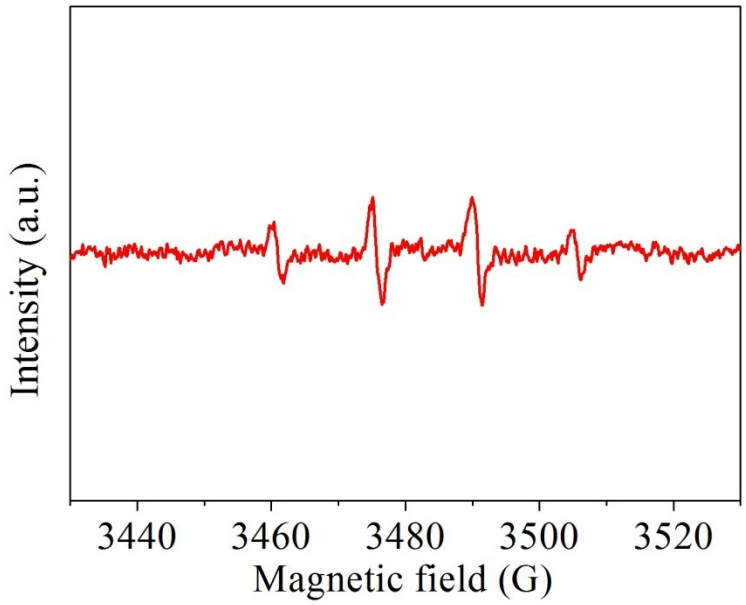


Fig. S6. ESR spectra of DMPO−•OH adduct in H-Cu_2O\Au@CeO_2 aqueous dispersions with visible light irradiation.

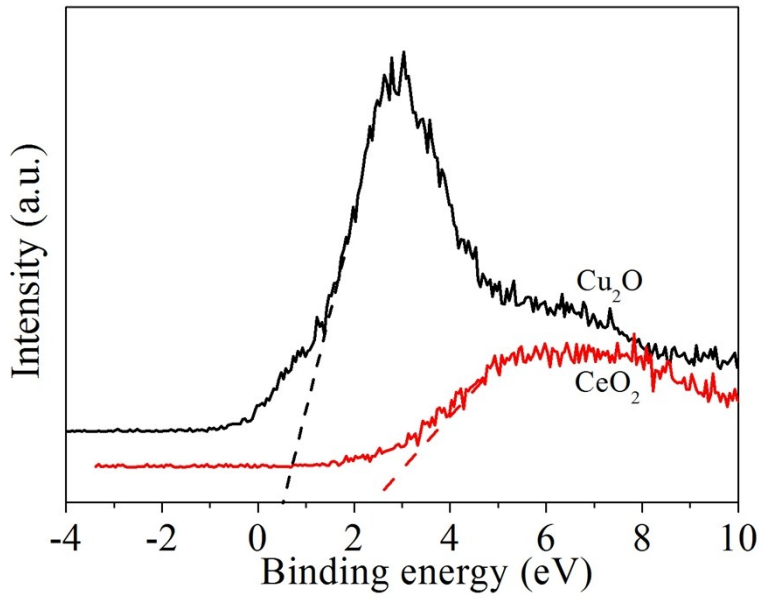


Fig. S7. XPS valence band spectra of different samples.

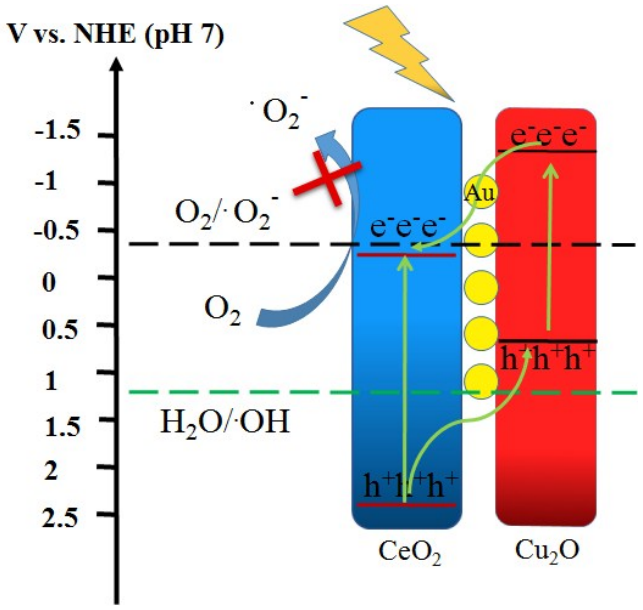


Fig. S8. One possible photoinduced charge transfer and separation processes for the H-Cu_2O\Au@CeO_2 under visible-light irradiation (λ >400 nm).

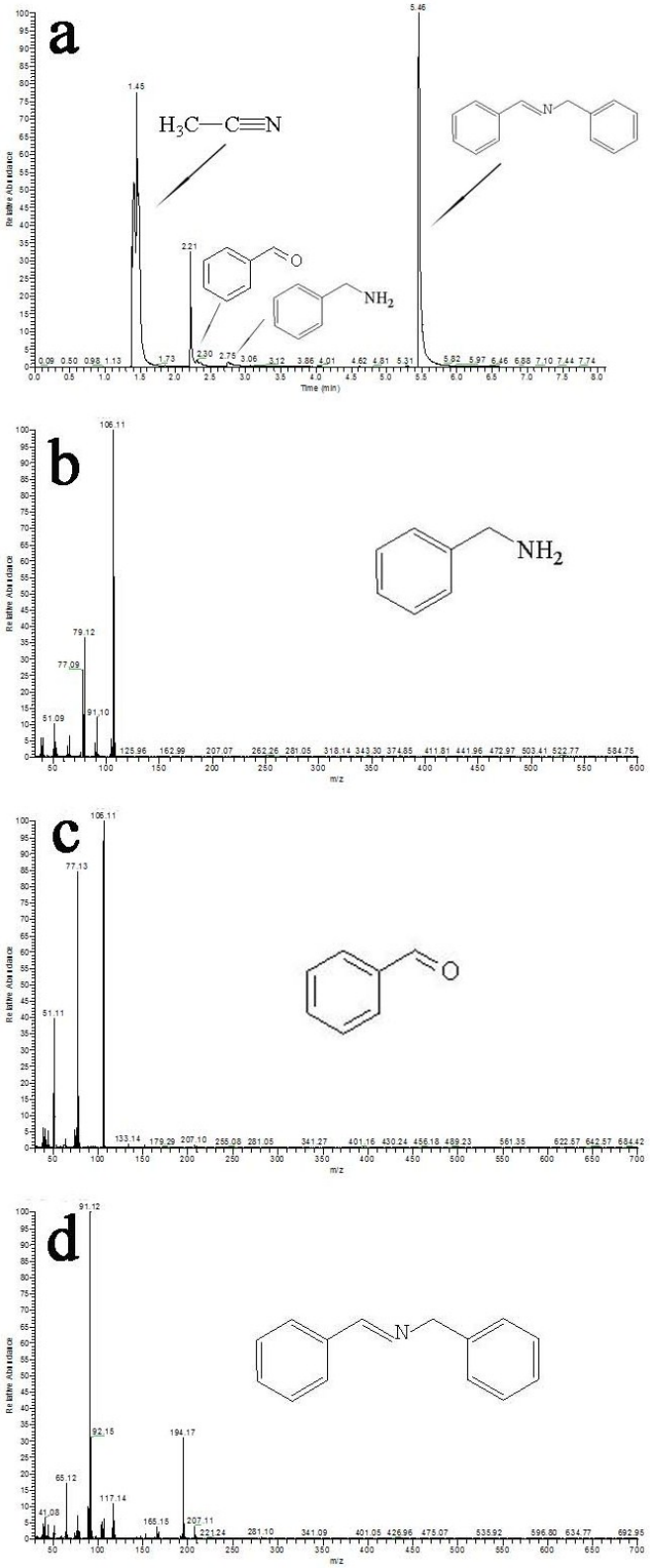


Fig. S9. Photocatalytic oxidation of benzylic amines over H-Cu_2O\Au@CeO_2 under visible light irradiation (5 h) in the presence of O_2 and H-Cu_2O\Au@CeO_2. (a) gas chromatogram of products, mass spectrograms of aldehyde (b), benzylamine (c) and N-benzylidene benzylamine (d).

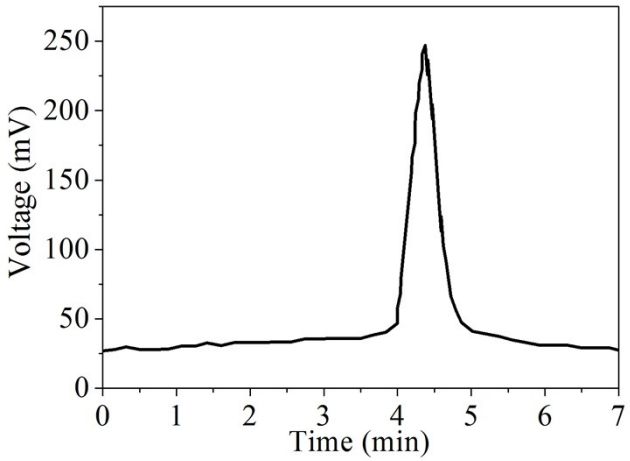


Fig. S10. Chromatogram of NH_4^+.

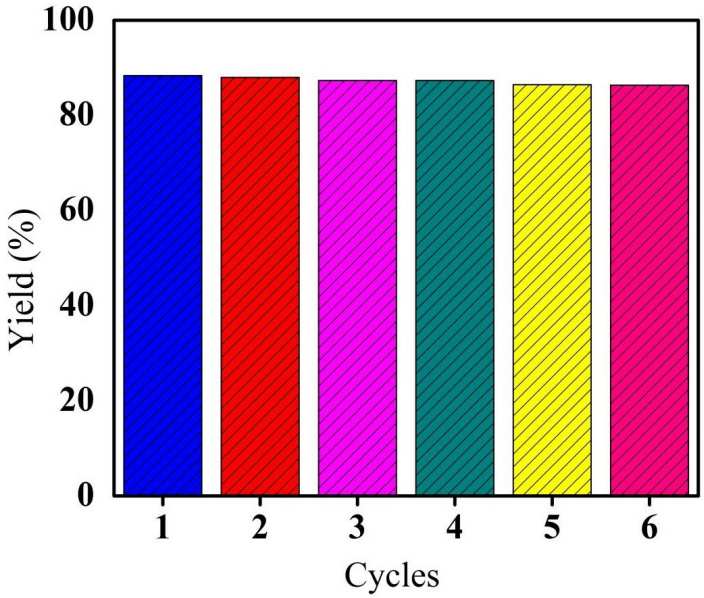


Fig. S11. The photocatalytic cycling stability of the H-Cu_2O\Au@CeO_2 in the photocatalytic oxidation of benzylamine.

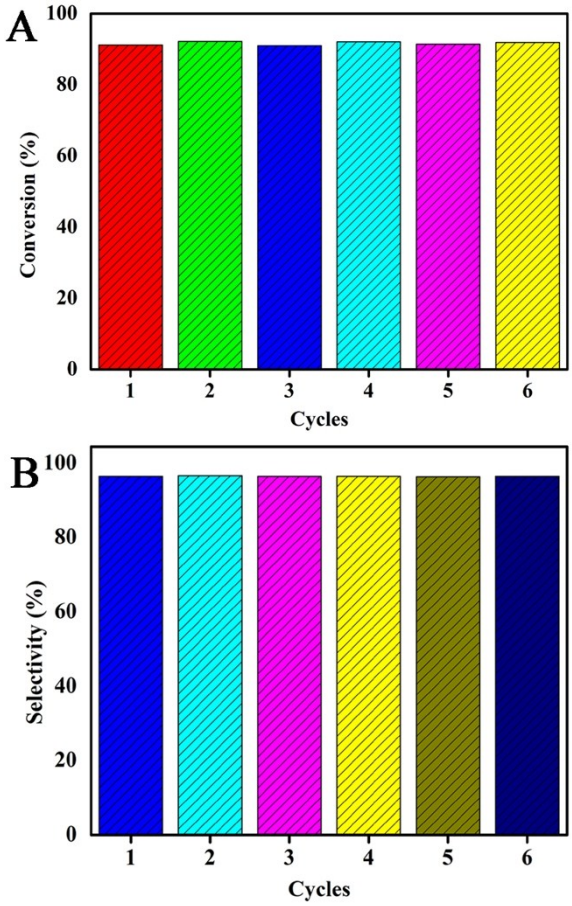


Fig. S12. Conversion and selectivity for the reusability test of the H-Cu_2O/Au@CeO_2.

Table S1 Summary of the photoluminescence decay time (τ) and their relative intensities of the different samples.

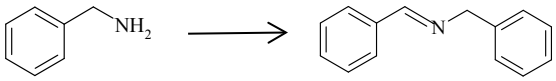
sample	τ_1(ns)	τ_2(ns)	I_1 (%)	I_2 (%)	Average lifetime (τ, ns)
H-Cu_2O\Au@CeO_2	6.93	13.07	36.52	63.48	11.63
Cu_2O@CeO_2\Au	6.05	11.50	38.86	61.14	10.13
Cu_2O\Au@CeO_2	5.75	11.41	35.96	64.04	9.98
Cu_2O@CeO_2	4.50	10.33	37.27	62.73	9.10
CeO_2	4.14	7.96	38.98	61.02	7.01

The average lifetime was calculated using equation: $<\tau>=(I_1\tau_1^2 + I_2\tau_2^2)/(I_1\tau_1 + I_2\tau_2)$

Table S2 Summary of the benzylamine adsorption capacity of the different samples.

sample	adsorption capacity (%)
H-Cu_2O\Au@CeO_2	4.9
Cu_2O@CeO_2\Au	4.3
Cu_2O\Au@CeO_2	4.1
Cu_2O@CeO_2	3.6
CeO_2	3.5

Table S3. The listing of photocatalytic oxidation of benzylamines over the catalysts of correlative references.



Entry	Photocatalyst	Solvent	Conversion (%)	Selectivity (%)	Reaction time (h)	Temperature (^oC)	Ref.
1	[Au_{25}]/TiO_2	CH_3CN	98	99	1.5	30	1
2	Au-Pd/ZrO_2	CH_3CN	99	96	96	45	2
3	Cu/graphene	C_2H_5O H	99	93	6	40	3
4	mpg-C_3N_4	CH_3CN	99	99	3.5	80	4
5	Nb_2O_5	C_6H_6	99	97	50	RT	5
6	TiO_2	CH_3CN	99	85	9	--	6
7	TiO_2 (Degussa P25)	H_2O	81	63	9	RT	7
8	H-Cu_2O\Au@CeO_2	H_2O	91	97	5	20	This work

"--" : Not given

References:

1 H. J. Chen, C. Liu, M. Wang, C. F. Zhang, N. C. Luo, Y. H. Wang, H. Abroshan, G. Li and F. Wang, *ACS Catal.*, 2017, **7**, 3632–3638.

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3 Z.-Y. Zhai, X.-N. Guo, G.-Q. Jin and X.-Y. Guo, *Catal. Sci. Technol.*, 2015, **5**, 4202−4207.

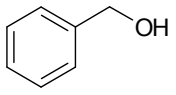
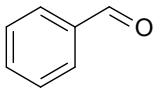
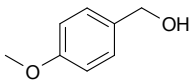
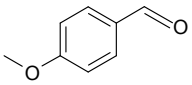
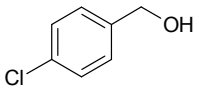
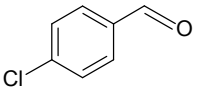
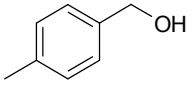
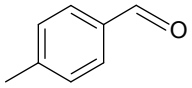
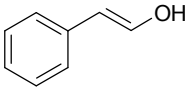
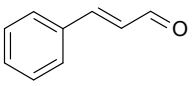
4 F. Z. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. C. Wang and S. Blechert, *Angew. Chem. Int. Ed.*, 2011, **50**, 657−660.

5 S. Furukawa, Y. Ohno, T. Shishido, K. Teramura and T. Tanaka, *ACS Catal.*, 2011, **1**, 1150–1153.

6 X. J. Lang, H. W. Ji, C. C. Chen, W. H. Ma and J. C. Zhao, *Angew. Chem. Int. Ed.*, 2011, **50**, 3934−3937.

7 N. Li, X. J. Lang, W. H. Ma, H. W. Ji, C. C. Chen and J. C. Zhao, *Chem. Commun.*, 2013, **49**, 5034-5036.

Table S4. The listing of photocatalytic oxidation of aromatic alcohols over H-Cu_2O\Au@CeO_2 under visible light irradiation. Reaction conditions: 15 mg H-Cu_2O\Au@CeO_2, 15 uL of substrates, 1.5 mL toluene, O_2, irradiation time is 5h.

Entry	Substrate	Product	Yield (%)	Selectivity(%)
1			74.4	99.9
2			78.7	99.9
3			61.1	78.6
4			77.9	99.9
5			80.9	99.9

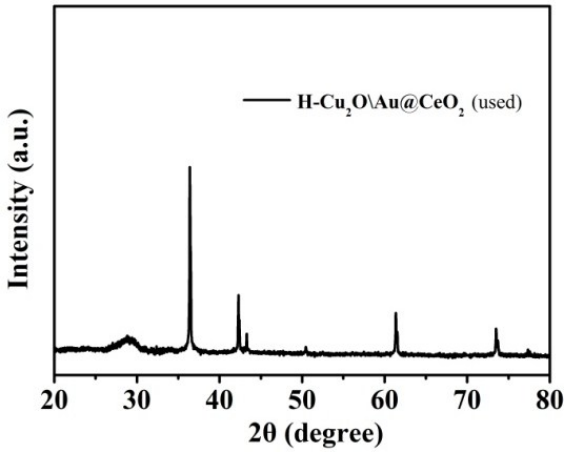


Fig. S13. The XRD patterns of H-Cu_2O\Au@CeO_2 after test**.**

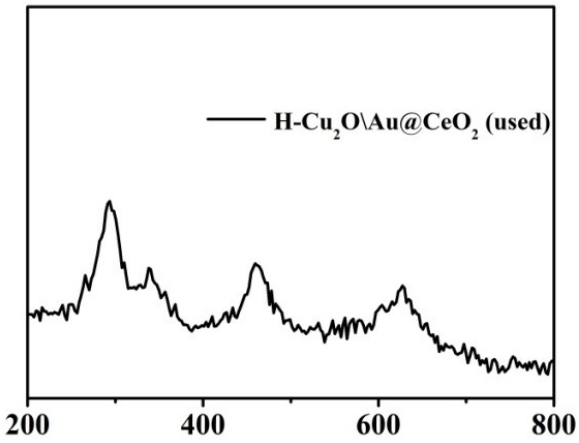


Fig. S14. The Raman spectrum of H-Cu_2O\Au@CeO_2 after test.

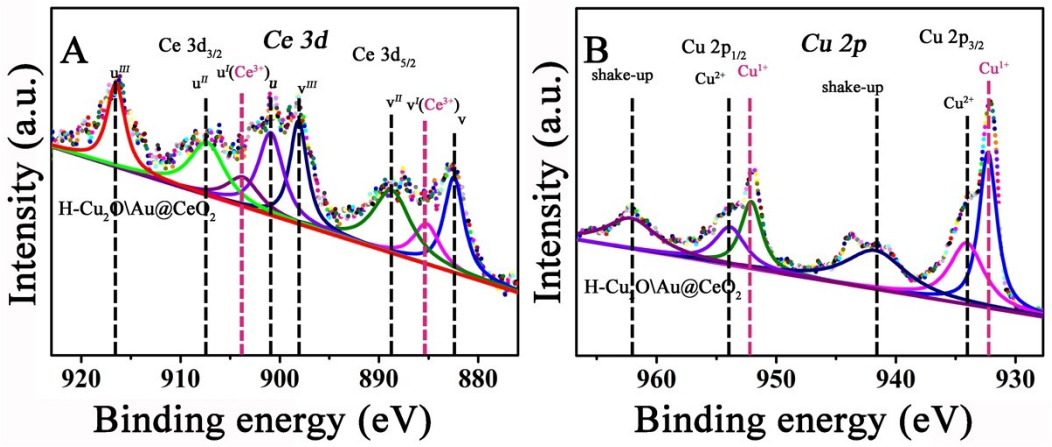


Fig. S15. XPS spectra of (A) Ce 3d, (B) Cu 2p of H-Cu_2O\Au@CeO_2 after test.

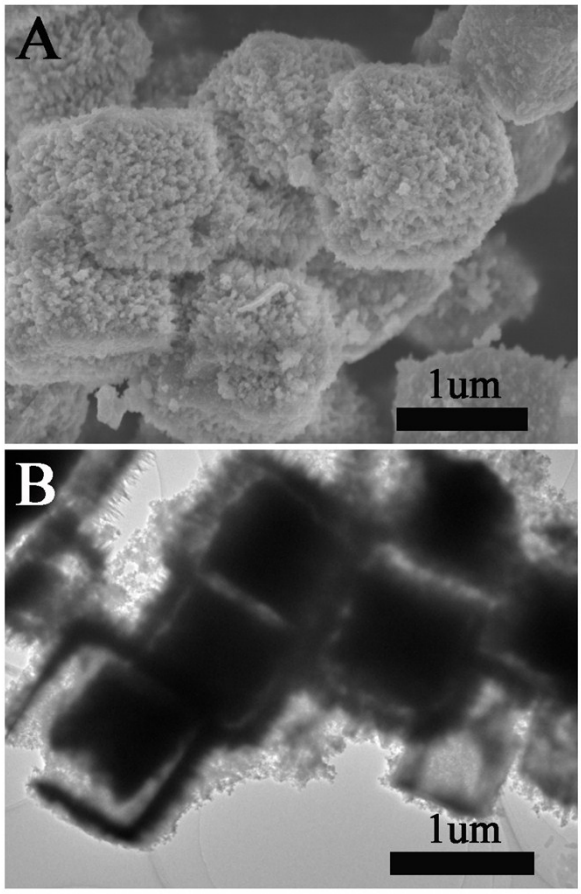


Fig. S16. The SEM (A) and TEM (B) images of H-Cu_2O\Au@CeO_2 after test.