Supporting Information

Photothermal conversion enhances selective hydrogenation over MOF-derived Cu-MoO$_2$ interfaces at ambient condition

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Experimental section

Materials and reagents

L-Glutamic acid (L-Glu, Aladdin, 99.5%), copper (II) acetate monohydrate ($Cu(OAc)_2·H_2O$, Aladdin, AR, 99%), 1,3,5-benzenetricarboxylic acid (H_3BTC, Aladdin, 98%), phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}$, Adamas, 98%), phosphotungstic acid hydrate ($H_3PW_{12}O_{40}$, Adamas, 99%), hydrochloric acid (HCl, Nanchang Xinguang Chemical Works, 36-38 wt%), 4-nitrostyrene (4-NS, Adamas, 98%), gold chloride hydrate ($HAuCl_4·H_2O$, J&K Chemical, Au: 49–51%), and silver nitrate ($Ag(NO_3)_3$, Aladdin, AR, 99.8%) was purchased and used without any further treatment.

Ammonia borane (AB, Innochem, 97%) requires further purification before use. AB (2.5 g) was placed into a round-bottom flask, followed by adding 300 mL anhydrous diethyl ether ($C_2H_5OC_2H_5$, AR) to dissolve, and then ultrasonicated for 1 hour. The solution was filtered, and the filtrate was subjected to rotary evaporation to yield white solid. Finally, the solid was dried overnight in a vacuum oven to obtain purified AB.

Characterization of catalysts

Scanning electron microscopy (SEM, Hitachi Limited S-3400N), and transmission electron microscopy (TEM, JEM-2100) were used to determine the morphology, microstructure, size, and composition of the samples. The crystalline shape of the catalysts was characterized using a Rigakurt-2000 X-ray diffractometer with Cu Ka as the radiation source. The X-ray photoelectron spectroscopy (XPS) for the analysis of the electronic valence of metal particles on the catalyst surface was performed on a Thermo Fisher Scientific 250xi X-ray photoelectron spectrometer, which operates with an Al Ka radiation source. The products of reaction were detected and analyzed by gas chromatography (GC, Fuli 9790II). Inductively coupled plasma-optical emission spectrometry (ICP-OES) was recorded on Agilent 730. Brunauer–Emmett–Teller (BET) surface area and pore-size measurements were performed on a Micromeritics ASAP 2020M instrument at 77 K. UV-visible (UV-vis) spectra of the samples were

analyzed using a Shanghai Lengguang 725s spectrometer. A photocatalytic equipment bought from Zhongjiao Jinyuan Technology Company of Beijing was used as the visible light source to trigger the catalytic reaction.

Preparation of catalysts.

Synthesis of MoO$_2$@C. The copper particles were removed by dispersing the annealed sample in 1.0 M HCl and kept stirring for 2 hours. The resulting MoO$_2$@C was collected by centrifugation repeatedly with deionized water until the pH value of the centrifuged solution reached 7, and finally dried under vacuum at 40 °C overnight.

Synthesis of Cu-BTC, Cu@C. In a typical synthesis, Cu(OAc)$_2$·H$_2$O (1 mmol, 0.2 g) was dissolved in 40 mL deionized water. After stirring for 1 hour under ambient conditions, a 40 mL ethanol solution containing H$_3$BTC (0.67 mmol, 0.14 g) was added to the above solution under vigorous stirring. After stirring for 14 hours, the resulting blue precipitates were collected by centrifugation, washed twice with deionized water and ethanol, respectively, and dried under vacuum at 40 °C overnight to obtain Cu-BTC. The as-prepared Cu-BTC was placed in a tubular furnace, which was heated to 800 °C at a ramp rate of 5 °C min^{-1} and kept for 180 min under Ar atmosphere to yield Cu@C.

Synthesis of Ag-MoO$_2$@C. First, 20 mg Cu-MoO$_2$@C was added into 5 mL of AgNO$_3$ (0.1 mmol) aqueous solution and stirred for 1 hour under dark conditions. Then the above solution was collected by centrifugation, washed three times with water, and dried under vacuum at 40 °C overnight.

Synthesis of Au-MoO$_2$@C. First, 20mg Cu-MoO$_2$@C was added into 5 mL of HAuCl$_4$ (0.05 mmol) aqueous solution and stirred for 15 min. Then the above solution was collected by centrifugation, washed three times with water, and dried under vacuum at 40 °C overnight.
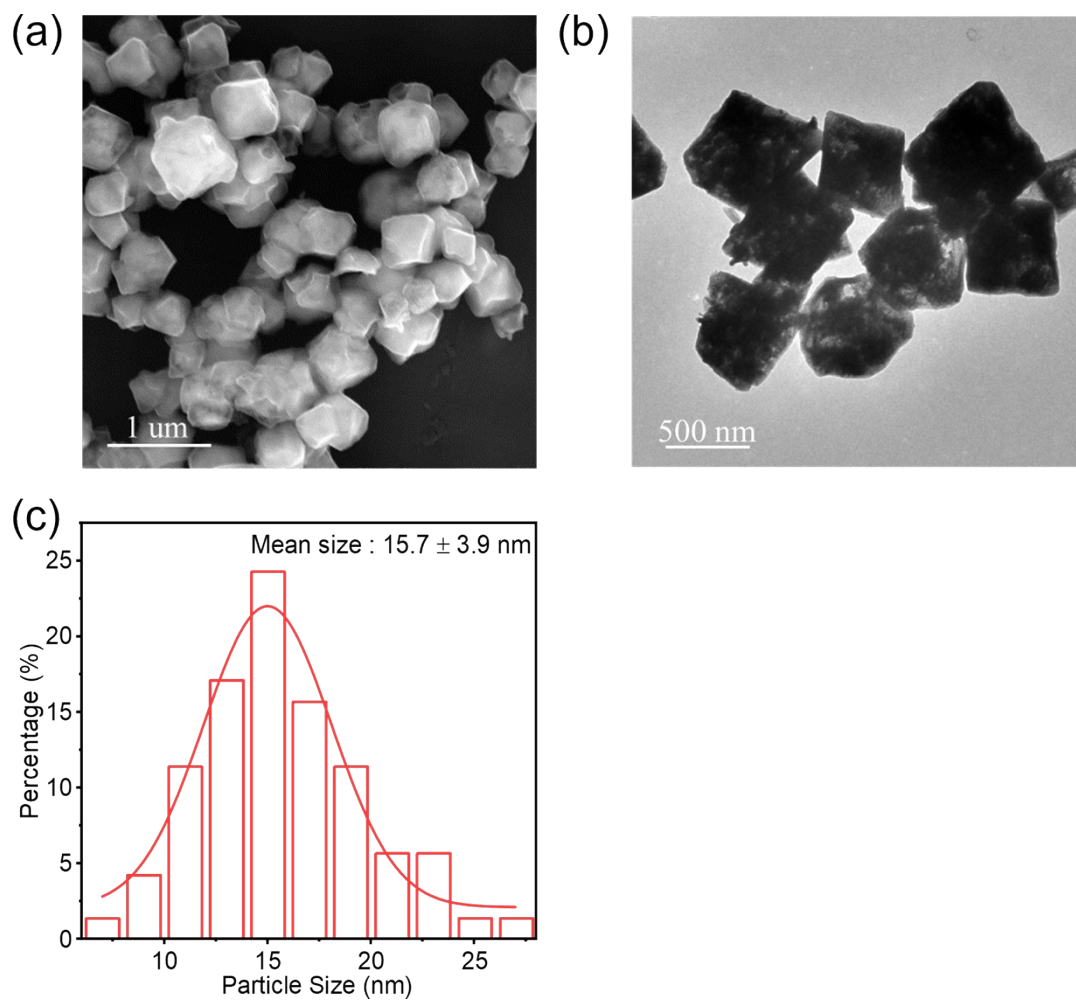
Synthesis of Cu-WO$_3$@C. The conditions and steps are the same as the synthesis of Cu-MoO$_2$@C, except that H$_3$PMo$_{12}$O$_{40}$ was replaced with H$_3$PW$_{12}$O$_{40}$.
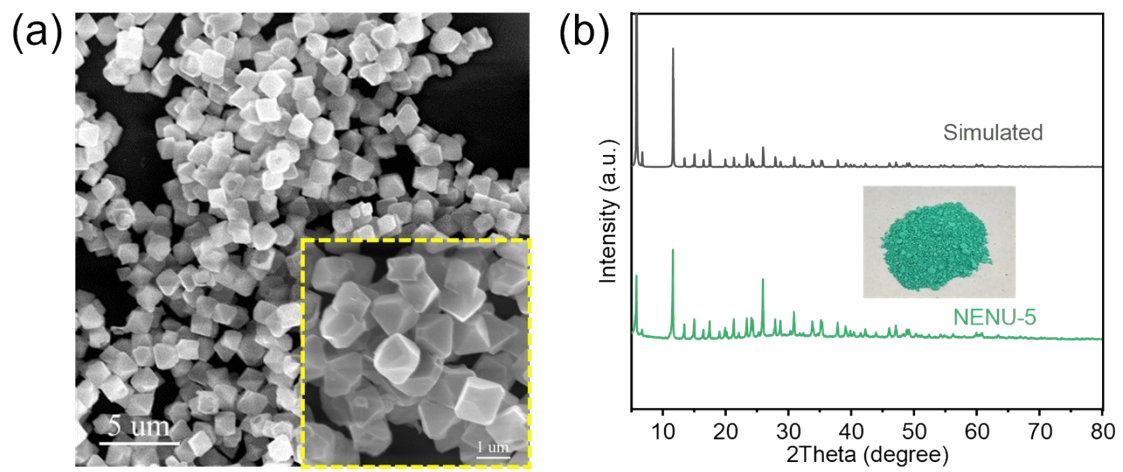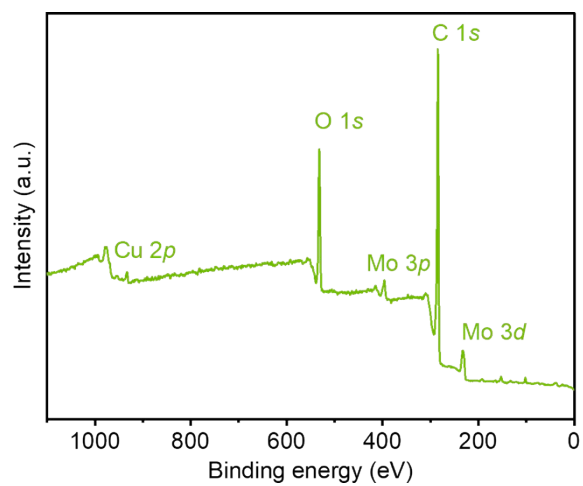
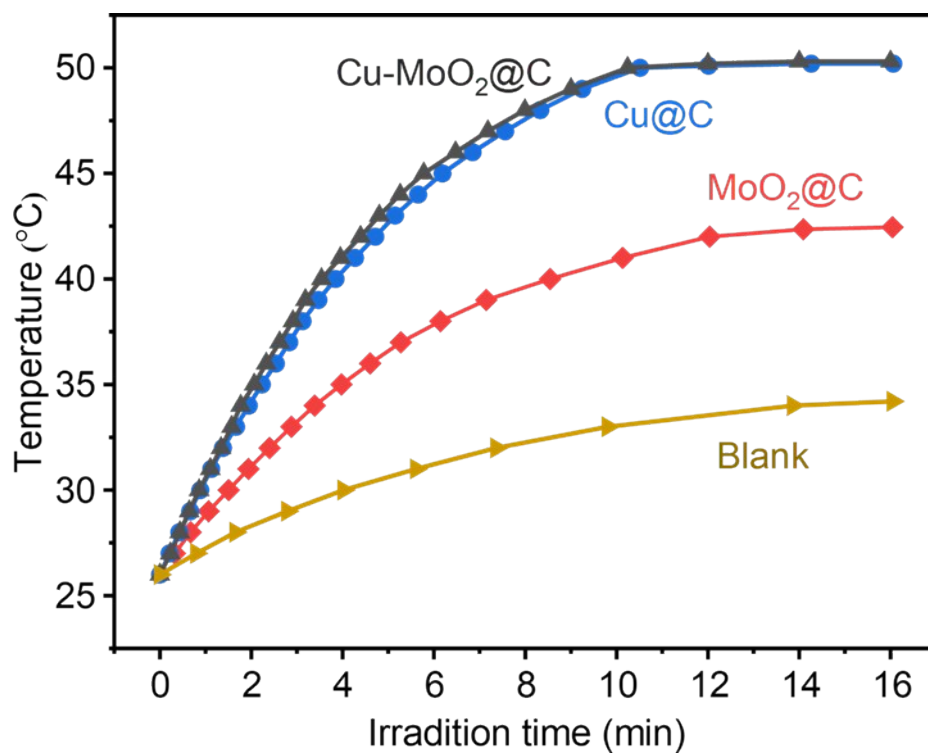**Fig. S1** (a) SEM images, and (b) XRD pattern (photograph) of NENU-5.
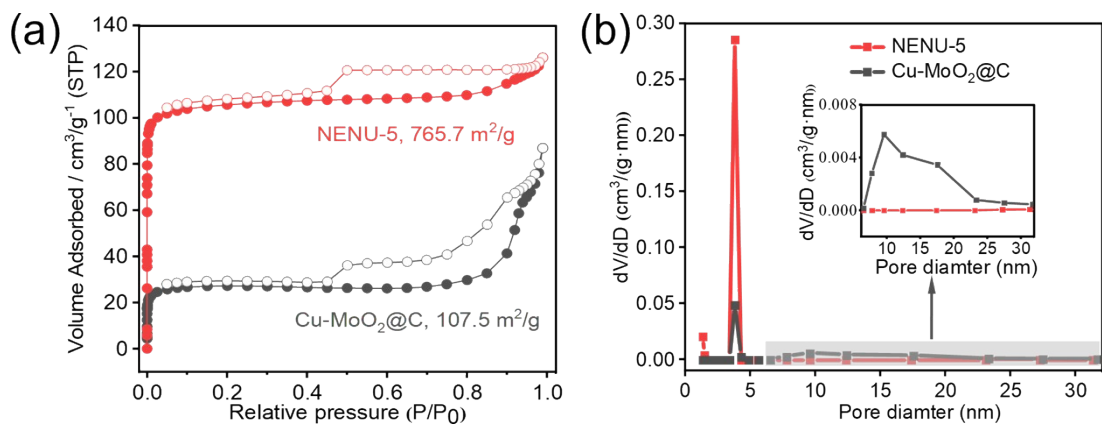
Fig. S2 (a) N$_2$ adsorption-desorption isotherms, and (b) corresponding pore-size distributions of NENU-5 and Cu-MoO$_2$@C.

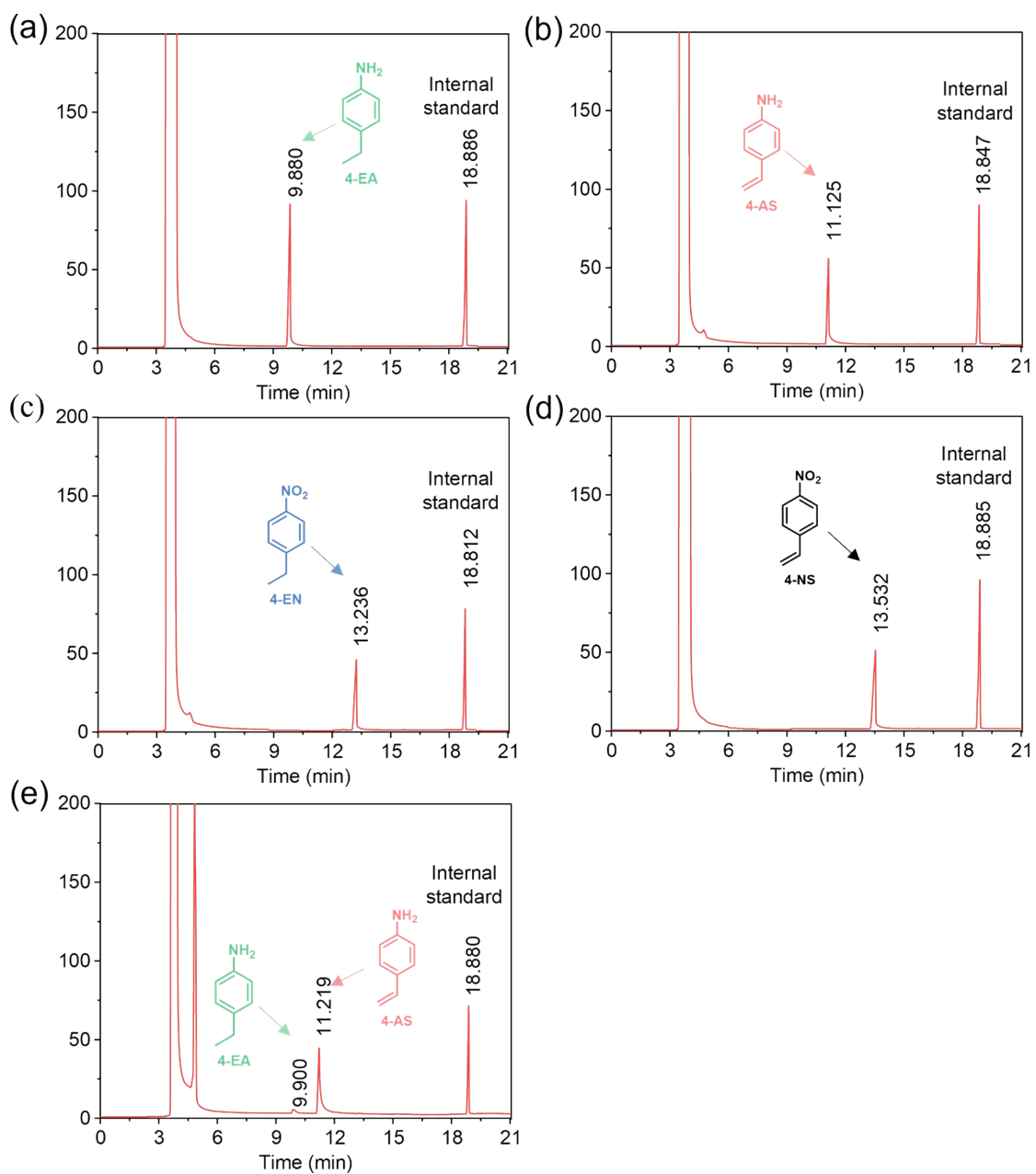**Fig. S3** (a) SEM image, (b) TEM image, and (c) particle size distribution of Cu-MoO$_2$@C.

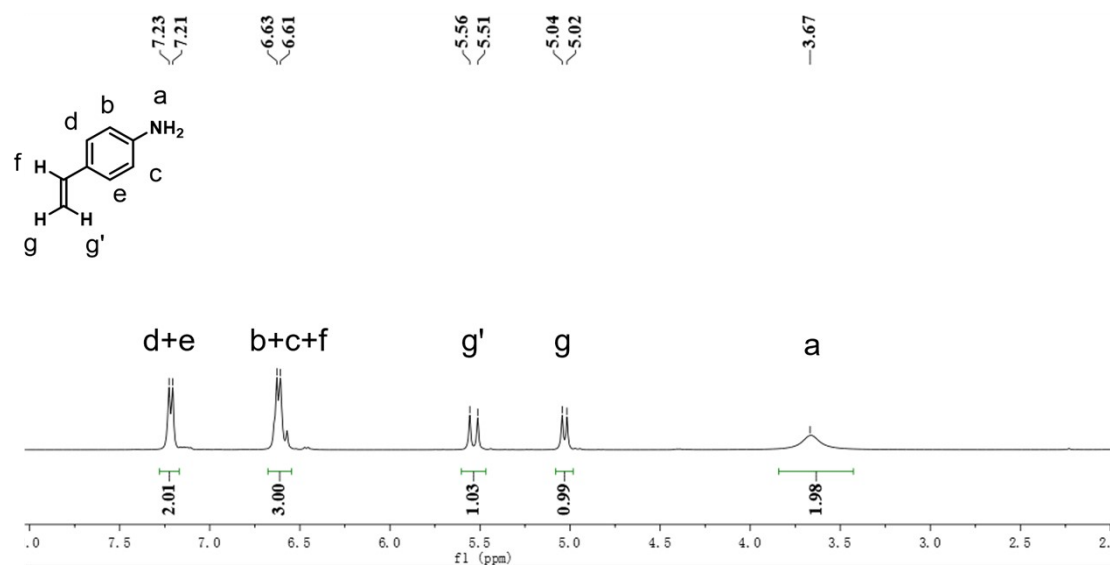**Fig. S4** XPS survey spectra of Cu-MoO$_2$@C.

Fig. S5 Temperature variation of the solution along with the light irradiation in the blank or in the presence of MoO_2@C, Cu@C, and Cu-MoO_2@C.
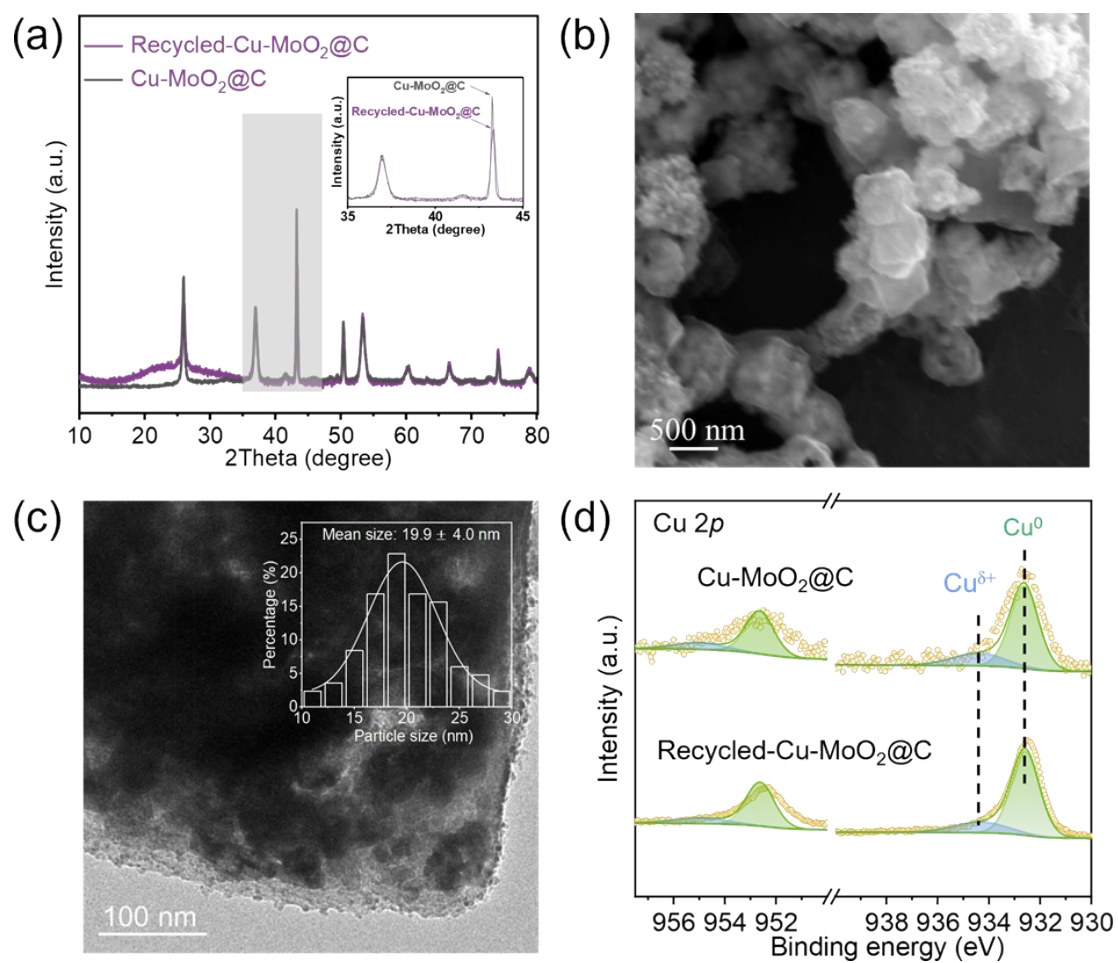
Fig. S6 The GC spectrum of (a) 4-ethylaniline, (b) 4-aminostyrene, (c) 4-ethylnitrobenzene, (d) 4-nitrostyrene, and (e) the production after reaction. Hexadecane as an internal standard.
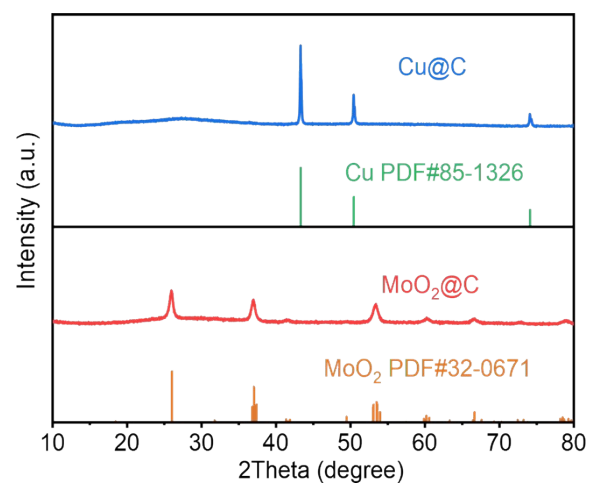
^{1}H NMR (400 MHz, Chloroform-d) δ 7.22 (d, J = 8.0 Hz, 2H), 6.62 (d, J = 8.0 Hz, 3H), 5.53 (d, 1H), 5.03 (d, J = 8.0 Hz, 1H), 3.67 (s, 2H).
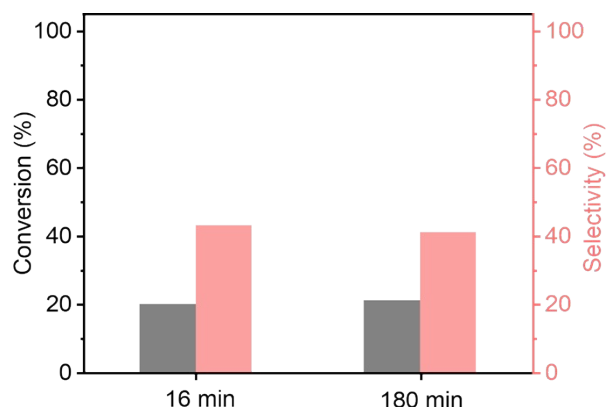
Fig. S7 ^{1}H Nuclear Magnetic Resonance (NMR) spectra of the product in CDCl$_3$.

Fig. S8 (a) Powder XRD pattern, (b) SEM image, (c) TEM image (inset: particle size distribution), and (d) XPS spectra of Cu $2p$ in Cu-MoO$_2$@C after cycling test.

Fig. S9 XRD pattern of MoO_2@C and Cu@C.

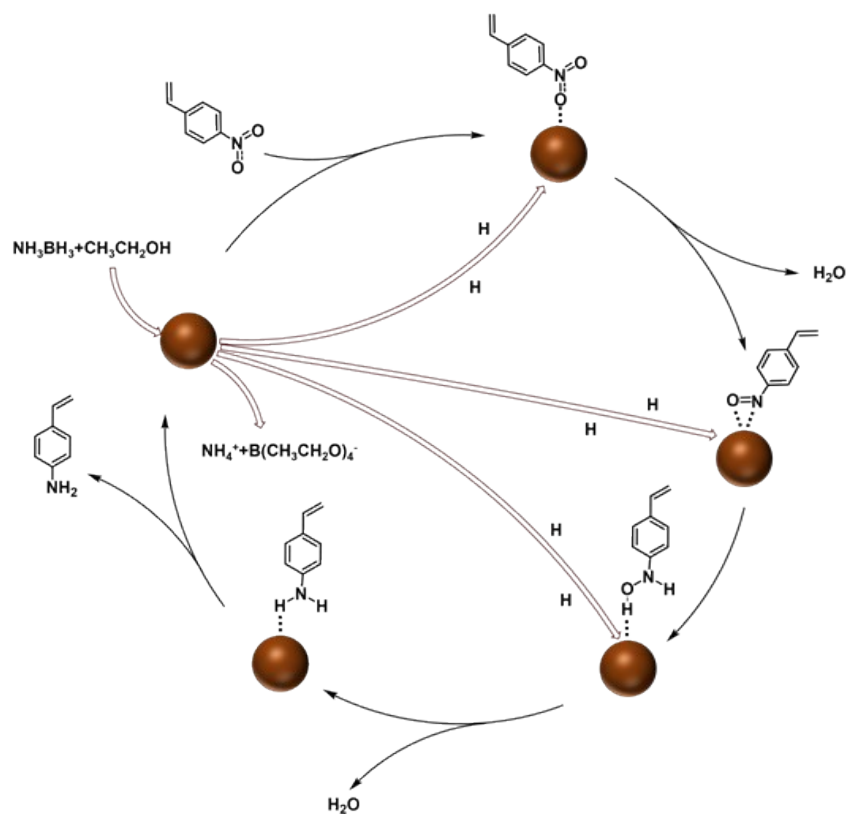**Fig. S10** Catalytic performance of 4-NS selective hydrogenation without catalyst under light irradiation.

Fig. S11 Proposed mechanism of 4-NS hydrogenation over Cu-MoO$_2$@C under light irradiation.
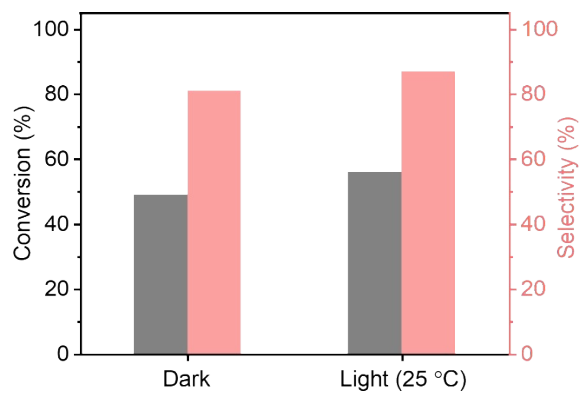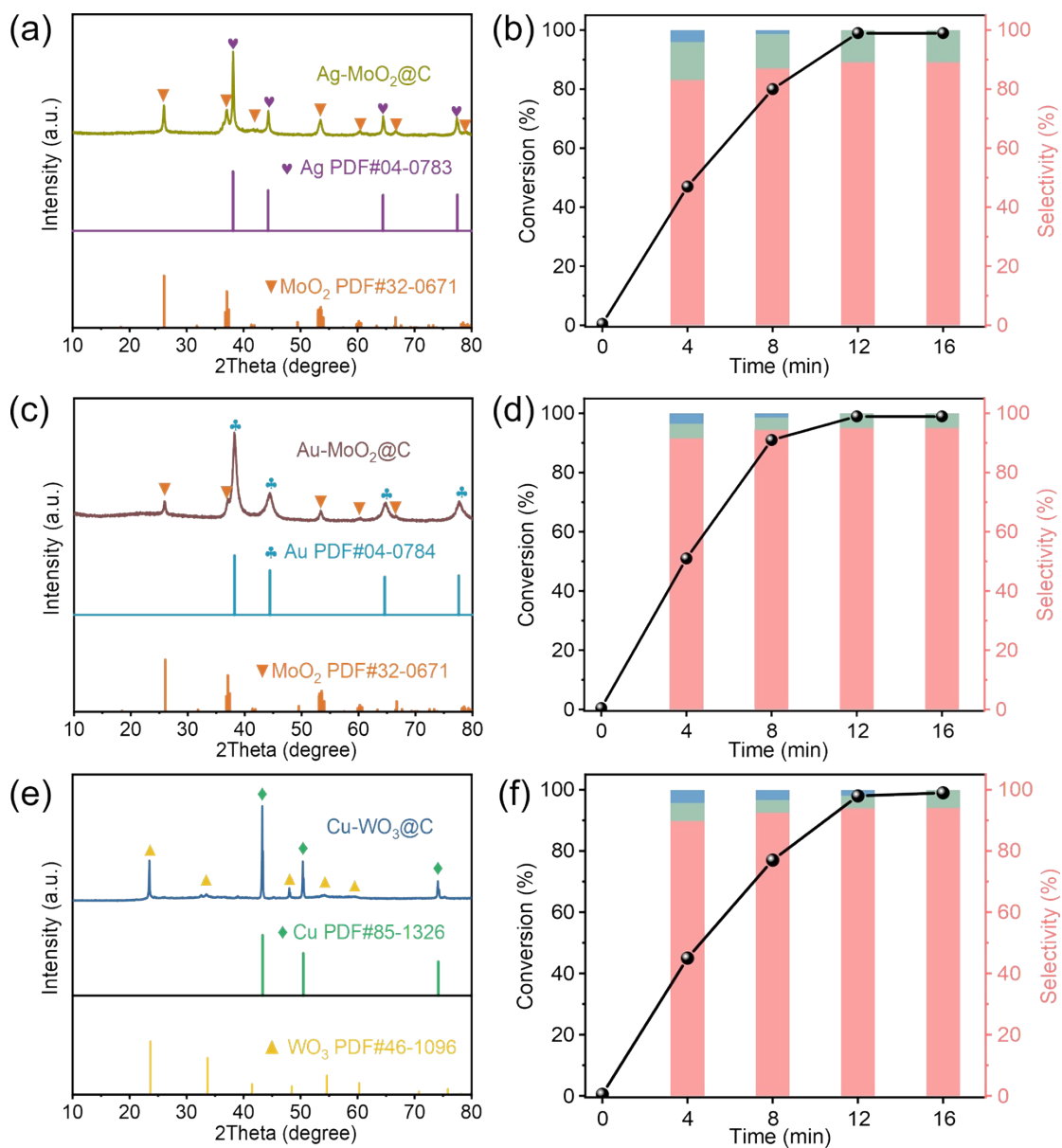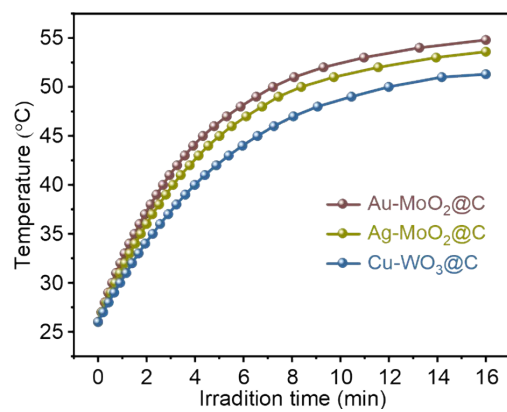
Fig. S12 The catalytic performance of Cu-MoO$_2$@C at dark condition and under irradiation at a controlled temperature of 25 °C.

Fig. S13 XRD pattern of (a) Ag-MoO$_2$@C, (c) Au-MoO$_2$@C, and (e) Cu-WO$_3$@C. Catalytic performance of 4-NS selective hydrogenation over (b) Ag-MoO$_2$@C, (d) Au-MoO$_2$@C, and (f) Cu-WO$_3$@C under light irradiation.

Fig. S14 Temperature variation of the solution along with the light irradiation over Ag-MoO$_2$@C, Au-MoO$_2$@C, and Cu-WO$_3$@C.

Table S1 Elemental analysis results of Cu-MoO$_2$@C.

Catalyst	Actual loading (wt%)	
	Cu	Mo
Cu-MoO$_2$@C	35	30

**Table S2** Comparison of the catalytic performance of nitrostyrene hydrogenation with other literatures.

Entry	Catalyst	Substrate	Reaction conditions	TOF (h^{-1})	Ref.
1	Cu-MoO$_2$@C	4-NS	AB, 25 °C, 16 min	22.3	This
		3-NS		21.4	work
2	Co@NC	4-NS	N$_2$H$_4$·H$_2$O, 80 °C, 1.5 h	10.1	S1
3	Ni$_{0.75}$Fe$_{0.25}$/SiO$_2$	4-NS	1 bar H$_2$, 70 °C, 3 h	10.8	S2
4	Cu NPs/CN	4-NS	20 bar H$_2$, 100 °C, 8 h	13.0	S3
5	Co$_4$Zn$_2$@CN	3-NS	1 MPa H$_2$, 80 °C, 1.5 h	18.2	S4
6	Co-100-NAC	3-NS	2 MPa H$_2$, 80 °C, 5 h	19.7	S5
7	Co@NC-800	3-NS	3 MPa H$_2$, 80 °C, 4 h	14.8	S6

Table S3 The hydrogenation of 4-nitrostyrene over Cu-MoO$_2$@C with H$_2$ as the hydrogen source.
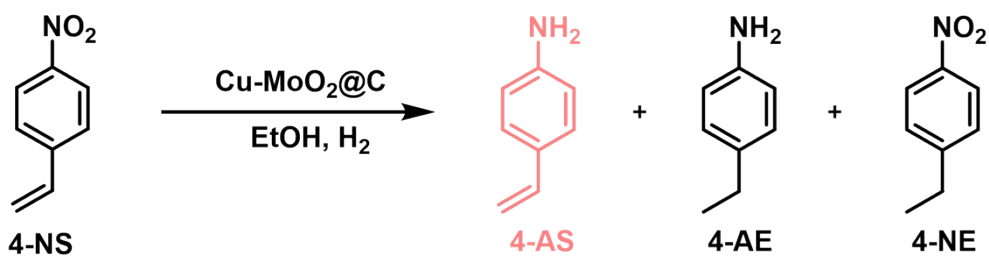
Entry	Hydrogen source	Conversion (%)	Yield (%)
1[a]	H$_2$	<1	0
2[b]	H$_2$	<1	trace

[a] Reaction conditions: 4-nitrostyrene (0.1 mmol), Cu-MoO$_2$@C (5 mg) in EtOH under H$_2$ atmosphere and 300 W Xe lamp irradiation for 16 min. [b] 2 h.
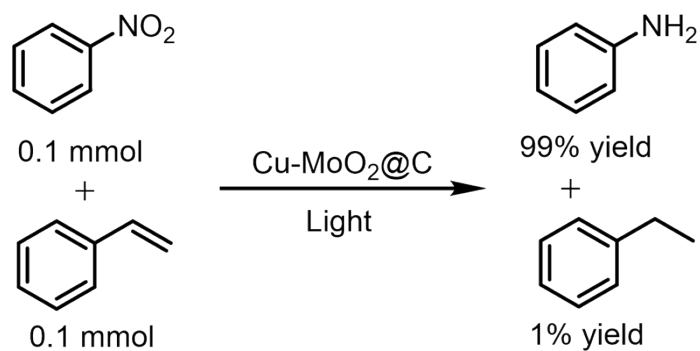
Scheme S1 Catalytic performance towards to the hydrogenation of styrene and nitrobenzene over Cu-MoO$_2$@C. Reaction conditions: nitrobenzene (0.1 mmol), styrene (0.1 mmol), Cu-MoO$_2$@C (5 mg) with NH$_3$BH$_3$ (15 mg) in EtOH (3 mL) under N$_2$ atmosphere and 300 W Xe lamp irradiation.

References

S1　S. Chen, L. L. Ling, S. F. Jiang and H. Jiang, Selective hydrogenation of nitroarenes under mild conditions by the optimization of active sites in a well defined Co@NC catalyst, *Green Chem.*, 2020, **22**, 5730-5741.

S2　M. Miyazaki, K. Ariyama, S. Furukawa, T. Takayama and T. Komatsu, Chemoselective hydrogenation of nitroarenes using Ni-Fe alloy catalysts at ambient pressure, *Chemistryselect*, 2021, **6**, 5538-5544.

S3　H. Liu, X. Li, Z. Ma, M. Sun, M. Li, Z. Zhang, L. Zhang, Z. Tang, Y. Yao, B. Huang and S. Guo, Atomically dispersed Cu catalyst for efficient chemoselective hydrogenation reaction, *Nano Lett.*, 2021, **21**, 10284-10291.

S4　Y. Cao, H. Wen, Q. Guan, H. Li, Q. Zhang and H. Zhang, Engineering the structure of ZIF-derived hierarchically porous CoZn catalysts for efficient selective hydrogenation of nitroarenes, *Ind. Eng. Chem. Res*., 2023, **62**, 13421-1343.

S5　Y. Lin, R. Nie, Y. Li, X. Wu, J. Yu, S. Xie, Y. Shen, S. Mao, Y. Chen, D. Lu, Z. Bao, Q. Yang, Q. Ren, Y. Yang, F. Liu, L. Qi, W. Huang and Z. Zhang, Highly efficient and anti-poisoning single-atom cobalt catalyst for selective hydrogenation of nitroarenes, *Nano Res.*, 2022, **15**, 10006-10013.

S6　H. Wei, H. Song, Y. Ren, X. Yan, G. Fang, W. Wang, W. Ren, M. Zhu and J. Lin, Solvent-free synthesis of Co@NC catalyst with Co-N species as active sites for chemoselective hydrogenation of nitro compounds, *Sci. China Mater*., 2023, **66**, 169-178.