Electronic Supplementary Material (ESI) for Nanoscale.

Atomic-Scale Engineering of MOFs Array Confined Au nanoclusters for Enhanced Heterogeneous Catalysis

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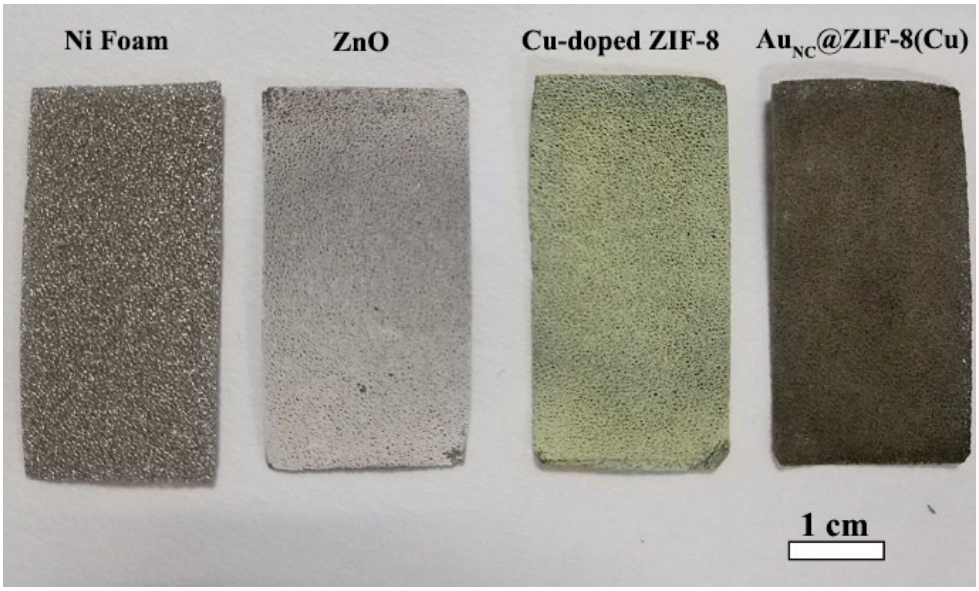

Fig. S1 The sample's photo of NF, ZnO NRs, ZIF-8(Cu) NRAs and Au_{NC}@ ZIF-8(Cu) NRAs.

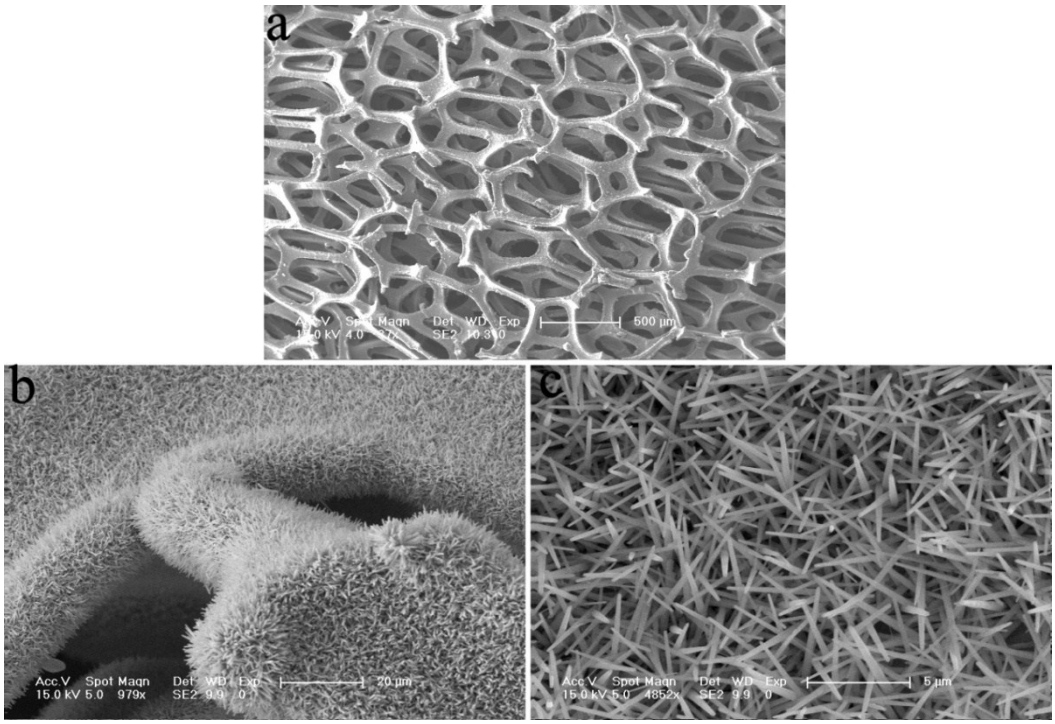

Fig. S2 (a) The SEM image of NF. (b-c) The SEM image of ZnO NRs.

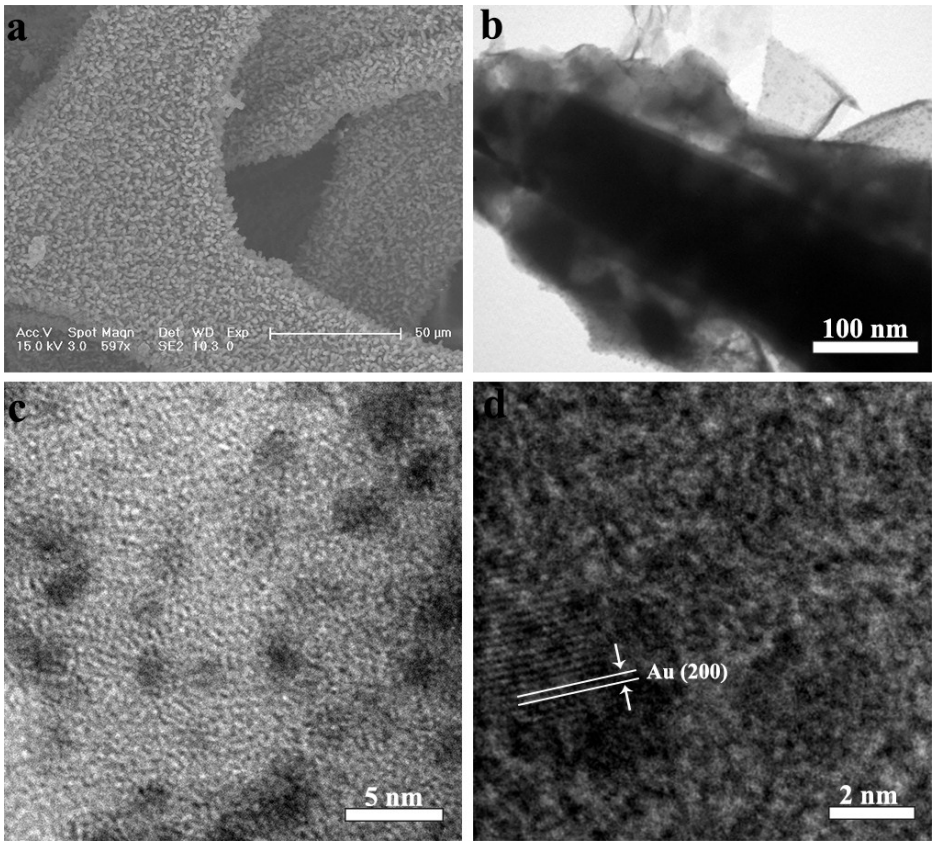

Fig. S3 (a) The SEM image of Au_{NC}@ZIF-8(Cu) NRAs. (b) The TEM image of Au_{NC}@ZIF-8(Cu) NRAs. (c-d) The HRTEM image of Au_{NC}@ZIF-8(Cu) NRAs.

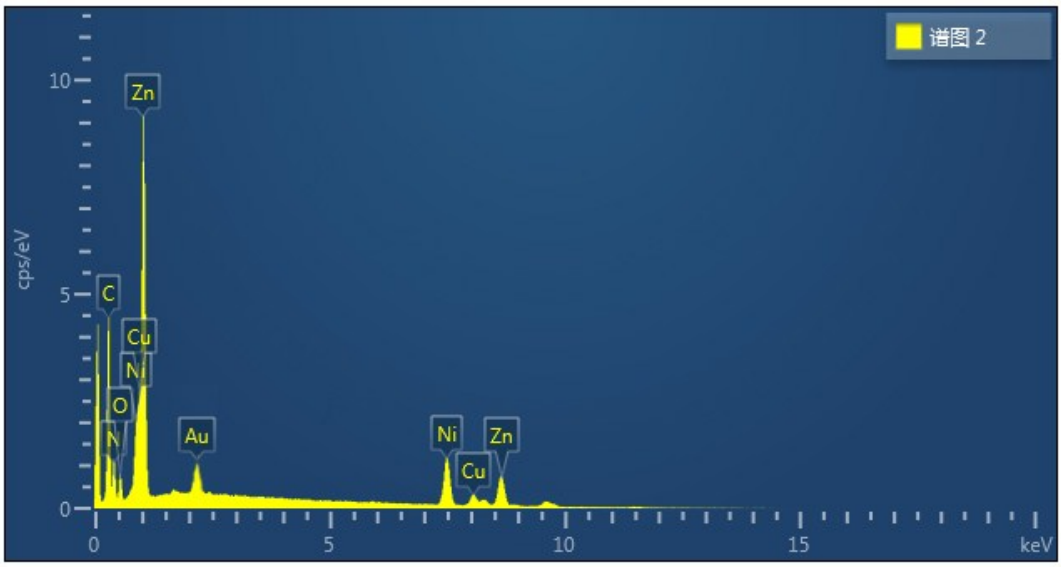

Fig. S4 The EDS spectrum of Au_{NC}@ZIF-8(Cu) NRAs.

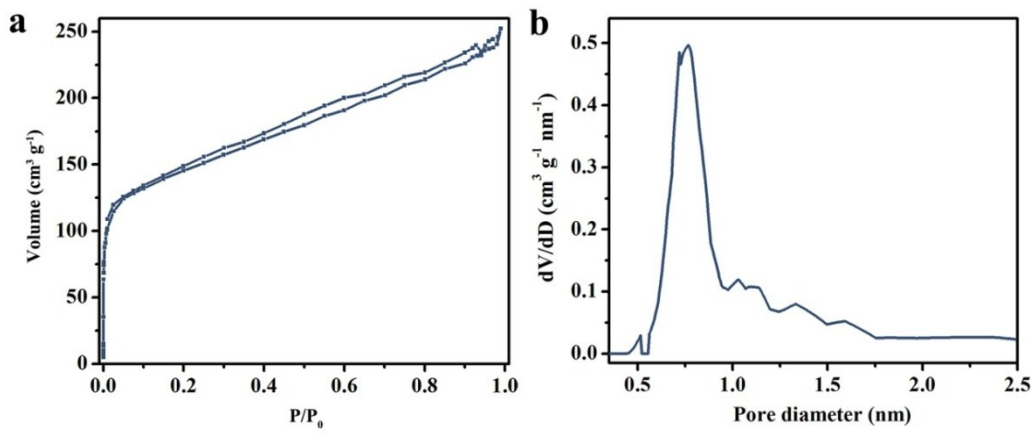

Fig. S5 (a) The N_2 adsorption/desorption isotherms and (b) pore size distribution curve of ZIF-8(Cu) NRAs.

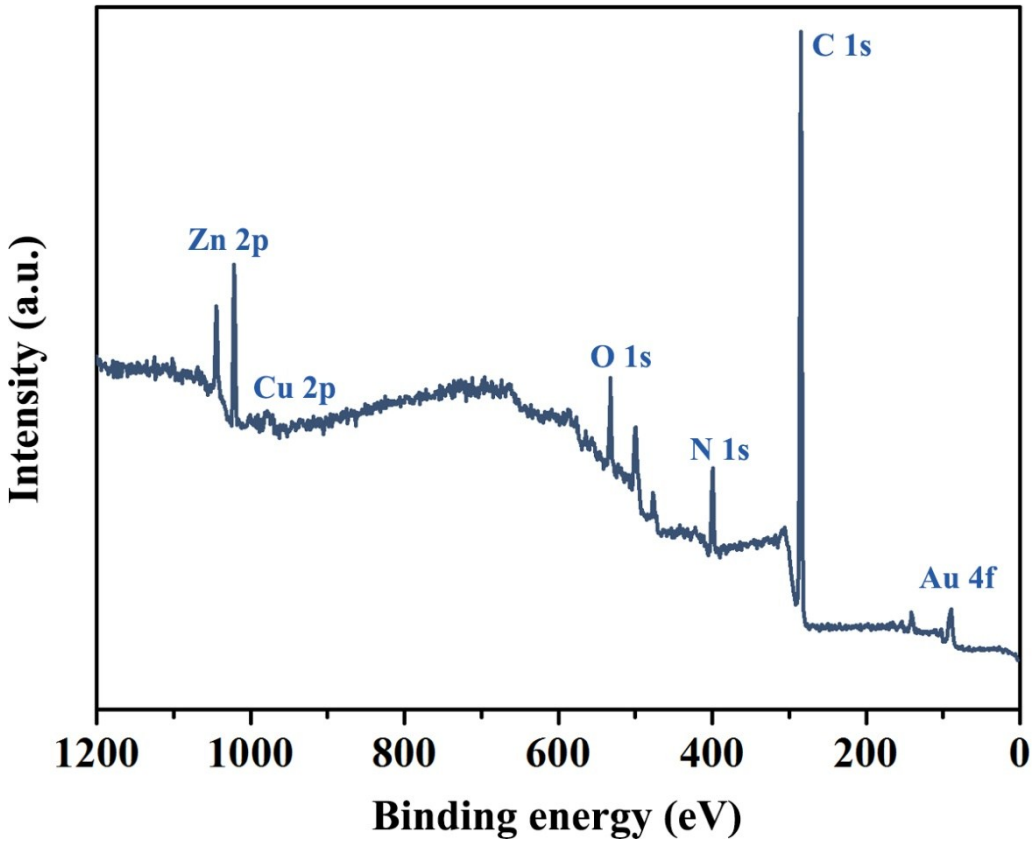

Fig. S6 The survey spectrum of Au_{NC}@ZIF-8(Cu) NRAs.

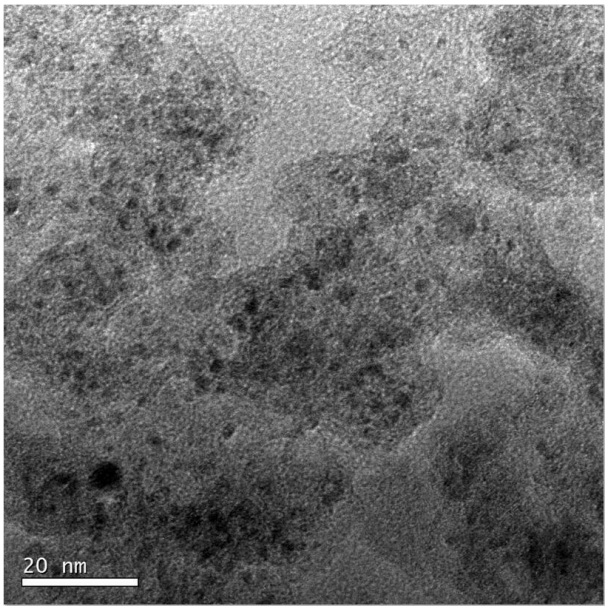

Fig. S7 The TEM image of Au NP.

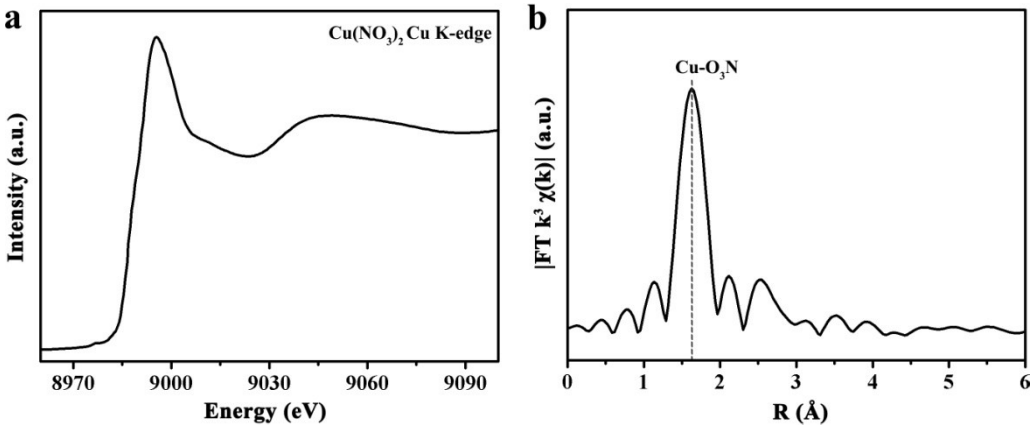

Fig. S8 (a) Normalized XANES spectra at Cu K-edge of $Cu(NO_3)_2$, and (b) the corresponding k^3-weighted Fourier transform spectra.

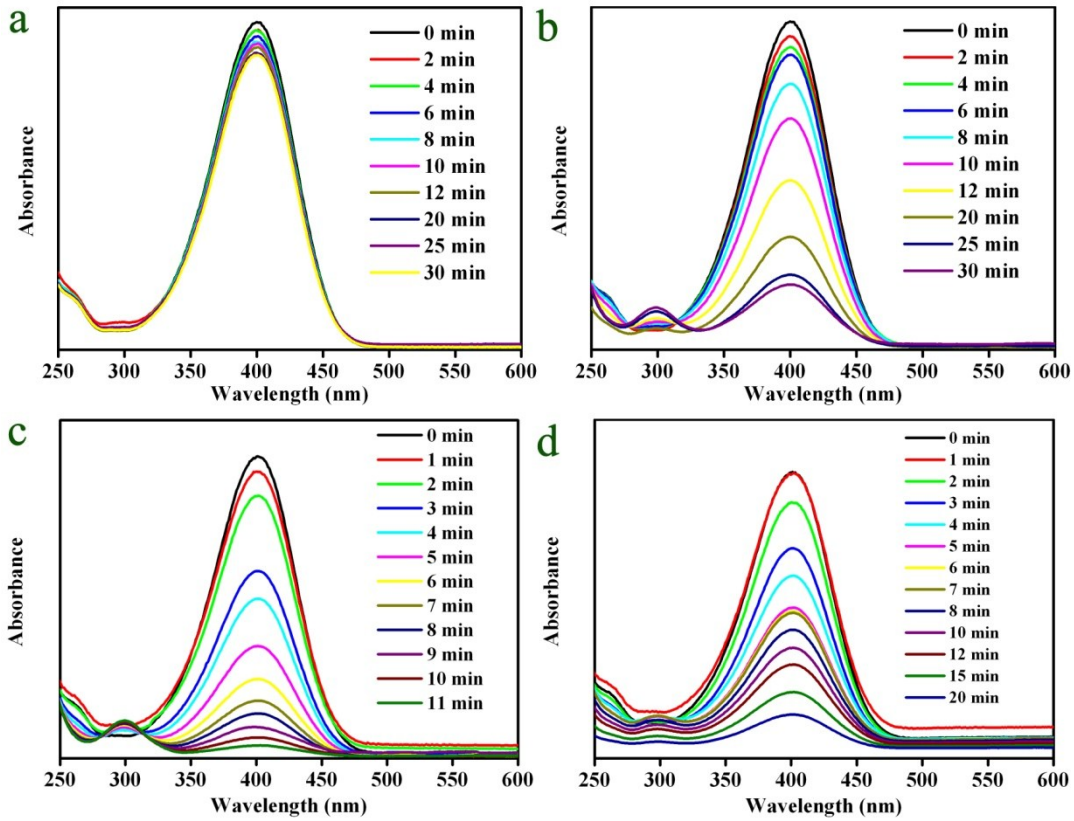

Fig. S9 Absorption spectra of 4-NP over (a) ZnO NRs, (b) ZIF-8(Cu) NRAs, (c) Au_{NC}@ZIF-8 NRAs and (d) Au NP.

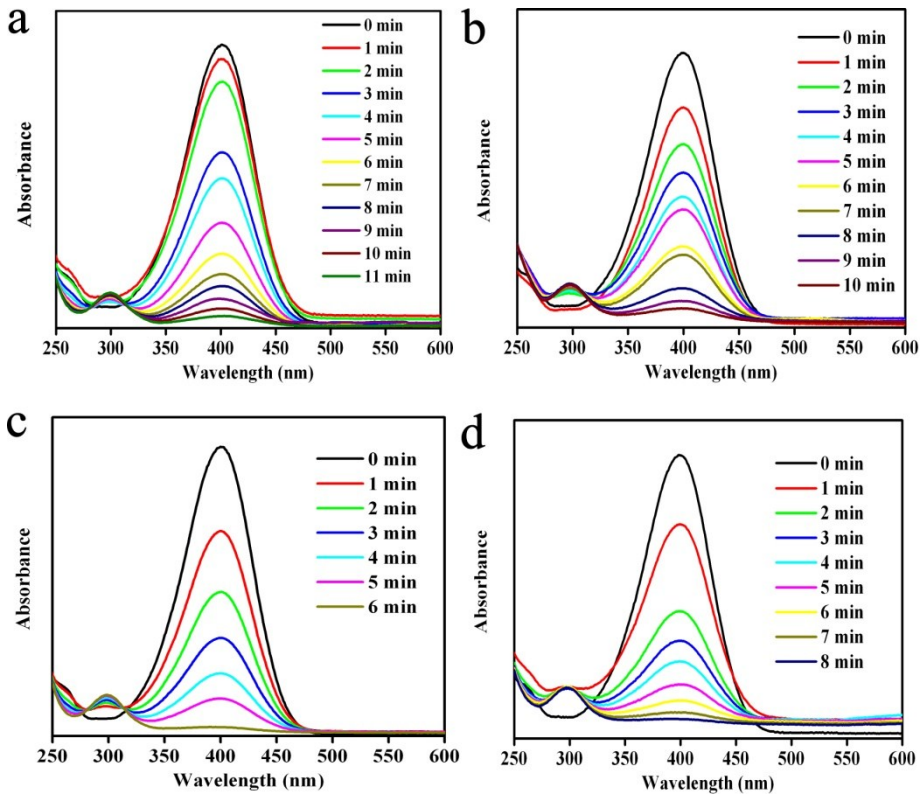

Fig. S10 Absorbance spectra of 4-NP over different Cu content of Au_{NC}@ZIF-8(Cu) NRAs (a) 0 mg, (b) 5 mg, (c) 10 mg and (d) 15 mg.

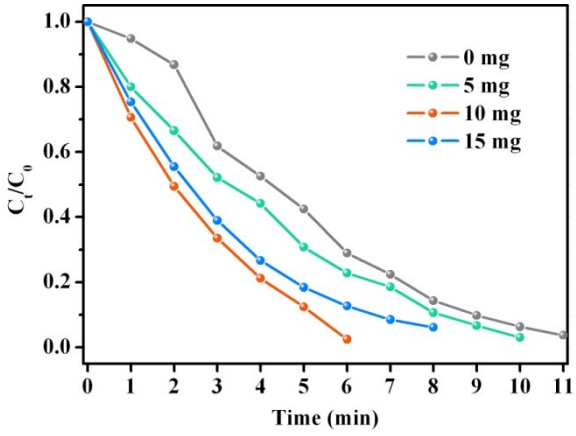

Fig. S11 The catalytic activity of reduction 4-NP over over different Cu content of Au_{NC}@ZIF-8(Cu) NRAs.

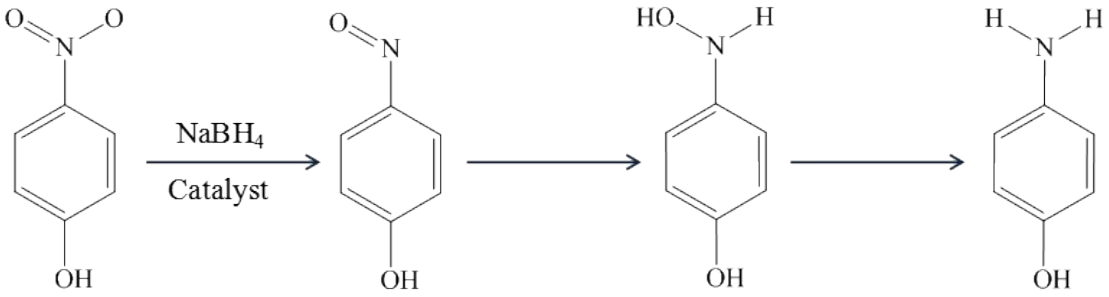

Fig. S12 The reaction scheme of 4-NP reduction.

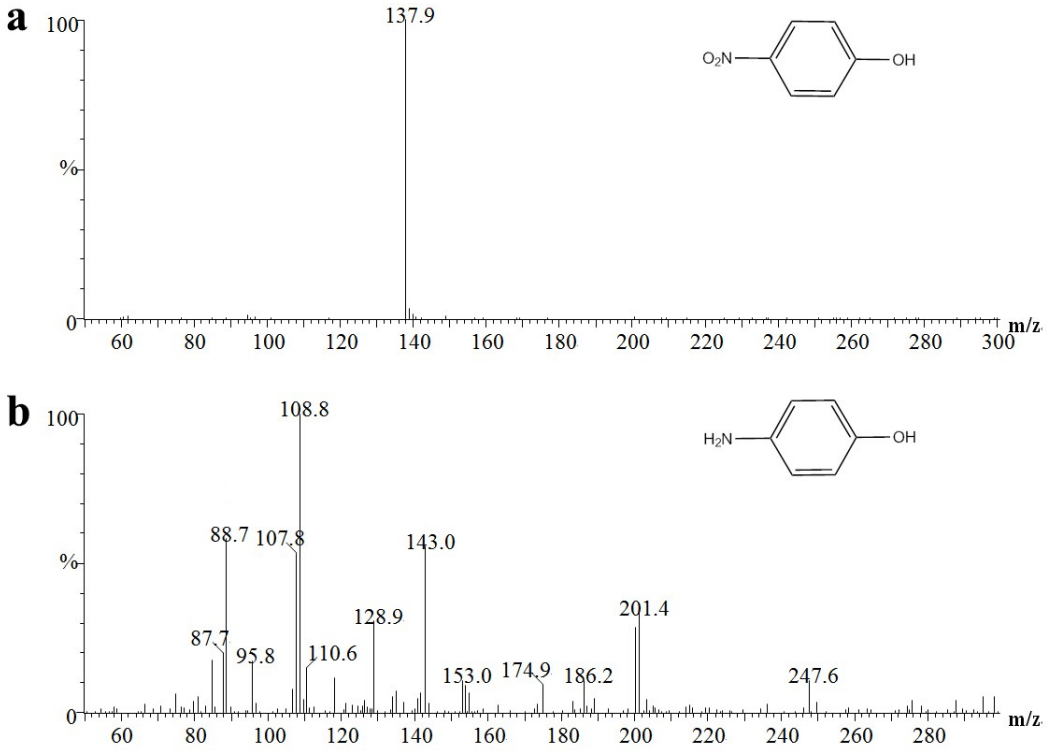

Fig. S13 The MS result of (a) 4-NP and (b) 4-AP.

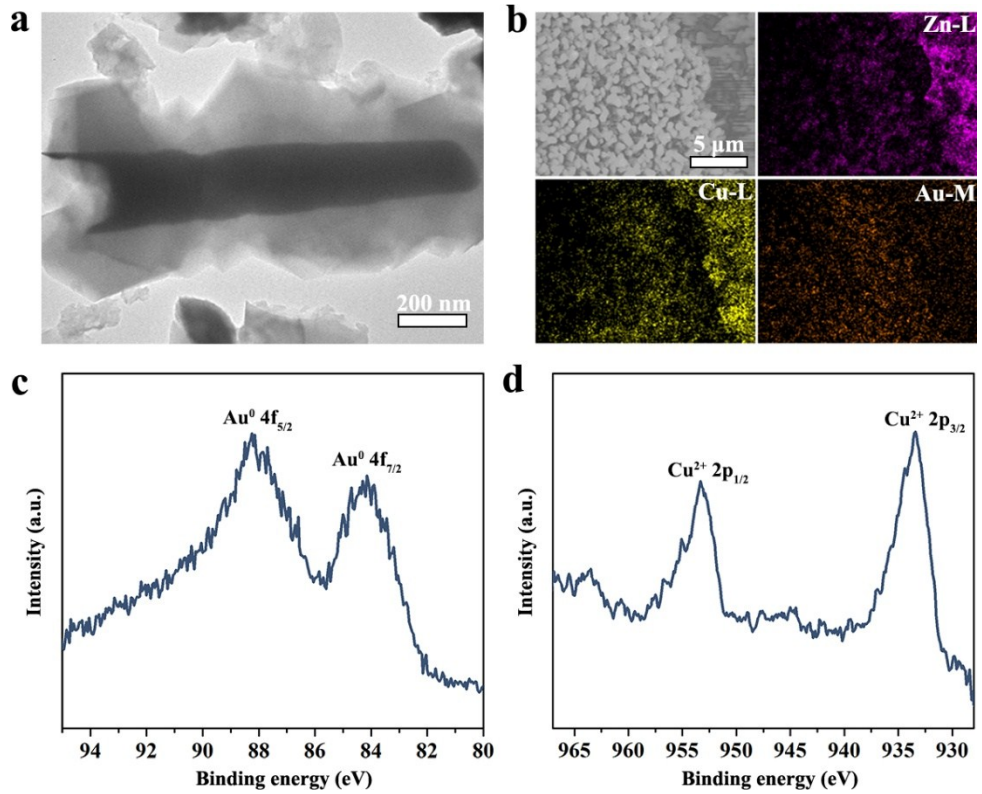

Fig. S14 The (a) TEM image, (b) element mapping of Zn, Cu and Au, (c) XPS Au 2p spectrum and (d) XPS Cu 2p spectrum of Au_{NC}@ZIF-8(Cu) NRAs after 10 cycles.

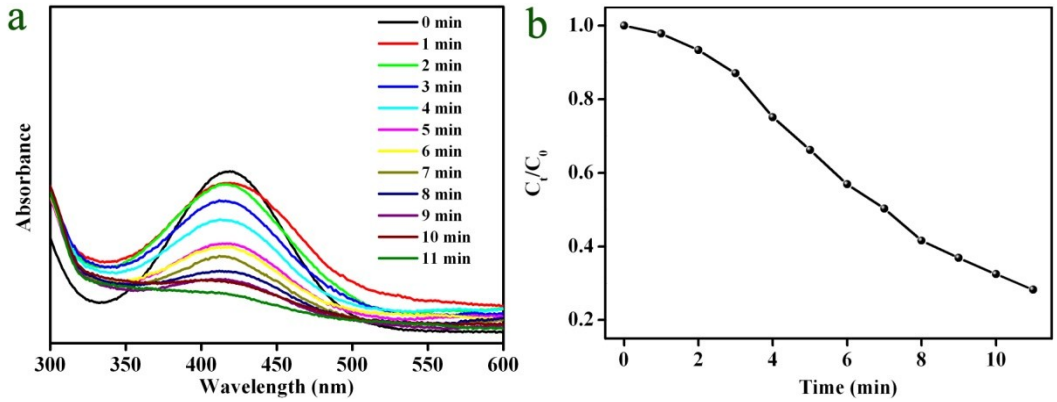

Fig. S15 (a) Absorption spectra of 2-NP over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction 2-NP over Au_{NC}@ZIF-8(Cu) NRAs.

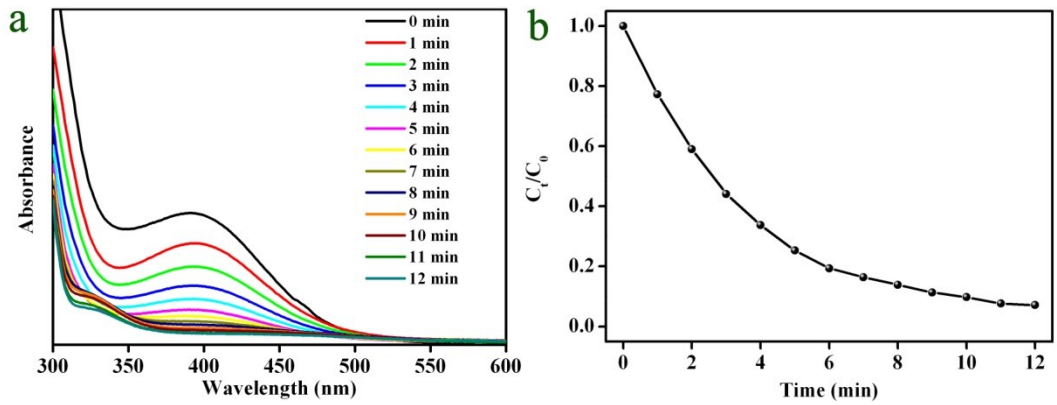

Fig. S16 (a) Absorption spectra of 3-NP over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction 3-NP over Au_{NC}@ZIF-8(Cu) NRAs.

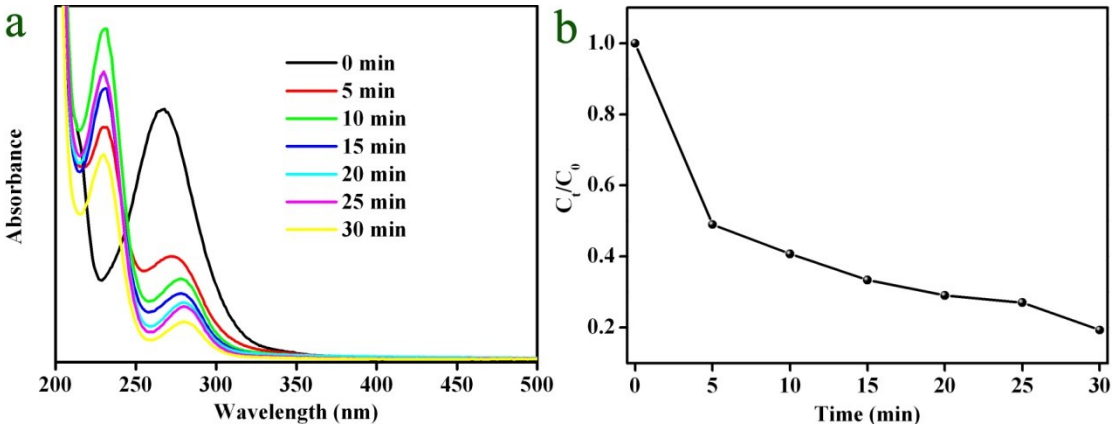

Fig. S17 (a) Absorption spectra of nitrobenzene over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction nitrobenzene over Au_{NC}@ZIF-8(Cu) NRAs.

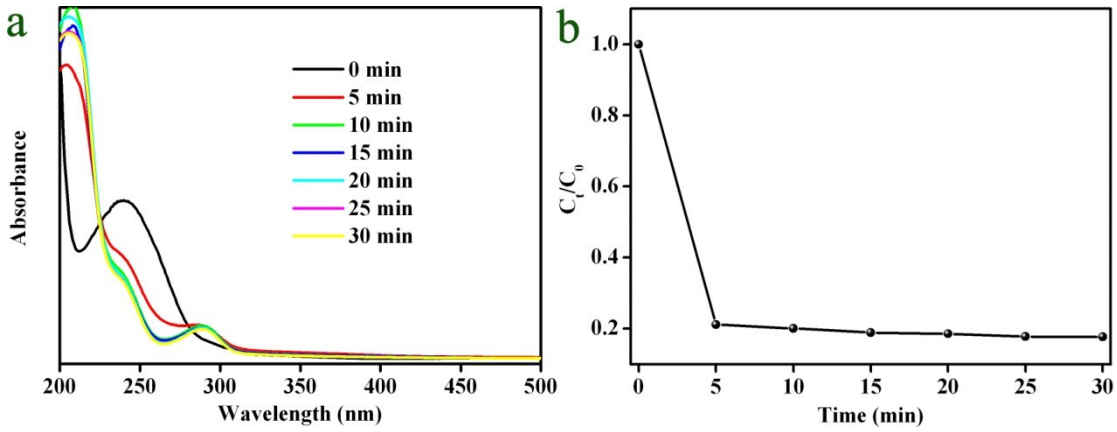

Fig. S18 (a) Absorption spectra of m-dinitrobenzene over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction m-dinitrobenzene over Au_{NC}@ZIF-8(Cu) NRAs.

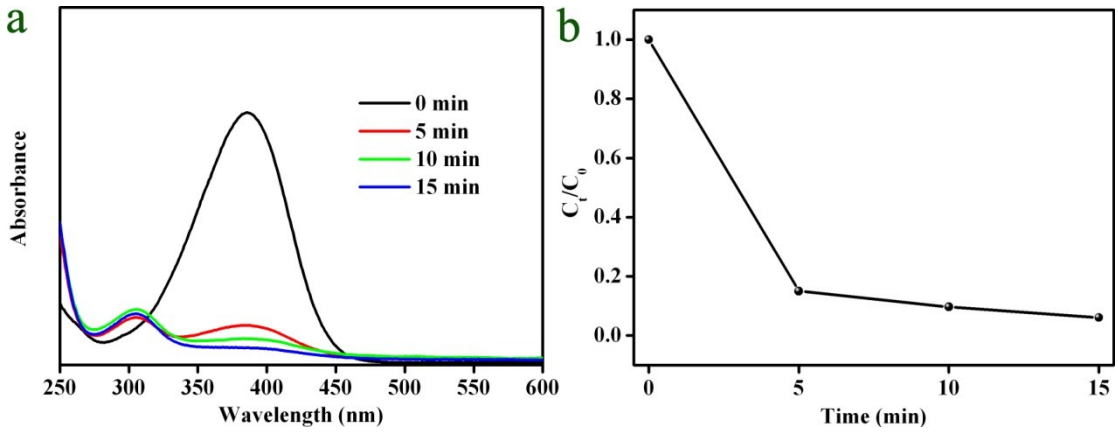

Fig. S19 (a) Absorption spectra of p-nitroaniline over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction p-nitroaniline over Au_{NC}@ZIF-8(Cu) NRAs.

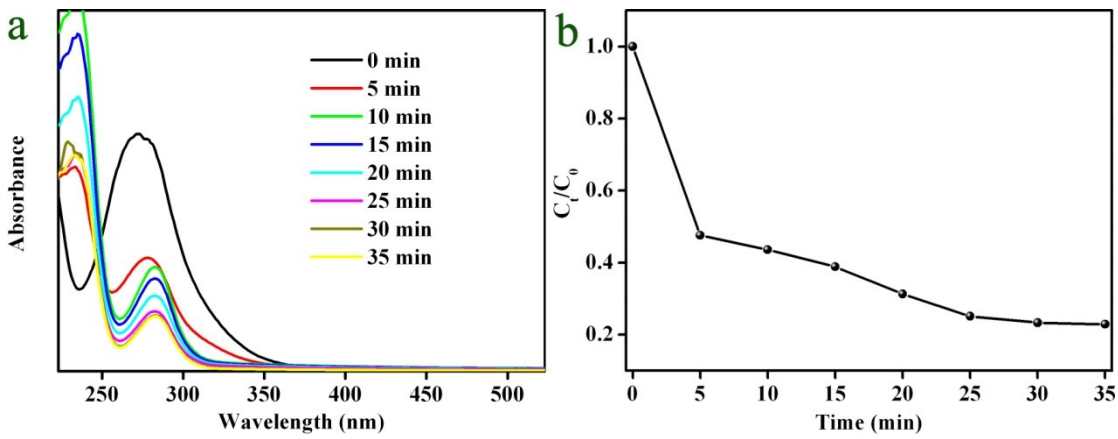

Fig. S20 (a) Absorption spectra of m-nitrotoluene over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction m-nitrotoluene over Au_{NC}@ZIF-8(Cu) NRAs.

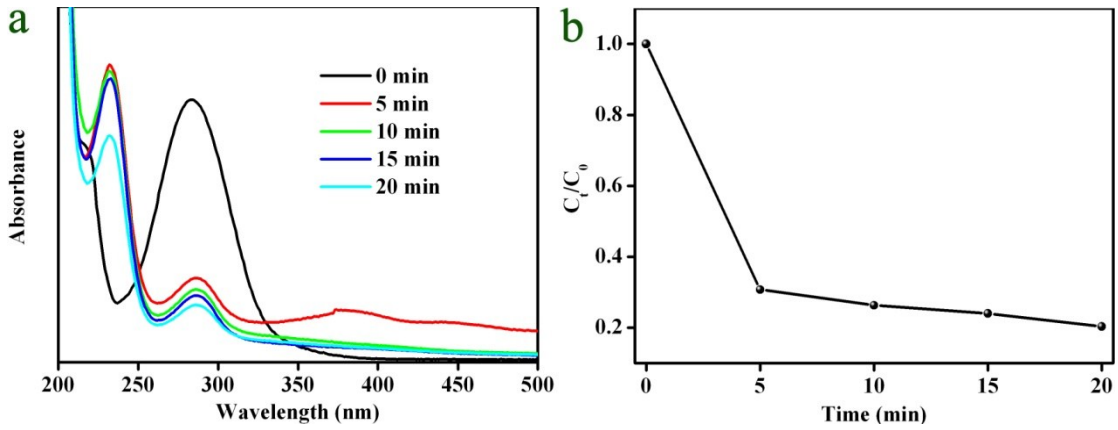

Fig. S21 (a) Absorption spectra of p-nitrotoluene over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction p-nitrotoluene over Au_{NC}@ZIF-8(Cu) NRAs.

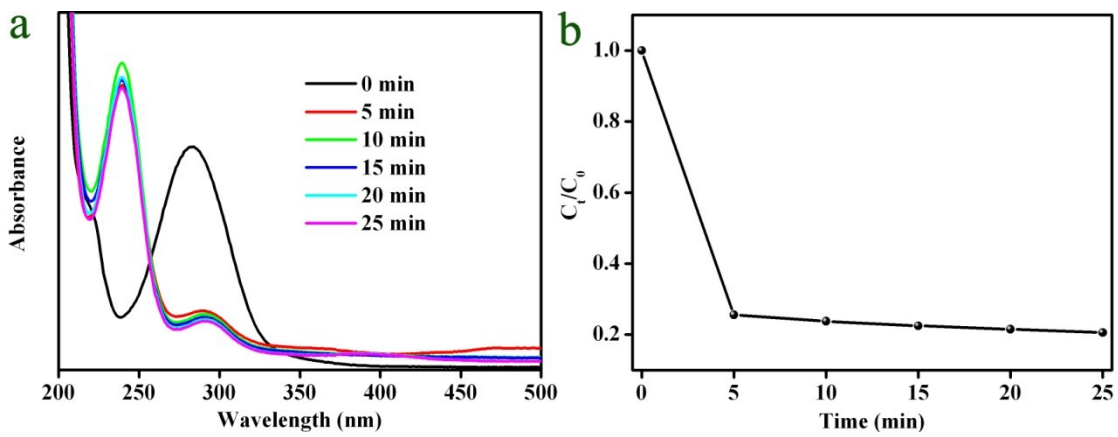

Fig. S22 (a) Absorption spectra of p-nitrobromobenzene over Au_{NC}@ZIF-8(Cu) NRAs. (b) The catalytic activity of reduction p-nitrobromobenzene over Au_{NC}@ZIF-8(Cu) NRAs.

Table S1. Catalytic performance of various catalysts in hydrogenation reduction of 4-NP under the same conditions.

Catalyst	Time	Conversion	k(min^{-1})
Au_{NC}@ZIF-8(Cu)	6 min	98%	0.489
Au_{NC}@ZIF-8	11 min	96%	0.305
Au NP	20 min	87%	0.103
ZIF-8(Cu)	30 min	81%	0.061
ZnO	30 min	13%	0.0035

Table S2. Comparison of 4-NP reduction by various catalysts from the literature.

Catalyst	4-NP (mmol/L)	$NaBH_4$ (mol/L)	Au (%)	Conversion (%)	Time (min)	Ref
Au_{NC}@ZIF-8(Cu) NRAs	0.1	0.05	3%	98%	6 min	This work
Au/graphene hydrogel	0.1	0.1	24%	90%	12 min	1
Au nanoparticles	7	0.16	100%	100%	27 min	2
ZIF-8-1000	1.8	0.17	-	92%	60 min	3
ZIF-8	0.125	1.3	-	-	600 min	4
ZIF-8 NC@Au	0.125	1.3	-	90%	28 min	5
2%Au@2%Ag/ZIF-8	0.18	1.3	2%	98%	13.5 min	6
2%Au/ZIF-8	0.18	1.3	2%	-	62 min	6
Au NPs@ZIF-8	0.1	5	-	70%	180 min	7
$Au_{25}(SG)_{18}$/ZIF-8	0.125	1.3	-	95%	10 min	4

Reference

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