

Supporting Information

Morphology tuning of assembled Au-Cu nicotinate rings by ligand coordination and used as efficient catalyst

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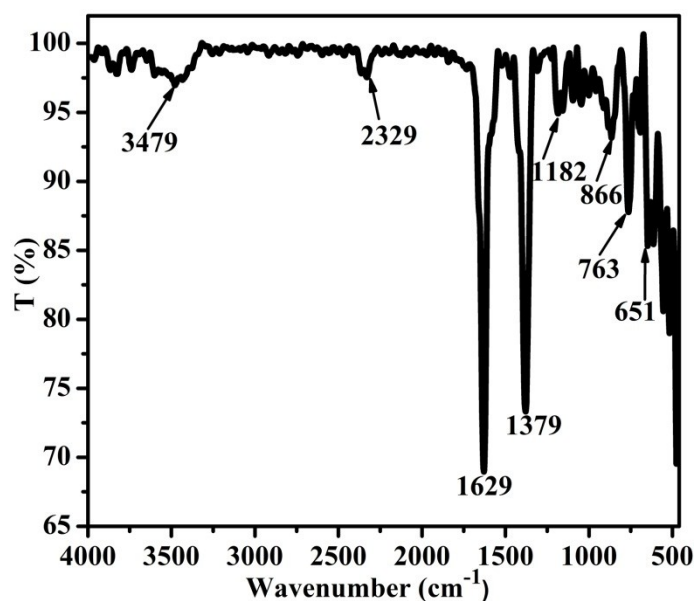


Fig. S1 FTIR spectra of the Au-Cu NRs.

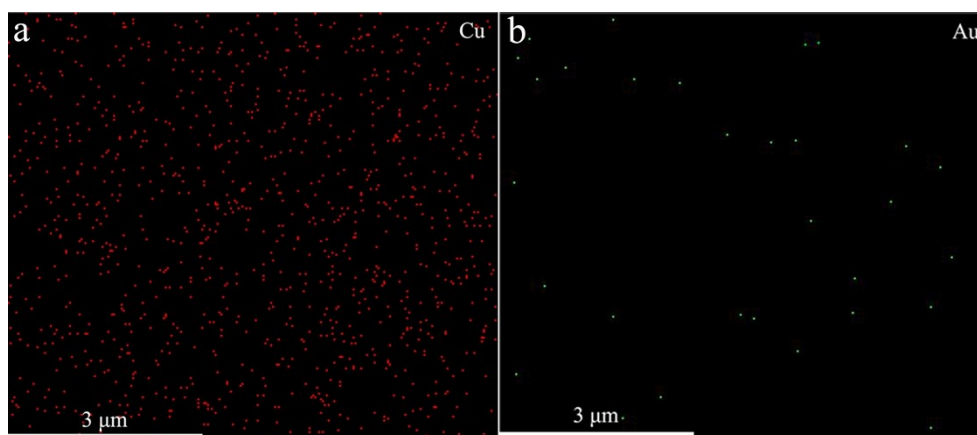


Fig. S2 SEM-EDS mapping of the Au-Cu NRs, corresponding (e) Cu and (f) Au.

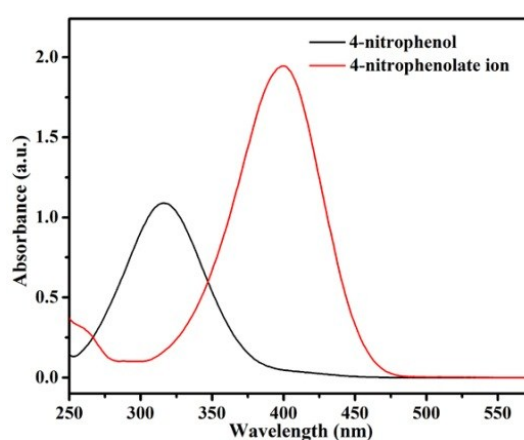


Fig. S3 The UV-vis characteristic peaks of freshly prepared 4-nitrophenol and 4-nitrophenolate ion aqueous solution at 317 and 400 nm, respectively.

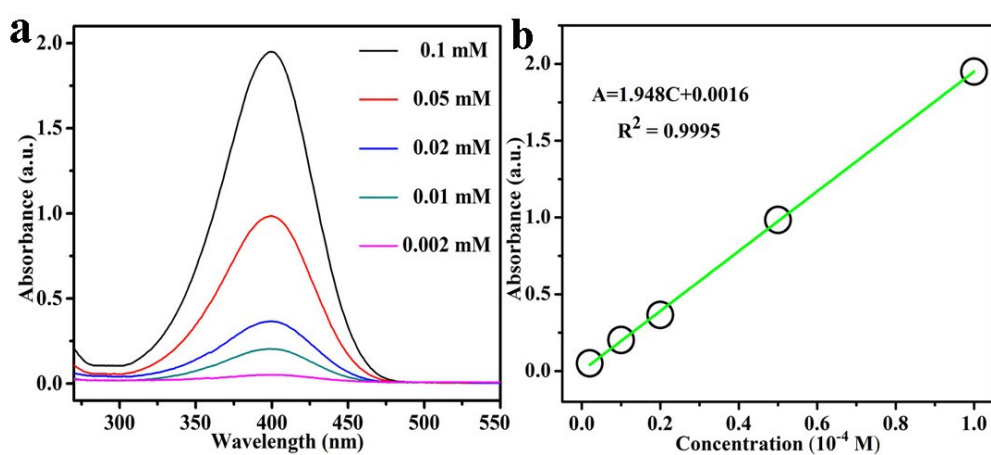


Fig. S4 (a) Absorption spectra of aqueous mixture solutions of 4-NP and NaBH_4 at different concentrations of 4-NP. (b) Plot of the peak absorbance against the concentration of 4-NP.

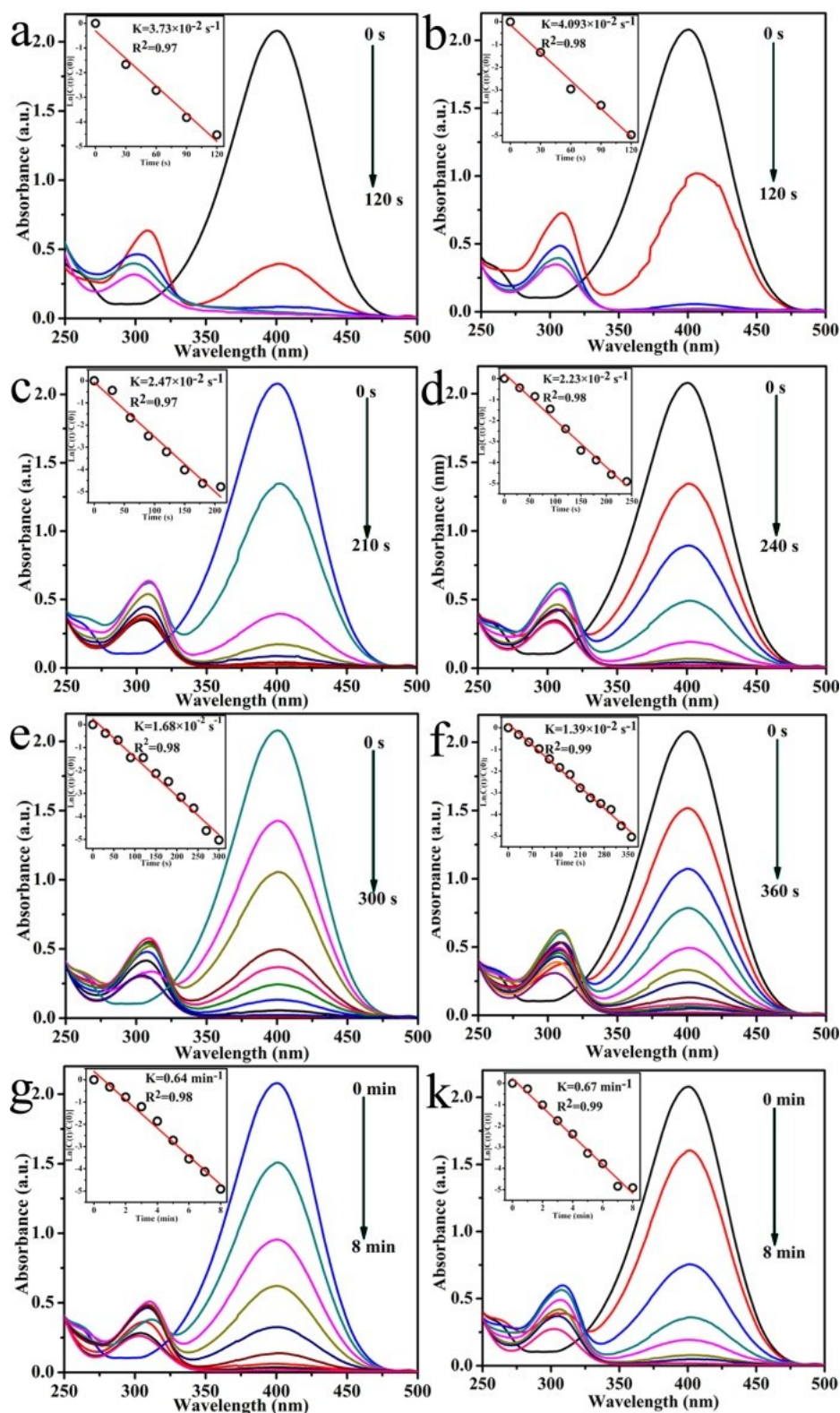


Fig. S5 UV-vis spectra of the reduction of 4-NP by NaBH_4 in the presence of Au-Cu NRs (0.2 M nicotinic acid) recorded for the 2nd (a), 3rd (b), 4th (c), 5th (d), 6th (e), 7th (f), 8th (g), 9th (k), insets: the corresponding $\ln(C(t)/C(0))$ versus reaction time for reduction of 4-NP.

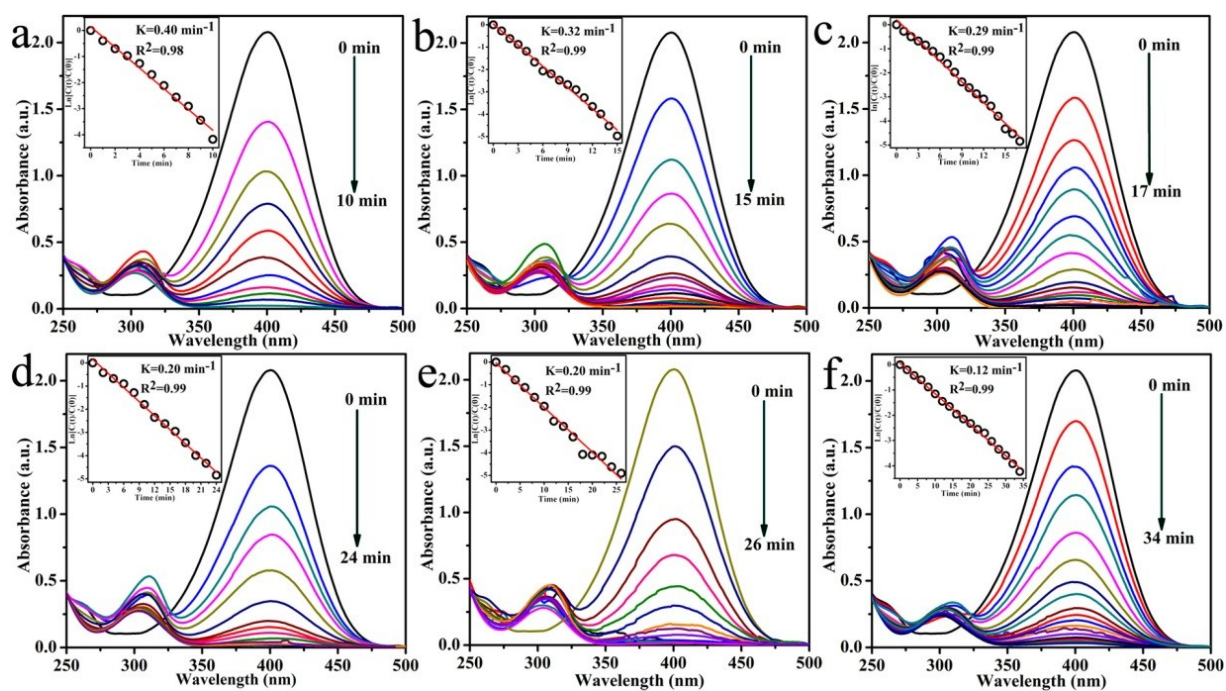


Fig. S6 UV-vis spectra of the reduction of 4-NP by NaBH_4 in the presence of Au-Cu NRs (0.2 M nicotinic acid) recorded for the 10th (a), 11th (b), 12th (c), 13th (d), 14th (e), 15th (f), insets: the corresponding $\ln(C_t/C_{(0)})$ versus reaction time for reduction of 4-NP.

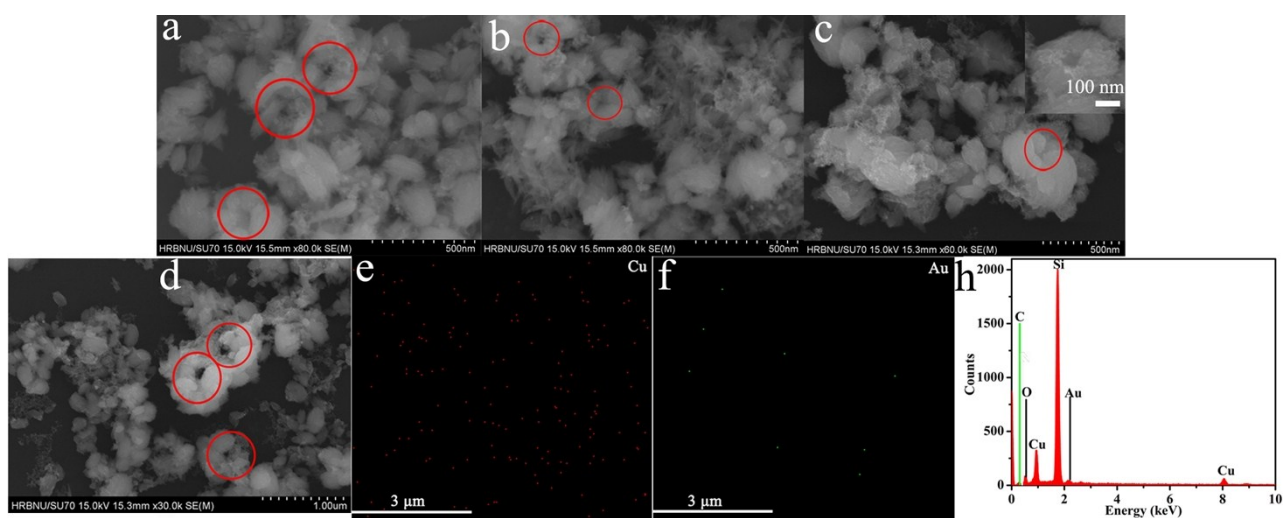


Fig. S7 The SEM (a, c, b, d) of the Au-Cu NRs as catalyst after reused 3rd, 5th, 10th, 15th times, respectively, SEM-EDS mapping of (e) Cu and (f) Au after the Au-Cu NRs as catalyst, (h) EDS of the Au-Cu NRs as catalyst after reused 15th times.

In order to validate the possible mechanism we deduced, according to the suggestion, we supplied the XPS data of the formation the samples before the addition of 4-NP (in the process of III). The XPS data of the Au-Cu NRs were obtained by pretreatment as follows: adding 200 μ L of fresh NaBH_4 solution after the Au-Cu NRs dispersed in to deionized water (1 mg/mL) without any stirring and ultrasonic dispersion, then the Au-Cu NRs was separated from the solution by centrifugation and dried in oven.

The full-scan XPS spectrum for the Au-Cu NRs after adding the reduce agent NaBH_4 was illustrated in Fig. S8. Peaks corresponding to C and O can be clearly observed which were located at 284.6, 399.5 and 529.25 eV, corresponding to C 1s, N 1s and O 1s, respectively. The Au4f high resolution spectra represent the XPS signature of the $4f_{7/2}$ and $4f_{5/2}$ peaks, separately located at 83.65 and 87.25 eV. The main Cu 2p XPS peaks were observed at 933.25 eV (Cu $2p_{3/2}$) and 953.2 eV (Cu $2p_{1/2}$) can be observed in Fig. S7. Compared with the as-prepared Au-Cu NRs, the XPS data of sample treated by NaBH_4 occurred displacement in all atom. The Cu 2p XPS spectrum of sample showed shakeup satellite peaks of the Cu $2p_{3/2}$ at 943.1 and Cu $2p_{1/2}$ at 962.3 eV, which conformed the presence of Cu(II) and Cu (I) species. The raw areas of the shakeup satellite peaks were grew up due to the adding NaBH_4 compared with the before and after catalysis (Fig. 2 and Fig. S9). This result proved that the change of the state from the Cu^{2+} to Cu^+ by reduced was existed in the catalysis. It is seemed that the state of the Au4f have no obvious transformation due to the content of Au in the Au-Cu NRs was much less. The solution of NaBH_4 can only get in touch with the surface of Au-Cu NRs, so, the Au^{3+} and Cu^{2+} on the surface of Au-Cu NRs can be reduced to Au^{2+} and Cu^+ , respectively. Generally, the characteristic shakeup satellite is peculiar to the Cu(II) species, which relates to d9 configuration of Cu. Thus, the XPS of the Au-Cu NRs indicated that the Au and Cu were still existed mixed valence state.

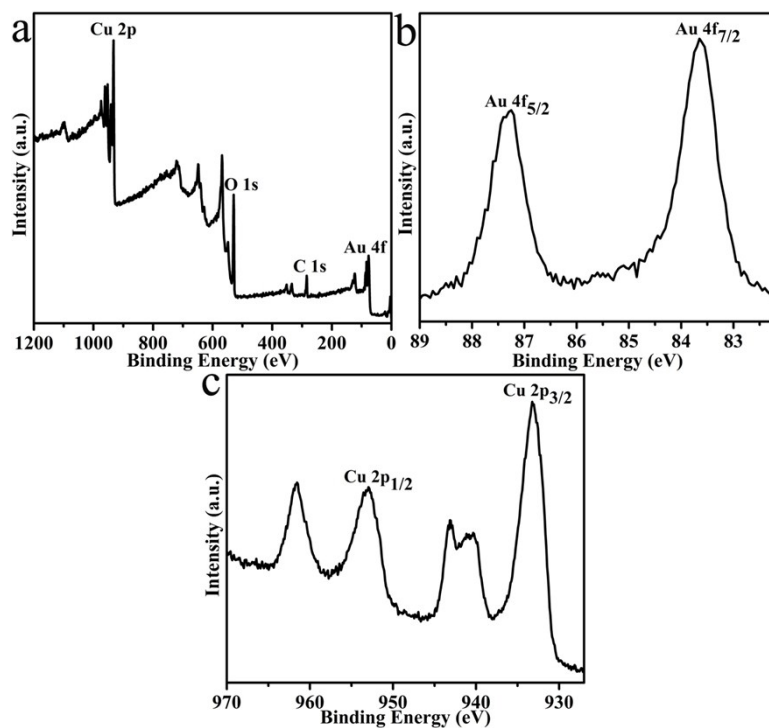


Fig. S8 (a) XPS spectrum of Au-Cu NRs (0.20 M nicotinic acid) as catalyst before the addition of 4-NP, (b) Au 4f high-resolution XPS spectrum, and (c) Cu 2p peak.

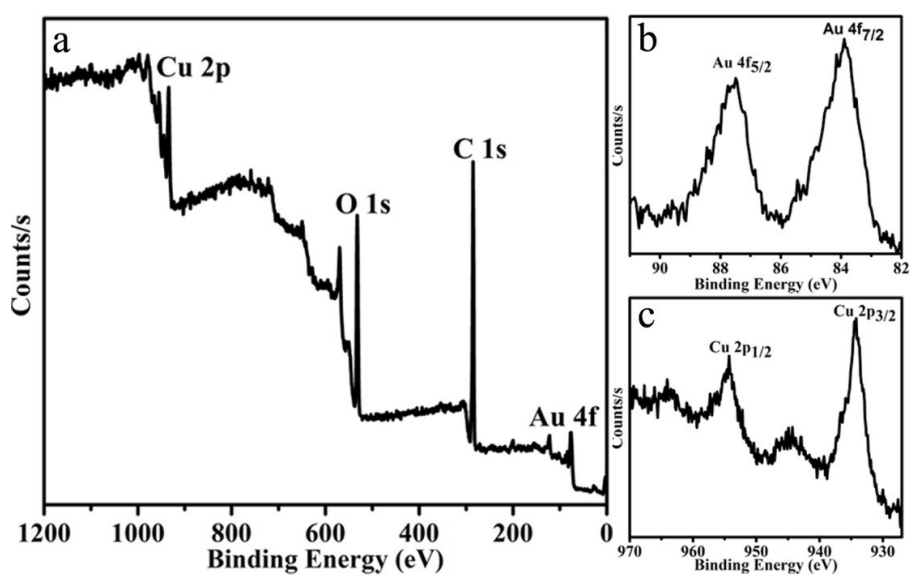


Fig. S9 (a) XPS spectrum of Au-Cu NRs (0.20 M nicotinic acid) as catalyst after reused 15th times, (b) Au 4f high-resolution XPS spectrum, and (c) Cu 2p peak.

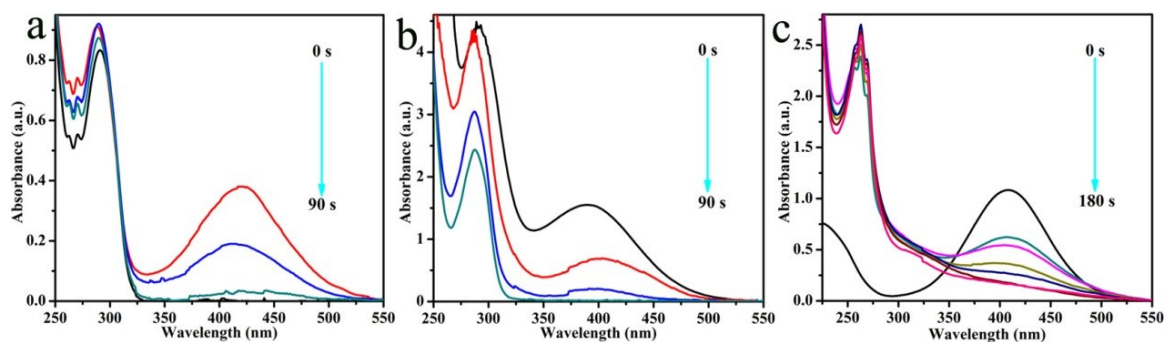


Fig. S10 UV-vis spectra of the reduction of (a) 2-NP, (b) 3-NP and (c) 4-NTP by NaBH₄ in the presence of Au-Cu NRs.

Table S1 Elemental analysis of Au-Cu NRs.

Element Name	Cu	Au	N	C	H
Content (%)	1.65	0.28	8.802	45.7588	2.1465

Table S2 The reduction of 4-NP in the presence of varying amount of Au-Cu NRs catalysts

Catalyst	Type	Concentration of 4-NP	Amount of catalyst	TOF ^a	References
Au-Cu NRs	Nanosheets	0.01 M, 30 μ L	0.025 mg	$2.17 \times 10^{-2} \text{ s}^{-1}$	This work
TiO ₂ /0.1 mol% Au	Supported	0.1 M, 30 μ L	2 mg	84 min ⁻¹	1
Au@RMF NSs	Nanostructures	17 mL, 2.0×10^{-4} M	0.2 mg	279.2 s ⁻¹	2
yolk-like SiO ₂ @Fe ₃ O ₄ /C@Au	Microspheres	0.1 mL, 5×10^{-3} M	0.05 mg	17.4 min ⁻¹	3
Fe ₃ O ₄ @SiO ₂ -Au@mSiO ₂	Microspheres	0.10 mL, 0.005 M	3 mg	0.1 min ⁻¹	4
AuNPs	Nano	0.30 mM	0.0286 mg/mL	260 h ⁻¹	5
Au NPs@CNs	nanocrystal	50 mL, 0.12 mM	1 mL, total Au content: 0.2 μ mol	109 h ⁻¹	6
Pd@Au CSNTPs	core-shell	2 mL, 1.0×10^{-5} M	0.005 mg	$2.46 \times 10^{-2} \text{ s}^{-1}$	7

^a The TOF is defined as the moles of reduced 4-NP molecules per mole of the surface noble metal atoms per second.

Reference:

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