Supplementary Information

Facile preparation of a variety of bimetallic dendrites with high catalytic activity by two simultaneous replacement reactions

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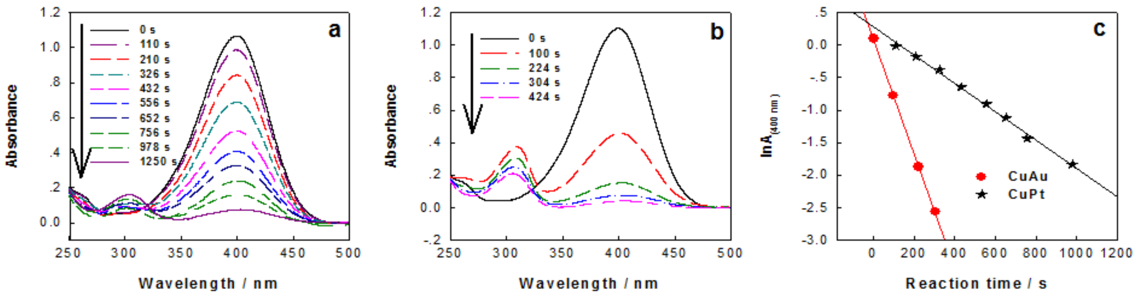

Fig. S1 UV-vis adsorption spectra during catalytic reduction of 4-NP by $NaBH_4$ in (a) 1950 mL of 7×10^{-5} M 4-NP + 50 mL of 0.2 M $NaBH_4$ + 2 mg CuPt and (b) 200 mL of 7×10^{-5} M 4-NP + 10 mL of 0.2 M $NaBH_4$ + 2 mg CuAu. (c) Plots of logarithm of absorbance at 400 nm vs. reaction time for the two systems, where the points of high and low absorbance were removed.

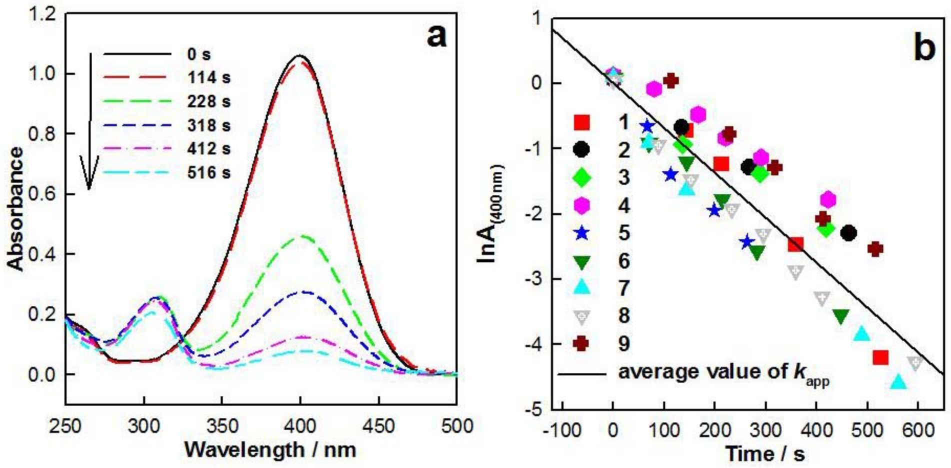

Fig. S2 (a) UV-vis adsorption spectra for the catalytic reduction of 4-NP by $NaBH_4$ using 1 mg CuPd catalyst in 400 mL of 7×10^{-5} M 4-NP + 20 mL of 0.2 M $NaBH_4$. (b) Plots of logarithm of absorbance at 400 nm vs. reaction time for the nine repeated experiments of CuPd catalyst, where the points of high and low absorbance were removed.

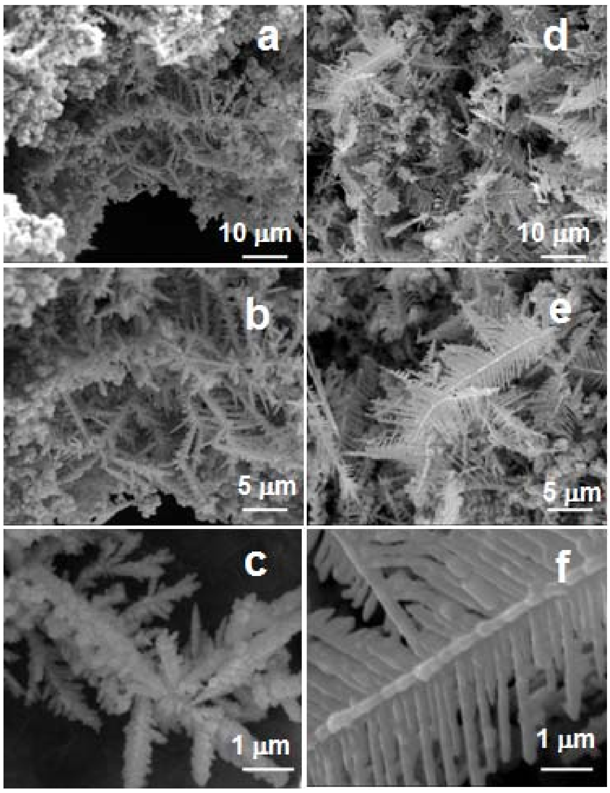

Fig. S3 SEM images with different enlargement scales for the monometallic (a-c) Ag and (d-f) Cu dendrites.

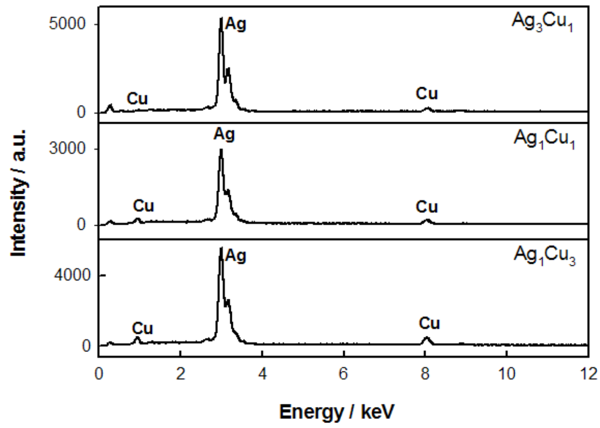

Fig. S4 EDX spectra for the dendrites of Ag_3Cu_1, Ag_3Cu_1 and Ag_3Cu_1 in Fig. 1.

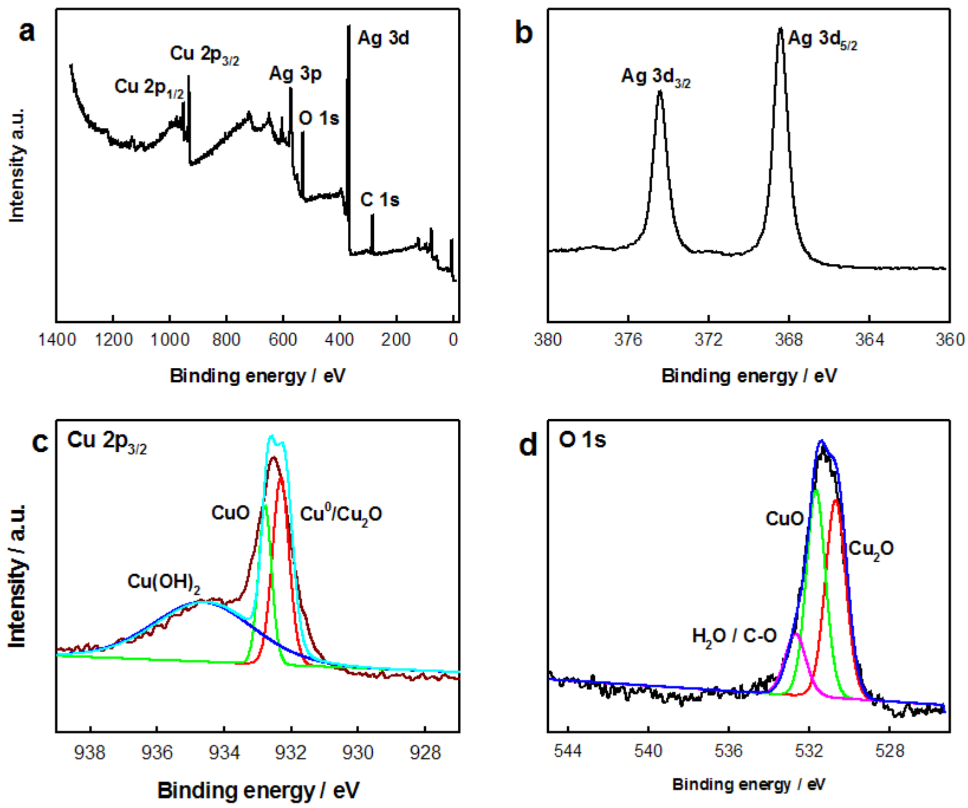

Fig. S5 XPS of the Ag_1Cu_1 catalyst. (a) A survey spectrum, (b) Ag 3d, (c) Cu $2p_{3/2}$ and (d) O 1s.

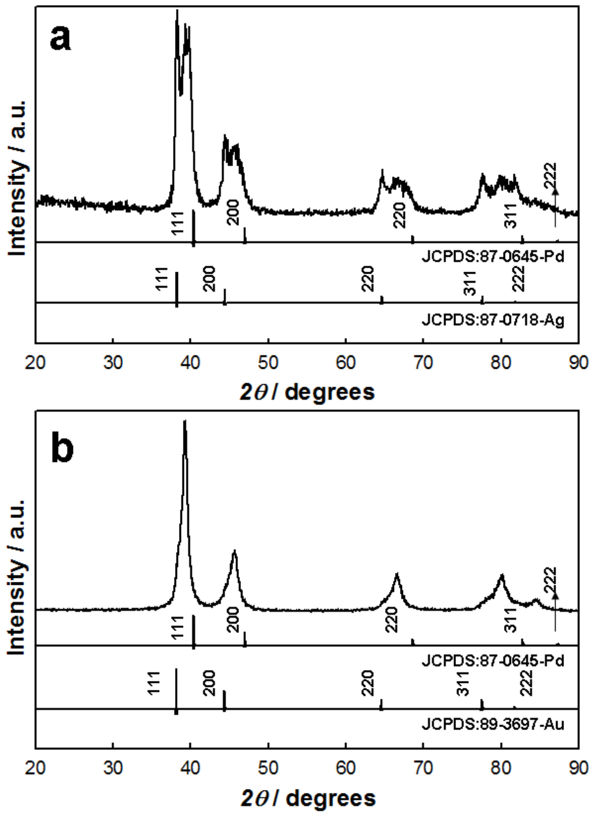

Fig. S6 XRD patterns for the prepared bimetallic dendrites of (a) AgPd and (b) AuPd in Fig. 7a and 7b, respectively.

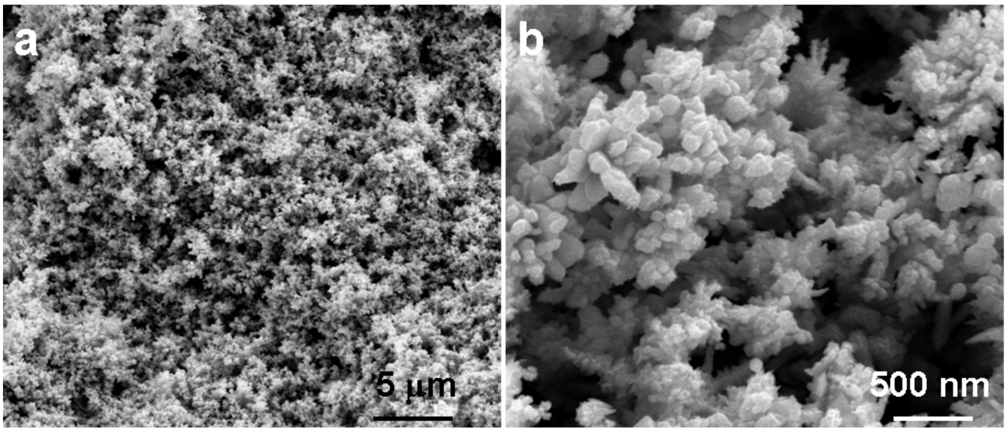

Fig. S7 SEM images with different enlargement scales for the prepared monometallic Pd.

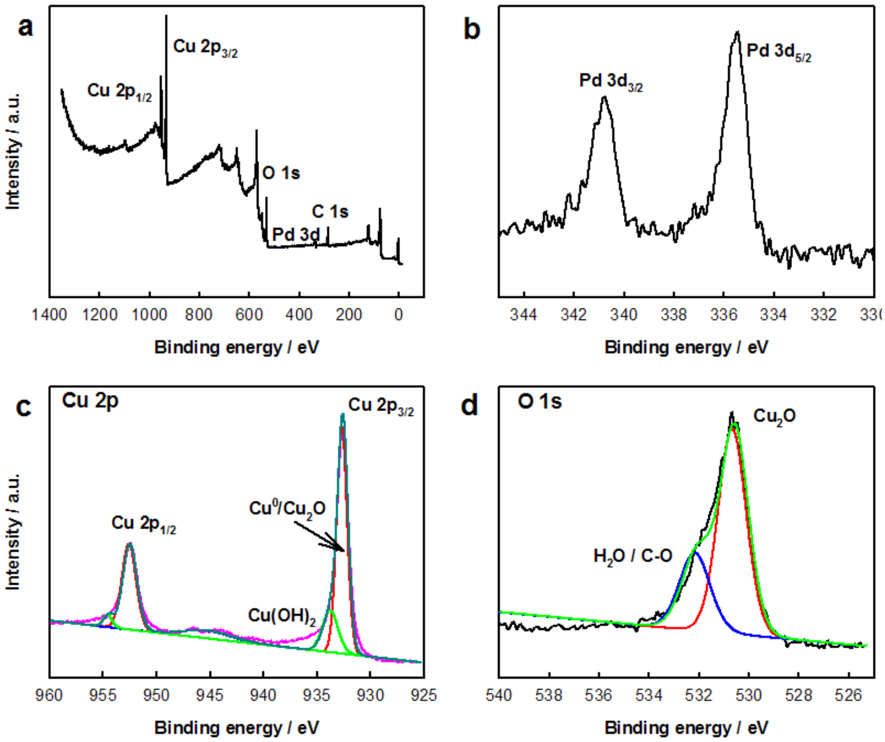

Fig. S8 XPS spectra of the CuPd catalyst. (a) A survey spectrum, (b) Pd 3d, (c) Cu 2p and (d) O 1s.

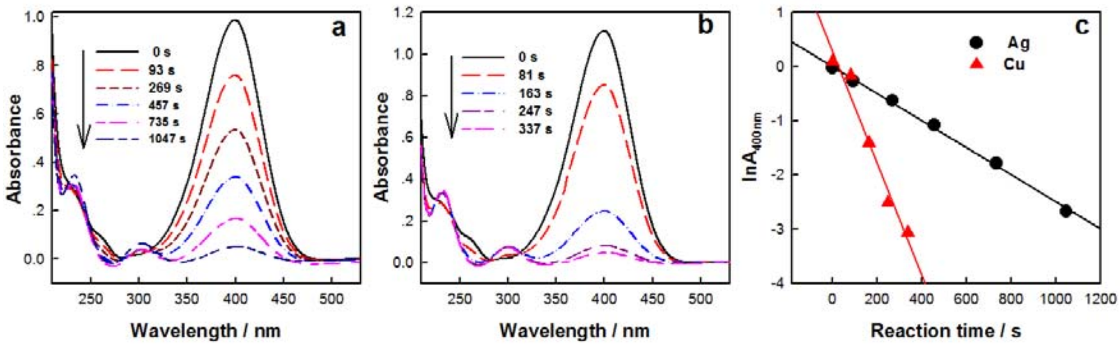

Fig. S9 UV-vis adsorption spectra during the reduction of 4-NP by $NaBH_4$ in the presence of monometallic dendrites of (a) Ag and (b) Cu. (c) Plots of logarithm of absorbance at 400 nm vs. reaction time for the two monometallic dendrites.

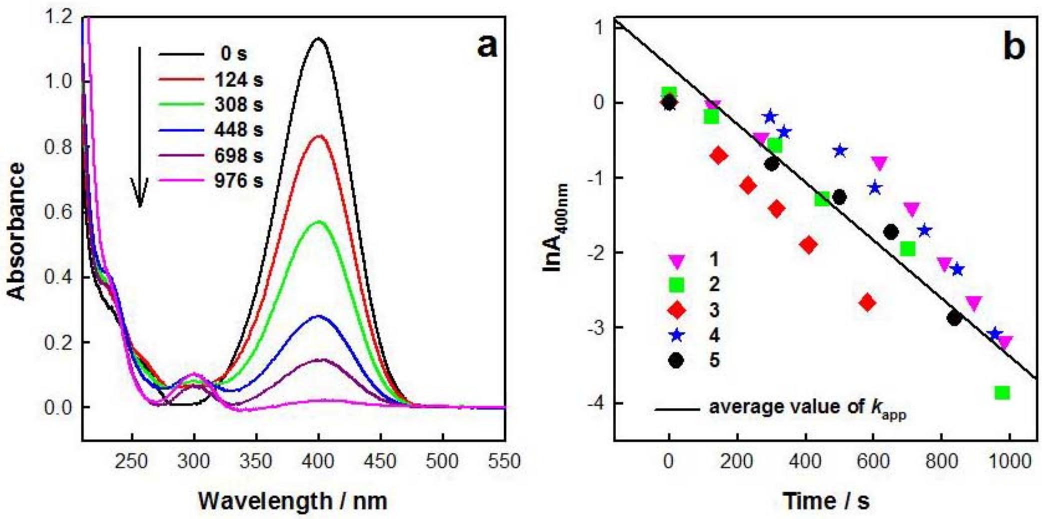

Fig. S10 (a) UV-vis adsorption spectra for the catalytic reduction of 4-NP by $NaBH_4$ using 2 mg Pd catalyst in 400 mL of 7×10^{-5} M 4-NP + 20 mL of 0.2 M $NaBH_4$. (b) Plots of logarithm of absorbance at 400 nm vs. reaction time for five repeated experiments, where the points of high and low absorbance were removed.

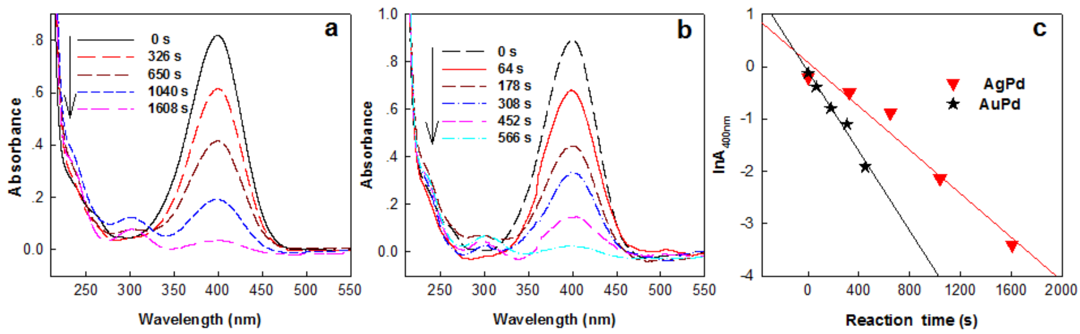

Fig. S11 UV-vis adsorption spectra during reduction of 4-NP by $NaBH_4$ in the presence of (a) AgPd and (b) AuPd dendrites. (c) Plots of logarithm of absorbance at 400 nm vs. reaction time for the two dendrites.

Table S1. Some relevant standard potentials vs. SHE from the handbook [S1].

Redox pair	Ag^+/Ag	$Ag(NH_3)_2^+/Ag$	Ag(I)EDTA/Ag*	Pd^{2+}/Pd	$AuCl_4^-/Au$
E^Θ /V	0.799	0.373	0.366	0.951	1.002
Redox pair	Cu^{2+}/Cu	$Cu(NH_3)_4^{2+}/Cu$*	Cu(II)EDTA/Cu*	$PtCl_6^{2-}/Pt$*	Mg^{2+}/Mg
E^Θ /V	0.342	−0.00178	−0.214	0.718	−2.37

*The standard electrode potential of $PtCl_6^{2-}/Pt$ was calculated from that of $PtCl_4^{2-}/Pt$ and $PtCl_6^{2-}/ PtCl_4^{2-}$ couples [S1]. The standard electrode potential of $Cu(NH_3)_4^{2+}/Cu$ was calculated from that of Cu^{2+}/Cu and the stability constants of $Cu(NH_3)_4^{2+}$ (K^Θ) according to

$$E^\Theta[Cu(NH_3)_4^{2+}/Cu] = E^\Theta(Cu^{2+}/Cu) + (0.05916/2)\log(1/K^\Theta)$$

The standard electrode potentials of Ag(I)EDTA/Ag and Cu(II)EDTA/Cu were also obtained in the same way.

Table S2. The atomic percentage of Ag (at.%) in the feeding solutions and AgCu bimetallic dendrites.

Sample	Feeding solution	Dendrite
Ag_3Cu_1	75.00	90.01
Ag_1Cu_1	50.00	81.66
Ag_1Cu_3	25.00	77.98

Table S3. 2θ angles (in degree) of the prepared bimetallic AgCu dendrites.

Sample	Ag(111)	Ag(200)	Ag(220)	Ag(311)	Ag(222)	Cu(111)	Cu(200)	Cu(220)	Cu(311)
Ag_1Cu_3	38.09	44.19	64.35	77.55	81.61	43.19	50.29	74.16	89.92
Ag_1Cu_1	38.09	44.19	64.35	77.55	81.61	/	/	74.16	/
Ag_3Cu_1	38.09	44.19	64.35	77.55	81.61	/	/	/	/

Table S4. Some relevant stability constants [S2].

Complex	$Ag(NH_3)_2^{+}$	$Cu(NH_3)_4^{2+}$	Ag(I)EDTA	Cu(II)EDTA
log K^{Θ}	7.23	12.67	7.32	18.80

Table S5. Comparison of normalized kinetic parameters (k_n) for the reduction of 4-NP reported in literature

Reference	Catalyst	m / 10^{-3}g	V / mL	c_0 / mM	k_{app}	k_n / 10^{-3} mmol g^{-1} s^{-1}
4	Ag dendrites	1.00	2.8	7.1×10^{-2}	10.4×10^{-3} s^{-1}	2.07
	Pd-Ag dendrites				39.1×10^{-3} s^{-1}	7.77
	Pd-Ag particles				8.3×10^{-3} s^{-1}	1.65
	Au-Ag dendrites				10.7×10^{-3} s^{-1}	2.13
53	$Ni_{33.8}Co_{66.2}$	1.00	10	0.1	0.07348 min^{-1}	1.23
	$Ni_{33.4}Co_{66.6}$				0.05717 min^{-1}	0.953
54	RGO-Co	6.00	2	5	27.16×10^{-3} min^{-1}	0.754
	RGO-$Ni_{25}Co_{75}$				93.22×10^{-3} min^{-1}	2.59
	RGO-$Ni_{50}Co_{50}$				7.73×10^{-3} min^{-1}	0.215
	RGO-$Ni_{75}Co_{25}$				29.06×10^{-3} min^{-1}	0.807
	RGO-Ni				37.26×10^{-3} min^{-1}	1.04
55	Au/Ag-8 min	0.60	2.8	7.10×10^{-2}	6.07×10^{-3} s^{-1}	2.01
56	Au-replicas(fresh)	0.30	100	7.82×10^{-3}	23.5×10^{-2} min^{-1}	10.2
	Au-replicas (recycled)				16.7×10^{-2} min^{-1}	7.25
57	Au-Fe_3O_4	2.00	0.04	10	0.63 min^{-1}	2.10
58	Ni	8.00	3	0.1	3.5×10^{-2} min^{-1}	0.022
	Ni@Au-30 min				4.1×10^{-2} min^{-1}	0.026
	Ni@Au-4 h				7.6×10^{-2} min^{-1}	0.048
	Ni@Au-12 h				4.2×10^{-3} min^{-1}	0.0026

c_0: initial concentration of 4-NP, V: volume of 4-NP solution, m: weight of catalyst.

References

S1 D. R. Lide, *CRC Handbook of Chemistry and Physics*, ed. P. Vanýsek, CRC Press: Boca Raton, FL, 87th edn., 2006/2007, Vol. 8, Iss. 8, pp. 20-29.

S2 Groups in Central China Normal University, Northeast Normal University; Shaanxi Normal University and Beijing Normal University, *Analytical Chemistry (3rd edn. of Chinese version)*, Higher Education Press: Beijing, 2006, Vol. 1, pp. 344-345.