Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2017

Supporting Information

3D structure-preserving galvanic replacement to create hollow Au microstructures

Harnchana Gatemala, Sanong Ekgasit, Prompong Pienpinijtham*

Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, 254 Phyathai Road, Patumwan, Bangkok 10330, Thailand

*Corresponding author: prompong.p@chula.ac.th

KEYWORDS: hollow gold microstructures; nanoporous silver microstructures, silver chloride complex, galvanic replacement, catalytic reduction of p-nitrophenol

Table S1: Atomic contents of microstructures after 24 hours of galvanic replacement using DI water (the samples in Fig. 2A1) and saturated NaCl solution (the samples in Fig. 2A2) as galvanic replacement media with different washing steps.

[NaCl]/M	Washing step	Atomic content (%Atom)		
		Au	Ag	Cl
0	DI water	21.38 ± 0.01	47.85 ± 0.01	30.77 ± 0.01
	5 M NH_4OH	82.85± 0.00	16.42± 0.04	0.72 ± 0.73
	65% HNO_3	97.47 ± 0.00	2.53 ± 0.14	N.D.
Saturated solution (~6.14 M)	DI water	68.24 ± 0.01	26.56 ± 0.02	5.21 ± 0.11
	5 M NH_4OH	91.90 ± 0.01	8.05 ± 0.09	0.05 ± 12.84
	65% HNO_3	96.82 ± 0.00	2.97 ± 0.13	0.21 ± 1.65
	65% HNO_3 for 24 h	97.06 ± 0.01	2.94 ± 0.26	N.D.

Note: N.D. represents “not detected”.

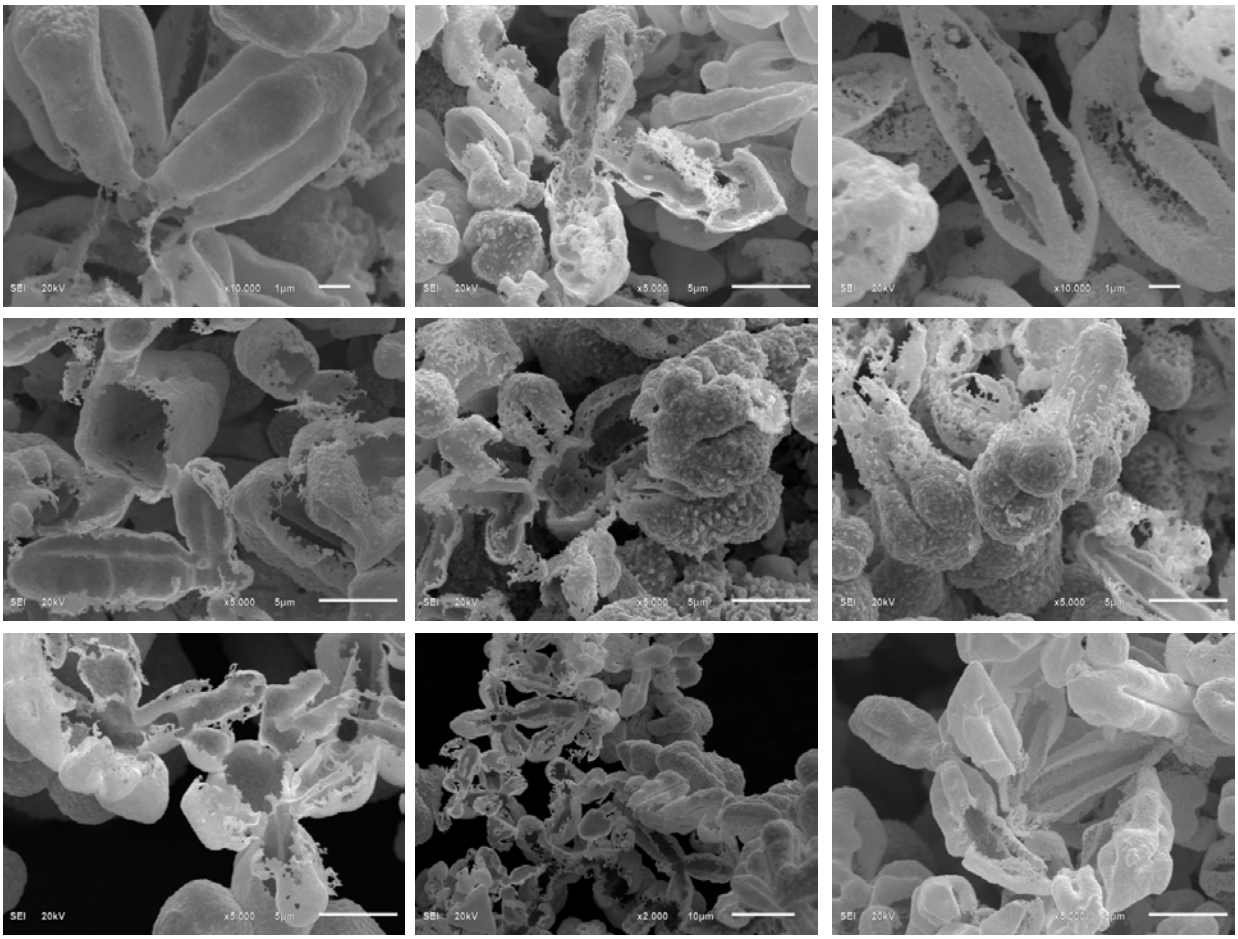

Fig. S1 SEM micrographs show the hollow structure of Au of sample synthesized under the same condition as Fig. 2A4.

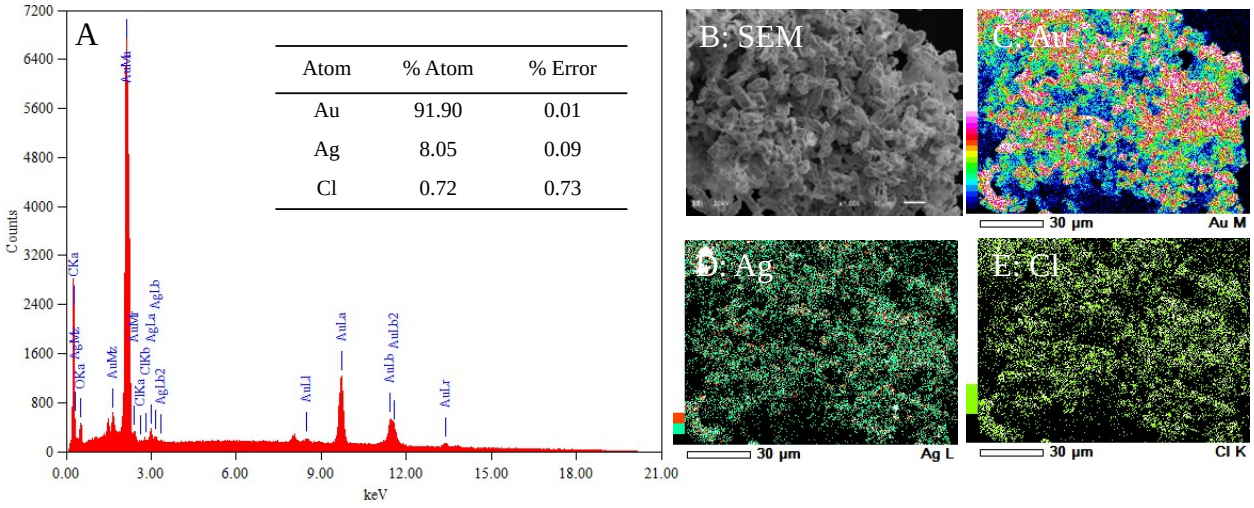

Fig. S2 (A) EDS spectrum of HL-6pAuMSs synthesized in saturated NaCl media after washing with 5 M NH_4OH. The corresponding (B) SEM micrograph and elemental maps representing the distribution of (C) Au, (D) Ag and (E) Cl on HL-6pAuMSs.

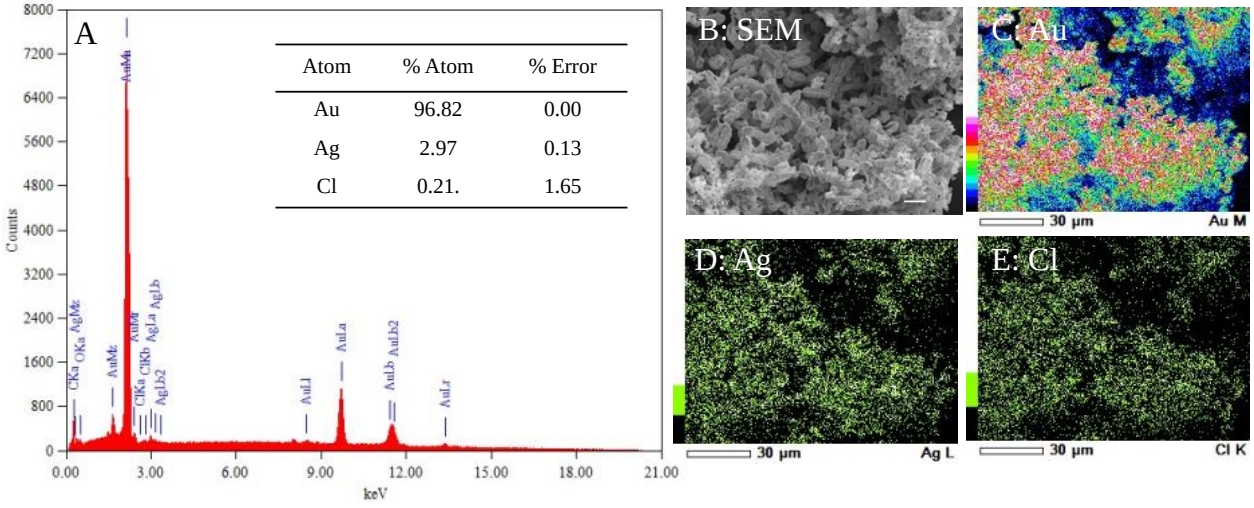

Fig. S3 (A) EDS spectrum of SEM micrograph of HL-6pAuMSs synthesized in saturated NaCl media after washing with 65% HNO_3. The corresponding (B) SEM micrograph and elemental maps representing the distribution of (C) Au, (D) Ag and (E) Cl.

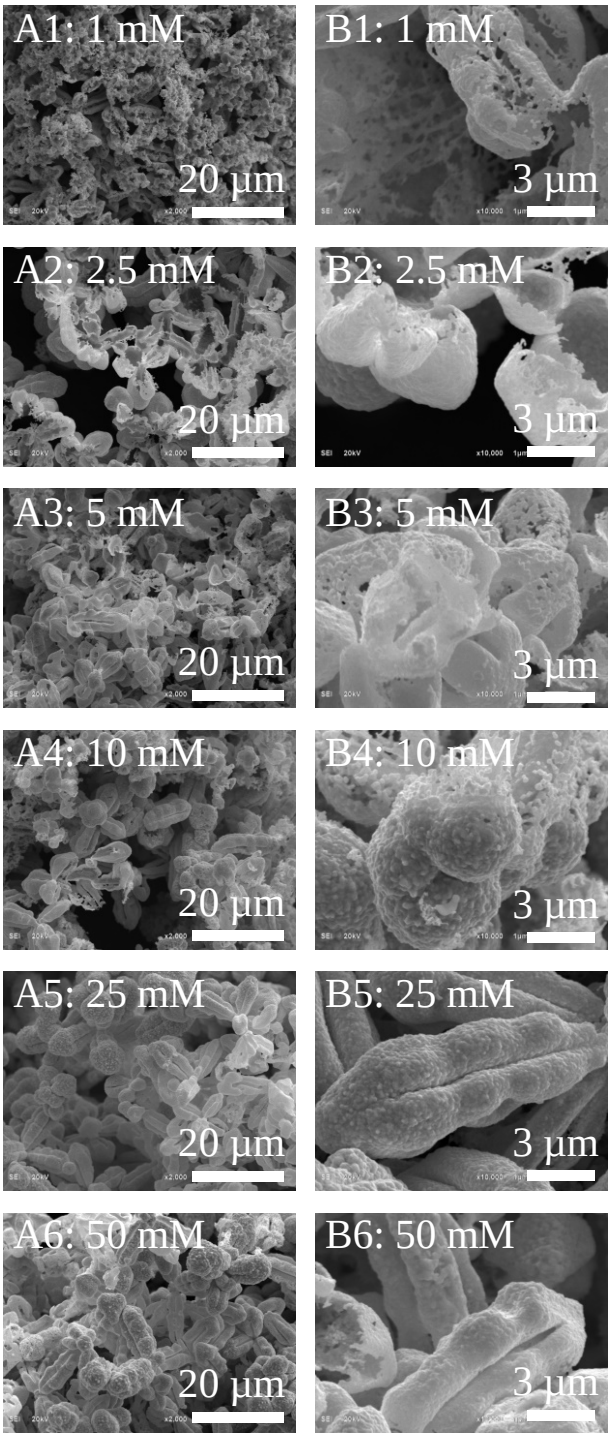

Fig. S4 SEM micrographs of HL-6pAuMSs synthesized using saturated NaCl solution as a galvanic replacement media with different $HAuCl_4$ concentrations (A1) 1 mM, (A2) 2.5 mM, (A3) 5 mM, (A4) 10 mM, (A5) 25 mM and (A6) 50 mM. The corresponding high magnification images of A1−A5 are shown in B1−B5.

Table S2: Elemental composition determined by EDS technique of the microstructures galvanically replaced using different Au^{3+} concentrations and different washing steps.

[Au^{3+}] (mM)	**Washing step**	**Atomic content (%Atom)**		
		Au	**Ag**	**Cl**
1	DI water	14.29 ± 0.01	85.26 ± 0.00	0.45 ± 0.45
	5 M NH_4OH	24.28 ± 0.01	75.59 ± 0.00	0.13 ± 1.62
	65% HNO_3	95.98 ± 0.00	3.47 ± 0.12	0.54 ± 0.68
5	DI water	68.24 ± 0.01	26.56 ± 0.02	5.21 ± 0.11
	5 M NH_4OH	91.90 ± 0.01	8.05 ± 0.09	0.05 ± 12.84
	65% HNO_3	96.82 ± 0.00	2.97 ± 0.13	0.21 ± 1.65
25	DI water	21.67 ± 0.01	40.79 ± 0.00	38.06 ± 0.00
	5 M NH_4OH	91.57 ± 0.00	7.35 ± 0.07	1.07 ± 0.46
	65% HNO_3	96.37 ± 0.00	3.57 ± 0.11	0.06 ± 6.00
50	DI water	21.16 ± 0.01	40.79 ± 0.01	38.06 ± 0.01
	5 M NH_4OH	90.71 ± 0.00	8.77 ± 0.04	0.51 ± 0.68
	65% HNO_3	96.79 ± 0.00	3.13 ± 0.13	0.07 ± 4.87

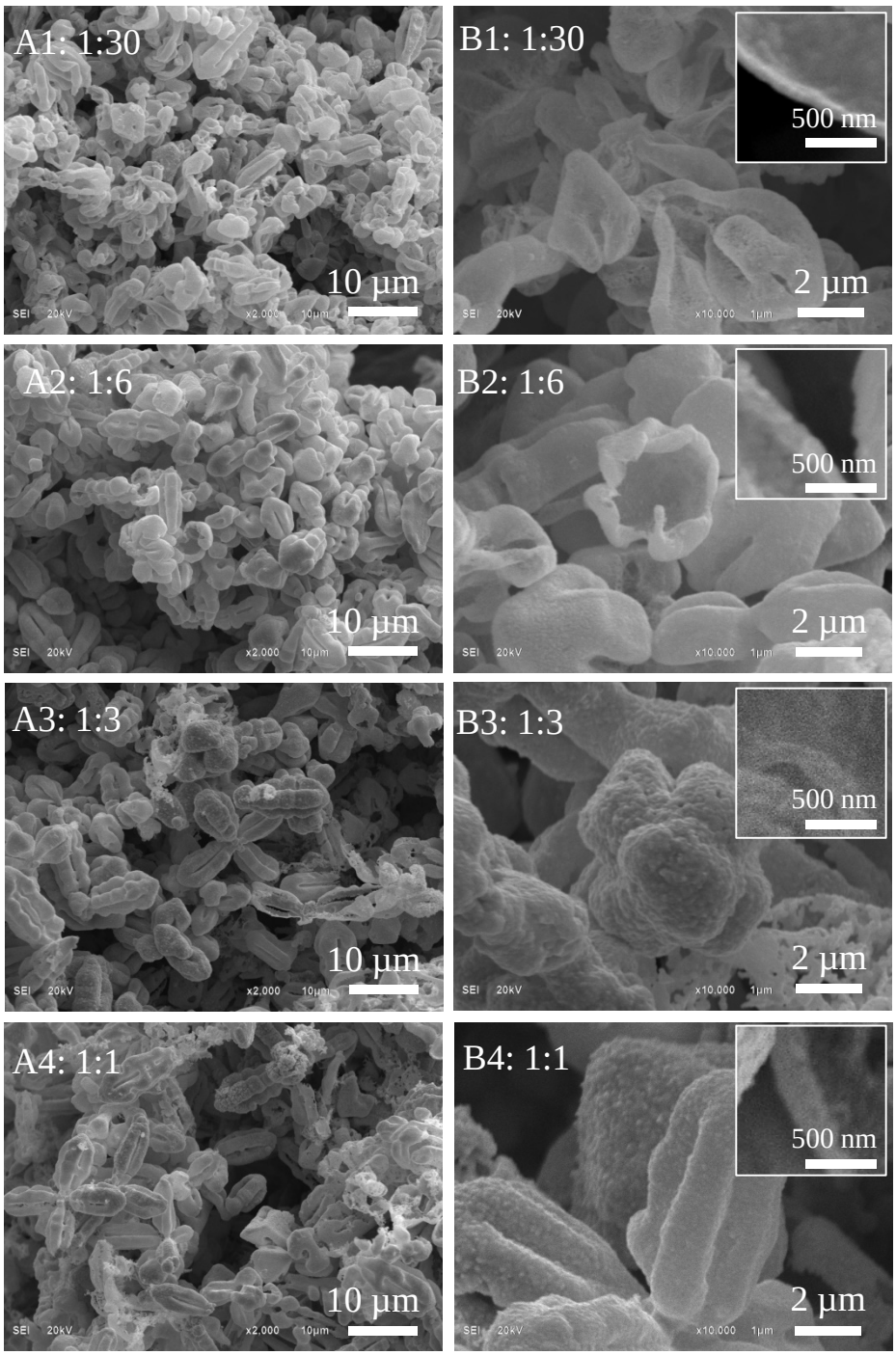

Fig. S5 SEM micrographs of HL-6pAuMSs synthesized using saturated NaCl solution as a galvanic replacement media with different mole ratio of Au^{3+}:Ag concentrations (A1) 1:30, (A2) 1:6, (A3) 1:3 and (A4) 1:1. The corresponding high magnification images of A1−A4 are shown in B1−B4. The inset SEM micrographs show the wall thickness of HL-6pMSs.

Table S3: Elemental composition determined by EDS technique of the microstructures galvanized using different Au^{3+} concentrations and different washing steps.

Au^{3+}:Ag	Washing step	Atomic content (%Atom)		
		Au	Ag	Cl
1 : 30	5 M NH_4OH	4.61 ± 0.03	94.92 ± 0.00	0.47 ± 0.41
	65% HNO_3	95.21 ± 0.00	4.67 ± 0.11	0.12 ± 3.84
1 : 6	5 M NH_4OH	23.02 ± 0.01	76.09 ± 0.00	0.89 ± 0.22
	65% HNO_3	93.39 ± 0.00	6.61 ± 0.06	N.D.
1 : 3	5 M NH_4OH	70.72 ± 0.01	28.28 ± 0.03	1.01 ± 0.72
	65% HNO_3	93.09 ± 0.01	6.44 ± 0.27	0.47 ± 3.29
1 : 1	5 M NH_4OH	93.17 ± 0.01	6.18 ± 0.12	0.65 ± 1.05
	65% HNO_3	94.71 ± 0.01	4.82 ± 0.27	0.47 ± 3.29

Note: N.D. represents “not detected”.

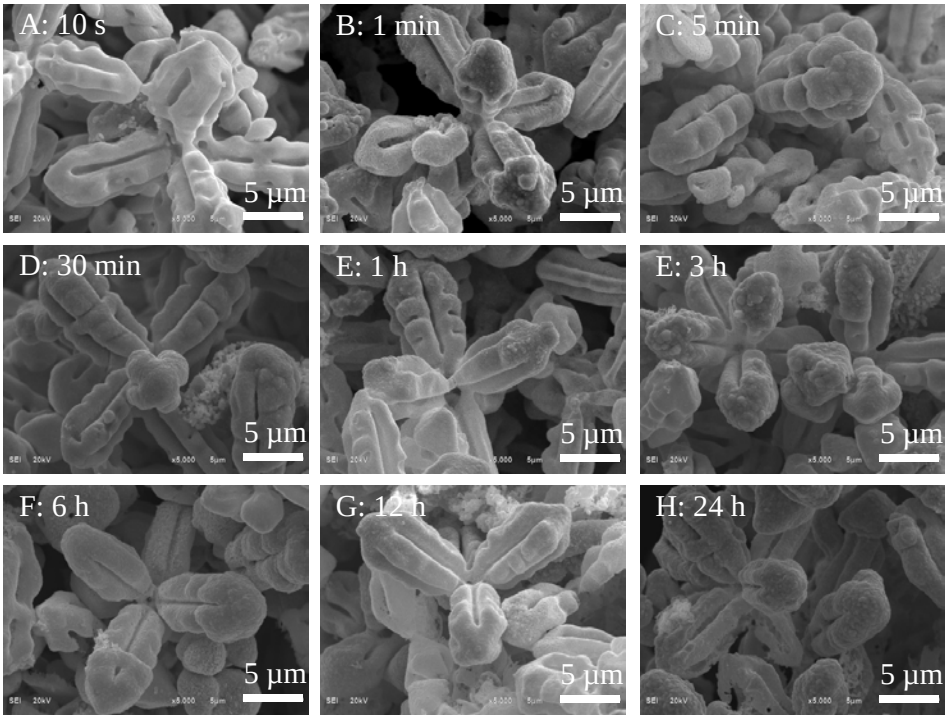

Fig. S6 The time dependent structural evolution of HL-6pAuMSs synthesized under the condition of saturated NaCl as a media, $[Au^{3+}]$ = 25 mM, mole ratio of Au^{3+}:Ag = 1:1. The scale bars are 5 µm.

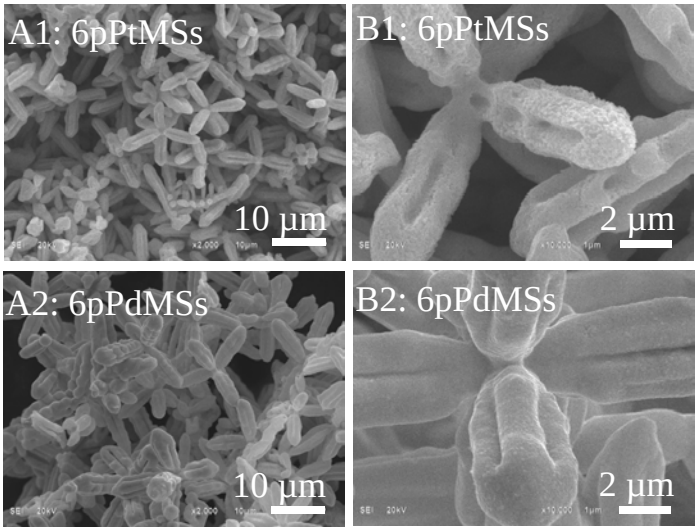

Fig. S7 SEM micrographs of microstructures galvanically replaced with 25 mM (A1) $[PtCl_4]^{2-}$ and (A2) $[PdCl_4]^{2-}$ for 24 hours. All samples were synthesized using saturated NaCl solution as a galvanic replacement media with mole ratio of precious metal:Ag of 1:1. The corresponding high magnification images of A1 and A2 are shown in B1 and B2.

Table S4: Elemental composition determined by EDS technique of the microstructures galvanically replaced using $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$ after washing.

Precious metal	Washing step	Atomic content (%Atom)		
		Precious metal	Ag	Cl
Pt	DI water	17.64 ± 0.01	45.62 ± 0.01	36.75 ± 0.01
	5 M NH_4OH	47.53 ± 0.00	50.94 ± 0.00	1.54 ± 0.15
	65% HNO_3	93.20 ± 0.00	6.80 ± 0.06	N.D.
Pd	DI water	29.50 ± 0.02	54.16 ± 0.01	16.34 ± 0.04
	5 M NH_4OH	42.86 ± 0.03	56.34 ± 0.02	0.81± 1.39
	65% HNO_3	N.A.	N.A.	N.A.

Note: N.D. represents “not detected”

N.A. represents “not analyzed” due to the dissolution of Pd metal in HNO_3.

Table S5: Elemental composition determined by EDS technique of the microstructures galvanically replaced using different np-AgMSs morphologies after washing with NH_4OH and HNO_3.

Morphology of Ag template	Atomic content (%Atom)		
	Au	**Ag**	**Cl**
np-6pAgMSs	97.21 ± 0.00	2.64 ± 0.11	0.15 ± 1.68
np-8pAgMSs	97.62 ± 0.01	1.71 ± 0.56	0.67 ± 1.26
np-CoAgMSs	93.63 ± 0.00	5.84 ± 0.08	0.53 ± 0.74
np-OhAgMSs	93.84 ± 0.00	5.46 ± 0.11	0.69 ± 0.78

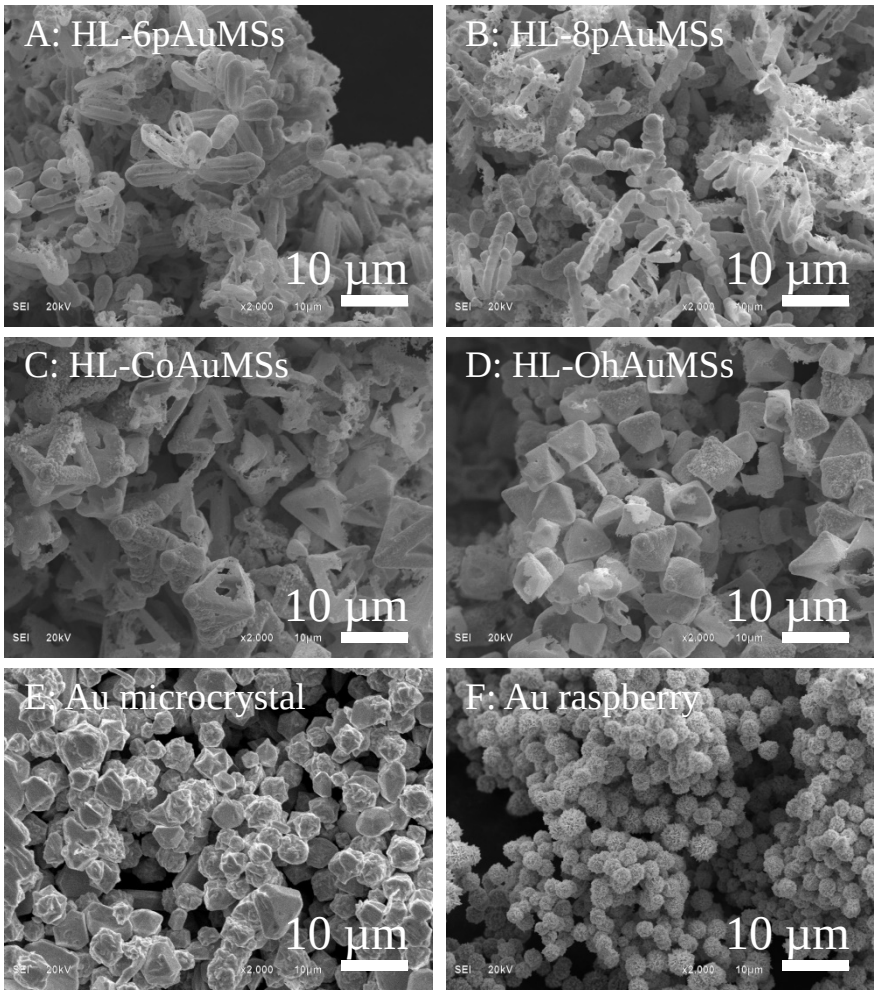

Fig. S8 SEM micrographs of Au microstructures employed as catalysts for the catalytic reduction of *p*-nitrophenol by $NaBH_4$ (A) HL-6pAuMSs, (B) HL-8pAuMSs, (C) HL-CoAuMSs, (D) HL-OHAuMSs, (E) Au microcrystals and (F) raspberry-like Au microspheres.

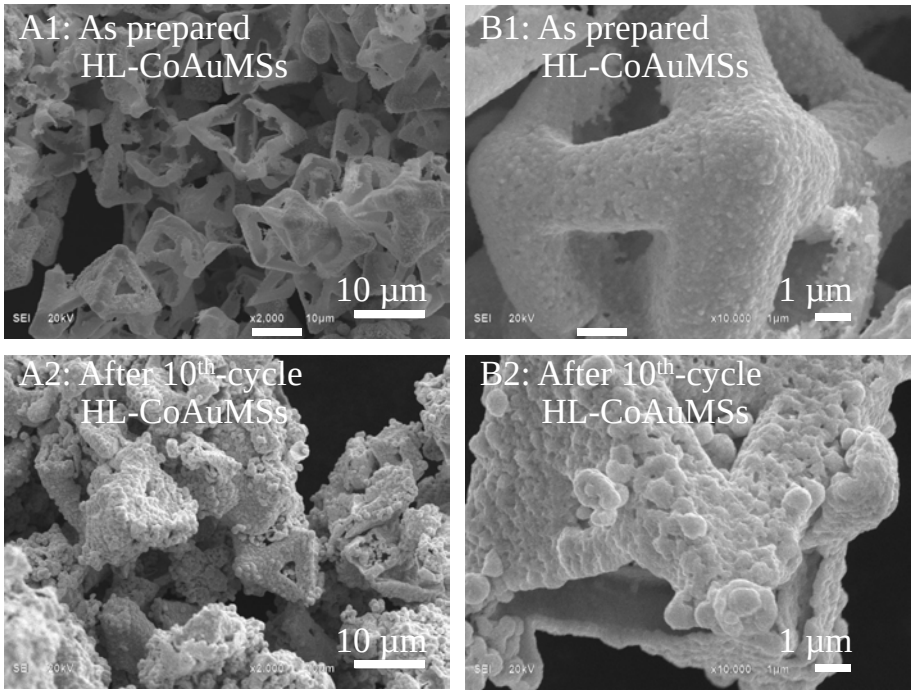

Fig. S9 SEM micrographs of (A1) as-prepared HL-CoAuMSs and (A2) HL-CoAuMSs after 10^{th} -cycle of the catalytic reduction. The corresponding high magnification images of A1 and A2 are shown in B1 and B2.