

Simultaneous Tunable Structure and Composition of PtAg Alloyed Nanocrystals as Superior Catalysts

Caihong Fang^{*†}, Jun Zhao[‡], Guili Zhao, Long Kuai, and Baoyou Geng^{*}

College of Chemistry and Materials Science, The Key Laboratory of Functional Molecular Solids,
Ministry of Education, Anhui Laboratory of Molecular-Based Materials, Anhui Normal University
Wuhu in Anhui Province 241000 (China)

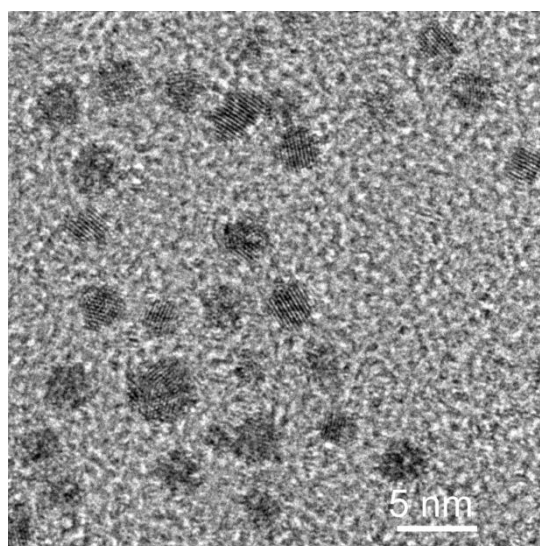


Fig. S1 TEM images of the Pt-nanoparticles seeds.

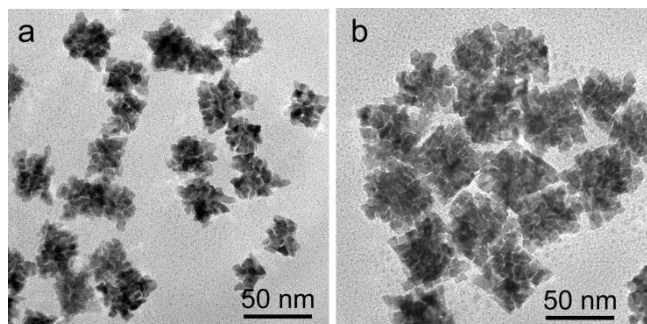


Fig. S2 TEM images of the porous PtAg NCs grown from grown solution with different ratios of AgNO_3 to H_2PtCl_6 that are controlled to 1:6.6, and 1:3.3, respectively.

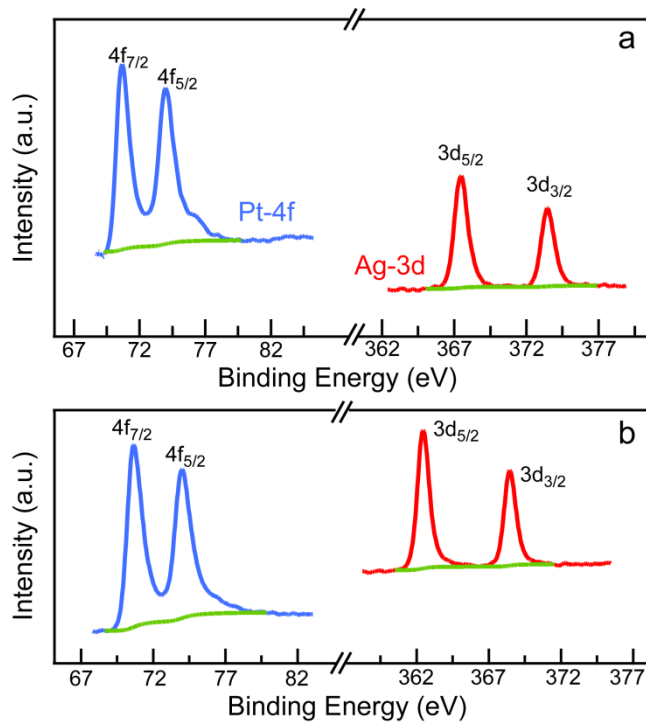


Fig. S3 (a,b) XPS spectra of Pt 4f and Ag 3d of the as-prepared PtAg multipetals and multioctahedral NCs, respectively. Pt 4f displays two strong peaks at 70.85 eV (Pt $4f_{7/2}$) and 74.15 eV (Pt $4f_{5/2}$) and Ag 3d show two peaks at 367.5 eV (Ag $3d_{5/2}$) and 373.45 eV (Ag $3d_{3/2}$) for PtAg multipetals. Pt $4f_{7/2}$ and Pt $4f_{5/2}$ of PtAg multioctahedra located at 70.65 (Pt $4f_{7/2}$) and 74 eV (Pt $4f_{5/2}$), respectively. Ag 3d of PtAg multioctahedra have two strong peaks at 70.45 eV (Ag $3d_{5/2}$) and 76.45 eV (Ag $3d_{3/2}$).

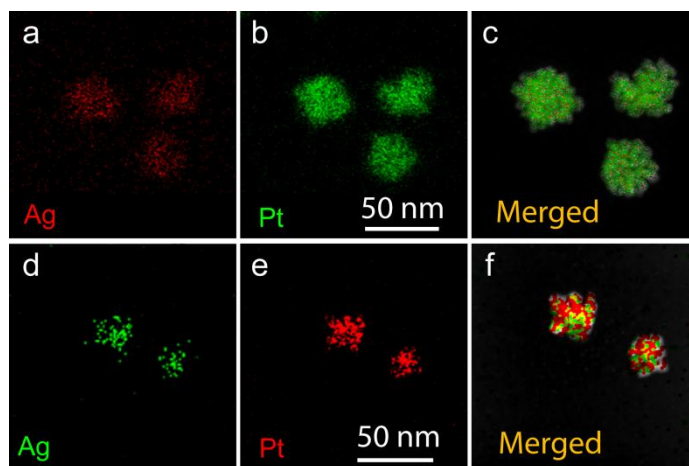


Fig. S4 Elemental mapping results of Pt₇₆Ag₂₄ (upper row) and Pt₆₆Ag₃₄ (bottom row) NCs.

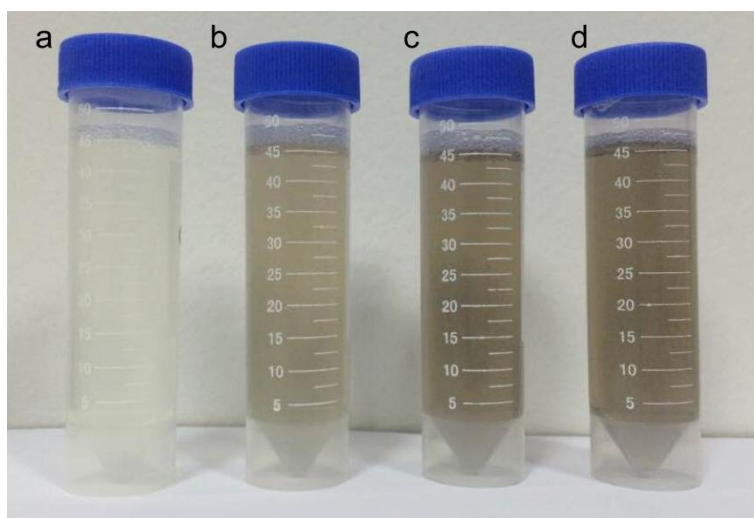


Fig. S5 Digital photograph of the resultant solution without (a) and with (b, c, and d) the addition of AgNO_3 in growth solution. 40, 400, and 1000 μL AgNO_3 (0.01 M) was respectively added in growth solution in b, c, and d with the pH values of 2.15.

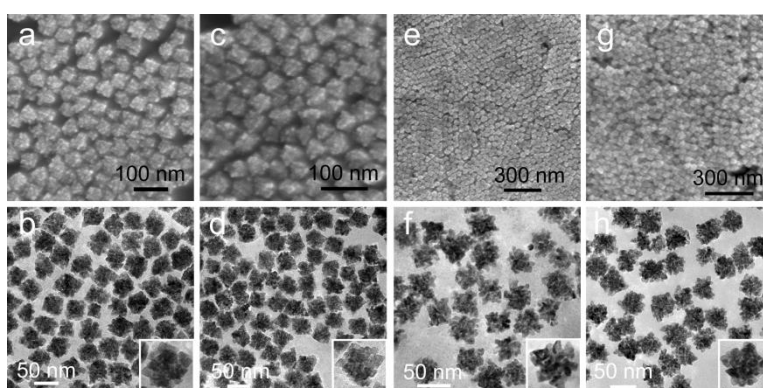


Fig. S6 Porous PtAg alloyed NCs produced by varying the pH values of the growth solution to be 1.95 (a,b), 2.44 (c,d), 3.47 (e,f) and 10.82 (g,h), respectively. (a, c, e and g) SEM and (b, d, f, and h) TEM images of the porous PtAg alloyed NCs obtained at different pH values. Scar bar in insert of b, d, e, and g is 10 nm. The average size were measured to be 47.6 ± 4.1 , 51.5 ± 4.6 , 53.2 ± 5.9 and 50.0 ± 5.2 , respectively. The samples were obtained by the addition of 400 μL AgNO_3 (0.01M).

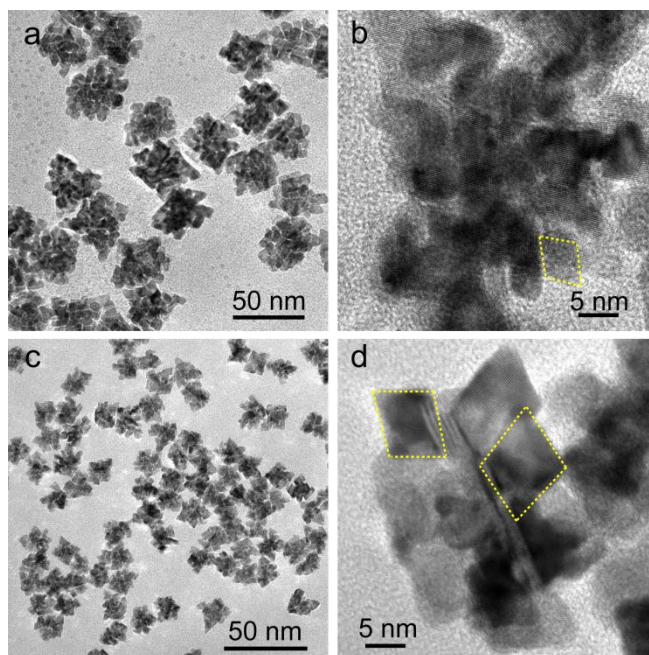


Fig. S7 Porous PtAg alloyed NCs produced by varying the amount of seed solution to be 500 μL (a,b) and 1000 μL (c,d), respectively. (a,c) TEM and (b,d) HRTEM images of the porous PtAg alloyed NCs respectively. The average size were measured to be 41.8 ± 4.1 and 34.5 ± 2.7 nm, respectively. The yellow lines indicate the margin of the porous structures in b, d, and f. We should declare that the samples were obtained by the addition of 400 μL AgNO_3 (0.01M).

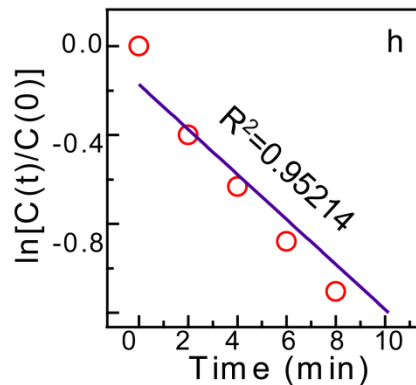
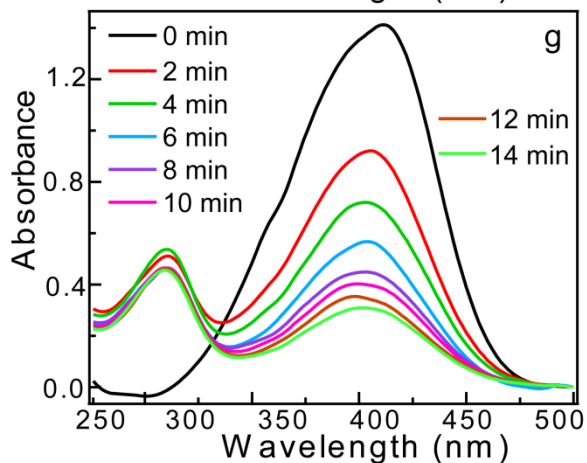
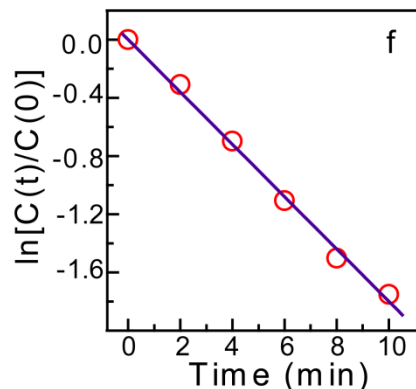
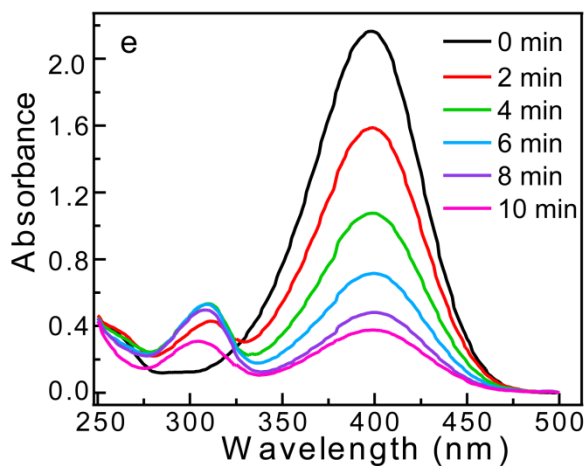
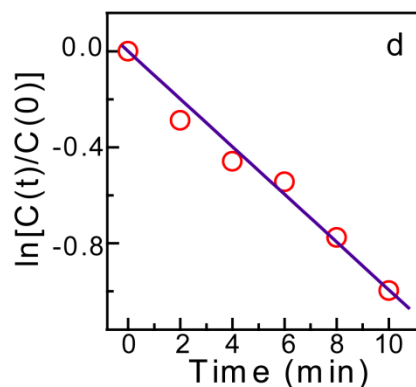
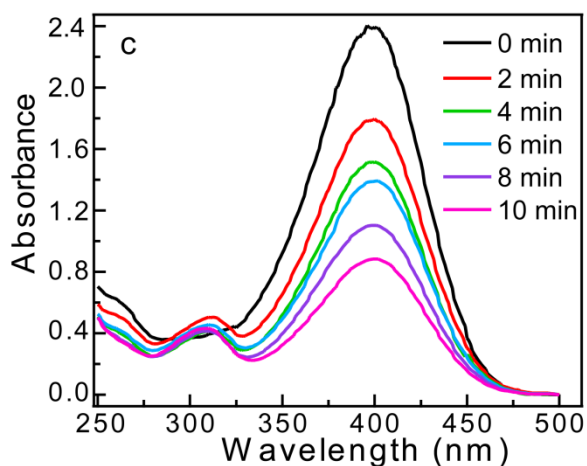
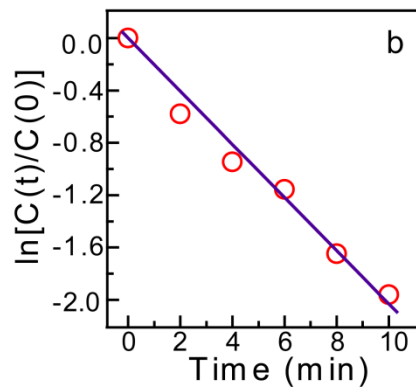
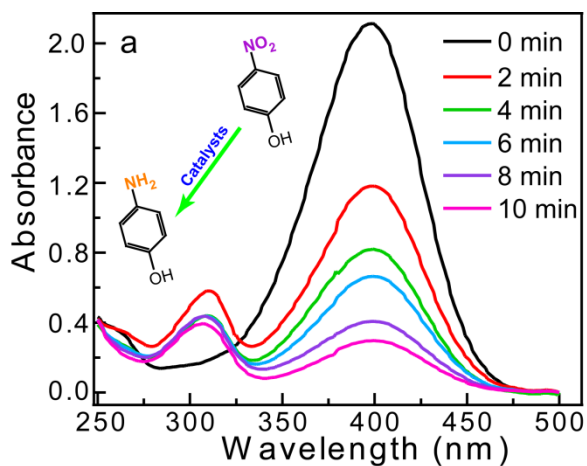


Fig. S8 Time-dependent absorption spectra and plots of $\ln[C(t)/C(0)]$ against the reaction time of the reduction of 4-NP to 4-AP using Pt₇₀Ag₃₀ (a and b), Pt₇₆Ag₂₄ (c and d), Pt₆₆Ag₃₄ NCs (e and f), and Pt black without support (1×10^{-4} M) (g and h) as the catalysts, respectively. The experiments were carried out in aqueous mixture of 4-NP (0.01 M, 30 μ L) and ice-cold NaBH₄ (0.5 M, 0.5 mL), PtAg alloyed catalysts, and DI water (2 mL) in a quartz cuvette with 1-cm optical length. The catalysts were dispersed into water in advanced. The cuvette was then immediately transferred into a spectrophotometer. The absorbance spectra were then monitored as a function of reaction time. The concentration of Pt loading of the added Pt₇₆Ag₂₄, Pt₇₀Ag₃₀, and Pt₆₆Ag₃₄ alloyed catalysts in cuvette was estimated from ICP-AES measurements to be 4.5×10^{-5} , 9.9×10^{-6} , and 1.1×10^{-5} M, respectively.

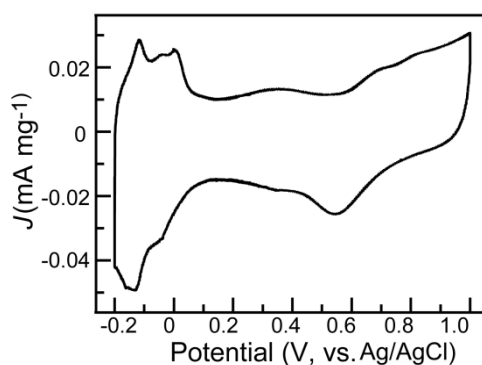


Fig. S9 CV curves for commercial Pt/C in N₂-saturated solution of H₂SO₄ (0.5 M) at a scanning rate of 20 mV·S⁻¹.

Table S1 Detailed constituent of the ink suspension and the mass loading in working electrode for various catalysts. The mass of catalysts in this table were estimated from ICP-AES tests.

	catalyst	XC-72 (mg)	water (μ L)	DMF (μ L)	Nafion(μ L)	Loading mass onto eletrodes(μ g)
Pt/C (20%)	0.1 mg	0.4	800	385	15	2.5
Pt ₇₆ Ag ₃₄	397 μ L	0.4	0.0	195	8.0	1.33
Pt ₇₀ Ag ₃₀	110 μ L	0.6	0.0	84.6	5.0	5.0
Pt ₆₆ Ag ₃₄	95.8 μ L	0.8	224.2	154	6.0	2.08