Electronic Supplementary Information (ESI) for

Morphological control and evolution of octahedral and truncated trisoctahedral Pt-Au alloy nanocrystals under microwave irradiation

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Experimental details

Reagent. Tetraethylene glycol (TEG) was purchased from Acros Chemicals Reagent Co., $HAuCl_4$ (99.8%), H_2PtCl_6 (98%), PVP (average molecular weight, M_w =30000) and KI were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used as received without further purification.

Synthesis. In a typical synthesis of truncated trisoctahedral Pt-Au alloy nanocrystals, 50 mg of PVP and 100 mg of KI were dissolved in 8 mL of TEG with rigorous stirring in a 50-mL round-bottomed flask at room temperature. Then, 1 mL of 0.01 M $HAuCl_4$ and 1 mL of 0.01 M H_2PtCl_6 solution in TEG were added. The final volume was 10mL. The molar ratio of the total metal species to PVP and KI was 1/15/30, and the total concentration of the Pt and Au precursors was 2 mM with a molar ratio of $H_2PtCl_6/HAuCl_4$ of 1/1. After stirring for 45 min, the resulting transparent orange-yellow solution was then put into a modified domestic microwave oven (Galanz, 1000W) and heated for 140 s with 100% output of the power and the earthy yellow colloids were obtained. After being cooled to room temperature, the resultant homogeneous colloids were separated by centrifugation at 15000 rpm for 15 min, washed several times with a mixed solvent of ethanol/acetone/water. The final products were re-dispersed in ethanol for characterization.

Under the same other conditions, similar experiments were conducted by altering the molar ratio of $H_2PtCl_6/HAuCl_4$ to 1/3 or 3/1, while the total concentration of Pt and Au precursor was maintained at 2 mM.

The microwave oven was modified without changing the power as described as follows: a water-cooled condenser outside the oven's cavity was connected by a glass joint of a glass round-bottomed flask set inside. A teflon stirrer was set in the flask and was driven by a motor. The power output was adjusted by the microwave machine with a routine on-off manner and the temperature didn't have to be controlled.

Characterization. Transmission electron microscopy (TEM) measurements were conducted on a FEI Tecnai G^2 20 transmission electron microscopy operated at 200 kV. High-resolution TEM (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray (EDX) analyses were performed using a JEM-2100 field emission transmission electron microscope (JEOL, Tokyo, Japan) operated at 200 kV. Diffractograms of HRTEM were obtained by

fast Fourier transformation. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer employing Cu Kα radiation with 40 kV and 50 mA. Ultraviolet-visible (UV-vis) absorption spectra were measured on a Lambda BIO35 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurement was conducted on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg *K*α radiation under a vacuum of 8×10^{-7} Pa. All binding energy values were determined with reference to carbon, C_{1s} = 284.6 eV.

Electrochemical Measurements. Cyclic voltammetry (CV) experiments were conducted using a CHI660E electrochemical workstation which was interfaced for data acquisition and analysis. All experiments were carried out at room temperature. The modified working electrodes were fabricated by depositing ethanol dispersion of the octahedral or truncated trisoctahedral Pt-Au alloy nanocrystals onto a glassy carbon electrode followed by natural drying. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. For the electro-oxidation of methanol, the cyclic voltammograms were recorded at a sweep rate of 50 $mV\cdot s^{-1}$ between -0.25 and 1.0 V in 0.1 M $HClO_4$ + 0.1 M CH_3OH. Before cyclic voltammetry measurements, 2 to 20 cycles of potential sweeps between -0.25 and 1.2 V were applied to clean the surfaces of the modified working electrodes in-situ. Both positive and negative CV scans were performed on each sample. The arrows in the CV curves indicated the scanning direction. The same electrochemical experiment was conducted for commercial Pt black. The chronoamperometry (CA) tests for the various catalysts were conducted in 0.1 M $HClO_4$ + 0.1 M CH_3OH at 0.62 V *vs* SCE.

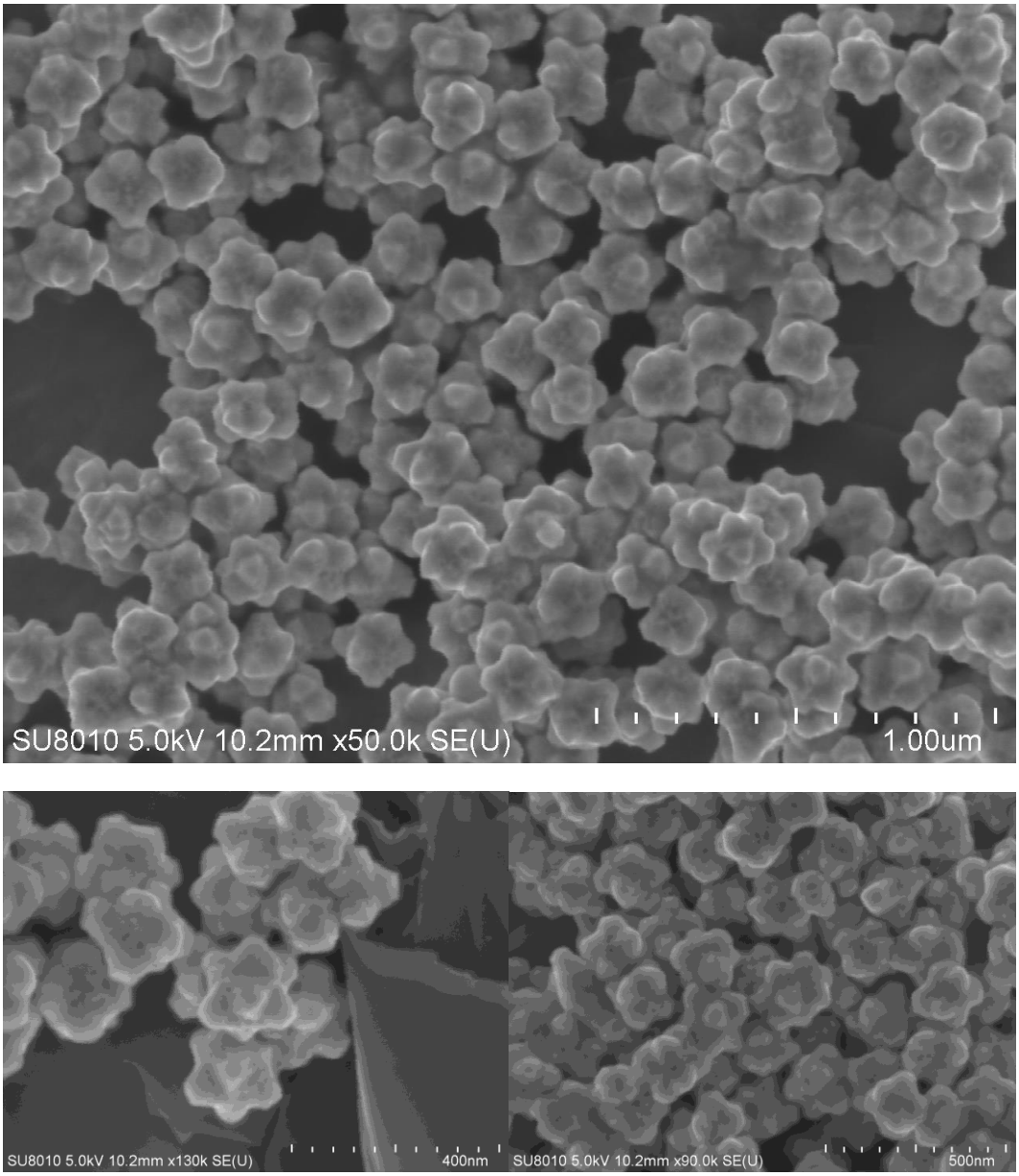


Fig. S1 SEM images of the as-prepared Pt-Au alloy truncated trisoctahedra.

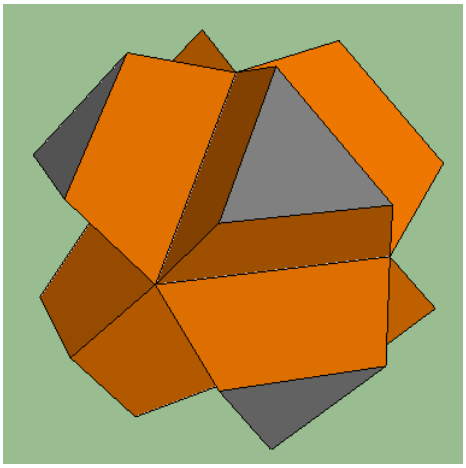


Fig. S2 The geometrical model of a truncated trisoctahedraon.

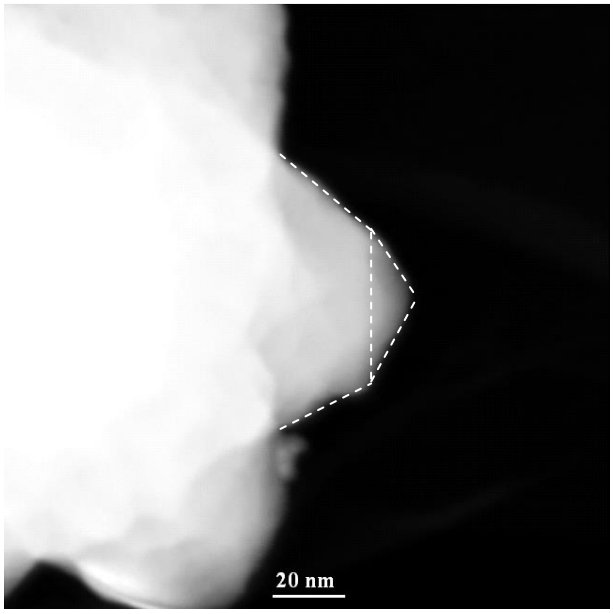


Fig. S3 HAADT-STEM image of one pod of a single Pt-Au alloy truncated trisoctahedral nanocrystal.

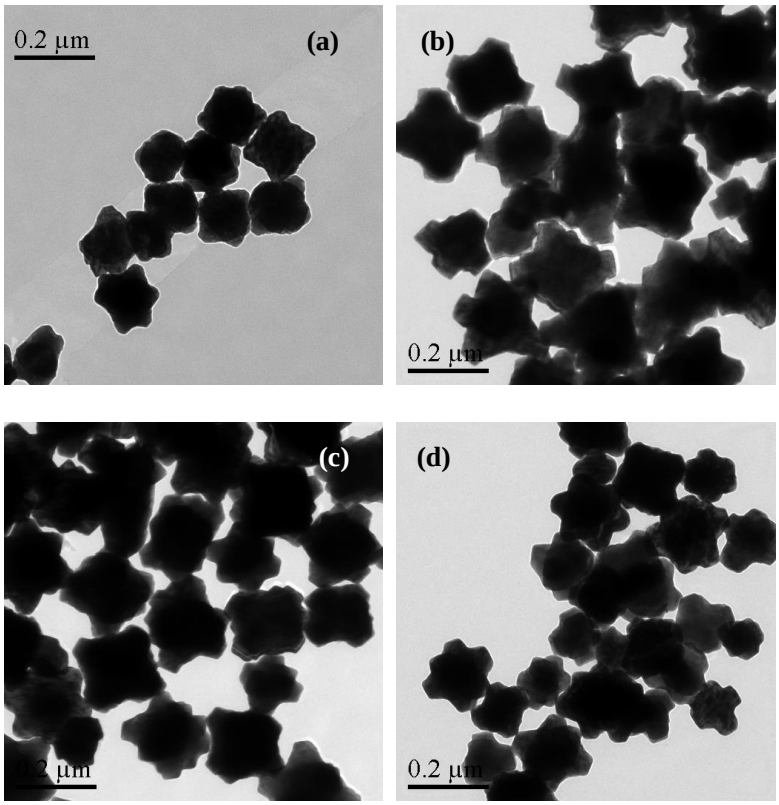


Fig. S4 TEM images of nanoparticles collected from the reaction system with the same conditions but different irradiation time. (a) 100 s; (b) 120 s; (c) 160 s; (d) 180 s.

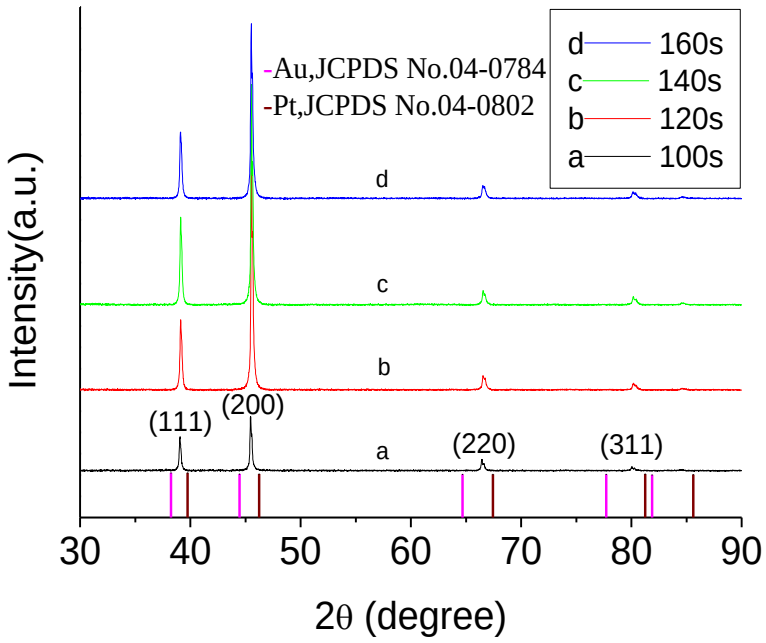
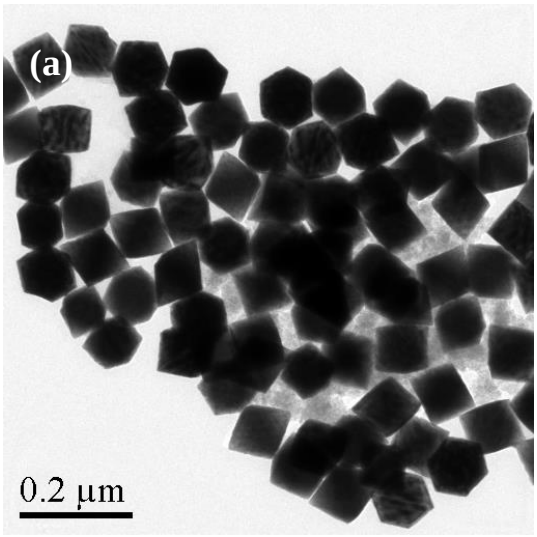


Fig. S5 XRD patterns of the samples collected from the reaction system with 1/1 of $H_2PtCl_6/HAuCl_4$ molar ratio at different irradiation time. (a) 100 s; (b) 120 s; (c) 140 s; (d) 160 s.

(a) **(b)**

Table S1 2θ values corresponding to XRD patterns of the samples at different time

Diffraction peaks		(111)	(200)	(220)	(311)
Diffraction angle			2θ(°)		
Au (JCPDS No. 04-0784)		38.185	44.393	64.578	77.549
Pt (JCPDS No. 04-0802)		39.765	46.244	67.456	81.289
Pt-Au particles	100 s	39.07	45.44	66.43	80.05
	120 s	39.13	45.44	66.53	80.18
	140 s	39.13	45.44	66.52	80.16
	160 s	39.13	45.44	66.53	80.15



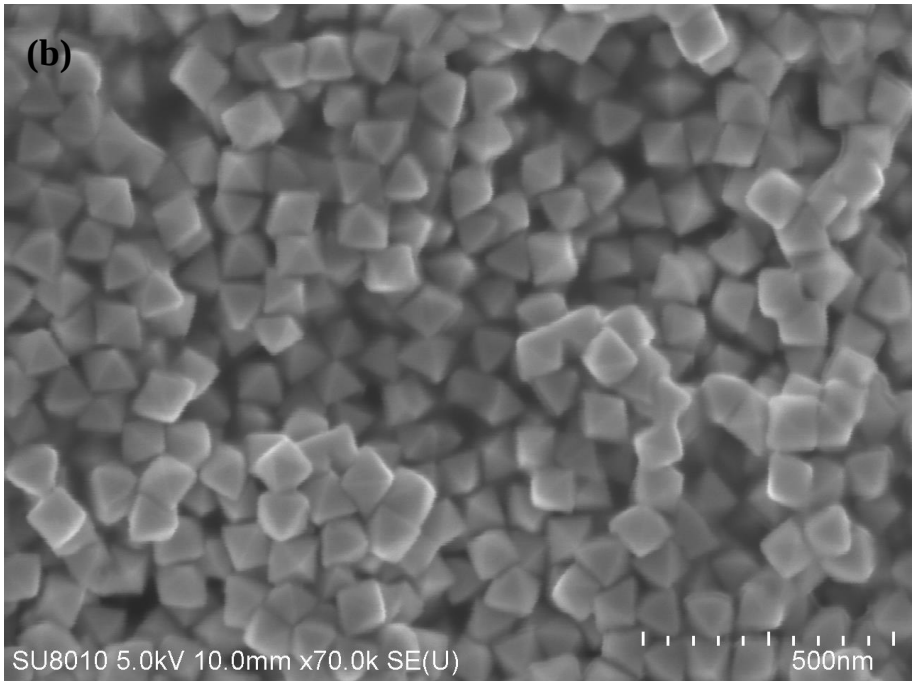


Fig. S6 TEM (a) and SEM (b) images of the as-prepared octahedral Pt-Au alloy nanocrystals in the case of reaction with an $H_2PtCl_6/HAuCl_4$ molar ratio of 1/3.

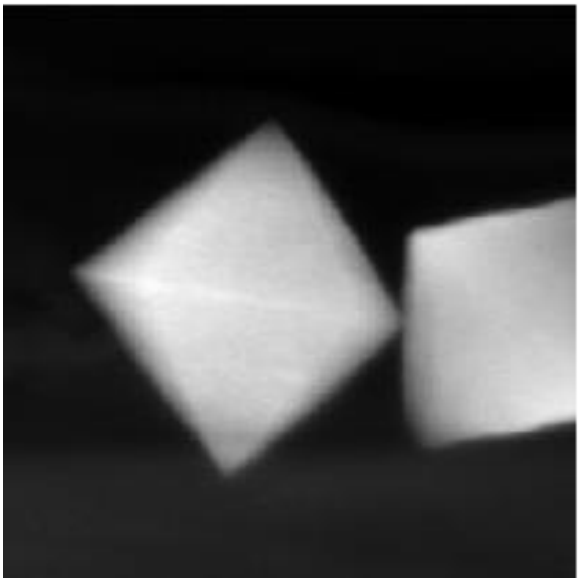


Fig. S7 HAADT-STEM image of the as-prepared Pt-Au alloy octahedral nanocrystals.

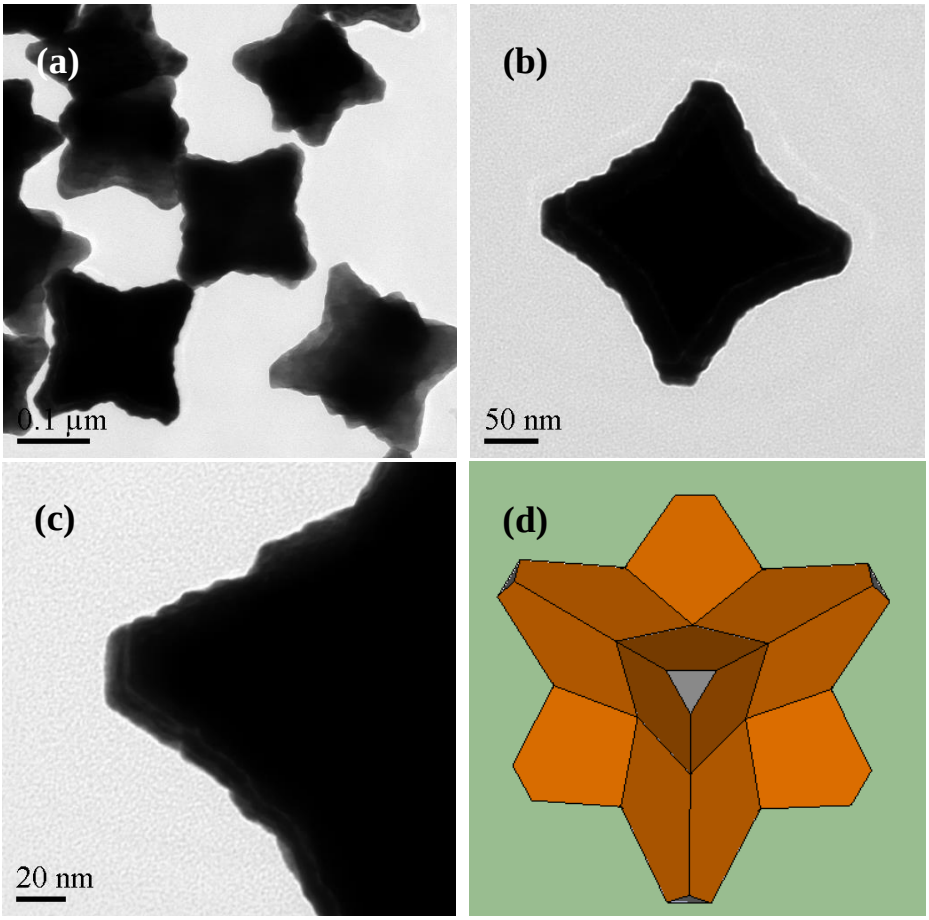


Fig. S8 (a) Typical TEM image of Pt-Au truncated octapods in the case of reaction with 3/1 of $H_2PtCl_6/HAuCl_4$ molar ratio. (b) Enlarged TEM of a single Pt-Au truncated octapod. (c) One pod of a single Pt-Au alloy truncated octapod nanocrystal. (d) The geometric model of a truncated octapod.

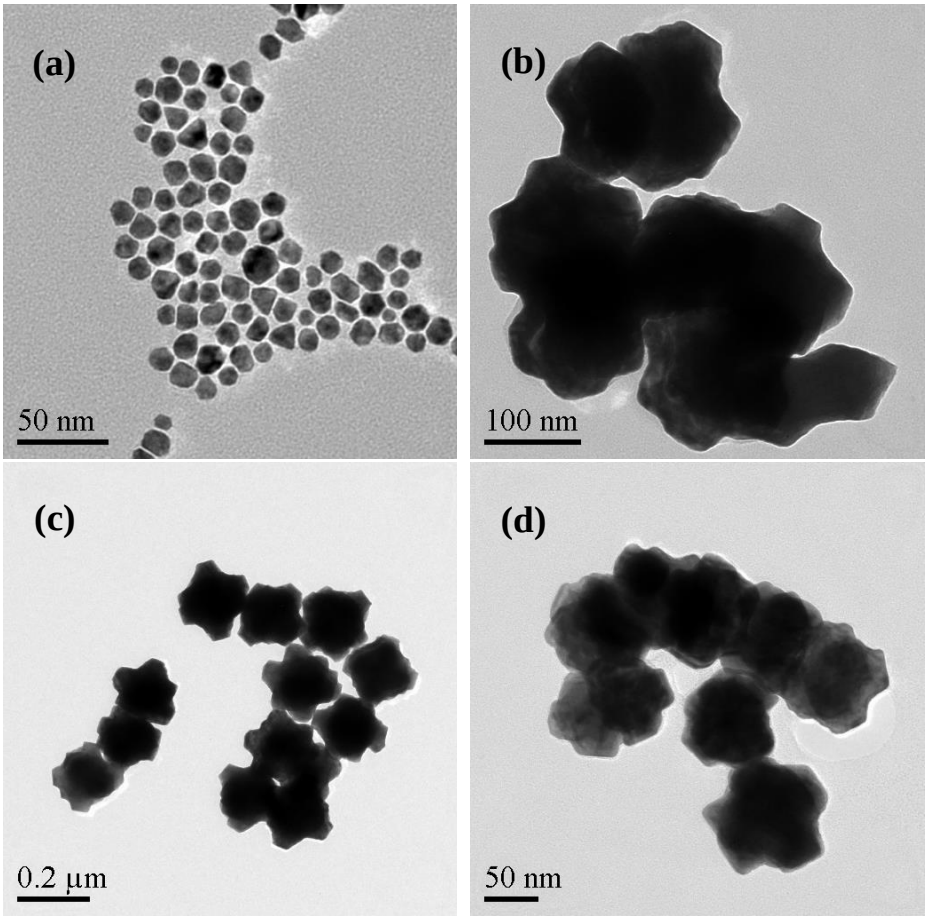


Fig. S9 TEM images of nanoparticles collected from the reactions in a molar ratio of H_2PtCl_6/$HAuCl_4$ of 1/1 with different amount of KI. (a) 0 mg; (b) 50 mg; (c) 100 mg; (d) 200 mg.

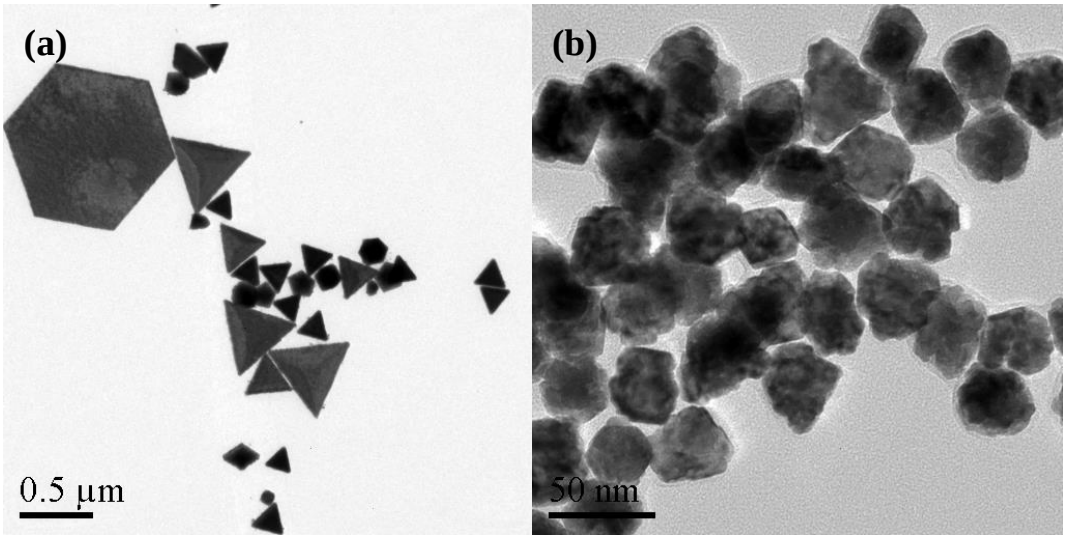


Fig. S10 TEM images of nanoparticles obtained with using an equal amount of KCl (a) or KBr (b) instead of KI under the same conditions.

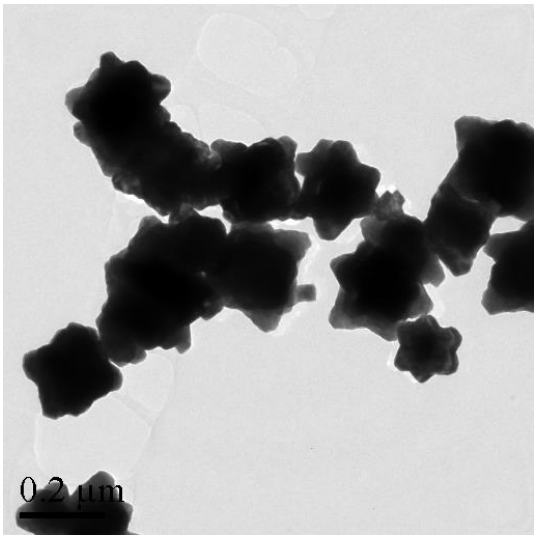


Fig. S11 TEM image of nanoparticles obtained in absence of PVP.

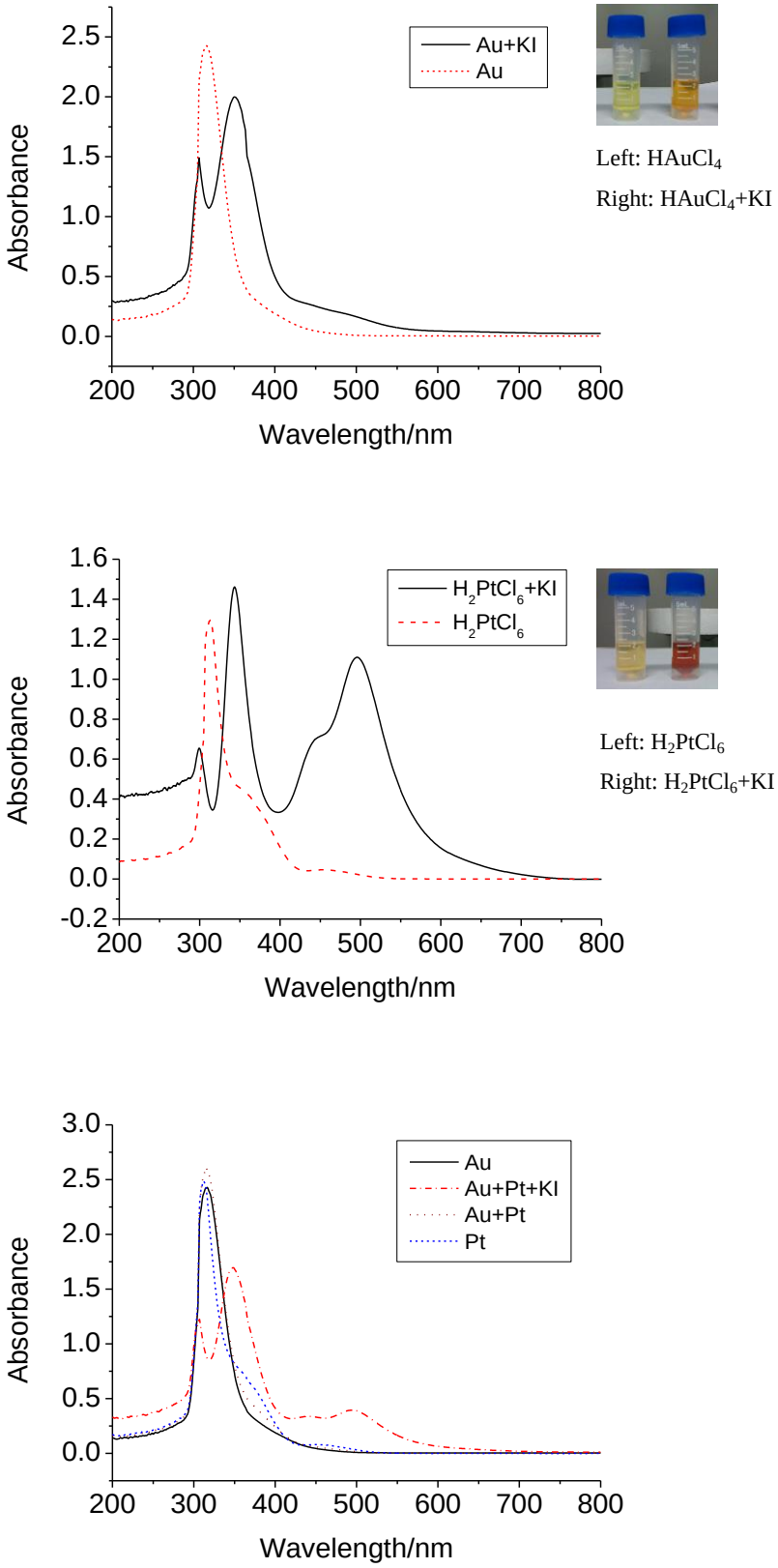


Fig. 12 UV-vis absorption spectra of Pt and Au species in different system in the presence or absence of KI.

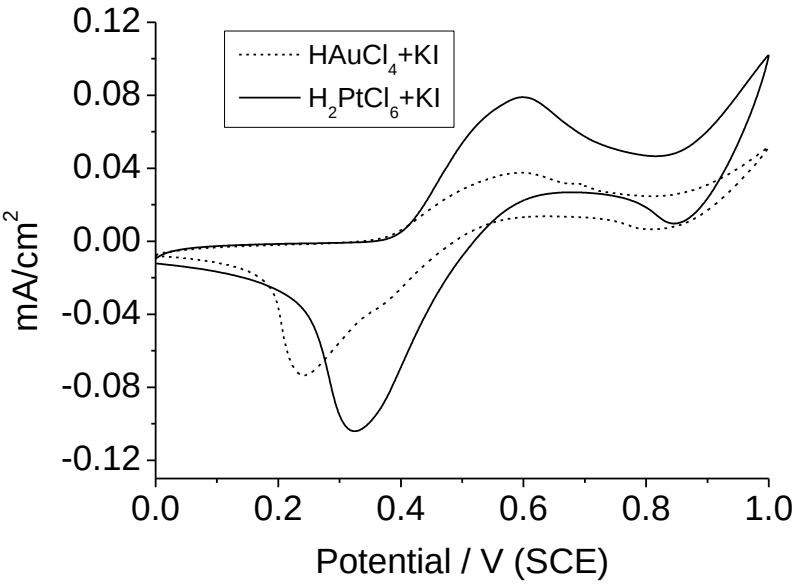


Fig. S13 CV curves of 0.001 M H_2PtCl_6 and 0.001 M $HAuCl_4$ solution in the presence of 0.03 M KI with the cyclic potential sweeping between 0 and 1.0 V at a sweep rate of 0.01mV·s^{-1}.

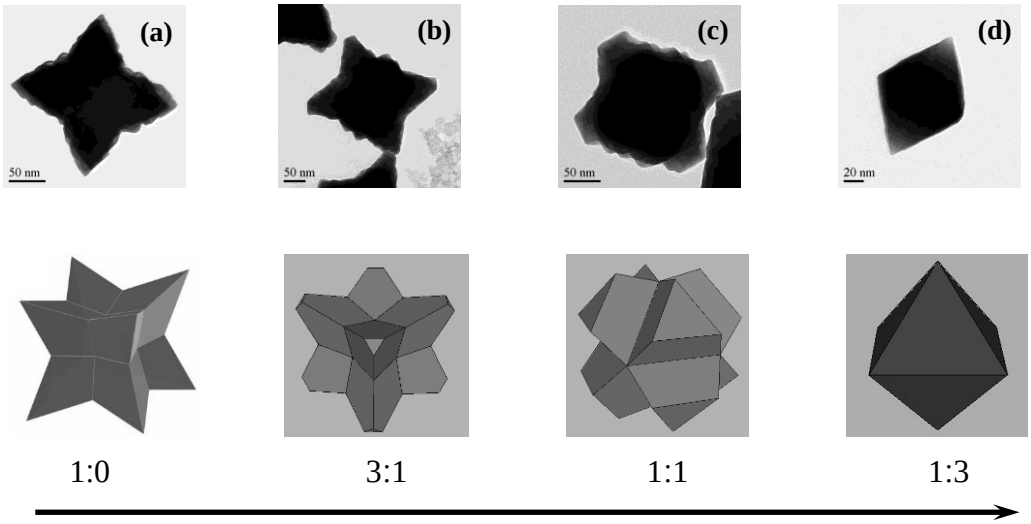


Fig. S14 The dependence of morphology evolution of Pt-Au nanocrystal upon the molar ratio of H_2PtCl_6/$HAuCl_4$. (a) 1:0; (b) 3:1; (c) 1:1; (d) 1:3.

Table S2 Detailed data on electrocatalytic oxidation of methanol on the as-prepared Pt-Au alloy truncated trisoctahedra, Pt-Au alloy octahedra and commercial Pt black. The geometric area of the glassy carbon electrode used for the deposition of the catalysts is 0.196 cm^2. I_f: current density for the forward scan, I_b: current density for the backward scan.

Catalysts	Catalyst loading (μg)	Specific ECSA(m^2/g)	area I_f (mA/cm^2)	area I_b (mA/cm^2)	I_f /I_b
Pt-Au alloy truncated trisoctahedra	7.80	1.82	1.09	0.85	1.28
Pt-Au alloy octahedra	7.83	3.76	0.82	0.89	0.92
Pt black	5	16	0.45	0.37	1.21

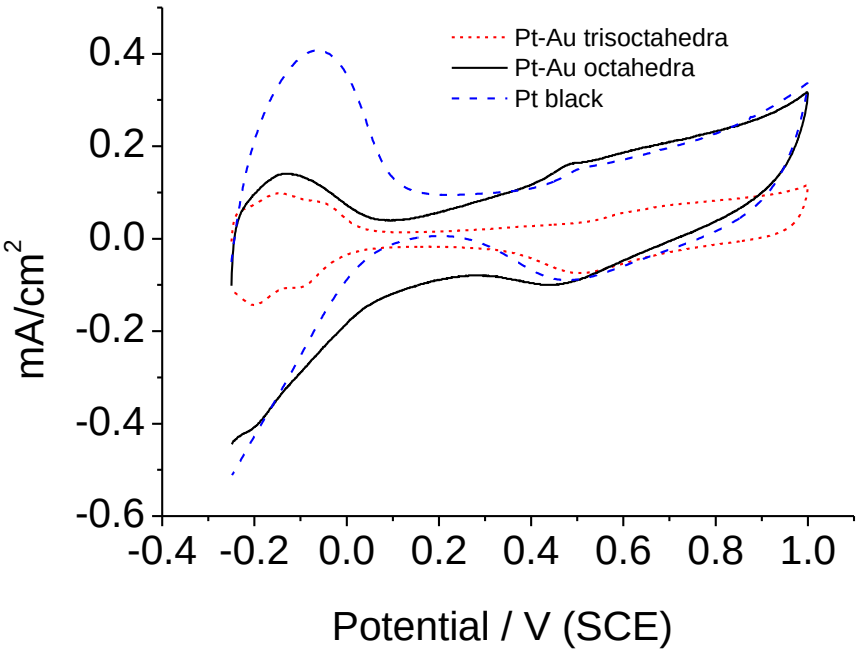


Fig. S15 CVs in 0.1 M $HClO_4$ of the as-prepared Pt-Au alloy truncated trisoctahedra, Pt-Au alloy octahedra and Pt black, respectively. Scan rate = 250 $mV \cdot s^{-1}$.

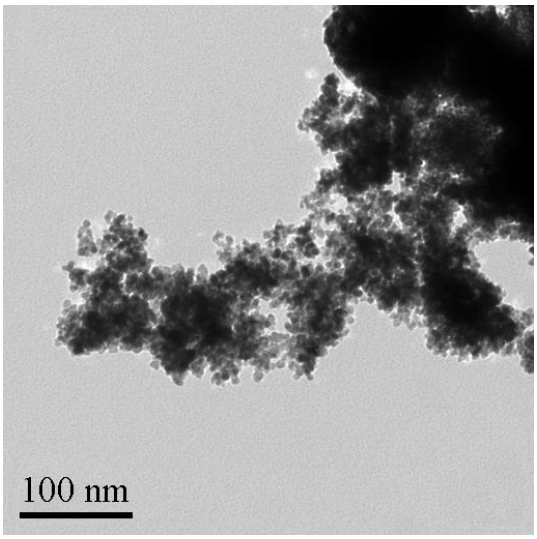


Fig. S16 TEM image of Pt black.