Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Facile synthesis of Au-Pt bimetallic nanocomplexes for direct oxidation of methanol and formic acid

Ruigang Xie, Muzi Chen, Jiaqing Wang, Sujuan Mei, Yue Pan*, Hongwei Gu*

Experimental Section

Chemicals and Materials: Oleylamine (OAm, >70%), were all purchased from Tokyo Chemical Industry Co. Ltd, Shanghai. Platinum acetylacetonate ($Pt(acac)_2$, 99.99%), octadecene (90%) and Nafion (5% w/w solution) were all obtained from Alfa Aesar. Formic acid(88%), oleic acid (OA), isopropanol (99.5%), $HAuCl_4{\cdot}4H_2O$, anhydrous ethanol, anhydrous methanol, concentrated sulfuric acid and hexane were purchased from Sinopharm Chemical Reagent Co., Ltd. 20 wt.% JM-Pt/C was purchased from Shanghai Hesen Electrical Co., Ltd. High purity hydrogen and nitrogen were purchased from Suzhou Jinhong gas Co., Ltd. All the chemicals were used as received without further purification.

Synthesis of 8 nm Au NPs: 0.302 g $HAuCl_4{\bullet}4H_2O$ and 30 mL oleylamine were mixed in 100 mL three-necked flask. Then the mixture solution was heated to 80℃and left at this temperature for 5 hours before the reaction was cooled to room temperature. The products were washed at least three times with ethanol and centrifuged at 4000 rpm for 10 min and finally dispersed in 3 mL n-hexane for further use.

Synthesis of Au-Pt nanocomplexes (NCs): 1 mL Au NPs n-hexane solution, 0.5010 g $Pt(acac)_2$ and 30 mL oleylamine were mixed in 100 mL three-necked flask .The system was sparged with nitrogen with a needle and then hydrogen was introduced to the system. The mixture solution was heated to 90 °C slowly. Aliquots were taken from the system by a syringe at 80 °C, 90 °C and followed by interval 10min, 20min, 30 min, 1 h, 2 h, 5 h respectively. The products were washed at least three times with ethanol and centrifuged at 4000 rpm for 10 min and finally dispersed in hexane for further use.

Characterization: The morphology of the nanostructures were obtained by a transmission electron microscopy (TEM) (TecnaiG220, FEI, American) equipped with a Gatan CCD794 camera operated at 200 KV. The powder wide angle X-ray diffraction pattern (XRD) were recorded on an X`Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). UV-vis absorption spectra was obtained with the UV-2812 spectrophotometer (Hitachi,Japan). The composition of Au NPs-Pt NCs was analyzed by an inductively coupled plasma-mass spectroscopy (ICP-MS, Varian 710-ES).

Catalysts treatment for electrochemical application: The catalyst ink was prepared by mixing catalysts (5 mg), ultrapure water (4 mL), isopropanol (1 mL) and Nafion (25 μL, 5% w/w solution).

Electrochemical measurements: Electrochemical measurements were performed by using a CS310 electrochemical workstation (Wu Han Corrtest Instruments Co.,Ltd). A convention three-electrode cell was used including a saturated calomel electrode (SCE) as the reference electrode, a platinum foil as the counter electrode, and a modified glassy carbon electrode (GCE) as the working electrode. The effective area of the glass carbon electrode is 0.0707 cm^2.

Preparation of working electrode: The GCE was polished successively with 1.0, 0.3, and 0.05 μm alumina power until a shiny, mirrorlike surface was obtained, and rinsed with deionized water. The GCE was allowed to dry under nitrogen atmosphere. Then, 5 μL of the catalysts ink (1mg/mL) was pipetted on the electrode and dried at ambient condition for at least 3 h before electrochemical experiments.

Measurement of methanol oxidation reaction: All the catalyst electrodes were pre-treated in N_2-saturated 0.5 M H_2SO_4 aqueous solution by 30 cyclic potential sweeps between -0.25 V and 1.0 V in order to remove any surface contamination. CV curves were recorded in the range of potentials from -0.25 V to 1.0 V in N_2-saturated 0.5 M H_2SO_4 aqueous solution. CV and Linear sweep voltammogram (LSV) measurement of methanol oxidation reaction were carried out at the potential between 0.0 V to 1.0 V and 0.0 V to 0.6 V in N_2-saturated 0.5 M H_2SO_4 + 0.5 M CH_3OH solution, respectively. Chronoamperometric curves for methanol electrooxidation are investigated in N_2-saturated 0.5 M H_2SO_4/0.5 M CH_3OH aqueous solution at the constant potential of 0.5 V for 900 s. All electrochemical measurements were carried out at a scan rate of 50 mV/s and room temperature.

Measurement of formic acid oxidation reaction: All the catalyst electrodes were pre-treated in N_2-saturated 0.5 M H_2SO_4 aqueous solution by 30 cyclic potential sweeps between -0.25 V and 1.0 V in order to remove any surface contamination. CV curves were recorded in the range of potentials from -0.25 V to 1.0 V in N_2-saturated 0.5 M H_2SO_4 aqueous solution. CV and Linear sweep voltammogram (LSV) measurement of methanol oxidation reaction were carried out at the potential between -0.25 V to 1.0 V and 0.0 V to 0.6 V in N_2-saturated 0.5 M H_2SO_4/0.5 M HCOOH solution, respectively. Chronoamperometric curves for methanol electrooxidation are investigated in N_2-saturated 0.5 M H_2SO_4/0.5 M HCOOH aqueous solution at the constant potential of 0.65 V for 900 s. All electrochemical measurements were carried out at a scan rate of 50 mV/s and room temperature.

Table S1. Composition of Au-Pt NCs at different reaction time determined by inductively coupled plasma spectroscopy (ICP).

	Au (mg/L)	Pt (mg/L)	Au% (mass)	Pt% (mass)	Au/Pt (mol/mol)	Au/Pt (mass/mass)
80°C	1.1608	0.4402	0.7250	0.2750	211/18	27/11
90°C-0 min	7.0958	14.0392	0.3357	0.6642	1/2	47/93
90°C-10 min	3.4567	12.5194	0.2164	0.7836	3 /11	8/29
90°C-20 min	1.9555	8.2775	0.1911	0.8089	11/47	13/55
90°C-30 min	1.5196	9.6027	0.1366	0.8634	8/51	3/19
90°C-1h	1.7179	14.7472	0.1043	0.8957	3/26	5/43
90°C-2h	3.3575	32.4491	0.09377	0.9062	4/39	3/29
90°C-5h	1.8546	21.0827	0.08086	0.9191	2 /23	8/91

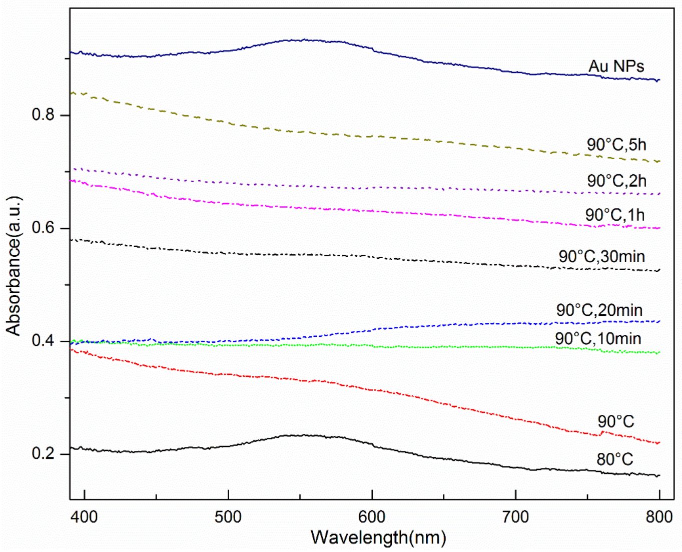

Figure S1. UV-vis spectra of the Au-Pt NCs at different reaction time and Au NPs respectively.

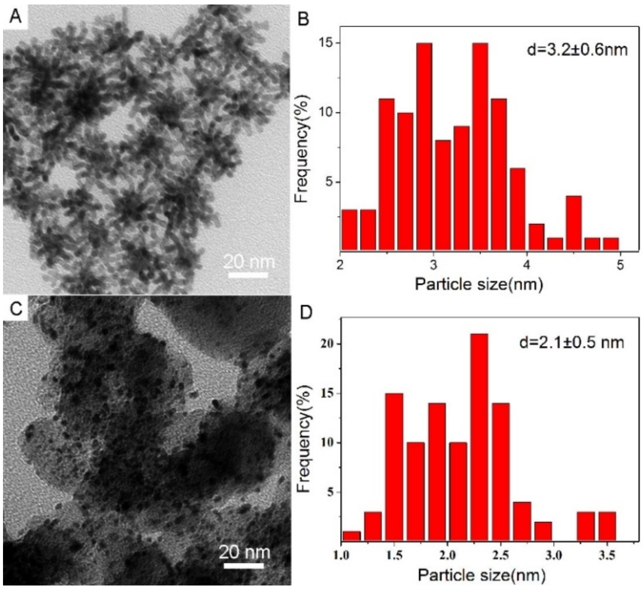

Figure S2. TEM images of Au-Pt NCs (A), 20% JM- Pt/C (C) and size distribution histogram of the Pt branch on Au-Pt NCs (B), JM- Pt/C (D).

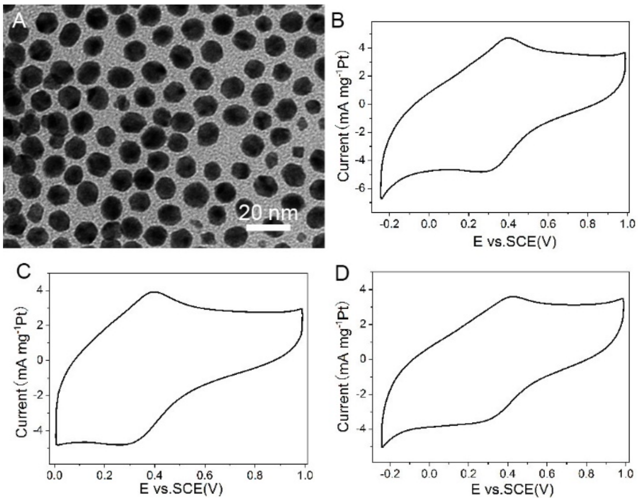

Figure S3. TEM image of Au-Pt NCs prepared at 80 ^oC (A), CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 (B), CVs of Au-Pt NCs in N_2-saturated 0.5 M CH_3OH + 0.5 M H_2SO_4 (C), CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 + 0.5 M HCOOH (D). Scan rate: 50 mVs^{-1}.

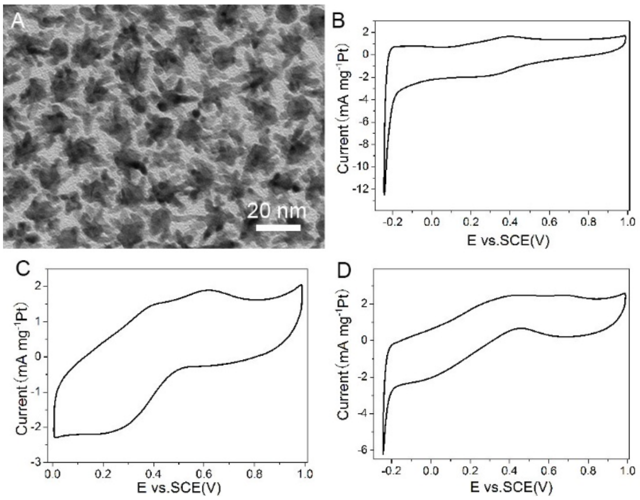

Figure S4. TEM image of Au-Pt NCs prepared at 90 °C for 10 min (A), CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 (B), CVs of Au-Pt NCs in N_2-saturated 0.5 M CH_3OH + 0.5 M H_2SO_4 (C), and CVs of Au-Pt in N_2-saturated 0.5 M H_2SO_4 + 0.5 M HCOOH (D). Scan rate: 50 mVs^{-1}.

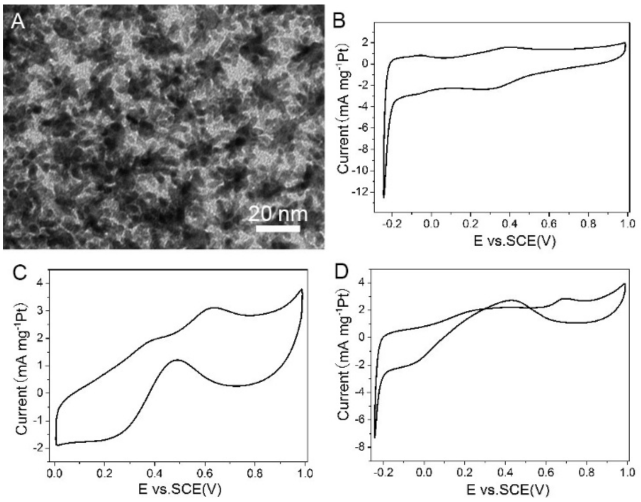

Figure S5. TEM image of Au-Pt NCs prepared at 90 °C for 20 min (A), CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 (B), CVs of Au-Pt NCs in N_2-saturated 0.5 M CH_3OH + 0.5 M H_2SO_4 (C), and CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 + 0.5 M HCOOH (D). Scan rate: 50 mVs^{-1}.

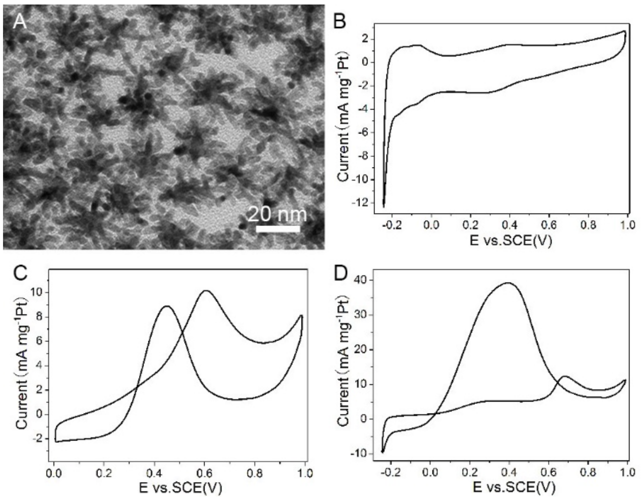

Figure S6. TEM image of Au-Pt NCs prepared at 90 °C for 30 min (A) , CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 (B), CVs of Au-Pt NCs in N_2-saturated 0.5 M CH_3OH + 0.5 M H_2SO_4 (C), and CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 + 0.5 M HCOOH (D). Scan rate: 50 mVs^{-1}.

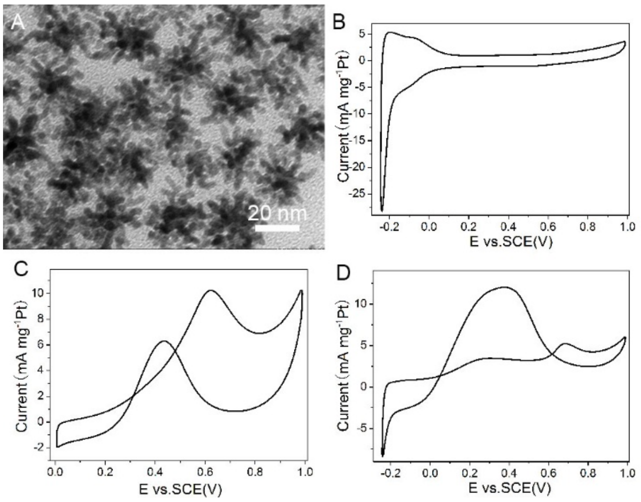

Figure S7. TEM image of Au-Pt NCs prepared at 90 °C for 1h (A), CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 (B), CVs of Au-Pt NCs in N_2-saturated 0.5 M CH_3OH + 0.5M H_2SO_4 (C), and CVs of Au-Pt NCs in N_2-saturated 0.5 M H_2SO_4 + 0.5 M HCOOH (D). Scan rate: 50 mVs^{-1}.

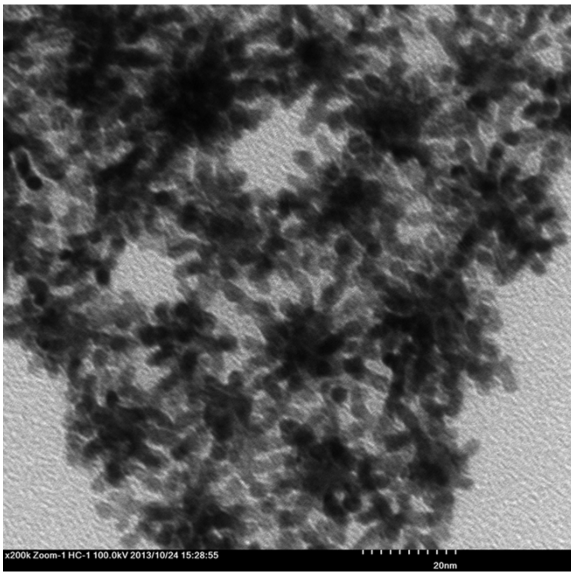

Figure S8. Typical TEM image of Au-Pt NCs prepared at 90 ^{o}C for 2h.

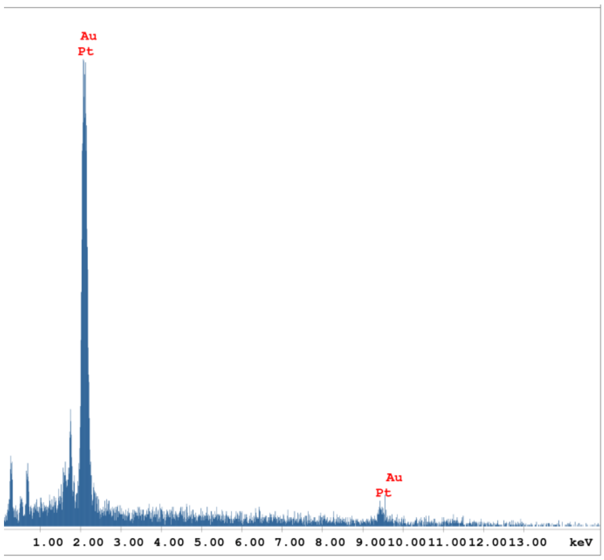

Figure S9. EDX data of Au-Pt NCs as synthesized.

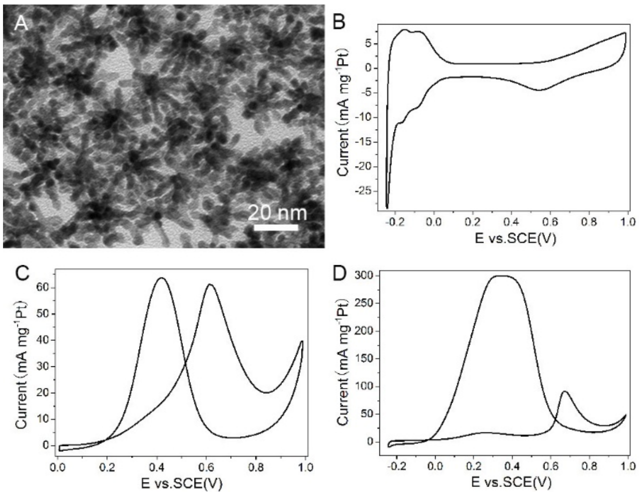

Figure S10. TEM image of Au-Pt NCs prepared at 90 °C for 5h (A), CVs of Au-Pt nanocomplexes in N_2-saturated 0.5 M H_2SO_4 (B), CVs of Au-Pt nanocomplexes in N_2-saturated 0.5 M CH_3OH + 0.5 M H_2SO_4 (C), and CVs of Au-Pt nanocomplexes in N_2-saturated 0.5 M H_2SO_4 + 0.5 M HCOOH (D). Scan rate: 50 mVs^{-1}.

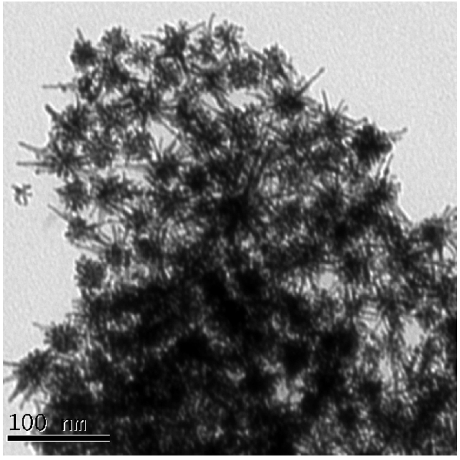

Figure S11. Typical TEM image of Au-Pt NCs after oxidation reaction.

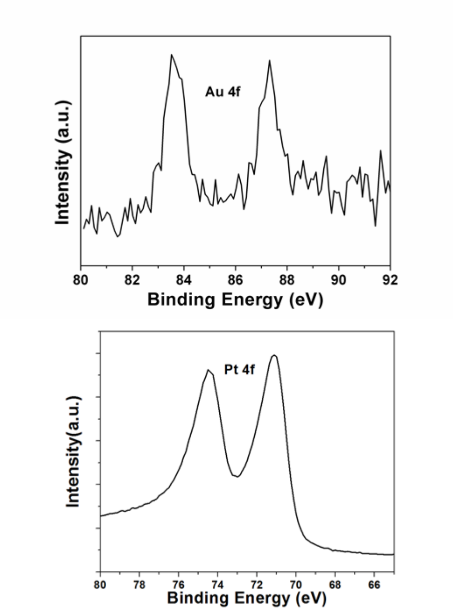

Figure S12. XPS data of Au-Pt NCs as synthesized.