

One-pot synthesis and enhanced catalytic performances of Pd and Pt nanocages *via* Galvanic Replacement Reactions

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Electronic Supplementary Information

Experimental details

Materials. Silver nitrate (AgNO_3), palladium chloride (PdCl_2), chloroauric acid (HAuCl_4), cetyltrimethylammonium bromide (CTAB), and poly(vinyl pyrrolidone) (PVP, MW=30,000) were obtained from Sigma-Aldrich. Other analytical grade reagents came from Guangdong Guanghua Chemical Reagent Co., such as ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, EG), acetylacetonone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$, acac), methanol, chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), ascorbic acid (AA), sodium chloride (NaCl), sodium hydroxide (NaOH), ferric nitrate ($\text{Fe}(\text{NO}_3)_3$), sodium sulfide (Na_2S) and concentrated sulfuric acid (H_2SO_4). All the reagents were used without further purification. Milli-Q water ($> 18.0 \text{ M}\Omega \text{ cm}$) was used to prepare all aqueous solutions.

Synthesis of Ag nanocubes solution. Ag nanocubes solution were synthesized by the reduction of AgNO_3 with EG in the presence of PVP and Na_2S .¹ Briefly, 0.166 g PVP was dissolved in 3 mL EG solution. Then, 60 μL 0.01 M Na_2S was introduced into the solution and kept stirring and refluxing for 5 min at 150 °C. Next, 3 mL 0.1 M AgNO_3 EG solution was slowly dripped. Finally, the Ag nanocubes solution was obtained through stirring and refluxing the mixture for 1.5 h at 175 °C.

Synthesis of metal (Au, Pd, Pt) nanocages. Metal (Au, Pd, Pt) nanocages were synthesized by galvanic replacement reactions of Ag nanocubes served as templates. Firstly, Ag nanocubes were synthesized by the reduction of AgNO_3 with EG in the presence of PVP and Na_2S . Meanwhile, 2.5 mM $\text{Au}(\text{acac})_4^{3+}$, $\text{Pd}(\text{acac})_2^{2+}$, or $\text{Pt}(\text{acac})_4^{4+}$ precursor solutions were prepared through mixing HAuCl_4 , PdCl_2 , or H_2PtCl_6 and acac solutions under vigorously stirring, respectively. Without centrifugation and separation, the freshly prepared nanocubes were cooled down to 120 °C, and 3 mL of 2.5 mM $\text{Au}(\text{acac})_4^{3+}$, $\text{Pd}(\text{acac})_2^{2+}$, or $\text{Pt}(\text{acac})_4^{4+}$ precursors were added through a syringe pump at the rate of 45 mL/h under continuously stirring. Next, the reaction mixture kept stirring at 120 °C for 1.5 h. Finally, the metal nanocages were obtained through dealloying with an overdose volume of 50 mM $\text{Fe}(\text{NO}_3)_3$ and washing with saturated NaCl solutions to remove AgCl and centrifuging several times to remove PVP and NaCl.²

Synthesis of Pd nanocubes. As control experiment, Pd nanocubes were synthesized as follow:³ 10 mM Na_2PdCl_4 solution was first prepared by dissolving 44.5 mg PdCl_2 in 5 mL 100 mM HCl and 19 mL ultrapure water, followed by the addition of 1 mL 500 mM NaOH. Then, 1 mL 10 mM PdCl_2 was mixed with 1 mL 10 mM CTAB, and the mixture was dropped into a flask containing 4 mL 25 mM AA over a period of 5 min and kept stirring for 1 h. Finally, the product was obtained through centrifuging and dispersing twice at 4000 rpm for 20 min.

Synthesis of Pt nanoparticles. As control experiment, Pt nanoparticles were prepared by seed-mediated growth strategy.⁴ Briefly, Pt seeds were first fabricated through refluxing 50 mL solution containing 6 mM H_2PtCl_6 , 0.6 mM PVP, 9.5 mL ultrapure water, and 40.5 mL methanol

for 3 h.⁵ Then, 2 mL Pt seeds were added into 10 mL 2 mM H₂PtCl₆, and the mixture was reduced with 2.4 mL 100 mM AA. The final product was acquired through centrifuging twice at 6000 rpm for 30 min.

Preparation of catalyst modified electrodes. Glassy carbon (GC) electrodes were first polished with alumina slurry of successively smaller particles (1.0, 0.3, and 0.05 μm diameters), respectively, and cleaned by ultrasonication. Then, 6 μL of 2 mg/mL catalyst solutions was deposited on the GC electrode surfaces with a 10-μL syringe and was allowed to dry at room temperature. Finally, uniform catalyst-nafion/GC modified electrodes were formed through casting 3 μL of 5% nafion onto the catalyst-modified electrode surfaces and putting overnight at room temperature.

Electrochemical measurements. All electrochemical experiments were conducted at (25 ± 2) °C with a CH Instruments (CHI 660C) electrochemical analyzer in a three electrode system with the modified GC electrode as the working electrode, a platinum wire as the auxiliary electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode, respectively. Methanol electrocatalytic oxidation measurements were performed in 0.5 M KOH solution containing 1 M methanol at the scan rate of 50 mV/s. All electrochemical experiments were commenced after degassing the electrolyte solutions with nitrogen for at least 20 min prior to measurements.

Instrumentation. Transmission electron microscopy (TEM) studies were performed by using a Hitachi H-7500 microscope operated at 80 kV. High-resolution TEM (HRTEM) was carried out with a JEM-2010 (HR) microscopy operated at 200 kV. X-ray diffraction (XRD) pattern was recorded on a powder sample using a D/max-III A (Japan) X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ=0.15418 nm) in ranging from 10° to 90°. X-ray photoelectron spectroscopy (XPS) measurement was performed using a Kratos Axis Ultra (DLD). UV-visible (UV-vis) absorption spectrum was acquired with a Hewlett-Packard 8452 diode array spectrometer (U-3010). Electrochemical experiments were carried out at room temperature using a CHI 660 electrochemical workstation (CH Instruments, Inc., Austin, USA)

References

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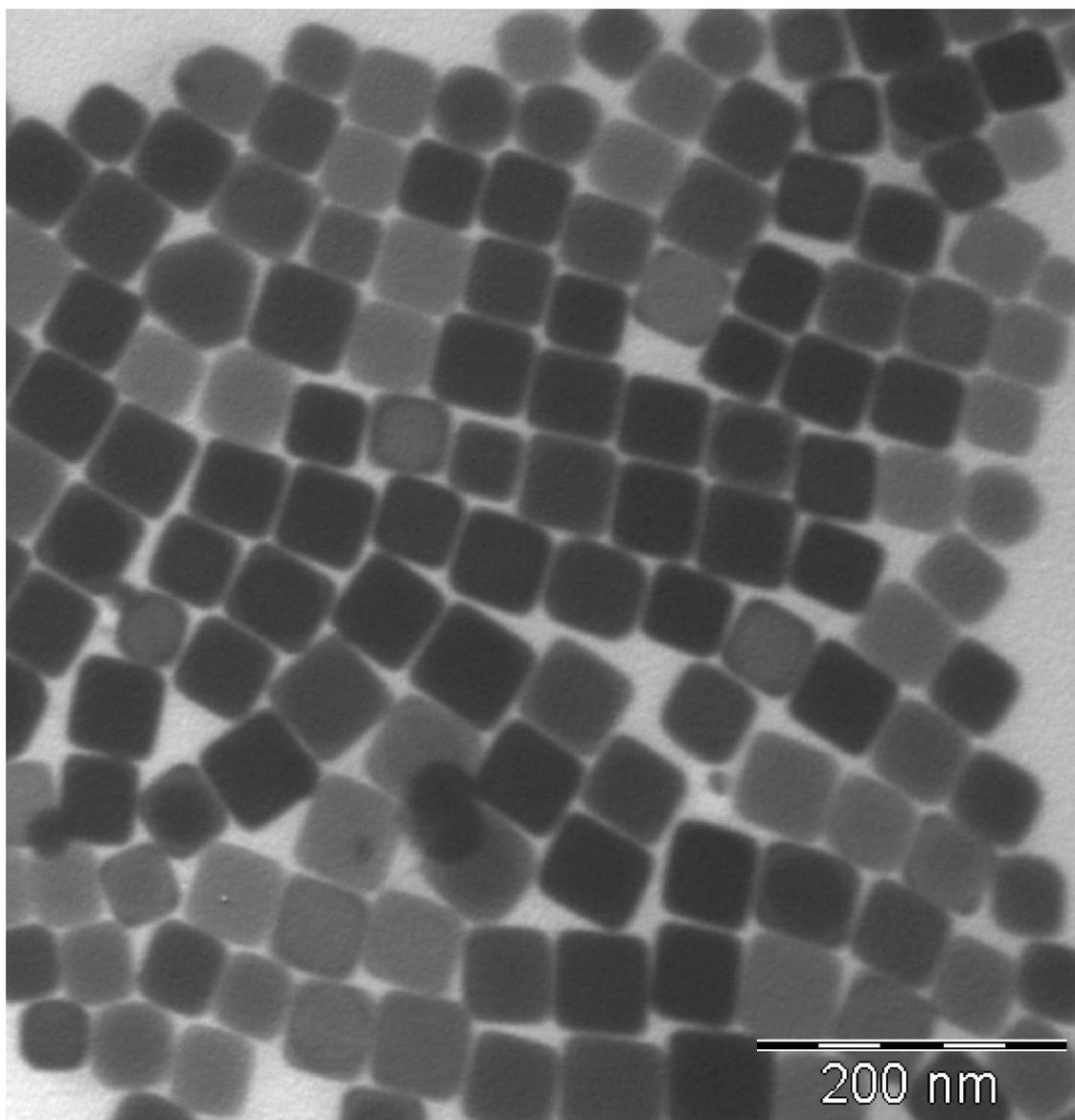


Fig. S1 TEM image of Ag nanocubes prepared by the glycol reduction method. Scale bar: 200 nm.

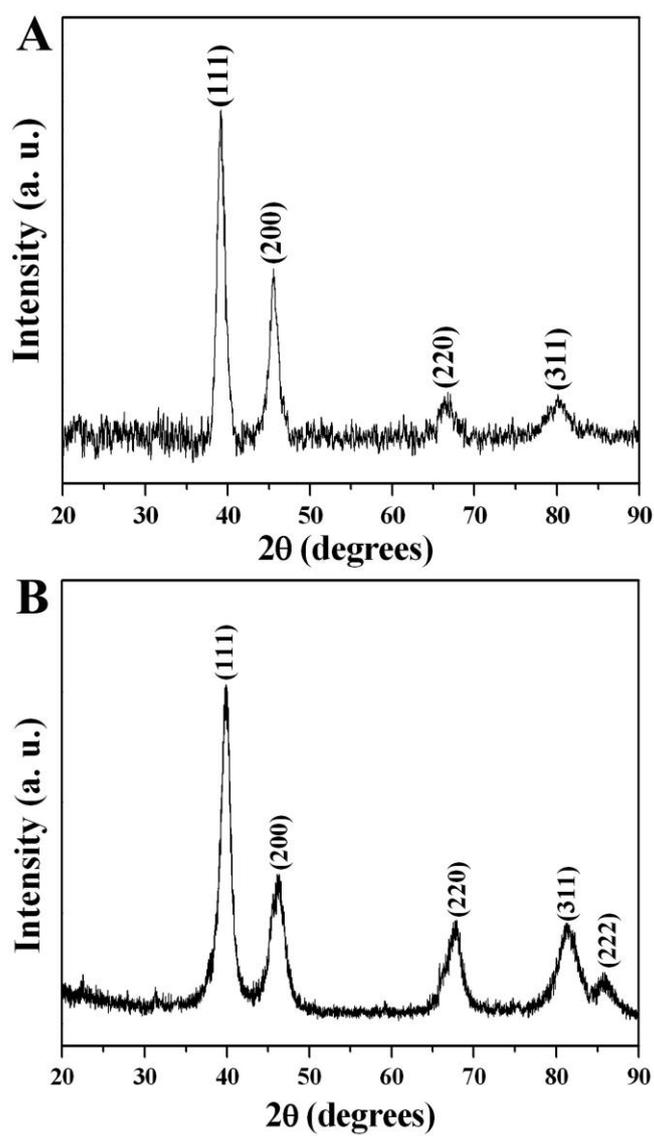


Fig. S2 (A,B) XRD patterns of Pd and Pt nanocages prepared by the present one-pot strategy, respectively.

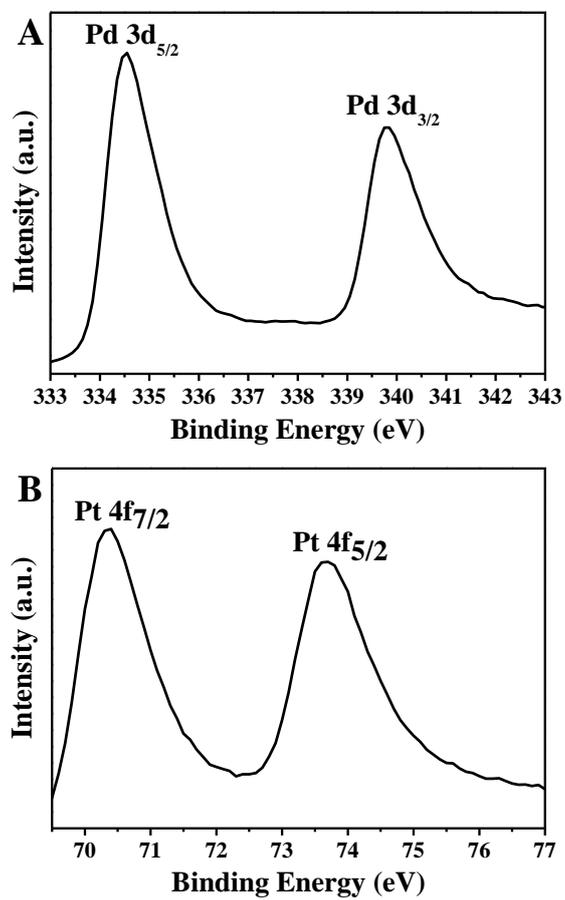


Fig. S3 XPS spectra of (A) Pd and (B) Pt nanocages prepared by the present one-pot strategy.

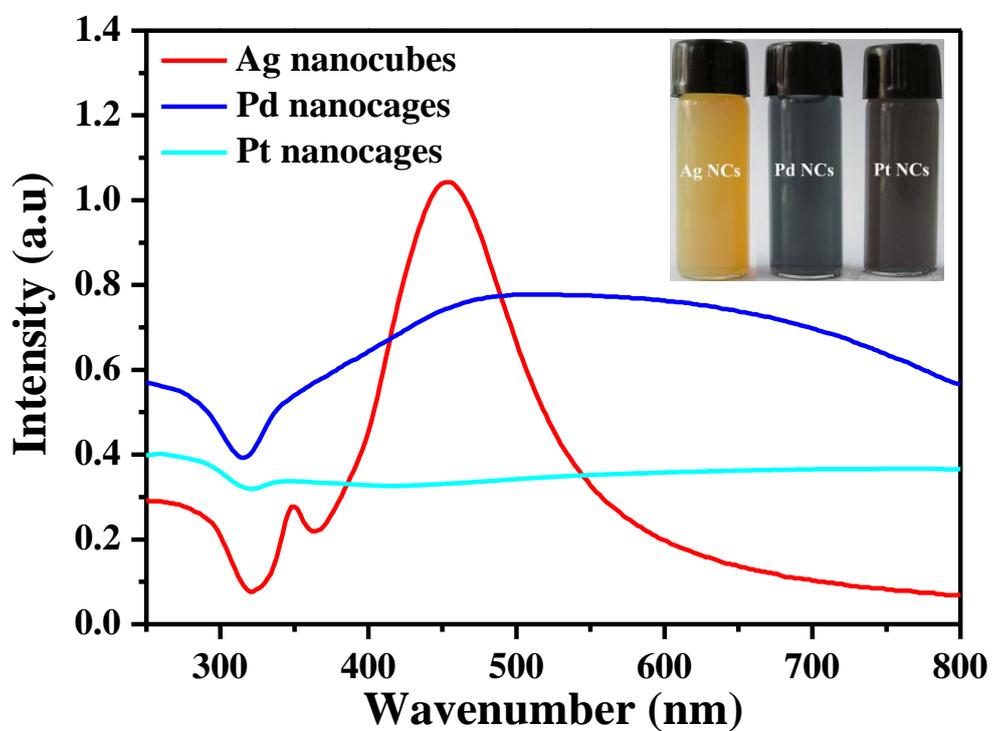


Fig. S4 UV-visible spectra of colloidal solutions containing Ag nanocubes and Pd and Pt nanocages prepared by the present one-pot strategy, respectively. The inset is their corresponding digital photos.

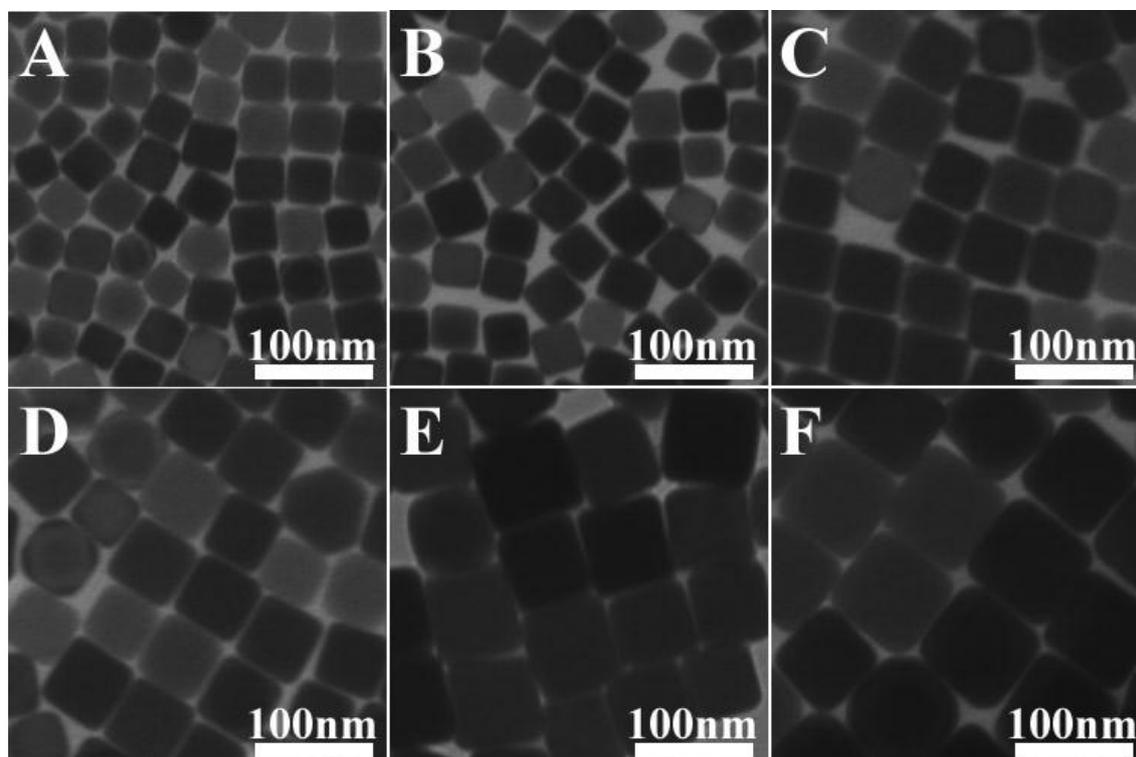


Fig. S5 TEM images of Ag nanocubes prepared using (A) 30, (B) 60, (C) 120, (D) 150, (E) 180, and (F) 240 μL 0.01 M Na_2S , respectively. Scale bar: 100 nm.

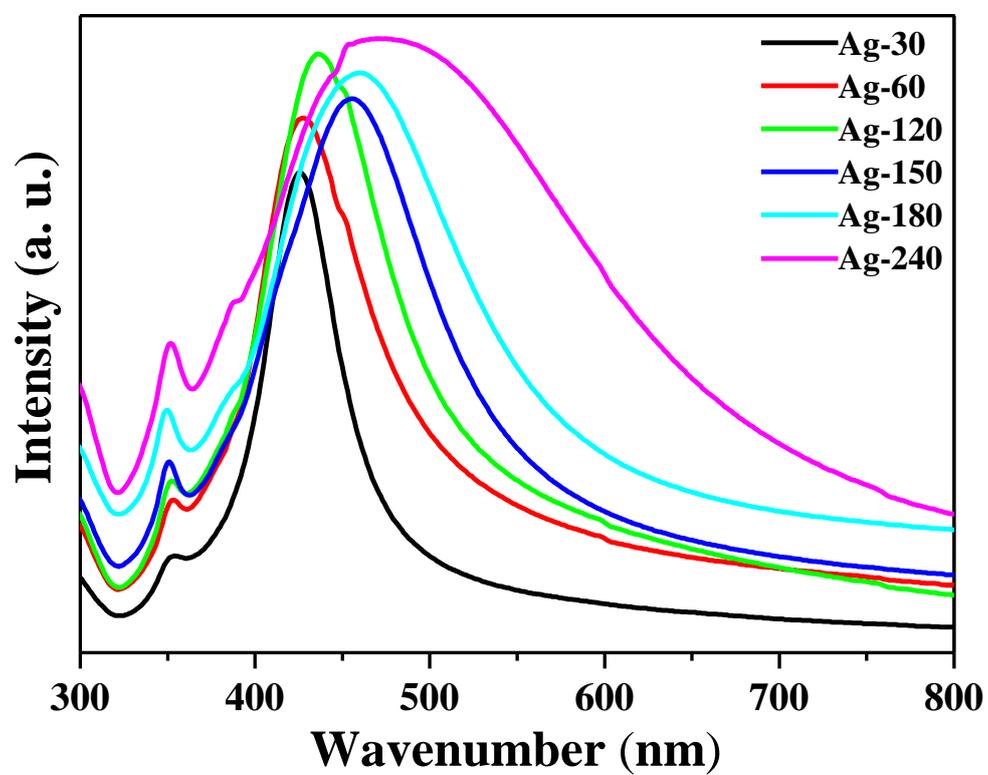


Fig. S6 UV-visible absorption spectra of the colloidal solutions containing the Ag nanocubes prepared using 30 (black), 60 (red), 120 (green), 150 (blue), 180 (cyan) and 240 (magenta) μL 0.01 M Na_2S , respectively.

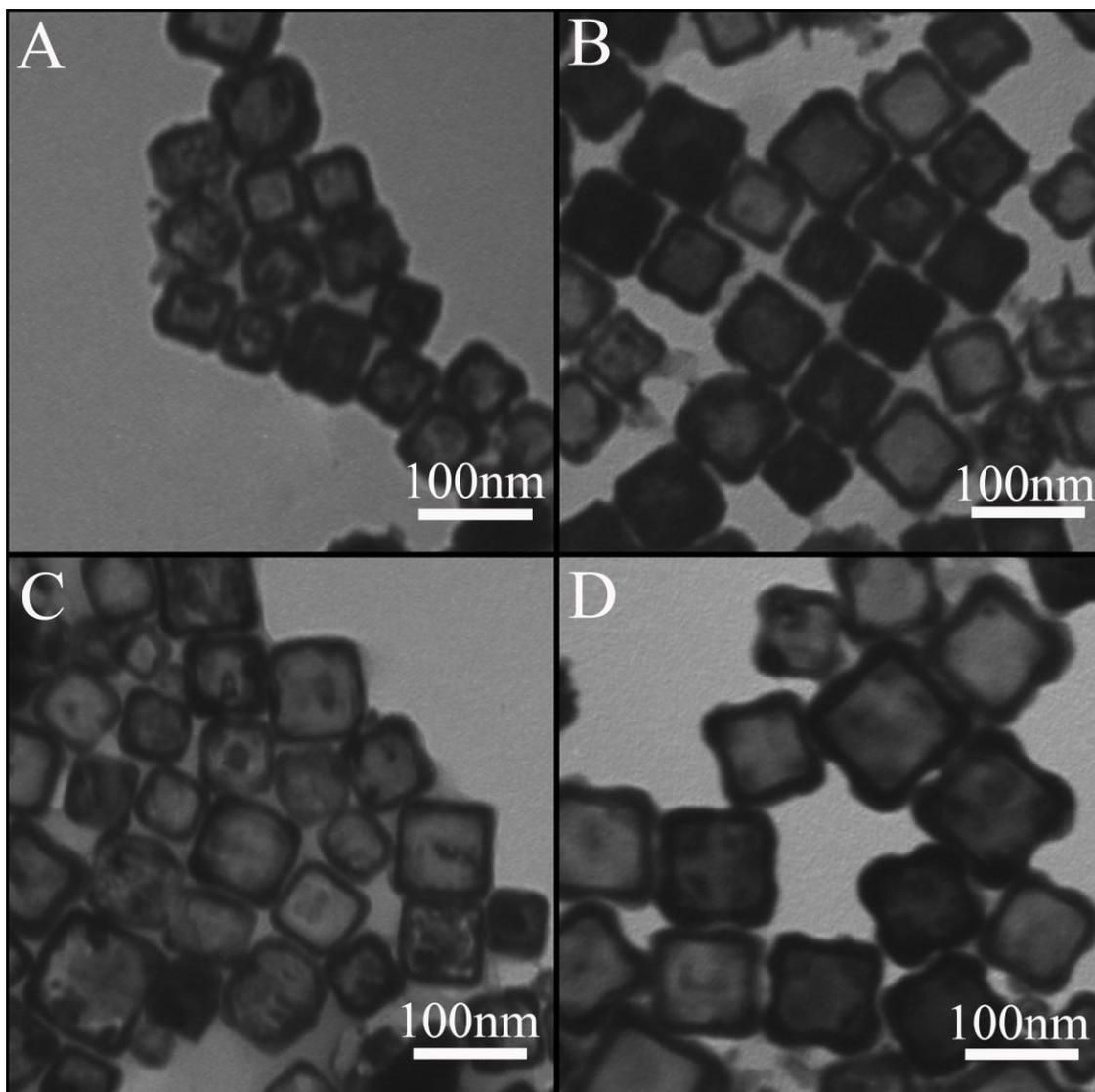


Fig. S7 TEM images of Pd nanocages prepared using the templates of Ag nanocubes with the edge lengths of (A) 51, (B) 57, (C) 67, and (D) 84 nm, respectively. Scale bar: 100 nm.

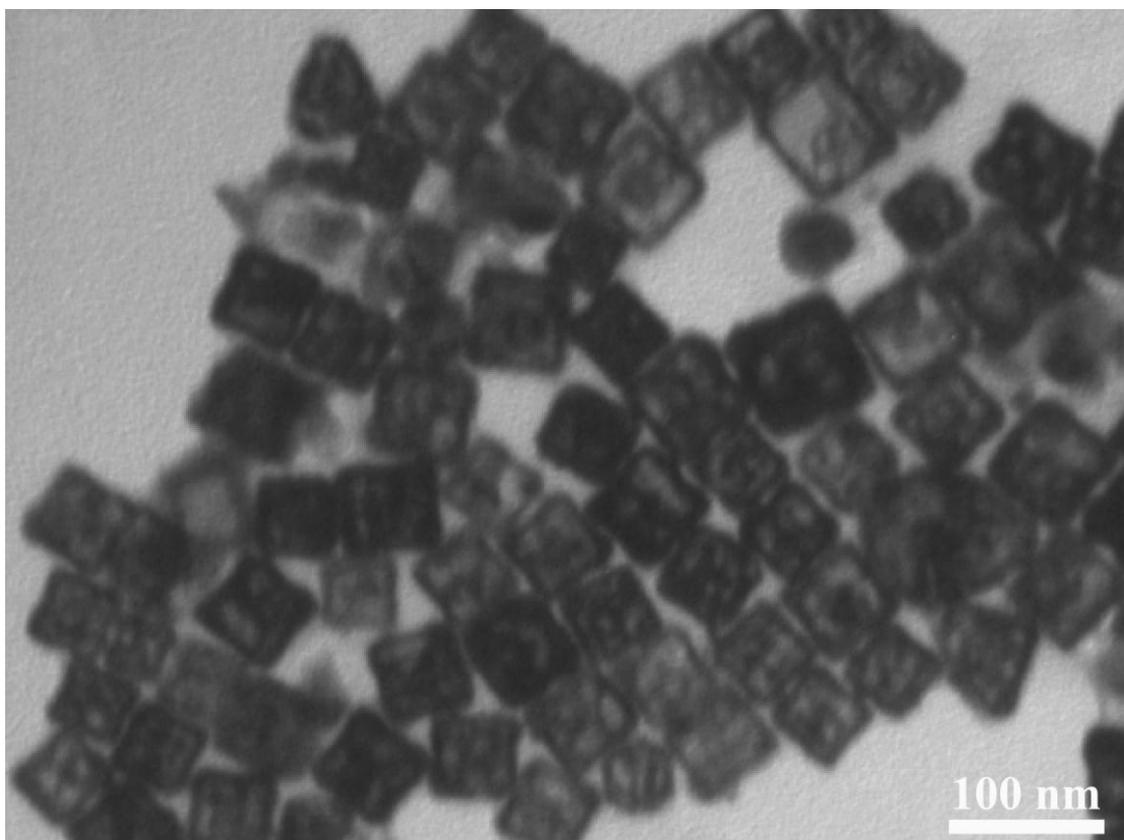


Fig. S8 TEM images of Pd nanocages prepared via the templates of the Ag nanocubes at the temperature of 70 °C. Scale bar: 100 nm.

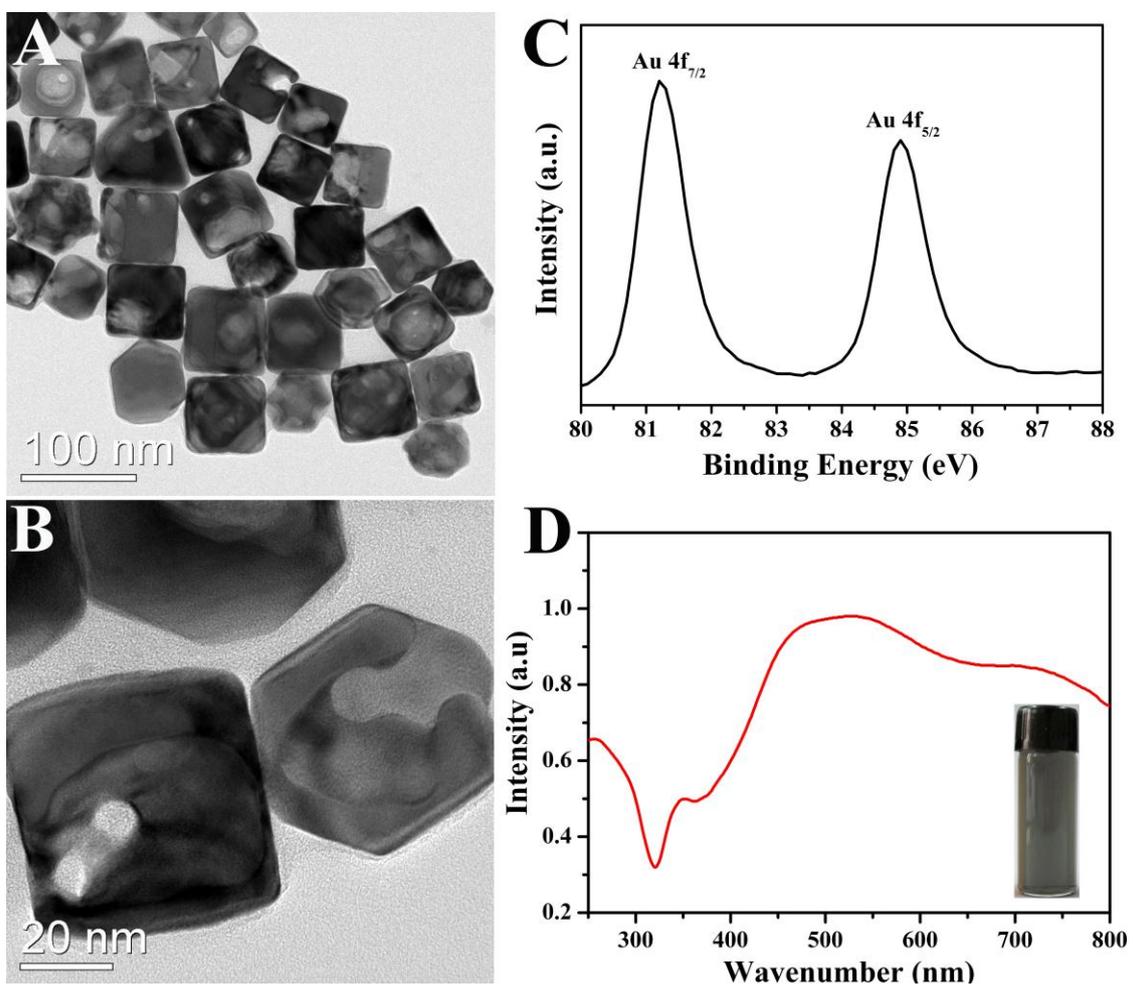


Fig. S9 (A) TEM and (B) HRTEM images and (C) XPS and (D) UV-visible spectra of Au nanocages prepared by the one-spot strategy, respectively. Scale bar: 100 and 20 nm; the inset is its corresponding digital photo.

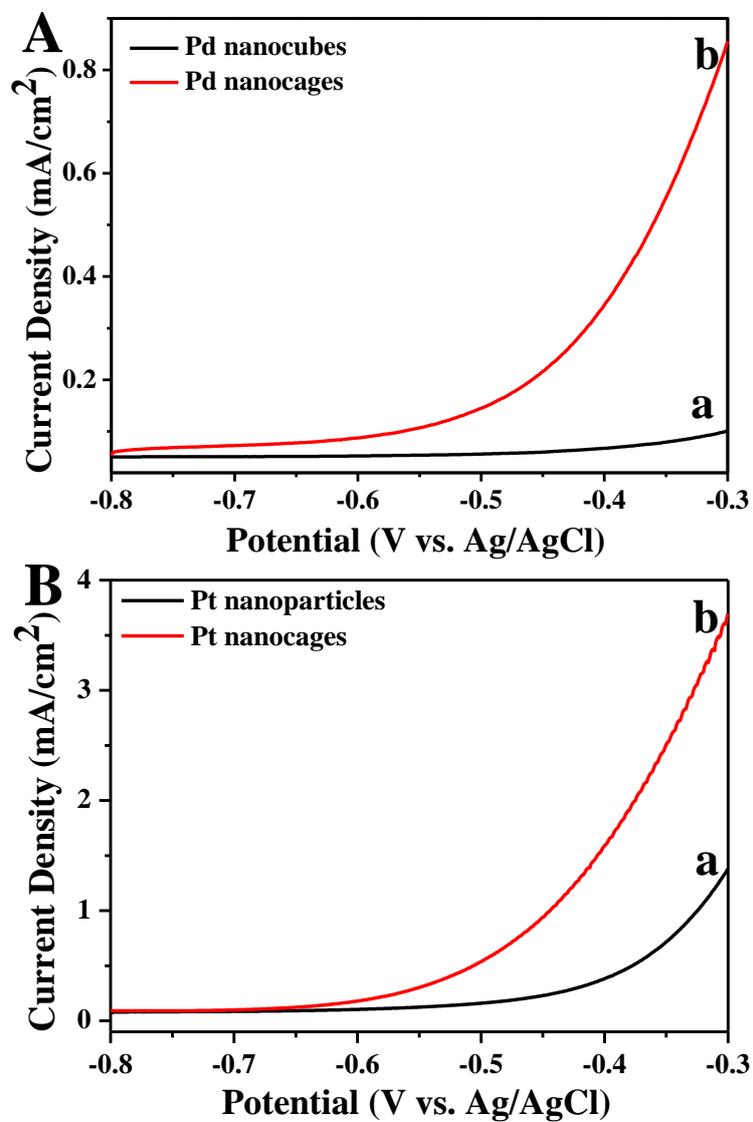


Fig. S10 Linear sweep voltammetry (LSV) of (A) Pd nanocubes (a) and Pd nanocages (b) and (B) Pt nanoparticles (a) and Pt nanocages (b) catalysts modified electrodes in 1 M CH₃OH + 0.5 M KOH at the scan rate of 50 mV/s, respectively.

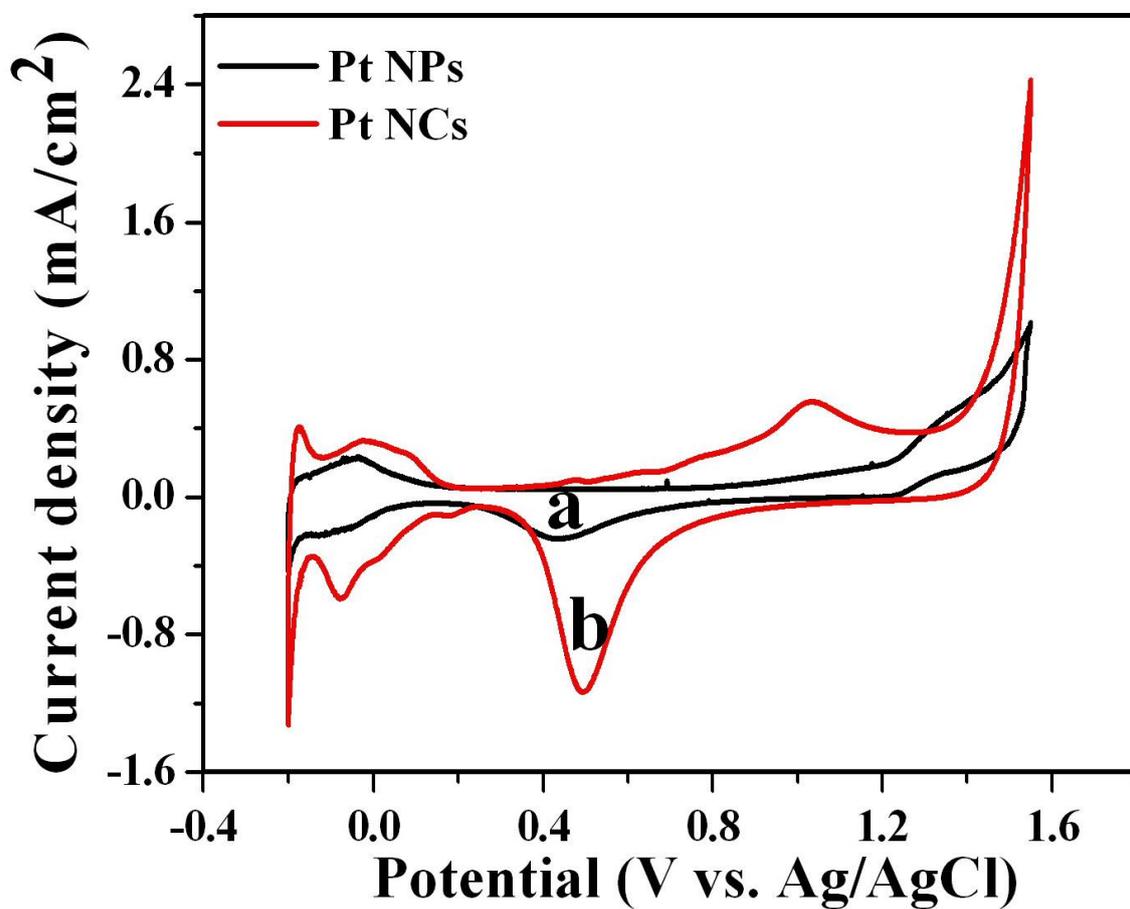


Fig. S11 Cyclic voltammograms of (a) Pt nanoparticles and (b) Pt nanocages in nitrogen-saturated 0.5 M H₂SO₄ at a scan rate of 50 mV/s.