Supporting Information

Facile Synthesis of PdPt Nanoalloys with Sub-2.0 nm Islandss as Robust Electrocatalysts for Methanol Oxidation

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Experimental section:

Chemicals: Chloroplatinic acid hydrate (99.9%), Palladium chloride (99.9%), Sodium chloride (99.99%), Cetyltrimethylammonium chloride (≥ 95%) and Citric acid monohydrate (99.9%) were purchased from Sigma-Aldrich. Pt black was purchased from Johnson Matthey. Perchloric acid (G.R.) and absolute methanol were purchased from China Medicine Shanghai Chemical Reagent Corp. Chemicals were used as received without further purification. The super pure water (18 MΩ cm) was used as solvent.

Synthesis of PdPt nanoalloys with sub-2.0 nm islands:

0.210 g of citric acid monohydrate and 0.256 g of CTAC were added into 9.0 mL of super pure water and stirred for several minutes. Then 0.1 M Na_2PdCl_4 and 0.1 M H_2PtCl_6 aqueous solution were added by the ratio of Pd to Pt of 1:1(Marked as $Pd_{50}Pt_{50}$), 1.5:1(Marked as $Pd_{60}Pt_{40}$) and 1:1.5 (Marked as $Pd_{40}Pt_{60}$), respectively (namely, 0.5 ml of 0.1 M Na_2PdCl_4 and 0.5 ml of 0.1 M H_2PtCl_6 aqueous solution; 0.6 ml of 0.1 M Na_2PdCl_4 and 0.4 ml of 0.1 M H_2PtCl_6 aqueous solution and 0.4 ml of 0.1 M Na_2PdCl_4 and 0.6 ml of 0.1 M H_2PtCl_6 aqueous solution) , after stirred several minutes , the resulting solution was transferred to a 15 ml Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 180 ˚C for 50 minutes before it was cooled to room temperature. The products were separated via centrifugation/washing cycles at 10000 rpm for 15 minutes for four times with super pure water. Finally, the collected product was vacuum drying for four days.

Characterizations: The TEM images of the samples were examined with FEI Tecnai T12 (120 KV). HRTEM, energy-dispersive X-ray spectroscopy (EDX), high-angle annular dark field scanning TEM (HAADF-STEM) and element line scanning were obtained with FEI Titan 80 (300 KV). X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ=1.5418 Å) with graphite monochromator (40 KV, 40 mA).X-ray photoelectroscopy (XPS) measurements were performed using a PHI Quantum 2000 Scanning ESCA Microprobe (PHYSICAL ELECTRONICS, USA), using Al Kα X-ray radiation (1486.6 eV) for excitation. The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of samples was performed on IRIS Intrepid II XSP (ThermoFisher).

***Characterization of electrocatalytic activity*:**

Electrochemical experiments were carried out in a standard three-electrode cell at room temperature (25 ºC) controlled by CHI 630E electrochemical analyzer (CHI Instruments, Shanghai, Chenghua Co., Ltd.). The super pure water (18 MΩ cm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.) was used as solvent. The working electrode is a glassy carbon (GC, Φ =5 mm) electrode embedded into a Teflon holder. Prior to the electrochemical test, the GC electrode was mechanically polished using successively alumina powder of size 5, 1, and 0.3 μm. It was then cleaned in an ultrasonic bath. Then took a certain amount of PdPt nanoalloys or Pt black powder and dispersed with super pure water under ultrasonic bath. The suspension of PdPt nanoalloys or Pt black was spread on the GC electrode. As soon as the electrode was dried under infrared lamp, 10 μL Nafion diluents (0.1 wt.% Nafion® solution) was coated onto the electrode surface. A Ag/AgCl electrode and a platinum foil were used as the reference and counter electrode, respectively.

The cyclic voltammograms (CVs) were obtained in nitrogen-saturated 0.1 M $HClO_4$ solution, and the potential was scanned from -0.25 to 1.0V (Ag/AgCl) at a scan rate 50 mV/s. The scan was repeated several times to ensure that a stable cyclic voltammetry (CV) was obtained. Voltammogram measurement for methanol oxidation was carried out in 0.1or 0.5 M CH_3OH + 0.1 M $HClO_4$ solution, and the potential was scanned from 0 to 0.9 V (Ag/AgCl) at a scan rate 50 mV/s.

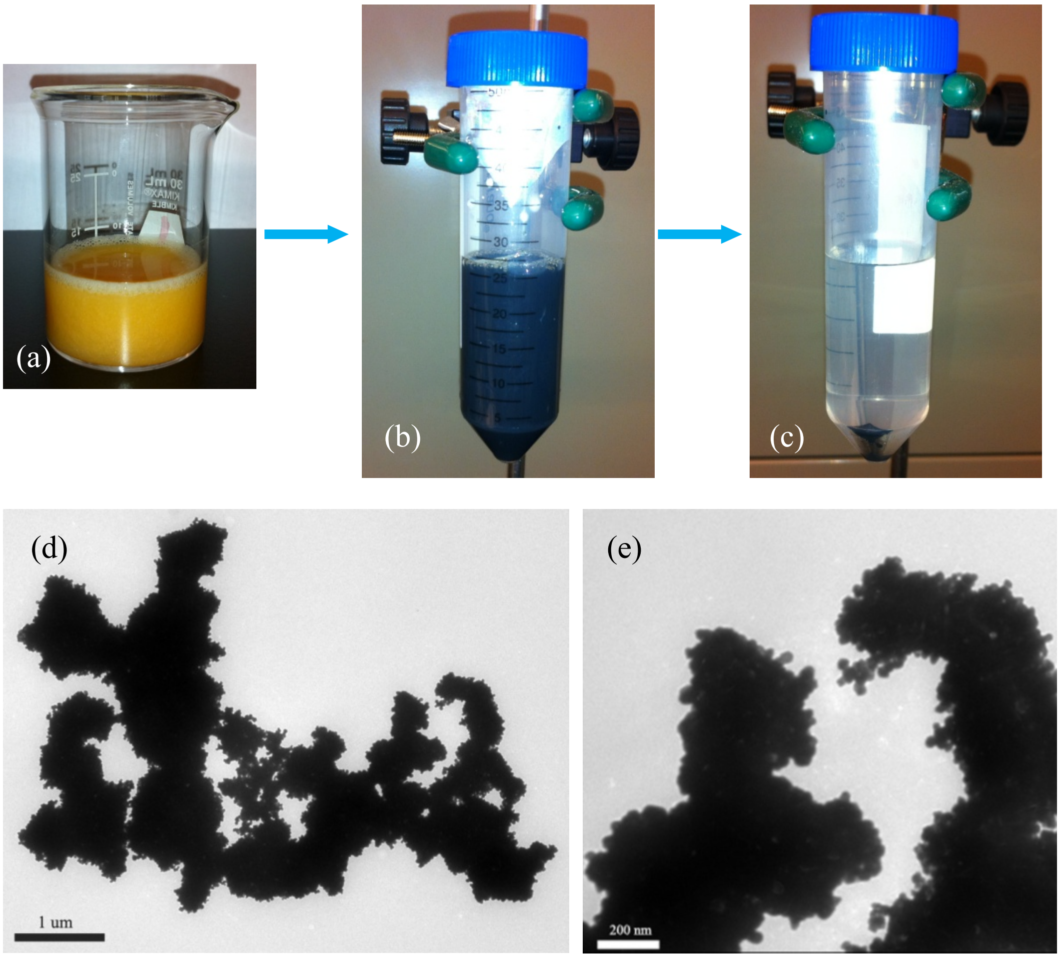

Fig. S1 Digital photos of as-synthesized $Pd_{50}Pt_{50}$ bimetallic nanoalloys. (a) Before reaction; (b) After reaction; (c) After centrifugation. (The transparent supernatant was detected by inductively coupled plasma optical emission spectrometry (ICP-OES). No Pd and Pt elements were detected. It means the Pd and Pt ions were fully reduced and formed the PdPt nanocrystals.) (d) and (e) The TEM images of as-synthesized $Pd_{50}Pt_{50}$ sample without CTAC. (The product is made of non-dispersed aggregates of particles, which implies that the CTAC act as surfactant in our present system.)

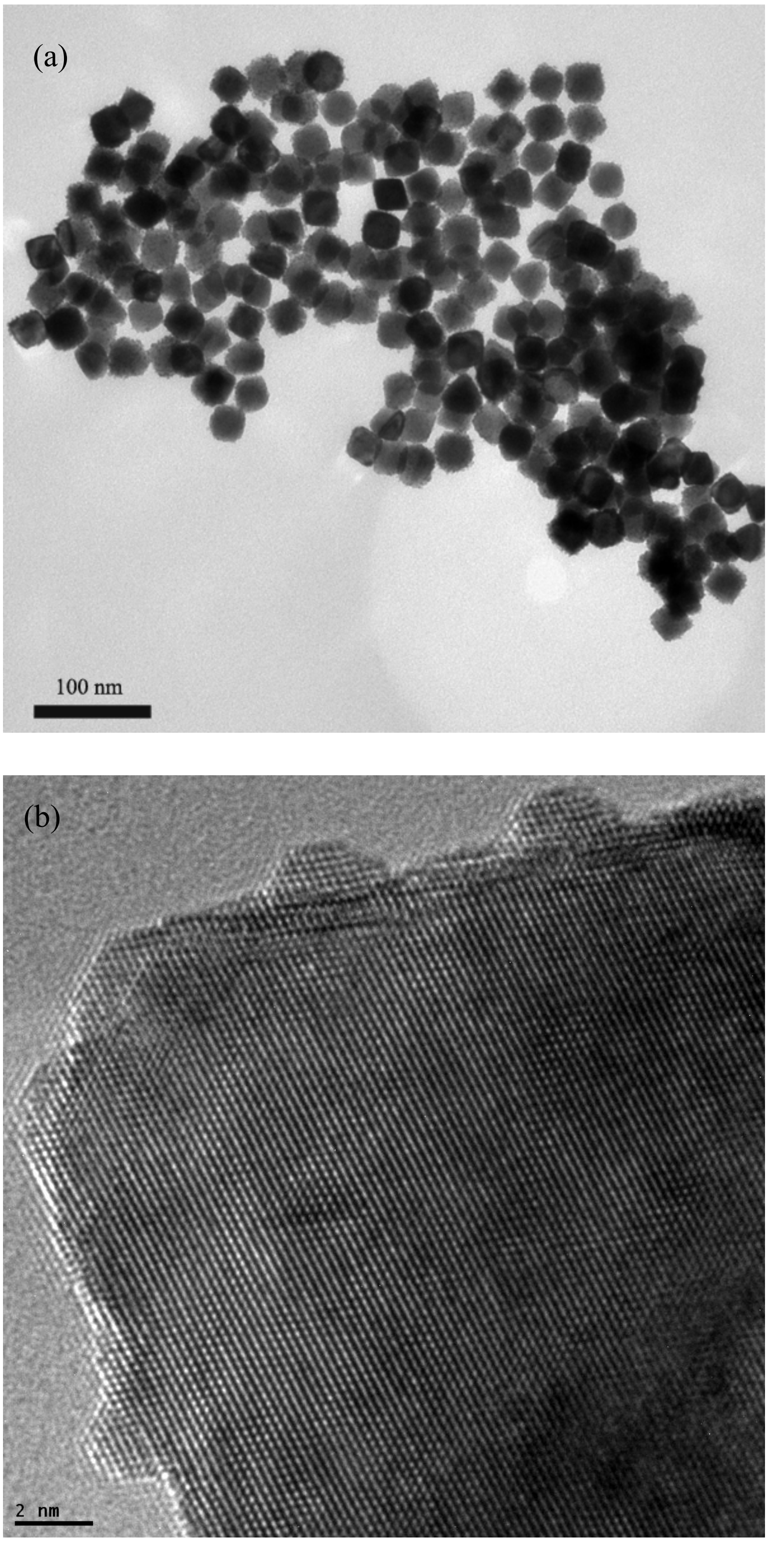

Fig. S2 The TEM (a) and HRTEM (b) images of as-synthesized $Pd_{50}Pt_{50}$ bimetallic nanoalloys.

Sample	Element	atom% feeding ratio	atom% (results from ICP)	atom% (results from XPS)
$Pd_{60}Pt_{40}$	Pd	60	59.6	61.7
	Pt	40	40.4	38.3
$Pd_{50}Pt_{50}$	Pd	50	50.7	51.3
	Pt	50	49.3	48.7
$Pd_{40}Pt_{60}$	Pd	40	39.2	41.6
	Pt	60	60.8	58.4

Table S1. The content of Pd and Pt of dendrite-like PdPt nanoalloys calculated from feeding ratio, ICP-OES and XPS.

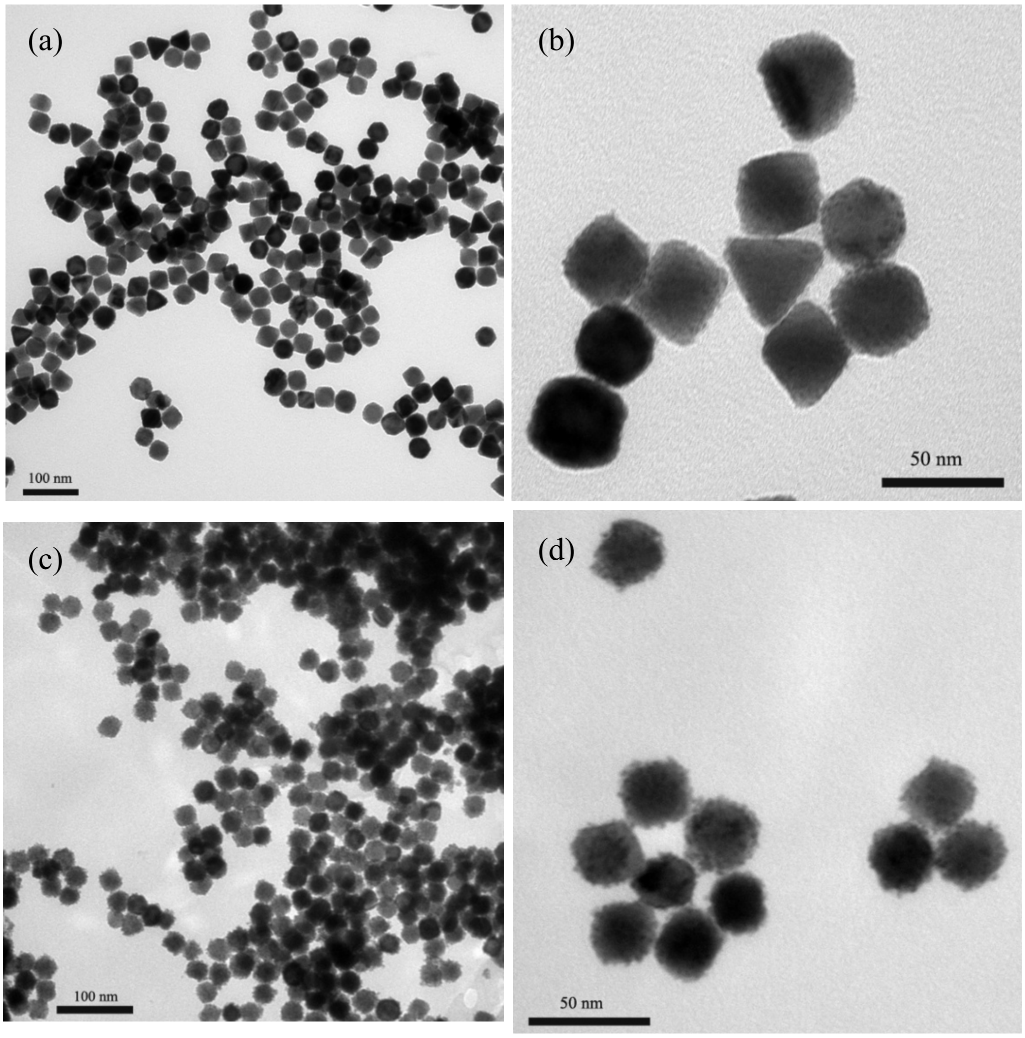

Fig. S3 TEM images of as-synthesized PdPt bimetallic nanoalloys. (a, b) The feeding ratio of Pd :

Pt is 1.5 : 1, marked as $Pd_{60}Pt_{40}$ (c, d) The feeding ratio of Pd : Pt is 1 : 1.5, marked as $Pd_{40}Pt_{60}$.

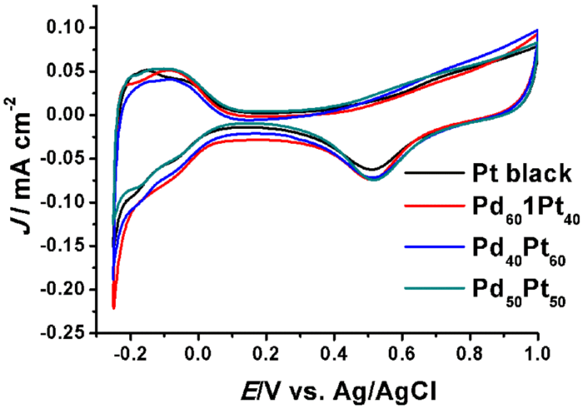

Fig. S4 The CVs of as-synthesized dendrite-like PdPt nanoalloys and commercial Pt black in 0.1 M $HClO_4$ solution. The specific ECSA for $Pd_{60}Pt_{40}$, $Pd_{40}Pt_{60}$, $Pd_{50}Pt_{50}$ and commercial Pt black was 7.2, 9.7, 11.3 and 21.7m^2/g, respectively. The lower ECSA for these PdPt nanoalloys is most likely due to their large nanoparticle sizes, about 35 ± 2.0 nm.

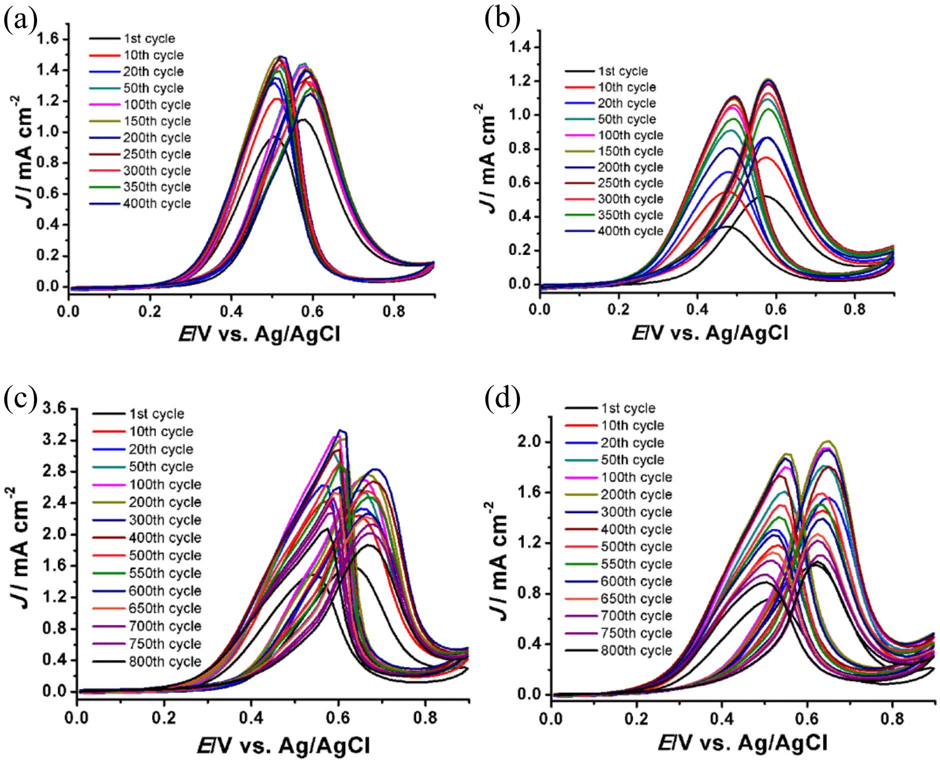

Fig. S5 The CVs of as-synthesized dendrite-like $Pd_{50}Pt_{50}$ nanoalloys and commercial Pt black. (a) $Pd_{50}Pt_{50}$ in 0.1 M $HClO_4$ + 0.1 M CH_3OH; (b) Pt commercial black in 0.1 M $HClO_4$ + 0.1 M CH_3OH; (c) $Pd_{50}Pt_{50}$ in 0.1 M $HClO_4$ + 0.5 M CH_3OH; (d) Pt commercial black in 0.1 M $HClO_4$ +

0.5 M CH_3OH.

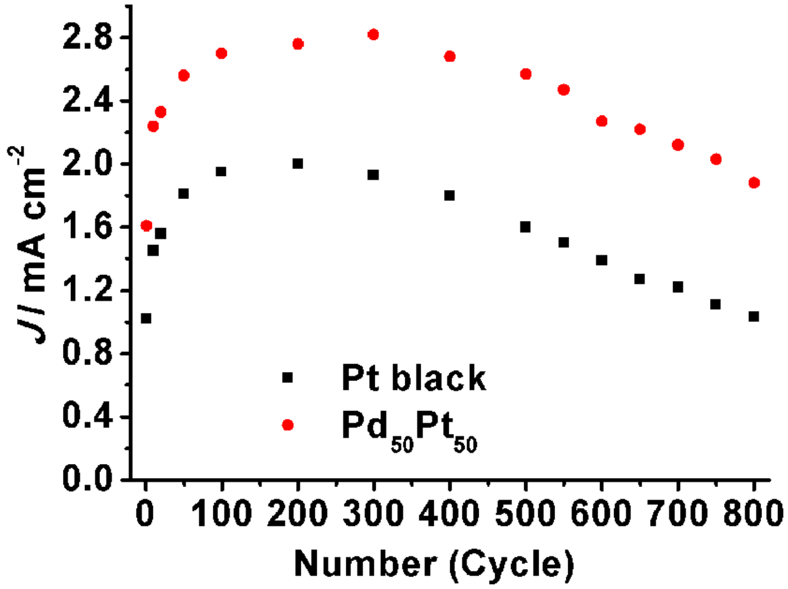

Fig. S6 The durability performance of $Pd_{50}Pt_{50}$ nanoalloys and commercial Pt black in 0.5 M CH_3OH + 0.1 M $HClO_4$ solution.