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Supplementary Information

Hollow ternary PtPdCu nanoparticles: a superior and durable cathodic electrocatalyst

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Experimental Section

Chemicals.

Pt(acac)₂ (acac = acetylacetonate), Cu(acac)₂, Nafion (5 wt%) were purchased from Sigma-Aldrich; PdCl₂, oleic acid (OA), hexane (≥ 97 wt%), acetic acid (98%), ethanol (≥ 99.7 wt%), HClO₄ (≈ 70–72 wt%), were commercially available from the Shanghai Chemical Reagent Co. Ltd; Oleylamine (OAm, 80-90%), 1-octadecene (ODE) was from Aladdin Reagent Co. Ltd (Shanghai). All chemical reagents were analytical grade and used without further purification.

Synthesis of PtPdCu alloyed nanoparticles with different compositions.

In a typical synthesis PtPdCu₁ nanoparticles (NPs), 0.05mmol of Pt(acac)₂, 0.05mmol of PdCl₂, 0.05mmol Cu(acac)₂, 4 mL OAm and 1mL OA were mixed together with 5 mL ODE in a 25 mL three-neck flask at room temperature. The mixture was then heated to 120°C with vigorous stirring. After 20 minutes, the mixed solution was subsequently heated to 230 °C at a heating rate of 10 °C /min and maintained at this temperature for 30 min. The black colloids

was cooled down to room temperature, and then isolated by adding a sufficient amount of ethanol followed by centrifugation at 8000rpm for 8min. After washed for several times to remove surfactants, the product was redispersed in hexane for further characterization.

PtPdCu_x NPs with other compositions were synthesized by modifying the molar ratios of Pt(acac)₂ : PdCl₂ : Cu(acac)₂ to 1:1:3, 1:1:6, and 1:1:9 for PtPdCu₃, PtPdCu₆ and PtPdCu₉, respectively. The other conditions were same with the method above.

PtPdCu_x NPs were then supported on Vulcan carbon to be used as electrocatalysts. The Pt content in the supported catalysts was controlled to be ~ 5 wt%. Then the corresponding certain amount of Vulcan carbon black was ultrasonically dispersed in 20 mL hexane for 15 min. At the same time, the as-prepared PtPdCu_x NPs were also ultrasonically dispersed in 20 mL hexane for 15 min. After that, the NPs were mixed with carbon black in the hexane solution and ultrasonically dispersed for another 1h. The supported catalysts were then collected by centrifugation at 5000 rpm for 5 min and then completely dried.

Acetic acid treatment of the PtPdCu_x nanoparticles.

The carbon supported PtPdCu_x catalysts were dispersed in pure acetic acid under an air atmosphere with vigorous stirring at room temperature for 24 h, and then collected by adding ethanol and centrifugation. The same procedure was performed under an N₂ atmosphere for comparison.

Preparation of unsupported dealloyed PtPdCu_x nanoparticles.

We directly treated the starting NPs by acetic acid, and then redispersed them in oleylamine and heated at 60°C for 1h after washing them with ethanol. The unsupported D_{N2}-PtPdCu₉ NPs also can be obtained in the same way.

Electrochemical Measurements.

The electrochemical measurements were carried out with a three-electrode system on an IM6ex electrochemical workstation (Zahner, Germany). All of the electrode potentials were recorded with respect to a reversible hydrogen electrode (RHE), which was calibrated with H₂ oxidation/evolution on a Pt-wire RDE electrode. A platinum foil and Ag/AgCl (3.5 M) were used as the counter and reference electrodes, respectively. To prepare the working electrode, ethanol suspensions of 0.5 mg of catalyst (recorded with metal Pt) per milliliter with 0.02 wt%

Nafion (diluted from 5 wt% Nafion, Sigma–Aldrich) were obtained by ultrasonic mixing for about 30 min. The metal-catalyst ink was transferred onto the RDE and dried in flowing argon. The Pt loadings of the $D_{\text{air}}\text{-PtPdCu}_9$ and $D_{\text{N}_2}\text{-PtPdCu}_9$ catalysts were both $10.2\mu\text{g cm}^{-2}$, and the Pt/C was $15.3\mu\text{g cm}^{-2}$. The electrochemical active process was carried out in an N_2 -saturated 0.1 M HClO_4 solution between 0.05 and 1.20 V at a sweep rate of 250 mV s^{-1} for 50 cycles at room temperature. The ECSA measurements were determined by integrating the hydrogen-adsorption/desorption-region charge of the cyclic voltammetry (CV) in an N_2 -saturated 0.1 M HClO_4 solution at the sweep rate of 50 mV s^{-1} . The ORR measurements were conducted in an O_2 -saturated 0.1M HClO_4 solution at the scan rate of 20 mV s^{-1} (1600 rpm). The durability testing was performed in air-saturated HClO_4 solution. The electrode was cycled from 0.6 V to 1.0 V at the sweep rate of 50 mV s^{-1} in 0.1 M HClO_4 and left open to the atmosphere to allow for the replenishment of the dissolved oxygen in the electrolyte.

Characterization.

The samples were characterized by powder X-ray power diffraction (XRD), using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$). The operation voltage and current were kept at 40 kV and 400 mA, respectively. Nanocrystals dispersed in hexane were drop-casted on carbon-supported Cu grids for transmission electron microscope (TEM) and high-resolution transmission electron microscope (HR-TEM) observation, which were performed on Hitachi H-7650 and JEOL-2010F with an acceleration voltage of 200 kV. Nanocrystals dispersed in hexane were drop-casted on carbon-supported Mo grids for scanning transmission electron microscopy energy dispersive spectrometer (STEM EDS) element mapping and line scan. Inductively coupled plasma (ICP) data were obtained using an Optima 7300 DV instrument. Electrochemical measurements were performed using an IM6ex electrochemical workstation (Zahner, Germany). The X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photo-electron spectrometer using Mg Ka radiation exciting source.

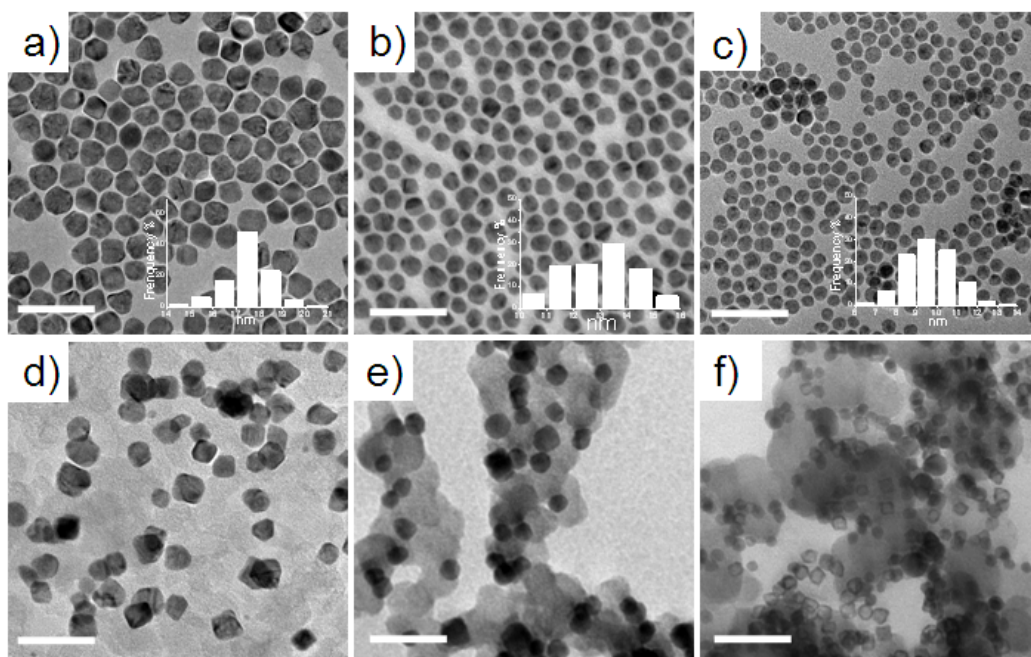


Fig. S1 (a-c) TEM images of as-prepared unsupported PtPdCu₁, PtPdCu₃ and PtPdCu₆ NPs. Insets show particle size distribution. (d-f) TEM images of D_{air}-PtPdCu₁, D_{air}-PtPdCu₃, and D_{air}-PtPdCu₆ catalysts. The scale bar is 100 nm.

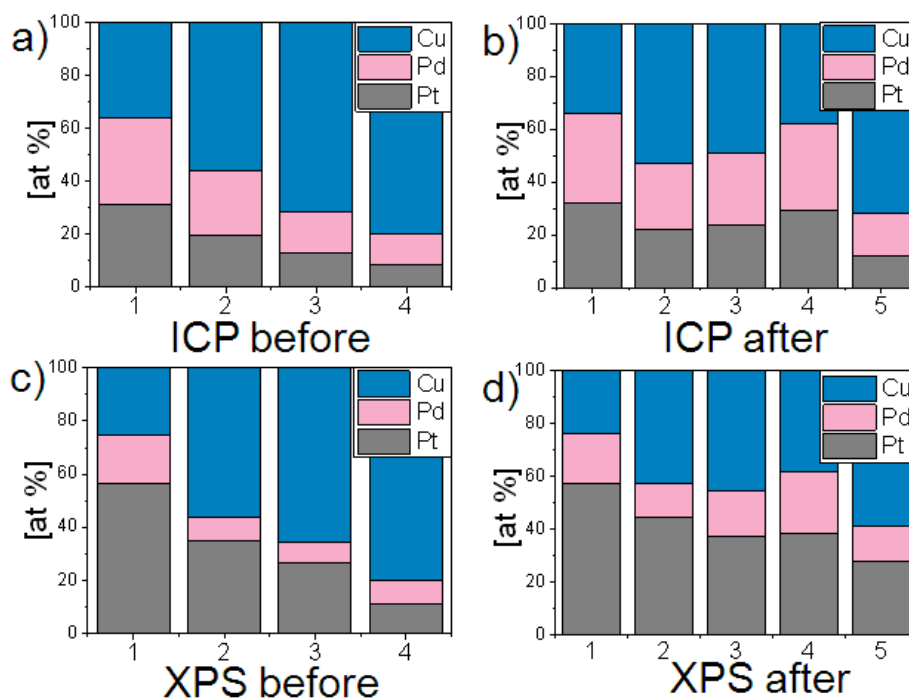


Fig. S2 The bulk Pt/Pd/Cu compositions of the catalysts were measured by ICP. Variations in the Pt/Pd/Cu ratio before and after acetic acid dealloying are shown in (a) and (b). The Pt/Pd/Cu atomic ratio in the near surface region before (c) and after (d) chemical dealloying were characterized by XPS. The sample 1-4 denotes these PtPdCu_x (x=1, 3, 6 and 9) catalysts with four atomic ratios. The sample 5 denotes the D_{N₂}-PtPdCu₉ catalyst.

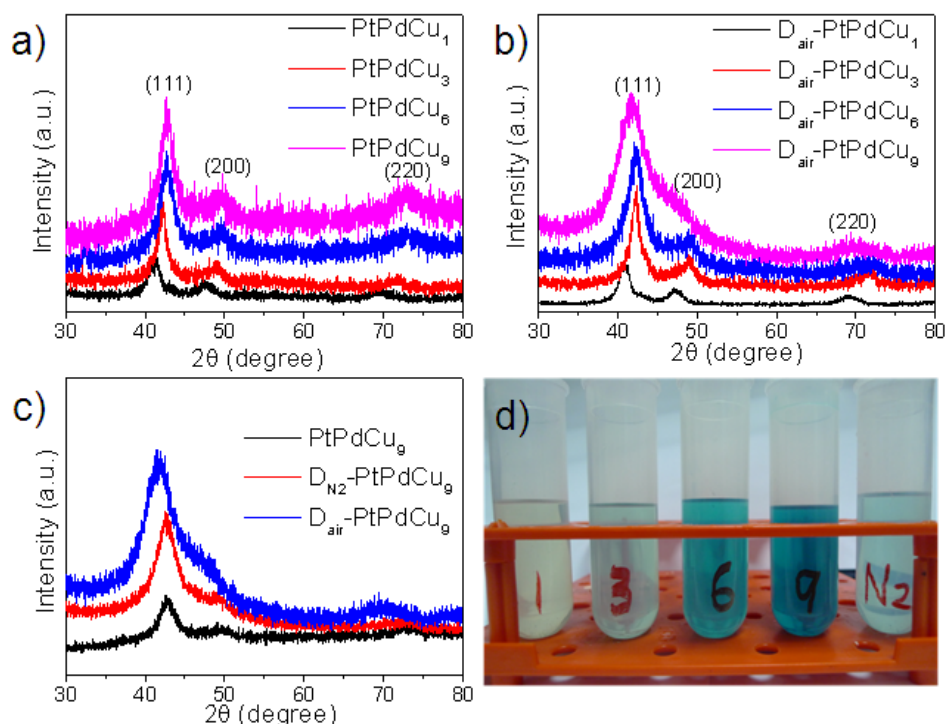


Fig. S3 XRD patterns of initial PtPdCu_x ($x=1, 3, 6$ and 9) NPs (a) and $\text{D}_{\text{air}}\text{-PtPdCu}_x$ ($x=1, 3, 6$ and 9) NPs (b). (c) XRD patterns for $\text{D}_{\text{N}_2}\text{-PtPdCu}_9$ and $\text{D}_{\text{air}}\text{-PtPdCu}_9$ in comparison with initial PtPdCu_9 NPs. (d) Comparison of the color of the top solution of dealloyed PtPdCu catalysts with different atomic ratios after centrifugation.

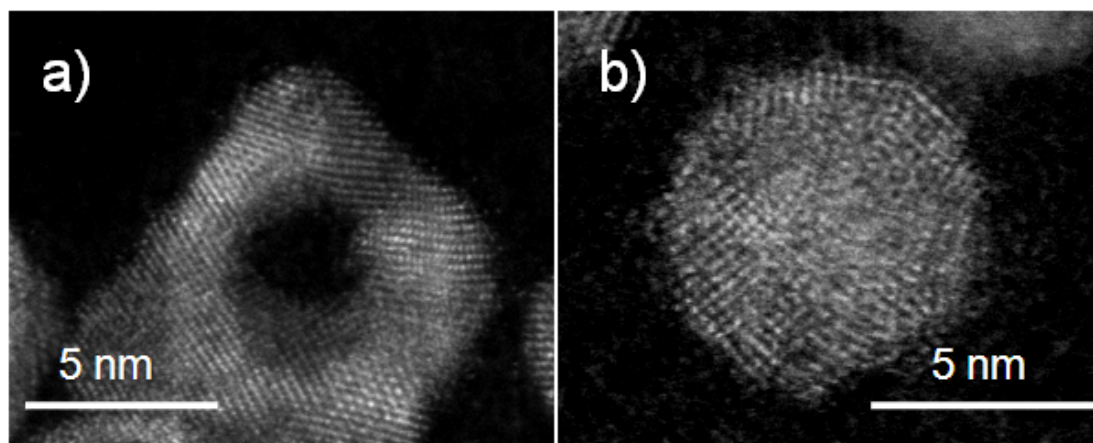


Fig. S4 HADDF-STEM images of a $\text{D}_{\text{air}}\text{-PtPdCu}_9$ NP (a) and a $\text{D}_{\text{N}_2}\text{-PtPdCu}_9$ NP (b).

Table S1. ICP results of Pt, Pd, Cu compositions in the top blue solution of the $\text{D}_{\text{air}}\text{-PtPdCu}_9$ after centrifugation.

Sample	Pt	Pd	Cu
($\mu\text{g/mL}$)	0.482	0.094	219.8

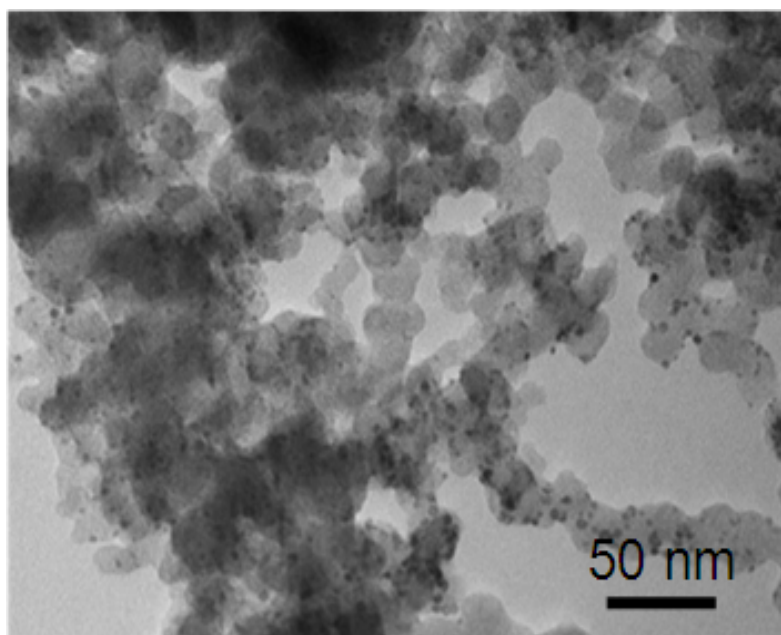


Fig. S5 TEM image of the carbon supported PtPdCu₉ catalyst dealloyed by 1M HCl aqueous solution.

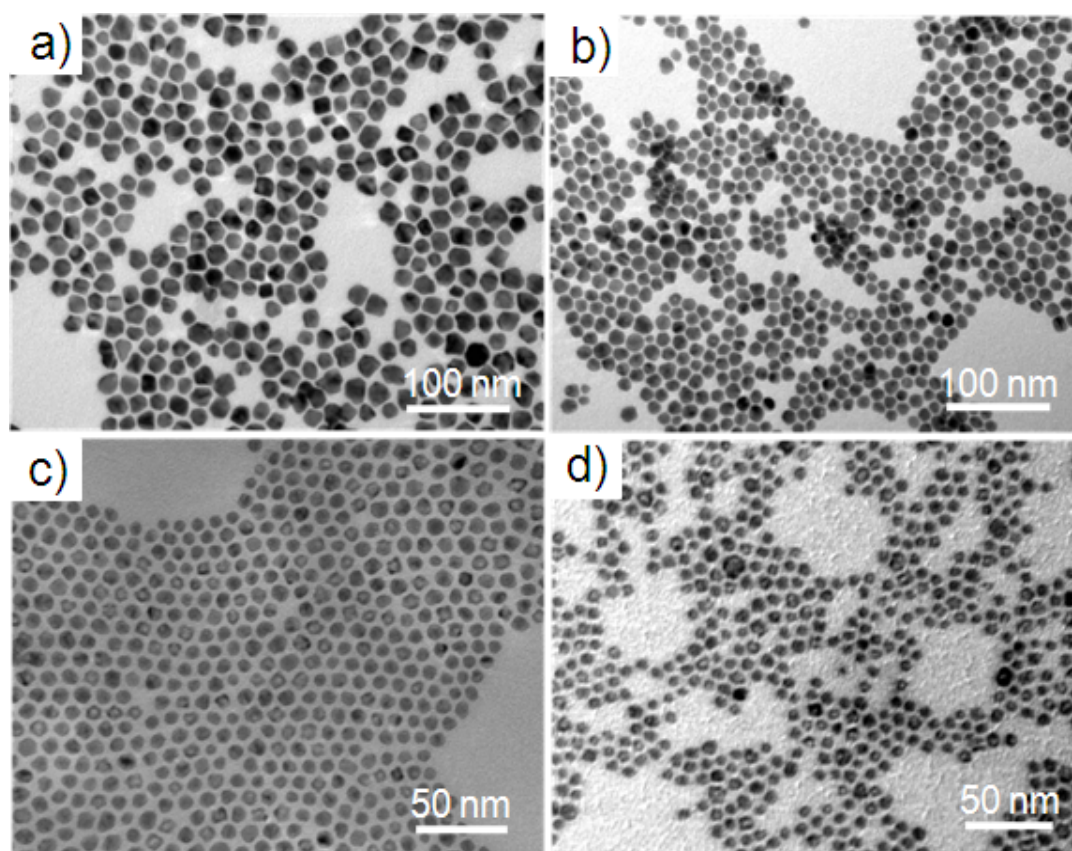


Fig. S6 (a-d) TEM images of unsupported PtPdCu₁, PtPdCu₃, PtPdCu₆ and PtPdCu₉ NPs which were chemically dealloyed in air.

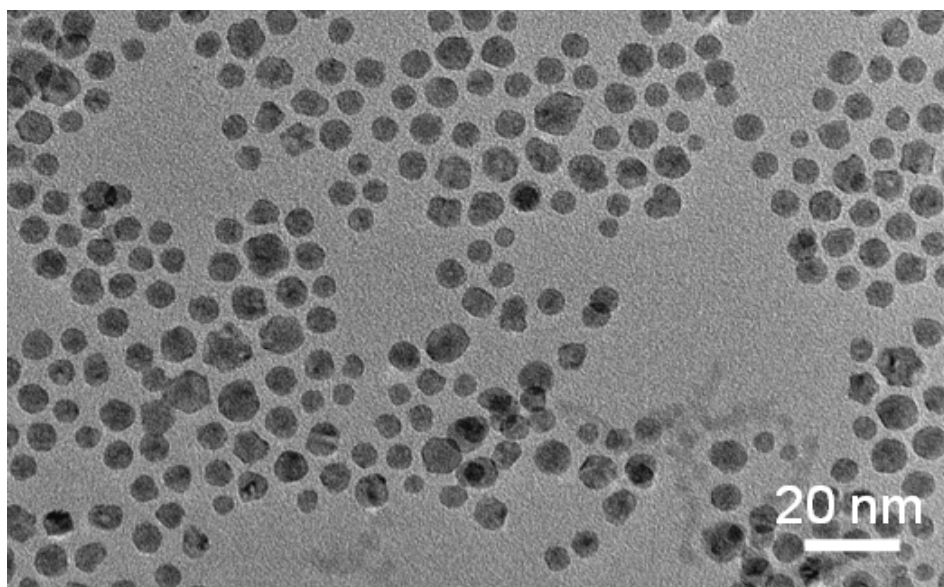


Fig. S7 TEM image unsupported of PtPdCu₉ NPs which was acid dealloyed under N₂ atmosphere.

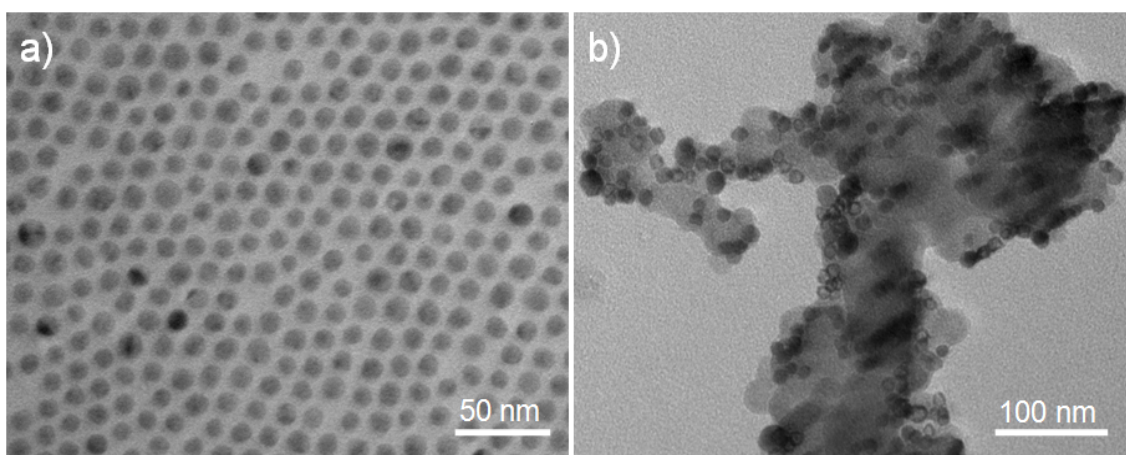


Fig. S8 (a) (b) TEM images of as-prepared unsupported PtPdCu₆ NPs at 270 °C and the corresponding obtained catalyst by acetic acid dealloying in air.

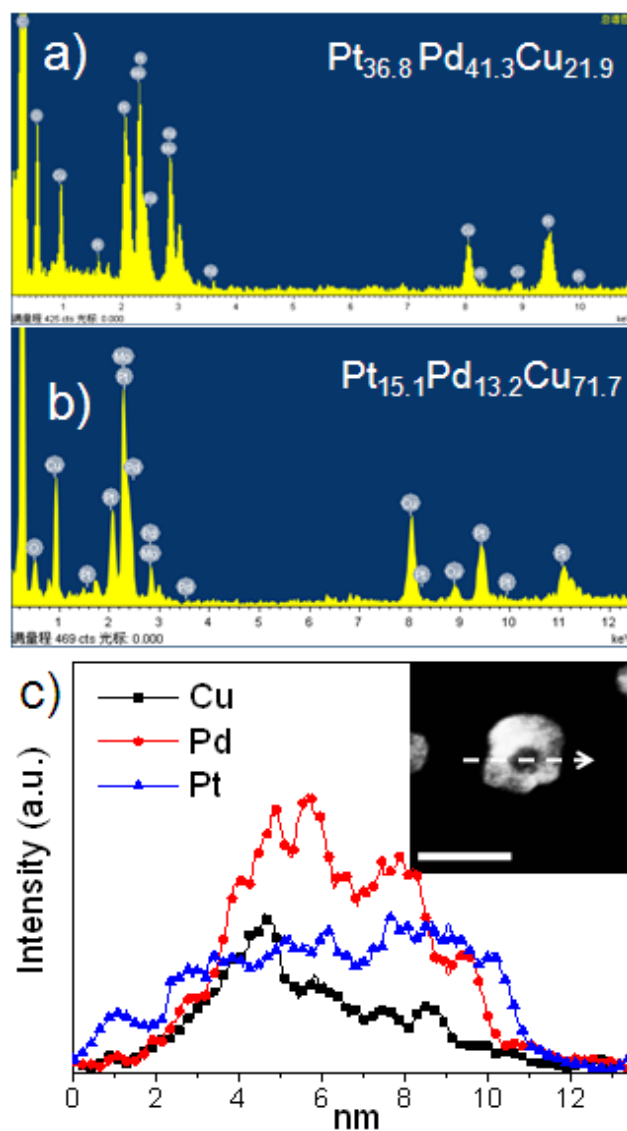


Fig. S9 (a) (b) EDS results of the two NPs in Figure 3a and 3b. (c) The EDX compositional line profile of another PtPdCu hollow NP. The scale bar is 20 nm.

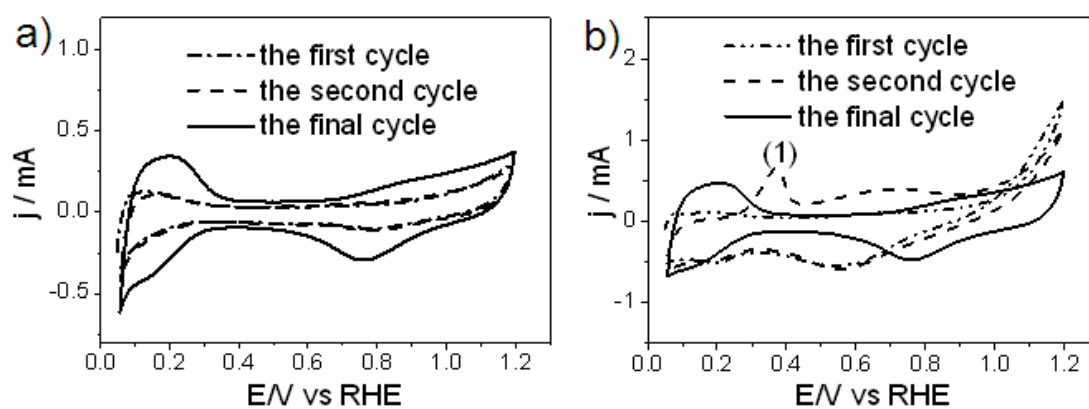


Fig. S10 CV profiles of (a) D_{air}-PtPdCu₉ and (b) D_{N₂}-PtPdCu₉ electrocatalyst before (the dashed line) and after (the solid line) the electrochemical activated process. Peak (1) in (b) indicates the surface dissolution of pure bulk Cu.

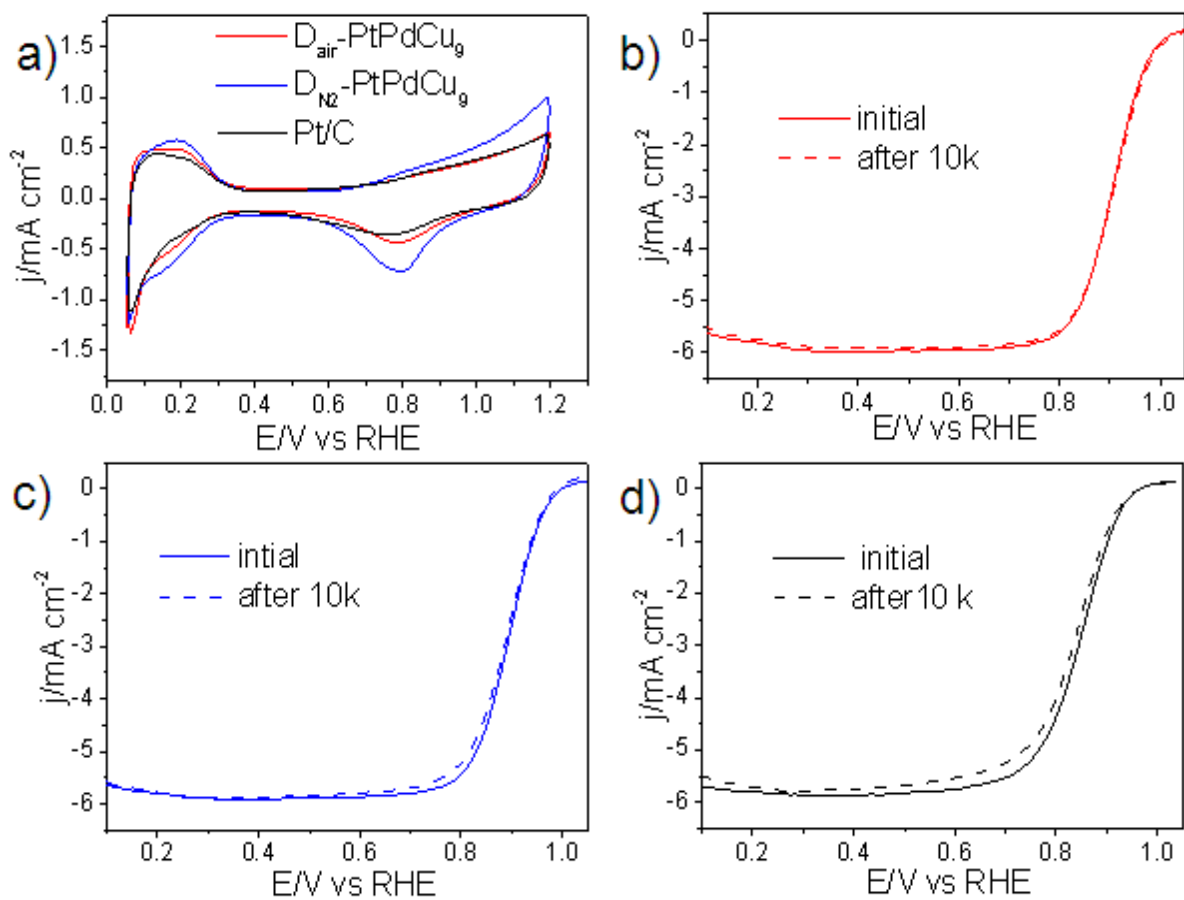


Fig. S11 (a) CV profiles of $\text{D}_{\text{air}}\text{-PtPdCu}_9$, $\text{D}_{\text{N}_2}\text{-PtPdCu}_9$ and commercial Pt/C electrocatalysts recorded in N_2 -saturated 0.1 M HClO_4 solution at the sweep of 50 mV s^{-1} . (b-d) ORR polarization curves before (solid) and after (dash) stability testing of $\text{D}_{\text{air}}\text{-PtPdCu}_9$, $\text{D}_{\text{N}_2}\text{-PtPdCu}_9$ and commercial Pt/C electrocatalysts, respectively.