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Supporting Information

Boosting Oxygen and Peroxide Reduction Reactions on PdCu Intermetallic Cubes

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Supporting Information

Phase transfer of Pd cubes

In a standard procedure, 8 mL of ethanol solution containing the Pd cubes, 5 mL of OLA and 3 mL of toluene were mixed in a 20 mL glass vial. After the reaction kept at 80°C over-night, the product was washed with ethanol by centrifugation and then re-dispersed in chloroform for further characterization.

Preparation of Carbon-Supported PdCu Catalysts Carbon

In a standard preparation, Carbon black (Vulcan XC-72) particles were dispersed in chloroform and sonicated for 1 h. A predetermined amount of PdCu nanoparticles (20% loading) was then added to this dispersion. This mixture was sonicated for additional 30 min and stirred overnight. The resultant solids were precipitated out by centrifugation at 5000 rpm for 5min and dried under a stream of argon gas.

The solid product was re-dispersed in 20 ml n-butylamine and stirred for 3 days to deoil before centrifuged at a rate of 5000 rpm for 5 min. The precipitate was re-dispersed in 10 mL methanol by sonication for 15 min, followed by centrifugation at 8000rpm for 3 times. The final samples were dried under a stream of argon gas.

Characterizations

XRD patterns were recorded in a scan range of 10-90° at a scan rate of 5.0° min⁻¹ by using X-Ray diffraction (Rigaku, Ultima IV) with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The TEM was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. The HRTEM and the corresponding EDS mapping analyses were performed on a JEOL JEM-ARM300F with a spherical aberration corrector.

The elemental ratio of PdCu were measured on ICP spectrometer on a 6300 instrument (Thermo Electron Corp.).

Electrochemical measurement

The three-electrode cell equipped with the CHI760E electrochemical analyzer (CH Instrument, Shanghai) was used to measure the electrochemical performance of catalysts.

Oxygen reduction reaction (ORR)

The glassy-carbon rotating disk electrode (RDE, area: $\sim 0.196 \text{ cm}^2$), a 4cm platinum wire and the Reversible hydrogen electrode (calibrated before test) were utilized as the working, counter, and reference electrodes, respectively.

The loading of the PdCu on the carbon black was confirmed by the TGA instrument (TG550). 5mg of PdCu catalysts, 4ml of deionized water, 1ml of isopropanol and 25 μL of 5% Nafion solution were mixed and sonicated for 15min. 48 μL of the ink (the loading amount of Pd is 6 μg) was added on the RDE and dried in the air naturally. For other catalysts ink, the loading amount of noble metal (Pd/Pt) was kept at 6 μg .

Before every electrochemical measurement, the CV measurement was carried in the 0.1M KOH to activate the electrode. The CV curves were recorded from 0.05V to 1V with the scan rate of 50mV/s. The electrochemical active surface area (ECSA) of Pt/C was calculated by integrating the hydrogen absorption charge on CV curves. ECSAs of Pd/C and PdCu/C catalysts were determined by CO stripping. The working electrode was immersed in the CO-saturated 0.1M KOH and held at 0.3V for 15min before plunged quickly into the Ar-saturated 0.1M KOH to run CV from 0 to 1.2 V using scan rate of 50mV/s. The ECSAs were calculated by subtracting the background charge (the second CV), assuming a charge density of $420 \mu\text{C cm}^{-2}$.

ORR LSV curves were obtained in the O₂-saturated 0.1M KOH at the rotating speed of 1600 rpm. The electrolyte was purged with oxygen for 30 min before test. The LSV curves were recorded at the scan rate of 10mV/s and repeated 20 times to be stable. IR-compensation was used to get the final LSV curves and calculate the kinetic current.

The accelerated stability test (ADT) was carried out between 0.6 V and 1.0 V at a scan rate of 100 mV/s^{-1} for 30000 cycles in Ar-saturated 0.1 M KOH solution.

Hydrogen peroxide reduction reaction

The glassy-carbon electrode (GCE, area: $\sim 0.071 \text{ cm}^2$), a 4cm platinum wire and the saturated calomel electrode (SCE) were utilized as the working, counter, and reference electrodes, respectively.

5mg of PdCu catalysts, 2ml of deionized water, 1ml of isopropanol and 25 μL of 5% Nafion solution were mixed and sonicated for 15min for making the catalyst ink. 10 μL of the ink (the loading amount of Pd is 2 μg) was added on the GCE and dried in the air naturally. For other catalysts ink, the loading amount of noble metal (Pd/Pt) was kept at 2 μg .

All the measurements were measured in the 15 ml bottle with 10 ml electrolyte. The CV same measurements were used to activate the catalysts in 0.1M HClO₄. Then the working electrode was switched to 0.1M PBS (PH=7) to record CV curves from -0.5 to 0.7V with the scan rate of 50mV/s. After drop 5 μL of H₂O₂ solution, CV curves were recorded with increasing scan rate (50,75,100,125 and 150 mV/s). CV curves with increasing H₂O₂ concentration (5,10,15,20,25mM) were recorded at the scan rate of 100mV/s. All the electrolytes were plunged with argon for 15min to make argon saturated in solution before measurements.

Density Functional Theory (DFT) Computational Model and Method

Analysis

Methodology

We carried out the density functional theory (DFT) calculations on the basis of the projector augmented wave (PAW) method^[1] by utilizing the Vienna ab initio simulation package (VASP)^{[2],[3]} with the generalized gradient approximation (GGA)^[4], the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in the treatment of electron-ion interactions and a cutoff energy of 520 eV for a plane wave expansion of

the wave functions. The PdCu (100) and (110) slabs were built to represent the cubic and spherical PdCu model on the base of the corresponding HAADF-STEM and HRTEM images. We use a 4×4 supercell slab with 7 atomic layers for PdCu (100) slab (Figure S1a), and use a 4×2 supercell slab with 6 atomic layers for PdCu (110) slab (Figure S1b), respectively. A Monkhorst-Pack grid of size of $2 \times 2 \times 1$ was used to sample the surface Brillouin zone^[5]. A vacuum region of 15 Å was added to give converged adsorption energies while the energy convergence criterion is 0.0001 eV/atom for electronic minimization steps. The slabs were shown in Figure S14.

Adsorption Energy Analysis on Oxygen Reduction Reaction

To clarify the effect of the shape of PdCu nanoparticles on activity of oxygen reduction reaction, we calculate the adsorption energy of oxygen atom. The detailed calculation method was similar to our previous work^[6]. And the stable adsorption site and energy were shown in Figure 4a and 4b.

Energy Barrier Analysis on H₂O₂ Decomposition

To discuss the shaped enhanced peroxide reduction reaction, we calculated the energy barrier of its rate-determining step, which is as follows,



The most stable adsorption energy for H₂O₂ were calculated on the surface of PdCu (100) and (111) slabs while the H₂O₂ molecules were allowed to relax. One of OHs, which prefers binding to the surface, was left on the slab surface, while another one, which will combine with H⁺ to form H₂O, were removed from the slab surface. The calculated results were listed in Figure 4c and 4d.

Table S1. Elements content of PdCu cubes and spheres

Sample	Before ADT test		After ADT test	
	Pd%	Cu%	Pd%	Cu%
	Atoms/Mass	Atoms/Mass	Atoms/Mass	Atoms/Mass
PdCu cubes	51.5/63.8	48.5/36.2	57.9/70.1	42.1/29.9
PdCu spheres	55.6/67.5	44.4/32.5	62.3/73.2	37.7/26.8

Table S2. Electrochemical parameters of catalysts before and after ADT

Samples	ECSA(m ² /g)	i _s (mA/cm ² _{Pd})	i _m (A/mg _{Pd})
PdCu cube/C	59.4	0.422	0.251
PdCu cube/C after ADT	35.4	0.483	0.171
PdCu Sphere/C	36.6	0.145	0.054
PdCu Sphere/C after ADT	17.0	0.183	0.031
Pd Cube/C	43.3	0.412	0.182
Pd Cube/C after ADT	33.3	0.306	0.101
Pd/C	51.5	0.116	0.061
Pd/C after ADT	31.9	0.122	0.039
Pt/C	63.2	0.086	0.056
Pt/C after ADT	30.3	0.069	0.021

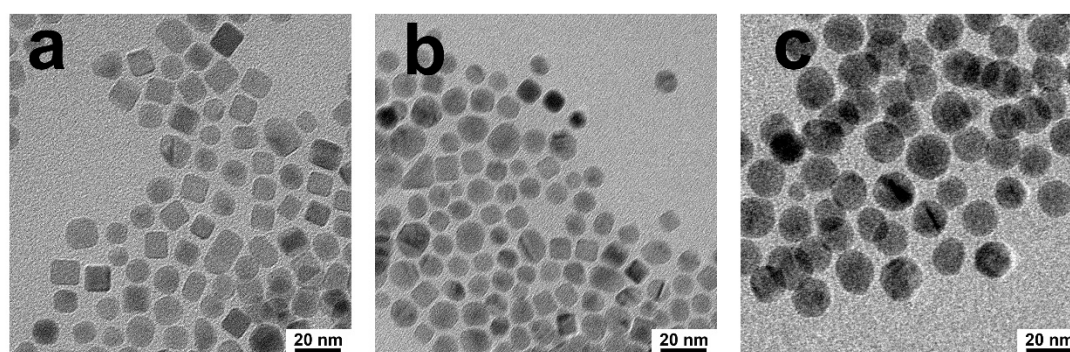


Figure S1. TEM images of PdCu nanoparticles at different temperature. (a)180°C (b)200°C (c) 220°C

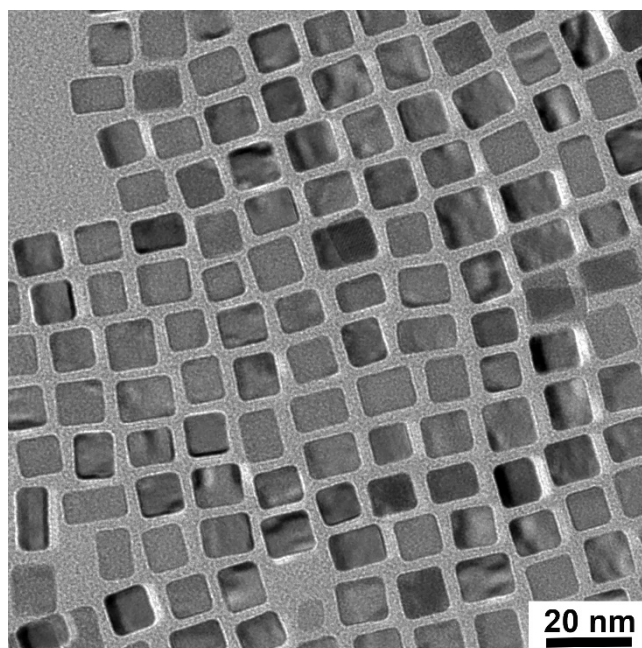


Figure S2. TEM image of Pd Cubes

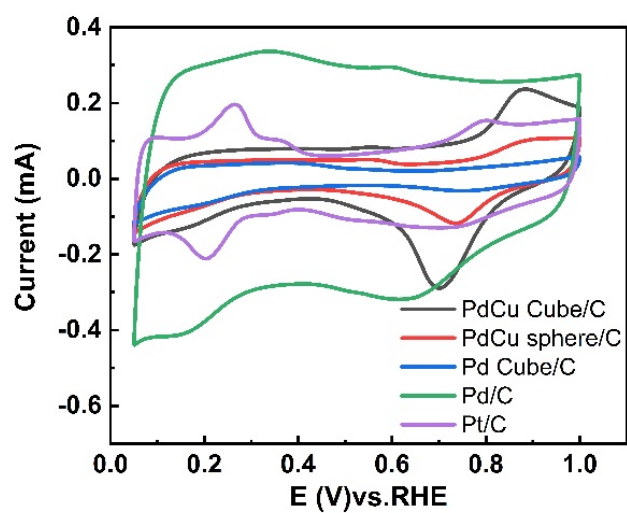


Figure S3. CV curves of the stated catalysts in 0.1M KOH

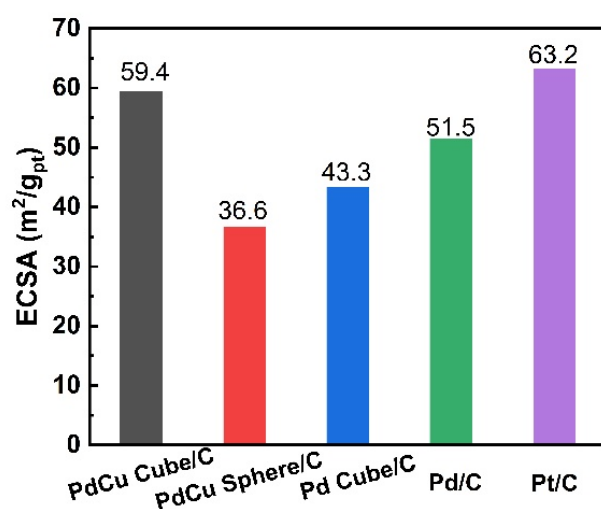


Figure S4. Initial ECSAs of the stated catalysts in 0.1M KOH

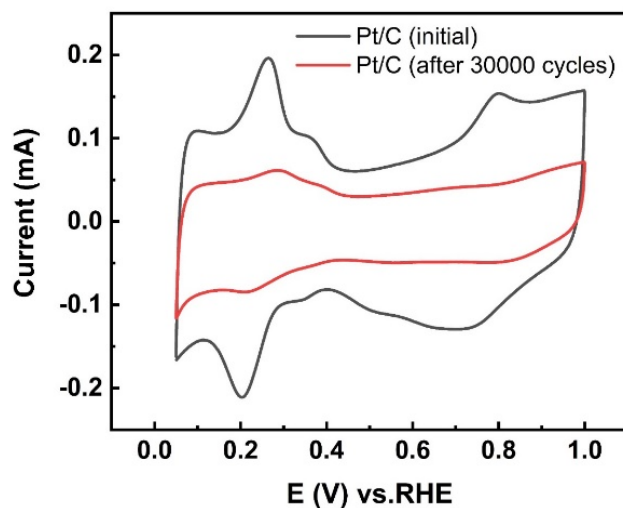


Figure S5. CV curves of the commercial Pt/C before and after 30000 cycles in 0.1M KOH

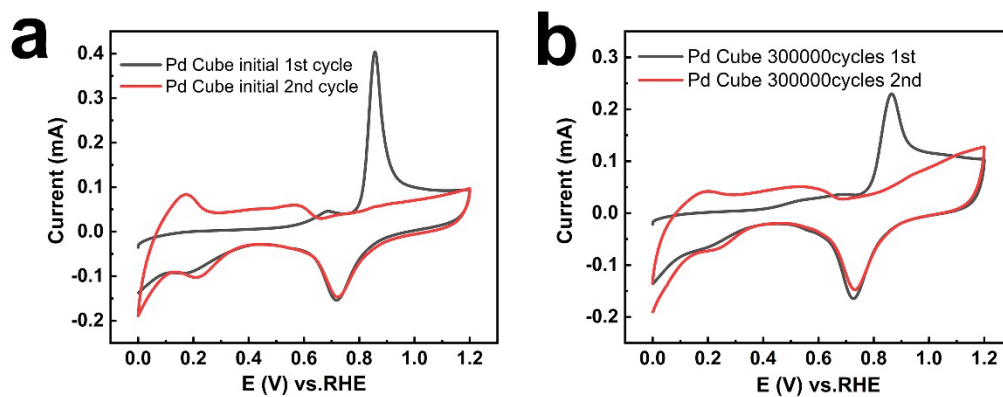


Figure S6. CO stripping curves of PdCu cube/C (a) before 30000 cycles (b) after 30000 cycles

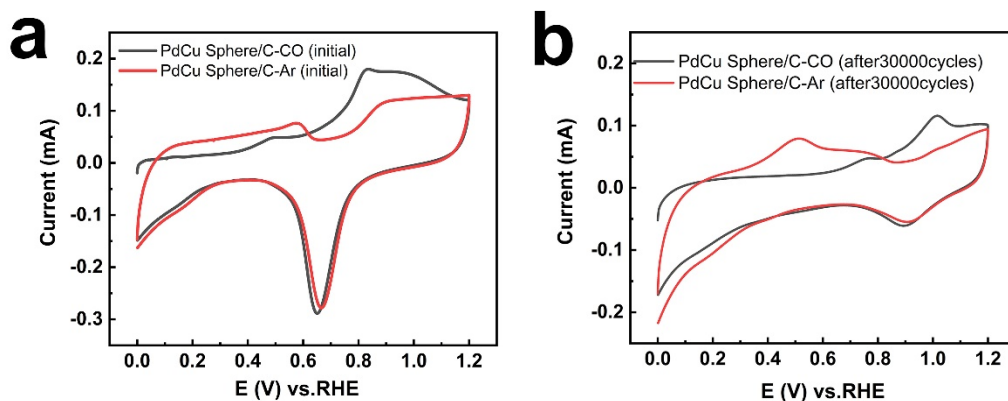


Figure S7. CO stripping curves of PdCu sphere /C (a)before 30000 cycles (b)after 30000 cycles

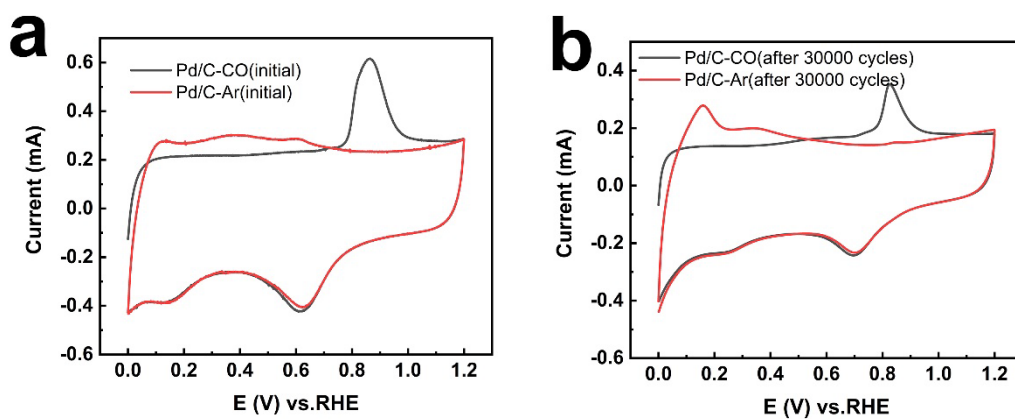


Figure S8. CO stripping curves of the commercial Pd/C (a)before 30000 cycles (b)after 30000 cycles

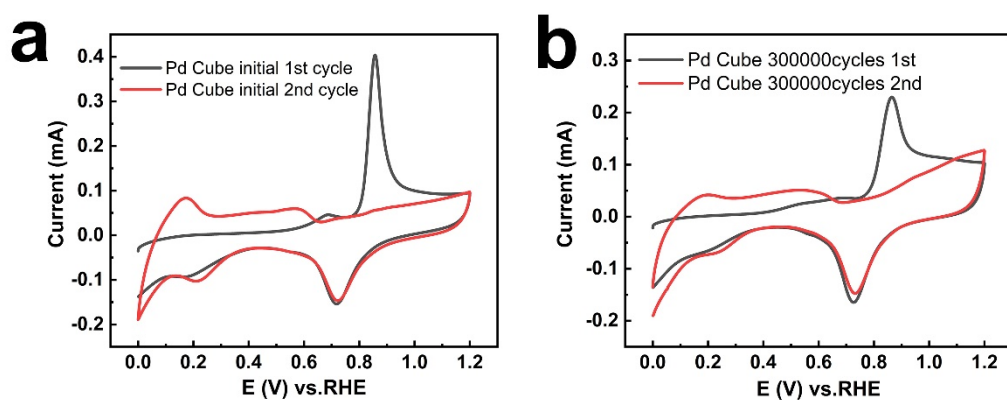


Figure S9. CO stripping curves of the Pd cube/C (a)before 30000 cycles (b)after 30000 cycles

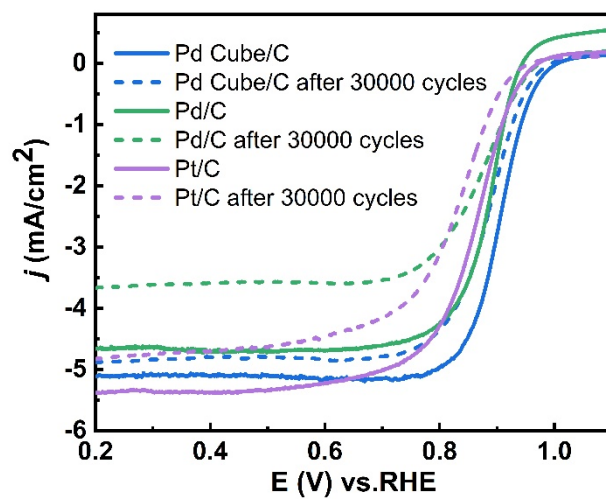


Figure S10. ORR polarization curves of Pd cube/C, commercial Pd/C and Pt/C before and after 30000 cycles

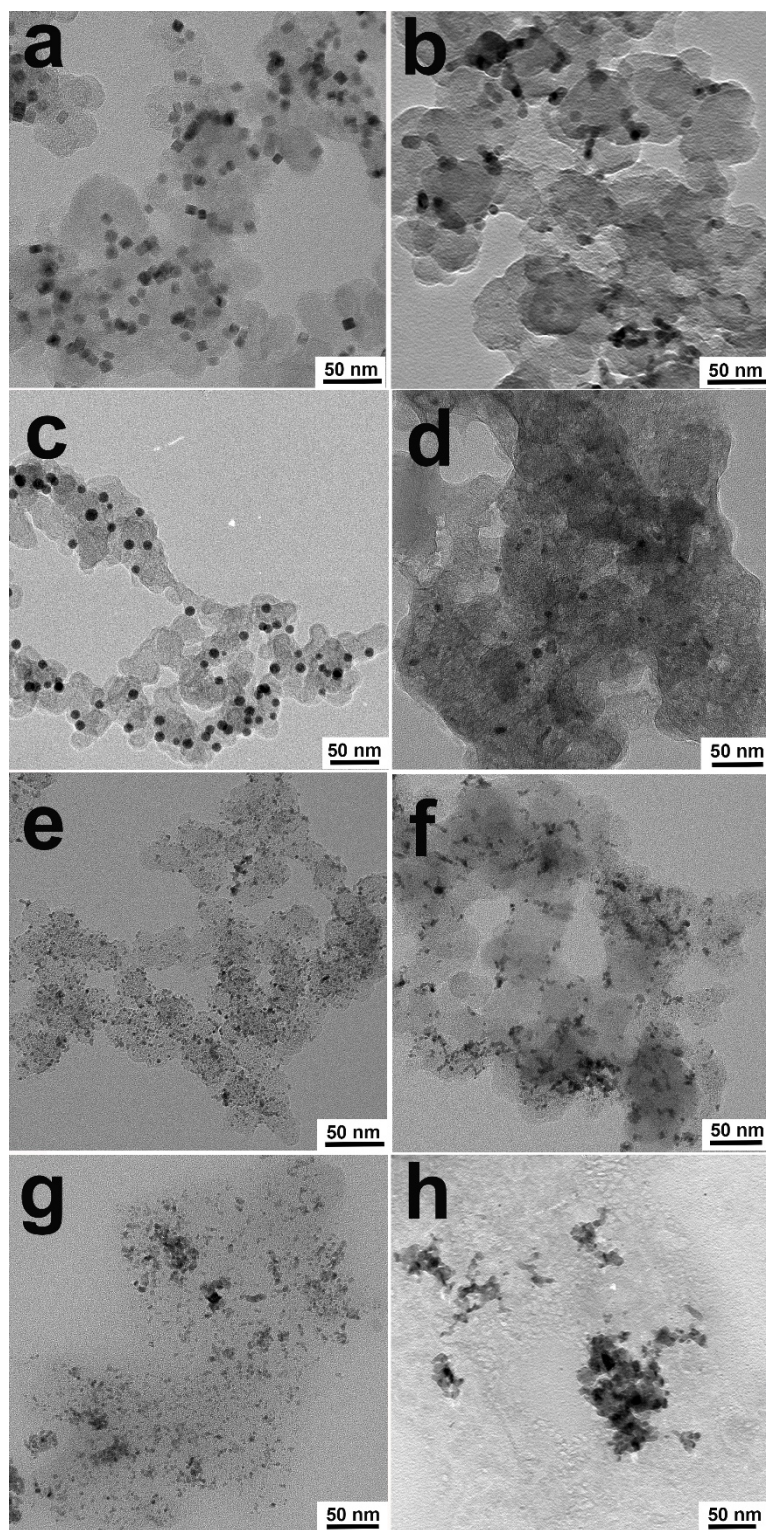


Figure S11. TEM images of PdCu cube/C (a,b) , PdCu sphere/C (c,d), Pt/C (e,f) and Pd/C (g,h) before (a,c,e,g) and after (b,d,f,h) 30,000 electrochemical cycles.

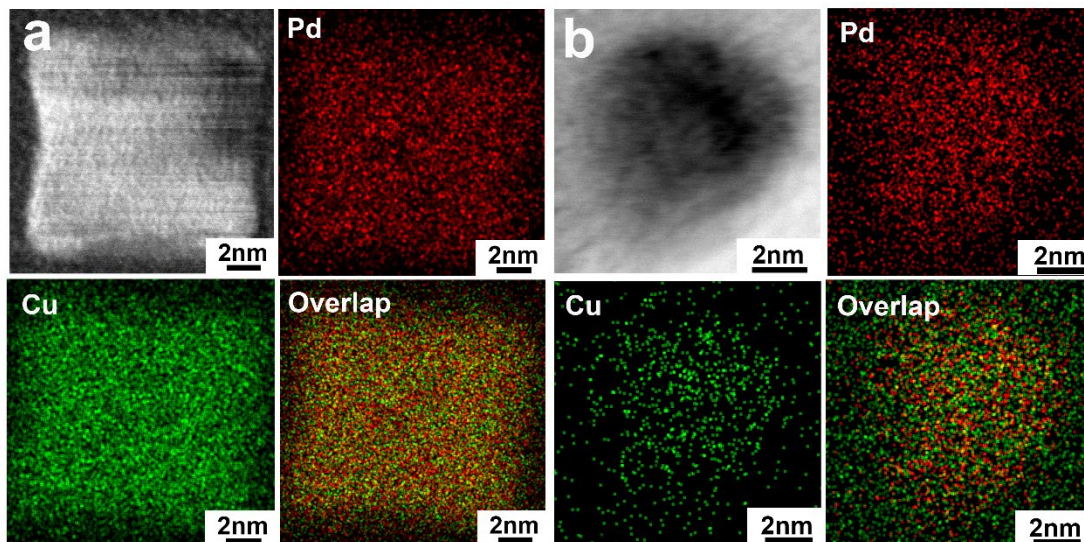


Figure S12. EDS mapping images of PdCu cube/C (a) , PdCu sphere/C (b) after (b,d,f,h) 30,000 electrochemical cycles.

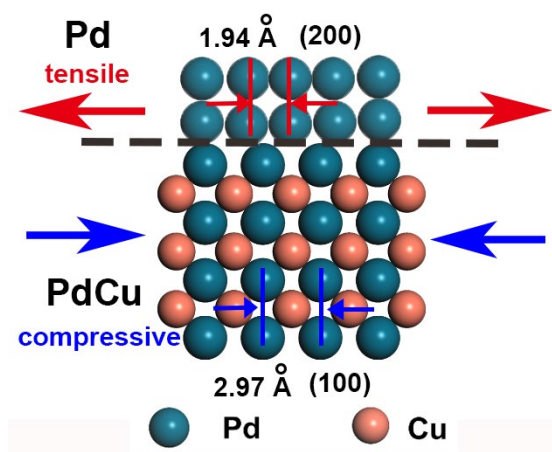


Figure S13. Stress analysis in the surface of PdCu cube (the top are the Pd atoms and inside are Pd and Cu atoms, side view)

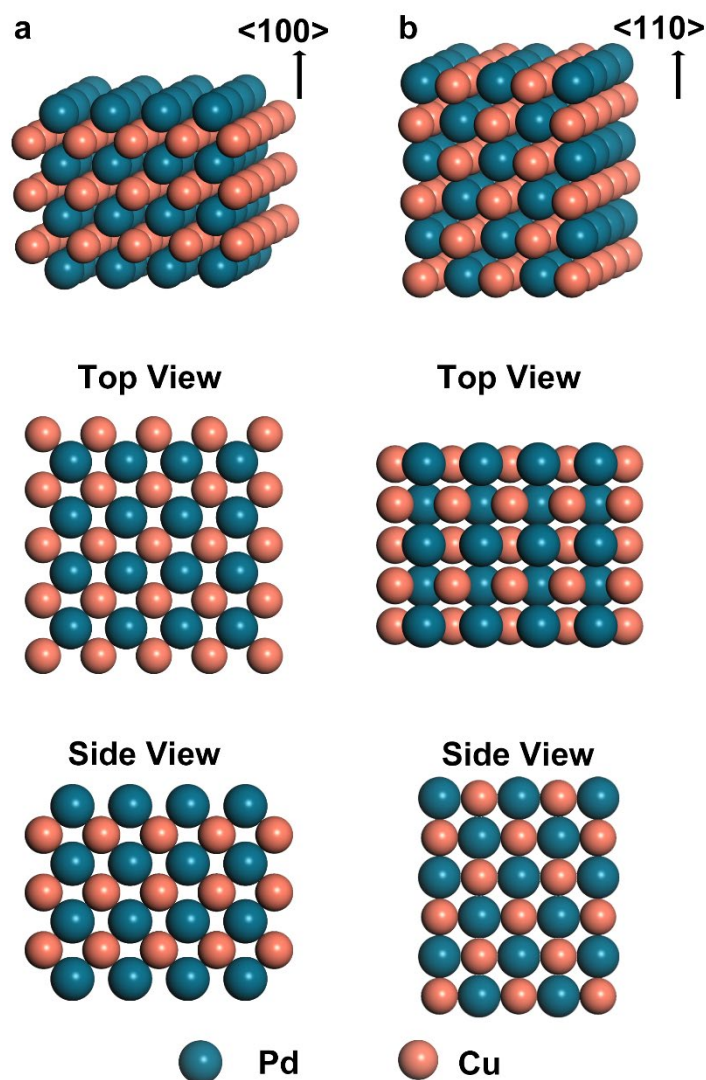


Figure S14. Periodic slab model, top view and side view of (a) PdCu (100) surface, (b) PdCu (110) surface.

References

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