

Supplementary Information

Direct evidence for active site-dependent formic acid eletro-oxidation by topmost-surface atomic redistribution in ternary PtPdCu electrocatalyst

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Experimental

Chemicals. NaNO₃, CuBr, PdCl₂, Dimethyl sulfoxide (99% wt.%), C₂H₅OH (≥99.7% wt.%), HClO₄ (70~72 wt.%) and NaOH were commercially available from Shanghai Chemical Reagent Co. Ltd, Nafion (wt.5%) from Sigma-Aldrich and PtCl₂ from J&K chemical Ltd. All the chemical reagents were analytical grade, and used as received without further purification.

Synthesis of ternary PdPtCu porous tubes. Au layer with a thickness of ~ 40 nm was deposited on the commercial anodic aluminum oxide template (AAO, Anodisc 47, Whatman Co., UK; ca. 300 nm in diameter measured by SEM) to form an annular base electrode at the bottom of the pores. The synthesis of PtPdCu was performed potentiostatically at -1.2 V in DMSO solvents mixed with 2 mM PtCl₂, 10 mM PdCl₂, 20 mM CuBr and 100 mM NaNO₃. The atomic fraction of the as-synthesized PtPdCu tubular materials depends on the starting molar ratio of Pt, Pd, and Cu precursors in bulk solutions and the applied potential. The thickness of the tube wall is mainly attributed to the applied potential. All electrode potentials were measured relative to an Ag/AgCl (3 M) reference electrode using a Pt foil as a counter electrode. After electrodeposition, the thin Au layer on one side of the AAO template was erased completely by alumina particles, and then washed with deionized H₂O and ethanol several times and finally dried for annealing.

Thermal annealing treatment. The AAO-template supported PtPdCu material was loaded on the bottom of a rectangular ceramic boat, and then annealed to maximum temperature of 500 °C for 8 hours (ramp at 5 °C/ min) in a flowing tube furnace (MTI GSL1400X) in 5% hydrogen

atmosphere (balanced with Ar). And then the products were exposed by immersing in 1.0 M NaOH solution for 1 h to completely remove the AAO template, and followed by washing with deionized H₂O and ethanol several times.

Electrochemical measurement. A glassy carbon rotating disk electrode (RDE) (PINE, 5 mm diameter, 0.196 cm²) was polished to a mirror finish and thoroughly cleaned. The preparation of the working electrode was performed as the following: ethanol suspensions of 1mg catalyst (recorded with metal Pt and Pd) per milliliter with 0.02 wt.% Nafion (diluted from 5 wt.% Nafion, Sigma-Aldrich) were obtained by ultrasonic mixing for about 20 min. The metal catalyst link was transferred onto the RDE. The loading of metal_(Pt+Pd) in PtPdCu catalyst is 28.7 μg/cm². Then, the as-prepared catalyst RDE was dried at room temperature. Then the electrochemical measurements were performed by using a three electrode system on an IM6ex electrochemical workstation (Zahner, Germany). A platinum foil and Ag/AgCl (3 M) were used as the counter and reference electrodes, respectively. All electrode potentials were recorded with respect to the reversible hydrogen electrode (RHE).

The electrochemical annealing process was carried out in Ar-saturated 0.1 M HClO₄ solution at the sweep rate of 250 mV/s at the room temperature. The initial cyclic voltammogram was recorded to monitor the surface Cu concentration. Then, the catalysts were electrochemical treated between 0.05 and 1.2 V at a scan sweep rate of 250 mV/s for different potential cycling numbers. Finally, the ECSA measurements were conducted upon the sweep rate of 50 mV/s from 0.05 to 1.2 V in Ar-saturated 0.1 M HClO₄ solutions at the interval of potential cycling, and the electric quantity of H_{upd} adsorption/desorption region was calculated by the attached electrochemical analysis software package of IM6ex electrochemical workstation. The component evolution on the top-most surface layer was detected in Ar-saturated 0.1 M HClO₄ and 0.1 M HCOOH solutions at the sweep rate of 50 mV/s from 0.05 to 1.2 V at the room temperature.

Characterization. The formed phase of the as-synthesized PtPdCu porous tubes was examined with XRD (Cu-K α radiation, λ = 0.154056 nm). XPS studies were performed on ESCALAB-MK- II . EDX were taken with a JEOJ-2010 transmission electron microscope with an acceleration voltage of 200 kV. TEM and HRTEM images were obtained using JEOL-2100F TEM. ICP data were obtained by Optima 7300 DV. Electrochemical measurements were performed on an IM6ex electrochemical workstation (Zahner, Germany).

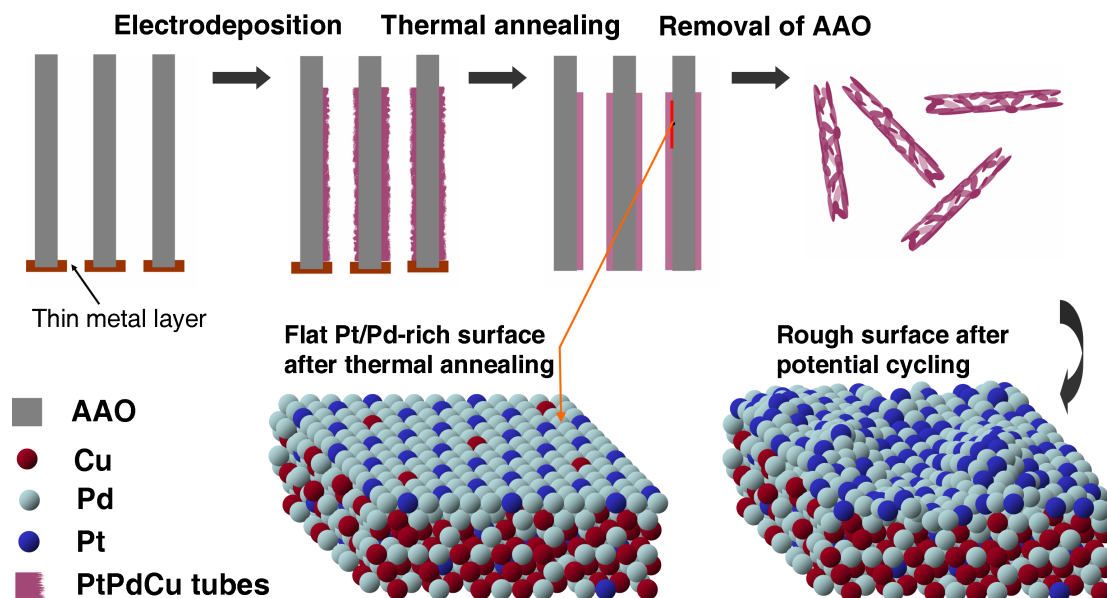


Fig. S1 Schematic of the synthesis of PtPdCu electrocatalysts. This highly active catalyst was prepared through a hydrogen-adsorption-induced compositional restructuring by thermal annealing in a dry environment and, especially, followed potential-induced geometric and compositional restructurings in acidic electrolyte. This electrochemical processing initially leached out the residual surface Cu and resulted in the formation of a mixed PtPd surface and, subsequently potential cycling induced highly increased surface active sites by geometric restructuring and enhanced Pt/Pd atomic ratio in topmost surface layers by compositional restructuring.

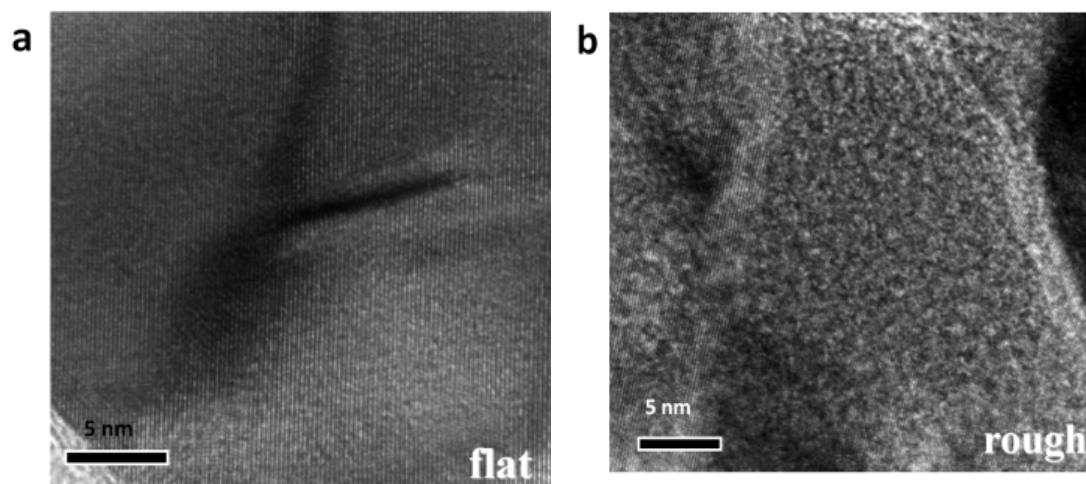


Fig. S2 (a) HRTEM image of the sample after thermal annealing treatment. (b), HRTEM image of the sample after followed 250 potential cycles in Ar-saturated 0.1 M HClO_4 with a sweep rate of 250 mV/s between $0.05 < E < 1.20$ V versus RHE.

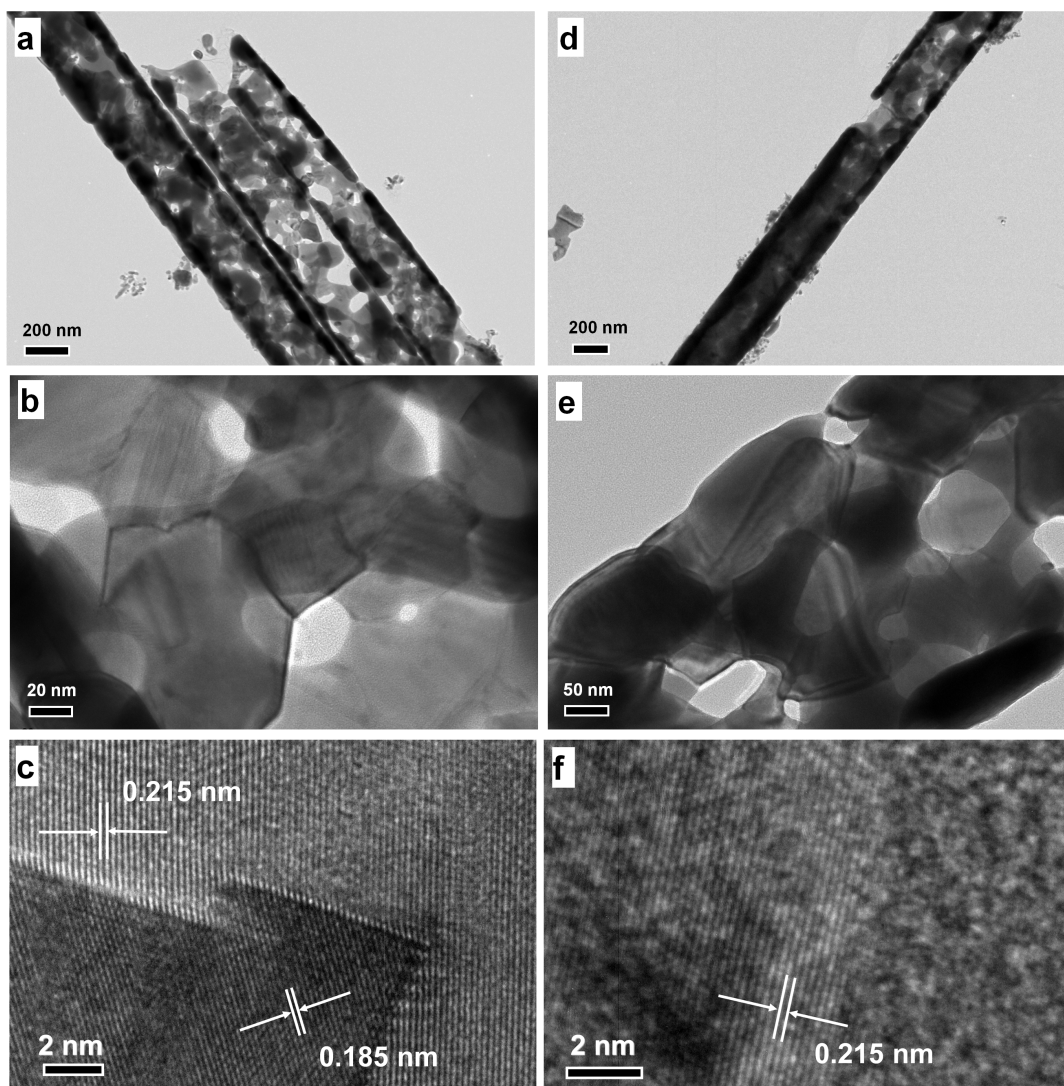


Fig. S3 TEM images of PtPdCu electrocatalyst before any cycling (**a**, **b**, and **c**) and after (**d**, **e**, and **f**) 250th potential cycles. The amplified TEM image (**b**) shows the obvious grain boundary before potential cycling. After 250th potential cycles, the roughing of the PtPdCu surfaces is evident compared to those before any cycling (**c** versus **f**).

This work is to demonstrate the topmost-surface atomic redistribution in acidic electrolyte. According to the reported papers, size and shape of nanoparticle electrocatalysts can be controlled well at nanoscale. Most of these nanoparticles have an organic capping layer which reduces the surface free energy of naked metal nanoparticles in synthesis. Unfortunately, the organic capping layer actually prevents it from XPS studies in many cases. Based on our studies, a reasonable XPS signal only can be achieved upon the removal of majority of carbon layers (carbon layers may form by thermal annealing in H₂/Ar atmosphere due to the carbonation of the capping agent).^{1, 2} The processes typically induce carbon diffusion and even the formation of metallic carbides. In contrast to metal nanoparticles, electrochemical surfactant-free synthesis of ternary electrocatalysts does not use organic capping agents, which make surface characterization and the studies of mechanism straightforward.

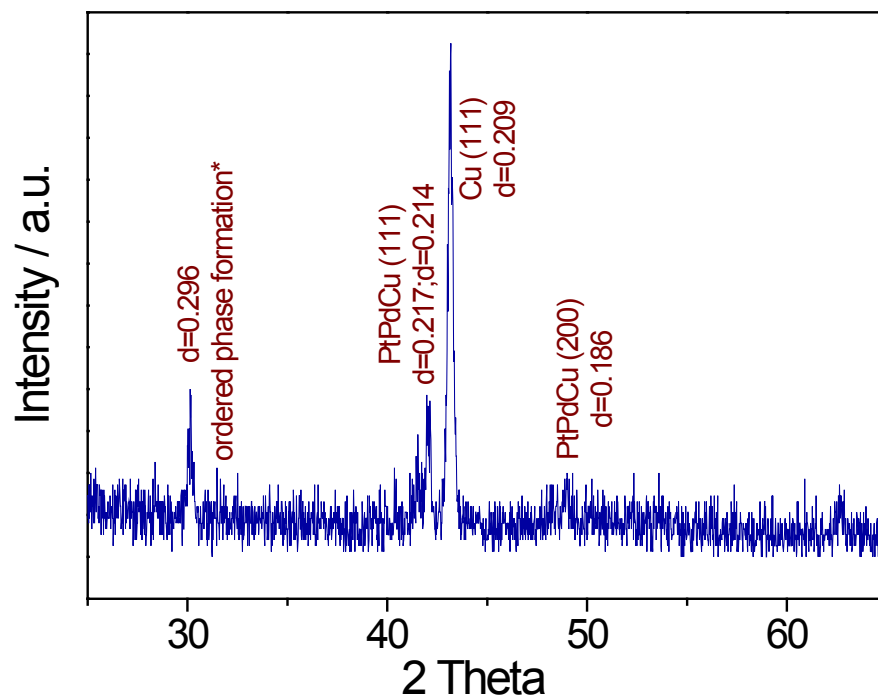


Fig. S4 XRD pattern of the PtPdCu porous tubes. Cu(111) diffraction pattern is clearly observed, which shows the existence of a crystallization of the Cu core due to the separation of Pd and Pt atoms during the thermal annealing at 500 °C in 5% H₂ balanced with Ar for 8 hours.

The differences in the adsorption energy of molecules on the three metals can induce the composition restructuring at high temperature. Here during thermal annealing at high temperatures in hydrogen, the PtPdCu alloy undergoes composition restructuring in which the Pt/Pd migrates to the surface region, forming a PtPd shell. This is because the adsorption enthalpy of H atoms on Pd and Pt is higher than that on Cu.³ The lattice spacing of about ca. 0.214-0.217 nm and 0.186 nm corresponds to the lattice spacing of the (111) and (200) planes in the PtPdCu system (PCPDF # 481550), respectively. The lattice spacing of about ca. 0.296 nm indicates that part of the PtPdCu may form an ordered intermetallic alloy.⁴

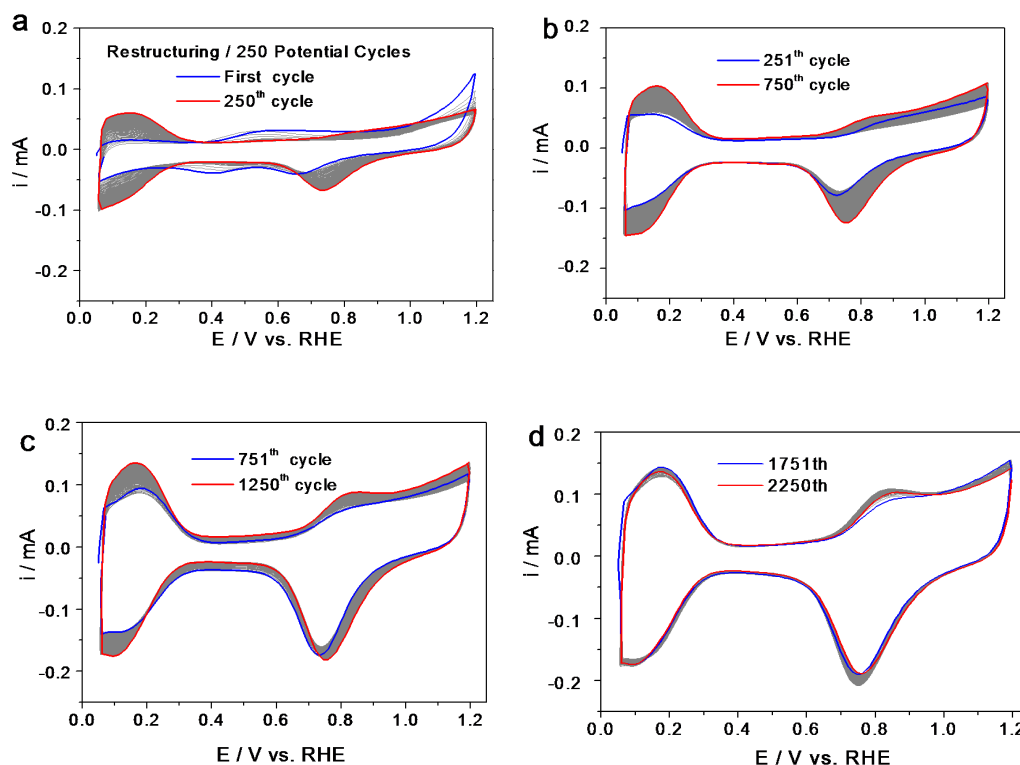


Fig. S5 CVs of the PtPdCu electrocatalyst were recorded with different potential cycle numbers at a scan rate of 250 mV/s in Ar-saturated 0.1 M HClO₄ solution. The ECSA and the polarization curves of formic acid oxidation were measured after 250th, 750th, 1250th, 1750th, and 2250th potential cycles.

After the leaching of surface Cu, the further Cu leaching was prevented by this PtPd-shell ternary system. Normally, after the initial several potential cycles, the surface redox peaks decrease in Figure S2a suggesting the formation of PtPd surface. The very few Cu leaching cannot result in the continuous increase of the ECSA in Figures S2a-c. The surface is PtPd shell with relative high coordination number. The surface energy of the compressive strain Pt-Pt and Pt-Pd bond on the surface should be high that induce rearrangement (ECSA increase) to decrease the surface strain by adsorbates in electrolyte.⁵ These results suggest the migration of Pt/Pd atoms in the surface region induced by potential cycling. We call it “morphology restructuring”. The highly rough surface was confirmed by HRTEM images in main text and supporting information.

On the other hand, atomic redistribution is another adsorbate-dependent or redox-dependent phenomenon for surface composition. In this study, the 2250 potential redox cycles was used to induce the atomic redistribution. Meanwhile, the oxygenated species such as hydroxyl will experience adsorption-desorption cycles on the mixed PtPd alloy surface. Then the Pt/Pd ratio increase with increasing the potential cycling. In this process, part of the surface Pd and Pt may dissolve into the solution, but we did not detect the change.

2250 potential cycles was also used to measure the composition stability (less Cu leaching), and test the structure stability (after 1250 cycles, from 1250 to 2250, ECSA almost keeps the same). Normally, for bimetallic system, upon only 200 cycles the composition of Pt-Cu electrocatalysts was decreased from Pt₂₅Cu₇₅ to Pt₅₅Cu₄₅.⁶ For this catalyst, there was no obvious Cu leaching after 2250 cycles. It clearly showed the composition stability of our low-Pt ternary catalysts.

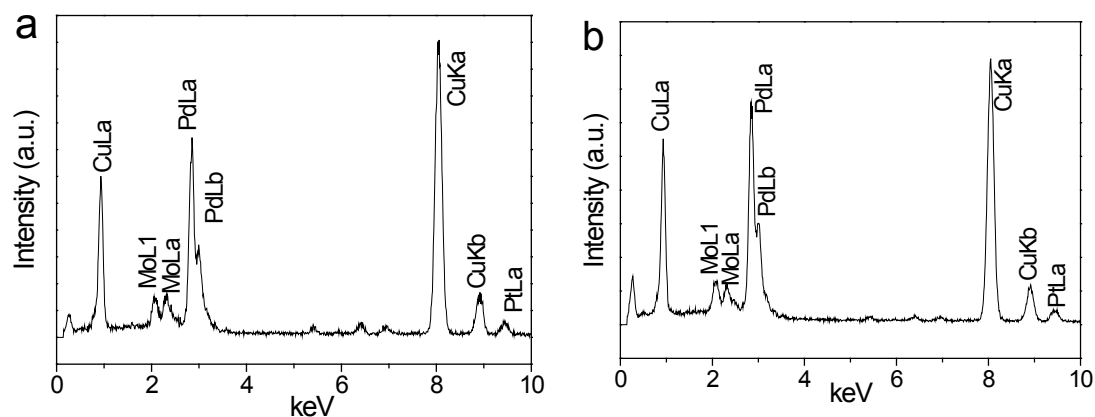


Fig. S6 EDX patterns of the PtPdCu tubes **a)** before and **b)** after potential cycling. It shows that Pd, Pt, and Cu were detected beside the Mo element from the Mo grid.

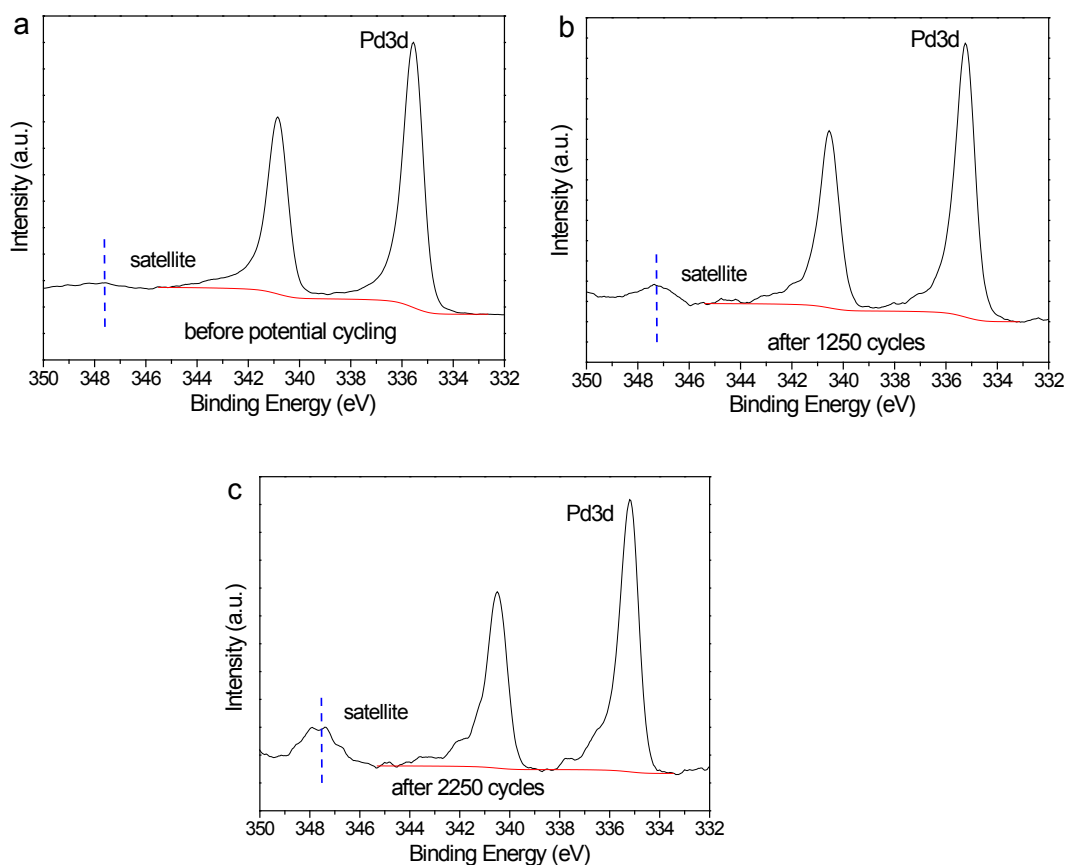


Fig. S7 Pd 3d XPS spectra of the PtPdCu tubes **a)** before potential cycling, **b)** after 1250th cycles, and **c)** after 2250th cycles.

Surface coverage of Pt on the top surface layer of catalysts and atomic fraction of Pt in a surface region

Surface coverage of Pt is defined to the ratio of the number of Pt atoms to the total number of atoms in the surface layer. The significant increase of i_c upon more potential cycling (Figure 4 in main text) suggests more Pt atoms segregate to the surface layer of the PtPdCu catalyst. Atomic fraction of Pt in a surface region is the ratio of the number of Pt atoms in surface region with certain thickness (for XPS using Al K α , the detected volume is from surface layer down to ~3 nm deep) to the total number of all metal atoms in this region. The compositions in the surface regions measured with XPS are listed in Figure 2b. The evolution of Pt surface coverage is monitored with the peak current density in the formic acid oxidation.

A potential technique to explore surface chemistry of electrode materials under a liquid layer

Many important reactions and processes such as electrochemistry in fuel cells and batteries occur at solid-liquid interfaces. In most of the cases, the surface chemistry and composition of these surfaces is the key in understanding the reaction mechanism, identification of their functions, and design of electrode materials. However, it is very challenging to explore the hidden surfaces. XPS is the main tool used to measure chemical composition and the oxidation state of a material's surface. Due to the significant decrease of a mean free path of photoelectrons exited by Al K α , it is impossible to study any surfaces under a liquid film with a thickness larger than 5 nm. One technique developed recently, ambient pressure XPS, can be used to study the surface chemistry of materials under a liquid layer of ~5 nm. A technique being developed by Franklin (Feng) Tao and a European analytical technique firm, called ambient pressure high energy XPS, can be used to study surfaces of materials under a liquid film with a thickness of 0.1-1 μm or even thicker by using high energy X-rays generated from a special anode material. The thickness of 0.1-1 μm of a liquid film will allow us to build micro-devices (fuel cells and batteries) with micro liquid environments for XPS studies. With this approach, the surface chemistry and composition of electrocatalysts can be studied in operando.⁷

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