Supplementary Material

Regulating Interfacial Water Structure by Tensile Strain to Boost Electrochemical Semi-hydrogenation of Alkynes

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Experimental Section:

Materials

Palladium(II) chloride ($PdCl_2$, A.R.), potassium bromide (KBr, A.R.), copper(II) chloride dihydrate ($CuCl_2·2H_2O$, A.R.), dichloromethane (CH_2Cl_2, A.R.), N,N-Dimethylformamide (DMF, ≥99.5 %), sodium chloride (NaCl, A.R.), glacial acetic acid ($C_2H_4O_2$, A.R.), ethanol (C_2H_6O, ≥99.7 %), 2-methyl-2-butanol (MBA, A.R.), sodium borohydride ($NaBH_4$, A.R.), ascorbic acid (AA, A.R.) and perchloric acid ($HClO_4$, 70-72 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. 1-penten-3-ol ($C_5H_{10}O$, ≥97.0 %), 3-buten-1-ol (C_4H_8O, ≥98 %), 1-hexene (C_6H_{12}, ≥97 %), 2-methyl-3-butyn-2-ol (C_5H_8O, A.R.), 2-methyl-3-buten-2-ol ($C_5H_{10}O$, ≥97 %), 4-methoxybenzyl alcohol ($C_8H_{10}O_2$, 98 %), commercial Pd/C (Pd≈10 wt.%) were obtained from J&K Chemicals. Polyvinylpyrrolidone (PVP, M.W.≈58000) and carbon black were purchased from Alfa Aesar. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.25 $M\Omega·cm^{-1}$.

Synthesis of PdCu nanocrystals/XC-72

In a typical synthesis of PdCu nanocrystals on carbon black with similar Pd/Cu raito with that of PdCu icosahedrons, 1.7 mg K_2PdCl_4, 0.25 mg $CuCl_2·2H_2O$ were dissolved in 2 mL H_2O. Then, 2 mg carbon black was added into the above solution and ultrasonic treatment for at least 30 min. After that, 1 mL $NaBH_4$ (10 mM) solution was added into the above solution and gently stirred for 1 h. The final product was collected by centrifugation and washed with ethanol and water three times, respectively. Finally, PdCu nanocrystals/XC-72 was re-dispersed in 1 mL

ethanol.

Synthesis of Pd icosahedrons/XC-72

The Pd icosahedrons catalyst was synthesized according to the previous work with mild modifications.[1] In a typical synthesis, 80 mg PVP was added to a 20 mL vial containing 2.0 mL ethylene glycol, and then preheated for 15 min under magnetic stirring in an oil bath at 115 °C. Subsequently, 1.0 mL ethylene glycol solution containing 17.2 mg Na_2PdCl_4 was rapidly injected using a pipette. After the reaction was proceeded for 8 h, the vial was naturally cooled in the air. Finally, the product was collected by centrifugation and washed with acetone/water twice, respectively. To obtain the final Pd icosahedrons/XC-72, the sample was re-dispersed in deionized water. Then, 1 mL of the sample was injected into 8 mL ethanol containing 2 mg carbon black. After ultrasound treatment for 30 min, the final product was collected by centrifugation and washed three times with ethanol and water, respectively.

Synthesis of Pd@PdCu octahedrons

The synthesis of Pd@PdCu core-shell octahedrons was carried out through a two-step atomic-layer-controlled epitaxial growth method. Pd octahedrons were firstly obtained, and then PdCu alloying layer was grown on Pd octahedrons by epitaxial growth method. Pd octahedrons were prepared according to the previous work with mild modifications.[2] Typically, 256 mg CTAC was dissolved in 8 mL deionized water in a three-necked flask, and then 60 mg AA and 60 mg citric acid were added into the above solution. After that, the solution was preheated to 100 °C and kept for another 10 min, and then K_2PdCl_4 aqueous solution (66.6 mg K_2PdCl_4 dissolved in 3 mL

water) was injected into the flask. The reaction was allowed to proceed at 100 °C for another 3 h. Finally, the product was collected by centrifugation and then re-dispersed in DMF. To perform PdCu alloy shell coating, $PdCl_2$ (1.4 mg), $CuCl_2$ (80 μL, 0.193 M) and KBr (15 mg) were firstly dissolved in 5 mL DMF as precursor solution. Then, 1 mL of Pd octahedrons solution was dispersed in 10 mL DMF with 200 mg PVP. After ultrasonic treatment for 30 min, 0.5 mL of the above precursor solution was added. The homogeneous solution was transferred in an autoclave with a Teflon liner, and was heated at 180 °C for 8 h. After it was naturally cooled to room temperature, the product was collected by centrifugation and washed with ethanol/water three times, respectively. Finally, Pd@PdCu octahedrons were re-dispersed in 1 mL ethanol.

Sample characterizations:

Prior to electron microscopy characterizations, a drop of the suspension of nanostructures in ethanol was placed on a piece of carbon-coated molybdenum grid and dried under ambient conditions. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and the corresponding energy-dispersive X-ray spectroscopy (EDS) mapping profiles were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images were collected on an FEI XL-30 ESEM scanning electron microscope operated at 5 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro Super X-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å). X-ray photoelectron spectra (XPS) were collected on an

ESCALab 250 X-ray photoelectron spectrometer with nonmonochromatized Al-Kα X-ray as the excitation source. The concentrations of Pd and Cu were measured with a Thermo Scientific PlasmaQuad 3 inductively coupled plasma atomic emission spectrometry (ICP-AES) after dissolving the samples with a mixture of HCl and HNO_3 (3:1, volume ratio).

In *situ* electrochemical Raman spectroscopy measurement

In *situ* Raman spectroscopy measurement was performed with the Raman microscopy system (WITEC alpha300 R confocal Raman system) using 633 nm He–Ne laser as the excitation source. The Raman emission was collected by an Olympus 10× objective. Each presented spectrum is an average of five continuously acquired spectra each with a collection time of 1 s.

Calculation of Faradaic efficiency

Faradaic efficiencies of MBE and MBA were calculated according to the following equations. Q_{MBE} and Q_{MBA} were obtained according to the amount of produced MBE or MBA. The production of 1 mol MBE or MBA will consume 2 or 4 mol electrons, respectively. Q_{all} was obtained according to the integration of *i*-*t* curves at the fixed potential.

$$FE_{MBE} = \frac{Q_{MBE}}{Q_{all}} \times 100\% \quad (1)$$

$$FE_{MBA} = \frac{Q_{MBA}}{Q_{all}} \times 100\% \quad (2)$$

$$Q_{all} = \int_0^t idt \quad (3)$$

Supplemental Figs.

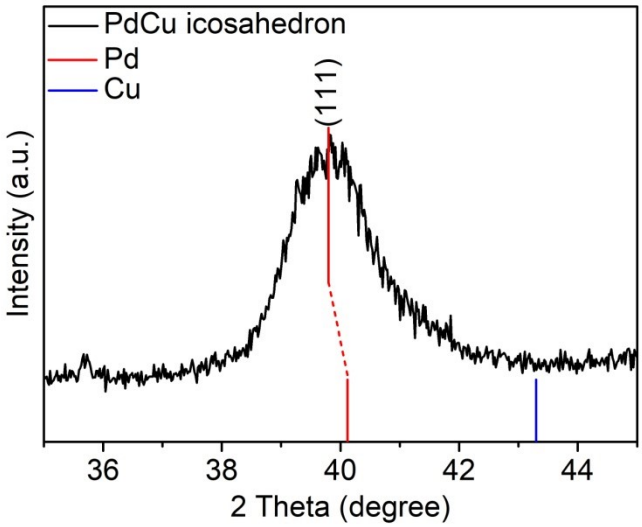

Fig. S1. The enlarged XRD pattern for PdCu icosahedrons.

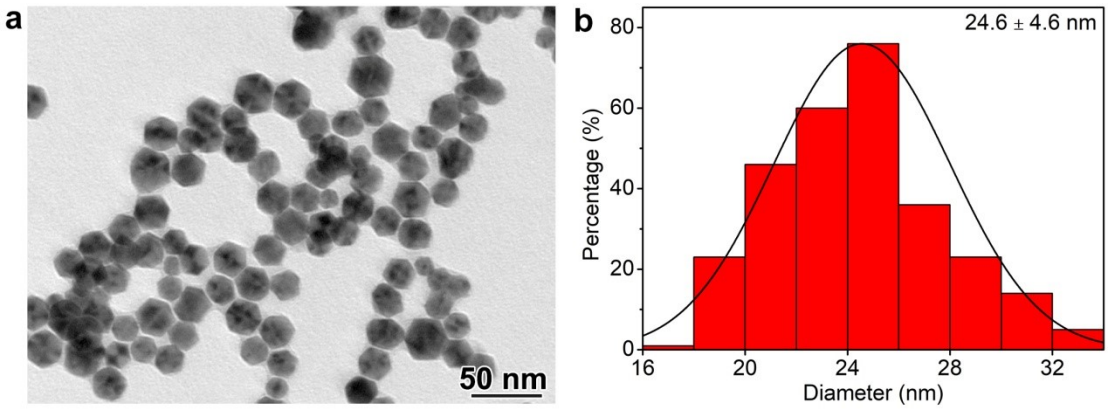

Fig. S2. (a) TEM and (b) the corresponding particle size distribution of PdCu icosahedrons.

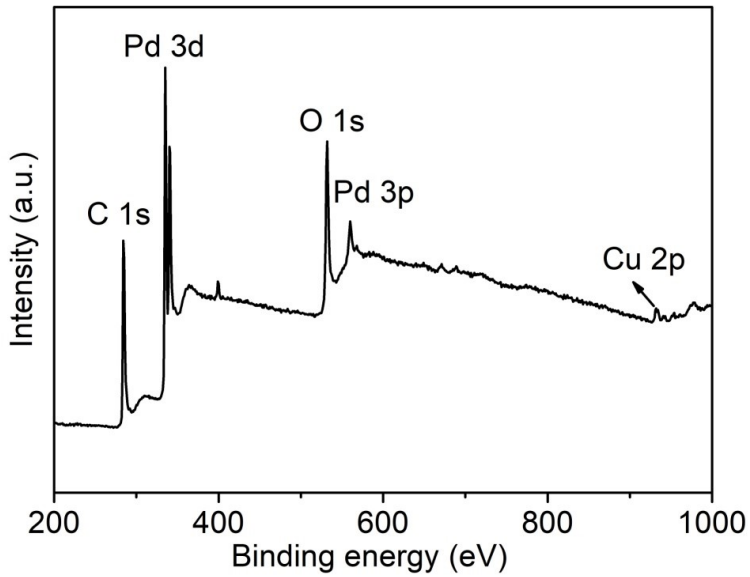

Fig. S3. XPS survey spectrum of PdCu icosahedrons.

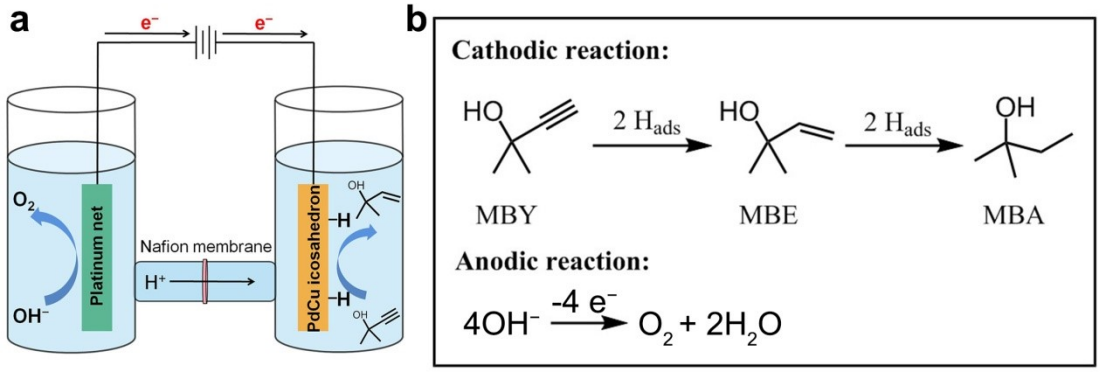

Fig. S4. Schematic illustration of electrolytic setup for ECSH tests.

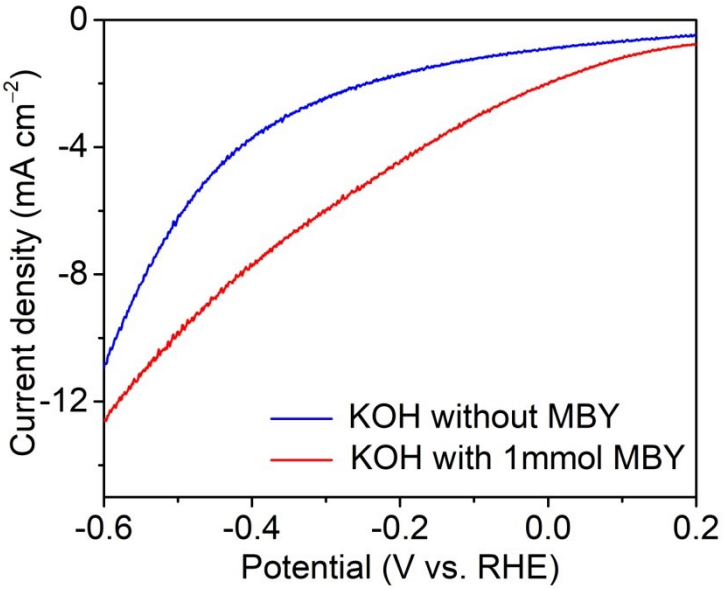

Fig. S5. LSV curves of PdCu icosahedrons recorded in 1 M KOH solution with or without MBY.

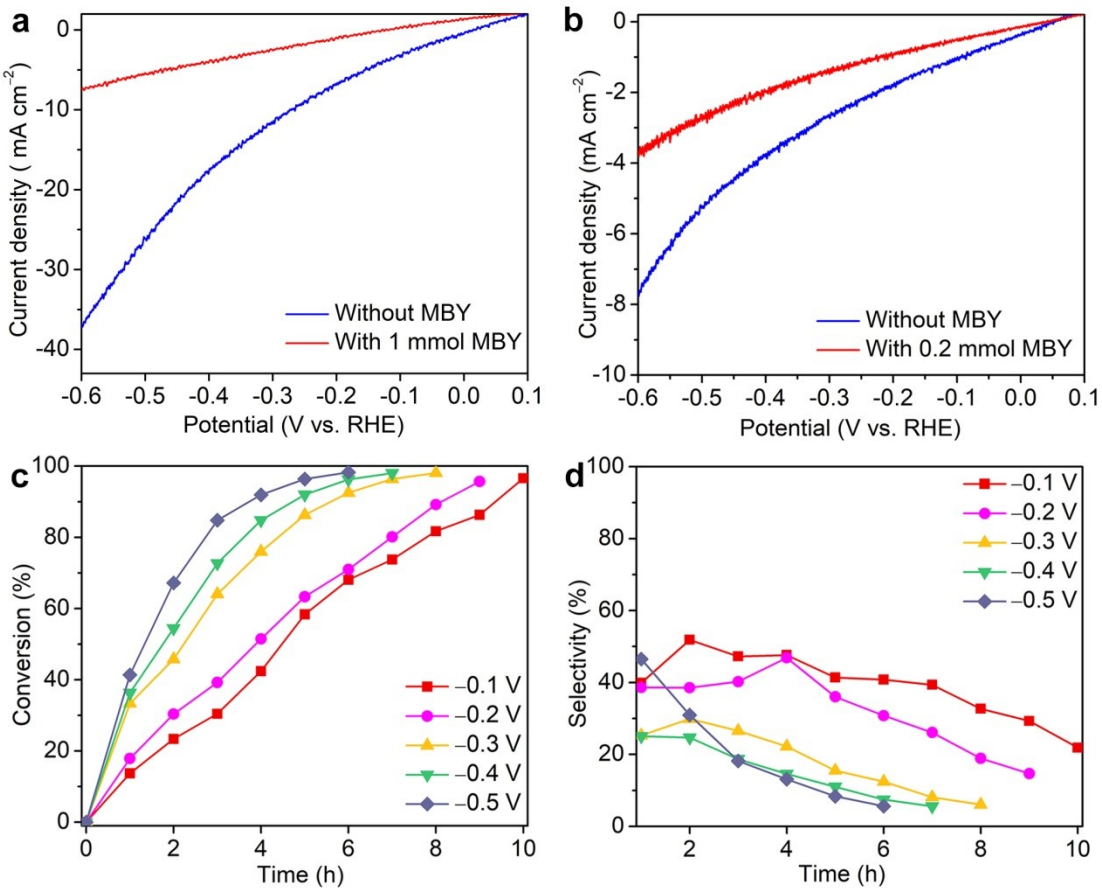

Fig. S6. LSV curves of commercial Pd/C recorded in (a) ethanol + KOH (1 M, V/V=2:1) and (b) KOH with or without MBY, respectively. (c) Time-dependent MBY conversion and (d) MBE selectivity in ECSH of MBY using commercial Pd/C as catalyst, respectively.

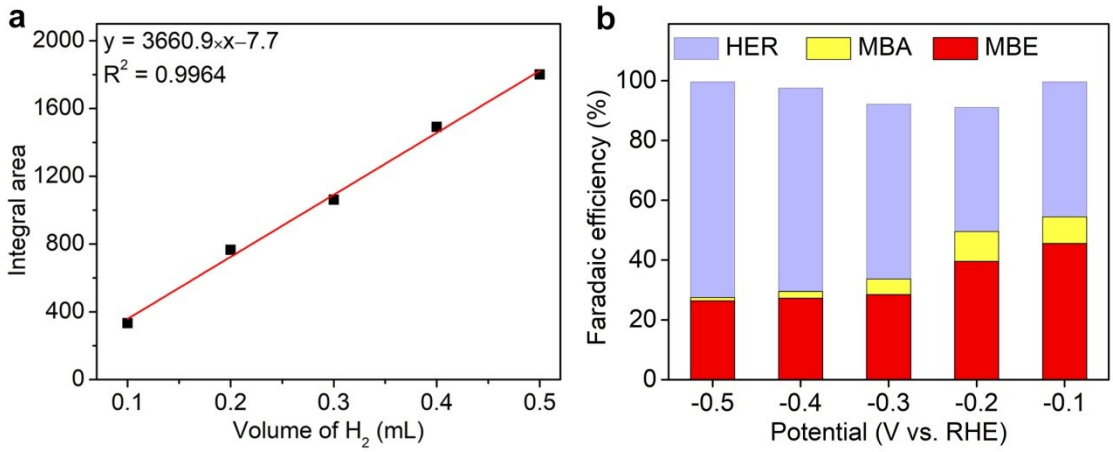

Fig. S7. (a) Calibration curve used for the calculation of H_2 evolution amount. (b) Faradaic efficiency diagram of different products.

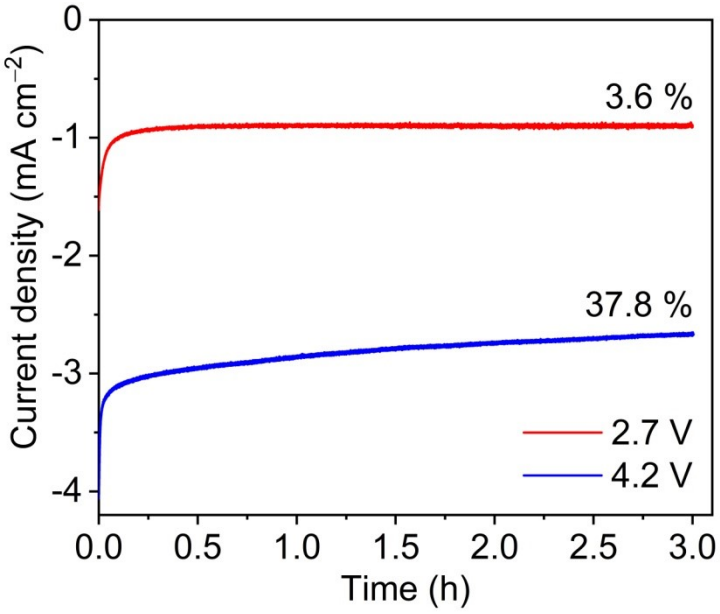

Fig. S8. *I-t* curves recorded by a two-electrode test and the corresponding energy efficiencies for MBE production at 2.7 and 4.2 V.

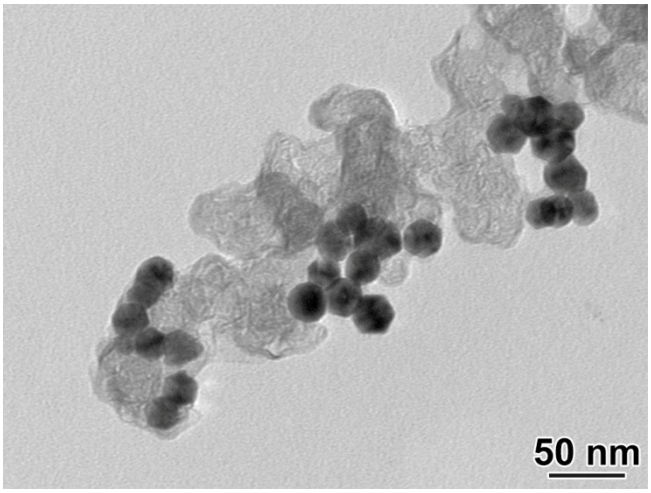

Fig. S9. TEM image of PdCu icosahedrons catalyst after durability test.

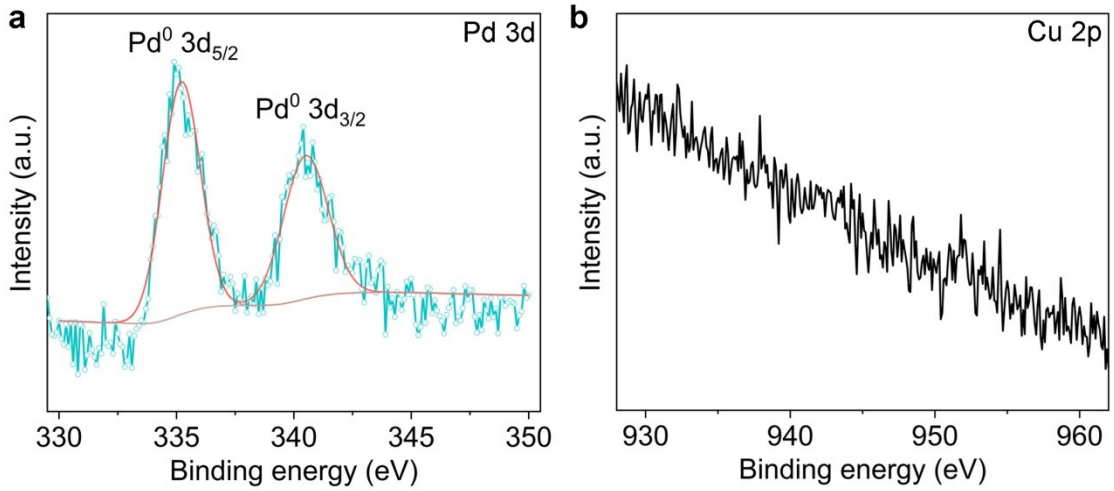

Fig. S10. (a) Pd 3d and (b) Cu 2p spectra of PdCu icosahedrons after durability test.

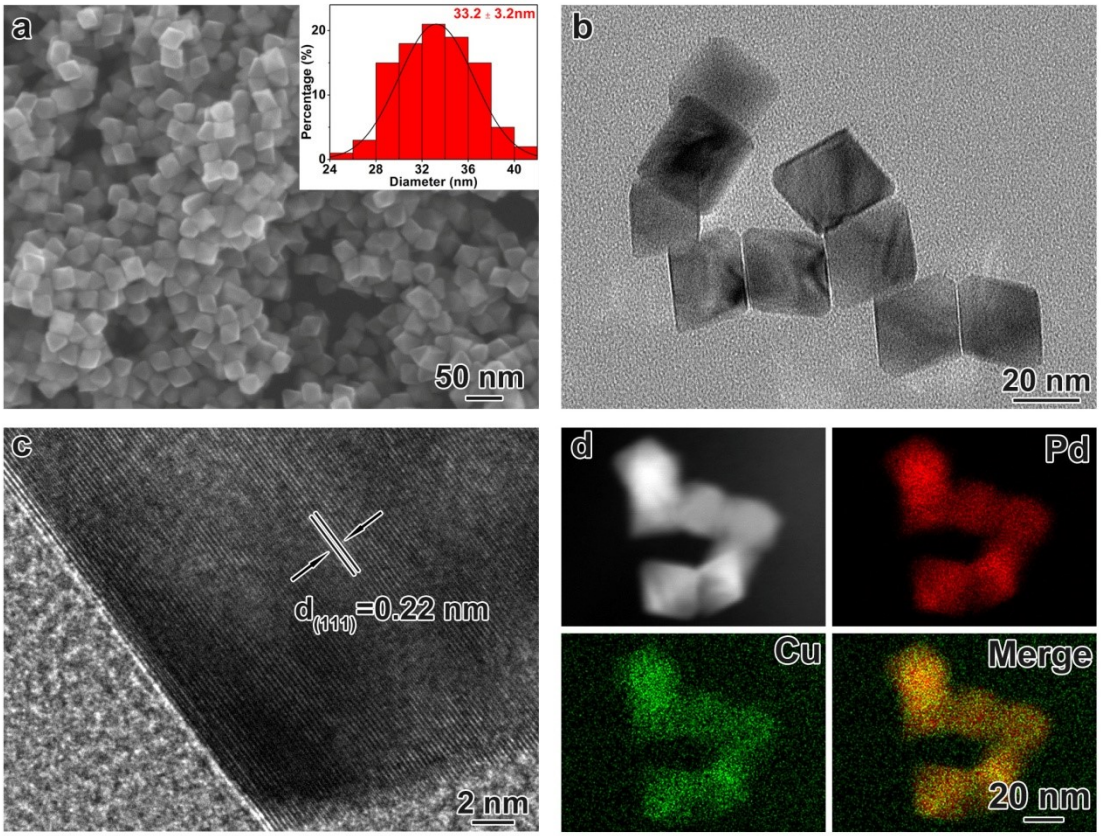

Fig. S11. (a) SEM image of Pd octahedrons (the inset: the particle size distribution diagram). (b) TEM, (c) HRTEM and (d) EDS mapping images of Pd@PdCu core-shell octahedrons, respectively.

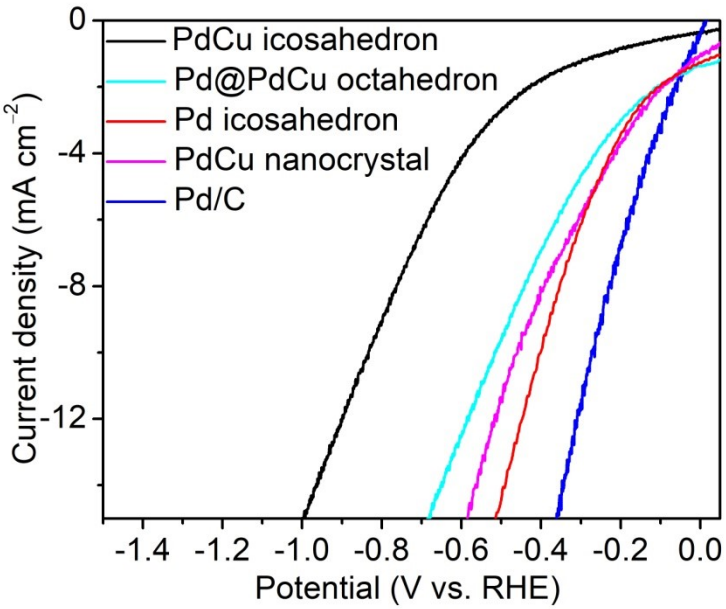

Fig. S12. LSV curves recorded in the optimal electrolyte for PdCu icosahedrons, Pd@PdCu octahedrons, Pd icosahedrons, PdCu nanocrystals and Pd/C.

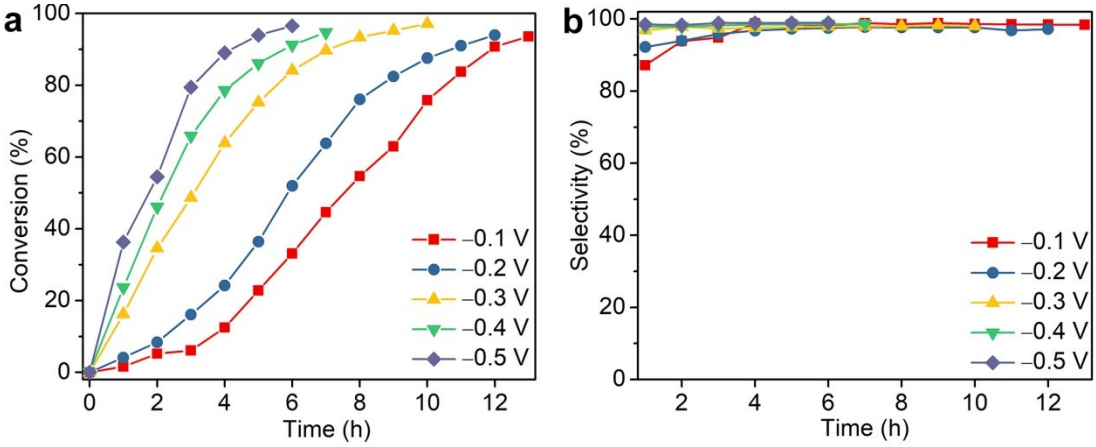

Fig. S13. (a) Time-dependent MBY conversion and (b) MBE selectivity for Pd@PdCu core-shell octahedrons, respectively.

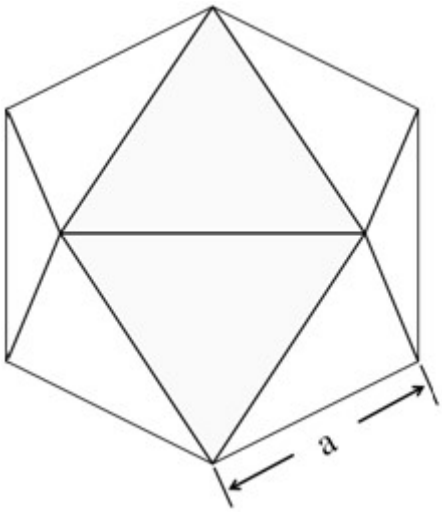

Fig. S14. Geometric model of icosahedrons structure.

The estimation of surface area of icosahedrons catalyst:

$$V_{total} = \frac{m_{Pd}}{\rho_{Pd}} + \frac{m_{Cu}}{\rho_{Cu}} \quad (4)$$

$$V_{icosahedron} = \frac{15 + 5\sqrt{5}}{12} \times a^3 \quad (5)$$

$$N = \frac{V_{total}}{V_{icosahedron}} \quad (6)$$

$$S_{icosahedron} = 5\sqrt{3}a^2 \quad (7)$$

$$S_{total} = N \times S_{icosahedron} \quad (8)$$

Where V is the volume, N is the number of icosahedrons, S is the surface area, a is the side length of icosahedron, m is the mass, and ρ is the density of a single metal (ρ_{Pd}=12.02, ρ_{Cu}=8.96 g cm^{-3}). Based on TEM results, a are 15.3 and 7.7 nm for PdCu and Pd icosahedrons, respectively. The total surface area of icosahedrons for a batch catalyst can be estimated according to Equation 8. The surface area of a single icosahedron can be calculated according to Equation 7. Therefore, the single $S_{\text{PdCu icosahedron}}$ is estimated to be 2.027×10^{-15} m^2. In order to figure up the total surface, the number of particles is calculated according to Equations 4-6, where $V_{\text{PdCu icosahedron}}$ is estimated to be 7.815×10^{-24} m^3. According to ICP-AES results, the amount of Pd and Cu were determined to be 0.5514 and 0.0226 mg, respectively. Therefore, $N_{\text{PdCu icosahedrons}}$ and S_{total} are estimated to be 6.19×10^{12} and 0.01255 m^2, respectively. The calculation method for Pd icosahedrons is similar to PdCu icosahedrons. $S_{\text{Pd icosahedrons}}$ and $V_{\text{Pd icosahedrons}}$ are estimated to be 5.135×10^{-16} m^2 and 9.961×10^{-25} m^3, respectively. The mass of Pd icosahedrons was estimated to 0.4800 mg. $N_{\text{Pd icosahedrons}}$ and S_{total} are estimated to be 4.0×10^{13} and 0.02057 m^2, respectively.

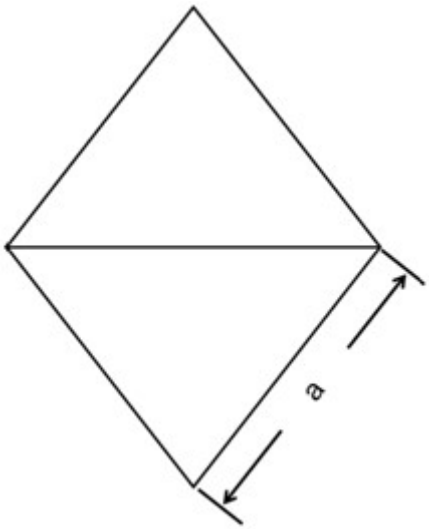

Fig. S15. Geometric model of octahedrons structure.

The estimation of surface area of octahedrons catalyst is based on the following calculation method.

$$V_{total} = \frac{m_{Pd}}{\rho_{Pd}} + \frac{m_{Cu}}{\rho_{Cu}} \quad (9)$$

$$V_{octahedron} = \frac{\sqrt{2}}{3} \times a^3 \quad (10)$$

$$N = \frac{V_{total}}{V_{octahedron}} \quad (11)$$

$$S_{octahedron} = 2\sqrt{3}a^2 \quad (12)$$

$$S_{total} = N \times S_{octahedron} \quad (13)$$

Where V is the volume, N is the number of octahedrons, S is the surface area, a is the side length of octahedron, m is the mass, and ρ is the density of a single metal (ρ_{Pd}=12.02, ρ_{Cu}=8.96 g cm^{-3}). Based on TEM and SEM results, the a is 24.3 nm for Pd@PdCu core-shell octahedrons. The total surface area and surface area of a single octahedron can be calculated according to Equations 13 and 12, respectively. Therefore, the single $S_{octahedron}$ is estimated to be 2.046×10^{-15} m^2. Then, N can be calculated according to Equations 9-11. According to ICP-AES results, the amount of Pd and Cu were estimated to 1.8045 and 0.0455 mg, respectively. As a result, $N_{octahedron}$ and S_{total} are estimated to be 2.294×10^{13} and 0.0469 m^2, respectively.

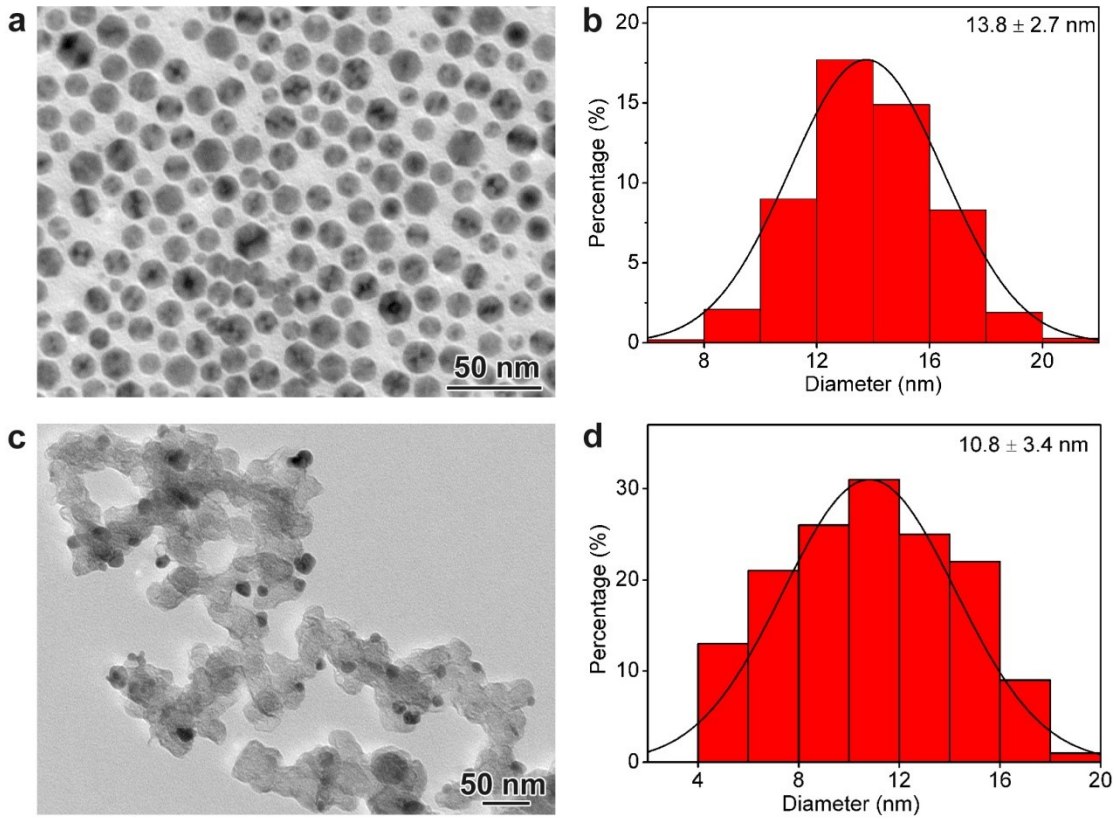

Fig. S16. TEM images and the corresponding particle size distributions: (a,b) Pd icosahedrons, (c,d) PdCu nanocrystals loaded on XC-72.

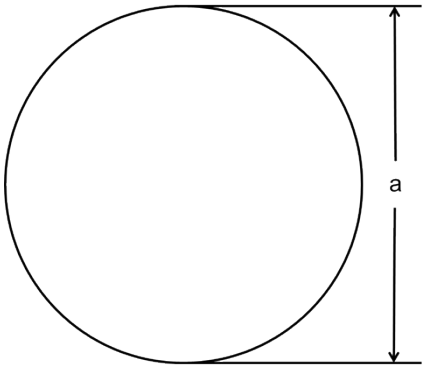

Fig. S17. Geometric model of spherical nanocrystal.

To simplify the calculation, PdCu nanocrystal is regarded as sphere. The estimation of surface area of nanocrystal catalyst is based on the following calculation method.

$$V_{total} = \frac{m_{Pd}}{\rho_{Pd}} + \frac{m_{Cu}}{\rho_{Cu}} \quad (14)$$

$$V_{NPs} = \frac{\pi}{6} {a_{NPs}}^3 \quad (15)$$

$$N = \frac{V_{total}}{V_{NPs}} \quad (16)$$

$$S_{NPs} = \pi {a_{NPs}}^2 \quad (17)$$

$$S_{total} = N \times S_{NPs} \quad (18)$$

Where V is the volume, S is the surface area and m is the mass. N is the number of nanocrystal, a is the diameter of the nanoparticle. Based on TEM result, a is 10.80 nm for PdCu nanocrystal. The total surface area and surface area of a single nanocrystal can be calculated according to Equations 18,17, respectively. Therefore, the single $S_{\text{PdCu NPs}}$ is estimated to be 3.66×10^{-16} m^2. Then, we calculated N according to Equations 14-16. According to ICP-AES results, the amount of Pd and Cu were estimated to 0.5510 and 0.0230 mg, respectively. As a result, $N_{\text{PdCu NPs}}$ and S_{total} are estimated to be 7.34×10^{13} and 0.0269 m^2, respectively. The calculation method for Pd/C is similar to PdCu nanocrystal. As a result, a is 4 nm for Pd/C. The single $S_{\text{Pd/C}}$ is estimated to be 5.027×10^{-17} m^2. The amount of Pd was estimated to 0.5520 mg. $N_{\text{Pd/C}}$ and S_{total} are estimated to be 1.373×10^{15} and 0.0688 m^2, respectively.

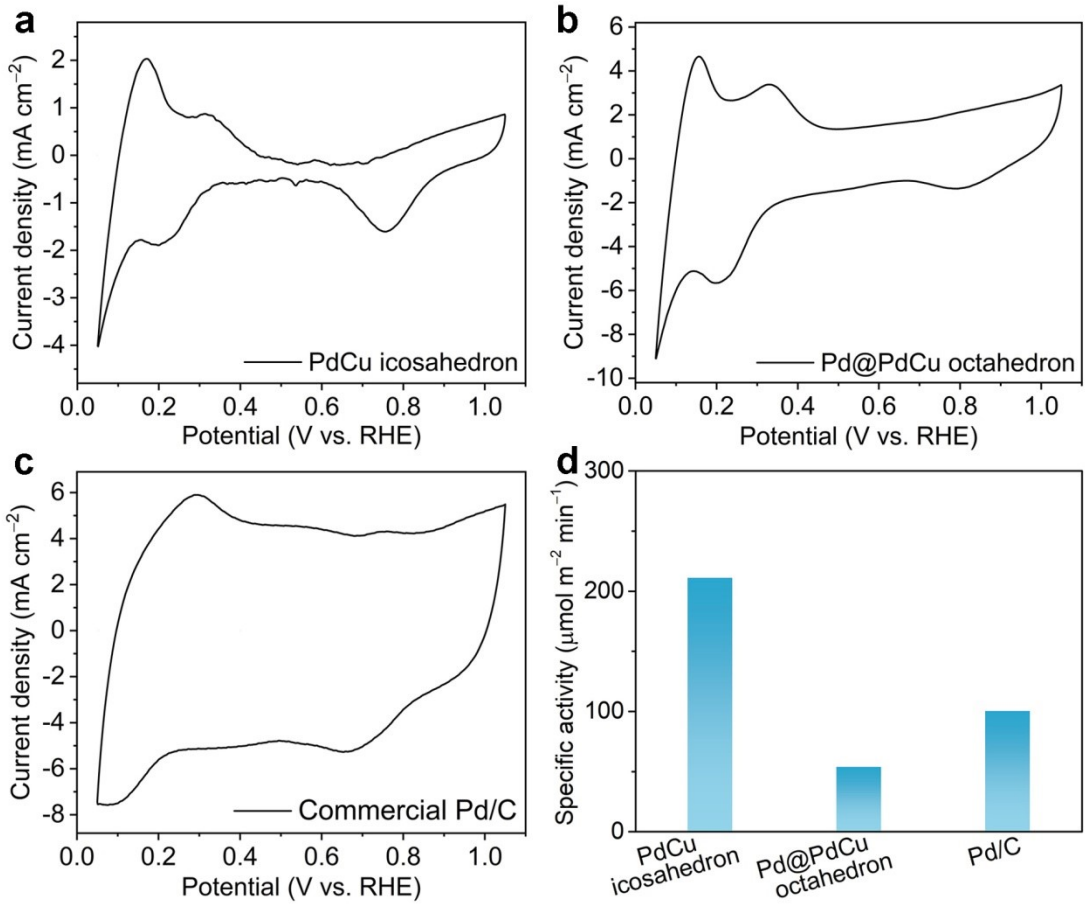

Fig. S18. CV curves of (a) PdCu icosahedrons, (b) Pd@PdCu octahedrons and (c) commercial Pd/C. (d) Specific activity normalized to ECSA at the initial 1 h.

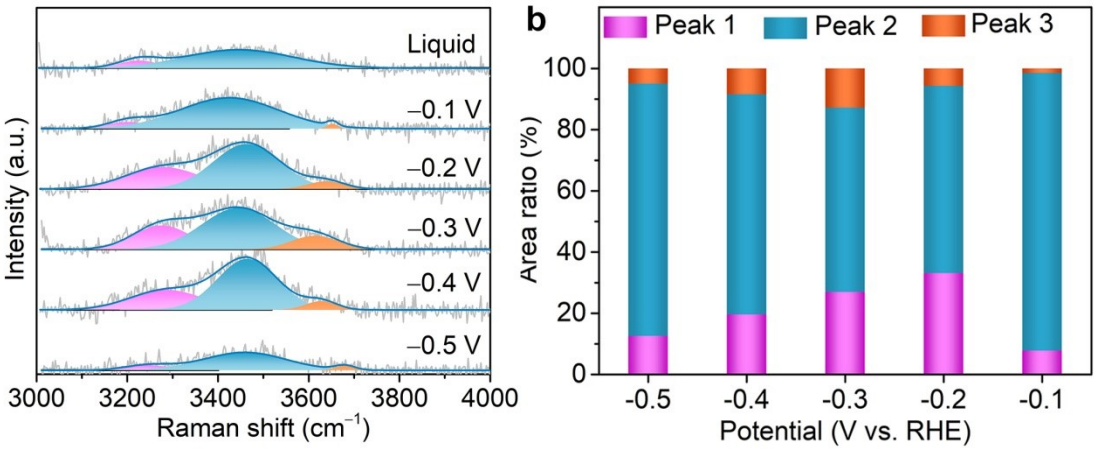

Fig. S19. (a) *In situ* electrochemical Raman spectra of the O–H stretching mode on PdCu icosahedrons surface recorded in KOH + ethanol solution at the fixed potential

and 15 min. (b) The corresponding area ratios of the three peaks (Peak 1: 4-HB·H_2O, Peak 2: 2-HB·H_2O and Peak 3: K·H_2O).

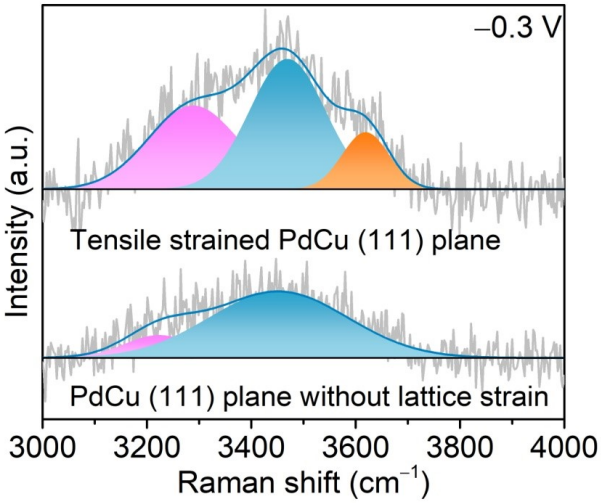

Fig. S20. Raman spectra recorded on tensile strained PdCu (111) plane and normal PdCu (111) plane.

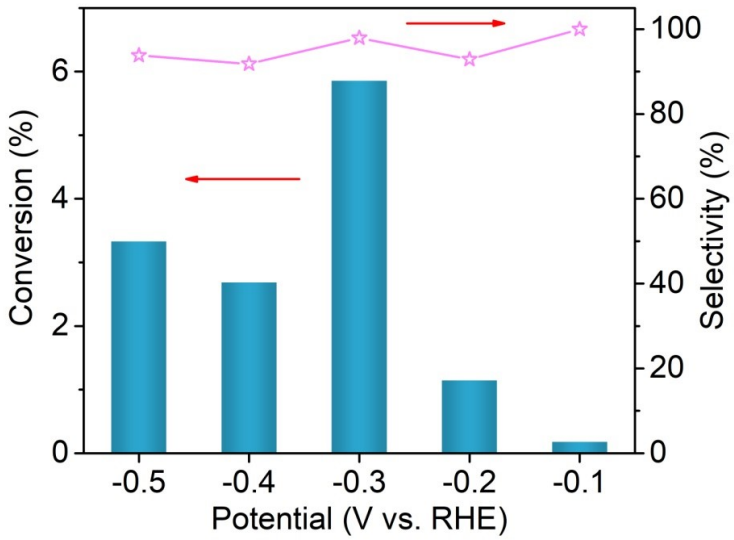

Fig. S21. Potential-dependent MBY conversion and MBE selectivity for PdCu icosahedrons in alkaline electrolyte at 15 min.

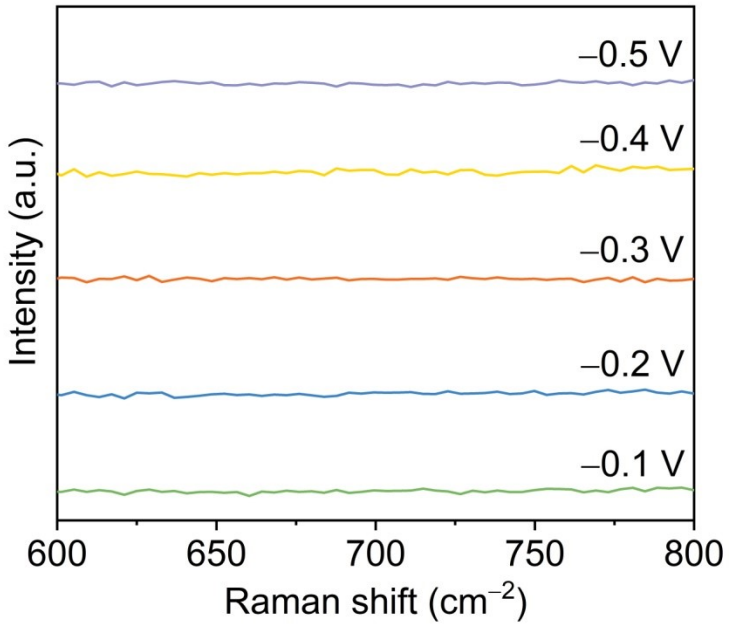

Fig. S22. Raman spectra for PdCu icosahedrons obtained at the potential range of –0.1 to –0.6 V.

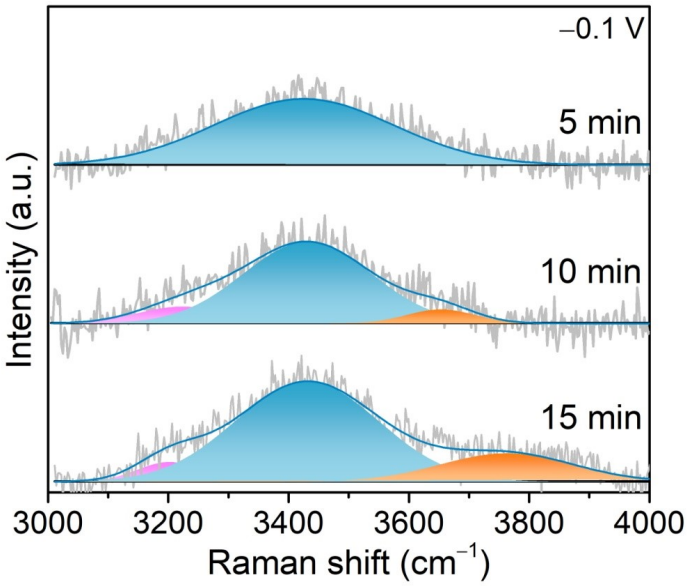

Fig. S23. The changes of interfacial water structure on PdCu icosahedrons surface recorded in ethanol + KOH solution at –0.1 V.

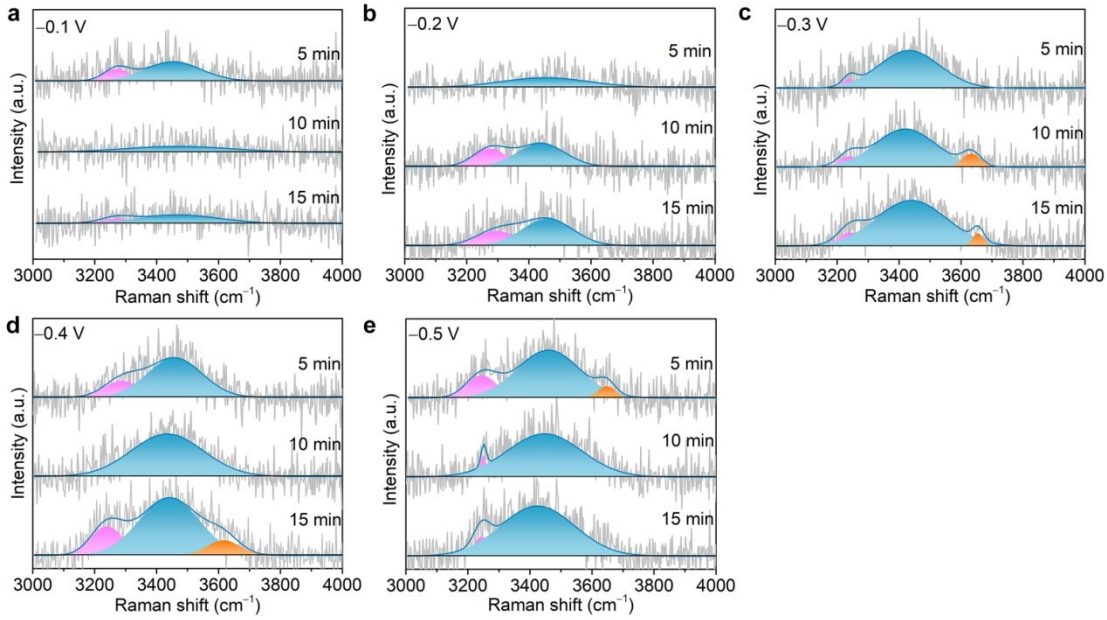

Fig. S24. Time-dependent Raman spectra of Pd@PdCu core-shell octahedrons at the fixed potential.

References

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2 Y. Xu, W. Bian, Q. Pan, M. Chu, M. Cao, Y. Li, Z. Gong, R. Wang, Y. Cui, H. Lin and Q. Zhang, Revealing the Active Sites of Pd Nanocrystals for Propyne Semihydrogenation: From Theory to Experiment, *ACS Catal.*, 2019, **9**, 8471-8480.