

Supporting Information

Ternary PdCoP nanoparticles with nanopore structures: synergic boosting of electrocatalytic activity for ethanol oxidation

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Experiment section

Chemical reagents

Palladium chloride (PdCl_2 , 99%) and tetraoctylammonium bromide (TOAB, 98%) were purchased from Energy Chemical. Cobalt (II) acetylacetonate ($\text{Co}(\text{acac})_2$, 97%), triphenylphosphine (TPP, 95%), Oleylamine (OAm, 80-90%) and potassium hydroxide (KOH, 95%) were purchased from Aladdin. Nafion (5 wt%) was obtained from Sigma Aldrich. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, AR, 99.7%), acetic acid (CH_3COOH , AR, 99.5%) and tetrahydrofuran (THF, AR, 99.5%) were gained from Sinopharm Chemical Reagent Co., Ltd. Dichloromethane (CH_2Cl_2 , AR, 99.5%) was obtained from WOHUA-CHEMICAL.

Synthesis of PdCoP NPs

In a typical preparation of $\text{Pd}_{31}\text{Co}_{44}\text{P}_{25}$ NPs, the whole reaction process was carried out in a 50 mL three-necked round bottom flask under carbon monoxide flow and magnetic stirring. First, 50 mg TPP was dissolved in 6 mL OAm in a three-necked round bottom flask and stirred at room temperature for 10 minutes. 10 mg PdCl_2 , 40 mg $\text{Co}(\text{acac})_2$ and 30.8 mg TOAB were added into 5 mL THF in centrifuge tube to form a mixed solution, and then transferred into the above formed TPP solution and continued to stir at room temperature for 10 minutes to completely dissolve the reactants. The resulting solution was heated to 90 °C and kept for about 12 minutes, and then the temperature was raised to 270 °C

within 20 minutes and maintained for 5 minutes. After the solution was cooled down to room temperature, the Pd₃₁Co₄₄P₂₅ NPs were collected and washed several times with ethanol/dichloromethane mixture. Finally, the product was dispersed in dichloromethane for further using.

Synthesis of PdCoP NPs/C

15 mg Vulcan XC-72 carbon was mixed with 6 mL dichloromethane in centrifuge tube and sonicated for 0.5 h to form uniform suspension. The Pd₃₁Co₄₄P₂₅ NPs (5 mg) were dispersed in dichloromethane (10 mL), and then added into the above formed suspension and sonicated for 1 h. The product was centrifuged at 8000 r.p.m. for 10 min and washed with a mixture of ethanol and acetic acid (denoted PdCoP-NPs-1). Finally, the PdCoP-NPs-1 sample was dried in the oven at 45 °C for 12 h. Similarly, the PdCoP-NPs-2 and PdCoP-NPs-3 can be obtained under the same synthetic method except for the addition of 70 mg and 40 mg TPP. The PdCo nanoalloys were synthesized under the analogous condition of PdCoP-NPs-1 without TPP, and the temperature was maintained at 250 °C for 5 minutes.

Characterization

Powder X-ray diffraction (PXRD) patterns were carried out on a Smart Lab 9 KW with Cu K α radiation. The transmission electron microscopes (TEM) together with high resolution TEM (HRTEM) images were implemented on the JEOL JEM-2010 transmission electron microscope at 200 kV. High-

angle annular dark-field scanning TEM (HAADF-STEM) mapping images were conducted by a JEOL JEM-F200 microscope. The content of elements was determined by the inductively coupled plasma optical emission spectroscopy ((ICP-OES) and scanning (electron) microscopy equipped with energy-dispersive X-ray (EDS). The X-ray photoelectron spectroscopy (XPS) tests were operated on a Thermo ESCALAB 250.

Electrocatalytic measurements

Electrochemical measurements were performed at room temperature on a CHI660E electrochemical workstation with a three-electrode system. The appropriate amount of the catalysts powders was dispersed in the mixed solution containing 400 μL of ethanol, 100 μL of ultrapure water and 20 μL of Nafion (5%). Next, 5 μL of catalyst ink was dropped onto the clean glassy carbon electrode (5 mm in diameter) and dried naturally at room temperature. Estimation of Pd loading is based on overall Pd ratio within catalyst determined by ICP-OES, and Pd loading is about 4.1 μg for the tested Pd based alloy samples. The catalyst-modified glassy carbon electrode was used as working electrode, and a Pt sheet and Hg/HgO were employed as counter electrode and reference electrode, respectively. The activation process was performed in a N_2 -saturated 1.0 M KOH solution at a scan rate of 50 mV s^{-1} . The CV curves for EOR were recorded at a scan rate of 50 mV s^{-1} in N_2 -saturated solution containing 1.0 M KOH and 1.0 M $\text{C}_2\text{H}_5\text{OH}$. Commercial Pd/C catalyst was tested as described above and

used as a comparative catalyst. For CO-stripping experiments, CO gas was bubbled into N₂-saturated 1.0 M KOH while holding the catalyst-modified glassy carbon electrode potential at -0.1 V (vs RHE) for 20 min. After that, the electrode was moved into fresh N₂-saturated 1.0 M KOH solution for CO stripping tests. The CV curves were recorded in the potential range between -0.1 and 1.4 V (vs RHE) at a scan rate of 10 mV s⁻¹.

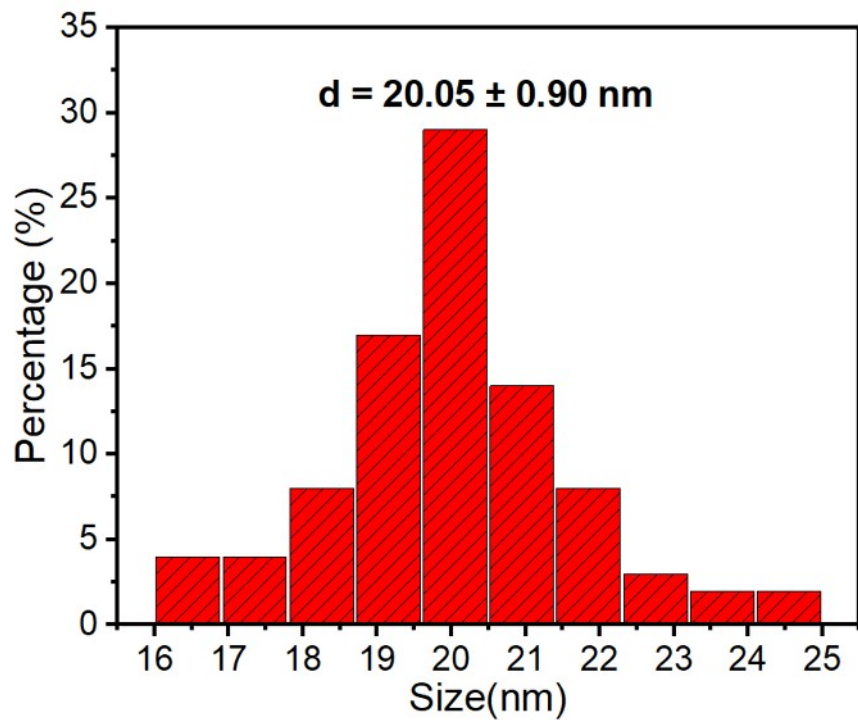


Figure S1. The size distribution diagram of Pd₃₁Co₄₄P₂₅ NPs.

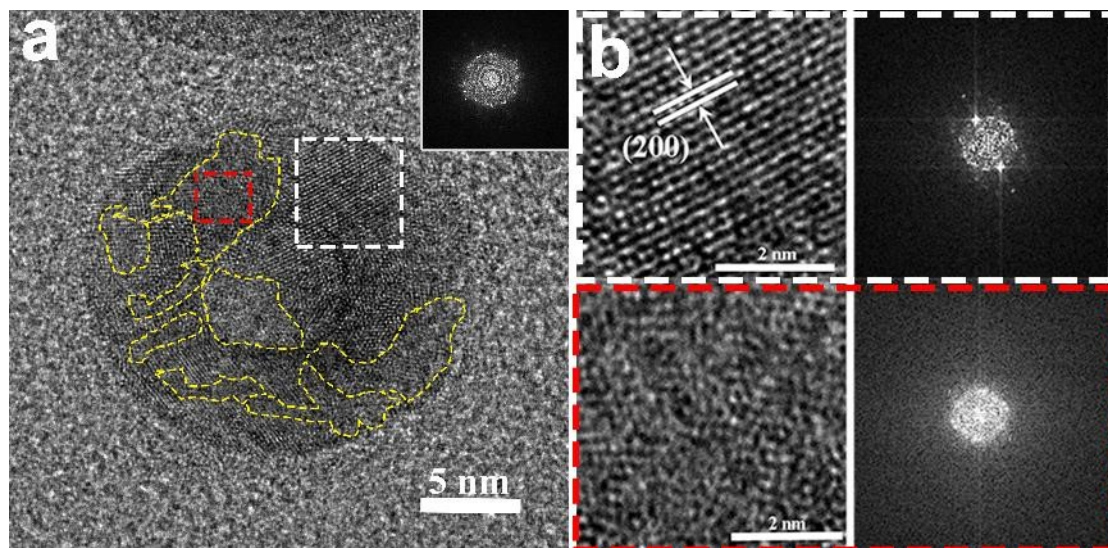


Figure S2. (a, b) HRTEM and FFT images of Pd₃₁Co₄₄P₂₅ NPs (amorphous regions are marked by the yellow dotted lines).

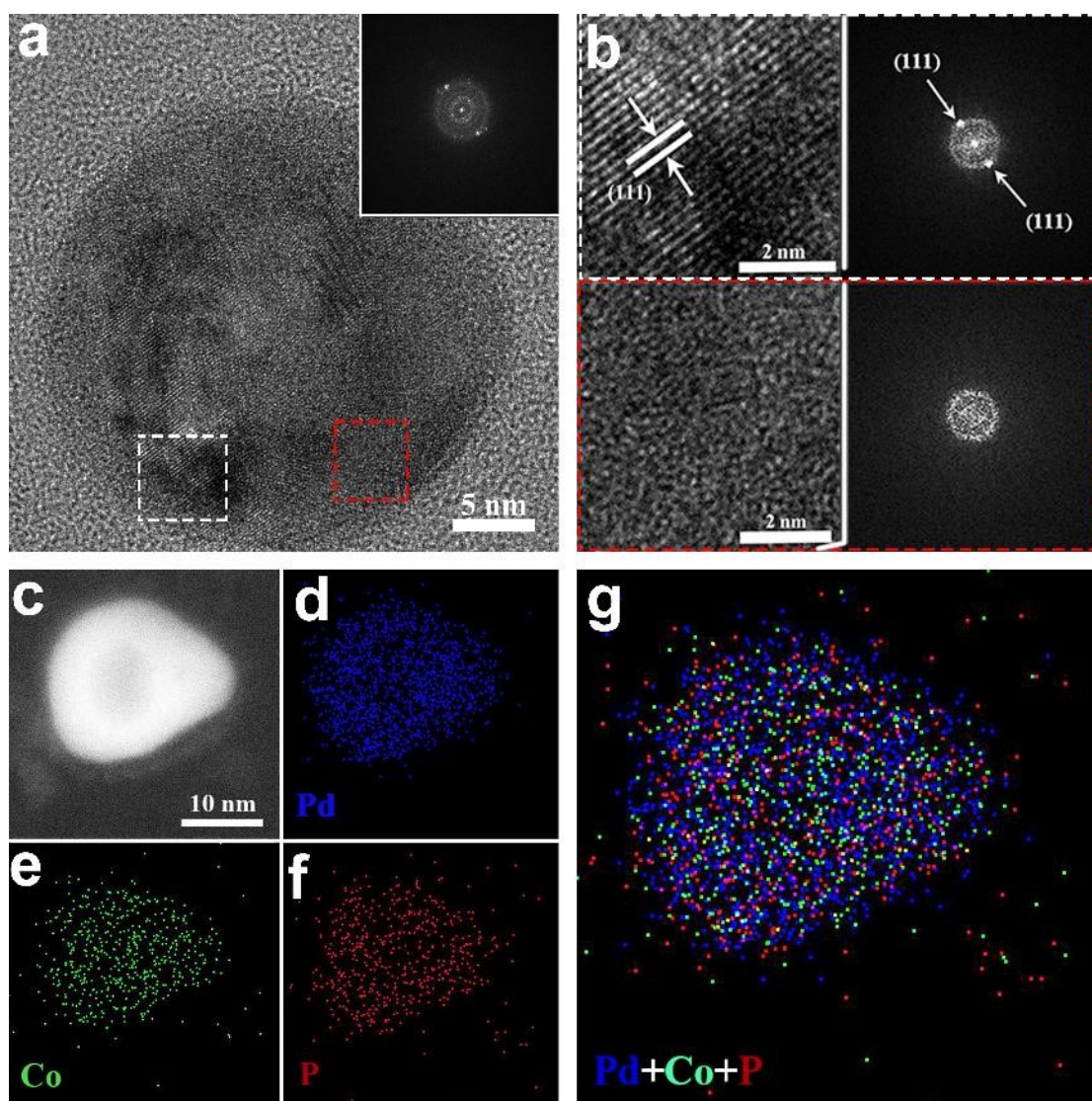


Figure S3. (a-b) HRTEM and FFT images, (c-g) HADDF-STEM image and the corresponding element mapping images of PdCoP-NPs-1: Pd (blue), Co (green) and P (red).

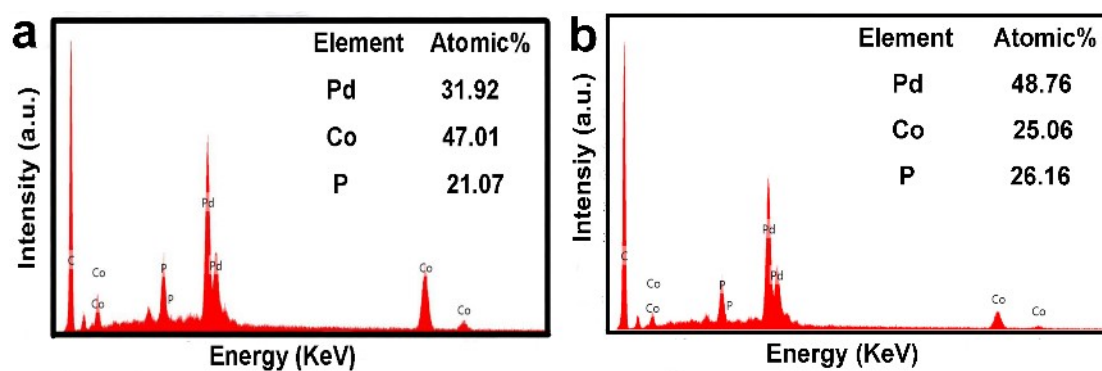


Figure S4. EDS composition analysis: (a) Pd₃₁Co₄₄P₂₅ NPs, (b) PdCoP-NPs-1.

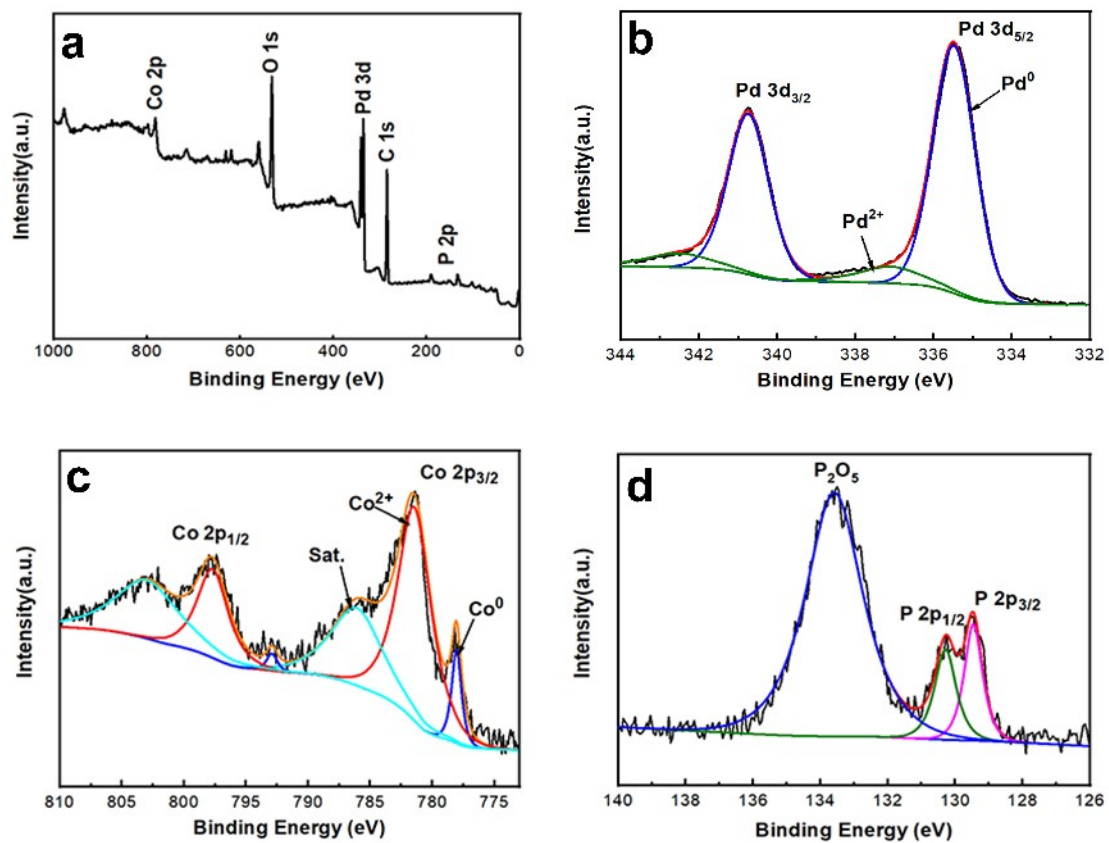


Figure S5 (a) XPS survey spectrum of PdCoP-NPs-1. (b) Pd 3d, (c) Co 2p, and (d) P 2p XPS spectra of PdCoP-NPs-1.

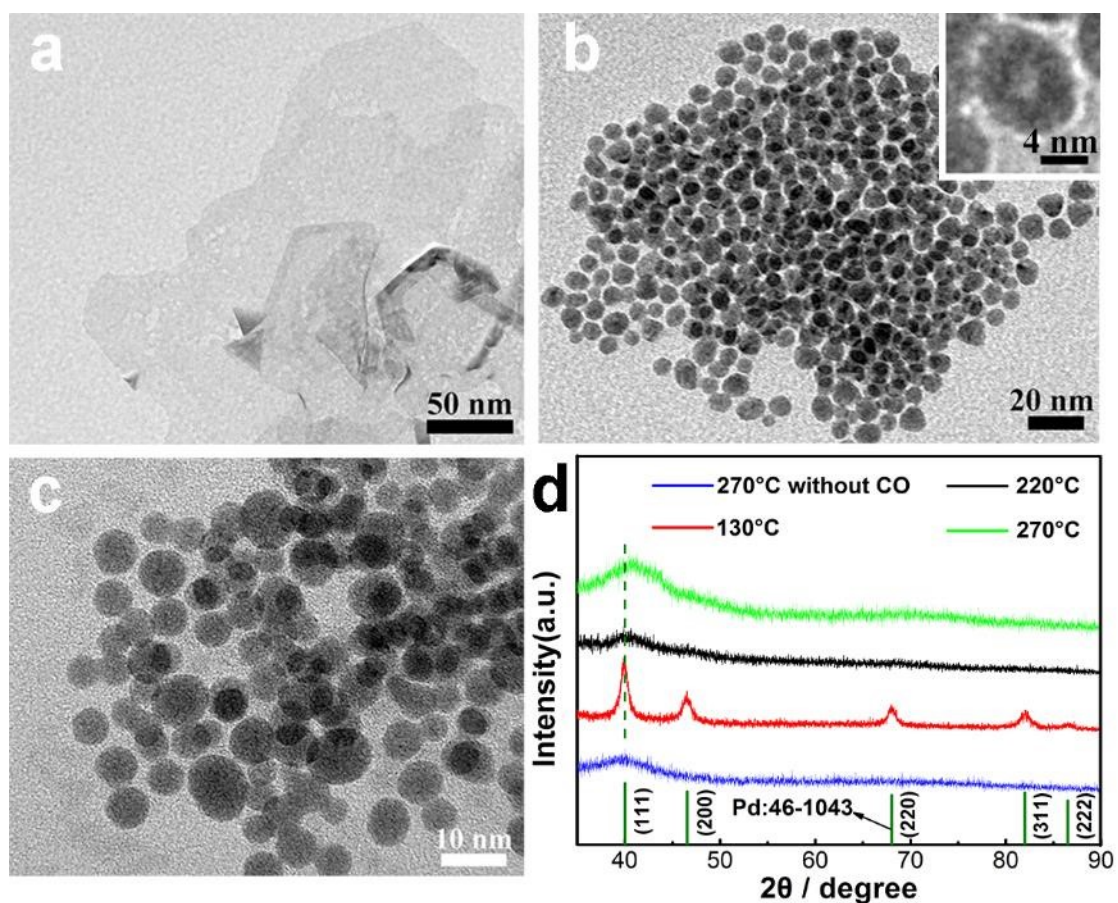


Figure S6. Representative TEM images of $\text{Pd}_{31}\text{Co}_{44}\text{P}_{25}$ NPs intermediates collected at different reaction temperature: (a) 130 °C, (b) 220 °C. (c) TEM image of the product without introducing CO under the same synthesized condition of $\text{Pd}_{31}\text{Co}_{44}\text{P}_{25}$ NPs. (d) PXRD patterns of the intermediates at 130 °C (red line), 220 °C (dark line), 270 °C (green line) and the product at 270 °C without CO (blue line).

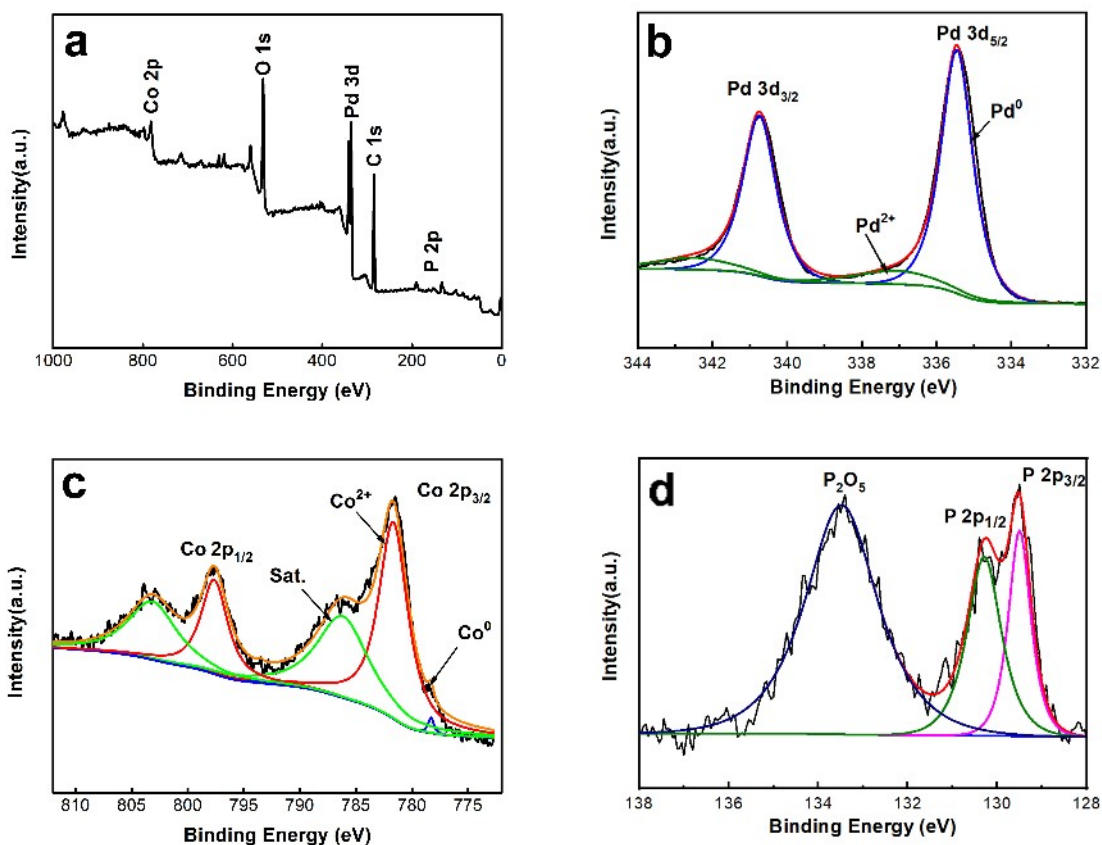


Figure S7. (a) The survey XPS spectrum, (b) Pd 3d, (c) Co 2p, (d) P 2p XPS spectra of the intermediate tracked at 220 °C in the preparation of Pd₃₁Co₄₄P₂₅ NPs.

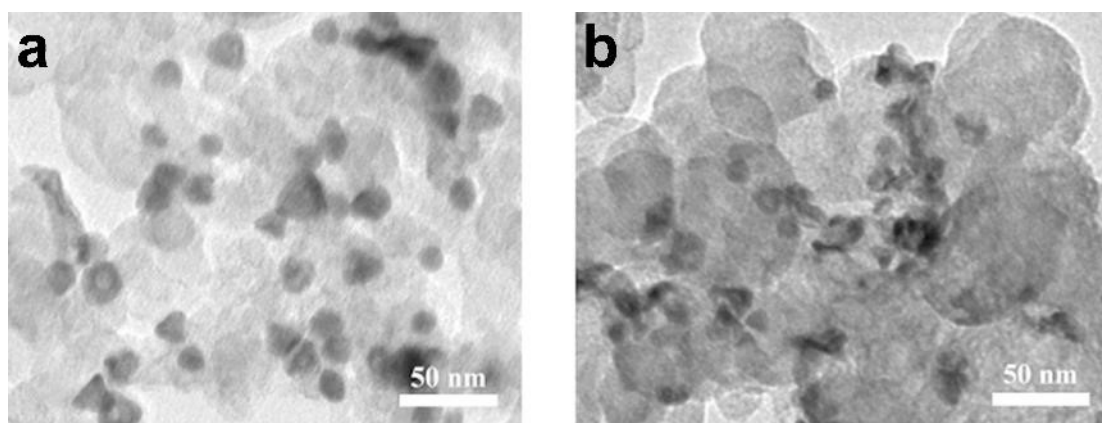


Figure S8. (a) and (b) TEM images of the PdCoP-NPs-1 before and after the electrochemical test, respectively.

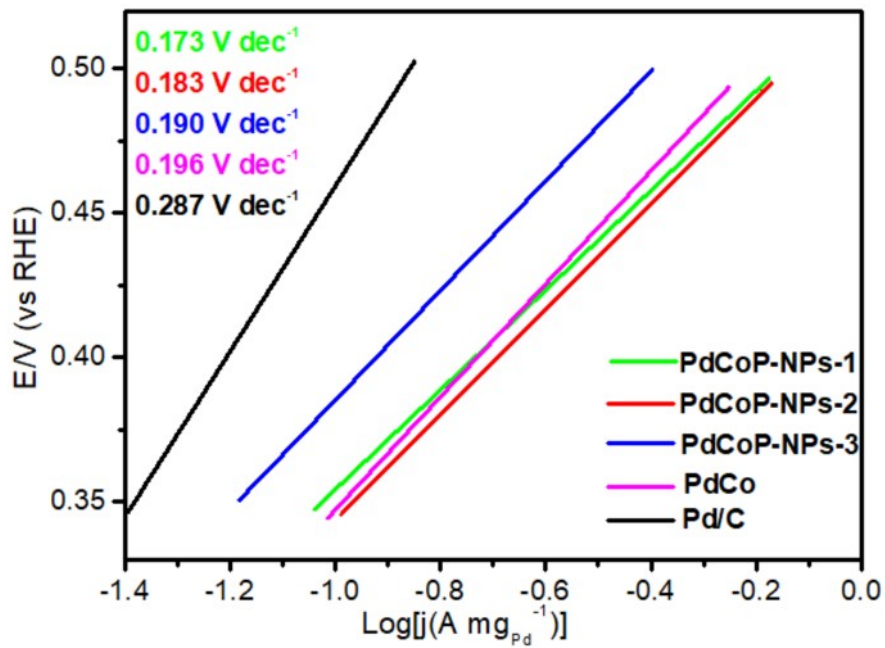


Figure S9. Tafel plots of PdCoP-NPs-1, PdCoP-NPs-2, PdCoP-NPs-3, PdCo catalysts and commercial Pd/C.

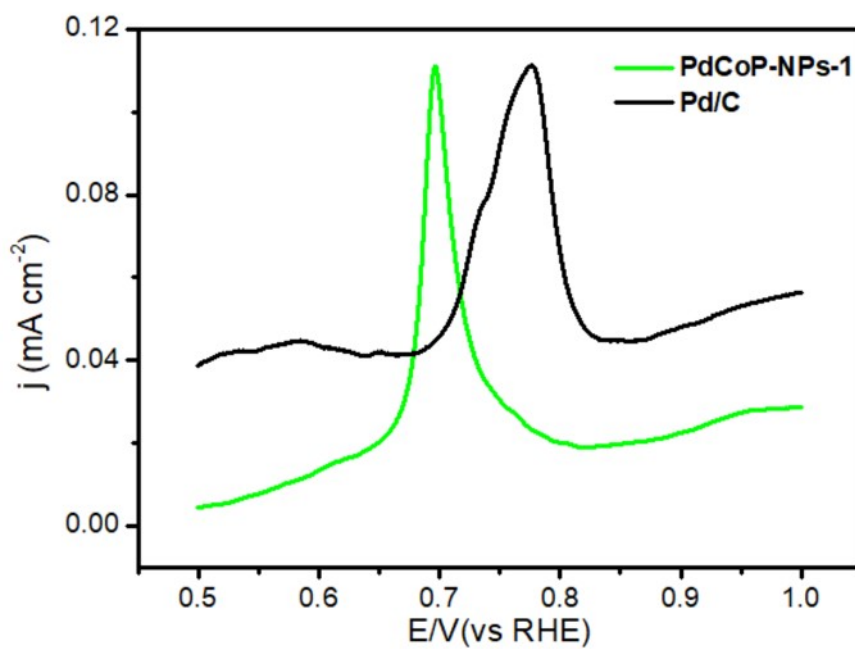


Figure S10. CV curves of PdCoP-NPs-1 and commercial Pd/C for CO-stripping in 1.0 M KOH at a scan rate of 10 mV s⁻¹.

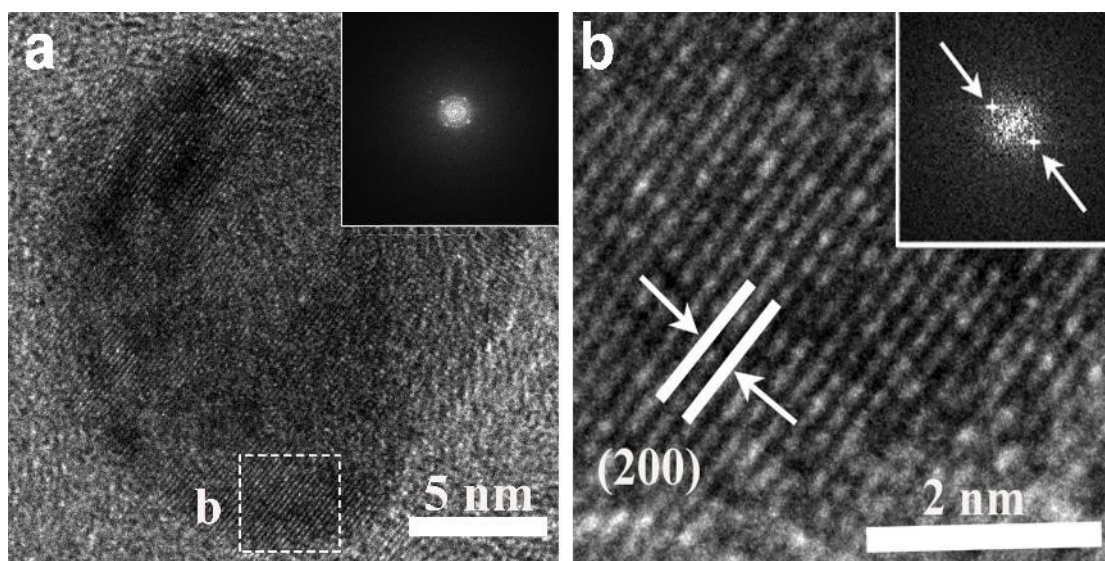


Figure S11. (a) HRTEM and FFT images of PdCoP-NPs-1-300. (b) HRTEM and FFT patterns taken from the corresponding regions in (a).

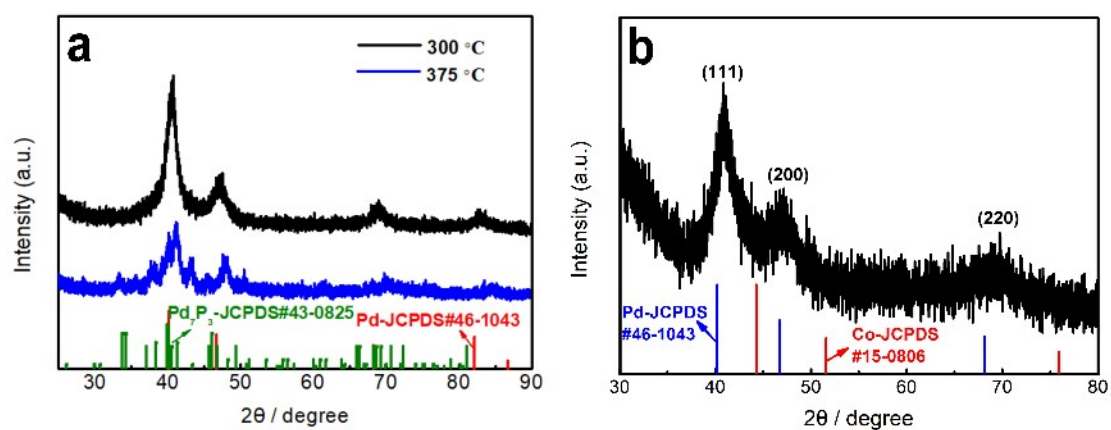


Figure S12. The as-synthesized $\text{Pd}_{31}\text{Co}_{44}\text{P}_{25}$ NPs were annealed at different temperature for 2 h under gas (95% N_2 /5% H_2) atmosphere: (a) XRD patterns (blue line:375 °C, black line:300 °C). (b) XRD pattern of the as-synthesized PdCo alloy catalyst.

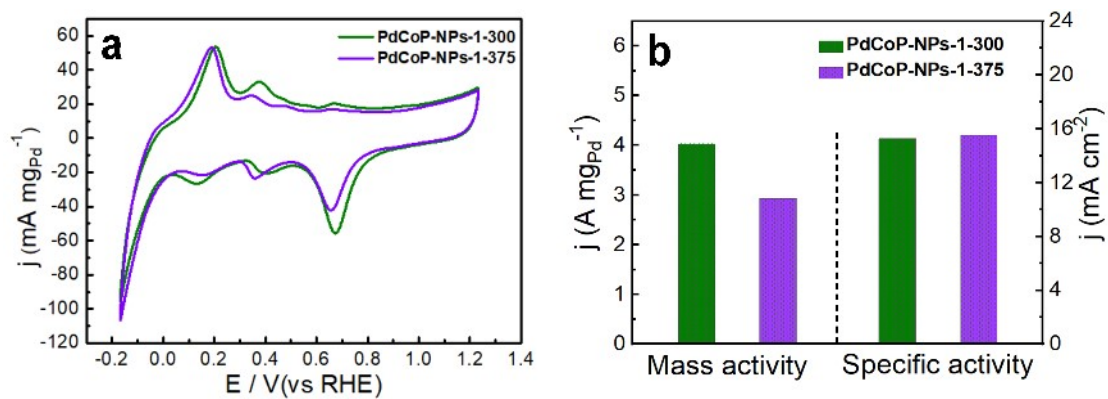


Figure S13. (a) CVs of PdCoP-NPs-1-300 and PdCoP-NPs-1-375 in 1.0 M KOH at a scan of 50 mV s⁻¹. (b) mass activities and specific activities of PdCoP-NPs-1-300 and PdCoP-NPs-1-375 in 1.0 M KOH + 1.0 M C₂H₅OH solution at a scan rate of 50 mV s⁻¹.

Table S1. EDS and ICP-OES composition comparisons of Pd₃₁Co₄₄P₂₅ NPs before and after acetic acid treatment.

PdCoP NPs	EDS	ICP-OES
Before	Pd ₃₂ Co ₄₇ P ₂₁	Pd ₃₁ Co ₄₄ P ₂₅
After	Pd ₄₉ Co ₂₅ P ₂₆	Pd ₄₉ Co ₂₆ P ₂₅

Table S2. Summarization of ethanol electrochemical properties of on Pd-based catalysts in alkaline media.

Catalysts	Mass activity (A mg _{Pd} ⁻¹)	Reference
PdCoP NPs/C	5.97	This work
Pd/CuO-Ni(OH) ₂ /C	3.74	1
TS-Pd/C	1.85	2
Pd NPs@Ni SAC	1.09	3
IL/Pd ₅₀ Bi ₁	5.74	4
Pd/NCB@NGS-2	2.69	5
CoP/RGO-Pd10	4.59	6
Pd/a-SrRuO ₃	4.00	7
PdP nanosheets	3.20	8
c-Pd-Ni-P@a-Pd-Ni-P nanoplates	3.05	9
CuPdNiP NHs	1.19	10
Ultrathin Pd ₂ Ag ₁ sNWs	2.84	11
2D PdAg Alloy Nanodendrites	2.60	12

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