

## Supporting information

### Unique one-pot strategy for PdH<sub>0.706</sub> nanoparticles with enhanced stability and activity towards ethanol oxidation†

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## Part I: Experimental

**Materials and reagents:** Palladium(II) acetylacetonate ( $\text{Pd}(\text{acac})_2$ ), Platinum (II) acetylacetonate ( $\text{Pt}(\text{acac})_2$ ), Ruthenium(III) acetylacetonate ( $\text{Ru}(\text{acac})_3$ ), Iron(III) acetylacetonate ( $\text{Fe}(\text{acac})_3$ ), Nickel(II) acetylacetonate ( $\text{Ni}(\text{acac})_2$ ), Cobalt(II) acetylacetonate ( $\text{Co}(\text{acac})_2$ ), Molybdenyl(IV) acetylacetonate ( $\text{Mo}(\text{acac})_6$ ), Cupric(II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ ), Tungsten hexacarbonyl ( $\text{W}(\text{CO})_6$ ), and benzyl alcohol ( $\text{C}_7\text{H}_8\text{O}$ ), and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Iminodiacetonitrile ( $\text{C}_4\text{H}_5\text{N}_3$ ) was bought from Alfa Aesar Chemical Reagent Co., Ltd. Nafion (5 wt.%) was purchased from Sigma-Aldrich Chemical Reagent Co. Ltd. Commercial Pd black was purchased from Johnson Matthey Corporation. Deionized water (DI water,  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was employed throughout all experiments. All chemicals were of analytical reagent grade and used without further purification.

**Synthesis of  $\text{PdH}_{0.706}$  nanoparticles (NPs):** In a typical synthesis, 30 mg of  $\text{Pd}(\text{acac})_2$  and 200 mg of iminodiacetonitrile were dissolved in 30 mL of benzyl alcohol and further ultrasonicated uniformly. The resulting solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and kept at  $160 \text{ }^\circ\text{C}$  for 10 h. After being cooled to room temperature, the  $\text{PdH}_{0.706}$  NPs were acquired via centrifugation at 9,000 rpm for 5 min and further purified by washing three times with ethanol.

**Synthesis of Pd NPs:** The Pd NPs were prepared using the same synthetic process without the introduction of iminodiacetonitrile.

**Synthesis of MPdH NPs:** The MPdH ( $\text{M} = \text{Pt}, \text{Ru}, \text{Fe}, \text{Ni}, \text{Co}, \text{Mo}, \text{Cu}, \text{and W}$ ) NPs were prepared using the same synthetic process with the additional introduction of 15 mg  $\text{Pt}(\text{acac})_2$ ,  $\text{Ru}(\text{acac})_3$ ,  $\text{Fe}(\text{acac})_3$ ,  $\text{Ni}(\text{acac})_2$ ,  $\text{Co}(\text{acac})_2$ ,  $\text{Mo}(\text{acac})_6$ ,  $\text{Cu}(\text{acac})_2$ , and

W(CO)<sub>6</sub>.

**Materials characterizations:** Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired on a JEOL JEM-2100F transmission electron microscopy which operated at an accelerating voltage of 200 kV. The crystallinity of the samples was verified by recording X-ray diffraction (XRD) patterns on a Model D/max-RC X-ray diffractometer using Cu K $\alpha$  radiation source ( $\lambda = 1.5406$  Å) and operating at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were proceeded on a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al K $\alpha$  X-ray source. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. The composition of the catalyst was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

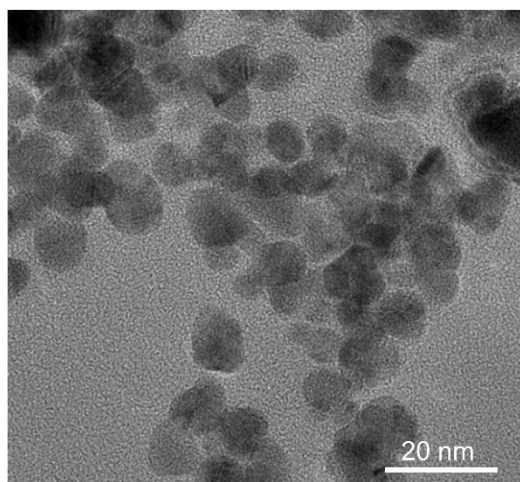
**Electrochemical measurements:** All electrochemical measurements were conducted at ambient temperature using a CHI 760E electrochemical analyzer (CH Instruments, Shanghai Chenhua Co., Ltd.) in a standard three-electrode system. The working electrode was a glassy carbon electrode (3 mm diameter) modified with the catalyst, the auxiliary electrode was a graphite rod, and a saturated calomel electrode (SCE) served as the reference electrode, protected by a Luggin capillary filled with saturated KCl solution. To prepare the catalyst inks, 2 mg of catalysts or commercial Pd black were dispersed in 1 mL of a mixed solvent comprising 0.90 mL ethanol and 0.10 mL Nafion solution (5 wt.%), followed by 30 minutes of ultrasonic agitation. Then, 6  $\mu$ L of the mixed catalyst ink was dropped on the glassy carbon electrode to acquire the working electrode. The ethanol oxidation reaction (EOR) tests were performed in N<sub>2</sub>-saturated 1.0 M KOH + 1.0 M CH<sub>3</sub>CH<sub>2</sub>OH solution at a scan rate of 50 mV s<sup>-1</sup>. Electrochemical surface area (ECSA) of the Pd-based catalysts was calculated based

on the CV curves acquired in 1.0 M KOH solution, where we assume a value of 0.21 mC cm<sup>-2</sup> for the charge for a monolayer of adsorbed hydrogen. The specific formula is as follows:

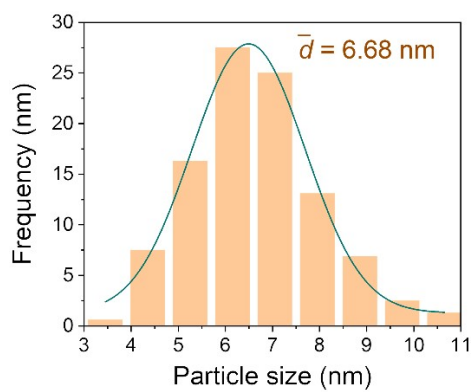
$$\text{ECSA} = Q / (0.21 \text{ mC cm}^{-2} \times m_{\text{Pd}}) \quad (1)$$

in which Q on behalf of the integrated charge of the PdO reduction peak in the CV curves acquired in 1.0 M KOH solution while the  $m_{\text{Pd}}$  represents the mass of the metal Pd applied to the working electrode. The accelerated durability test (ADT) of CVs was performed for 1000 cycles in N<sub>2</sub>-saturated 1.0 M KOH + 1.0 M CH<sub>3</sub>CH<sub>2</sub>OH solution with a scan rate of 100 mV s<sup>-1</sup>. CO stripping experiments were conducted in 1.0 M KOH solution. The electrolyte was first bubbled with CO while holding the working electrode at 0.1 V for 30 min. Then, the CV cycles were carried out at 50 mV s<sup>-1</sup> to record the CO stripping voltammetry in the fresh solution.

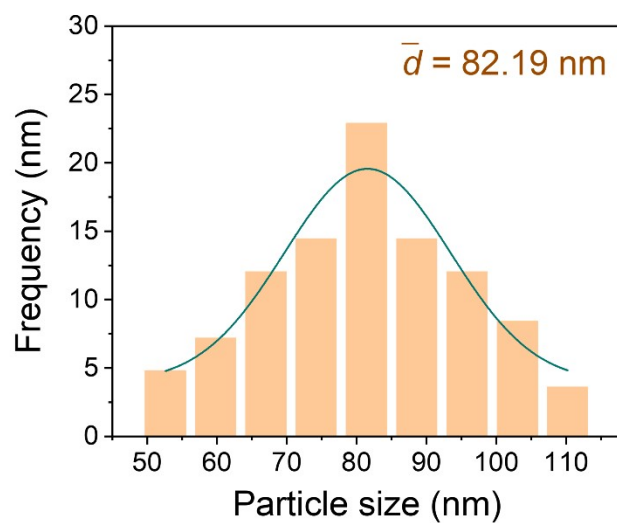
## Part II: Figures and Tables



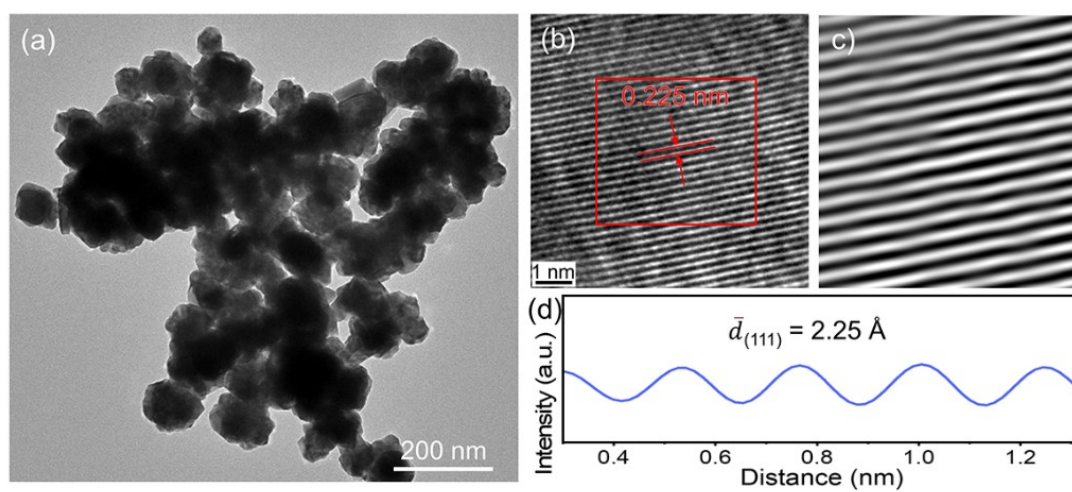
**Figure S1.** TEM image of the PdH<sub>0.706</sub> NPs.



**Figure S2.** The size distribution histogram of the PdH<sub>0.706</sub> NPs.



**Figure S3.** The size distribution histogram of the Pd NPs.



**Figure S4.** (a) TEM image, (b) HRTEM image, (c) HRTEM image after noise elimination and (d) corresponding integrated pixel intensities of Pd NPs.

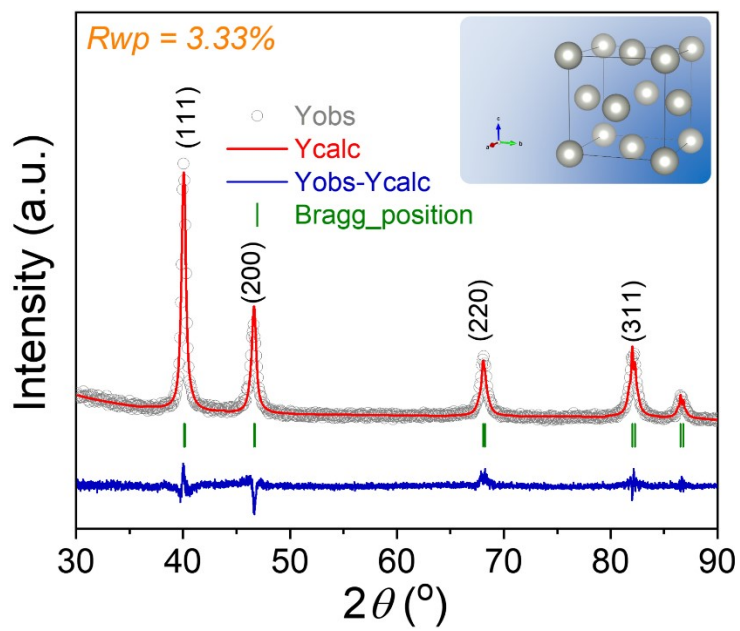


Figure S5. XRD refinements of Pd NPs.

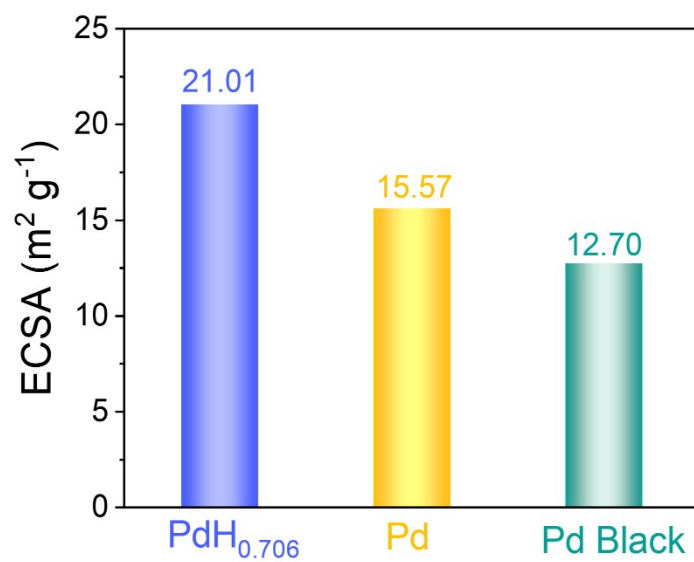
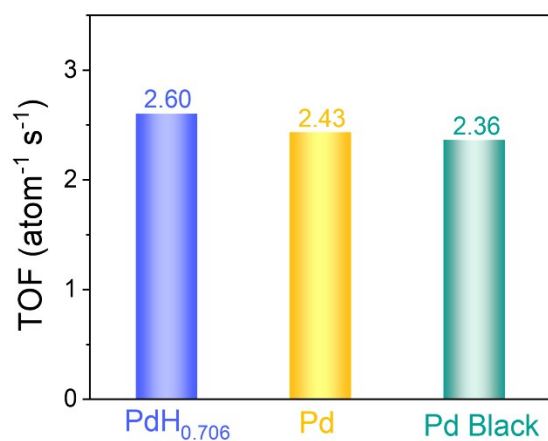
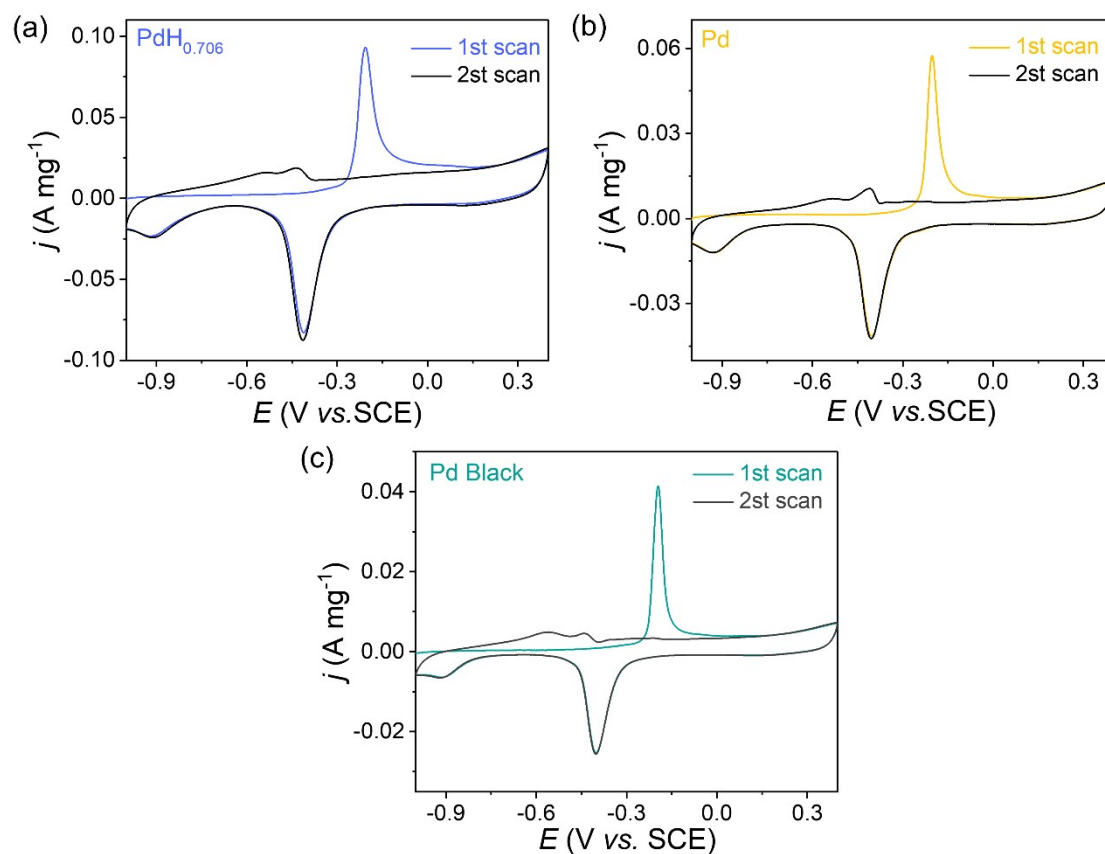


Figure S6. The contrast histogram of ECSA of catalysts.

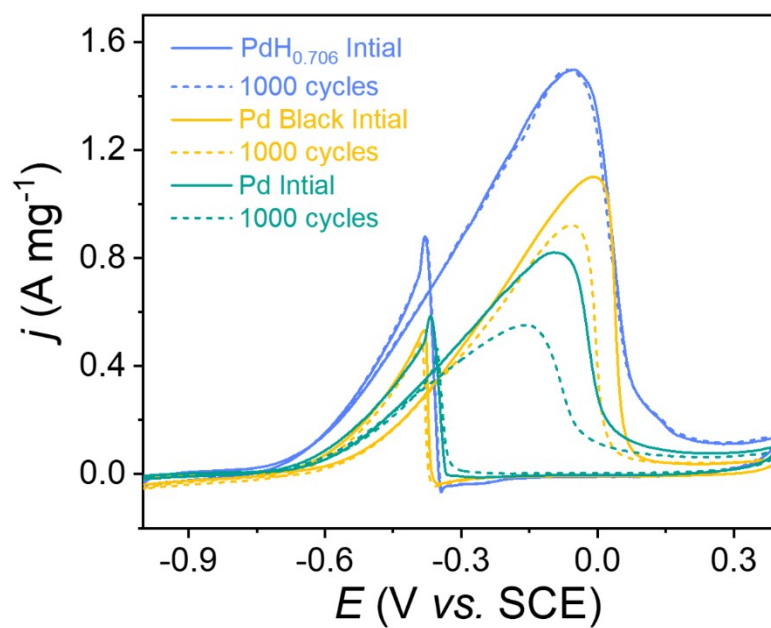


**Figure S7.** The contrast histogram of TOFs of catalysts.

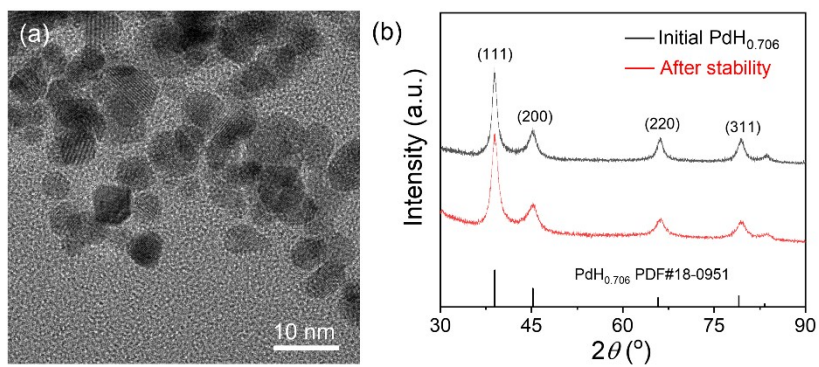


**Figure S8.** CO-stripping curves of (a) PdH<sub>0.706</sub> NPs, (b) Pd NPs, and (c) commercial Pd black obtained in 1.0 M KOH solution at a scan rate of 50 mV s<sup>-1</sup>.





**Figure S9.** The EOR curves of the catalysts before and after the ADT test (1000 cycles).

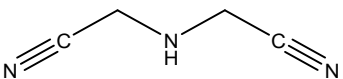
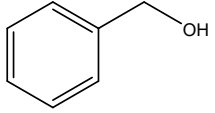
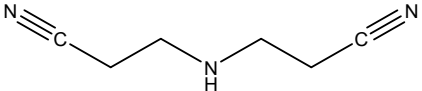
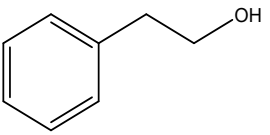
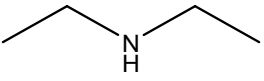
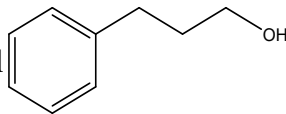
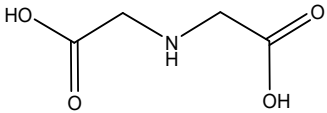
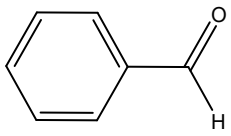
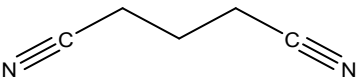
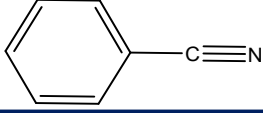


**Figure S10.** (a) TEM image and (b) XRD pattern of PdH<sub>0.706</sub> NPs after the stability test.

**Table S1.** The lattice parameters of PdH<sub>0.706</sub> and Pd NPs derived from the XRD refinement.

Samples	Cell parameters (Å)			V(Å <sup>3</sup> )
	<i>a</i>	<i>b</i>	<i>c</i>	
PdH <sub>0.706</sub>	3.98675	3.98675	3.98675	63.366
Pd	3.89333	3.89333	3.89333	59.015

**Table S2.** The chemical structures of the molecules used in the mechanism exploration part of this work.

Name	Structural formula	Name	Structural formula
<b>Iminodiacetonitrile</b>		<b>Benzyl alcohol</b>	
Iminodipropionitrile		Phenethyl alcohol	
Diethylamine		Phenylpropanol	
Iminodiacetic acid		Benzaldehyde	
Glutaronitrile		Benzonitrile	

**Table S3.** The atomic ratios of the prepared MPdH NPs.

MPdH	Pd ( <i>at.%</i> )	M ( <i>at.%</i> )
PdH	100	0
PtPdH	98.1	1.9
RuPdH	96	4
FePdH	90.2	9.8
NiPdH	88.2	11.8
CoPdH	87.3	12.7
MoPdH	84.9	15.1
CuPdH	83.1	16.9
WPdH	68.4	31.6

**Table S4.** Comparison of the ethanol oxidation performance of the PdH<sub>0.706</sub> NPs with other recently reported noble metal catalysts in alkaline media.

Catalysts	Mass Activity (A mg <sup>-1</sup> )	Electrolyte	References
<b>PdH<sub>0.706</sub> NPs</b>	<b>1.51</b>	<b>1.0 M KOH + 1.0 M EtOH</b>	<b>This work</b>
<b>Pd NPs</b>	<b>1.10</b>	<b>1.0 M KOH + 1.0 M EtOH</b>	<b>This work</b>
<b>Pd black</b>	<b>0.87</b>	<b>1.0 M KOH + 1.0 M EtOH</b>	<b>This work</b>
PdPt@s-EPS	1.13	1.0 M KOH + 1.0 M EtOH	Small 2024, 20, 2308283.
Pt <sub>6</sub> Ru MAs	1.26	1.0 M KOH + 0.5 M EtOH	App. Surf. Sci. 2024, 652, 159277.
RhCuBi TMEs	1.10	1.0 M KOH + 1.0 M EtOH	Adv. Energy Mater. 2024, 14, 2400112.
PtPd/CNTs	0.28	1.0 M KOH + 1.0 M EtOH	Electrochim. Acta 2023, 437, 141531.
g-PtPd-NPs	0.99	1.0 M KOH + 1.0 M EtOH	Int. J. Hydrog. Energy 2023, 48, 21686.
C, S, N-polymer-Pd	0.95	1.0 M KOH + 1.0 M EtOH	Adv. Funct. Mater. 2022, 33, 2210877.
twin boundary-Pd/C	1.50	1.0 M KOH + 1.0 M EtOH	Adv. Energy Mater. 2022, 12, 2103505.
PtCu NF/C	1.50	1.0 M KOH + 0.5 M EtOH	ACS Catal. 2022, 12, 11402.
Pd NPs@Ni SAC	1.09	1.0 M KOH + 1.0 M EtOH	J. Mater. Chem. A, 2022, 10, 6129-6133.
PdBi MCs	1.02	1.0 M KOH + 1.0 M EtOH	Chem. Sci. 2022, 13, 3819.
Pd/Hemin-rGO	1.05	0.1 M NaOH + 0.1 M EtOH	Int. J. Hydrog. Energy 2022, 47, 3801.
Holey Pt nanotubes	1.00	1.0 M KOH + 1.0 M EtOH	Sci. Bull. 2021, 66, 2079.
PtPdNiCu TNTPs	1.02	1.0 M KOH + 1.0 M EtOH	J. Colloid Interface Sci. 2020, 575, 425.