Electronic Supplementary Information

Introducing oxophilic metal and interstitial hydrogen into Pd lattice to boost electrochemical performance of alkaline ethanol oxidation

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1. Experimental Section

1.1 Chemicals and Materials

Palladium (II) acetylacetonate ($[Pd(acac)_2]$) and cobalt (II) acetylacetonate ($[Co(acac)_2]$) was purchased from Kunming Noble Metal Institute; Molybdenum carbonyl (Mo (CO)₆) was purchased from J&K Chemicals; N, N-dimethylformamide (DMF), sodium hydroxide (NaOH, AR) and ethanol (C_2H_6O , AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Mixed gas (4% CO+96% N₂) and nitrogen (N₂, 99.99%) were purchased from Linde Industrial Gases. All reagents were used without further purification.

1.2 Syntheses of PdCoH NSs, PdCo NSs and PdH NSs

In a typical synthesis of PdCoH NSs, 10.0 mg (0.033 mmol) of Pd(acac)₂, 8.5 mg (0.033 mmol) of Co(acac)₂ and 20 mg (0.076 mmol) of Mo(CO)₆ were dissolved in 10 mL of DMF under magnetic stirring. When the mixture turned into a homogeneous solution, 2.0 mL of n-butylamine was added. The mixture was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 25 ml after 15 min stirring. The sealed vessel was then heated to 200 °C in 60 min and kept for 12 h before it was cooled to room temperature. The product was collected by centrifugation and washed several times with ethanol. The PdH NSs were prepared with the same synthesis procedure of PdCoH NSs but in the absence of Co(acac)₂.

1.3 Calculation of H content

The content of H atoms was calculated by the following equation:

For PdCoH NSs

$$x_0 = (a_{PdCoH} - a_0) / 0.214$$

Where x_0 is the atom ratio of H / (Pd+Co), a_{PdCoH} is the lattice parameter of PdCoH NSs (3.9685 Å), a_0 is the lattice parameter of Pd₈₄Co₁₆ alloy (3.8349 Å)

For PdH NSs

$$x_1 = (a_{PdH} - a_1) / 0.214$$

Where x is the atom ratio of H/Pd, a_{PdH} is the lattice parameter of PdH NSs (3.9980 Å), a_1 is the lattice parameter of Pd (3.8933 Å) and the 0.214 is inferred from the lattice parameter of Pd (JCPDS No. 46-1043), PdH_{0.43} (JCPDS No. 87-0637), PdH_{0.58}¹,

 $PdH_{0.64}^2$, and $PdH_{0.75}^2$ based on lattice parameter and composition relationship within PdH_x system (Figure S16).

1.4 Characterization of samples

The morphology and crystal structure of the as-prepared samples were observed by scanning electron microscopy (SEM, Hitachi S4800), and transmission electron microscopy (TEM, JEOL JEM 2100). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDS), cross-sectional compositional line profile and elemental energy-dispersive X-ray spectroscopy mapping were performed with a FEI TECNAI F30 microscope operated at 300 kV. All TEM samples were prepared by drop-casting the diluted suspension in ethanol on carbon film coated molybdenum grid. The crystal phases of the samples were determined by powder X-ray diffraction (XRD) patterns, using a Rigaku Ultima IV X-ray diffractometer (Cu K α , $\lambda = 1.54056$ Å). The compositions of the samples were determined by the inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher iCAPQ). The X-ray photoelectron spectroscopy was carried out on PHI Quantum-2000, and all the spectra were calibrated with the C1s peak at 284.6 eV for internal standard. All the XPS spectra were corrected using the Shirley background. The d band center for the valence band spectra by the formula of

$$\varepsilon_d = \frac{\int N(\varepsilon)\varepsilon d\varepsilon}{\int N(\varepsilon)d\varepsilon}$$
 in the range of 0~9.0 eV, where $N(\varepsilon)$ is the density of states.

1.5 Electrochemical Measurement

Preparation of carbon - supported catalysts

The as-prepared PdCoH NSs and 10 mg of carbon supports (Vulcan XC-72) were firstly dispersed in 6 mL and 12 mL of n-butylamine and kept sonicating for 30 min, respectively. The two suspensions were then mixed and stirred for 2 h to obtain a well-dispersed suspension. The carbon supported PdCoH NSs catalyst was collected through centrifugation and washed several times with ethanol, and then kept at 60 °C in a vacuum drying oven. The carbon supported PdH NSs catalysts were obtained with the same method. The carbon supported PdCo NSs were obtained by heat treatment of the

PdCoH NSs at 300 °C for 3 hours in argon atmosphere to remove the lattice hydrogen.

The carbon-supported catalysts were dispersed in a mixed solvent containing isopropanol and Nafion (0.5%) with a concentration of 2 mg mL⁻¹. A well-dispersed electrochemical ink was obtained by ultrasonic stirring the mixture for 2 h.

Electrochemical test

All the electrochemical measurements were recorded at an electrochemical workstation (CHI 650E, Shanghai Chenhua Co., China) with three-electrode system. A carbon rod was employed as the counter electrode and a Hg/HgO (1.0 M KOH) electrode was used as the reference electrode, and a glass carbon electrode with diameter of 5 mm was served as the working electrode. Before each experiment, the working electrode was carefully polished and cleaned. Next, the electrochemical ink was added to form a catalyst film evenly coated on the surface of the glassy carbon electrode. The loading amounts of Pd for PdCoH NSs, PdH NSs, PdCo NSs, and commercial Pd/C on the working electrode was 1.6 μ g, 1.6 μ g, 2 μ g and 2 μ g, respectively, which were determined by the ICP-MS.

For the ethanol oxidation reaction test, the cyclic voltammogram (CV) curve was scanned until stable in a N₂-saturated NaOH solution (1.0 M) with a scan rate of 50 mV s⁻¹ from -1.0 V to 0.2 V (vs Hg/HgO). The ethanol oxidation test was then performed in the N₂-saturated solution of 1.0 M NaOH + 1.0 M C₂H₅OH at a scan rate of 50 mV s⁻¹ between -0.7 V and 0.2 V (vs. Hg/HgO).

For Pd-O region:

The electrochemical active surface area (ECSA) was calculated from the curve in 1.0 M NaOH using the following equation:

$$ECSA = Q_{PdO} / (q_o \cdot m_{Pd})$$
(1)

Where Q_{PdO} is the charge by integrating oxygen desorption peaks of Pd, q_o corresponding to the assumption of the adsorption charge of oxygen on the polycrystalline Pd surface is 405 μ C cm⁻², m_{Pd} is the Pd loading mass).

For CO-stripping experiment:

The ECSA were determined by the according to the equation:

$$ECSA = Q_{CO} / (q_{CO} * m_{Pd})$$
 (2)

Where the Q_{co} is the charge by integrating CO oxidation peaks of Pd, q_{co} represents the charge of CO desorption per unit area is 420 μ C cm⁻², m_{Pd} is the Pd loading mass).

Electrochemical in situ Fourier Transform infrared spectroscopy

Electrochemical in situ FTIR spectroscopy were recorded on a Nexus 870 FTIR spectrometer (Nicolet), equipping with a liquid-nitrogen-cooled MCT-A detector, an EverGlo IR source, with a spectral resolution of 8 cm⁻¹. The resulting spectra were recorded as relative change according to the following equation:

$$\frac{\Delta R}{R} = \frac{R(E_s) - R(E_R)}{R(E_R)} \tag{3}$$

where $R(E_S)$ and $R(E_R)$ is the single-beam spectrum collected at sample potential E_S and reference potential E_R . These in situ FTIR studies were performed at a solution of 1.0 M NaOH +1.0 M C₂H₅OH. The counter electrode and the reference electrode were a carbon rod and a Hg/HgO (1.0 M KOH) electrode. The E_R was fixed at -0.8 V (vs. Hg/HgO). The CO₂ selectivity (η) were calculated by the following equation:

$$\eta(CO_2) = \frac{[CO_3^{2^-}]}{2[CH_3COO^-] + [CO_3^{2^-}]}$$
(4)

where the $[CO_3^{2-}]$ and $[CH_3COO^-]$ represent the relative concentration (C_R) of CO_3^{2-} and CH_3COO^- by using the quantitative analytical method.

2. Supplementary results



Figure S1.SEM image of the as-prepared PdCoH NSs.



Figure S2.TEM image of the PdCoH NSs after 3 min of beam exposure.



Figure S3. XRD patterns of the PdCoH NSs and the PdH NSs.



Figure S4. EDS analysis of the PdCoH NSs.



Figure S5. a) XRD patterns of PdCoH NSs obtained at initial and after being aged in ambient conditions for 6 months, b) in-situ XRD patterns of the PdCoH NSs at different temperature.



Figure S6. TEM image of PdH NSs synthesized in the absence of Co(acac)₂.



Figure S7. a) TEM image and b) XRD pattern of the PdCo NSs.



Figure S8. CV curves in 1.0 M NaOH at a scan rate of 50 mV s⁻¹ for a) PdCoH NSs; b) PdH NSs,c) PdCo NSs and d) Pd/C.



Figure S9. CV curves of CO-stripping in 1.0 M NaOH at a scan rate of 10 mV s⁻¹ for a) PdCoH NSs; b) PdH NSs, c) PdCo NSs and d) Pd/C.

There are two anodic peaks in the first cycle, the first peak in the range of -0.6 to -0.3 V (vs. Hg/HgO) and the second peak in the range of -0.2 to 0 V (vs. Hg/HgO). During the CO stripping experiment, we set the initial potential at -1.0 V (vs. Hg/HgO) and purged gaseous CO into the solution for 25 min to let CO adsorb on the surface of the catalyst, and then purged gaseous N₂ to remove the CO in the solution. However, at this potential (-1.0 V vs. Hg/HgO), the H atoms will infiltrate into the lattice of Pd. It is reported when the electrode potential negative to reversible H⁺/H₂ potentials (-0.924 vs. Hg/HgO), there will appear a broad anodic peak assigned to the desorption peaks which may overlaying the UPD-H or the absorbed H desorption in the range of -0.6 V to -0.3 V^{3,4}. And the second peak in the range of -0.2 V to 0 V was due to the oxidation of CO.



Figure S10. a) TEM image, b) XRD pattern of PdCoH NSs after durability test.



Figure S11. The schematic diagram of ethanol oxidation process.



Figure S12. The setup for in situ FTIR experiments.



Figure S13. Illustration of the subtraction procedure of IR spectra (a₀: the in situ FTIR spectrum of EOR of PdCoH NSs at 0.2 V; b₀: transmission IR spectrum of 0.1 M CH₃COONa as the subtrahend; c₀: the resultant subtraction spectrum; d₀: transmission IR spectrum of 0.1 M Na₂CO₃).



Figure S14. XPS characterization of Co 2p for PdCoH NSs and PdCo NSs.

The area ratio of Co^{x+}/Co for PdCoH NSs is 23; the area ratio of Co^{x+}/Co for PdCo NSs is 20.



Figure S15. XPS characterization of Pd 3d for a) Pd/C, b)PdH NSs, c) PdCo NSs and d) PdCoH NSs.



Figure S16. The relationship between lattice constant and H content.

Table S1. Detailed data for electrochemical active surface area (ECSA), specific mass current density (mass activity) and specific area current density (specific activity) of the four catalysts towards ethanol electro-oxidation.

	ECSA (m^2/g)	ECSA (m^2/g)	Mass activity	Specific activity
	(Pa-O)	(CO-stripping)	(mA/mg)	(mA/cm ⁻²)
PdCoH NSs/C	58.2	54.8	6263.7	11.0
PdH NSs/C	57.2	52.0	4569.4	8.0
Pd/C	38.5	36.1	1460	3.8
PdCo NSs/C	30.0	29.3	2617.1	8.7

Table S2. Summary of the EOR performance of Pd-based catalysts reported in recent years.

Catalyst	Mass Activity	Condition	Ref.
	(mA mg ⁻¹)		
PdCoH NSs/C	6263.7	1M NaOH+ 1MC₂H₅OH	This work
PdBi	5740	1М КОН + 1 М С ₂ н5ОН	Adv. Funct. Mater. 2021, 2103465
PdMoH bimetallene	4260	1 М КОН+1М С ₂ н₅он	ACS Energy Lett. 2021, 6, 1912–1919
Pd ₂ Sn:P/C	5030	0.5 M KOH + 0.5 M ethanol	Nano Energy, 2020, 77, 105116
PdPb ₃ nanochains	2523	1M NaOH + 1M C ₂ H ₅ OH	Rare Metals, 2020, 39, 792–799
PdZn NSs	2730	1M NaOH+ 1 MC ₂ H ₅ OH	ACS Nano 2019, 13, 14329-14336

PdAg nanodendrites	2600	1M KOH +	Adv. Mater. 2018,
		1 M C ₂ H ₅ OH	1706962
Ultrathin Palladium	5400	1M KOH+	Angew. Chem., Int. Ed.
Nanomesh		1M C ₂ H ₅ OH	2018, 57, 3435–3438
Pd aerogel	3700	1M NaOH+	J. Mater. Chem. A,
		1MC ₂ H ₅ OH	2017, 5, 10244–10249
	1500	1 M KOH +	Adv. Mater. 2017, 29,
Pa/NI(OH) ₂ /IGO		1 M EtOH	1703057
DdNiD nononortialog	4950	1 M NaOH +	Nat. Commun. 2017, 8,
POINTP nanoparticles		1 M EtOH	14136
Au/Pd	2920	1 M KOH +	Adv. Mater. 2017, 29,
		1 M EtOH	1701331

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