

Supplementary Information

Electrooxidation of Veratryl Alcohol to Veratraldehyde by Pd-Ni(OH)₂

Hybrid Nanoarrays via Interfacial Engineering

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1. Materials and methods

Chemicals

Veratryl alcohol (VA, 98%) was purchased from Macklin Biochemical Co. Ltd (Shanghai, China). Dimethyl sulfoxide (DMSO, 99.9%) and deuterium oxide (D_2O , 99.9%) were supplied from Energy Chemical Reagent Co., Ltd. Palladium chloride ($PdCl_2$, Pd 59-60%) were purchased from Aladdin Co., Ltd. Ar (99.9%) was purchased from Dalian Special Gases Co., Ltd. Potassium hydroxide (KOH) and ethanol (C_2H_5OH , AR) were purchased from Sinopharm Shanghai Chemical Reagent Company. Unless otherwise specified, all chemicals were directly used without further purification.

Catalysts preparation

Synthesis of $Ni(OH)_2$ nanosheets

Nickel foam (NF) was used as matrix for growing $Ni(OH)_2$ nanosheets array. Initially, NF (15*15*1.5 mm) was ultrasonically cleaned in ethanol (50 mL) for 5 min and rinsed by deionized water, then it was etched by 2 M HCl (50 mL) for 1 h and ultrasonically cleaned by deionized water for 5 min. Subsequently, the treated NF was further put in deionized water (40 mL) for 24 hours at 60 °C to *in-situ* grow $Ni(OH)_2$ nanosheets.

Synthesis of $Pd/Ni(OH)_2$ and Pd/NF

The Pd species were electrodeposited onto NF supported $Ni(OH)_2$ nanosheets at -1.0 V vs Ag/AgCl for 10 min in a three-electrode system using Ag/AgCl (with saturated KCl) reference electrode, Pt foil as counter electrode, and NF supported $Ni(OH)_2$ nanosheets as working electrode, with an aqueous electrolyte containing 0.5 M H_3BO_3 and 10 mM H_2PdCl_4 , getting the $Pd/Ni(OH)_2$ catalyst.

The Pd/NF catalyst was prepared via the similar electrodeposition method on NF.

Preparation of Pd NPs/ $Ni(OH)_2$ control catalyst

The catalyst ink was obtained by ultrasonically dispersing 1 mg of the Pd powder from electrolyte after electrodeposition in a suspension containing water/ethanol solution ($V_{water} = 400 \mu L$, $V_{ethanol} = 75 \mu L$) and 25 μL of Nafion solution (5 wt.%). Then, the catalyst ink was dropped on the $Ni(OH)_2/NF$.

Catalysts characterizations

The morphology of the samples was characterized using SU5000 SEM operated at 10.0 kV and JEM-F200 TEM operated at 200.0 kV. The Fourier transform infrared (FT-IR) spectra were acquired from a Thermo Scientific Nicolet 6700 FTIR spectrometer.

Powder X-ray diffraction (XRD) measurements were conducted with a PANalytical X'Pert3 powder diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was conducted on Scientific K-Alpha, Thermo Ltd with a monochromatic X-ray source (Al K α). The liquid nuclear magnetic resonance spectra (NMR) were collected on a Vaian DLG 400 MHz in deuterium oxide.

Electrochemical measurements

All electrochemical measurements were performed on an Ivium-n-Stat electrochemical workstation at room temperature using a standard three-electrode cell with a working electrode, a platinum sheet (2.25 cm^2) as the counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. Additionally, the anode and cathode chambers were separated by a Nafion 117 membrane. The as-synthesized catalysts on NF electrodes (Pd/Ni(OH) $_2$, Pd/NF, Ni(OH) $_2$ and bare NF) were used directly as working electrodes (2.25 cm^2). The potentials were converted to RHE through the Nernst equation: $E \text{ (RHE)} = E \text{ (Ag/AgCl)} + 0.197 \text{ V} + 0.0591 \times \text{pH}$. The cathodic compartment contained an aqueous 0.1 M KOH solution, whereas the anodic compartment was filled with 0.1 M KOH electrolyte supplemented with 0.1 M VA. To evaluate the electrocatalytic activity of the catalysts toward VA oxidation, the polarization curves were normalized with respect to the corresponding electrode surface areas. All curves were measured at a scan rate of 5 mV s^{-1} with 85%-iR compensation.

Product Analysis

The liquid products can be analyzed by nuclear magnetic resonance (NMR) spectrometer. ^1H NMR spectra were recorded on a Vaian DLG 400 MHz, in which 500 μL electrolyte was added 50 μL D $_2$ O with 50 μL DMSO used as an internal standard. The Faraday efficiency (FE) of the VAId formation can be determined by the following equation:

$$FE (\%) = \frac{n * eF}{Q}$$

where e is the electrons transfer number and Q (C) is the total charge passed during the electrochemical reaction. n (mol) and F (96485 C mol^{-1}) are the total moles of the product formed and Faraday constant, respectively.

2. Supplementary Figures

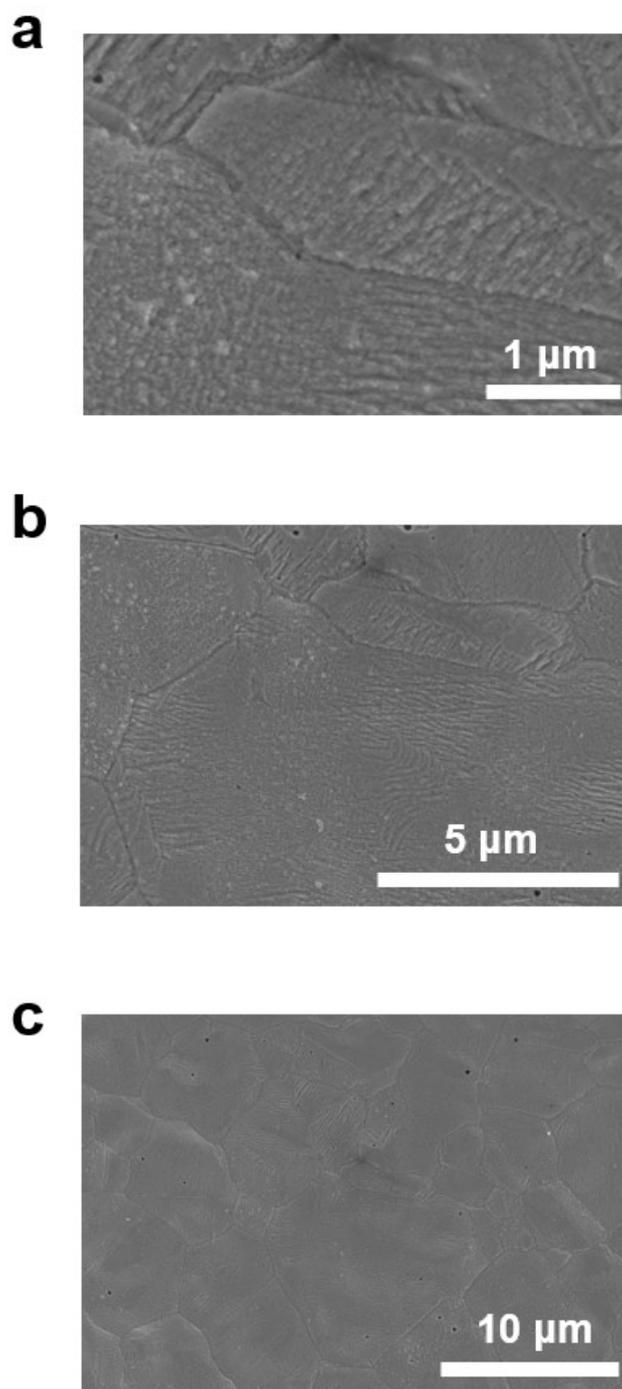


Fig. S1. SEM images of NF.

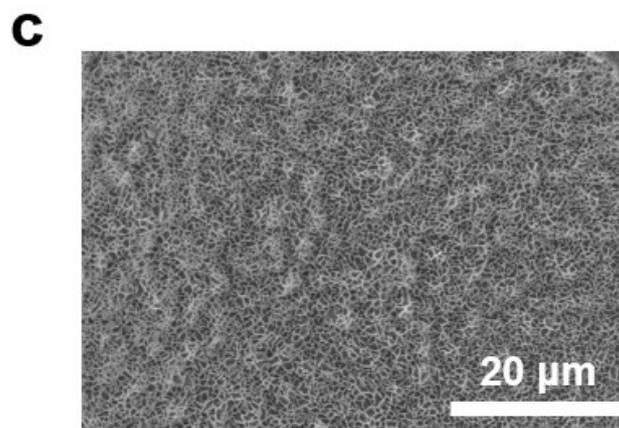
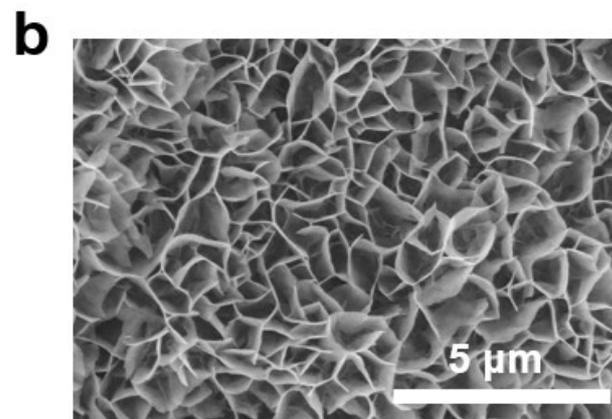
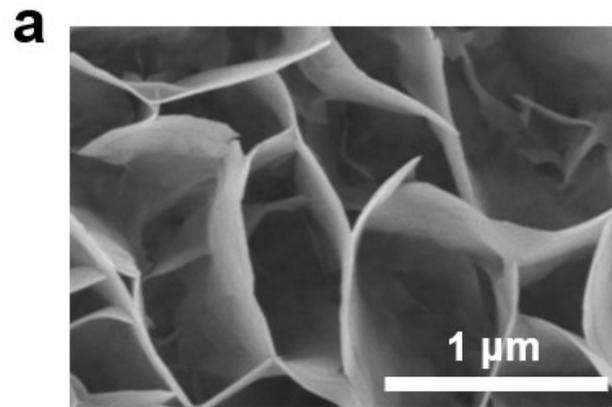


Fig. S2. SEM images of $\text{Ni}(\text{OH})_2$.

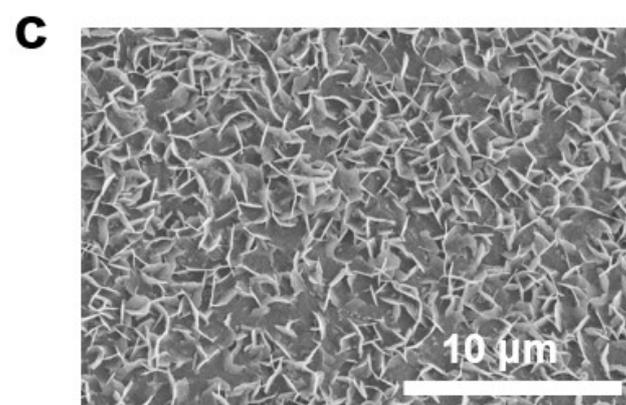
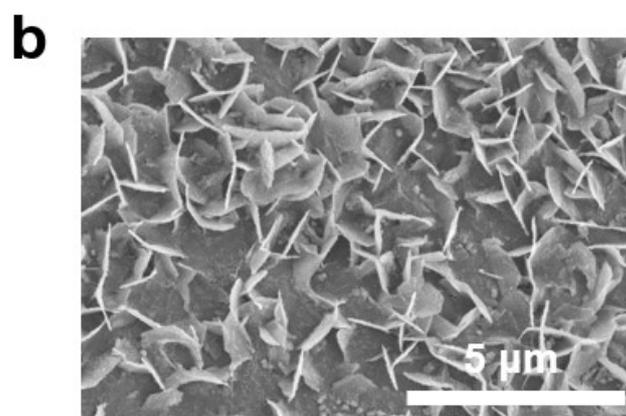
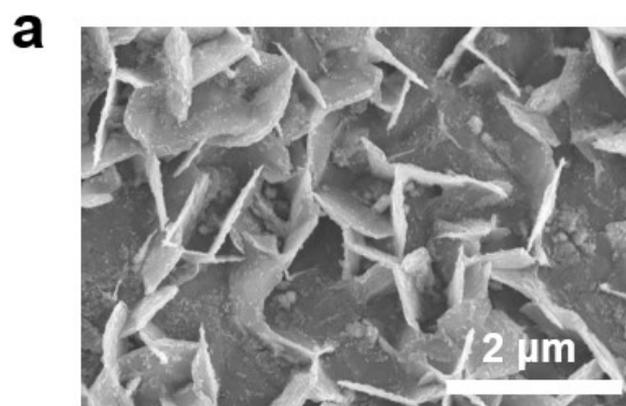


Fig. S3. SEM images of Pd/Ni(OH)₂.

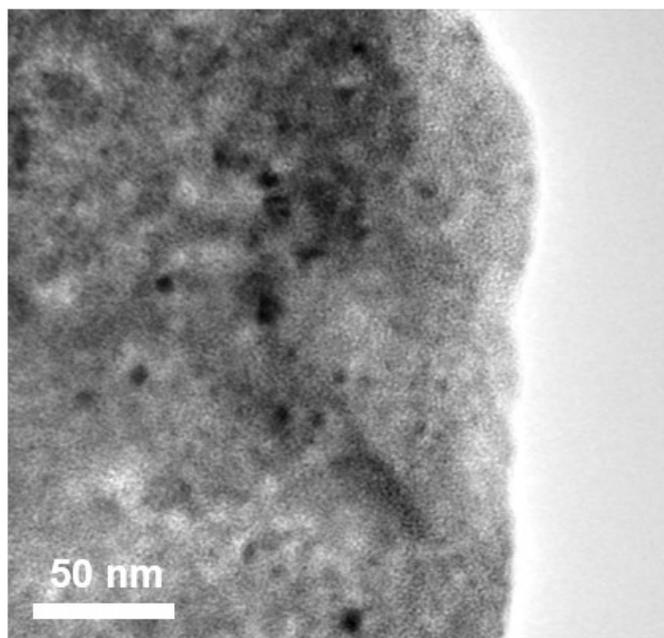


Fig. S4. TEM image of Pd/Ni(OH)₂.

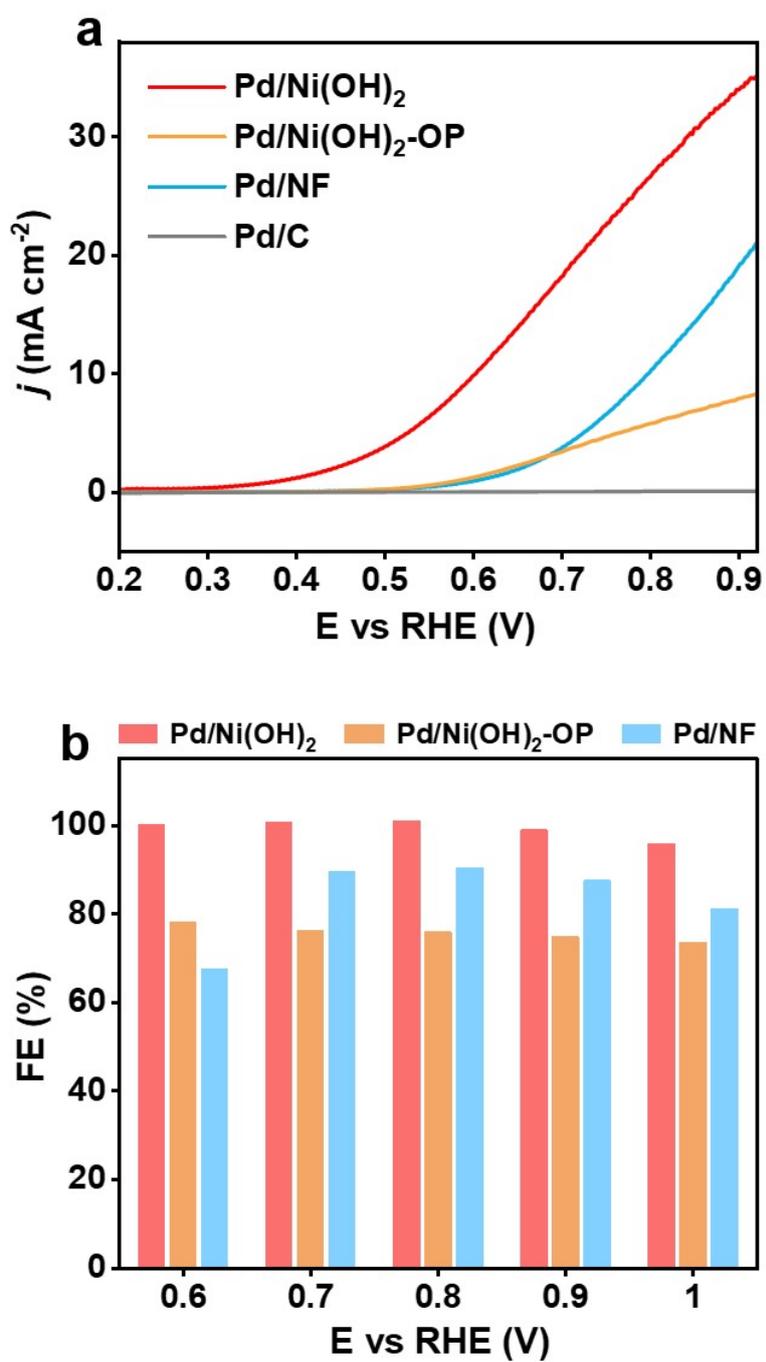


Fig. S5. (a) LSV curves of Pd/Ni(OH)₂, Pd/Ni(OH)₂-OP, Pd/NF and Pd/C; (b) FE of Pd/Ni(OH)₂, Pd/Ni(OH)₂-OP, Pd/NF.

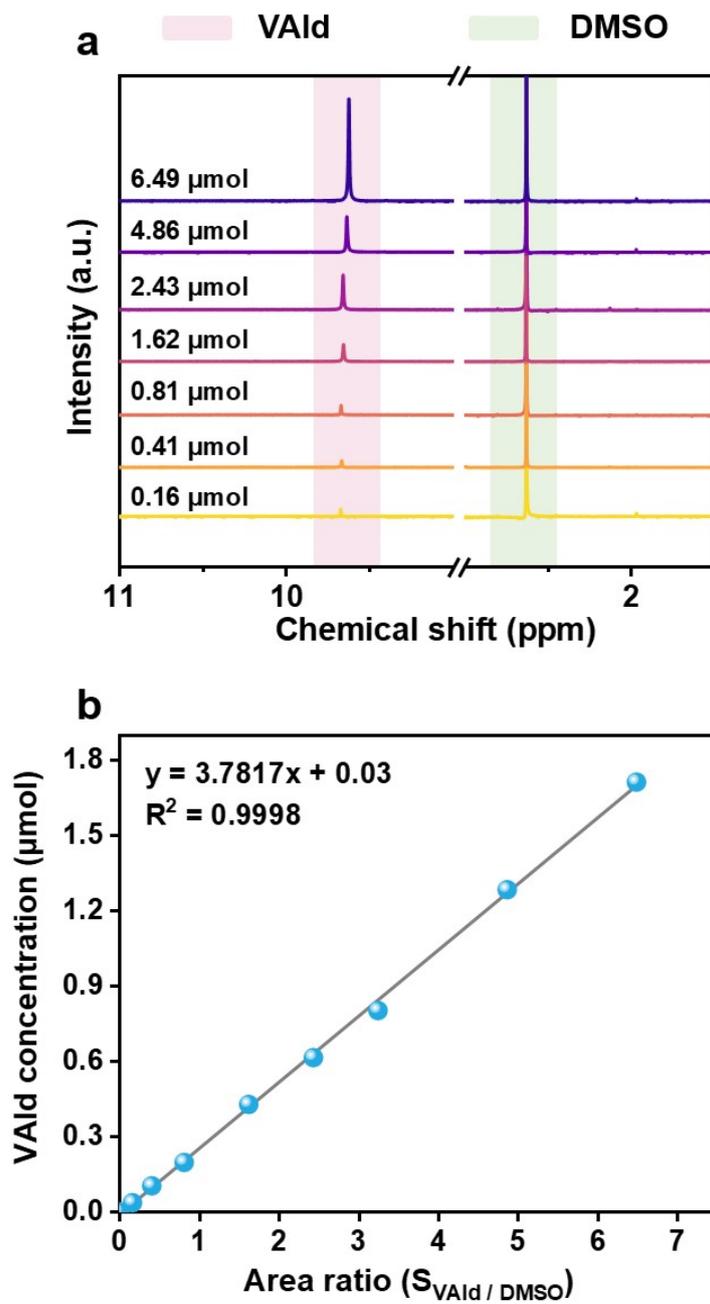


Fig. S6. ¹H NMR spectra and standard curve of veratraldehyde (VAld). (a) ¹H NMR spectra of VAld and (b) standard curve of VAld. The standard curve of VAld shows the good linear relationship and follow the linear equation: $y=3.7817x+0.03$ ($R^2 = 0.9998$).

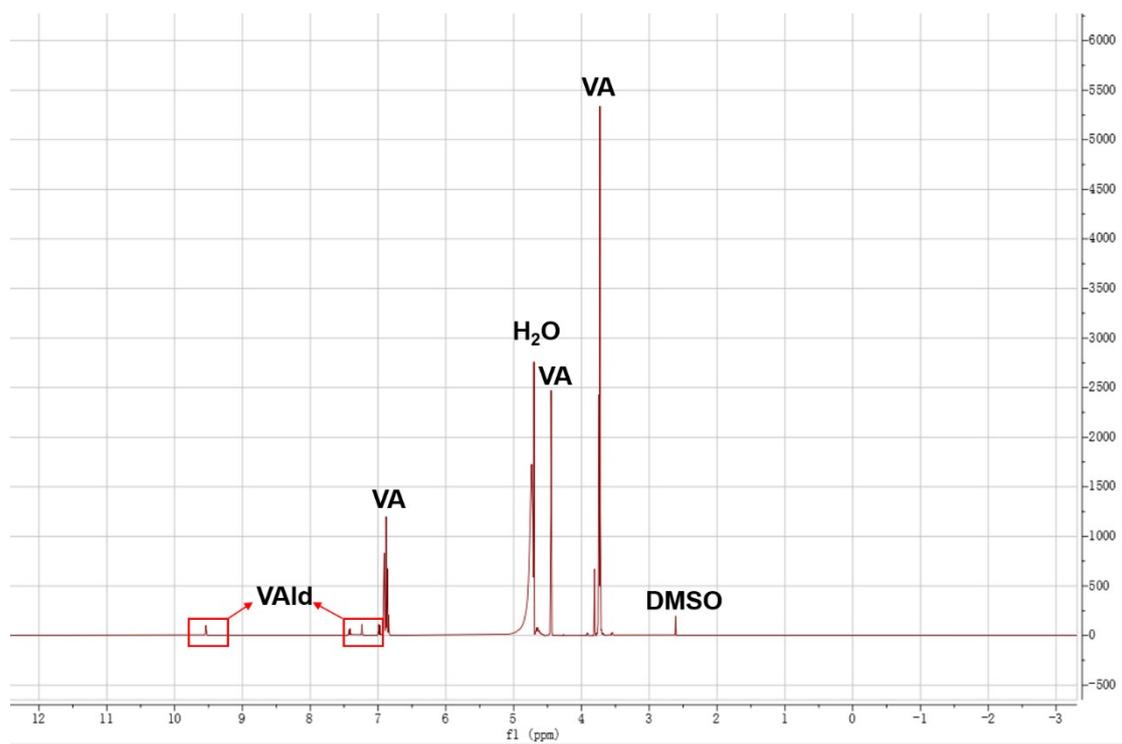


Fig. S7. ^1H NMR spectrum of the electrolysis product.

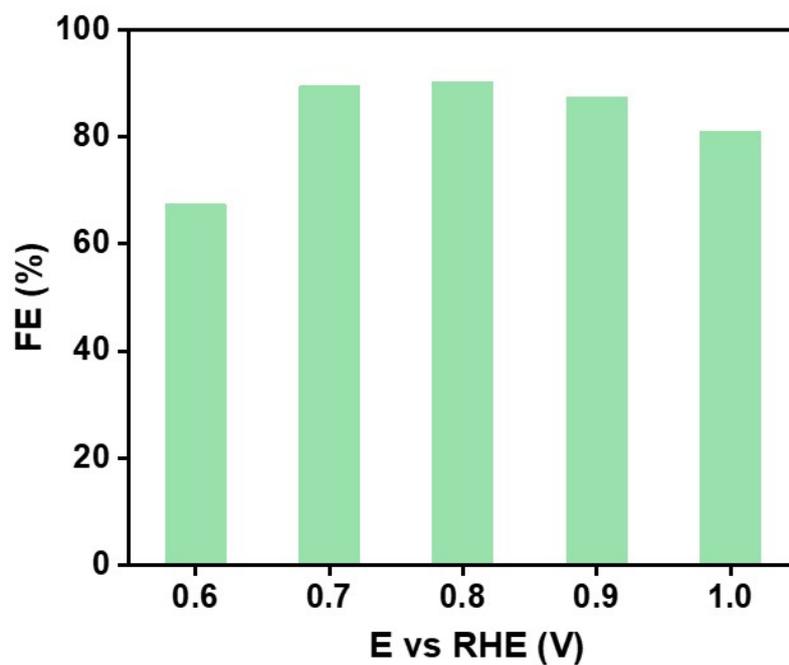


Fig. S8. FE of Pd/NF at 0.6-1.0 V vs RHE.

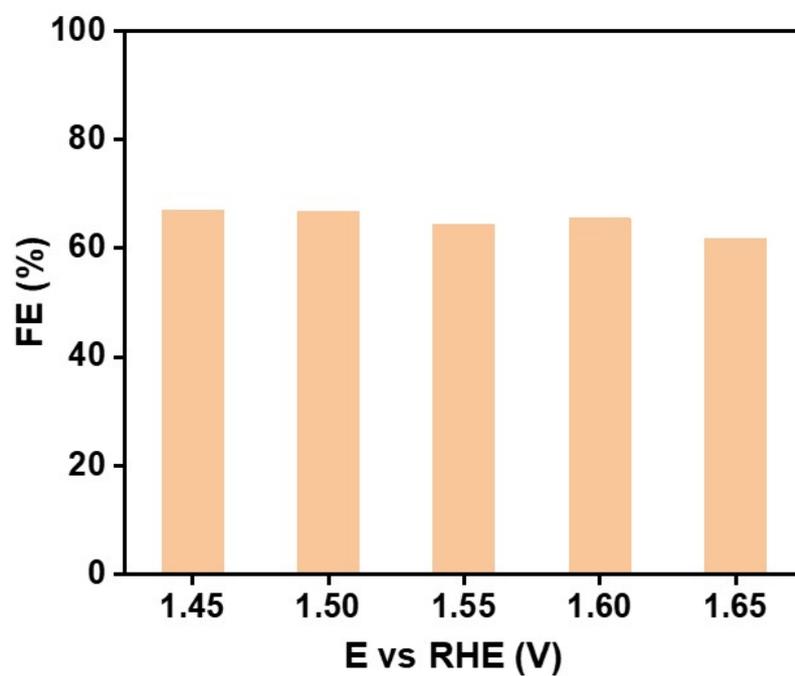


Fig. S9. FE of Ni(OH)₂ at 1.45-1.65 V vs RHE.

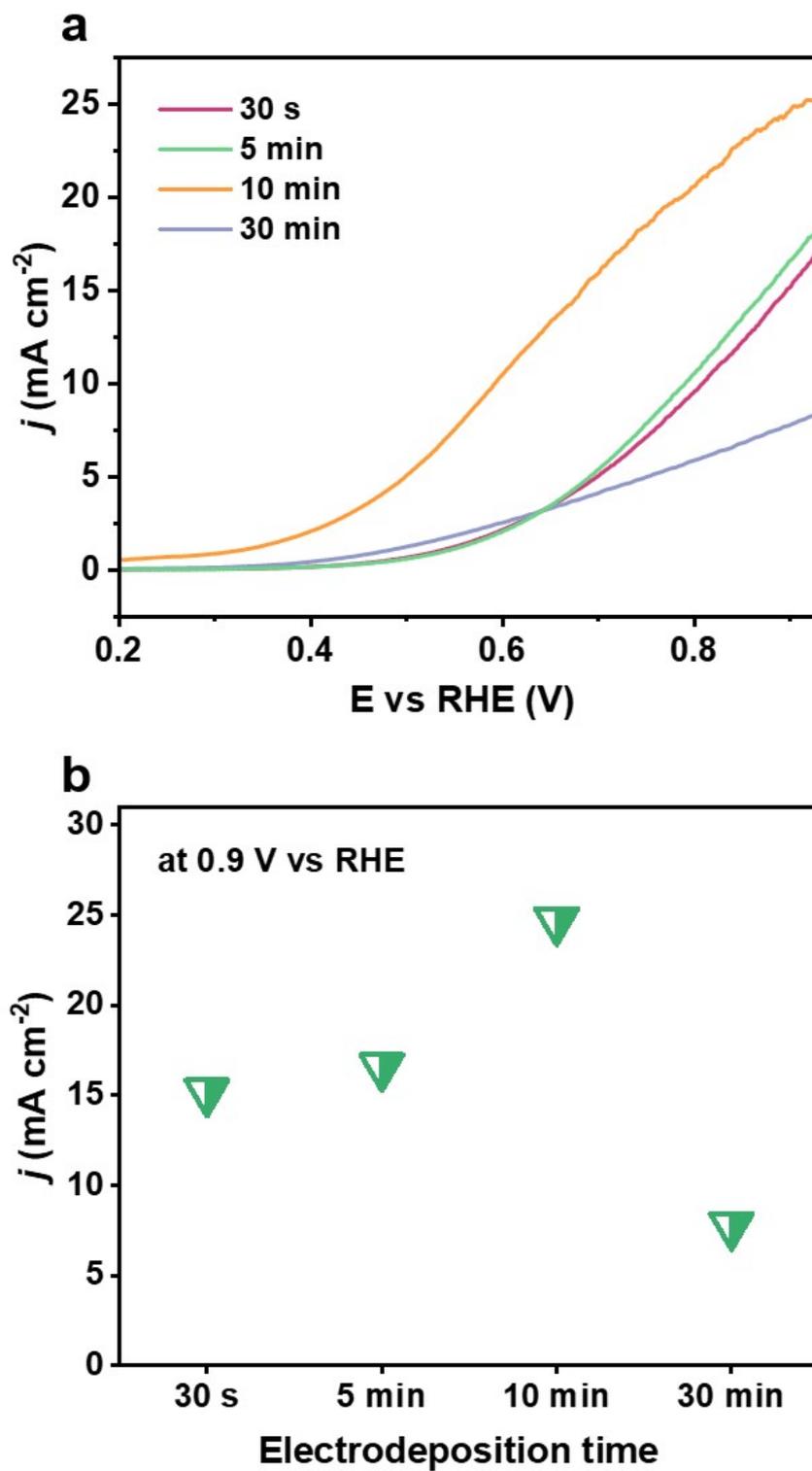


Fig. S10. (a) LSV curves of Pd/Ni(OH)₂ catalysts with different electrodeposition time; (b) The current densities of the catalysts prepared with different electrodeposition times at 0.9V vs RHE.

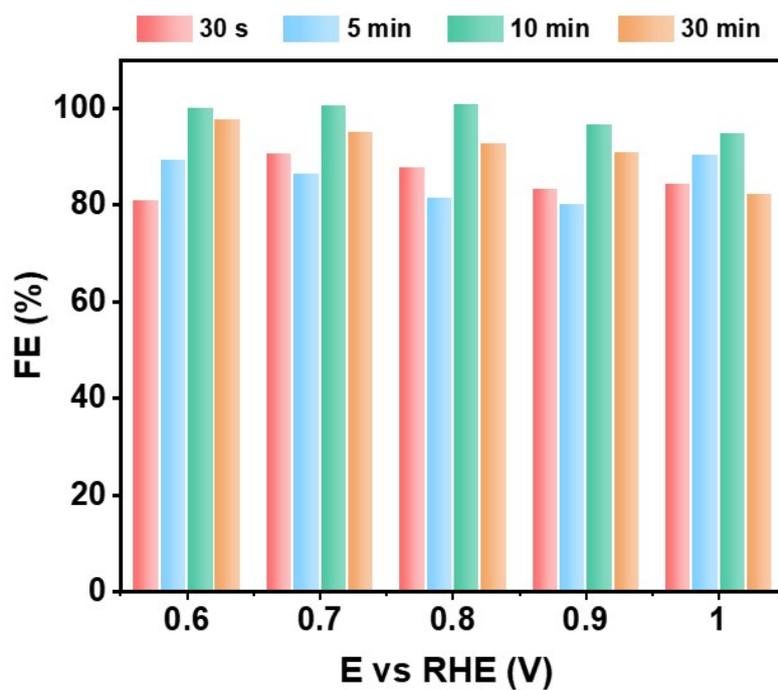


Fig. S11. FE of Pd/Ni(OH)₂ catalysts prepared with different electrodeposition time.

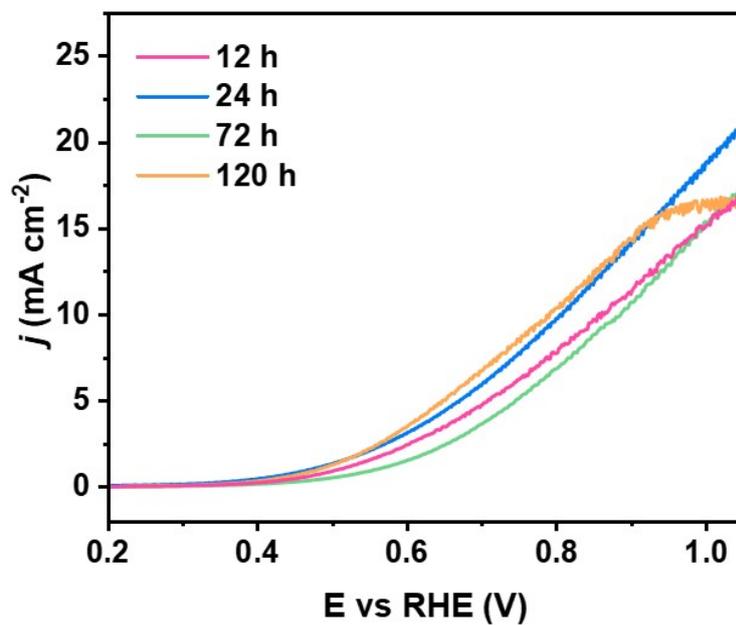


Fig. S12. LSV curves of Pd/Ni(OH)₂ catalysts with different hydrothermal synthesis time.

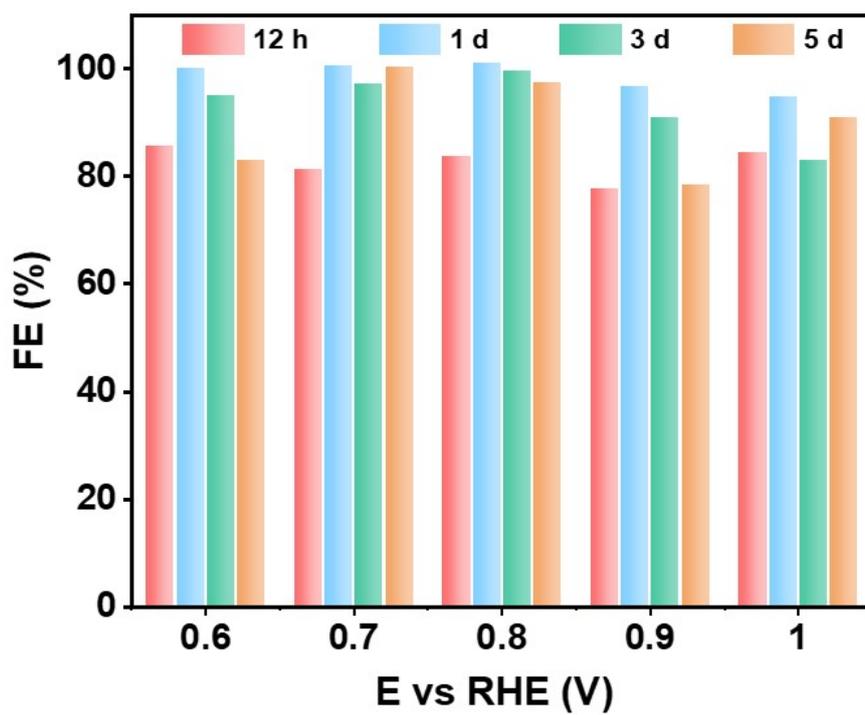


Fig. S13. FE of Pd/Ni(OH)₂ catalysts prepared with different hydrothermal synthesis duration.

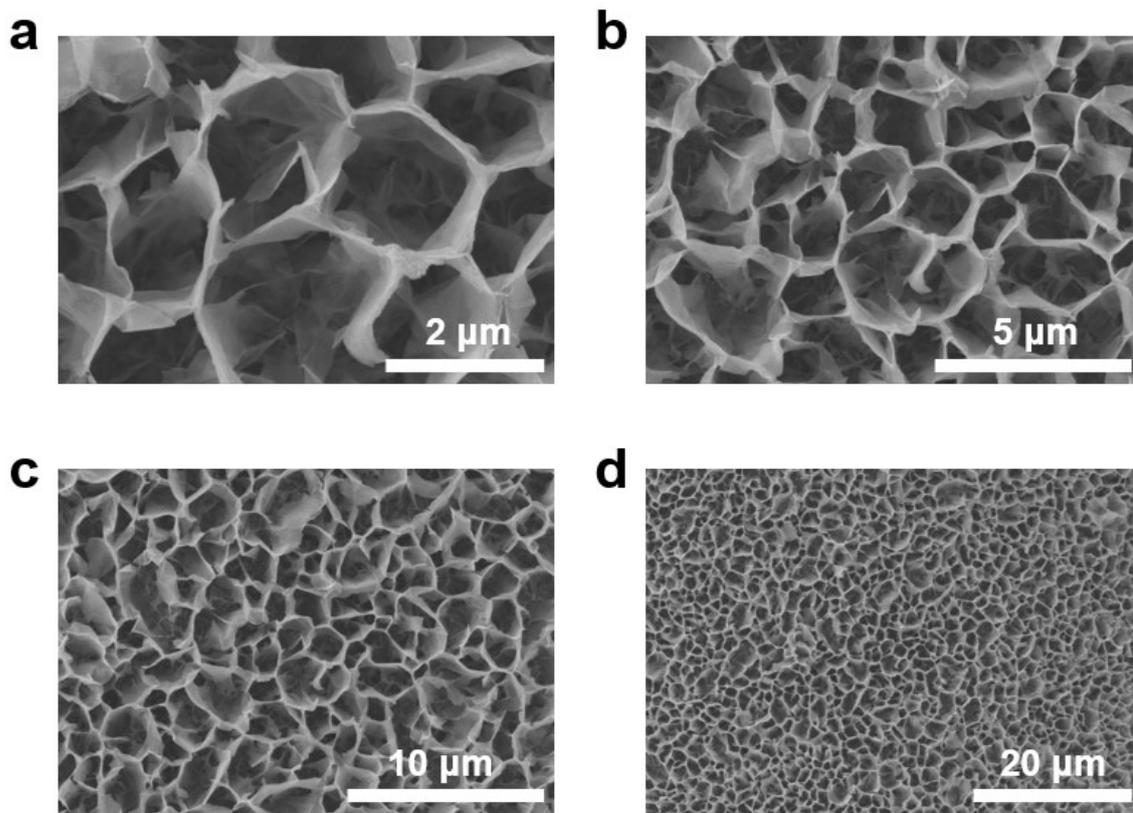


Fig. S14. SEM images of the Pd/Ni(OH)₂ catalyst prepared with a 72 h hydrothermal synthesis duration.

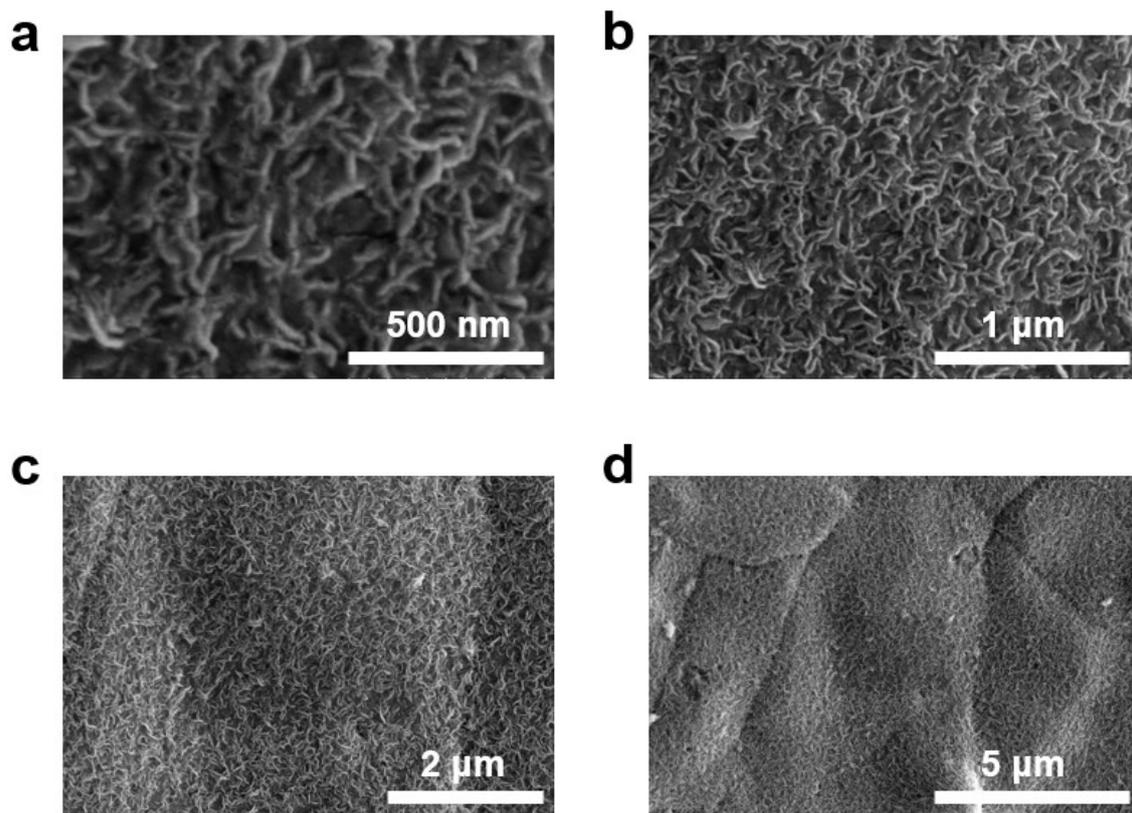


Fig. S15. SEM images of the Pd/Ni(OH)₂ catalyst prepared with a 120 h hydrothermal synthesis duration.

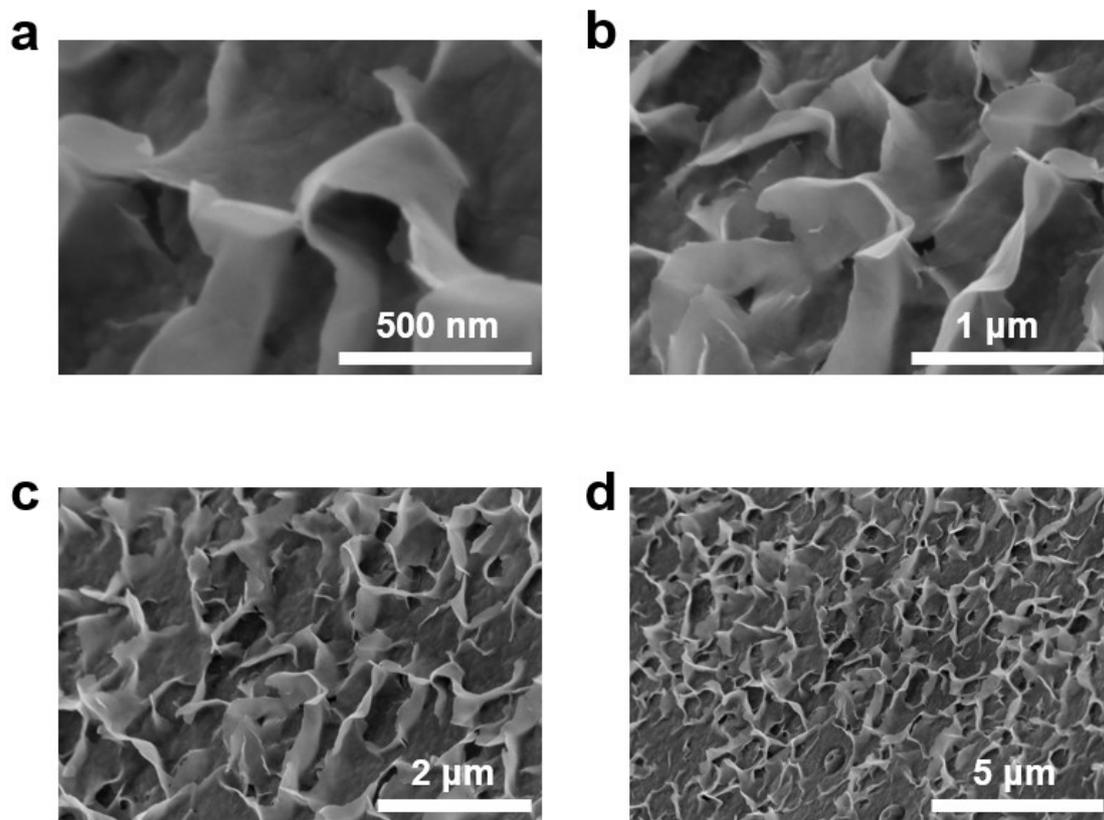


Fig. S16. SEM images of the Pd/Ni(OH)₂ catalyst prepared with a 12 h hydrothermal synthesis duration.

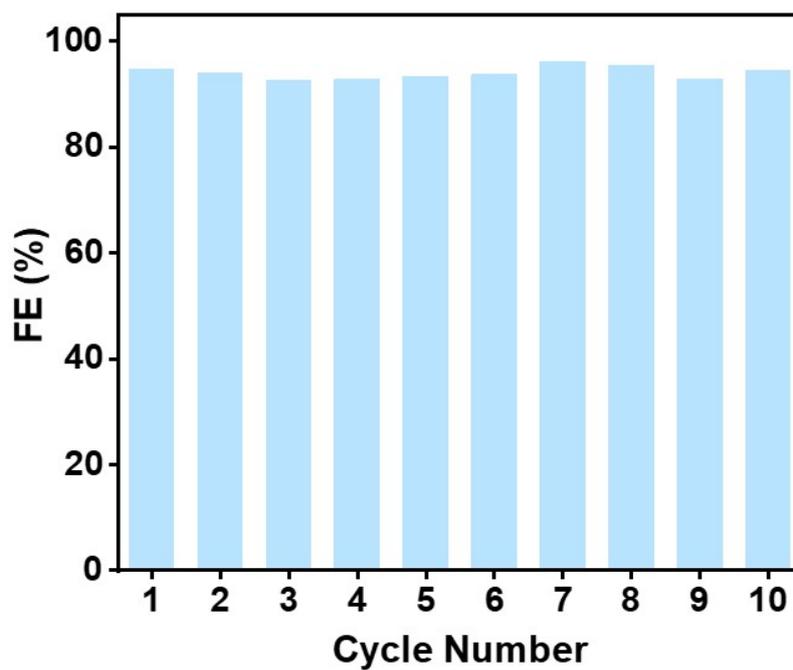


Fig. S17. Recyclability test of the Pd/Ni(OH)₂ catalyst for VA oxidation. The FE of VALd were recorded over 10 consecutive cycles at an applied potential of 0.9 V vs RHE.

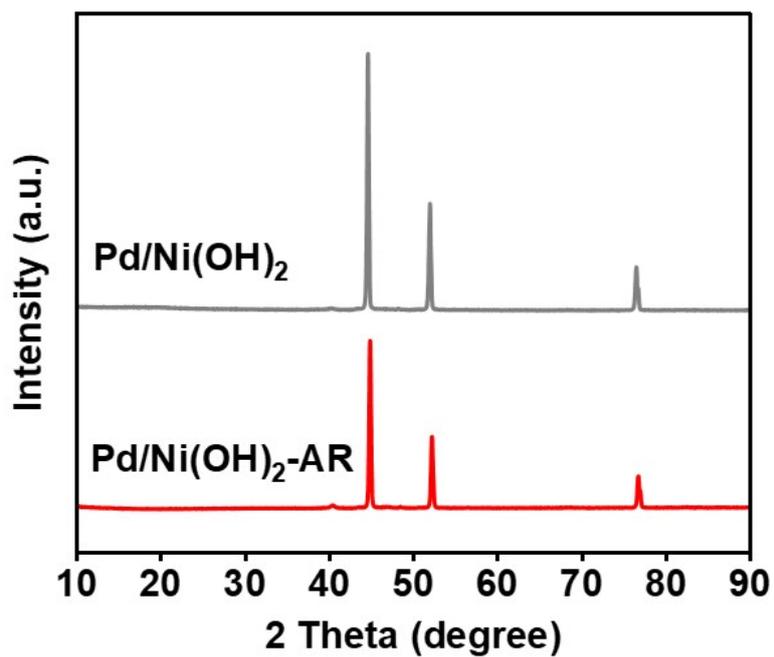


Fig. S18. XRD patterns of the Pd/Ni(OH)₂ catalyst before and after the recyclability test.

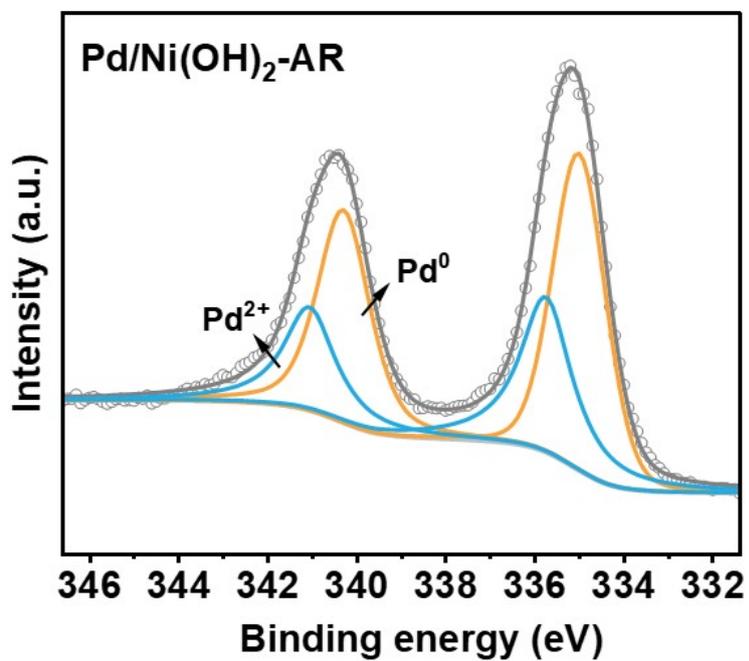


Fig. S19. High-resolution Pd 3d XPS spectrum of the Pd/Ni(OH)₂-AR.

3. Supplementary Tables

Tab. S1. The Pd content for the two catalysts.

Catalyst	ICP (wt.%)	Pd mass (mg)
Pd/Ni(OH) ₂	0.78	0.51
Pd/NF	0.68	0.55

Tab. S2. The integrated charge of the two catalysts.

Catalyst	Q (mC)
Pd/Ni(OH) ₂	0.12
Pd/NF	0.08

Tab. S3. Comparison of catalytic performance for VA oxidation.

Catalyst	Method	Exogenous oxidant	Reaction pressure	Reaction temperature (°C)	Selectivity (%)	References
Pd/Ni(OH)₂	Electro-catalysis	--	--	RT	100	This work
Ru/Al ₂ O ₃	Thermo-catalysis	Air	5 bar	160	89	[1]
RuCo/rGO	Thermo-catalysis	O ₂	3 bar	100	92.2	[2]
Ru@ZIF-8 + CuO	Thermo-catalysis	O ₂	5 bar	130	95	[3]
CuO/SBA-15	Thermo-catalysis	TBHP	1 bar	80	100	[4]
TiO ₂ /SO ₄ /Ni @SBA-15	Thermo-catalysis	TBHP	10 bar	90	100	[5]
Fe-Ni/Mordenite	Thermo-catalysis	TBHP	10 bar	90	99	[6]
Mn-Zn/AC	Thermo-catalysis	TBHP	15 bar	90	98	[7]
Ni/SO ₄ /ZrO ₂	Thermo-catalysis	TBHP	10 bar	90	100	[8]

4. References

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