

Supporting information

In Situ Growth Engineering Ultrathin Dendritic PdNi Nanosheets on Nitrogen-doped V_2CT_x MXene for Efficient Hydrogen Evolution

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1. Experimental section

1.1 Chemicals and Materials:

Palladium (II) chloride ($PdCl_2$, 99%), nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), sulfuric acid (H_2SO_4 , 98%), hydrochloric acid (HCl, 98%), docosyltrimethylammonium chloride (BTAC), tetrabutylammonium hydroxide (TBAOH) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Diethanolamine (DEA) and methanol (MT) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). L-ascorbic acid (AA) was purchased from Alfa Aesar (China) Co., Ltd. Vanadium carbide (V_2CT_x) multilayer nanosheets were purchased from XFNano Materials Tech Co., Ltd. Pd/C (20 wt%) and Nafion (5 wt%) were provided by Sigma-Aldrich. The experiments' ultra-pure water (18.2 M Ω ·cm) was obtained from a Millipore purification system (Simplicity).

1.2 Preparation of TBA- V_2CT_x :

To prepare TBA- V_2CT_x , 1 g of V_2CT_x was dispersed in 10 mL of tetrabutylammonium hydroxide and shaken for 8 hours at room temperature (25°C). The resulting solid product was obtained by centrifugation at a speed of 11,000 r/min and subsequently washed with 40 mL of ultrapure water through repeated centrifugation 3 times. The resulting TBA- V_2CT_x aqueous solution was then freeze-dried to obtain TBA- V_2CT_x powder.

1.3 Preparation of N-TBA- V_2CT_x :

To prepare N-TBA- V_2CT_x , 0.5 g of TBA- V_2CT_x powder was mixed with 15 mL of diethanolamine (DEA) and 6 mL of methanol (MT) in a hydrothermal reaction vessel and stirred until well mixed. The mixture was then heated at 180°C for 20 hours. After complete cooling of the solution, the resulting solid product was obtained by centrifugation at a speed of 11,000 r/min. The product was then washed with 40 mL of ultrapure water through repeated centrifugation 3 times to obtain N-TBA- V_2CT_x aqueous solution. Finally, the solution was freeze-dried to obtain N-TBA- V_2CT_x powder.

1.4 Preparation of N- V_2CT_x :

To prepare N- V_2CT_x , 0.5 g of V_2CT_x powder was mixed with 15 mL of diethanolamine (DEA) and 6 mL of methanol (MT) in a hydrothermal reaction vessel and stirred until well mixed. The mixture was then heated at 180°C for 20 hours. After complete cooling of the solution, the resulting solid product was obtained by centrifugation at a speed of 11,000 r/min. The product was then washed with 40 mL of ultrapure water through repeated centrifugation 3 times to obtain N-TBA- V_2CT_x aqueous solution. Finally, the solution was freeze-dried to obtain N- V_2CT_x powder.

1.5 Preparation of PdNi/N-TBA- V_2CT_x :

To prepare the H_2PdCl_4 solution, mix 1 g of $PdCl_2$, 1.143 g of HCl, and 562.857 g of ultrafiltration water in a reagent bottle, and shake for 3 hours at 60°C. In the typical synthesis of PdNi/N-TBA- V_2CT_x , H_2PdCl_4 (6 ml, 0.01 M), $NiCl_2$ (4 ml, 0.01 M), and 0.5 g of N-TBA- V_2CT_x powder were sequentially added to a BTAC aqueous solution (0.01 M, 200 ml) and then sonicated for 15 minutes to mix the solution evenly. Next, quickly add 10 ml of 0.1 M AA to the mixed solution, and react for 8 hours at 35°C. After the reaction, the resulting solid product was obtained by centrifugation at a speed of 11,000 r/min for 30 minutes, followed by three washes with ultrapure water. The preparation of

$\text{Pd}_x\text{Ni}_y/\text{N-TBA-V}_2\text{CT}_x$ was essentially the same as that of $\text{Pd}_{58}\text{Ni}_{42}/\text{N-TBA-V}_2\text{CT}_x$, except that the total amount of Pd and Ni precursors was kept at 10 ml and the ratio of Pd/Ni precursors added was once ($x: y = 2:8, 3:7, 4:6, 5:5, 7:3, 8:2$). The compositions prepared were $\text{Pd}_{28}\text{Ni}_{72}/\text{N-TBA-V}_2\text{CT}_x$, $\text{Pd}_{33}\text{Ni}_{67}/\text{N-TBA-V}_2\text{CT}_x$, $\text{Pd}_{52}\text{Ni}_{48}/\text{N-TBA-V}_2\text{CT}_x$, $\text{Pd}_{58}\text{Ni}_{42}/\text{N-TBA-V}_2\text{CT}_x$, $\text{Pd}_{64}\text{Ni}_{36}/\text{N-TBA-V}_2\text{CT}_x$, and $\text{Pd}_{75}\text{Ni}_{25}/\text{N-TBA-V}_2\text{CT}_x$.

1.6 Preparation of PdNi:

The preparation of various proportions of PdNi was similar to the process described above for $\text{PdNi}/\text{N-TBA-V}_2\text{CT}_x$, except that MXenes were not added during the preparation process. Specifically, a typical process for the preparation of $\text{Pd}_{58}\text{Ni}_{42}$ is given as an example. H_2PdCl_4 (6 ml, 0.01 M), and NiCl_2 (4 ml, 0.01 M) were sequentially added to a BTAC aqueous solution (0.01 M, 200 ml) and then sonicated for 15 minutes to mix the solution evenly. Next, quickly add 10 ml of 0.1 M AA to the mixed solution, and react for 8 hours at 35°C. After the reaction, the resulting solid product was obtained by centrifugation at a speed of 11,000 r/min for 30 minutes, followed by three washes with ultrapure water.

1.7 Material characterization:

The crystal structure was examined using X-ray diffraction by X Pert-Pro MPD diffractometer (Netherlands PANalytical) with a $\text{Cu K}\alpha$ X-ray source ($\lambda = 1.540598 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer) was performed to measure the elemental compositions and chemical states in samples. The inductively coupled plasma optical emission spectrometer (ICP-OES, Varian 710-ES) determined the contents of elemental metals. The Hitachi HT7700 at an acceleration voltage of 120 kV was adopted to collect low-magnification transmission electron microscopy (TEM) images. SEM images were received from Hitachi SU8010. High-resolution TEM (HRTEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were obtained from the FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. An atomic force microscopy (AFM) image was collected on a Bruker Dimension Icon. Fourier transform infrared spectra were obtained by FT-IR (Thermo Nicolet iS50).

1.8 Zeta potential tests:

The zeta potential tests were performed using a Zetasizer Nano ZS Malvern Laser Particle Sizer. Before tests, the as-synthesized $\text{N-TBA-V}_2\text{CT}_x$ and $\text{Pd}_{58}\text{Ni}_{42}/\text{N-TBA-V}_2\text{CT}_x$ were washed with ultra-filtered water one time to remove free BTAC from the solution. After that, the solution was directly sent for zeta potential tests.

1.9 Electrochemical Measurements:

Electrochemical experiments were performed on a CHI 660E potentiostat at room temperature. The working electrode, reference electrode, and counter electrode are glassy carbon electrode (GCE, 3 mm in diameter), saturated calomel electrode (SCE), and graphite rod in turn. For fabricating $\text{PdNi}/\text{N-TBA-V}_2\text{CT}_x$ electrocatalyst ink, a certain amount of $\text{PdNi}/\text{N-TBA-V}_2\text{CT}_x$ solution freeze-dried into $\text{PdNi}/\text{N-TBA-V}_2\text{CT}_x$ powder. Afterward, 3 mg powder was dispersed into a solution containing 400 μl H_2O , 560 μl ethanol, and 40 μl Nafion solution and then subjected to vigorous ultrasonication for 30 min to form a uniform ink. For other catalysts. As for the Pd/C (20 wt%) catalyst, 3 mg 30 wt% commercial Pd/C was weighed. Subsequently, 5 μl of the electrocatalyst ink was drop-cast on the GCE and dried naturally in the air. Before HER measurements, the electrolyte was bubbled with N_2 for at least 30 min to remove residual O_2 . Linear sweep voltammetry (LSV) curves were tested at a scan rate of 5 mV s^{-1} in the 0.5 M H_2SO_4 electrolyte, and obtained with 50% iR compensations through instrument automatic settings. All recorded potentials (overpotentials) were converted to the reversible hydrogen electrode (RHE). The long-term durability of all electrocatalysts was examined by potentiostatic electrolysis at an overpotential with a current density of 10 mA cm^{-2} . Electrochemical impedance spectra (EIS) measurements were carried out at 0 V vs. RHE from 10^5 Hz to 0.1 Hz at an amplitude of 5 mV.

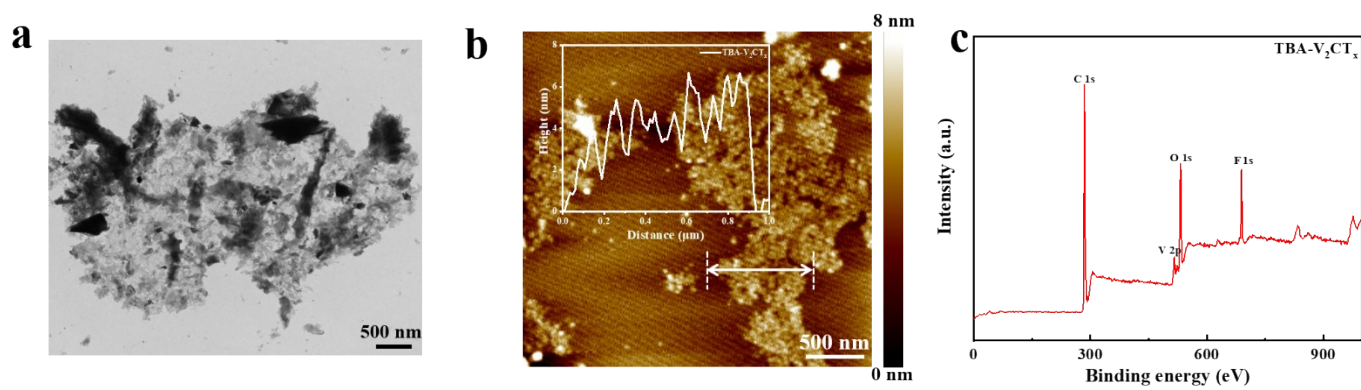


Fig. S1 (a) TEM image of TBA-V₂CT_x. (b) AFM image of TBA-V₂CT_x and its corresponding height profile. (c) XPS survey spectrum of TBA-V₂CT_x.

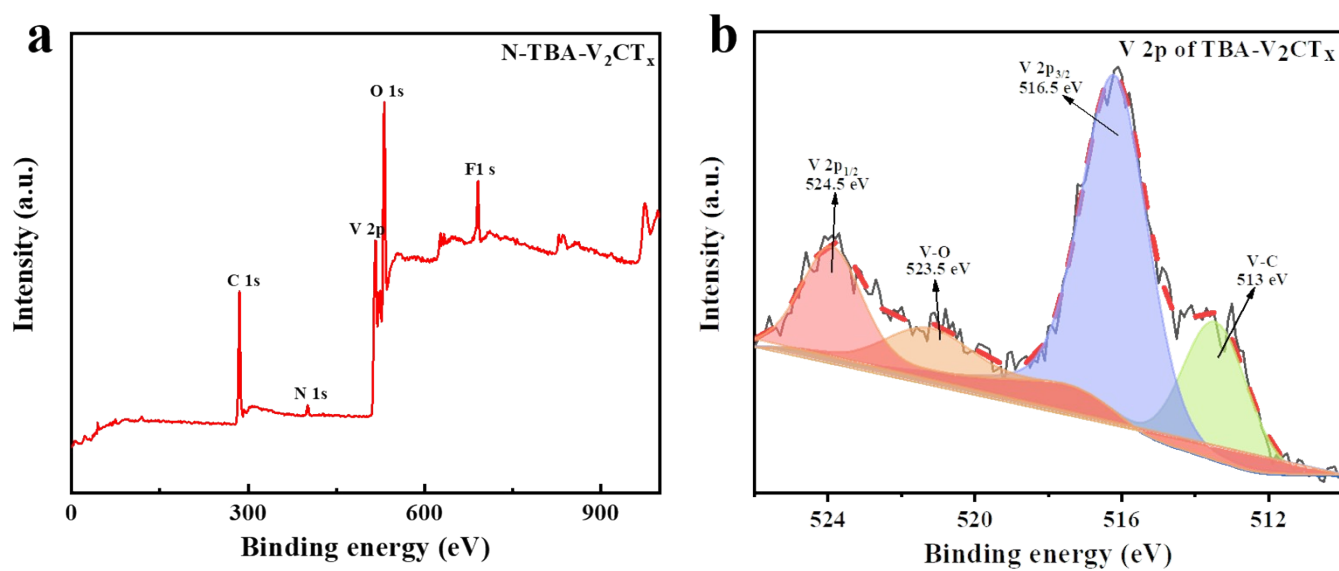


Fig. S2 (a) XPS survey spectrum of N-TBA-V₂CT_x. (b) High-resolution XPS spectrum of TBA-V₂CT_x.

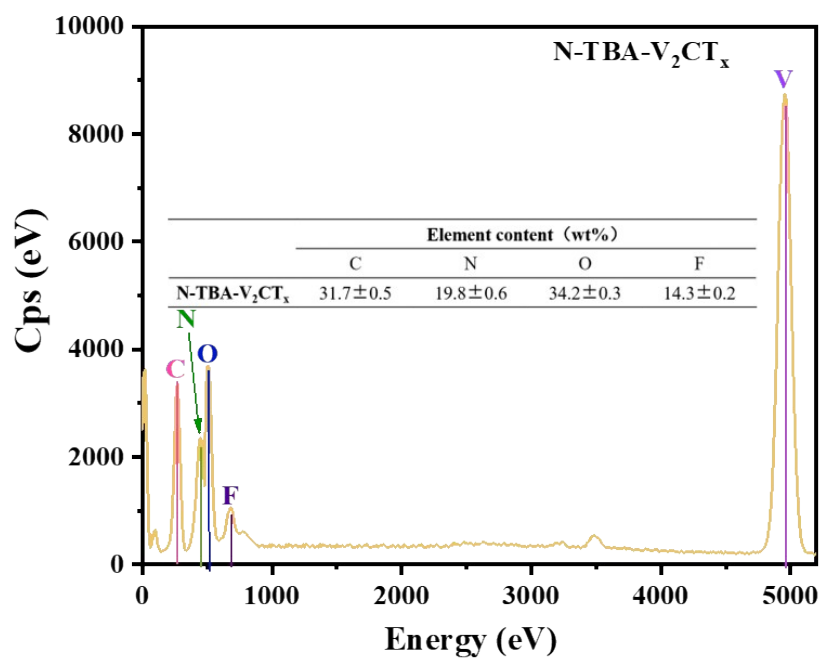


Fig. S3 The element content of N-TBA-V₂CT_x.

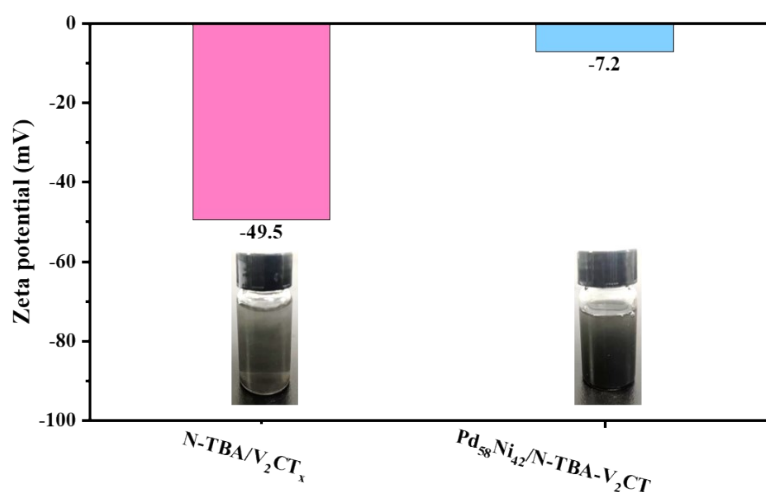


Fig. S4 Zeta potentials of N-TBA-V₂CT_x and Pd₅₈Ni₄₂/N-TBA-V₂CT_x aqueous solution.

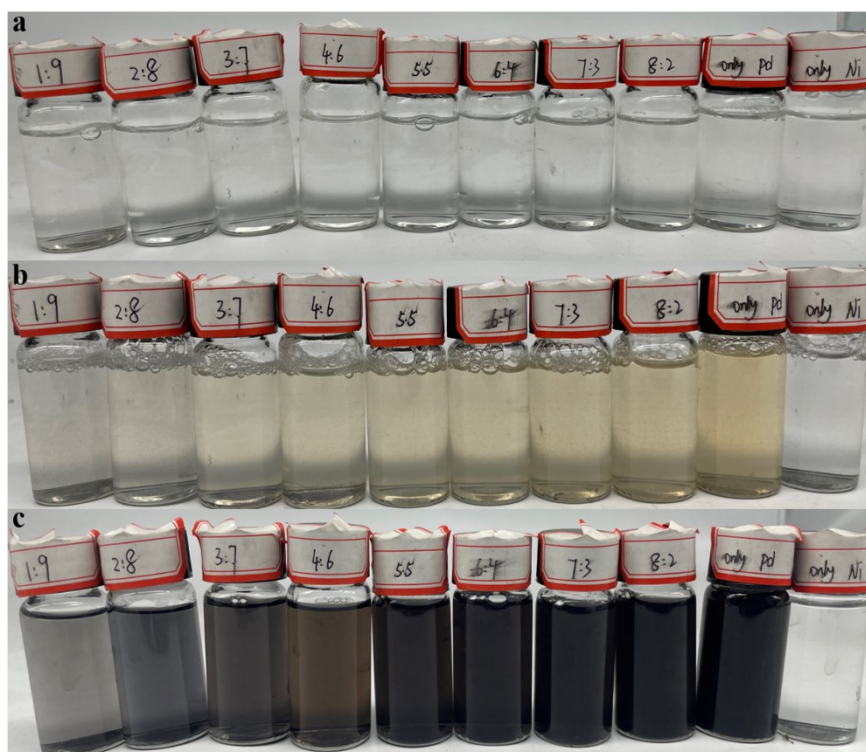


Fig. S5 Photographs of BTAC solutions containing different ratios of precursors and fixed ratios of N-TBA-V₂CT_x, with the metal precursor Pd: Ni added in ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, and 8:2 from left to right, Pd precursor only, and Ni precursor only. (a) Pure BTAC solution without metal precursors and N-TBA-V₂CT_x. (b) BTAC solution after further addition of two metal precursors and N-TBA-V₂CT_x. (c) The reaction was at 35 °C for 8 h after adding the reducing agent AA.

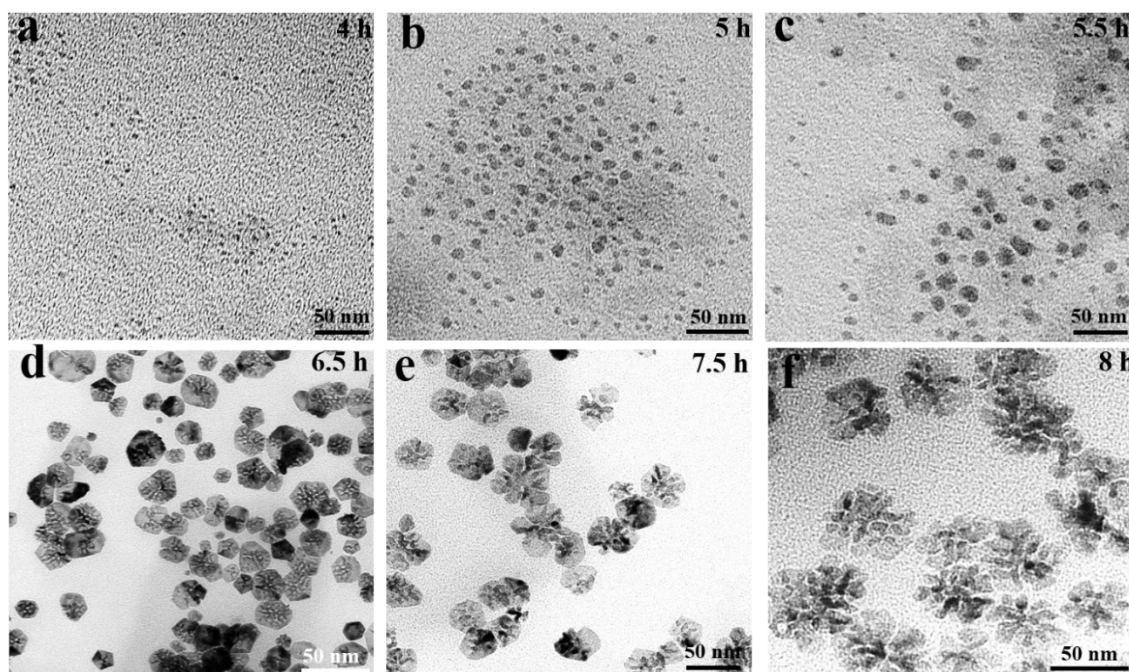


Fig. S6 TEM images of Pd₅₈Ni₄₂/N-TBA-V₂CT_x at different reaction times.

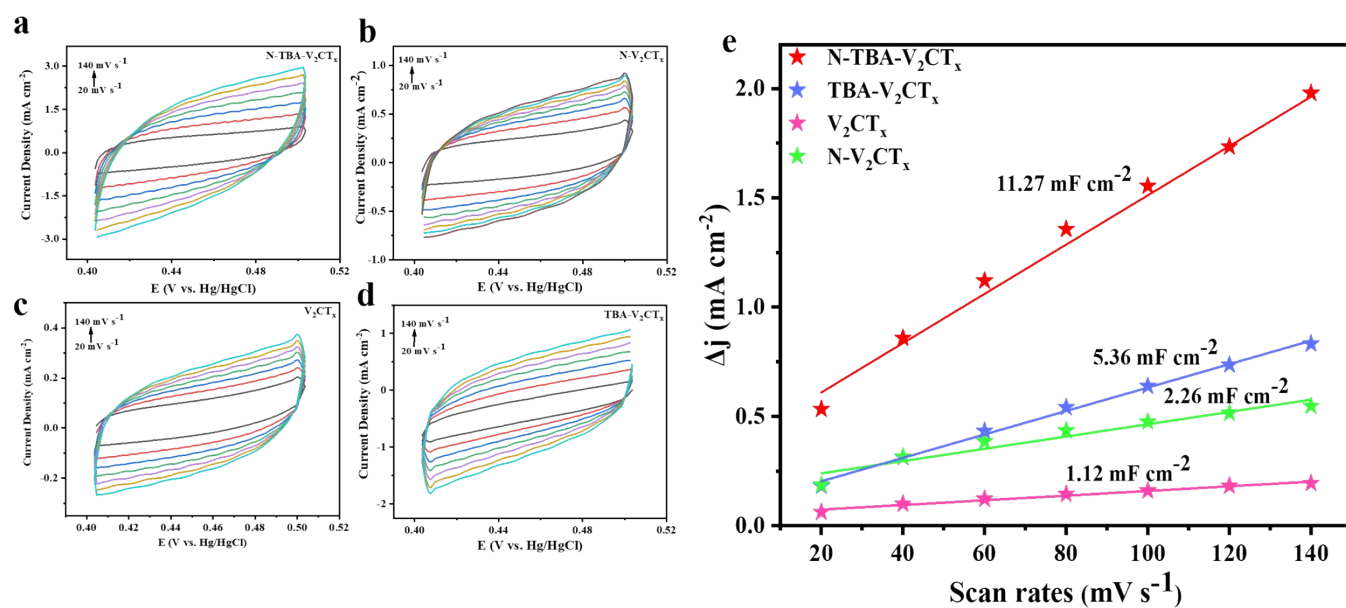


Fig. S7 (a-d) The cyclic voltammograms (CV) for V₂CT_x, TBA-V₂CT_x, N-V₂CT_x and N-TBA-V₂CT_x with scan rate from 20 to 140 mV·s⁻¹. (e) Capacitive current versus scan rate for V₂CT_x, TBA-V₂CT_x, N-V₂CT_x and N-TBA-V₂CT_x electrocatalysts.

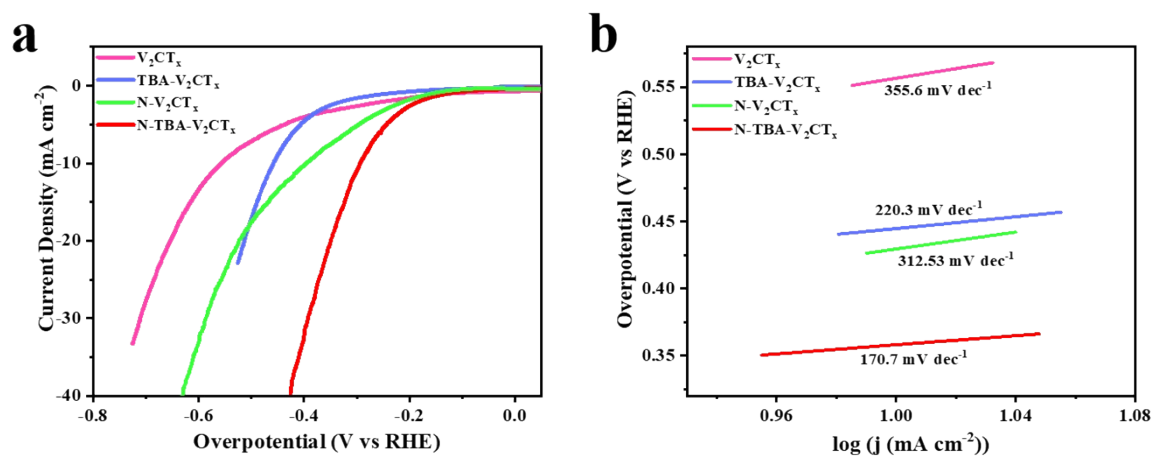


Fig. S8 (a) LSV curves for V₂CT_x, TBA-V₂CT_x, N-V₂CT_x and N-TBA-V₂CT_x in 0.5 M H₂SO₄ at a scan rate of 5 mV s⁻¹. (b) Tafel slope of V₂CT_x, TBA-V₂CT_x, N-V₂CT_x and N-TBA-V₂CT_x.

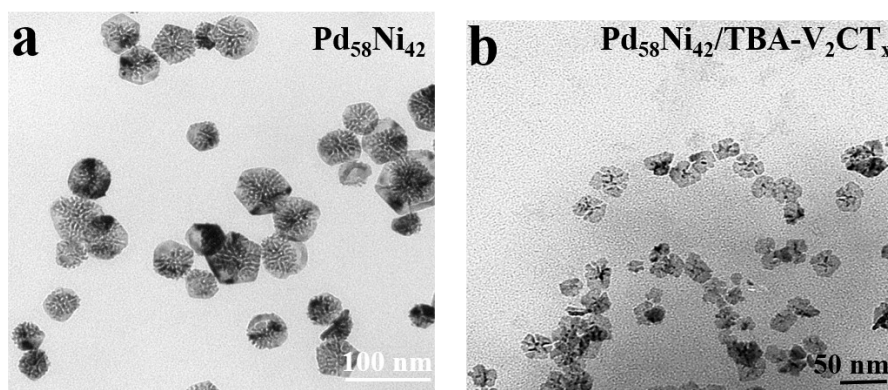


Fig. S9 (a) TEM image of Pd₅₈Ni₄₂. (b) TEM image of Pd₅₈Ni₄₂/TBA-V₂CT_x.

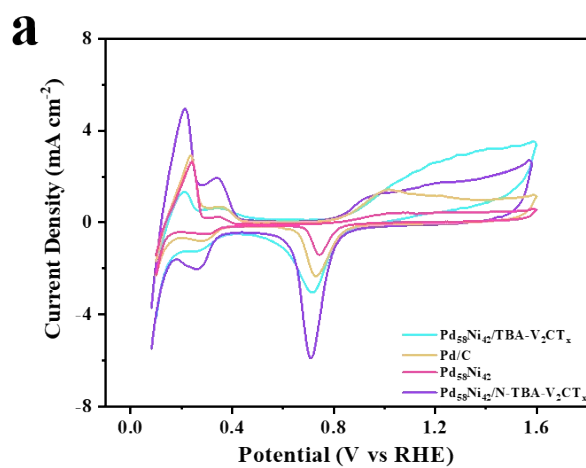


Fig. S10 (a) CV curves of Pd₅₈Ni₄₂/N-TBA-V₂CT_x, Pd₅₈Ni₄₂/TBA-V₂CT_x, Pd/C and Pd₅₈Ni₄₂ in N₂-saturated 0.5 M H₂SO₄ solution.

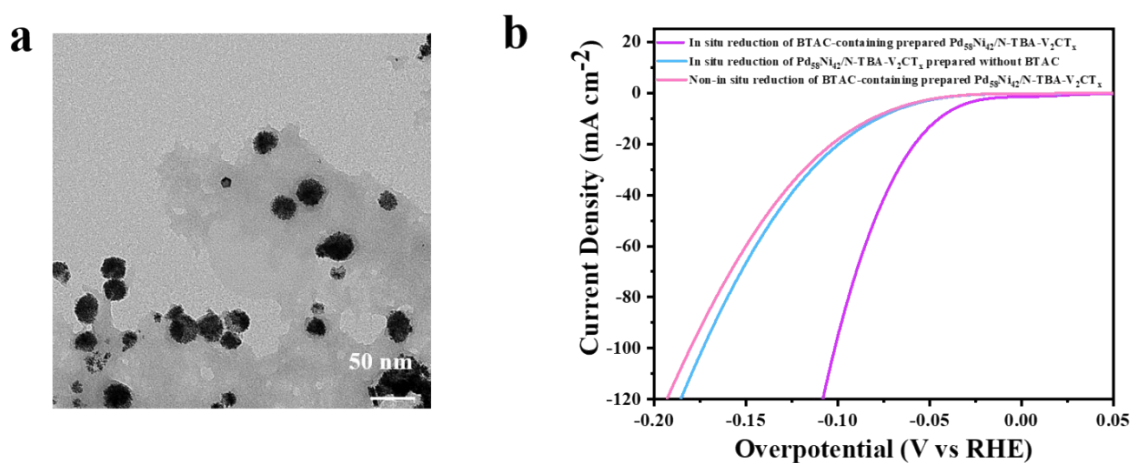


Fig. S11 (a) TEM image of Pd₅₈Ni₄₂/N-TBA-V₂CT_x prepared without surfactant BTAC. (b) LSV curves of spherical Pd₅₈Ni₄₂/N-TBA-V₂CT_x, mixing Pd_aNi_b/N-TBA-V₂CT_x, and Pd₅₈Ni₄₂/N-TBA-V₂CT_x prepared by in-situ engineering.

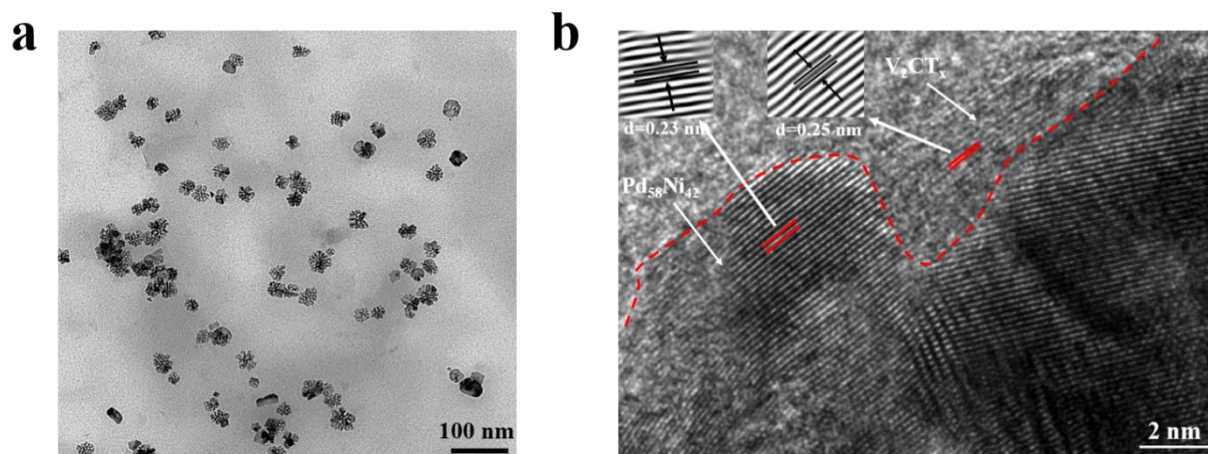


Fig. S12 (a) TEM image of Pd₅₈Ni₄₂/N-TBA-V₂CT_x after 50 h of continuous operation. (b) HRTEM image of Pd₅₈Ni₄₂/N-TBA-V₂CT_x after 50 h of continuous operation.

Table S1. Summary of ICP results and corresponding atomic ratios of different electrocatalysts

Electrocatalysts	Pd at%	Ni at%
Pd ₁₉ Ni ₈₁ /N-TBA-V ₂ CT _x	19	81
Pd ₂₈ Ni ₇₂ /N-TBA-V ₂ CT _x	28	72
Pd ₃₃ Ni ₆₇ /N-TBA-V ₂ CT _x	33	67
Pd ₅₂ Ni ₄₈ /N-TBA-V ₂ CT _x	52	48
Pd ₅₈ Ni ₄₂ /N-TBA-V ₂ CT _x	58	42
Pd ₆₄ Ni ₃₆ /N-TBA-V ₂ CT _x	64	36
Pd ₇₅ Ni ₂₅ /N-TBA-V ₂ CT _x	75	25
Pd ₉₃ Ni ₇ /N-TBA-V ₂ CT _x	93	17
Pd/N-TBA-V ₂ CT _x	100	0

Table S2. Summary of Pd mass loadings of all investigated catalysts

Electrocatalysts	Pd mass loading ($\mu\text{g}_{\text{Pd}} \text{cm}^{-2}$)
$\text{Pd}_{19}\text{Ni}/\text{N-TBA-V}_2\text{CT}_x$	13.56
$\text{Pd}_{28}\text{Ni}_{72}/\text{N-TBA-V}_2\text{CT}_x$	19.97
$\text{Pd}_{33}\text{Ni}_{67}/\text{N-TBA-V}_2\text{CT}_x$	23.67
$\text{Pd}_{52}\text{Ni}_{48}/\text{N-TBA-V}_2\text{CT}_x$	37.18
$\text{Pd}_{58}\text{Ni}_{42}/\text{N-TBA-V}_2\text{CT}_x$	41.47
$\text{Pd}_{64}\text{Ni}_{36}/\text{N-TBA-V}_2\text{CT}_x$	45.76
$\text{Pd}_{75}\text{Ni}_{25}/\text{N-TBA-V}_2\text{CT}_x$	53.64
$\text{Pd}_{93}\text{Ni}_7/\text{N-TBA-V}_2\text{CT}_x$	66.40
$\text{Pd}/\text{N-TBA-V}_2\text{CT}_x$	71.43
Pd/C	43.86

Table S3. Summary of the overpotential and Tafel plots of $\text{Pd}_{58}\text{Ni}_{42}/\text{N-TBA-V}_2\text{CT}_x$ and the recently reported metal/MXene electrocatalysts.

Electrocatalyst	Overpotential $_{\eta_{10}}$ (mV vs. RHE)	Tafel plots (mV dec^{-1})	Ref.
$\text{Pd}_{58}\text{Ni}_{42}/\text{N-TBA-V}_2\text{CT}_x$	44.1	39.4	This work
$\text{Pd}/\text{Ti}_3\text{C}_2\text{T}_x\text{-CNT}$	158	50	1
$\text{Pt}/\text{Ti}_3\text{C}_2\text{T}_x$	226	59	2
Ni-GF/VC	111	20	3
MXene/Pt-3	302	79	4
TBA- $\text{Ti}_3\text{C}_2\text{T}_x$ -Pt-20	70	65	5
40Pt-TBA- $\text{Ti}_3\text{C}_2\text{T}_x$	67.8	69.8	6
$\text{Pt}_{\text{NPs}}/\text{Ti}_3\text{C}_2\text{T}_x$	226	60	2
S-M-5Pt	62	78	7
$\text{Ru-Ti}_3\text{C}_2\text{T}_x$	96	59.8	8
$\text{Pd}@/\text{MoS}_2\text{-Mo}_2\text{TiC}_2\text{T}_x$	92	60	9

Notes and References:

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