

Electronic Supplementary Information

Oxidized indium with transformable dimension for CO₂
electroreduction toward formate aided by oxygen vacancies

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Experimental section

Synthesis of InOOH Nanosheets

In a typical procedure, 270 mg $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ and 2 g urea were dissolved in 60 ml ethanol under stirring for 30 min. 65 mg conductive carbon black (Vulcan XC72R) was dispersed in the obtained solution by stirring and ultrasonic operation for 15 min and 30 min respectively. The suspension mixture was then transferred into a sealed 100 ml Teflon-lined autoclave and statically heated at 90 °C for 12 h. The autoclave was rapidly cooled to room temperature and the sample was collected by filtration, washed with distilled water and ethanol until $\text{pH} = 7$ and then dried overnight under vacuum. The samples for CO_2 adsorption tests were prepared without Vulcan XC72R.

Synthesis of V_o -rich Nanosheets and Nanoparticles of Oxidized Indium

The V_o -rich nanosheets and nanoparticles of oxidized indium were synthesized by heating the obtained InOOH nanosheets directly at 320 °C in a muffle furnace for 2 min and 15 min, respectively. The calcined samples were removed immediately, and naturally cooled to room temperature.

Electrochemical Tests

The working electrode used in this study was fabricated by covering a catalyst layer onto a gas diffusion electrode which was self-made by brushing carbon black ink (Vulcan XC72R mixed with 15% PTFE) onto a piece of Toray carbon paper. The as-obtained catalysts together with Nafion ionomer solution was suspended in a

water/ethanol mixture after ultrasonic operation and then painted onto the gas diffusion electrode at 70 °C. The loadings of the carbon black ink and the catalyst layer were about 1 mg cm⁻² and 2 mg cm⁻² respectively, and the content of Nafion in the catalyst layer was 10 wt%. The working electrode would be cut into a rectangular piece in size of 1 cm × 2 cm before being assembled to the electrolysis cell.

Electrochemical tests were carried out in a gastight H-shaped two-compartment electrolytic cell separated by cation-exchange membrane (Nafion 115) at room temperature. Each compartment contained 30 ml 0.1 M KHCO₃ solution as electrolyte which was bubbled with pure CO₂ for at least 30 min to achieve CO₂ saturation (pH 6.8) prior to the electrochemical tests. The electrolysis was proceeding with uninterrupted mixed gas flow (CO₂/N₂=95%/5%) at 20 ml min⁻¹ under stirring at 800 rpm. All electrochemical measurements were controlled by an electrochemical workstation (CHI760E) using a platinum wire as the counter electrode and a Ag/AgCl reference electrode. All potentials in this work were converted to the RHE reference scale by the formula $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.197 \text{ V} + 0.0591 \times \text{pH}$.

LSV tests were conducted in a three-electrode cell from 0 V vs. RHE to -1.1 V vs. RHE with a scan rate of 30 mV s⁻¹ in CO₂ or N₂ atmosphere. The electroreduction of CO₂ was performed by Fixed Potential Amperometry method. The electrolysis at applied potential was conducted for an hour. The uncompensated solution resistance R_u was compensated for 85% during electrolysis, and the R_u was determined by both EIS tests and the direct internal resistance compensation module of the electrochemical

workstation. The current densities were determined relative to the geometric projected electrode area.

The gas products from cathodic compartment were monitored by an online gas chromatography (GC) equipped with a TCD detector using 5% N₂ as an internal standard. The electrolyte after test was collected and analyzed with hydrogen nuclear magnetic resonance (¹H-NMR, Bruker 400 MHz) to determine the liquid products.

Catalysts Characterization

Environmental transmission electron microscope (ETEM) technique was performed on HITACHI H-9500 at an accelerating voltage of 300 kV. Samples are monitored in situ under vacuum at 320 °C as a function of time. Scanning electron microscopy (SEM) was carried out on a HITACHI S-4700 microscope. SEM-EDX was conducted on ZEISS SIGMA FE-SEMs 300. Transmission electron microscope (TEM) was performed on a field emission transmission electron microscope (FEI Tecnai G2 20S Twin microscopy) at an accelerating voltage of 300 kV. The sample was suspended in ethanol and dispersed on a copper grid coated with lacey carbon film. X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advanced X-ray diffractometer using Cu K α radiation at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Fisher Scientific ESCALAB 250 equipped with a monochromatic Al k α radiation. High-resolution and survey scans were executed at pass energies of 30 and 200 eV respectively. ESR studies were performed on a JES-FA200 ESR Spectrometer. Thermogravimetric analysis and

differential thermal gravimetric (TG/DTG) analysis were carried out on a NETZSCH STA 449 C analyzer at a ramp of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $600\text{ }^{\circ}\text{C}$. CO_2 adsorption measurements were performed on a modified Micromeritics ASAP 2460 Version 2.01 surface area and porosity analyzer. The samples were degassed at 393 K under vacuum of $1.33\times 10^{-3}\text{ Pa}$ for 10 h and then switched to the analysis station for adsorption analysis at 298 K . The adsorption process was conducted from 0 to 100 kPa .

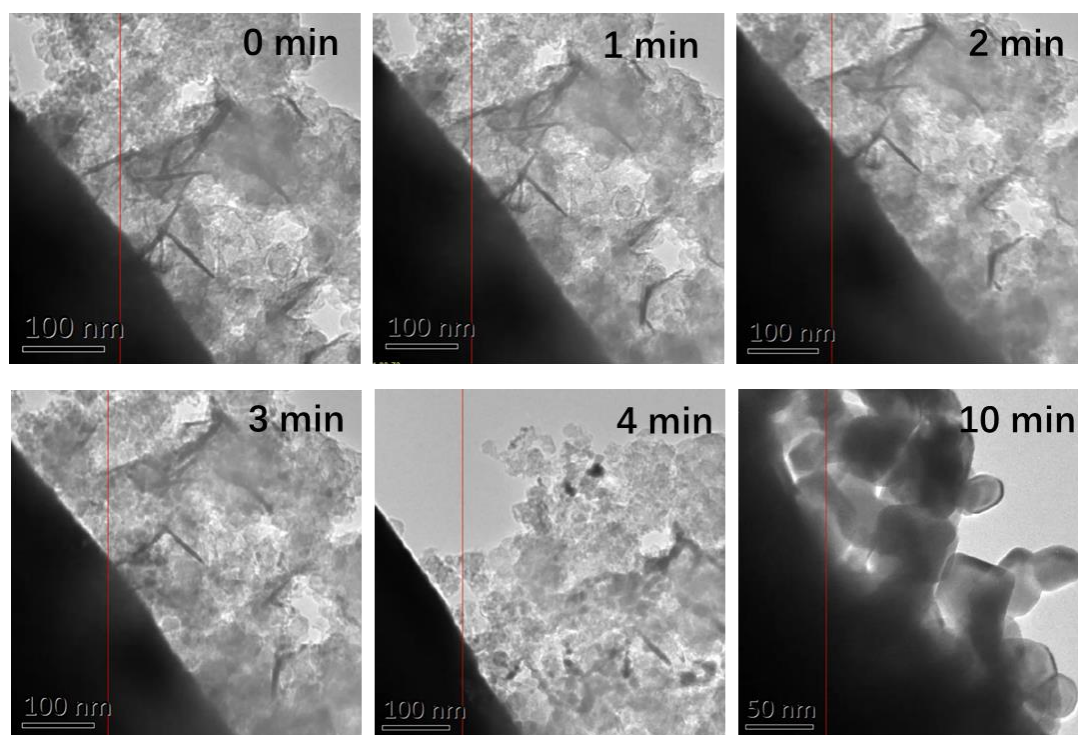


Figure S1. *In situ* ETEM images of InOOH nanosheets heated in 320 °C under vacuum as a function of time.

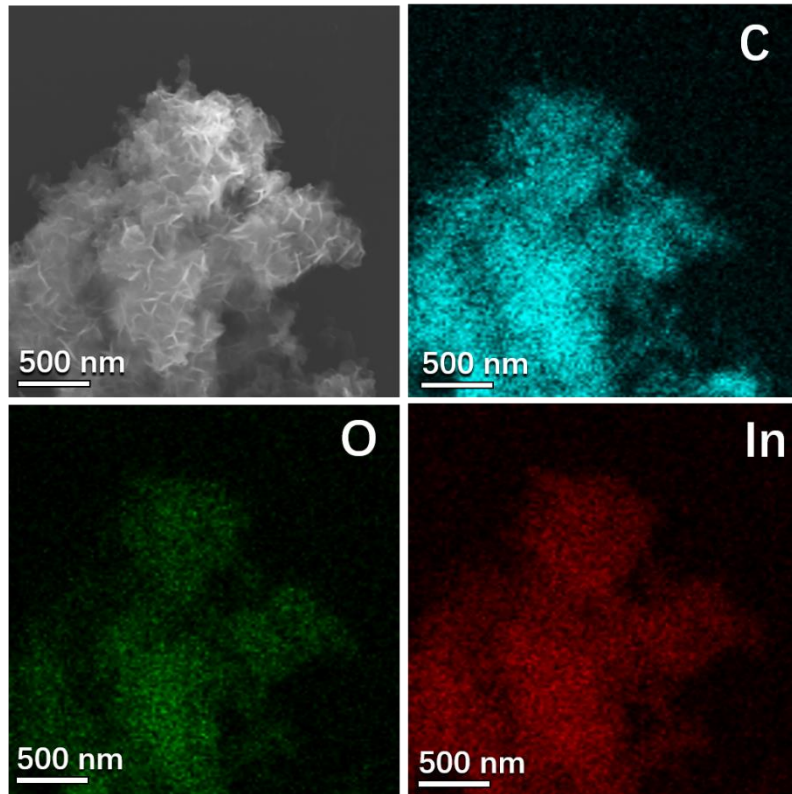


Figure S2. SEM-EDX elemental mappings showing the composition of nanosheets.

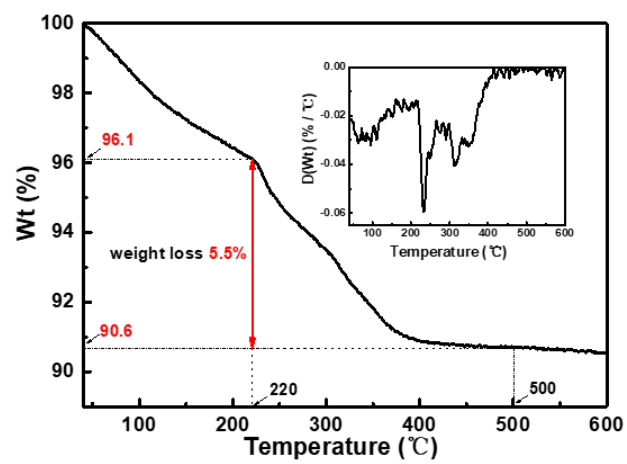


Figure S3. TG/DTG analysis over nanosheets.

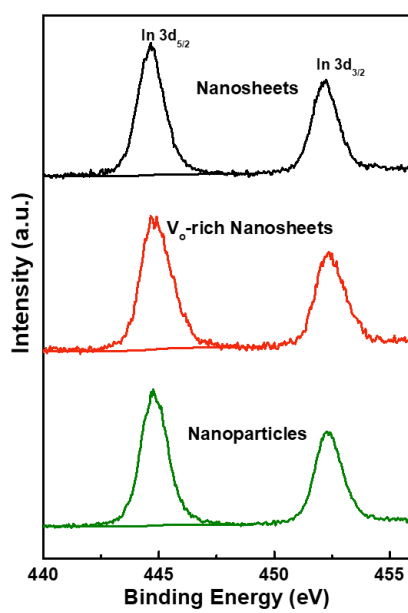


Figure S4. In 3d XPS spectra of the catalysts. The two peaks located at around 444.3 eV and 452.0 eV could be attributed to the characteristic spin-orbit split of In $3d_{5/2}$ and In $3d_{3/2}$, corresponding to oxidized states.

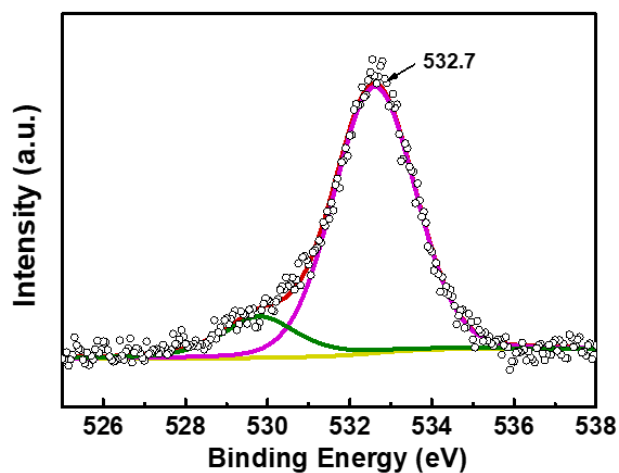


Figure S5. O 1s XPS spectra of the sample of In(OH)₃. In(OH)₃ was prepared by an aqueous ammonia precipitation method: 270 mg In(NO₃)₃·4H₂O was dissolved in 60 ml deionized water under stirring for 30 minutes. 65 mg conductive carbon black (Vulcan XC72R) was dispersed in the obtained solution by ultrasonic operation for 60 min. During the ultrasonic operation, 8 ml aqueous ammonia (37 wt %) was added very slowly into the mixture. The mixture was then aged for 2 h followed by filtration and thorough washing. After dried under vacuum at 60 °C overnight, the sample of In(OH)₃ was obtained.

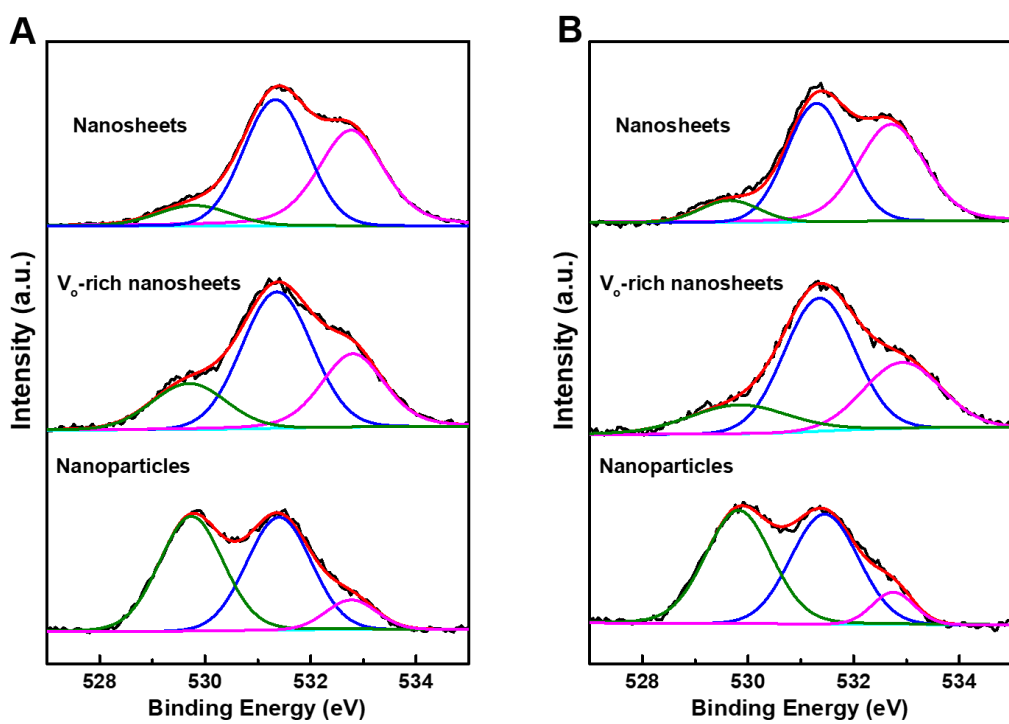


Figure S6. O 1s XPS spectra of another two batches of synthesized samples.

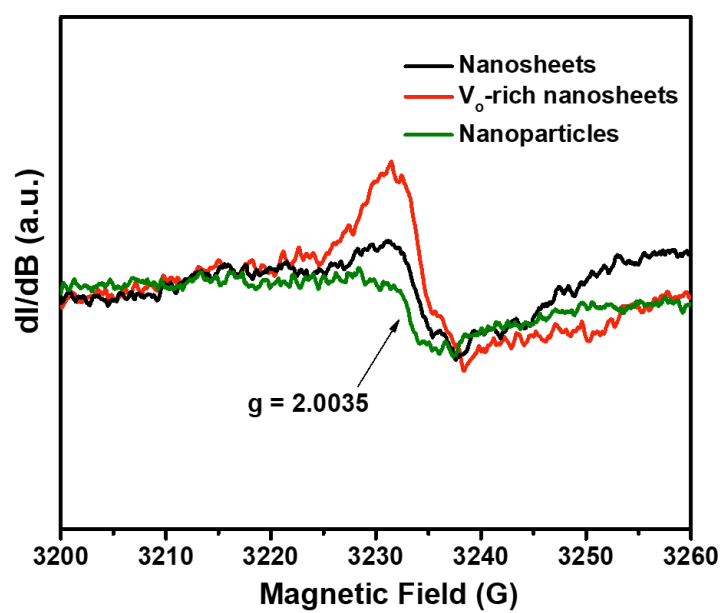


Figure S7. Electron spin resonance spectra of prepared catalysts.

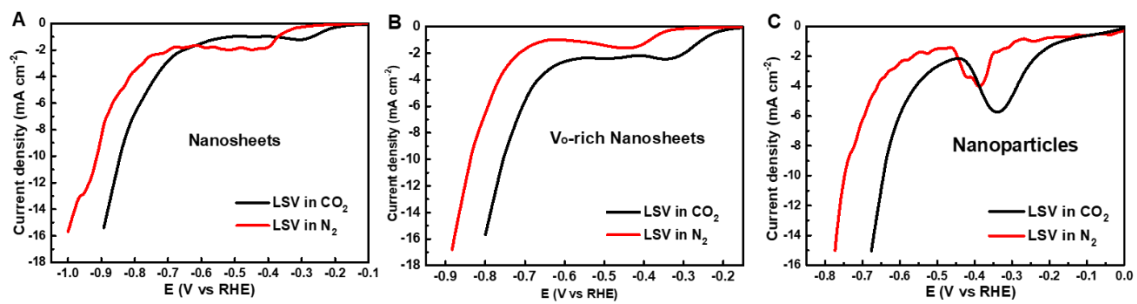


Figure S8. LSV tests in CO₂-saturated and N₂-saturated electrolyte of (A) nanosheets, (B) V_o-rich nanosheets and (C) nanoparticles.

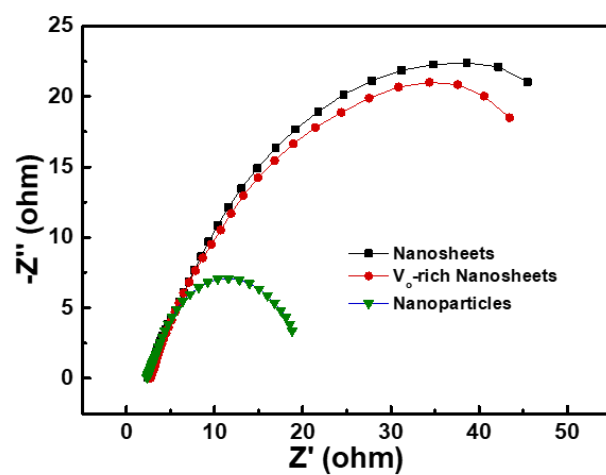


Figure S9. EIS measurements on nanosheets, V_o-rich nanosheets and nanoparticles. The EIS plot was obtained at the same CO₂RR potential (-0.65 V vs RHE) with small AC amplitude of 10 mV in the frequency range of 1 to 10⁵ Hz.

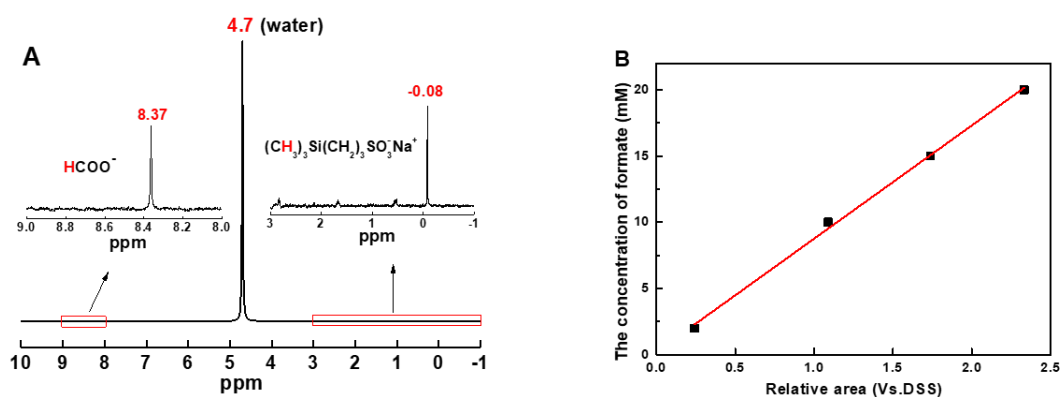


Figure S10. (A) $^1\text{H-NMR}$ spectra for formate determination; (B) Linear relationship between the formate concentration and relative area vs. DSS.

Each liquid sample for $^1\text{H-NMR}$ test contained 0.1 ml D_2O , 0.1 ml 6 mM DSS (1-Propanesulfonic acid 3-(trimethylsilyl) sodium salt) solution and 0.5 ml electrolyte after electrolysis. The area ratio of the formate peak to the DSS peak was compared to the standard curve to quantify the concentration of formate. The standard curve was obtained by testing sodium formate ($\text{HCOONa}\cdot 2\text{H}_2\text{O}$) solution in different concentration (from 2 mM to 20 mM).

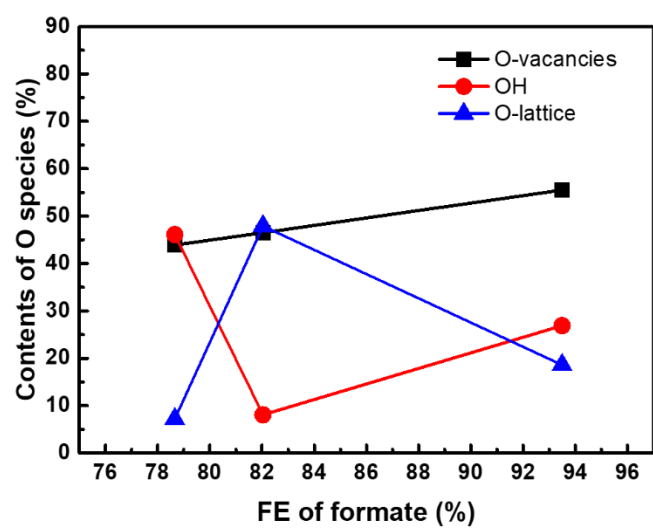


Figure S11. The relationship between contents of three O species and FE of formate.

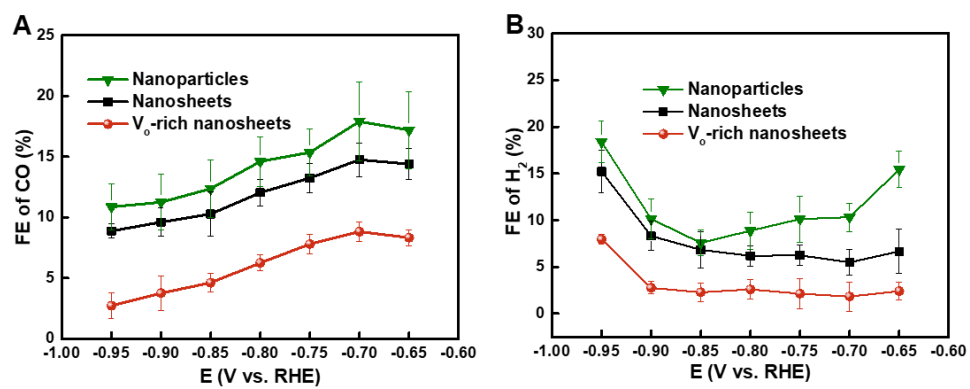


Figure S12. FE of CO and H₂ for nanosheets, V_o-rich nanosheets and nanoparticles.

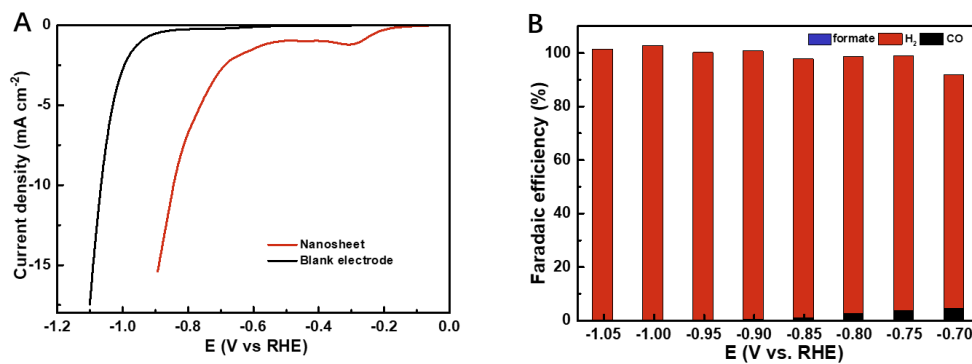


Figure S13. (A) LSV curve and (B) Faradaic efficiency of blank electrode. A blank electrode was fabricated by brushing carbon black instead of prepared catalysts onto gas diffusion electrode in same proportion and condition.

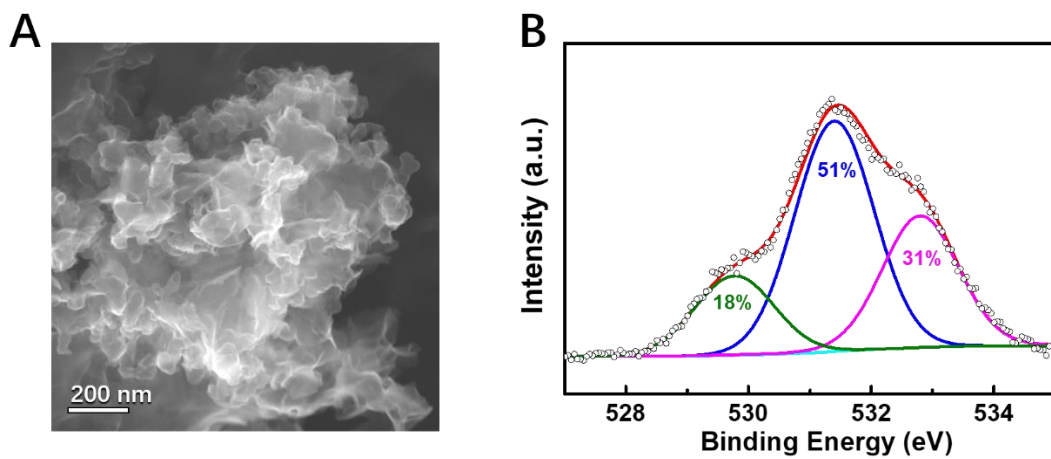


Figure S14. Characterization of V_o-rich nanosheets after stability test. (A) SEM image; (B) O 1s spectrum.

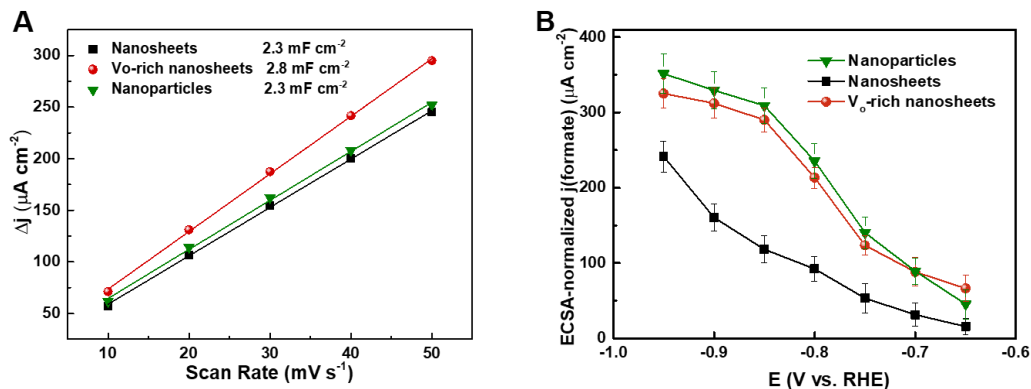


Figure S15. (A) Charging current density differences plotted against scan rates. (B) The ECSA normalized $j(\text{formate})$.

ECSA was calculated by the formula of $\text{ECSA} = R_f S$, where R_f denoted the roughness factor of the working electrode and S represented the geometric surface area of the carbon paper electrode (2 cm^2 in this work). The double-layer capacitance of ideal smooth oxide surface is $60 \mu\text{F cm}^{-2}$ [S1], leading to the relation of $R_f = C_{dl}/60$. C_{dl} was obtained by plotting the $\Delta j = j_a - j_c$ at 0.05 V vs RHE against the scan rates, in which j_a and j_c represented the anodic and cathodic current density, respectively. The C_{dl} value equaled to the half of the linear slope.

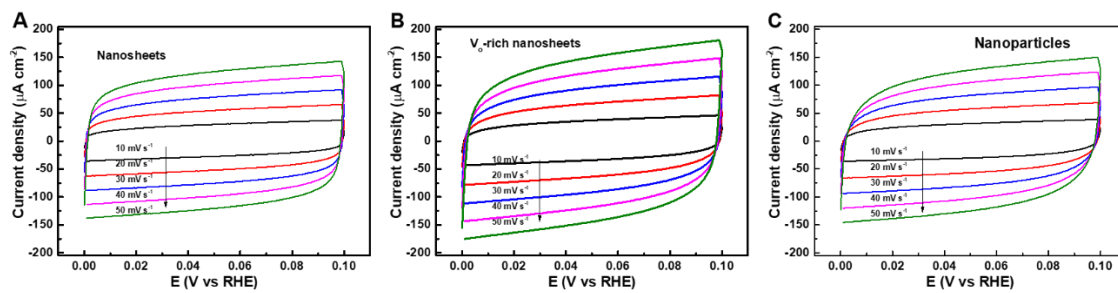


Figure S16. Cyclic voltammograms (CV) curves. CV measurements were conducted from 0 to 0.1

V vs RHE (0.1 M KHCO_3) at various scan rates of 10, 20, 30, 40, and 50 mV s^{-1} .

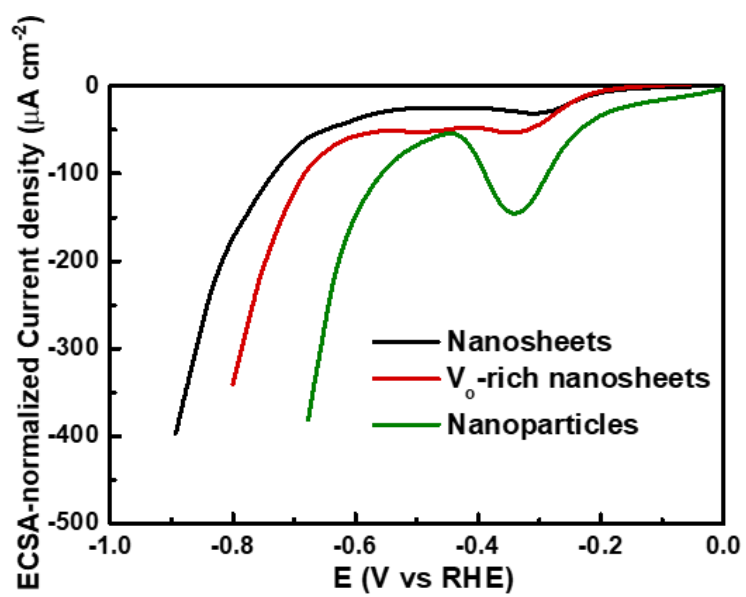


Figure S17. ECSA-normalized electrolysis current densities.

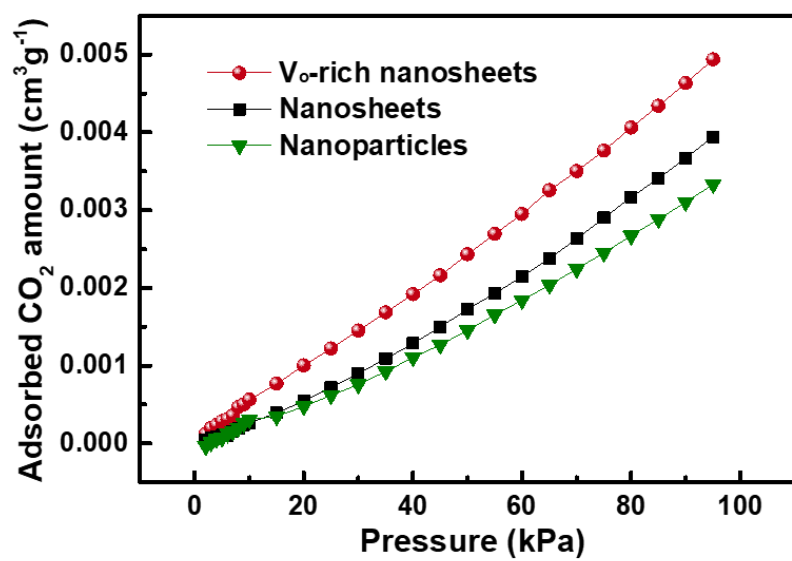


Figure S18. CO₂ adsorption isotherms of the prepared samples.

Table S1: Contents of various O species in nanosheets, V_o-rich nanosheets and nanoparticles over three independent batches of synthesized samples.

	Batches	O-lattice	O-vacancies	OH
Nanosheets	1	5.7%	46.5%	47.8%
	2	8.0%	47.0%	45.0%
	3	8.0%	46.0%	46.0%
	Average	7.2%	46.6%	46.1%
V _o -rich nanosheets	1	19.9%	56.5%	23.7%
	2	17.0%	54.0%	29.0%
	3	19.0%	54.0%	28.0%
	Average	18.6%	54.6%	26.9%
Nanoparticles	1	49.8%	42.9%	7.2%
	2	47.0%	44.0%	9.0%
	3	47.0%	45.0%	8.0%
	Average	47.9%	43.9%	8.1%

Table S2. Recent works based on metal oxide for CO₂ electronic reduction to formate.

Catalysts	Electrolyte	Applied potentials (V vs SCE)	FE (%)	j (formate) (mA cm ⁻²)	Ref.
SnO ₂ /graphene	0.1 M NaHCO ₃	-1.8	93.6	10.2	[16]
Oxidized Co 4-atom-thick layers	0.2 M Na ₂ SO ₄	-0.85	90.1	10.5	[15]
SnO ₂ nanosheets	0.5 M NaHCO ₃	-1.6	89	45	[12]
Vacancy-rich Co ₃ O ₄ layers	0.1M KHCO ₃	-0.87	87.6	2.7	[14]
SnO ₂ porous nanowire	0.1M KHCO ₃	-0.8 (V vs RHE)	80.1	4.8	[13]
V _o -rich InOOH nanosheets	0.1M KHCO ₃	-0.9 (V vs RHE)	93.5	> 14	This work

Reference:

[S1] B. S. Levine.; A. L. Smith. *Discuss. Faraday Soc.* **1971**, 52, 290-301