

Supplementary Information for:

Metallic Ni₃N nanosheets with exposed active surface sites for efficient hydrogen evolution

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Experiment and calculation details

Active Sites Calculation: The number of active sites (n) is examined using CVs with pH=7 phosphate buffer at a scan rate of 50 mV s⁻¹. When the number of voltammetric charges (Q) is obtained after deduction of the blank value, n (mol) can be calculated with the equation of $n=Q/2F$, where F is Faraday constant (96485 C mol⁻¹). TOF (S⁻¹) is calculated with the equation of $\text{TOF}=I/(2Fn)$ where I (A) is the current of the polarization curve obtained from the LSV measurements.^{1,2}

Capacitance measurements and relative comparison of active surface area

To estimate the differences in electrochemically active surface areas of various catalysts, the cyclic voltammetry (CV) method was employed to measure the electrochemical double-layer capacitance (EDLC), C_{dl} .³ The C_{dl} is respected to be linearly proportional to effective active surface area relatively. And this is an appropriate strategy because the number of active sites often scales with the catalyst surface area. Cyclic voltammetry curves were obtained at various scan rates (20, 40, 60, etc. mV/s) at -0.2~0 V vs the RHE region. The halves of the positive and negative current density differences $\Delta j/2$ ($\Delta j=j_a-j_c$) at the center of the scanning potential ranges are plotted vs the voltage scan rate.

Computational details: Density functional theory (DFT) calculations in our case were performed using the Vienna *ab initio* simulation package (VASP) and the Perdew–Burke–Ernzerhof exchange correlation functional correction.^{4,5} A 520-eV kinetic energy cutoff was chosen for plane-wave basis set, and Monkhorst–Pack k -point sampling was used.⁶ Residual forces were within 0.02 eV/Å for geometry optimizations. The Gibbs free energy change (ΔG_{H^*}) is expressed as follows: $\Delta G_{\text{H}^*} = \Delta E_{\text{H}^*} + \Delta E_{\text{ZPE}} - T\Delta S$, where ΔE_{H^*} , ΔE_{ZPE} and ΔS are the adsorption energy of atomic hydrogen on the given surface, zero point energy correction and entropy change of H* adsorption, respectively. The zero point energy correction can be estimated by the equation $\Delta E_{\text{ZPE}} = E_{\text{ZPE}}(\text{H}^*) - 1/2 E_{\text{ZPE}}(\text{H}_2)$, where $E_{\text{ZPE}}(\text{H}^*)$ and $E_{\text{ZPE}}(\text{H}_2)$ are calculated by vibration frequency calculation. At 1 bar and 300 K, $T\Delta S$ is approximately -0.205 eV. The value of ΔE_{H^*} is calculated as $\Delta E_{\text{H}^*} = E_{\text{tot}} - E_{\text{sub}} - 1/2 E_{\text{H}_2}$, where E_{tot} and E_{sub} are the energies of H absorbed systems and the clean given surface, respectively, and E_{H_2} is the energy of molecular H₂ in the gas phase.⁷

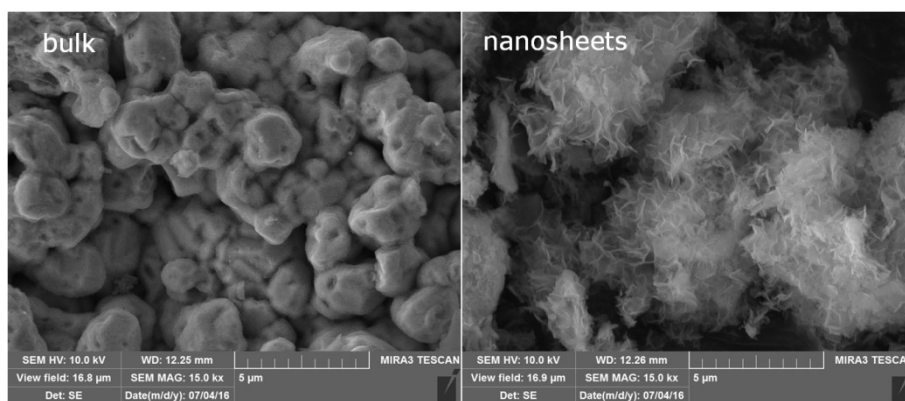


Figure S1. SEM images of Ni_3N bulk and nanosheets.

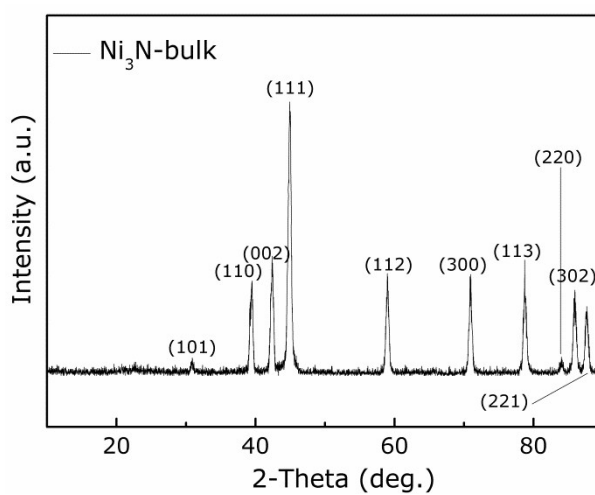


Figure S2. XRD result of Ni_3N bulk.

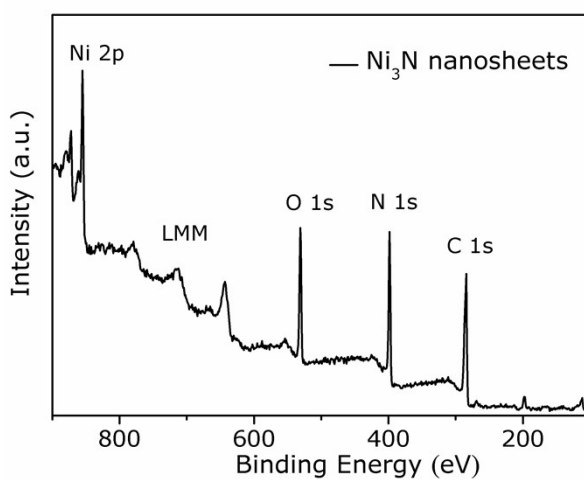


Figure S3. wide XPS spectra for Ni_3N nanosheets.

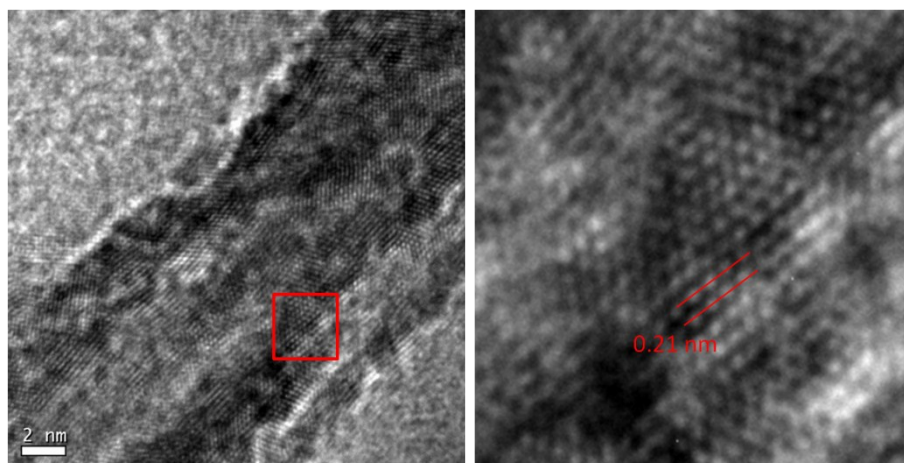


Figure S4. HRTEM image for Ni_3N nanosheets.

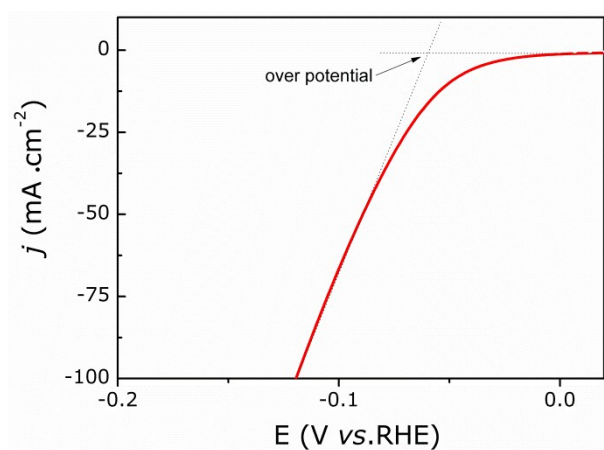


Figure S5. The defined onset potential for our sample.

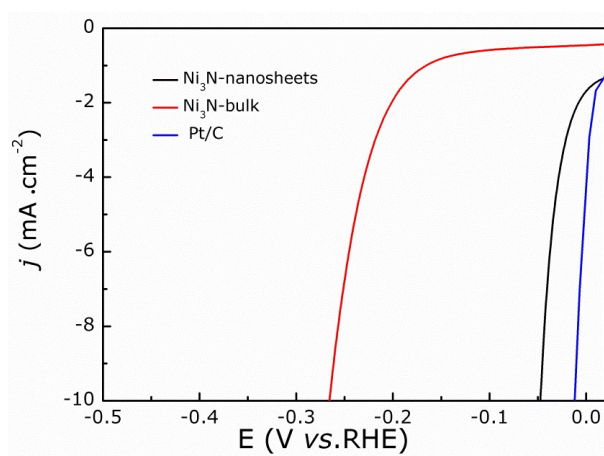


Figure S6. The polarization curves of Ni_3N bulk and nanosheets electrocatalyst in low j value.

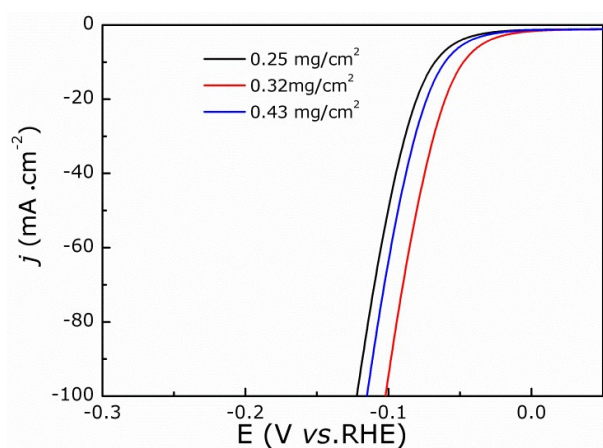


Figure S7. The polarization curves of Ni_3N nanosheets electrocatalyst with different loading amounts.

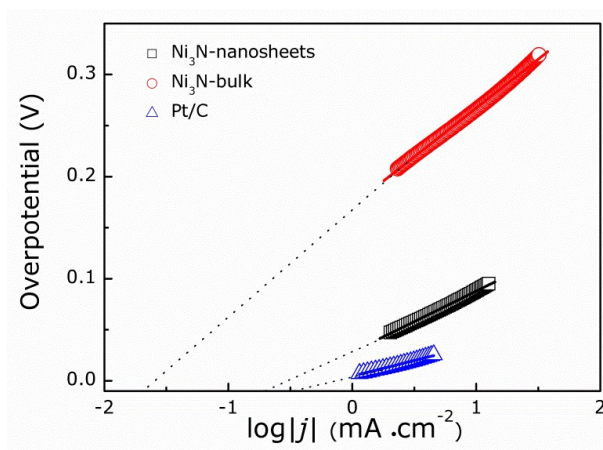


Figure S8. Calculated exchange current density for Ni_3N bulk, nanosheets and Pt/C.

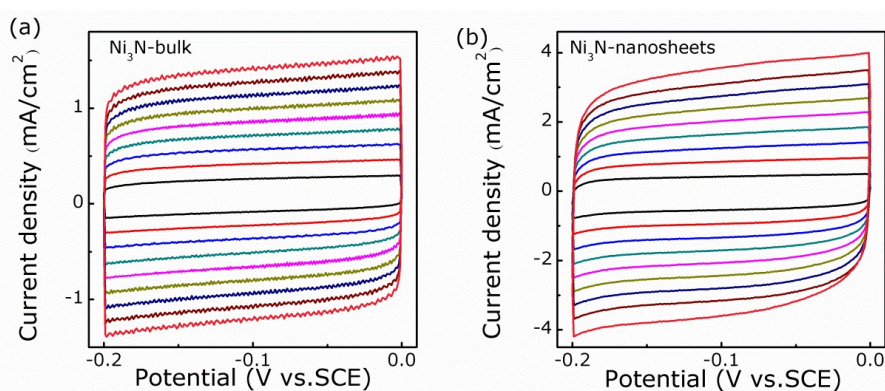


Figure S9. CV for Ni_3N (a) bulk and (b) nanosheets electrocatalysts at different scan rates from 5 to 100 mV s^{-1} , respectively.

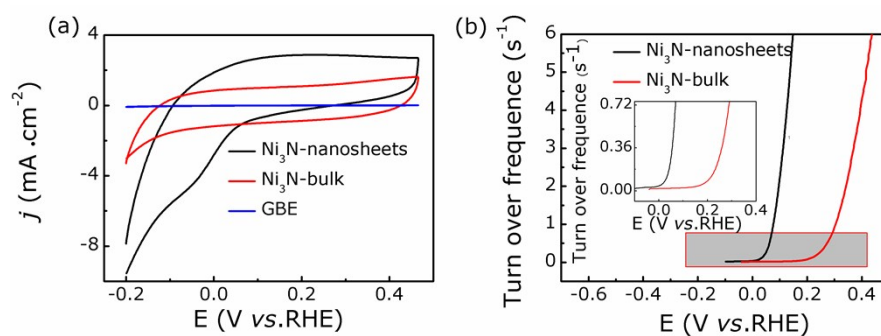


Figure S10. The CV curves in 1.0 M PBS and (b) the polarization curves of Ni_3N bulk and nanosheets normalized by the active sites and expressed in terms of TOF.

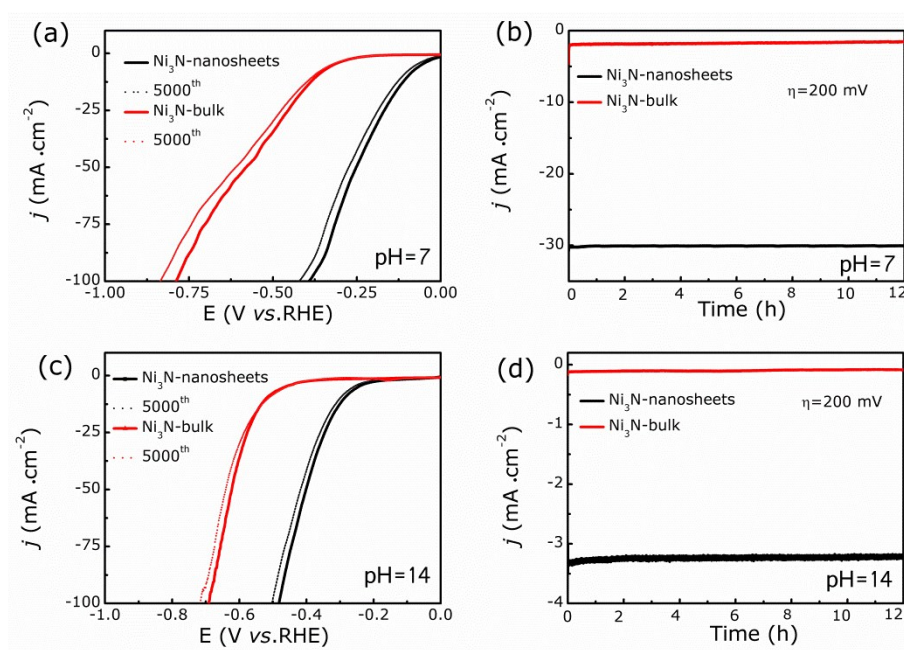


Figure S11. Polarization curves recorded for Ni_3N nanosheets and its bulk form before and after 5000 CV cycles in (a) 1.0 M PBS and (c) 1.0 M KOH. Potentiostatic measurements of Ni_3N samples at an overpotential of 200 mV in (b) 1.0 M PBS and (d) 1.0 M KOH.

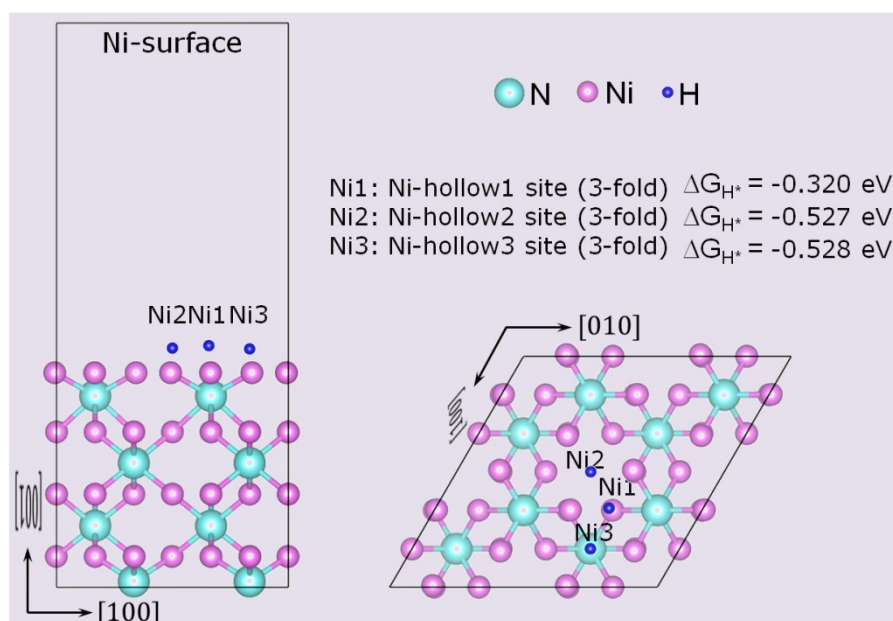


Figure S12. ΔG_{H^*} of the different active site with Ni surface exposing for Ni_3N based on the DFT calculations.

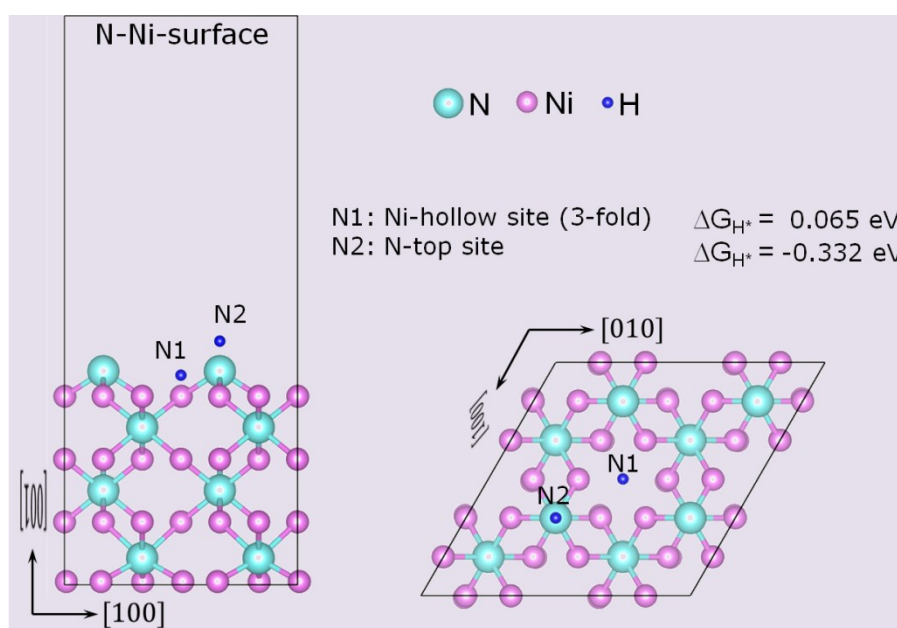


Figure S13. ΔG_{H^*} of the different active site with N-Ni surface exposing for Ni_3N based on the DFT calculations.

Table S1. Comparison of HER performance of Ni₃N nanosheets with various non-precious HER electrocatalysts reported in the literature.

	Loading density (mg cm ⁻²)	$\eta@j = 10$ mA cm ⁻² (mV vs RHE)	J_0 (exchange current density) (mA cm ⁻²)	Ref.
Ni ₃ N nanosheets	0.32	50	0.32	This work
TiN@Ni ₃ N (pH=14)		25	0.0125	J. Mater. Chem. A, 2016, 4, 5713
NiMoN (pH=14)	~1.1	109	0.92	Adv. Energy Mater., 2016, 6
Ni ₃ N (pH=14)	~1	208	0.123	Adv. Energy Mater., 2016, 6
MoON (pH=14)	~1	146	0.217	Adv. Energy Mater., 2016, 6
β -Mo ₂ C (0.1 M HClO ₄)	0.28	205 (1 mA cm ⁻²)	0.01729	Angew. Chem. Int. Ed. 2014, 126, 6525.
Co _{0.6} Mo _{1.4} N ₂	0.24	200	0.00023	J. Am. Chem. Soc. 2013, 135, 19186
Mo ₂ C nanoparticles	0.102	198		J. Mater. Chem. A 2015, 3, 8361
Mo ₂ N/CNT-GR	0.65	186	0.039	ACS Nano 2014, 8, 5164
CoN _x /C	2	133	0.07	Nat. Commun. 2015, 6, 7992
Ni ₃ N (pH=14)	N.A.	96	N.A.	J. Mater. Chem. A 2015, 3, 8171.

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