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Supporting Information

Efficient Ammonia Photosynthesis from Nitrate by Graphene/Si Schottky Junction Integrated with Ni-Fe LDH Catalyst

Chun-Hao Chiang,‡[a] Yu-Ting Kao,‡[a] Po-Hsien Wu,[a] Ting-Ran Liu,[a] Jia-Wei Lin,[b] Po-Tuan Chen,[c] Jr-Wen Lin,[a] Shan-Chiao Yang,[a] Hsuen-Li Chen,[a] Shivaraj B. Patil,[d] Di-Yan Wang *[d] and Chun-Wei Chen *[abe]

[a] Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

[b] Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan

[c] Department of Vehicle Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

[d] Department of Chemistry, Tunghai University, Taichung 40704, Taiwan

[e] Center of Atomic Initiative for New Materials (AI-MAT), National Taiwan University, Taipei 10617, Taiwan

‡ These authors contributed equally to this work.

Corresponding author: Di-Yan Wang (E-mail: diyanwang@thu.edu.tw), Chun-Wei Chen (chunwei@ntu.edu.tw)

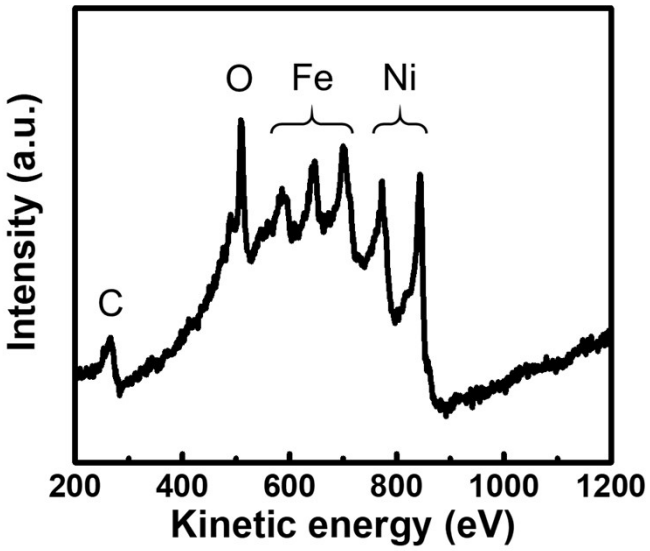


Figure S1. The Auger spectrum of the as-deposited Ni-Fe LDH on graphene/Si heterojunction.

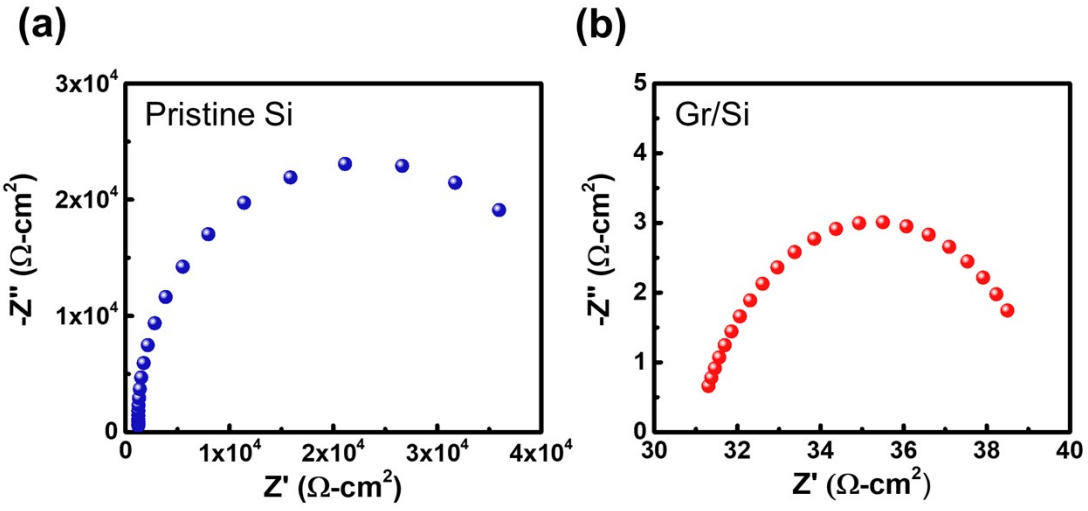


Figure S2. The EIS analysis of the (a) pristine Si and (b) graphene/Si junction in the electrodeposition solution of Ni-Fe LDH.

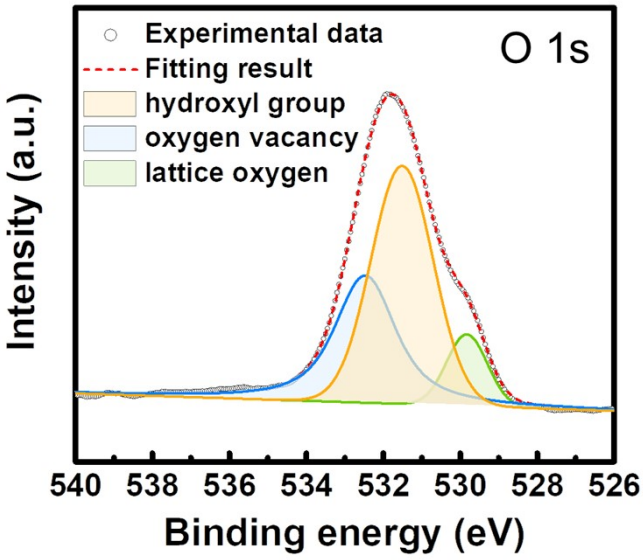


Figure S3. The XPS O 1s spectrum of the as-deposited Ni-Fe LDH.

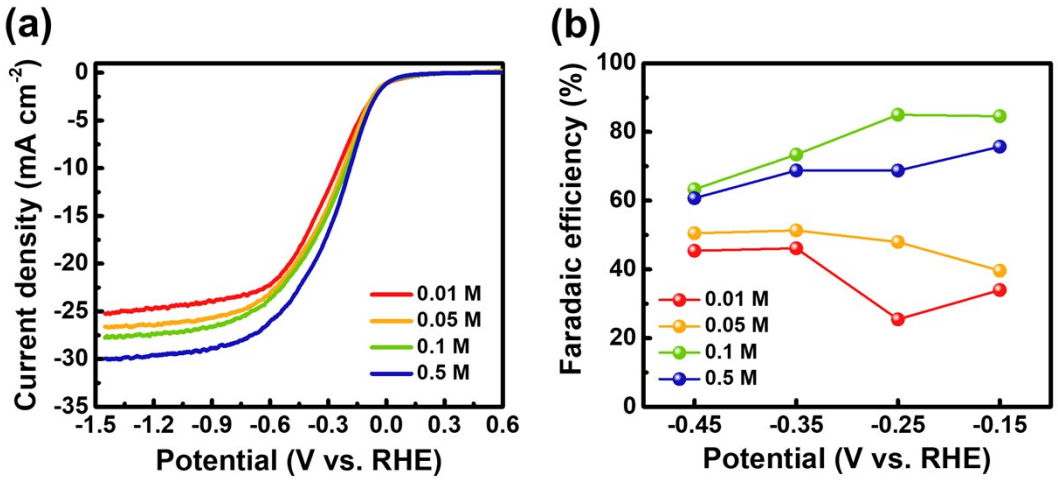


Figure S4. The PEC performances of the Ni-Fe LDH/graphene/Si heterojunction photocathode in 0.5 M Na_2SO_4 with various nitrate concentrations (0.01 M, 0.05 M, 0.1 M, and 0.5 M). (a) Polarization curves and the (b) corresponding Faradaic efficiencies of the PEC device.

Potential (V vs. RHE)	-0.15	-0.25	-0.35	-0.45
FE_{NH3} (%)	84.57	84.98	74.08	73.01
FE_{NO2-} (%)	3.08	1.78	1.93	2.04

Table S1. The Faradaic efficiencies of NH_3 and NO_2^- products of the Ni-Fe LDH/graphene/Si PEC cathode under -0.15 V, -0.25 V, -0.35 V, and -0.45 V (vs. RHE) in 0.5 M Na_2SO_4 and 0.1 M $NaNO_3$.

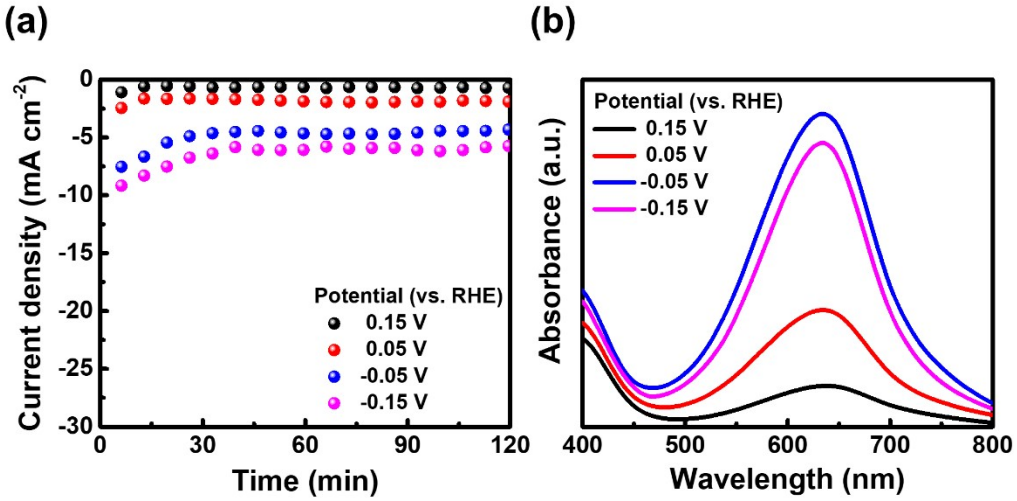
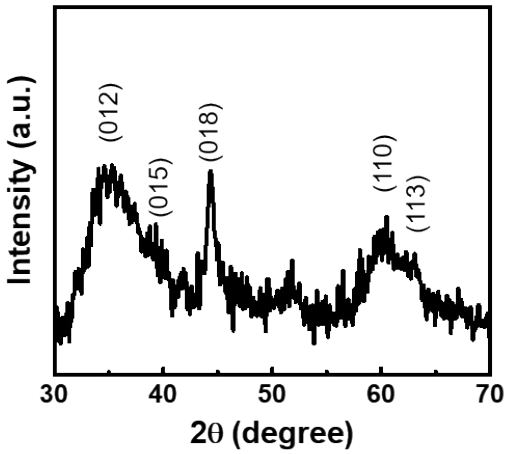


Figure S5. (a) The chronoamperometric curves and (b) absorbance spectra with indophenol indicator for two-hour measurements of the Ni-Fe LDH/graphene/pyramid Si heterojunction photocathode.



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53 **Figure S6.** The XRD spectrum of Ni-Fe LDH electrodeposited on pyramid Si.

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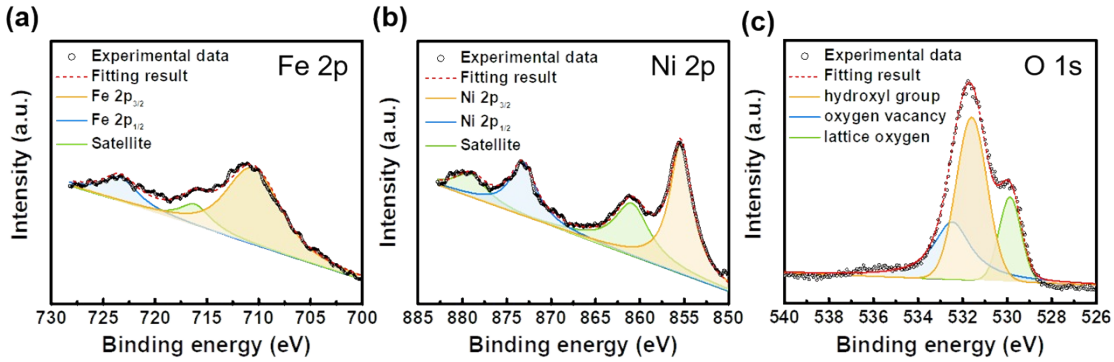

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57 **Figure S7.** The XPS (a) Fe 2p, (b) Ni 2p, and (c) O 1s spectra of Ni-Fe LDH

58 electrodeposited on pyramid Si.

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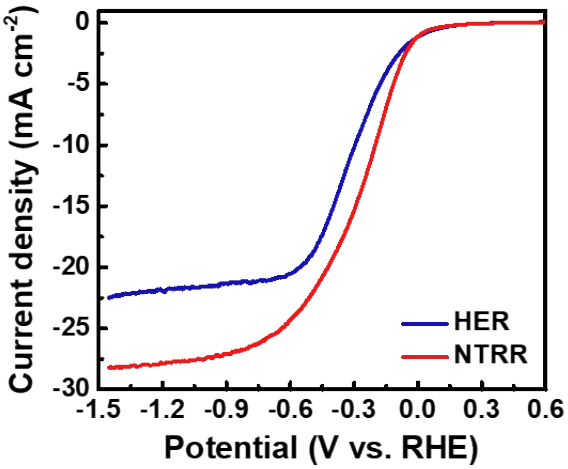

Figure S8. The PEC LSV curves of the Ni-Fe LDH/graphene/Si for HER and NTRR. For HER, the electrolyte is 0.5 M Na_2SO_4. For NTRR, the electrolyte is prepared by 0.5 M Na_2SO_4 and 0.1 M $NaNO_3$.

DFT calculation:

The NTRR on Ni-Fe LDH surface model with oxygen vacancy was simulated using Vienna ab initio simulation package (VASP). The model has the vacuum space of larger than 10 Å. The electron-ion interaction was evaluated via the projector augmented-wave (PAW) pseudopotential method, and the exchange-correlation energy functional was covered with the generalized gradient approximation (GGA). The Monkhorst pack k-point grid was set as 2 × 2 × 1 in our calculations for each model. An energy cutoff of 500 eV was used for the plane-wave basis set, and structural relaxation was iteratively performed until the force of each atom was reduced to within 0.01 eV $Å^{-1}$. The intermediated states are chosen referred to the literature (ACS Catal. 2019, 9, 7052−7064).

For reactions involving proton and electron transfer,

$$A + H^+ + e^- \rightarrow AH \qquad (1)$$

the reaction free energies were estimated through the computational hydrogen electrode model. Specifically, the free energy dependence of the proton−electron pair on the electrode potential was determined using the linear free energy dependence of the electron energy at this potential, which shifts the electron energy by −eU,

$$\mu(H^+) + \mu(e^-) \rightleftharpoons 1/2\ \mu(H_2) - eU \qquad (2)$$

where e is the elementary positive charge ($1.602176634 \times 10^{-19}$ C) and U is the electrode potential on the RHE scale. The free energy change for a specific electrochemical hydrogenation reaction i as a function of potential, $\Delta G_i(U)$, was computed as

$$\Delta G_i(U) \rightleftharpoons \Delta E_i + \Delta ZPE - T\Delta S + eU \qquad (3)$$

where ΔE_i is the DFT-computed electronic adsorption energy of adsorbate i.

For computing potential-dependent kinetics, we follow the procedure for nonelectrochemical surface hydrogenation,

$$A^* + H^* \rightleftharpoons AH^* + * \qquad (4)$$

the activation energy (E_a) can be obtained by DFT calculations of the reactant's minimum-energy geometry and the corresponding hydrogenation transition state. For the corresponding electrochemical step, at equilibrium $H^+ + e^- + * \rightleftharpoons H^*$ conditions, the activation energy $E_a(U^0)$ for $A^* + H^+ + e^- \rightleftharpoons AH^*$ equals E_a. U^0 is the equilibrium potential at which the analogous nonelectrochemical state, $\mu(H^*)$, is in equilibrium with its equivalent electrochemical state, $\mu(H_{(aq)}^+ + e^-)$. Here, U^0 equals the hydrogen

adsorption free energy (ΔG_H) for a given surface at 0 V vs. RHE. The free energy change for the electrochemical surface hydrogenation can then be computed by $U^0 = [G(AH^*) - G(A^*) - 1/2G(H_2)]/e$.

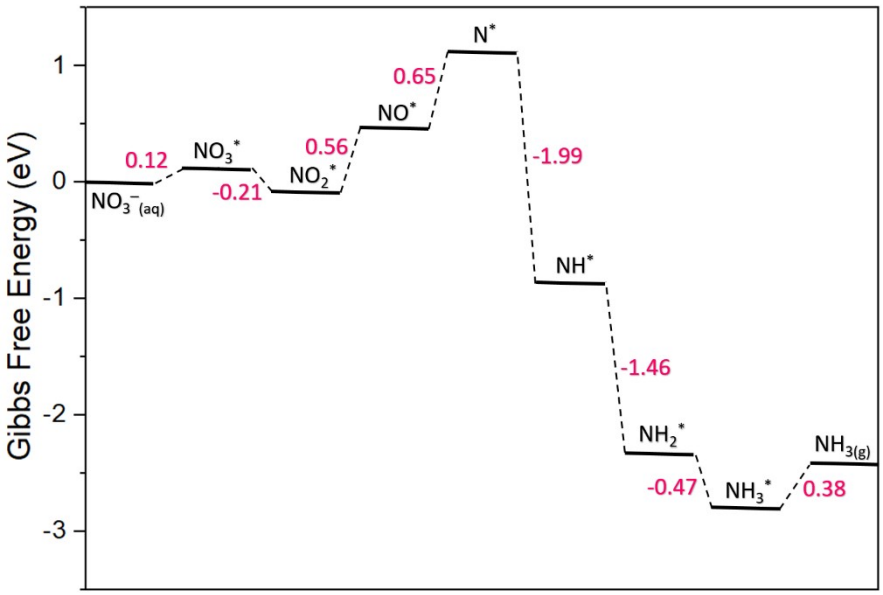

Figure S9. The reaction Gibbs free energy diagram of the Ni-Fe LDH with oxygen vacancy on basal plane for nitrate-to-ammonia conversion. The reaction energy barrier of the rate-determining step resulting from NO* to N* intermediates is 0.65 eV.