Electronic Supplementary Informations

Synthesis of highly twinned ZnSe nanorods for Enhancing N_2 Electrochemical Conversion to NH_3

Kangwen Qiua*, Yuning Hana, Wenbo Guoa, Licun Wanga, Jinbing Chengb*, Yongsong Luob,c

1.Experimental

1.1 Materials synthesis

Preparation of T-ZnSe nanorods: Firstly, ZnO nanorods were grown on carbon fiber paper (CFP) by hydrothermal method, similar to that described in the literature.¹ Subsequently, CFP substrate loaded with ZnO nanorods was placed in the center of a quartz tube and Se powder was placed 5 cm upstream from the tube center. After the quartz tube was outgassed under vacuum, it was heated to 550 °C, held for 1 h, and cooled down to the room temperature.

Preparation of R-ZnSe: For R-ZnSe, A quartz tube consisted of two temperature zones: zone A at 800 °C and zone B at 650 °C. The ZnSe powders was placed in the centre of zone A, and a gold (Au)-coated (0001) Si substrate were located in zone B. The nitrogen (N_2) gas flow rate (100 sccm) was introducted into the system. The synthesis was performed for 1 h, and then cool down to room temperature.

1.2 Characterizations

X-ray diffraction (XRD) spectrum was performed on a Bruker D8 Advance diffractometer with Cu Kα radiation. Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) imaging were carried out on a Hitachi S-4800 SEM and a JOEL 2100 TEM, respectively. X-ray photoelectron spectroscopy (XPS) was characterized on ESCALAB250Xi. 1H nuclear magnetic resonance (NMR) was performed on Varian Inova 500 MHz. IR spectra was measured on a Fourier transform infrared spectrometer (Nicolet IS50, Thermo Fisher Scientific Co., Ltd) with a MCT detector and a Pike Technologies VeeMAX III ATR accessory.

1.3 Electrochemical measurements

The electrochemical measurements were carried out in an H-type electrolytic cell, which was separated by Nafion 115 membrane. Before using, the Nafion membrane was boiled in 5 % H_2O_2 and ultrapure water at 80 °C, respectively. Ag/AgCl and Pt electrodes were used as the reference and counter electrodes, respectively. The T-ZnSe nanorods grown on CFP was directly used as the

working electrode. During NRR tests, highly purified N₂ (99.9999%), ${}^{15}N_2$ (99%,98 atom% ${}^{15}N_2$), and Ar (99.999%) were continuously purged into a gas cleaning plant containing copper-exchanged zeolites (Cu-SSZ-13) and 0.1 M H₂SO₄ solution to remove possible nitrogen oxide impurities and possible ammonia. The gas flow rate was 25 mL min⁻¹.

1.4 ¹⁵N isotope labelling experiment

In order to identify the source of ammonia, the ${}^{15}N_2$ isotope labelling experiment was carried out using ${}^{15}N_2$ as the feed gas. The electrochemical experimental condition was the same as that in ${}^{14}N_2$. After chronoamperometry tests at -0.5 V versus RHE for 12 h, the electrolyte was concentrated into 5 mL, and then mixed with H₂SO₄ and dimethyl sulfoxide-d6 to adjust the pH of the concentrated electrolyte for ¹H NMR test.

1.5 Calculation of Faradaic efficiency and NH₃ yield of catalysts

The Faradaic efficiency was calculated by the following equation:

$$Faradaic \ efficiency = \frac{3F \times n \times V}{17 \times Q}$$

where *F* is Faraday constant (96485 C mol⁻¹), *n* is the concentration of NH₃ production, *Q* is the quantity of the electric charge for one electron, and *V* is the volume of the electrolyte. The NH₃ yield was calculated as follows:

$$NH_3$$
 yield rate = $\frac{n \times V}{m \times t}$

where *m* is the mass of the catalyst, *t* is the reaction time.

1.6 Computation Methods

DFT calculations implemented in the Vienna Ab-initio Simulation Package (VASP) were performed to simulate the ground state properties. The projector augmented-wave (PAW) pseudopotentials were adopted in this work, and the cutoff energy was set to 500 eV for the plane-wave basis set. The local density approximation (LDA) method was employed to describe the exchange-correlation term. The Gaussian smearing method with a width of 0.1 eV was employed. The relaxations of atom positions were achieved with a force convergence criterion of 0.05 eV Å⁻¹, using the conjugate-gradient algorithm. The energy convergence criteria were 10⁻⁴ eV between two consecutive self-consistent steps. All calculations use normal dipole correction to eliminate the pseudo-electrostatic interaction between adjacent slabs.

For bulk calculations, GAMMA-centered K grids with subdivisions of $(7 \times 7 \times 7)$ were used. The equilibrium lattice constant of bulk ZnSe was calculated to be 5.58 Å with an energy gap of 1.57 eV,

which is in agreement with the previous study. For surface stimulation, a slab model of (111) surface with four-unit cell thickness was utilized. The bottom layer of the slab was fixed while the other atoms were allowed to relax. A vacuum layer of 10 Å was introduced to avoid periodic image interactions. A *k*-mesh of $(1 \times 3 \times 1)$ was set for p (6 × 2) slab. The lower surface is passivated with pseudo-hydrogen to revivify the semiconductor property of bulk ZnSe and prevent the influence of the unrealistic gap states on the adsorption properties. ZnSe (111) surface with atomic steps was constructed according to the stoichiometric ratio.

The adsorption energy (E_{ads}) was calculated as

$$E_{ads} = E_{total} - E_{slab} - E_{moleculo}$$

where E_{total} is the energy of molecule-slab adsorption configuration, E_{slab} and E_{molecule} is the energy of clean surface and isolate molecule, respectively. A negative Eads reflects an exothermic process.

For the HER reaction, we tested the HER performance of T-ZnSe, the results were shown in Fig.S. According to the HER kinetic model,² the Tafel slope of 79 mV dec⁻¹ is between the theoretical values for the rate-determining Volmer (120mV dec⁻¹) and Heyrovsky (40mV dec⁻¹) cases and thus indicates that the HER is proceeding via a Volmer-Heyrovsky reaction (Volmer: H⁺ + e⁻ \rightarrow H^{*}; Heyrovsky: H^{*} + H⁺ + e⁻ \rightarrow H₂ + *). We used the method of computational hydrogen electrode (CHE) to simulate the electrochemical reaction properties. Setting the reversible hydrogen electrode (RHE) to the reference potential, the chemical potential of proton-electron pair (μ (H⁺) + μ (e⁻)) is equal to that of 1/2H₂ – eU at a given U versus RHE, at any pH. The Gibbs free energy changes (ΔG) for elemental steps were calculated by $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the energy difference, ΔZPE and ΔS are the changes in zero-point energy and entropy, respectively. The zero-point energies and entropies are obtained from the vibrational frequency calculations and NIST database (*T*=300K). To avoid the periodic spurious interactions between two images, we placed the adsorbate at a position above 5 Å from the active site of the surface to align the vacuum energy levels of the two to analyze the changes in the electronic structure before and after adsorption.

Element	Mass ratio (%)	Atomic ratio (%)
Zn K	45.14	49.84
Se K	54.86	50.16
ОК	0	0
Total	100.00	100



Fig. S1. Structural characterizations of R-ZnSe nanorods. (a) XRD pattern. (b) SEM image. (c) TEM image. (d) HRTEM image.



Fig. S2. Electrochemical active surface area (ECSA) measurement. (a) and (b) CV curves of T-ZnSe and R-ZnSe, respectively, measured at the scan rates of 10, 20, 30, 40 and 50 mV s⁻¹. The insets show current densities at 0 V versus RHE as a function of the scan rate.



Fig. S3. Digital photograph of the homemade NRR testing system. Note that the gas cleaning cell contains copper-exchanged zeolites (Cu-SSZ-13) and 0.1 M H_2SO_4 solution to remove possible nitrogen oxide impurities and possible ammonia.



Fig. S4. Multi-step control experiments for NRR test. (a) Flow diagram of experimental protocol for reliable proof that NH_3 production over the investigated catalysts. (b) ¹H NMR analysis of the electrolyte fed by ¹⁴N₂ and ¹⁵N₂ as the isotopic N₂ source for NRR; (c) NH₃ contents tested in ultrapure water, 0.10 M KOH electrolyte, N₂-saturated electrolyte, Nafion dispersed liquid, and multi-step control experiments.



Fig. S5. UV-vis absorption spectra of NO_x with different concentration solution; (b) Standard concentrationabsorbance curve of the NO_x obtained from (a).



Fig. S6. The UV-vis absorption spectra of the 0.1 M KOH background and the ultra-high N_2 (99.9999 % purity) purged in 0.1 M KOH electrolyte; using N-(-1-naphthyl)-ethylenediamine dihydrochloride spectrophotometric method.¹⁹ The result show that NO_x does not exist in the N₂ purged gas.



Fig. S7. Ammonia-sensitive electrode method. (a) Digital photograph of the ammonia-sensitive electrode instrument. (b) Standard curve of the NH_4Cl solutions detected by the ammonia-sensitive electrode.



Fig. S8. (a-e) *I-t* curves of T-ZnSe nanorods at -0.3~-0.7 V vs. RHE, respectively. The calculated NH₃ yield rate and Faradaic efficiency of T-ZnSe are provided in Fig. 4c, d.



Fig. S9. Ion chromatography method. (a) Standard curve for the standard NH₄Cl solution with different content detected by ion chromatography. (b) Faradaic efficiency and NH₃ yield rate of T-ZnSe catalyst.



Fig. S10. XRD pattern. of T-ZnSe after NRR test.



Fig. S11. (a) UV-Vis absorption spectra of the N_2H_4 with different concentrations. (b) Standard concentration-absorbance curve of the N_2H_4 obtained from (a), with the inset showing the digital photograph of N_2H_4 solutions with different concentrations. As shown, no hydrazine was produced over T-ZnSe catalyst during NRR.



Fig. S12. (a) LSV curves and (b) Tafel plots for the catalytic HER process of T-ZnSe.



Fig. S13. NRR pathways.



Fig. S14. (a) Atomic models of ZnSe (111) and (111)-AT. (b) DFT calculated energy barrier of water dissociation process on ZnSe (111) and (111)-AT.



Fig. S15. Calculated HER free energy diagrams on ZnSe (111) and T- ZnSe (111).



Fig. S16. The Free-energy diagrams of N_2 adsorption on possible active sites of ZnSe. The result indicates that Zn shows higher N_2 adsorption affinity during NRR.



Fig. S17. DFT calculated free energy diagrams of overall NRR on T-ZnSe (111) with and without H* .

references

- H.Zhang, T. Ling, X. W. Du, Gas-Phase Cation Exchange toward Porous Single-Crystal CoO Nanorods for Catalytic Hydrogen Production, *Chemistry of Materials* 27, 352-357 (2015).
- [2] Z. Qiu, C. W. Tai, G. A. Niklasson, T. Edvinsson, Energy & Environmental Science, 2019, 12, 572-581.