

Computational Methodology

The 4×4×1 BN-based supercell with 20 Å vacuum was constructed for simulation. The Perdew-Burke-Ernzerhof (PBE)¹ generalized-gradient approximation (GGA) functional was selected for exchange-correlation. All calculations were spin-polarized and the cutoff energy for the plane-wave-basis was 520 eV. The Gaussian smearing was employed with a smearing width of 0.05 eV. Gamma centered Monkhorst-Pack² k-points sampling of 3×3×1 and 9×9×1 were adopted for structural relaxation and electronic structural calculations, respectively. The global break condition for the electronic self-consistency and ionic relaxation loops were set to 1×10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. Grimme's DFT-D3 correction method with Becke-Jonson damping was used to describe van der Waals interactions. The effects of an implicit solvation were also tested using VASPsol^{3,4} with a relative permittivity of solvent set to 78.4 for water. The ab initio molecular dynamic (AIMD) simulations were performed using the NVT ensemble with the Nosé-Hoover thermostat⁵⁻⁷ at 500 K for 10 ps.

Bader charge analysis⁸ was done using the code developed by Henkelman group⁹⁻¹². Crystal Orbital Hamilton Populations (COHP)^{13,14} was calculated using LOBSTER¹⁵⁻¹⁷ program. In addition, VASPKIT¹⁸ was used for post-processing of results. VESTA¹⁹ program was used to visualize structural models and electron densities.

The stabilities of the doped BN structures are indicated by the formation energy (E_f), dissolution potential (U_{diss})²⁰ and AIMD. For the formation energy, it is defined as:

$$E_f = E_{M@BN} - E_{\text{defective BN}} - E_M$$

where $E_{M@BN}$, $E_{\text{defective BN}}$, and E_M are the total energies of M@BN, BN with B defect, and per metal atom in bulk.

The binding energy of heterostructures is defined as:

$$E_b = E_{M@BN/GR} - E_{M@BN} - E_{GR}$$

where $E_{M@BN/G}$, $E_{M@BN}$, and E_{GR} are the total energies of M@BN/GR, M@BN, and graphene.

Computational hydrogen electrode (CHE) framework advanced by Nørskov *et al.*²¹ was used to calculate Gibbs free energy change (ΔG) of elementary reaction steps involving $H^+ + e^-$. The ΔG can be calculated as

$$\Delta G = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S + eU + \Delta G_{\text{pH}}$$

where ΔE_{DFT} is adsorption enthalpy, ΔE_{ZPE} and ΔS are the changes in zero-point energy, and entropy at $T = 298.15$ K, respectively. U and e are the electrode potential and the number of electrons transferred. The ΔG_{pH} is the free energy correction of H^+ ions:

$\Delta G_{\text{pH}} = kT \ln 10 \times \text{pH}$ (The k is the Boltzman constant and pH is set as 0 in this work)

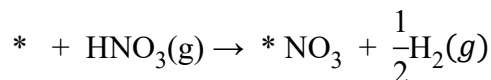
The limiting potential (U_L) is defined as

$$U_L = -\Delta G_{\text{max}}/e$$

which is needed to make all steps downhill in free energy.

To calculate accurately the adsorption energy of dissolved NO_3^- , the scheme proposed by Calle-Vallejo *et al.*²² was adopted. That is, the adsorption Gibbs free

energy $\Delta G_{\text{NO}_3}^{\text{DFT}}$ of NO_3^- is calculated with respect to gas phase HNO_3 and H_2 based on equation:



Then, correcting the $\Delta G_{\text{NO}_3}^{\text{DFT}}$ with experimental data²³:



Furthermore, the error for formation free energies of HNO_3 is also corrected with experimental value²⁴:

$$|\Delta G_{\text{exp}}^0 - \Delta G_{\text{DFT}}^0| = |-0.77 - (-1.91)| = 1.14 \text{ eV}$$

Taken together, the corrected $\Delta G_{\text{NO}_3}^{\text{EC}}$ on the electrochemical scale is as follows:

$$\Delta G_{\text{NO}_3}^{\text{EC}} = \Delta G_{\text{NO}_3}^{\text{DFT}} - 0.748$$

Additional data

Table S1 The formation energy (E_f) and dissolution potential (U_{diss} , versus SHE) of the Zn@BN

System	E_f / eV	U_{diss} / V
Zn@BN	-3.40	0.94

Table S2 Binding energies of Zn@BN/graphene heterostructure

System	E_b / eV (AA stack)	E_b / eV (AB stack)
Zn@BN/G	-1.53	-1.72
R		

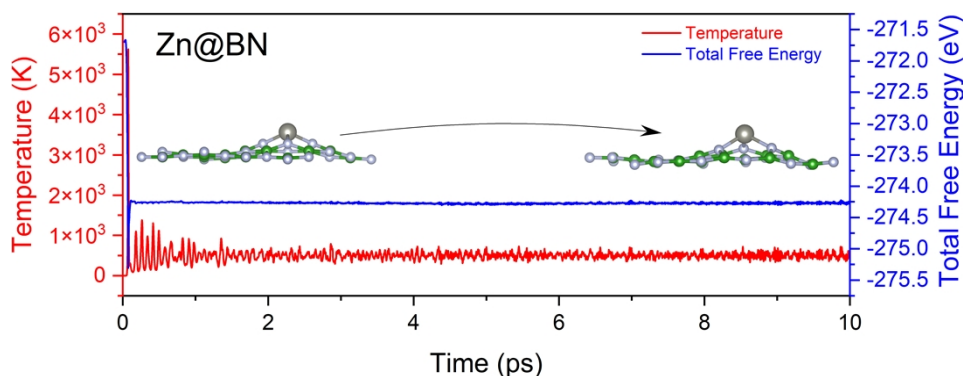


Figure S1 The temperature and energy progress of Zn@BN with time (10 ps with time step of 2 fs) in AIMD simulations at 500 K.

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