Tunable Ferroelectric Diatomic Catalysis on In_2Se_3 Monolayers for NO Reduction

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Table S1 The binding Characteristics of TM Atomic Clusters, including the binding energies of TM atom(Eb-TM in eV/atom), the d band center of TM atom (Ed-band in eV) and the charge lost from (positive values) or gained by (negative values) the adsorbed TM atoms (QTM in e/atom).

	$E_{b\text{-}TM}$ (eV)				$E_{d\text{-}band}$ (eV)				Average Q_{TM} (eV)			
	1	2	3	4	1	2	3	4	1	2	3	4
Pt/In_2Se_3(↑)	-3.28	-4.22	-4.35	-4.55	-1.59	-2.48	-2.47	-2.58	-0.16	-0.64	+0.09	-0.05
Pt/In_2Se_3(↓)	-4.11	-4.35	-5.31	-4.73	-1.96	-1.93	-2.28	-2.40	-0.06	+0.30	+0.40	+0.15
Pd/In_2Se_3(↑)	-2.28	-2.36	-2.94	-2.86	-1.27	-1.51	-2.35	-2.20	+0.01	+0.04	+0.10	-0.04
Pd/In_2Se_3(↓)	-2.29	-3.18	-2.95	-3.14	-1.26	-2.03	-1.64	-1.91	+0.09	+0.43	+0.8	+0.29
Ag/In_2Se_3(↑)	-1.20	-1.49	-1.64	-1.74	-4.19	-3.34	-4.60	-3.62	+0.16	-0.01	+0.10	+0.02
Ag/In_2Se_3(↓)	-2.10	-1.97	-2.06	-2.05	-4.10	-4.02	-3.86	-3.79	+0.31	+0.20	+0.15	+0.15
Au/In_2Se_3(↑)	-1.37	-2.03	-1.96	-2.25	-2.82	-1.95	-3.76	-2.34	-0.13	-0.18	-0.06	-0.09
Au/In_2Se_3(↓)	-2.05	-2.17	-2.38	-2.49	-3.29	-2.46	-3.27	-3.07	+0.04	-0.09	-0.02	+0.01
Ir/In_2Se_3(↑)	-3.90	-6.57	-5.00	-5.28	-1.91	-2.51	-2.26	-2.34	-0.15	+0.17	+0.01	+0.01
Ir/In_2Se_3(↓)	-5.21	-6.60	-5.50	-6.23	-2.30	-2.22	-2.45	-2.65	-0.07	+0.55	+0.11	+0.24
Rh/In_2Se_3(↑)	-3.23	-5.20	-4.62	-3.84	-1.37	-2.12	-2.06	-1.92	-0.01	+0.18	+0.24	+0.01
Rh/In_2Se_3(↓)	-4.26	-3.58	-5.24	-4.58	-1.81	-1.65	-2.16	-1.96	+0.07	+0.15	+0.41	+0.22
Ru/In_2Se_3(↑)	-4.20	-5.88	-5.32	-5.39	-1.81	-2.74	-2.47	-2.45	-0.2	+0.77	+0.11	+0.10
Ru/In_2Se_3(↓)	-5.60	-5.54	-6.27	-6.04	-2.05	-2.80	-2.62	-2.61	+0.2	+0.29	+0.43	+0.34

Table S2. Comparison of relative energies for different adsorption sites of a single atom (e.g., Pt) under two polarization directions.

	The Bridge site	The Se-Hollow site	The Top site
M/In2Se3(↑)/eV	-307.5493	-307.9654	-307.6257
M/In2Se3(↓)/eV	-308.0233	-308.2974	-308.1149

Figure S1 Optimized geometric structures: (a) Top view of Ag atomic clusters adsorbed on

In_2Se_3.(b) Top and side views of transition metal (TM) diatomic species (TM = Pt, Pd, Au) adsorbed on In_2Se_3.

Figure S2 Optimized geometries: (a) Top and side views of TM triatomic clusters adsorbed on In_2Se_3; (b) Top and side views of TM tetratomic clusters adsorbed on In_2Se_3 (TM = Pt, Pd, Au, Ir, Rh, Ru).

Figure S3 (a) presents the free energy diagram for all reaction pathways of the nitric oxide reduction reaction (NORR) on the dual-atom Ir catalyst (DAC). (b) shows the free energy diagram for the NORR reaction pathways on the dual-atom Rh catalyst (DAC).

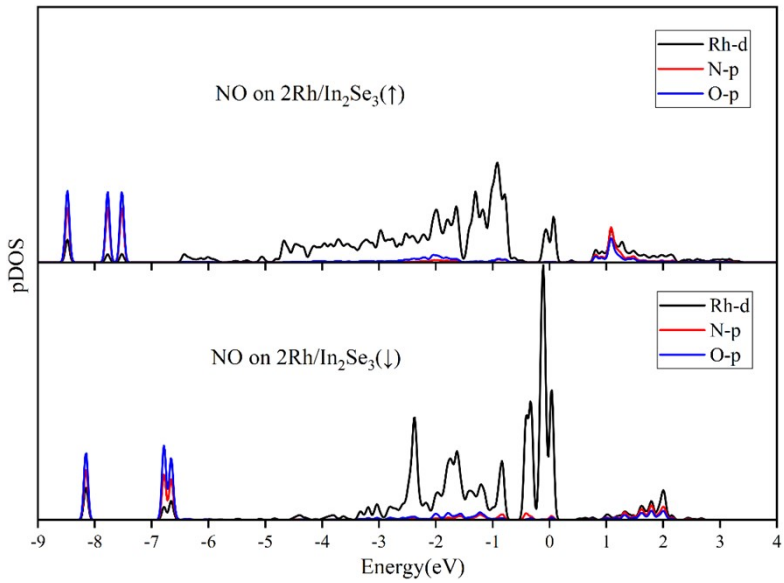

Figure S4 The spin-up projected density of states (PDOS) for the Rh d, N p, and O p orbitals in $2Rh/In_2Se_3$, and for the Rh d, N p, and O p orbitals in M/In_2Se_3.

Figure S5 Top and side views of the Bridge site, Se-Hollow site and Top site.

Section S1: Detailed Methodology for Electric Polarization Calculation

1. Theoretical Framework and Computational Implementation

The spontaneous electric polarization (P) values reported in the main text were computed using the modern theory of polarization (Berry phase formalism):

$$\delta p = p^f - p^0$$

$$= \frac{1}{\Omega}\sum_i \left[q_i^f r_i^f - q_i^0 r_i^0\right] - \frac{2ie}{(2\pi)^3}\sum_n^{occ}\left[\int_{BZ} d^3k e^{-ik\cdot R}\left\langle u_{nk}^f \middle| \frac{\partial u_{nk}^f}{\partial k}\right\rangle - \left\langle u_{nk}^0 \middle| \frac{\partial u_{nk}^0}{\partial k}\right\rangle\right]$$

where f and 0 indicate the final (polar) and intial (high symmetry) positions/wavefunctions.

This approach calculates the change in polarization (ΔP) along an adiabatic path connecting a reference structure to the ferroelectric ground state of interest, as implemented in the VASP code.

2. Calculation Pathway via λ-Path Integration

Reference State (λ = 0): A hypothetical centrosymmetric reference structure was constructed by enforcing inversion symmetry on the atomic positions of the In_2Se_3 monolayer.

Polarized State (λ = 1): The fully optimized ferroelectric ground-state structure of the α-In_2Se_3 monolayer.

For each image, a self-consistent field (SCF) calculation was performed with high-precision settings (ENCUT = 420 eV, EDIFF = 1E-7 eV) to obtain converged wavefunctions.

The total change in polarization ΔP was computed by VASP through the discretized Berry phase formula evaluated along the λ-loop.

3. k-Point Convergence

The precision of the Berry phase integral is highly sensitive to Brillouin zone sampling. We rigorously tested the convergence of the calculated polarization with respect to the k-point mesh. The results confirmed that the chosen 10 × 10 × 1 Monkhorst-Pack grid is sufficient, yielding polarization values converged to within < 2.0 pC/m of the values obtained with a denser 12 × 12 × 1 grid.

4. Directional Components of the Polarization Vector

The calculation directly outputs the full polarization vector P with its three Cartesian components (Px, Py, Pz). The reported in-plane polarization value (324.5 pC/m) corresponds to the Px component. The out-of-plane polarization value (27.5 pC/m) corresponds to the Pz component. The Py component was negligible, consistent with the structural symmetry.

5. Key VASP Parameters

The standalone Berry phase calculation was performed using the following key parameters in the INCAR file:

- LCALCPOL = .TRUE. ! Activate Berry phase calculation
- IDIPOL = .TRUE. and IDIPOL = 3 ! Apply dipole correction along the z-axis to eliminate spurious interactions between periodic images
- High-precision electronic settings: ENCUT = 420, EDIFF = 1E-7, ISMEAR = 0, SIGMA = 0.05

The final polarization values were extracted from the OUTCAR file upon successful completion of the calculation.