Supporting Information for

Enhanced OER catalytic activity of single metal atom supported by pentagonal NiN_2 monolayer：insight from density functional calculations

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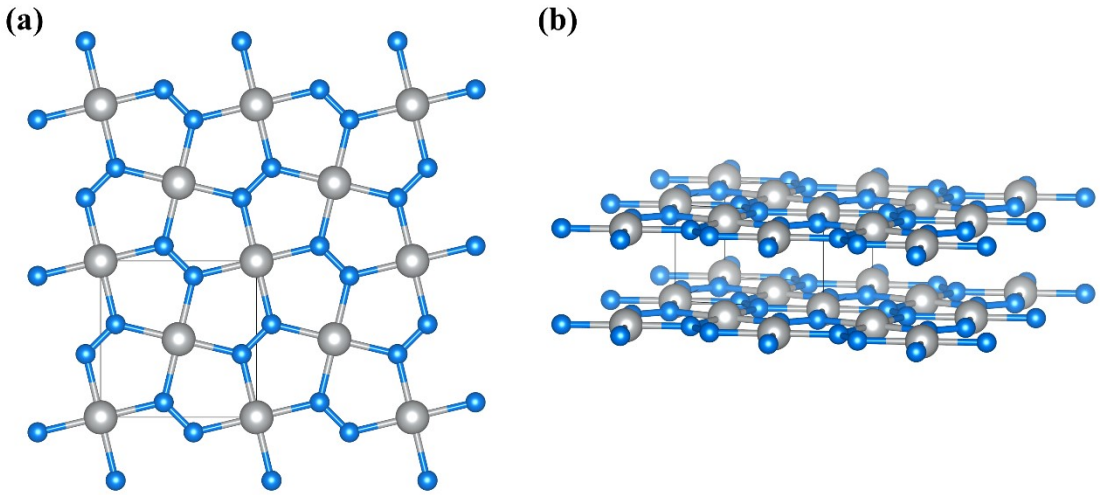

Figure S1. Bulk pentagonal NiN_2 structure. Blue and gray balls show the positions of N and Ni atoms, respectively. (a) Top view of bulk pentagonal NiN_2. (b) Normal view of bulk pentagonal NiN_2.

Each Ni atom locate on planar coordination with four N atoms, while each N atom locate on planar triangular coordination with two Ni atoms and one N atom. NiN_2 monolayer can be obtained by peeling off from the pentagonal bulk NiN_2 material.

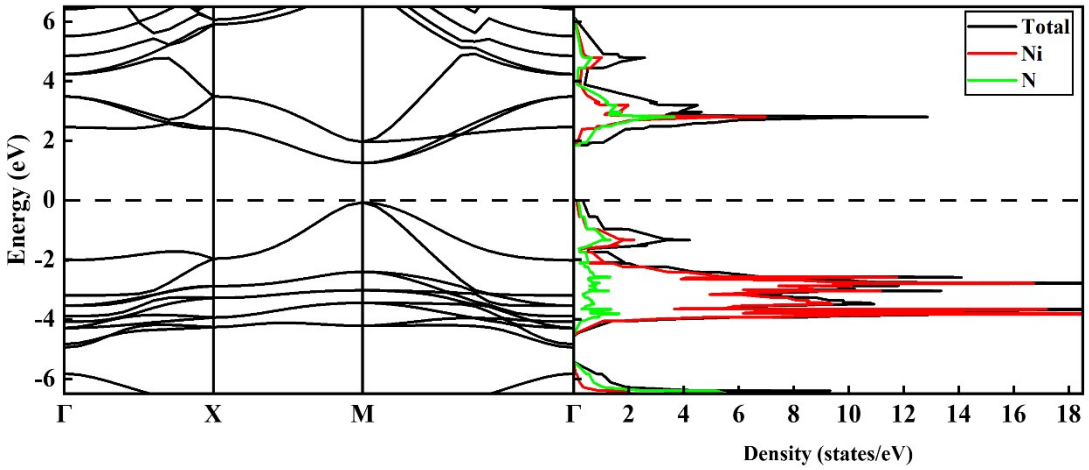

Figure S2. Band structure and DOS of NiN_2 monolayer calculated by functional. The black, red and green line represent the total density of states, the density of states projected onto Ni and N, respectively. The black dashed line represents the position of the Fermi level.

The HSE06 band structure of NiN_2 monolayer indicates that it is a direct bandgap semiconductor with a bandgap of 1.32 eV. The calculated bandgap is slightly higher than 1.10 eV in previous study (*Appl. Surf. Sci.*, 2019, 469, 456-462). Both the valence band maximum (VBM) and conduction band minimum (CBM) located on the M point.

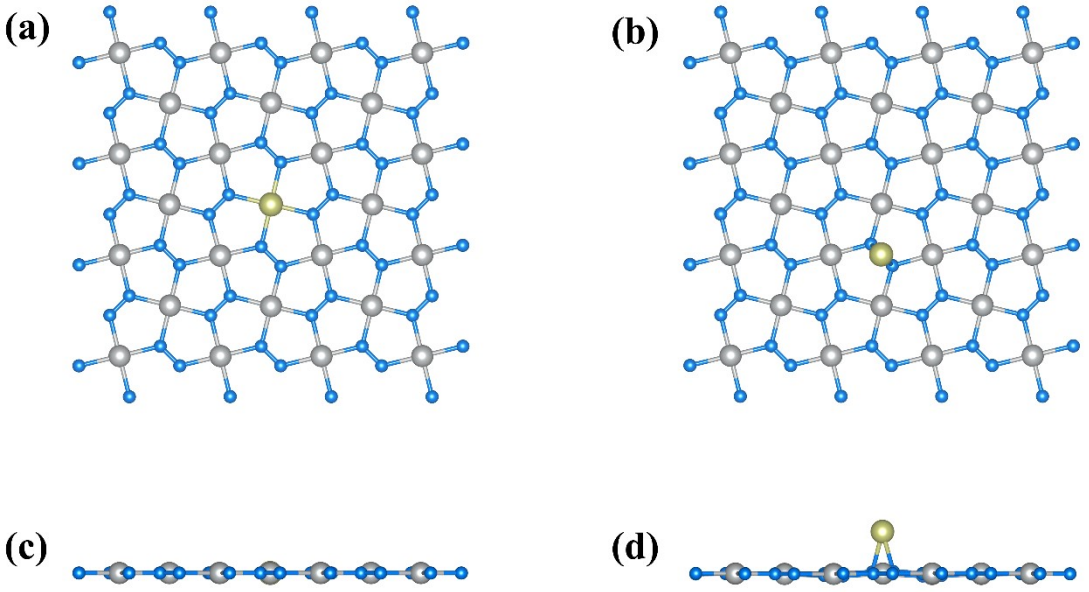

Figure S3. The Ir doped and Ir adsorbed NiN_2 monolayer. Yellow, gray, and blue represent Ir, Ni, and N atoms, respectively. (a) Top view of Ir doped NiN_2 monolayer. (b) Top view of Ir adsorbed NiN_2 monolayer. (c) Side view of Ir doped NiN_2 monolayer. (d) Side view of Ir adsorbed NiN_2 monolayer.

The calculated binding energy of Ir doped and Ir adsorbed NiN_2 monolayer were -9.62 eV and -3.71 eV, respectively. Thus, Ir doped NiN_2 monolayer is more stable than that of Ir adsorbed NiN_2 monolayer.

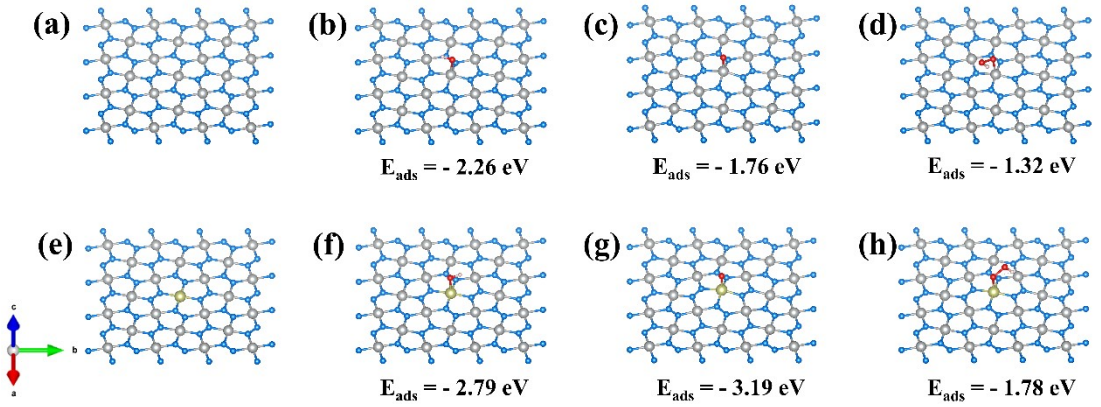

Figure S4. The intermediate adsorption configuration of pristine NiN_2 and Ir@NiN_2. Yellow, gray, and blue represent Ir, Ni, and N atoms, respectively. (a-d) pristine NiN_2 monolayer, *OH intermediate adsorption, *O intermediate adsorption, and *OOH intermediate adsorption on NiN_2 monolayer, respectively. (e-h) Ir@NiN_2 monolayer, *OH intermediate adsorption, *O intermediate adsorption, and *OOH intermediate adsorption on Ir@NiN_2 monolayer, respectively.

The *O, *OH, and *OOH intermediates adsorbed on the top of Ni atoms in NiN_2 monolayer. While, the *O, *OH, and *OOH intermediates adsorbed on the top of Ir atoms in Ir@NiN_2 monolayer.

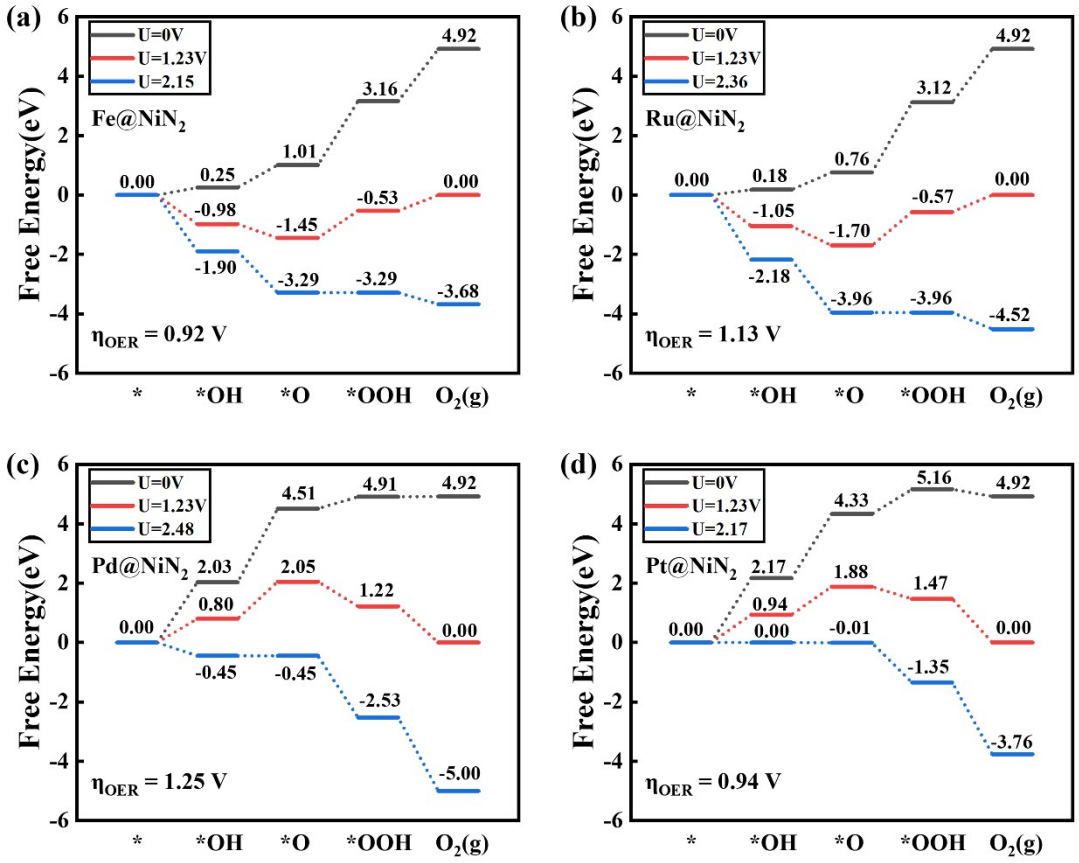

Figure S5. (a-d) OER Gibbs free energy step diagram of Fe@NiN_2, Ru@NiN_2, Pd@NiN_2, Pt@NiN_2, respectively (pH=0). Black lines refer to the initial state, red lines indicate the equilibrium potential, and blue lines represent the potential required to initiate the reaction.

For $Fe@NiN_2$ and $Ru@NiN_2$, the rate-determining step (RDS) is the step from *O to *OOH. While, the RDS of $Pd@NiN_2$ and $Pt@NiN_2$ is the step from *OH to *O and * to *OH, respectively. The calculated OER overpotentials for $Fe@NiN_2$, $Ru@NiN_2$, $Pd@NiN_2$ and $Pt@NiN_2$ are 0.92 V, 1.13 V, 1.25 V and 0.94 V, respectively.

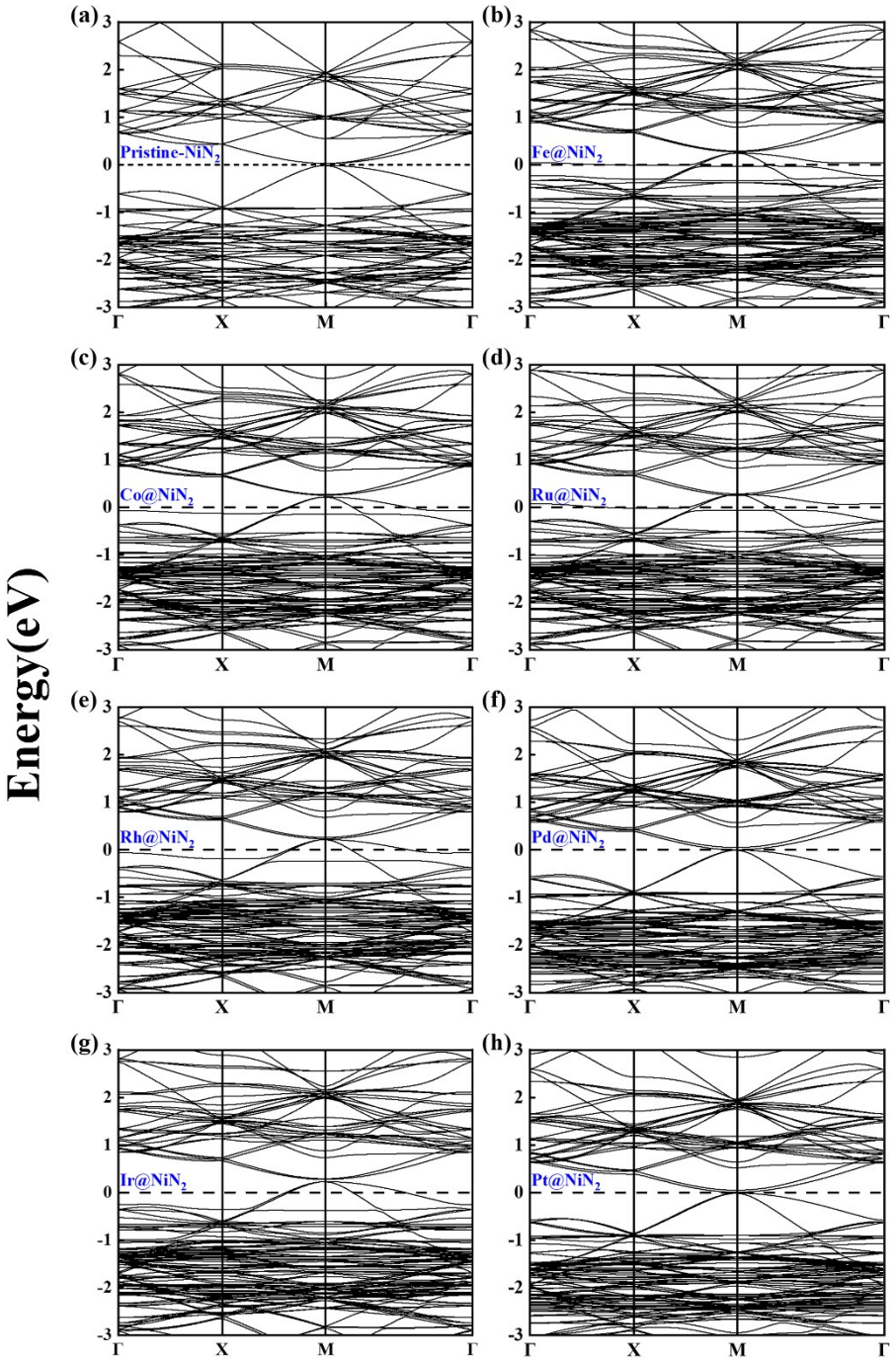

Figure S6. (a-h) Band structure of pristine NiN_2 monolayer and $TM@NiN_2$ (TM = Fe, Co, Ru, Rh, Pd, Ir, Pt) by PBE functional. The black dashed line represents the position of the Fermi level.

TM doping does not significantly alter the band structure of NiN_2 monolayer. All the band structures of $TM@NiN_2$ were similar to the initial band structure of NiN_2 monolayer.

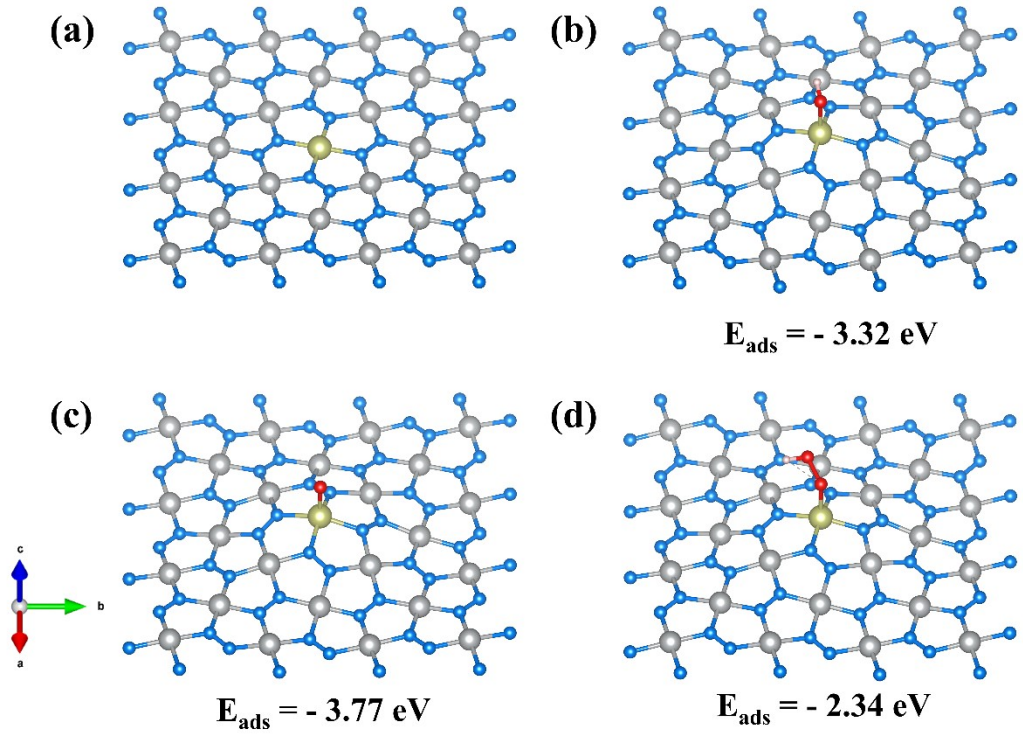

Figure S7. (a-d) Ir@NiN_2 monolayer, *OH intermediate adsorption, *O intermediate adsorption, and *OOH intermediate adsorption on Ir@NiN_2 monolayer under -2% biaxial strain, respectively. Yellow, gray, and blue represent Ir, Ni, and N atoms, respectively.

The *O, *OH, and *OOH intermediates still adsorbed on the top of Ir atoms in Ir@NiN_2 under -2% biaxial strain.