Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Information for High Excellent hydrogen evolution characteristics and novel mechanism of two-dimensional tetra-phase $OsN_2$ and $ReN_2$

## Surface Pourbaix Diagram

In the model of the theoretical standard hydrogen electrode, the surface is regarded in equilibrium with protons and the liquid water at 298 K, so that oxygen, hydroxyl and hydrogen may be exchanged between the surface and the reference electrolyte through the following steps：

$$H_2O + * \rightarrow OH^* + H^+ + e^- \quad (1)$$

$$H_2O + * \rightarrow O^* + 2H^+ + 2e^- \quad (2)$$

At finite pH and potential, the free energy changes of the reactions eqn. (1),(2)

$$\Delta G(OH) = \Delta G_0(OH) - eU_{SHE} - k_B T \ln 10 \times pH$$

$$\Delta G(O) = \Delta G_0(O) - 2eU_{SHE} - 2k_B T \ln 10 \times pH$$

respectively, where $\Delta G_0(O)$, $\Delta G_0(OH)$ are the free energy changes of equation (1), (2) at U=0 and pH = 0 respectively. It's the same algorithm as the hydrogen adsorption free energy, as

$$\Delta G_{nOH} = \Delta E_{nOH} + \Delta E_{ZPE} - T\Delta S$$

and

$$\Delta G_{nO} = \Delta E_{nO} + \Delta E_{ZPE} - T\Delta S$$

respectively.

Table S1. Charge for each element, average charge and net charge for donor atom. N* denoted as the N-atom attached to H-atom.

| System/atom | Re | N | $N^*$ | $N^*$ | $N^*$ | $N^*$ | H | $\Delta G_H$(eV) |
|---|---|---|---|---|---|---|---|---|
| $ReN_2$+slab | -1.81 | 0.905 | | | | | | |
| $ReN_2$+H | -1.775 | 0.923 | 1.13 | | | | -0.49 | -0.11 |
| $ReN_2$+2H | -1.730 | 0.923 | 1.11 | 1.11 | | | -0.42 | 0.001 |
| $ReN_2$+3H | -1.69 | 0.927 | 1.10 | 1.09 | 1.09 | | -0.38 | 0.25 |
| $ReN_2$+4H | -1.653 | 0.932 | 1.12 | 1.12 | 1.10 | 1.10 | -0.39 | 0.27 |

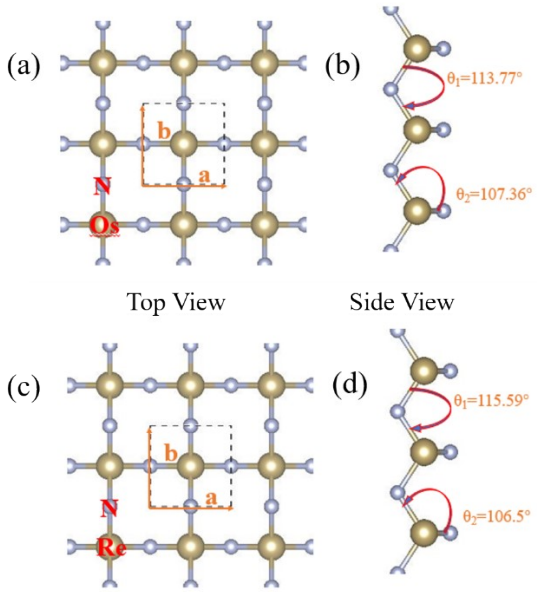



Fig. S1 Atomic structure of the $OsN_2$ and $ReN_2$. (a) and (b) are top view and side view of $OsN_2$ monolayer, (c) and (d) are top view and side view of $ReN_2$.

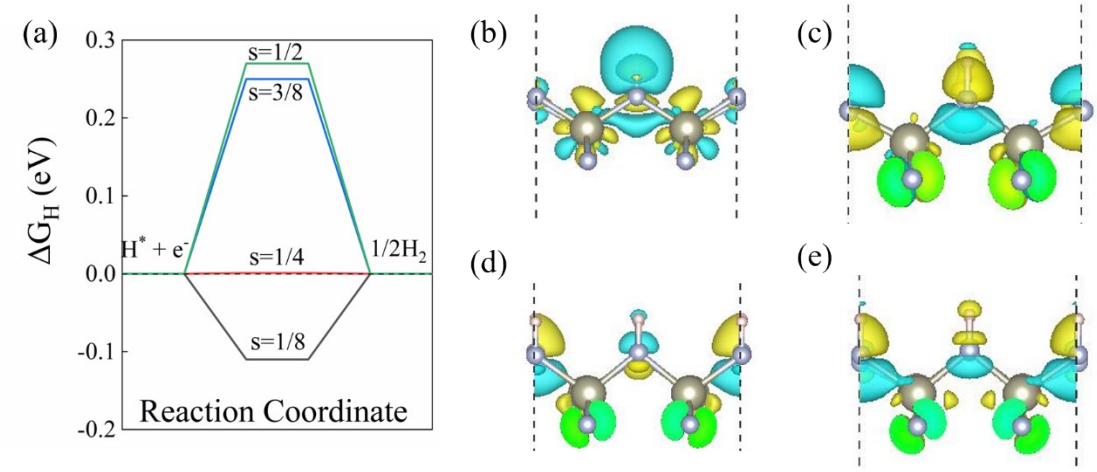



Fig. S2 (a) $\Delta G_H$ of $ReN_2$ monolayer under different coverage. Differential charge density diagram before and after hydrogen adsorption, (b) - (e) are adsorption H and 2H, 3H, 4H respectively, with the red/silver/white balls representing Re/N/H ( with isosurfaces of 0.01 eV/Å$^3$).

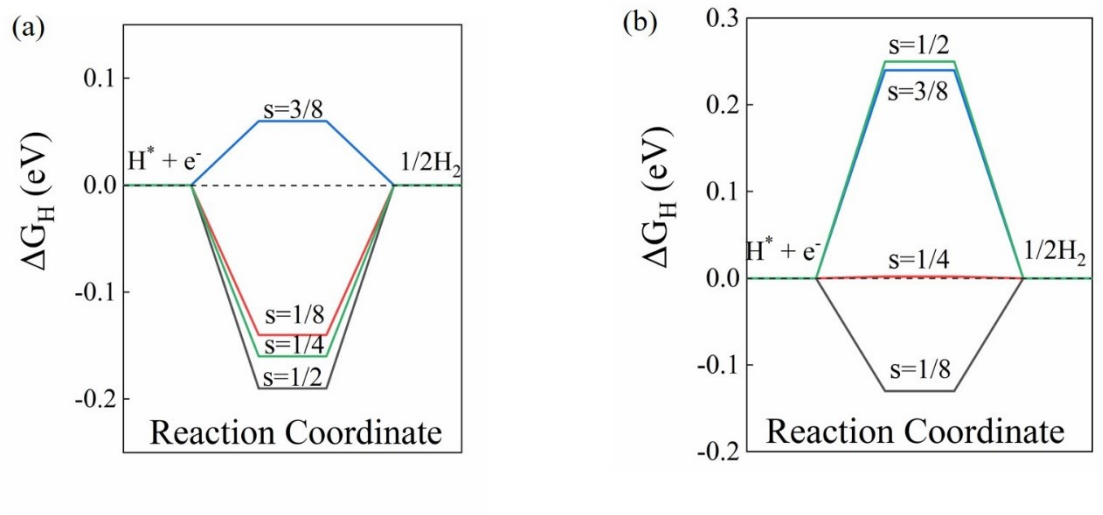



Fig. S3 $\Delta G_H$ of double-layer $OsN_2$ (a) and $ReN_2$ (b) at different coverage.

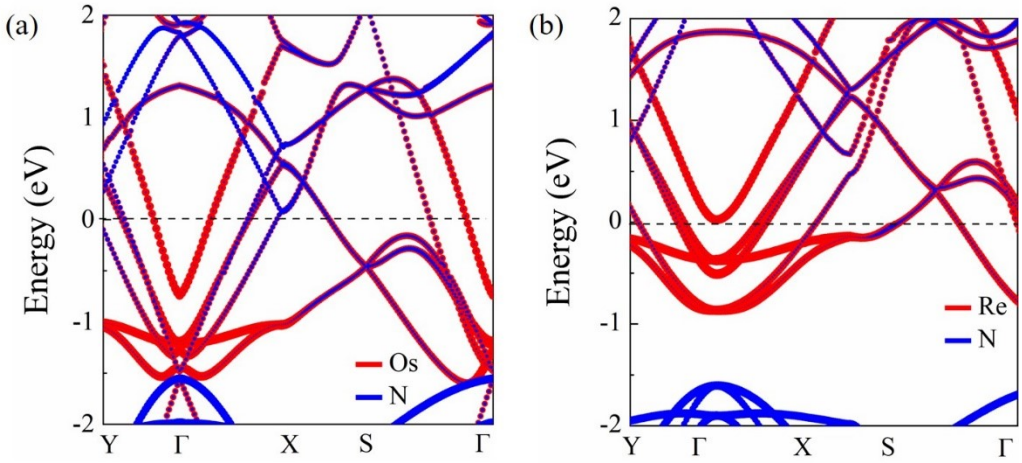
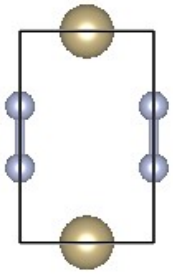
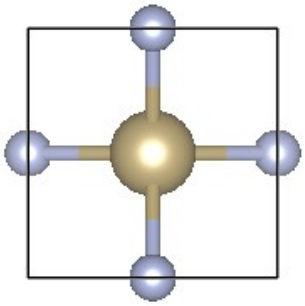
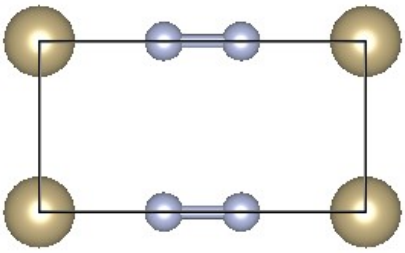
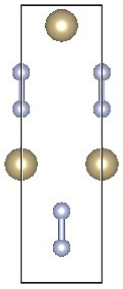
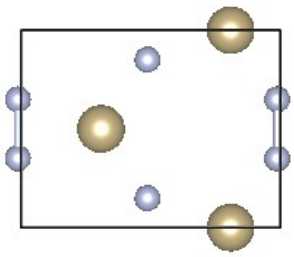
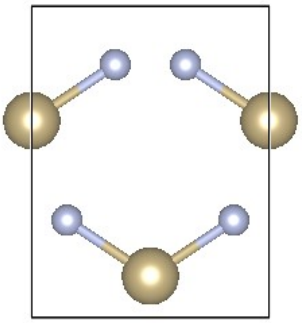



Fig. S4 Band structure of (a) $OsN_2$ and (b) $ReN_2$ monolayer Based on HSE06

Table S2 Configurations of $OsN_2$ from global searches based on CALYPSO package. The configuration of which the HER properties were studied is marked **in bold**.

| Configuration | Relative Energy (eV) | Space Group |
|---|---|---|
|  | 0 | Pmmm |

| | | |
|---|---|---|
|  | **0.045** | **P-4m2** |
|  | 0.080955 | Pmmm |
|  | 0.15642 | Cm2m |
|  | 0.34571 | C2mm |
|  | 0.3469 | Cm2m |

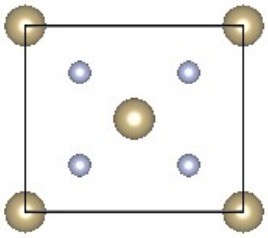
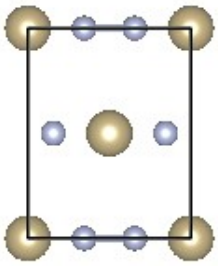
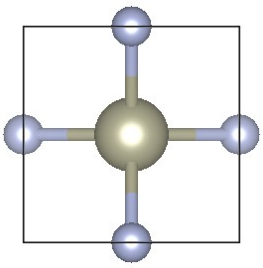
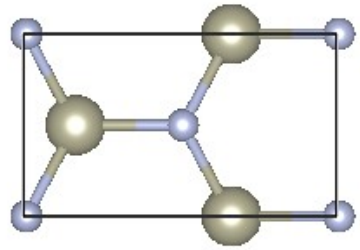
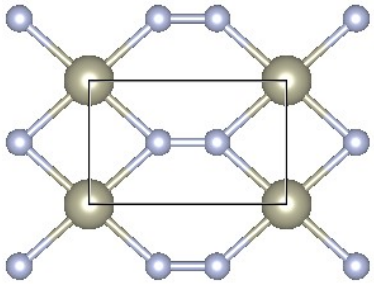
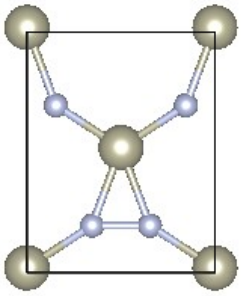
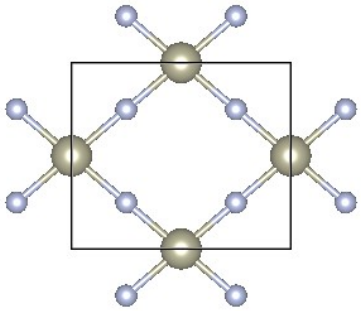
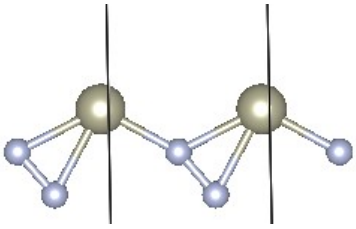
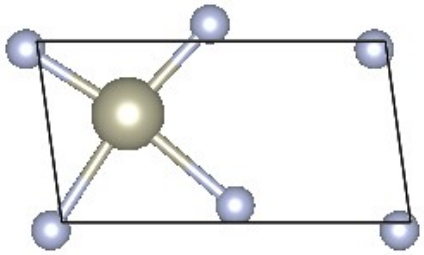
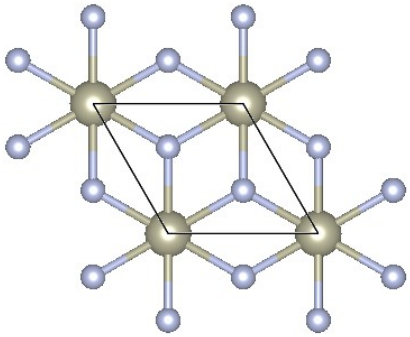
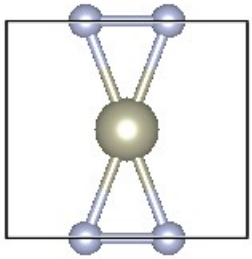
| | | |
|---|---|---|
|  | 0.53844 | Cmmm |
|  | 0.92264 | Cmm2 |

Table S3 Configurations of $ReN_2$ from global searches based on CALYPSO package. The configuration of which the HER properties were studied is marked **in bold**.

| Configuration | Relative Energy (eV) | Space Group |
|---|---|---|
|  | **0** | **P-4m2** |
| | 0.09 | Cm |

| | | |
|---|---|---|
|  | | |
|  | 0.3051 | Pmmm |
|  | 0.62047 | Cm2m |
|  | 0.77734 | Cmmm |
|  | 0.82168 | P1 |

| | | |
|---|---|---|
|  | 1.14912 | Pm |
|  | 1.30142 | P6mm |
|  | 1.32866 | Pmmm |