

# Supplementary information

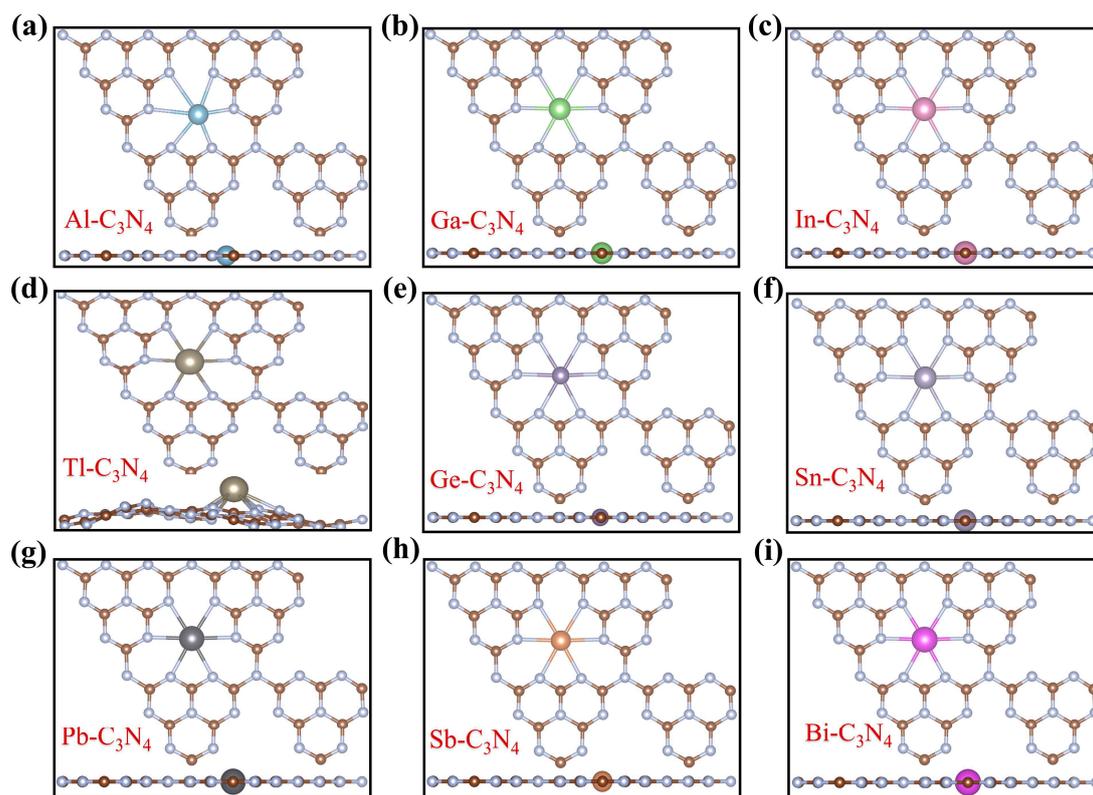
## Theoretical study of *p*-block metal single atom loaded carbon nitride catalyst for photocatalytic water splitting

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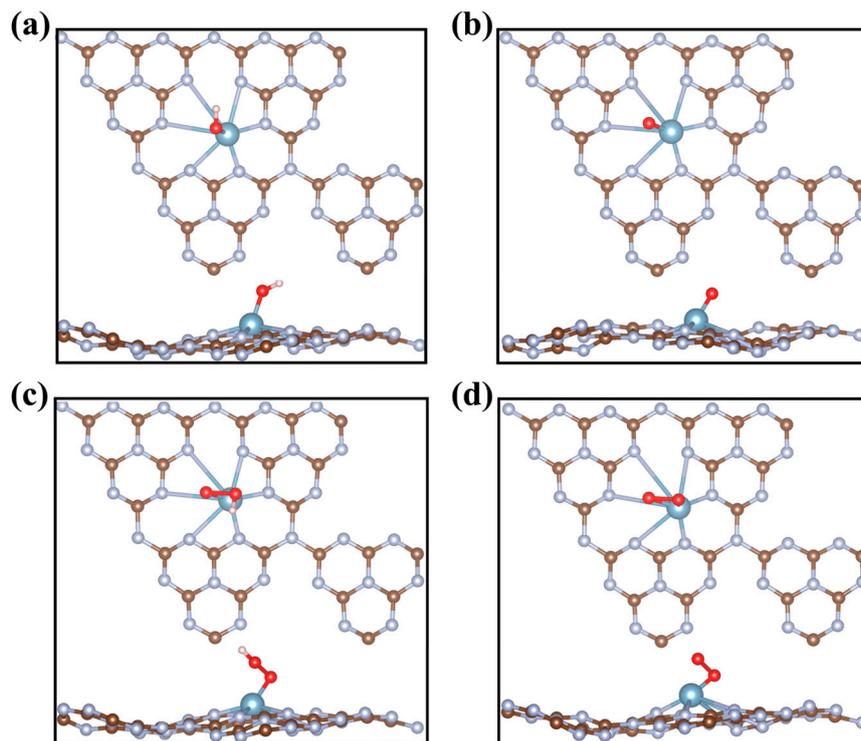
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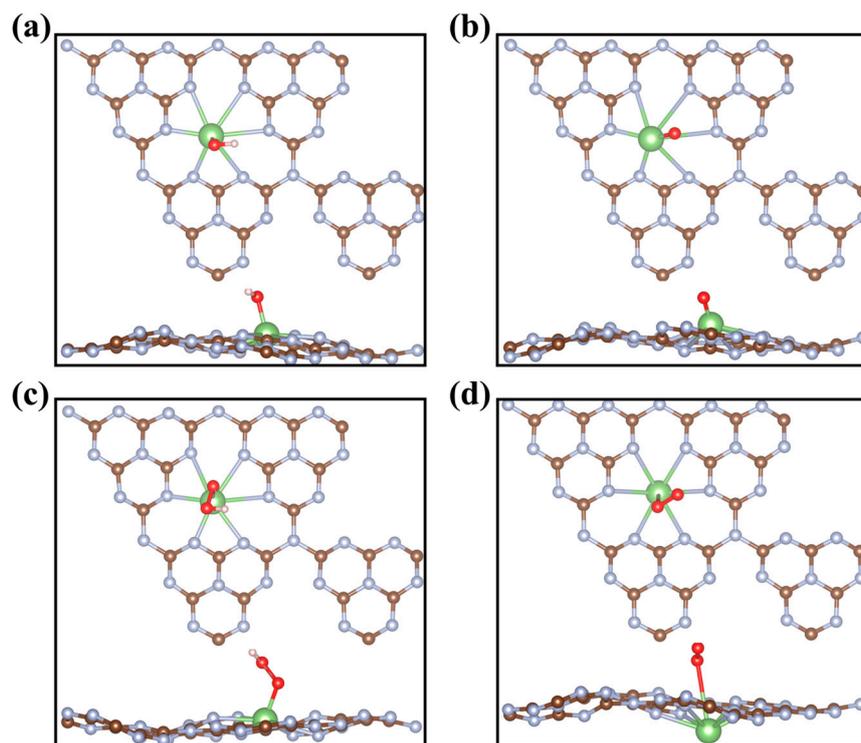
**Figure S1.** Optimized structures of PM-C<sub>3</sub>N<sub>4</sub> (PM = Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi). Color scheme: brown, carbon; greyish-white, nitrogen.

**Table S1.** The average bond length between the PM and nitrogen atoms in PM-C<sub>3</sub>N<sub>4</sub>.

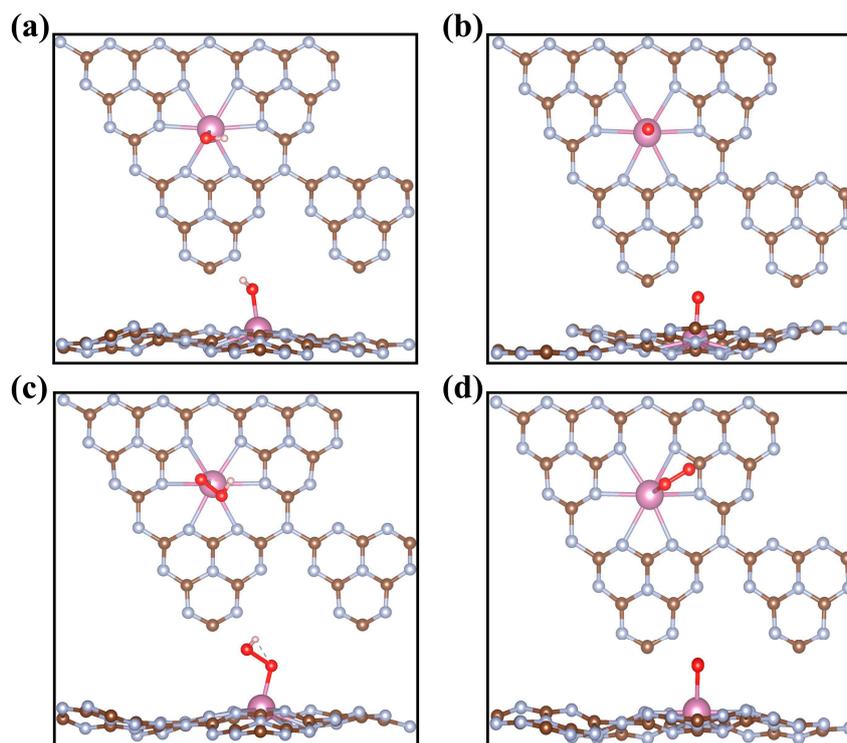
|                | <b>p-block metal (PM)</b> | <b>L(PM-N) (Å)</b> |
|----------------|---------------------------|--------------------|
| The IIIA group | Al                        | 2.39               |
|                | Ga                        | 2.40               |
|                | In                        | 2.42               |
| The IVA group  | Ge                        | 2.35               |
|                | Sn                        | 2.42               |
|                | Pb                        | 2.44               |
| The VA group   | Sb                        | 2.40               |
|                | Bi                        | 2.43               |



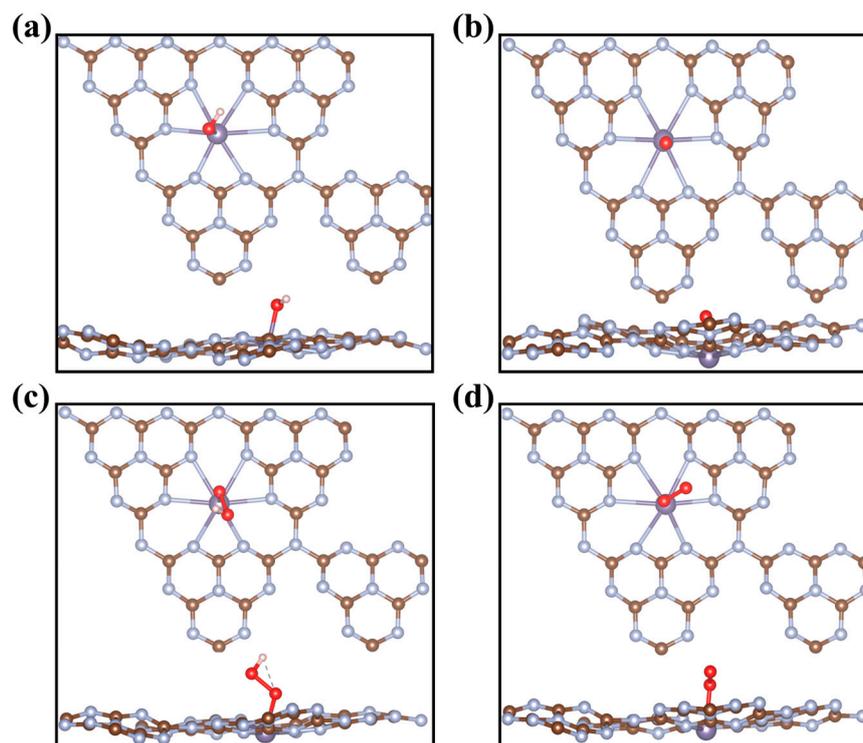
**Figure S2.** Optimized structures for intermediates during OER catalyzed by Al-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates. Color scheme: red, oxygen.



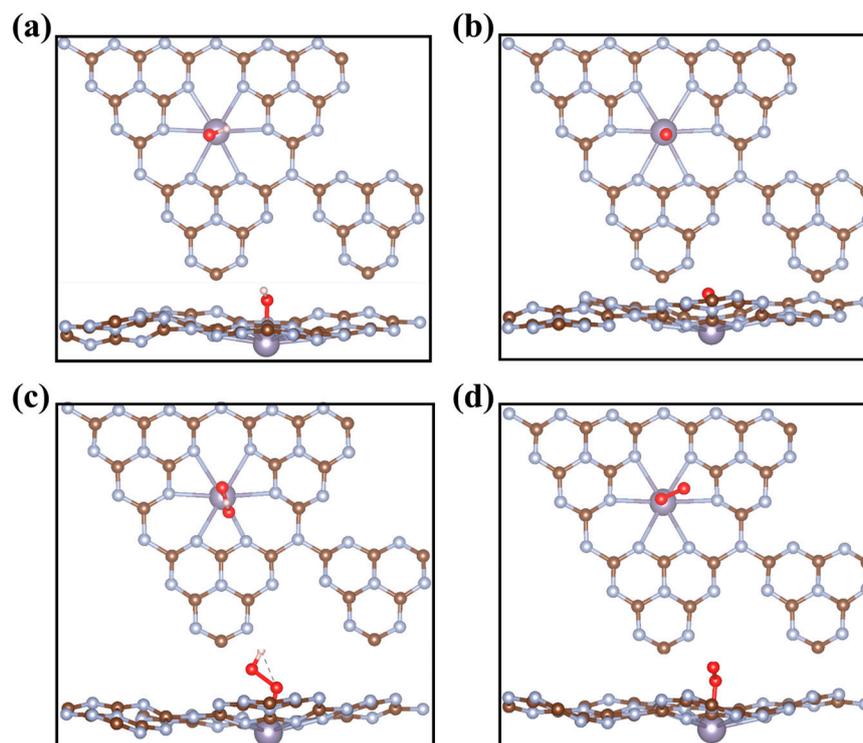
**Figure S3.** Optimized structures for intermediates during OER catalyzed by Ga-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates.



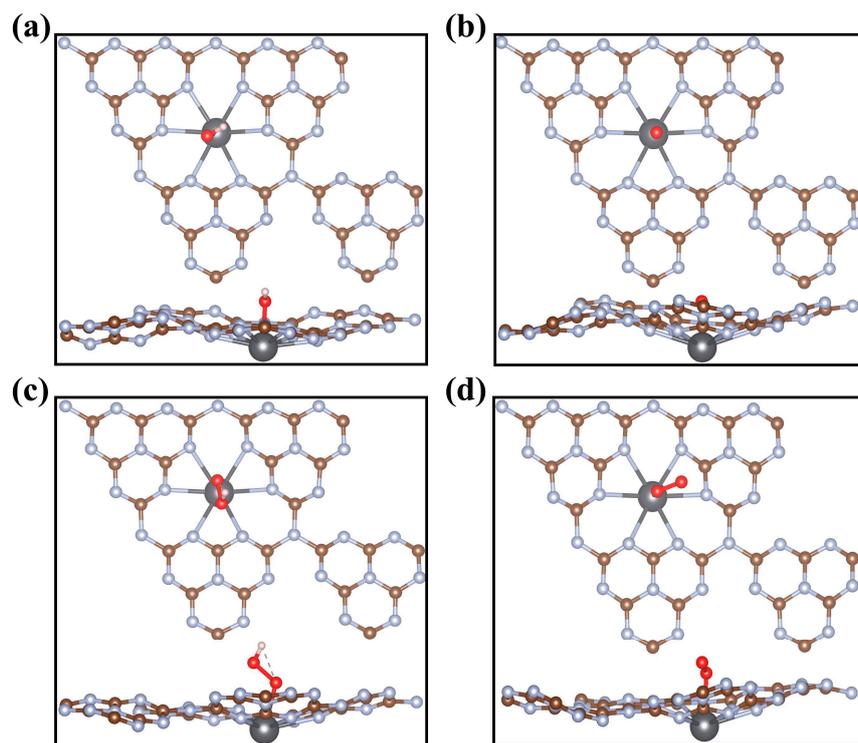
**Figure S4.** Optimized structures for intermediates during OER catalyzed by In-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates.



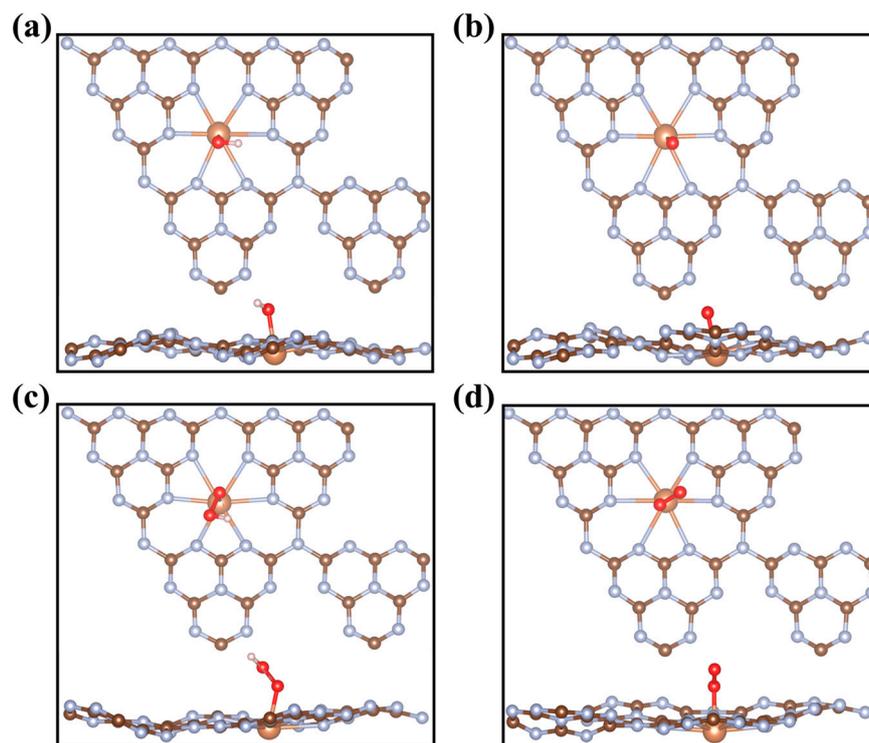
**Figure S5.** Optimized structures for intermediates during OER catalyzed by Ge-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates.



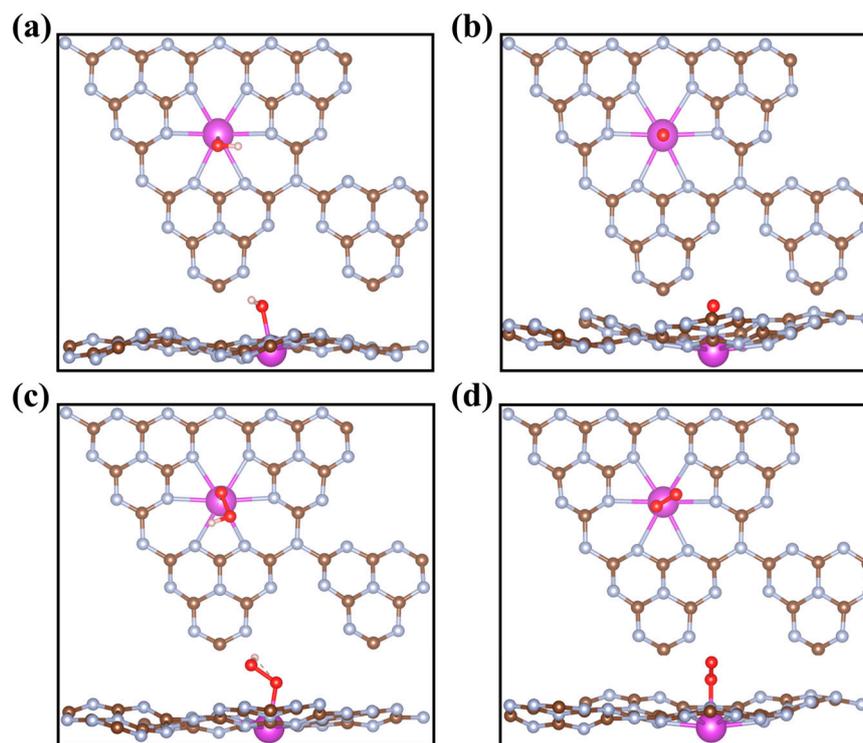
**Figure S6.** Optimized structures for intermediates during OER catalyzed by Sn-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates.



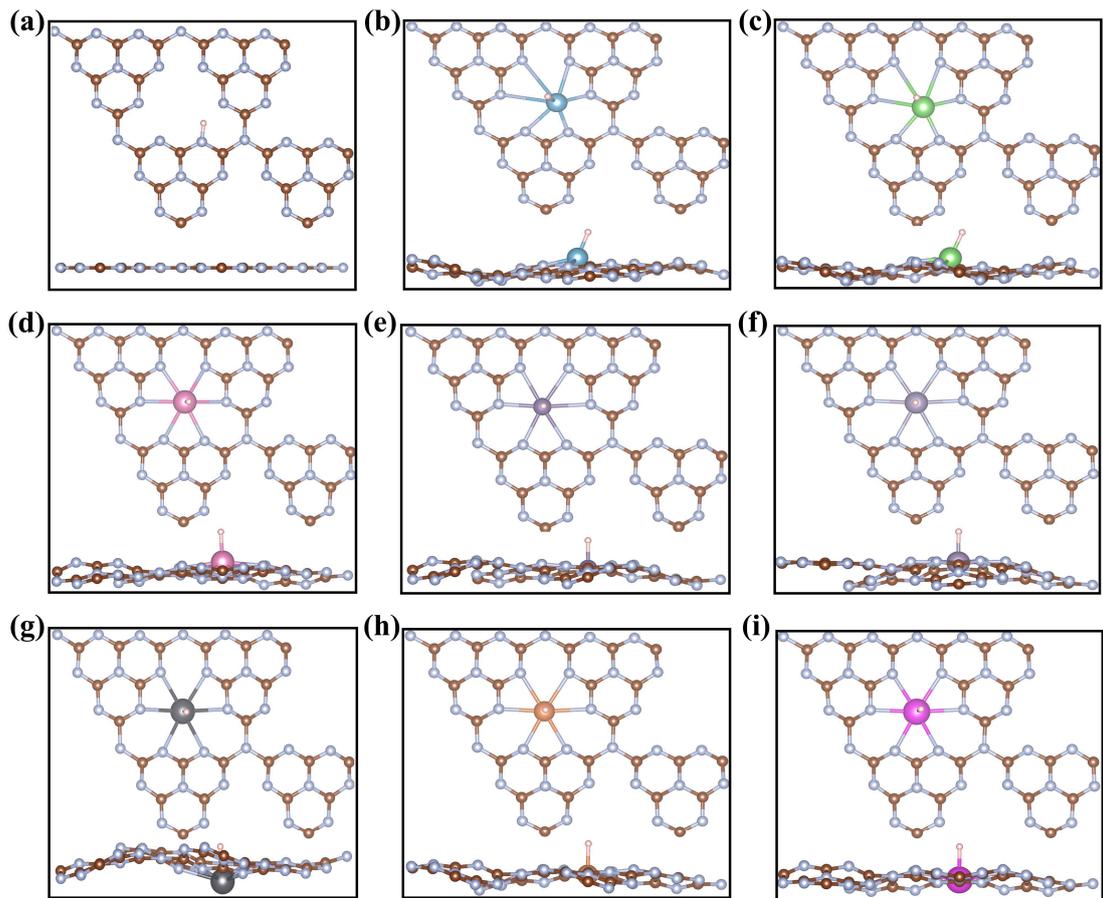
**Figure S7.** Optimized structures for intermediates during OER catalyzed by Pb-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates.



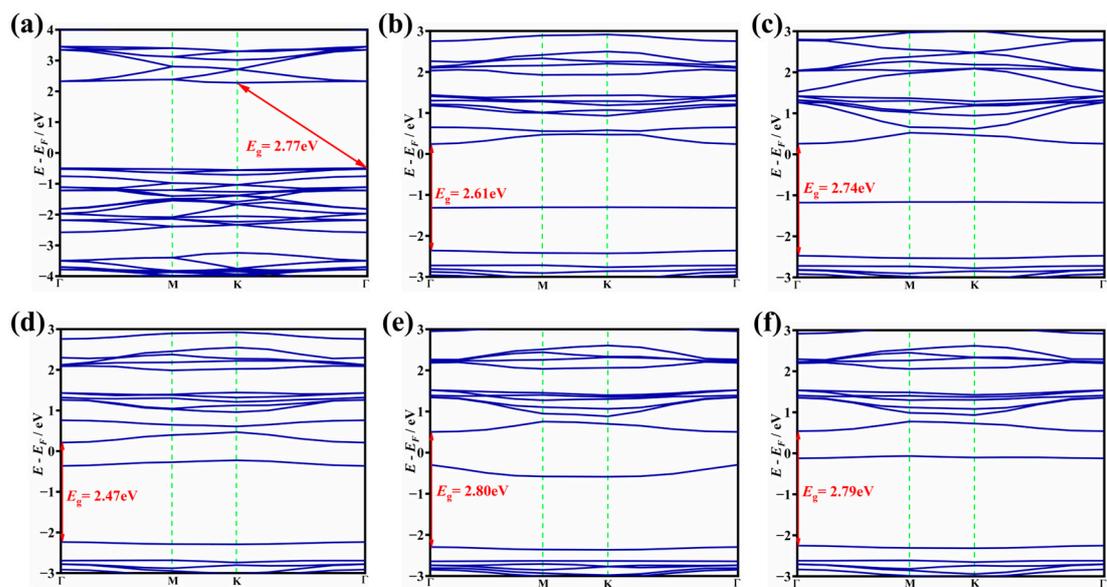
**Figure S8.** Optimized structures for intermediates during OER catalyzed by Sb-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates.



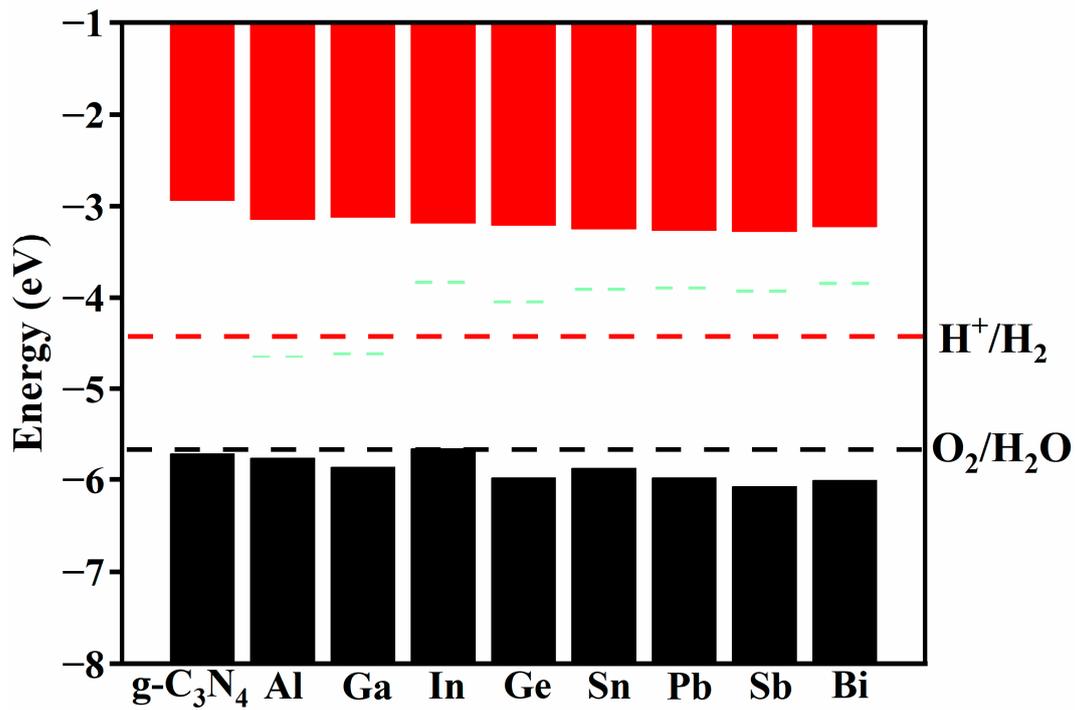
**Figure S9.** Optimized structures for intermediates during OER catalyzed by Bi-C<sub>3</sub>N<sub>4</sub>. (a) \*OH; (b) \*O; (c) \*OOH; (d) \*OO intermediates.



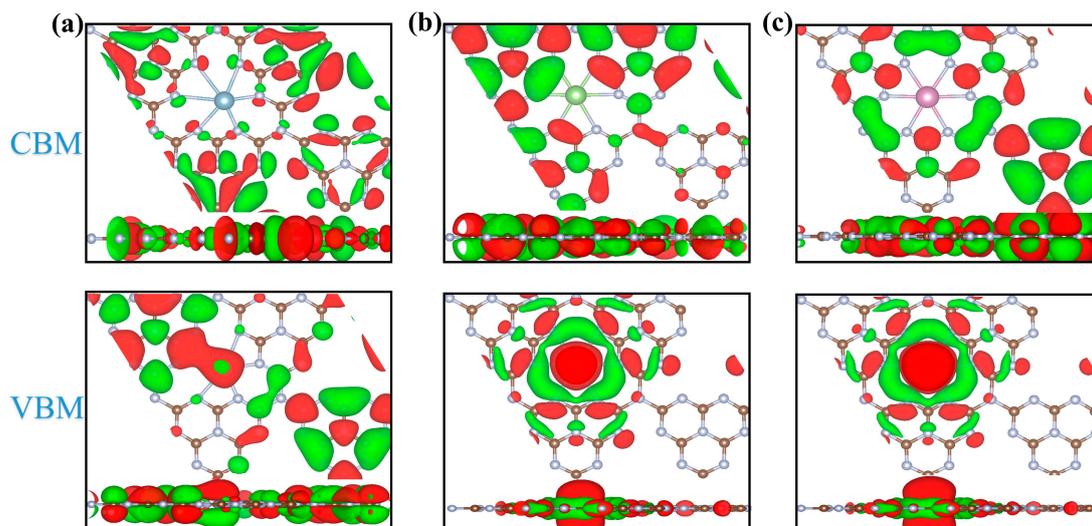
**Figure S10.** Optimized structures for \*H on  $g\text{-C}_3\text{N}_4$  and  $\text{PM-C}_3\text{N}_4$ . (a)  $g\text{-C}_3\text{N}_4$ ; (b)  $\text{Al-C}_3\text{N}_4$ ; (c)  $\text{Ga-C}_3\text{N}_4$ ; (d)  $\text{In-C}_3\text{N}_4$ ; (e)  $\text{Ge-C}_3\text{N}_4$ ; (f)  $\text{Sn-C}_3\text{N}_4$ ; (g)  $\text{Pb-C}_3\text{N}_4$ ; (h)  $\text{Sb-C}_3\text{N}_4$  and (i)  $\text{Bi-C}_3\text{N}_4$ .



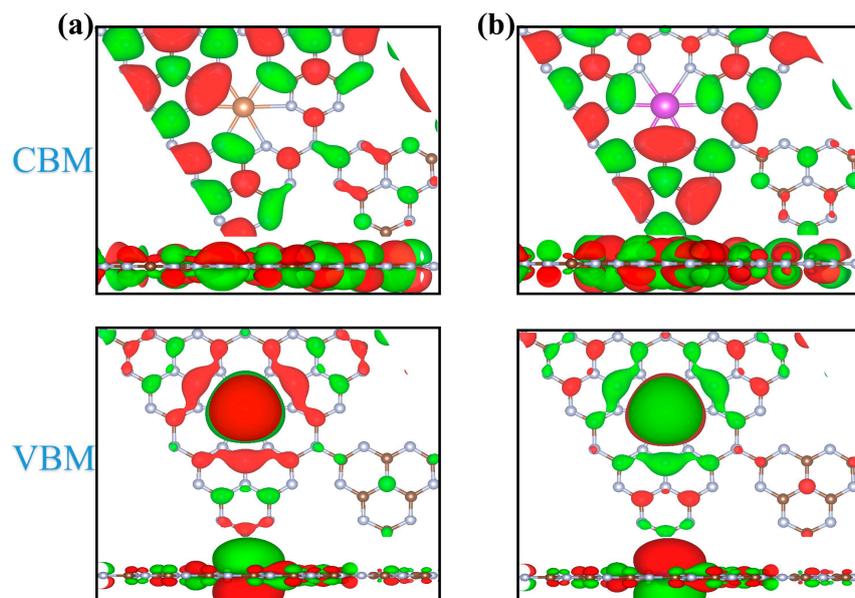
**Figure S11.** The electronic band structures of  $g\text{-C}_3\text{N}_4$  and  $\text{PM-C}_3\text{N}_4$ . (a)  $g\text{-C}_3\text{N}_4$ ; (b)  $\text{Al-C}_3\text{N}_4$ ; (c)  $\text{Ga-C}_3\text{N}_4$ ; (d)  $\text{In-C}_3\text{N}_4$ ; (e)  $\text{Sb-C}_3\text{N}_4$  and (f)  $\text{Bi-C}_3\text{N}_4$ .



**Figure S12.** Band edges (i.e., VBM and CBM) alignment of  $g\text{-C}_3\text{N}_4$  and PM- $\text{C}_3\text{N}_4$  corresponding to the redox potential for water splitting. The green dash-lines represent the doping energy level.



**Figure S13.** The isosurface (isolevel:  $0.008 \text{ e}/\text{\AA}^3$ ) of band-decomposed electron density for the CBM (upper) and VBM (bottom) of PM- $\text{C}_3\text{N}_4$  (PM=Al, Ga, In). (a) Al- $\text{C}_3\text{N}_4$ ; (b) Ga- $\text{C}_3\text{N}_4$  and (c) In- $\text{C}_3\text{N}_4$ .



**Figure S14.** The isosurface (isolevel:  $0.008 \text{ e}/\text{\AA}^3$ ) of band-decomposed electron density for the CBM (upper) and VBM (bottom) of PM-C<sub>3</sub>N<sub>4</sub> (PM=Sn, Bi). (a) Sn-C<sub>3</sub>N<sub>4</sub> and (b) Bi-C<sub>3</sub>N<sub>4</sub>.