

Electronic Supplementary Information

Two-dimensional MgX₂Se₄ (X=Al, Ga) Monolayer with Tunable Electronic Properties for Optoelectronic and Photocatalytic Applications

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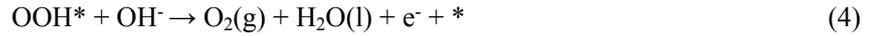
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Calculation method for photocatalytic OER and HER overpotentials

We compute the theoretical overpotential for the OER and HER by using DFT methods and the computational hydrogen electrode model.¹ This method has been shown to be successful in predicting trend of electrochemical activity on oxide surfaces^{2,3} and metal embedded nitrogen-doped graphene (M-NG)^{4,5}. For OER, the overall reaction scheme can be expressed as:



As for HER, the overall reaction scheme can be written as:



For each elementary step in OER and HER, the Gibbs reaction free energy ΔG is defined as the difference between free energies of the initial and final states, and is given by the following expression:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (6)$$

where ΔE is the computed reaction energy of reactant and product molecules adsorbed on catalyst surface; ΔZPE and ΔS are the change in zero-point energies and entropy in the reaction. The bias effect on the free energy of each initial, intermediate and final state involving electron transfer in the electrode is also taken into account by shifting the energy of the state by $\Delta G_U = -neU$, where U is the applied electrode potential, e is the transferred charge, and n is the number of proton-electron transferred pairs. The change in free energy due to the effect of pH value of the electrolyte is considered by the correction of H^+ concentration ($[\text{H}^+]$), $\Delta G_{pH} = -k_B T \ln [\text{H}^+] = pH \times k_B T \ln 10$, where k_B is the Boltzmann constant and T is the temperature (298 K). Given that the high-spin ground state of the oxygen molecule is poorly described in DFT calculations, the free energy of the O_2 molecule is determined by $G_{\text{O}_2}(\text{g}) = 2G_{\text{H}_2\text{O}}(\text{l}) - 2G_{\text{H}_2}(\text{g}) + 4 \times 1.23(\text{eV})$. The free energy of OH^- is derived as $G_{\text{OH}^-} = G_{\text{H}_2\text{O}}(\text{l}) + e^- - 1/2G_{\text{H}_2}(\text{g})$. The free energy of gas-phase water is calculated at 0.035 bars because this is the equilibrium pressure in contact with liquid water at 298 K. The free energy of gas-phase water at these conditions is equal to the free energy of liquid water.

To evaluate the adsorption strength of OH^* , O^* and OOH^* , the adsorption energy of these species is calculated by using DFT method with the equation:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{catalyst}} - E_{\text{adsorbate}}, \quad (7)$$

where, E_{catalyst} is the energy of the bare catalyst, $E_{\text{adsorbate}}$ is the energy of the free O, OH OOH or H species in the gas phase, and E_{total} is the total energy of the catalyst with adsorbents. Based on

the adsorption energies, we can obtain the adsorption free energy of O*, OH*, OOH* and H*. To obtain the exact free energy of O*, OH*, OOH* and H* radicals in the electrolyte solution, the adsorption free energies ΔG_{O^*} , ΔG_{OH^*} , ΔG_{OOH^*} and ΔG_{H^*} are relative to the free energy of appropriate stoichiometric amounts of H₂O (g) and H₂ (g), defined as follows:

$$\begin{aligned}\Delta G_{O^*} &= \Delta G(H_2O(g) + * \rightarrow O^* + H_2(g)) \\ &= (E_{O^*} + E_{H_2} - E_{H_2O} - E_*) + (E_{ZPE(O^*)} + E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(*)}) \\ &\quad - T \times (S_{O^*} + S_{H_2} - S_{H_2O} - S_*)\end{aligned}\tag{8}$$

$$\begin{aligned}\Delta G_{OH^*} &= \Delta G(H_2O(g) + * \rightarrow OH^* + 1/2H_2(g)) \\ &= (E_{OH^*} + 1/2E_{H_2} - E_{H_2O} - E_*) + (E_{ZPE(OH^*)} + 1/2E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(*)}) \\ &\quad - T \times (S_{OH^*} + 1/2S_{H_2} - S_{H_2O} - S_*)\end{aligned}\tag{9}$$

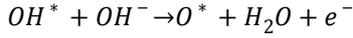
$$\begin{aligned}\Delta G_{OOH^*} &= \Delta G(2H_2O(g) + * \rightarrow OOH^* + 3/2H_2(g)) \\ &= (E_{OOH^*} + 3/2E_{H_2} - 2E_{H_2O} - E_*) + (E_{ZPE(OOH^*)} + 3/2E_{ZPE(H_2)} - 2E_{ZPE(H_2O)} - E_{ZPE(*)}) \\ &\quad - T \times (S_{OOH^*} + 3/2S_{H_2} - 2S_{H_2O} - S_*)\end{aligned}\tag{10}$$

$$\begin{aligned}\Delta G_{H^*} &= \Delta G(H^+ + e^- + * \leftrightarrow H^*) \\ &= (E_{H^*} - 1/2E_{H_2} - E_*) + (E_{ZPE(H^*)} - 1/2E_{ZPE(H_2)} - E_{ZPE(*)}) - T \times (S_{H^*} - 1/2S_{H_2} - S_*)\end{aligned}\tag{11}$$

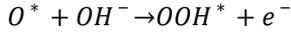
The reaction free energy of (1)-(4) for the OER can be determined from the following equations:

$$\begin{aligned}OH^- + * &\rightarrow OH^* + e^- \\ \Delta G_1 &= G_{OH^*} + G_{e^-} - G_{OH^-} - G_* \\ &= G_{OH^*} + G_{e^-} - (G_{H_2O}(l) + G_{e^-} - 1/2G_{H_2}(g)) - G_* \\ &= G_{OH^*} + 1/2G_{H_2}(g) - G_{H_2O}(l) - G_* \\ &= \Delta G_{OH^*}\end{aligned}$$

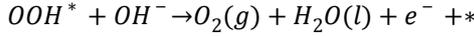
(12)



$$\begin{aligned} \Delta G_2 &= G_{O^*} + G_{H_2O} + G_{e^-} - G_{OH^-} - G_{OH^*} \\ &= G_{O^*} + G_{H_2O} + G_{e^-} - (G_{H_2O}(l) + G_{e^-} - 1/2G_{H_2}(g)) - G_{OH^*} \\ &= (G_{O^*} + G_{H_2} - G_{H_2O}(l) - G_{e^-}) - (G_{OH^*} + 1/2G_{H_2}(g) - G_{H_2O}(l) - G_{e^-}) \\ &= \Delta G_{O^*} - \Delta G_{OH^*} \end{aligned} \quad (13)$$



$$\begin{aligned} \Delta G_3 &= G_{OOH^*} + G_{e^-} - G_{O^*} - G_{OH^-} \\ &= G_{OOH^*} + G_{e^-} - G_{O^*} - (G_{H_2O}(l) + G_{e^-} - 1/2G_{H_2}(g)) \\ &= (G_{OOH^*} + 3/2G_{H_2}(g) - 2G_{H_2O}(l) - G_{e^-}) - (G_{O^*} + G_{H_2}(g) - G_{H_2O}(l) - G_{e^-}) \\ &= \Delta G_{OOH^*} - \Delta G_{O^*} \end{aligned} \quad (14)$$



$$\begin{aligned} \Delta G_4 &= G_{O_2}(g) + G_{H_2O}(l) + G_{e^-} + * - G_{OOH^*} - G_{OH^-} \\ &= (2G_{H_2O}(l) - 2G_{H_2}(g) + 4 \times 1.23) + G_{H_2O}(l) + G_{e^-} + * \\ &\quad - G_{OOH^*} - (G_{H_2O}(l) + G_{e^-} - 1/2G_{H_2}(g)) \\ &= 2G_{H_2O}(l) - 1/2G_{H_2}(g) + * - G_{OOH^*} \\ &= 4.92 - \Delta G_{OOH^*} \end{aligned} \quad (15)$$

With this approach, the theoretical overpotential (η^{OER}) at standard conditions is defined as:

$$\eta^{OER} = (G^{OER} / e) - 1.23 \quad (16)$$

where G^{OER} is the potential determining step defined as the highest free energy step in the process of OER and e is unit charge.

The HER performance is examined by computing the reaction free energy (ΔG_{H^*}) for H adsorption based on the computational hydrogen electrode model^[1] at 0 eV. That is, the equilibrium potential of the HER:

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE(H)} - T\Delta S_H \quad (17)$$

ΔE_H is the hydrogen adsorption energy based on DFT calculation. $\Delta E_{ZPE(H)}$ is the zero-point

energy difference between the hydrogen adsorbed state and the gas-phase state of hydrogen obtained from vibrational frequency calculation. ΔS_H is the entropy difference due to hydrogen adsorption. Here we approximate the entropy changes of hydrogen adsorption as $\Delta S_H \approx 1/2(\Delta S_{H_2})$, where S_{H_2} is the entropy of gas phase H_2 at standard conditions (25 °C, 1 bar). The theoretical overpotential η for HER is determined by ΔG_{H^*} :

$$\eta^{\text{HER}} = |\Delta G_{H^*}| / e \quad (18)$$

Like previous theoretical studies⁶, H^* , OH^* and OOH^* can form H-bonds with H_2O due to the solvent effect. Hence, their adsorption free energies decrease. Here, the correction energies are added to the electronic energy of the state to represent the total Gibbs free energy of the state. The latter will be used to calculate the Gibbs free energy of reaction.

Table S1. Computed zero-point energies, entropy and the corrections (ΔG_{corr} (eV)) of the adsorbates presented in the reaction.

	$\Delta ZPE(\text{eV})$		$T\Delta S(\text{eV})$	$\Delta G_{\text{corr}}(\text{eV})$
	MgGa_2Se_4	MgAl_2Se_4		
H_2O	0.57	0.57	0.58	
H_2	0.27	0.27	0.41	
H	0.13	0.13		0.11
O	0.07	0.07		
OH	0.34	0.41		0.30
OOH	0.37	0.37		0.40

Table S2. Computed adsorption free energy (eV) of the adsorbates in the reaction, and the overpotentials (V) for HER and ORR.

	$\Delta G_H(\text{eV})$	$\Delta G_O(\text{eV})$	$\Delta G_{OH}(\text{eV})$	$\Delta G_{OOH}(\text{eV})$	$\eta^{\text{HER}}(\text{V})$	$\eta^{\text{OER}}(\text{V})$
MgGa_2Se_4	0.82	2.17	1.28	4.50	0.70	0.82
MgAl_2Se_4	0.99	2.57	1.45	4.82	0.62	0.99

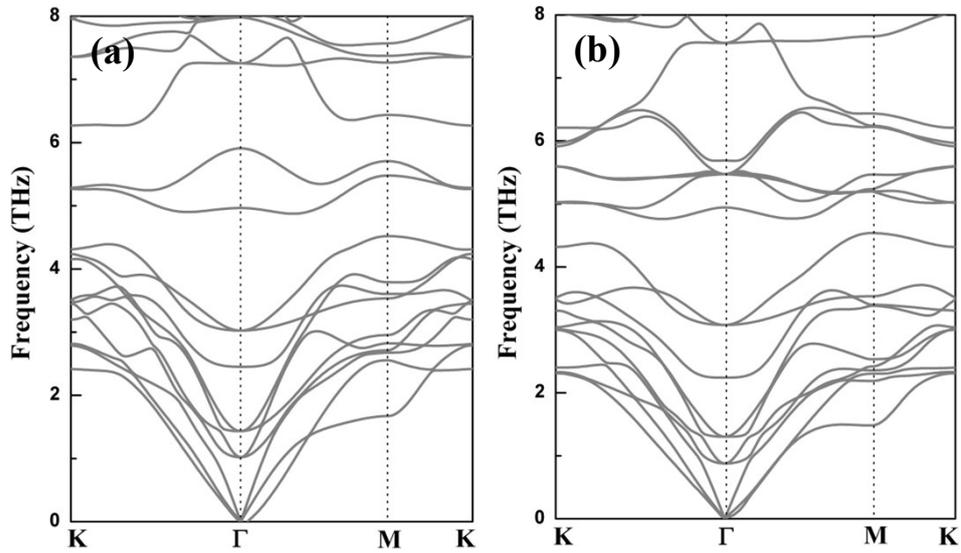


Figure S1. Computed phonon spectra of the monolayer (a) MgAl_2Se_4 and (b) MgGa_2Se_4 .

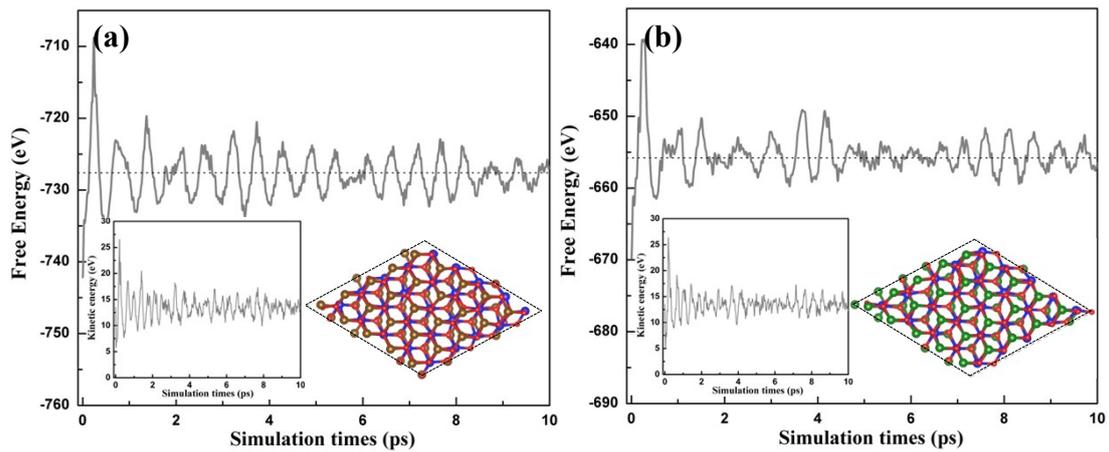


Figure S2. The free energy and kinetic energy versus the AIMD simulation steps; final equilibrium structures (inset) at $T = 600$ K for (a) monolayer MgAl_2Se_4 and (b) monolayer MgGa_2Se_4 , respectively.

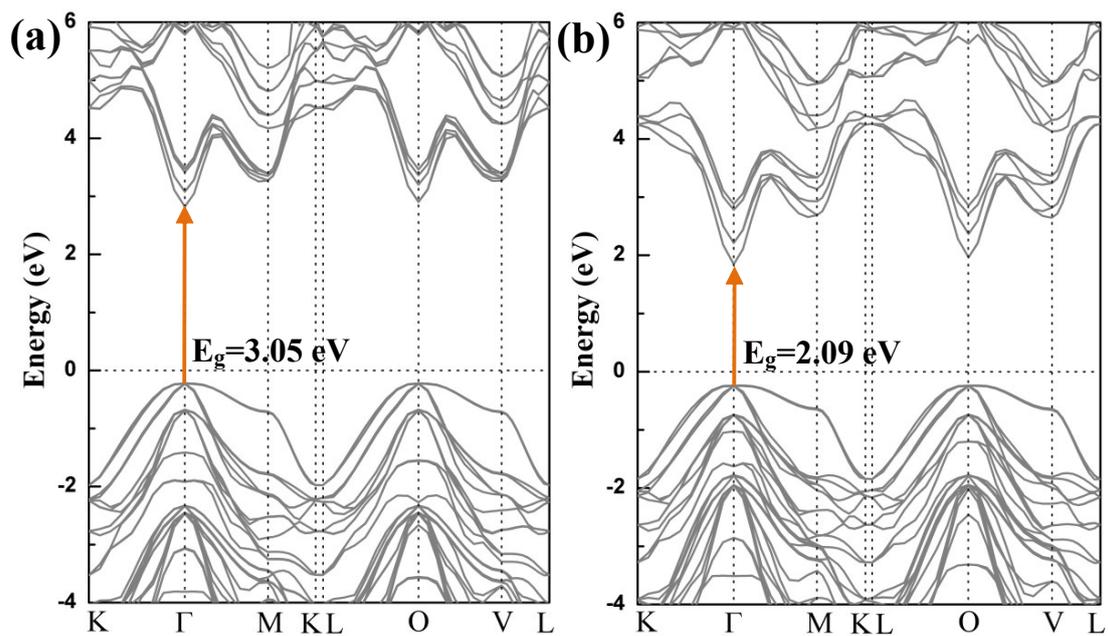


Figure S3. Computed band structures of (a) bulk MgAl_2Se_4 and (b) bulk MgGa_2Se_4 at the HSE06 level. The Fermi level is set to 0 eV.

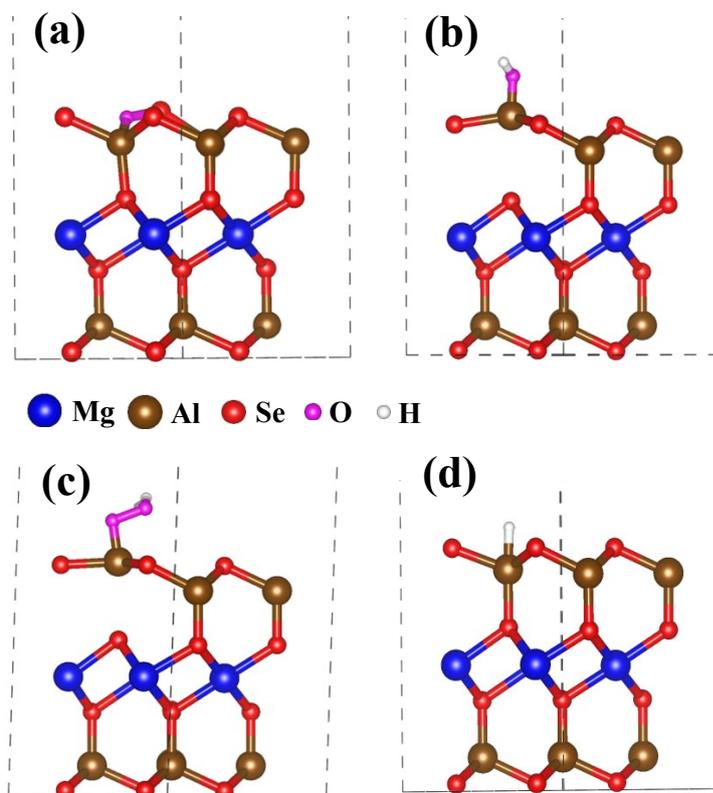


Figure S4. Atomic structure of adsorbate on the surface of monolayer MgAl_2Se_4 . (a) O, (b) OH, (c) OOH, (d) H.

Supplementary Reference

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