Supporting Information

Two-dimensional superatomic B_6O_2 monolayer for photocatalytic water splitting

Changcheng Wu[1], Qinqin Yuan[1*], Dan Li[1], and Longjiu Cheng[1,2*]

[1]*Department of Chemistry, Anhui University, Hefei, 230601, P. R. China.*

[2]*Key Laboratory of Structure and Functional Regulation of Hybrid Materials (Anhui University), Ministry of Education, Hefei, 230601, P. R. China.*

*Corresponding authors. Email: qinqinyuan@ahu.edu.cn, clj@ustc.edu

Contents

P13 References

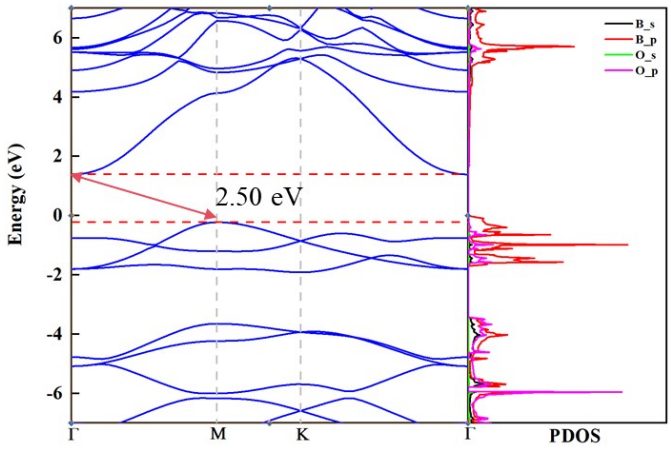

Fig. S1 Electronic band structure and PDOS of B_6O_2 monolayers by PBE.

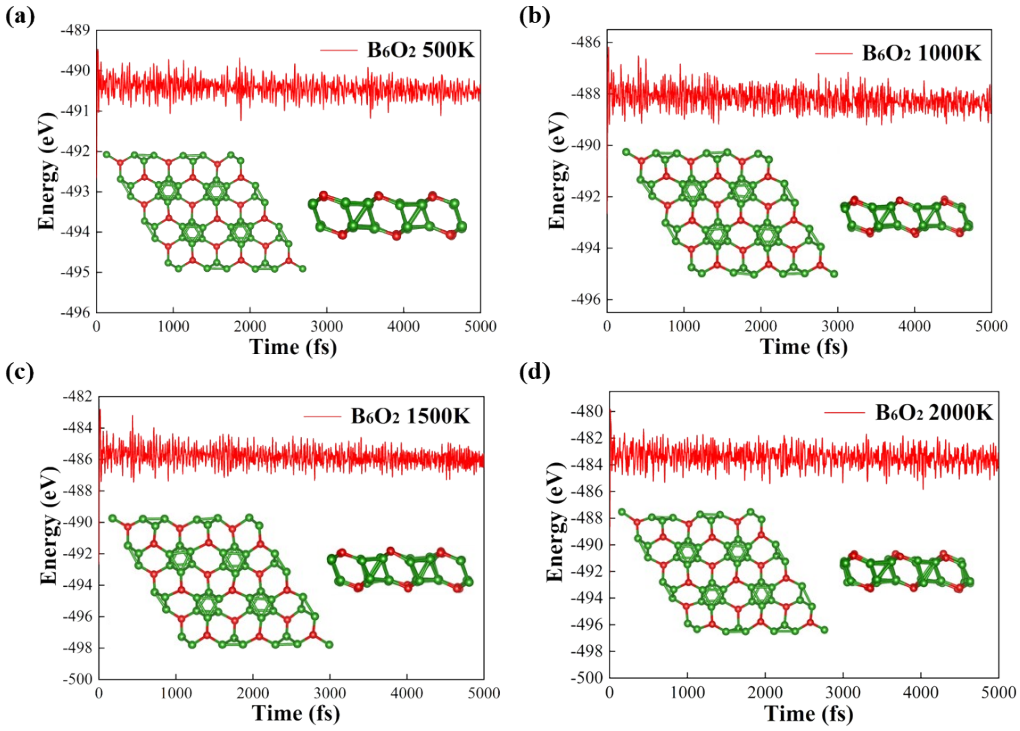

Fig. S2 AIMD simulation of B_6O_2 monolayer at (a) 500 K (b) 1000 K (c)1500 K (d) 2000 K showing energy fluctuation with time step and its snapshot image (top and side views).

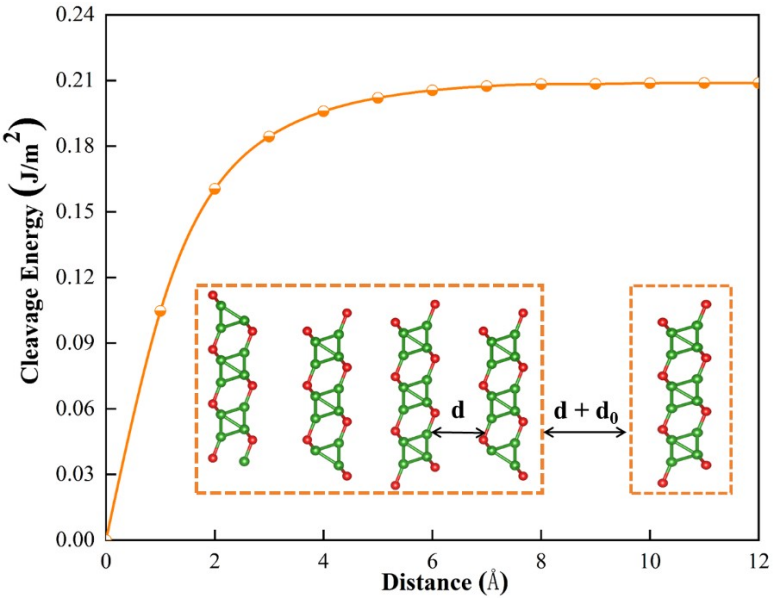

Fig. S3 Cleavage energy of B_6O_2 calculated by exfoliating the top layer from the five-layer slab.

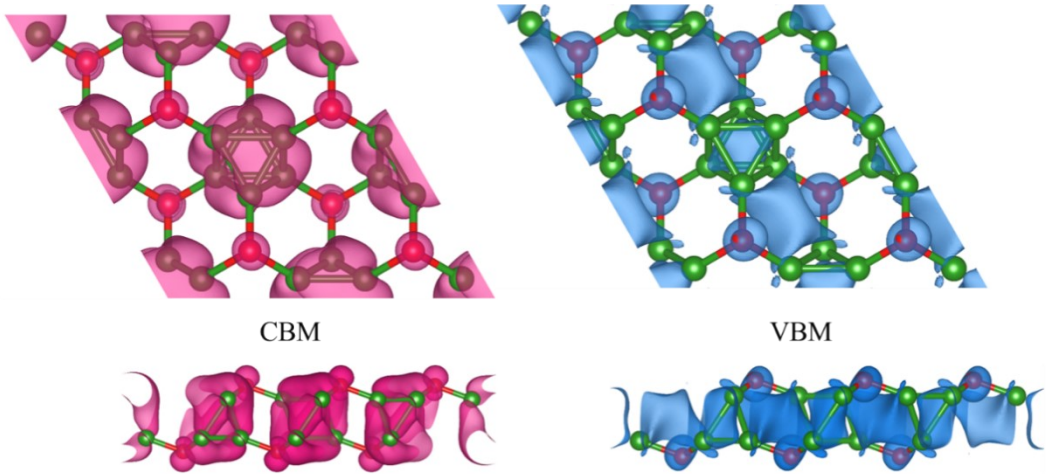

Fig. S4 The charge distributions of the B_6O_2 monolayer relative to the conduction band minimum (CBM) and valence band minimum (VBM) are represented by red and blue, respectively. The value of the isosurface is set to 0.007 e/Å^3.

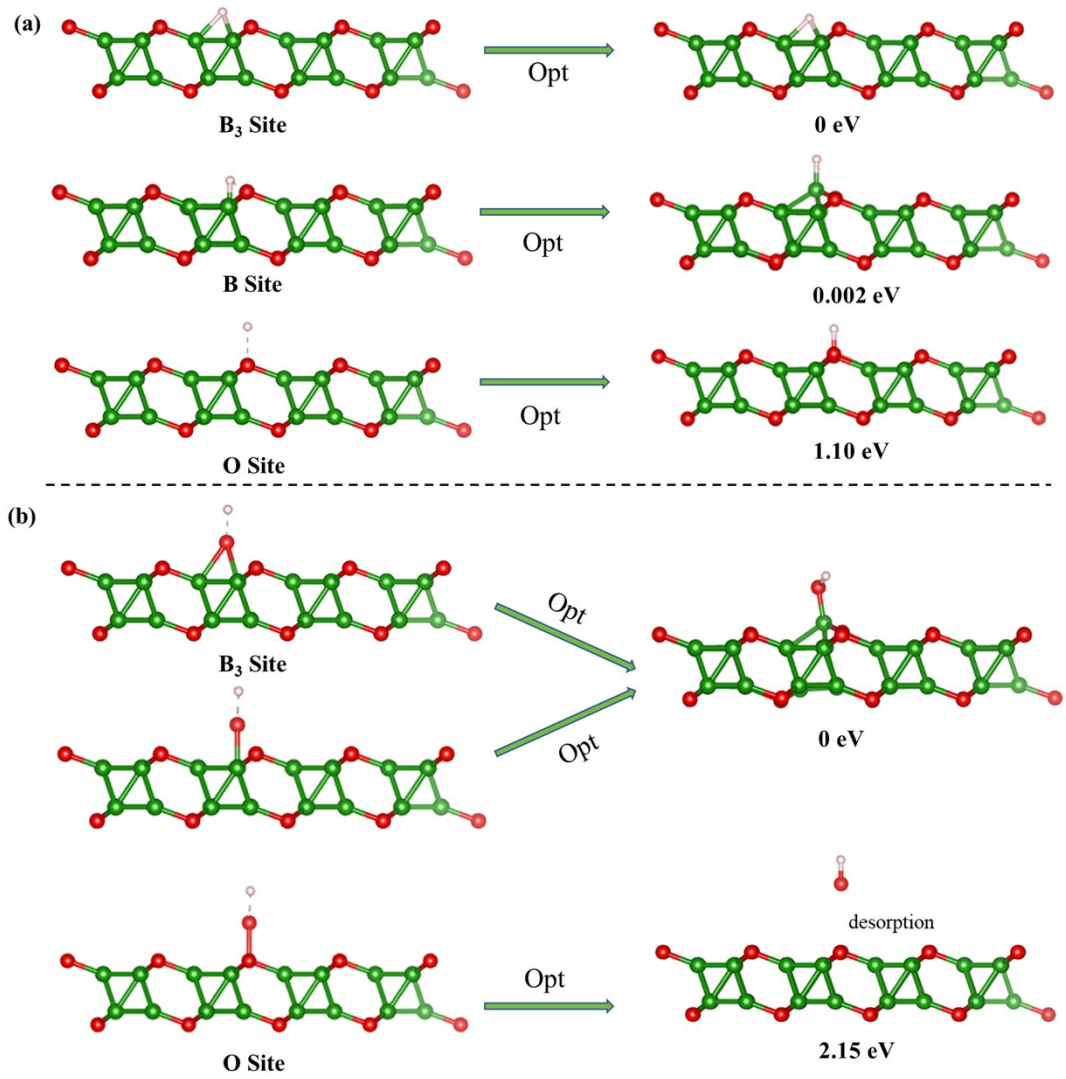

Fig. S5 The initial and optimized structures of three possible active sites on B_6O_2 monolayer for (a) *OH and (b) *H, respectively. B-site, O-site and B_3-site denote that *OH/*H is absorbed above the B atom, above the O atom, and above the center of the B_3. The relative energy (RE, in eV) is listed under the optimized structure.

TABLE S1 Optimized cell parameters and bond lengths (Å) of B_6O_2 monolayer at different biaxial strain values.

Strain	**a (Å)**	**b (Å)**	**Bond lengths (Å)**	
			B-B	B-O
+5%	4.32	4.32	1.76	1.54
+2%	4.20	4.2	1.76	1.51
0	4.12	4.12	1.75	1.49
-2%	4.03	4.03	1.75	1.48
-5%	3.91	3.91	1.74	1.46

TABLE S2: Total energy *(E)*, zero-point energy correction (ΔE_{zpe}), entropy contribution (TS, T = 298.15 K) and Gibbs free energy (G) of related species for water splitting on the B_6O_2 monolayer. All values are in eV.

Species	*E*	E_{zpe}	TS	*G*
H_2	-6.76	0.27	0.400	-6.89
H_2O	-14.22	0.57	0.670	-14.32
OH*	-509.20	0.39	0.072	-508.88
O*	-504.76	0.30	0.147	-504.61
OOH*	-513.26	0.46	0.181	-512.98
H*	-501.02	0.21	0.004	-500.81

TABLE S3: Structural information of the predicted B_6O_2 monolayer.

Space Group	Lattice Parameters (Å, °)	Atoms	Fractional Coordinates		
			x	y	z
Pm1	a = 4.11505	B1	0.48758	0.84452	9.27100
	b = 4.11505	B2	2.58857	2.05753	9.27100
	c = 20.0000	B3	0.48758	3.27053	9.27100
	α = 90.0000	B4	0.97517	0.00000	10.72900
	β = 90.0000	B5	3.07616	-1.21300	10.72900
	γ = 120.0000	B6	3.07616	1.21300	10.72900
		O1	2.37582	0.00000	11.24182
		O2	1.18791	2.05752	8.75818

1: Calculation the oxidation and reduction potential ($E^{oxd}_{O2/H2O}$ and $E^{red}_{H+/H2}$) for Photocatalytic Water Splitting

Standard redox potential exhibits a strong dependence on ambient pH, and this thermodynamic correlation can be mathematically described by the following equation[1]:

$$E^{oxd}_{O2/H2O} = -5.67 + pH \times 0.059 \text{ (eV)} \quad (1)$$

$$E^{red}_{H+/H2} = -4.44 + pH \times 0.059 \text{ (eV)} \quad (2)$$

When pH = 7, the oxidation potential of water is -5.26 eV and the reduction potential is -4.03 eV.

2: Calculation photogenerated electrons for hydrogen reduction reaction (U_e)/ holes for water oxidation (U_h)

Based on previous studies[2-3]:

$$U_h = VBM - 4.03 \text{ (eV)} \quad (3)$$

$$U_e = 4.03 - CBM \text{ (eV)} \quad (4)$$

3: Calculation details of the free energy difference (ΔG) for Photocatalytic Water Splitting on the B_6O_2 monolayer.

For the OER and HER processes, their free energy differences (ΔG) were evaluated according to the approach put forward by Norskov et al.[4], and the relevant formula is defined as follows:

$$\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S + \Delta G_{pH} + \Delta G_U$$

where ΔE is the adsorption energy, ΔE_{zpe} and ΔS are the difference in the zero-point energy and entropy between the adsorbed state and the gas phase, respectively. ΔG_{pH} ($\Delta G_{pH} = k_B T \times \ln_{10} \times pH$) represents the free energy contributed in different pH concentrations. Here T=298.15K. ΔG_U ($\Delta G_U = -eU$) denotes the extra potential bias provided by an electron in the electrode, where U is the electrode potential relative to the standard hydrogen electrode (SHE).

The OER take places via the following four steps:

$$* + H_2O \rightarrow OH* + H^+ + e^-$$

$$OH* \rightarrow O* + H^+ + e^-$$

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^-$$

$$OOH^* \rightarrow * + O_2 + H^+ + e^-$$

Meanwhile, HER can be decomposed into two steps, the reaction equation can be written as:

$$* + H^+ + e^- \rightarrow H^*$$

$$H^* + H^+ + e^- \rightarrow * + H_2$$

where * means the adsorbed materials, O*, OH*, OOH* and H* represent the adsorbed intermediates.

For each step of both the oxidation and hydrogen reactions, the free energy difference under the effect of pH and an extra potential bias can be written as:

$$\Delta G_1 = G_{OH^*} + 1/2G_{H2} - G_* - G_{H2O} + \Delta G_U - \Delta G_{PH}$$

$$\Delta G_2 = G_{O^*} + 1/2G_{H2} - G_{OH^*} + \Delta G_U - \Delta G_{PH}$$

$$\Delta G_3 = G_{OOH^*} + 1/2G_{H2} - G_{O^*} - G_{H2O} + \Delta G_U - \Delta G_{PH}$$

$$\Delta G_4 = G_* + 1/2G_{H2} + G_{O2} - G_{OOH^*} + \Delta G_U - \Delta G_{PH}$$

$$\Delta G_5 = G_{H^*} - 1/2G_{H2} - G_* + \Delta G_U + \Delta G_{PH}$$

$$\Delta G_6 = G_* + 1/2G_{H2} - G_{H^*} + \Delta G_U + \Delta G_{PH}$$

2: Calculation the in-plane stiffness (C_{2D}), effective mass (m^*), deformation potential constant (E_1), and carrier mobilities (μ) at 300 K.

The carrier mobility (μ) for the two-dimensional B_6O_2 monolayer was evaluated using the deformation potential theory, which is well-established for describing charge transport in 2D semiconductors. The expression for the directional mobility μ is given by:

$$\mu = e\hbar^3 C_{2D} / k_B T m^* m_d E_1^2$$

- e is the elementary charge.
- $\hbar$ is the reduced Planck constant.
- k_B is the Boltzmann constant.
- T is the temperature (here, 300 K).
- m^* denotes the effective mass along a specific transport direction.
- m_d represents the average (density-of-states) effective mass.
- C_{2D} is the in-plane elastic modulus along the corresponding transport direction.
- E_1 is the deformation potential constant, describing the shift of the band edge with respect to strain.

References：

1 X. Lv, W. Wei, Q. Sun, F. Li, B. Huang and Y. Dai, Two-dimensional germanium monochalcogenides for photocatalytic water splitting with high carrier mobility, *Appl. Catal. Environ.*, 2017, **217**, 275-284.

2 Qiao, J. Liu, Y. Wang, Y. Li and Z. Chen, PdSeO3 monolayer: promising inorganic 2D photocatalyst for direct overall water splitting without using sacrificial reagents and cocatalysts, *J. Am. Chem. Soc.*, 2018, 140, 12256-12262.

3 L. Ju, J. Shang, X. Tang and L. Kou, Tunable photocatalytic water splitting by the ferroelectric switch in a 2D $AgBiP_2Se_6$ monolayer, *J. Am. Chem. Soc.*, 2020, **142**, 1492-1500.

4 J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, Origin of the overpotential for oxygen reduction at a fuel-cell cathode, *J. Phys. Chem. B*, 2004, **108**, 17886-17892.