Full Length Article

Theoretical proposal of a revolutionary water-splitting photocatalyst: The monolayer of boron phosphide

Tatsuo Suzuki (鈴木達夫)

Tokyo Metropolitan College of Industrial Technology, 8-17-1, Minami-Senju, Arakawa-ku, Tokyo 116-8523, Japan

ARTICLE INFO

Keywords:
Water-splitting photocatalyst
Monolayer
Boron phosphide
Density-functional theory calculations
Hydrogen and oxygen
HSE06

ABSTRACT

Recently, hydrogen generation by water-splitting photocatalysts is attracting attention as a sustainable and clean energy resource. Photocatalytic hydrogen-generation systems are much simpler, cheaper, and easier to scale up than the coupled systems of electrolysis and solar cells, wind-power generation, etc. However, photocatalytic hydrogen generation is currently inefficient. This paper proposes the monolayer of boron phosphide as a stable highly-efficient water-splitting photocatalyst by high-precision density-functional theory calculations using a HSE06 functional with a solvent effect. The monolayer of boron phosphide has a direct allowed energy gap of about 1.4 eV, and functions as a one-step excitation photocatalyst. It absorbs sunlight with wavelengths below about 890 nm (ultraviolet, visible, and near-infrared light) and produces both hydrogen gas and oxygen gas from water at a suitable pH condition. By calculating the overpotentials of hydrogen and oxygen evolution reactions, its photocatalytic effectiveness was confirmed. The monolayers of boron phosphide will realize green hydrogen revolution.

1. Introduction

Fossil fuels cause global warming and will dry up in the future. Nuclear fuel has a risk of radioactive contamination such as Fukushima or Chernobyl. Recently, hydrogen generation by water-splitting photocatalysts [1] is attracting attention as a sustainable and clean energy resource to replace fossil fuels and nuclear fuel. Photocatalytic hydrogen-generation systems are much simpler, cheaper, and easier to scale up than the coupled systems of electrolysis and solar cells, wind-power generation, etc. Recently, Nishiyama et al. [2] reported solar hydrogen production from water on a 100 m²-scale using an aluminum-doped strontium titanate particulate photocatalyst. They demonstrated that safe, large-sale photocatalytic water splitting and gas collection and separation were possible; however, the hydrogen production was inefficient. Finding a stable highly-efficient photocatalyst is an urgent task for humankind to realize green hydrogen revolution.

In 2012, Sun et al. [3] reported the fabrication of large-area freestanding single layers of ZnSe with four-atomic thickness, which have an enhanced water-splitting efficiency and photostability. The ZnSe single layers exhibit a photocurrent density of 2.14 mA cm⁻² at 0.72 V versus Ag/AgCl under 300 W Xe lamp irradiation, 195 times higher than that of bulk ZnSe. Similarly, the efficiency of SnS₂ single layer is 72 times higher than bulk SnS [4]. These reports reveal that two-dimensional materials can be highly-efficient water-splitting photocatalysts. The possible reason is as follows. In the case of bulk photocatalysts, light penetrates deep inside the photocatalyst, where it generates electron-hole pairs. The generated electrons and holes can instantly react against the mutual Coulomb attraction in order to react with atoms or ions adsorbed on the surface. Therefore, bulk photocatalysts require mechanisms such as depletion layers or heterojunctions to separate electrons and holes; nevertheless, the electrons and holes still recombine, resulting in energy loss. However, in the case of two-dimensional photocatalysts, the generated electrons and holes can instantly react with atoms or ions adsorbed on the surface with little movement because two-dimensional photocatalysts are surface-only materials. Since Sun’s reports, many two-dimensional photocatalysts have been developed, and details are found in review articles [6,7,8].

2. Proposal

This paper theoretically proposes the monolayer of boron phosphide (BP) as a stable highly-efficient water-splitting photocatalyst (cf. Fig. 1 (a)). As a result of searching for various two-dimensional materials by high-precision density-functional theory (DFT) calculations, the revolutionary property of the BP monolayer was discovered. At present,
there are no reports that BP monolayers were synthesized. However, in 2019, on the surface of a cubic zinc-blend BP nanocrystal grown at 1250 °C through a solid state reaction route, graphite-like layers with the lattice spacing of 0.35 nm were observed in high-resolution TEM images [9]. These layers may become the precursors of BP monolayers. In 2020, Hernández et al. [10] theoretically proposed that BP monolayers can be exfoliated by incorporating arsenic in the (1 1 1) surface of a cubic zinc-blend BP.

Below, we investigate the property of the BP monolayer as a photocatalyst by two types of high-precision DFT calculations: a plane-wave (PW) basis calculation using a pseudo-potential and a Gaussian type orbital (GTO) basis calculation using all electrons. The PW basis calculation also include a solvent effect, i.e., a water polarization effect by an implicit solvation model based on the Poisson-Boltzmann equation. All calculations use Heyd-Scuseria-Ernzerhof (HSE06) hybrid density functionals [11,12] for both structural optimizations and energy bands calculation methods, and the error between the calculated energy gaps and the experimental values is less than 10% [13].

3. Important conditions

First, we confirm four important conditions that two-dimensional photocatalysts must satisfy for large-scale practical use; (a) stable in water against long exposure to strong sunlight, (b) made from earth-abundant elements, (c) one-step excitation using a single semiconductor because Z-scheme using two connected semiconductors requires double photons of one-step excitation, and PEC water splitting using two electrodes is difficult to deploy on a large scale due to the complexity of equipment, and (d) a direct allowed transition semiconductor with an energy gap $E_g$ that is larger than the theoretical limit $\Delta_{\text{limit}}$ but as small as possible. In order to achieve one-step excitation of (c), band edges (i.e., conduction band minimum $E_C$ and valence band maximum $E_V$) should straddle water redox potentials $E_{H_2/O_2}$ and $E_{O_2/H_2O}$; that is,

$$E_C \geq E_{H^+/H_2} \quad \text{and} \quad E_{O_2/H_2O} \geq E_V$$

(1)

And, $\Delta_{\text{limit}}$ of (d) is the redox potential difference; that is,

$$\Delta_{\text{limit}} = E_{\text{limit}} - E_{\text{limit}} = E_{H^+/H_2} - E_{O_2/H_2O}$$

(2)

Next, we confirm redox potentials $E_{H^+/H_2}$ and $E_{O_2/H_2O}$. The hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) are expressed in Eqs. (3) and (4), respectively.

$$2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2 \quad \langle E' = 0.000 \text{V vs. SHE} \rangle$$

(3)

$$2 \text{H}_2 \text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 e^- \quad \langle E' = +1.229 \text{V vs. SHE} \rangle$$

(4)

Water molecules H$_2$O and hydrogen ions H$^+$ adsorbed on the surface of the BP monolayer are transformed into various intermediates on the surface (cf. Fig. 1(b)-(h)), and are finally decomposed into hydrogen molecules H$_2$ and oxygen molecules O$_2$, as described in detail below. Here, $E'$ is the standard electrode potential relative to the standard hydrogen electrode (SHE). $E_{H^+/H_2}$ and $E_{O_2/H_2O}$ are expressed by the Nernst equation in Eqs. (5) and (6), respectively.

$$E_{H^+/H_2} = -0.44 - \frac{k_B T}{2e} \ln \left( \frac{[\text{H}^+]^{1/2}}{[\text{H}_2]} \right) = -4.445 + 0.0592 \text{pH (eV)}$$

(5)

$$E_{O_2/H_2O} = -4.44 - 1.229 - \frac{k_B T}{4e} \ln \left( \frac{[\text{H}_2O_2]}{[\text{H}^+]^4} \right) = -5.662 + 0.0592 \text{pH (eV)}$$

(6)

From the definition of the Nernst equation, $E_{H^+/H_2}$ and $E_{O_2/H_2O}$ are the potential energies of the electron in the BP monolayer, not the potential energies in the solution. The origin of these equations is the vacuum level, and $-4.44$ eV is the energy level of SHE relative to the vacuum level. $k_B$, $e$, and $[\text{H}^+]$ are Boltzmann constant, elementary charge, and the molar concentration of H$^+$ ions, respectively. Temperature $T = 298.15$ K, and pH = $-\log_{10}[\text{H}^+]$. The reaction vessel is filled with generated gas; therefore, the partial pressures of H$_2$ and O$_2$ are $p_{H_2} = \frac{3}{4}$ atm and $p_{O_2} = \frac{1}{4}$ atm, respectively. The theoretical limit $\Delta_{\text{limit}} = E_{H^+/H_2} - E_{O_2/H_2O} = 1.217$ eV.

4. Reviews of previous researches

First, we review the bulk crystal of BP, which has a cubic zinc-blend structure. The cubic zinc-blend BP is quite chemically stable and is resistant to chemical corrosion. It is not attacked by hot concentrated mineral acids or aqueous alkali solution [14]. It is also resistant to oxidation in air up to about 800–1000 °C [15]. The cubic zinc-blend BP is an indirect transition semiconductor with an energy gap of 2.0 eV, and functions as a photocatalyst for H$_2$ evolution [9,14,16]. The photocatalytic H$_2$ evolution reactions continue even in strong acid or strong alkaline, and the BP photocatalyst is stable under these extreme conditions [14]. These durable properties of the cubic zinc-blend BP originate in the strong covalent bonds between elements B and P. This durability

---

Fig. 1. Optimized structures of (a) BP monolayer, (b) O*, (c) OH*, (d) OOH*, (e) H*0, (f) H*1, (g) H*2, and (h) H*3. Black, green, red, and blue balls are boron, phosphorus, oxygen, and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
will be carried over to BP monolayers. Recently, Li et al. [17] prepared cubic zinc-blend BP nanosheets with a thickness of about 4 nm, and demonstrated that the BP nanosheets were well dispersed in water with a concentration of 0.2 mg/mL. Liang et al. [18] synthesized cubic zinc-blend BP single crystals larger than 1 mm, and evaluated their excellent thermal stability up to 1200°C.

Next, we review BP monolayers. The most stable structure of a BP monolayer is a hexagonal planar structure like a graphene or a h-BN monolayer (cf. Fig. 1(a)) [19]. Sahin et al. [20] performed DFT calculations using a PW basis and local-density approximation, and reported the bond length \( d = 1.83 \) Å and the direct energy gap \( E_g = 0.82 \) eV or 1.81 eV which is corrected by frequency-dependent GW calculations. They calculated the phonon dispersion of a BP monolayer also, and confirmed the dynamical stability of a BP monolayer. Suzuki & Yokomizo [21] calculated \( d = 1.87 \) Å and \( E_g = 1.912 \) eV using a GTO basis and a B3LYP/6-31G(d) functional. After that, the high-precision calculation method using a HSE06 functional became widespread. Zhuang & Hennig [22] calculated \( d = 1.855 \) Å and \( E_g = 1.854 \) Å using a GTO basis and a HSE06 functional. Wang & Wu [23] calculated the band edges of a BP monolayer in a vacuum using a PW basis and a HSE06 functional. Wu et al. [29] performed DFT calculations combined with \textit{ab initio} molecular dynamics (AIMD) simulations, and demonstrated that the physical and chemical stabilities of BP monolayers in a vacuum, and in oxygen, water, and oxygen-water environment.

5. Calculation methods

PW basis calculations use a plane-wave basis set, the projector augmented wave (PAW) potentials [30,31], a HSE06 functional, a 27 × 27 × 1 Monkhorst-Pack k-point mesh, the super-cell width of 18 Å, the cutoff energy of 800 eV for the PW basis, and VASP 5.4.1 package [32,33]. The convergence criteria of electronic self-consistent calculations and ionic relaxations are 10^{-6} and 10^{-5} eV, respectively. A solvent effect by the polarization of water is implemented as an implicit solvent approximation based on the Poisson-Boltzmann equation, and is performed by using VASPsol package [34,35]. GTO basis calculations use a Gaussian type orbital 6-31G(d,p) basis set and a HSE06 functional under the periodic boundary condition. A pseudo-potential is not used because of all-electron calculations. About 2000 k-points are requested in a unit cell. The convergences of electronic self-consistent calculations are that the maximum and the root mean square (RMS) of the variations of the density matrix are less than 10^{-5} and 10^{-7}, respectively, and that the variation of the total-energy is less than 10^{-5} Hartree. The convergences of ionic relaxations are that the maximum and RMS of force are less than 2 × 10^{-6} and 10^{-6} Hartree/Bohr, respectively, and that the maximum and RMS of displacement are less than 6 × 10^{-6} and 4 × 10^{-6} Bohr, respectively. The GTO basis calculation is performed by using Gaussian 09 package [36].

6. Results and considerations

This paper shows three types of calculated results: (a) PWsol using a PW basis with a solvent effect, (b) PWvac using a PW basis in a vacuum, and (c) GTOvac using a GTO basis in a vacuum.

First, we consider the shapes of BP monolayers after structural optimizations. The bond lengths of PWsol, PWvac, and GTOvac are 1.845, 1.846, and 1.854 Å, respectively. Comparing PWsol and PWvac, the bond lengths are almost the same with and without a solvent effect. Comparing PWvac and GTOvac, there is 0.4% difference in bond lengths due to the different calculation methods. These bond lengths are in good agreement with previous researches [22,23].

Next, we consider the results of PWsol in Fig. 2. An infinitely wide BP monolayer is placed on the x-y plane at \( z = 0 \). \( V(z) \) is the potential which is averaged within the unit cell.

\[
V(z) = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} V_{sol}(x,y,z) \, dx \, dy}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \, dx \, dy}
\]

where \( V_{sol}(x,y,z) \) is the entire local potential (ionic plus Hartree plus exchange correlation) with the solvent effect. The potential value at the midpoint of the spacer is vacuum level, and it is aligned with the origin of energy; that is, \( V(z = 9) = 0 \). \( n(z) \) is the averaged number density of valence electrons of the BP monolayer with the solvent effect, and \( n_0(z) \) is the averaged bound charge density of water. Drawn for comparison, \( V_{vac}(z) \) is the averaged potential of PWvac, i.e., the averaged potential without the solvent effect. \( V_{vac}(z) \) at the midpoint of the spacer is also aligned with the origin of energy; that is, \( V_{vac}(z = 9) = 0 \). We define \( V_d(z) = V(z) - V_{vac}(z) \), which is the potential difference caused by the polarization of water. Here, we notice that \( V(z) \) is the vacuum level when the solvent effect exists; that is, \( V(z) \) corresponds to the vacuum level of Anderson model [37] which explains the energy band profiles of semiconductor heterostructures. Therefore, \( V_{pzc} = \frac{V(z = 0)}{0.21} \) eV is the electrical double layer voltage. \( E_c = -3.85 \) eV and \( E_V = -5.17 \) eV are band edges with the solvent effect. \( E_{C1/V1} \) is the averaged potential of PWsol and PWvac are drawn under the same condition. Then, we consider energy bands in the left panel of Fig. 3. Here, the energy bands of PWvac in Fig. 2 are shifted with and without the solvent effect is small. The energy gap of PWvac is in good agreement with previous researches [22,23]. The band edges \( (E_C, E_V) \) of PWsol and PWvac are \((-3.85, -5.17)\) and \((-4.06, -5.39)\) eV, respectively. \( (E_C, E_V) \) are shifted only by the electrical double layer voltage \( V_{pzc} = 0.21 \) eV. Next, we compare PWvac and GTOvac. The energy gap of GTOvac is 1.47 eV, which is 10% larger than PWvac. This discrepancy is due only to the different calculation methods. \( (E_C, E_V) \) of GTOvac is \((-4.13, -5.60)\) eV. Despite the different calculation methods, the band edges \( (E_C, E_V) \) are located at almost the same energy levels, which are in good agreement with a previous research [23].

Then, we consider the relationship between band edges and redox potentials. The band edges in this paper are calculated under the condition that the BP monolayer is not charged, i.e., the pH of the solution is at the point of zero charge \( p_{Hz} \). It is unclear how the band edges of the BP monolayer depend on \( p_H \); that is, whether the band edges show a Nernstian dependence of 0.059 eV/pH like semiconducting metal oxides (e.g. TiO2 [38], or are pH-independent like a hydrogen-terminated diamond [39]). Therefore, we cannot estimate \( p_{Hz} \). In the right panel of Fig. 3, the redox potentials are drawn according to Eqs. (5) and (6). If
the pH_{zpc} of PWsol is in the range of 8.4–10.0, the BP monolayer functions as a photocatalyst because it satisfies Eq. (1). However, even if the pH_{zpc} is out of this range, the BP monolayer still functions as a photocatalyst. This is because the band edges E_C and E_V are very close to the redox potentials E_{H+/H^2} and E_{O_2/H_2O}, respectively; then, either band edge is pinned to the corresponding redox potential. The basis for this idea is the experiments by Chakrapani et al. [39]. They added hydrogen-terminated diamond particles into aqueous solutions and measured the changes in pH and oxygen concentrations. Their experiments show that electron exchange systematically occurs between diamond and the oxygen redox couple; that is, the electrochemical potential (Fermi energy) of the diamond is pinned by the oxygen redox potential. By the way, on the BP monolayer side of water–solid interface there is little charge to compensate for ions adsorbed on the water side because the BP monolayer does not have free electrons like metals nor does it form a depletion layer like bulk semiconductors. Furthermore, the covalent bonds between elements B and P are so strong that B or P does not dissolve as ions. Therefore, the BP monolayer will not be charged very much.

Then, we calculate the overpotentials of HER and OER by Nørskov approach [40,41,42]. Here, we consider an acidic reaction involving H^+; however, the results are the same for the alkaline reaction involving OH^–. HER pathways considered are (a) H^+ + e^- + H_2(g), (b) H^+ + e^- + H^* - H_2(g), and (c) 2H^+ - H_2(g) + 2 e^-; OER pathways are (d) H_2O(l) + e^- - OH^* + H^* + e^-, (e) OH^* - O^* + H^* + e^-, (f) 2OH^* - H_2O(l) + O^* + e^-, (g) H_2O(l) + O^* - OOH^* + H^* + e^-, (h) OOH^* - O_2(g) + * + H^* + e^-, and (i) 2OOH^* - O_2(g) + 2O^* + 2H^* + 2 e^- . Here, * denotes an adsorb-site on the BP monolayer. In the following, temperature T = 298.15 K. The Gibbs free energies per molecule of hydrogen gas and oxygen gas are G(H_2(g)) = G^0(H_2(g)) + ln(p_H^2) and G(O_2(g)) = G^0(O_2(g)) + ln(p_O_2), where G^0 is the Gibbs free energy at standard conditions. The Gibbs free energies of water is G(H_2O(l)) = G^0(H_2O(l)) - 0.088 eV [44].

\[ G^0(H_2O(l)) = G^0(H_2(g)) + G^0(O_2(g)) + \Delta H^0(H_2O(l)(0–T) - T S(H_2O(l))) \]
For all reactions included in a pathway, the maximum value of those threshold potential and the redox potential are the same pH dependent. Therefore, 

\[ \eta_{\text{HER}}(0-T) - \eta_{\text{OER}}(0-T) = \eta_{\text{HER}}(0-T) - \eta_{\text{OER}}(0-T) \]

This work was partially supported by Tokyo Metropolitan College of Industrial Technology.

### Acknowledgements

This work was partially supported by Tokyo Metropolitan College of Industrial Technology.

### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2022.153844.

### References

1. AKIRA Fujishima, KENICHI Honda, Electrochemical photocatalysis of water at a semiconductor electrode, Nature 238 (5388) (1972) 37–38.

2. H. Nishiyama, T. Yamada, M. Nakabayashi, Y. Maehara, M. Yamaguchi, Y. Kuromiya, Y. Nagatsuma, H. Tokudome, S. Akiyama, T. Watanabe, R. Narushima, S. Okuizumi, N. Shibata, T. Takata, T. Hisatomi, K. Domen, Photocatalytic solar hydrogen production from water on a 100–m2 scale, Nature 598 (7880) (2021) 304–307.

3. Y. Sun, et al., Fabrication of flexible and freestanding zinc chalcogenide single layers, Nat. Commun. 3 (2012) 1057.

4. Y. Sun, et al., Freestanding tin disulfide single-layer solar cells efficiently realizing visible-light water splitting, Angew. Chem. Int. Ed. 51 (2012) 8727–8731.

5. Y. Sun, et al., All-surface-atomic metal chalcogenide sheets for high-efficiency visible-light photocatalytic water splitting, Adv. Energy Mater. 4 (2014) 1300611.

6. Y. Li, C. Gao, R. Long, Y. Xiong, Photocatalyst design based on two-dimensional materials, Mater. Today 1 (2019) 197–216.

7. Y. Zhao, et al., Two-dimensional photocatalyst design: A critical review of recent experimental and computational advances, Mater. Today 34 (2020) 78–91.

8. K. Khan, et al., Recent progress, challenges, and prospects in two-dimensional photo-catalyst materials and environmental remediation, Nano-Micro Lett. 12 (2020) 167.

9. H. Sugiarto, et al., Size-dependent photocatalytic activity of cubic boron phosphide nanocrystals in the quantum confinement regime, J. Phys. Chem. C 123 (2019) 23226–23235.

10. O. Munive Hernandez, et al., Hexagonal boron phosphide monolayer exfoliation induced by arsenic incorporation in the BP (1 1 1) surface: a DFT study, Appl. Surf. Sci. 538 (2021) 148163.

11. J. Heyd, G.E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118 (2003) 8207.

12. J. Heyd, G.E. Scuseria, M. Ernzerhof, Erratum: “Hybrid functionals based on a screened Coulomb potential” [J. Chem. Phys. 118, 8207 (2003)], J. Chem. Phys. 124 (2006) 219906.

13. S. Park, B. Lee, S.H. Jeon, S. Han, Hybrid functional study on structural and electronic properties of oxides,Curr. Appl. Phys. 11 (2011) S337–S340.

14. Li Shi, P. Li, W. Zhou, T. Wang, K. Chang, H. Zhang, T. Kako, G. Liu, Y. Ye, n-type boron phosphide as a highly stable, metal-free, visible-light-active photocatalyst for hydrogen evolution, Nano Energy 28 (2016) 158–163.

15. F.V. Williams, R.A. Rauhwein, The preparation and properties of boron phosphides and arsenides I, J. Am. Chem. Soc. 82 (1960) 1330–1332.

16. J. Lee, A. Fujishima, K. Honda, Y. Kumashiro, Photoelectrochemical behavior of p-type boron phosphide photoelectrode in acidic solution, Bull. Chem. Soc. Jpn. 58 (1985) 2634–2637.

17. Z. Li, C. Cheng, H. Gong, Q. Liu, C. Huang, Water-dispersible boron phosphide nanosheets for enhancing the thermal conductivity of nanofluids, J. Mol. Liq. 309 (2020) 115925.
[18] W. Liang, et al., Growth of millimeter-size single-crystal boron phosphide by eutectic melt at 5.0 GPa and 3000 °C, Solid State Commun. 327 (2021) 114206.

[19] T. Suzuki, Theoretical discovery of stable structures of group III-V monolayers: the materials for semiconductor devices, Appl. Phys. Lett. 107 (2015) 213105.

[20] H. Sahin, S. Cahanlioglu, M. Topsisakal, E. Bekaroglu, E. Akturk, R.T. Senger, S. Ciraci, Monolayer honeycomb structures of group-V elements and III-V binary compounds: first-principles calculations, Phys. Rev. B 80 (15) (2009) 155453.

[21] T. Suzuki, Y. Yokomizo, Energy bands of atomic monolayers of various materials: possibility of energy gap engineering, Phys. E Low-dimensional Syst. Nanostuct. 42 (2010) 2620–2625.

[22] H.L. Zhuang, R.G. Hennig, Electronic structures of single-layer boron pnictides, Appl. Phys. Lett. 101 (2012) 153109.

[23] S.F. Wang, X.J. Wu, First-principles study on electronic and optical properties of graphene-like boron phosphide sheets, Chinese J. Chem. Phys. 28 (2015) 588–594.

[24] H. Shu, J. Guo, X. Niu, Electronic, photocatalytic, and optical properties of two-dimensional boron phosphide, Appl. Phys. Lett. 101 (2012) 153109.

[25] K. Ren, et al., First-principle study of electronic and optical properties of two-dimensional materials-based heterostructures based on transition metal dichalcogenides and boron phosphide, Appl. Surf. Sci. 476 (2019) 70–75.

[26] I. Shahid, et al., Electronic and photocatalytic performance of boron phosphide-blue phosphorene vdW heterostructures, Appl. Surf. Sci. 523 (2020) 146483.

[27] T.-N. Do, et al., Electronic and photocatalytic properties of two-dimensional boron phosphide/SiC van der Waals heterostructure with direct type-II band alignment: a first principles study, RSC Adv. 10 (2020) 32027–32033.

[28] C. Nguyen, N.V. Hoang, H.V. Phuc, A.Y. Sin, C.V. Nguyen, Two-dimensional boron phosphide/MoGeN_x van der Waals heterostructure: a promising tunable optoelectronic material, J. Phys. Chem. Lett. 12 (2021) 5076–5084.

[29] J. Wu, J.-H. Li, Y.-X. Yu, Stabilities of group-III phosphide (MP, M = B, Al, Ga and In) monolayers in oxygen and water environments, Phys. Chem. Chem. Phys. 22 (2020) 7633–7642.

[30] P.E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979.

[31] G. Kresse, D. Joubert, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953–17979.

[32] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B 47 (1993) 558–561.

[33] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186.

[34] K. Mathews, B. Sundararaman, K. Letchworth-Weaver, T.A. Arias, R.G. Hennig, Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways, J. Chem. Phys. 140 (2014) 084106.

[35] K. Mathews, V.S.C. Kolluru, S. Mula, S.N. Steinmann, R.G. Hennig, Implicit self-consistent electrolyte model in plane-wave density-functional theory, J. Chem. Phys. 151 (2019) 234101.

[36] M.J. Frisch, et al., Gaussian 09, Revision C.01, Gaussian, Inc, Wallingford CT, 2010.

[37] R.L. Anderson, Experiments on Ge-GaAs heterojunctions, IRE Trans. Electron Dev. 9 (1962) 509.

[38] Y. Xu, M.A.A. Schoonen, The absolute energy positions of conduction and valence bands of selected semiconducting minerals, Am. Min. 85 (2000) 543–556.

[39] V. Chakrapani, J.C. Angus, A.B. Anderson, S.D. Wolter, B.R. Stoner, G. U. Sumanasekera, Charge transfer equilibria between diamond and an aqueous oxygen electrochemical redox couple, Science 318 (2007) 1424–1430.

[40] J.K. Nørskov, et al., Origin of the overpotential for oxygen reduction at a fuel-cell cathode, J. Phys. Chem. B 108 (2004) 17868–17872.

[41] I.C. Man, H.-Y. Su, F. Calle-Vallejo, H.A. Hansen, J.I. Martinez, N.G. Inoglu, J. Kitchin, T.F. Jaramillo, J.K. Nørskov, J. Rossmeisl, Universality in oxygen evolution electrocatalysis on oxide surfaces, ChemCatChem 3 (7 (2011) 1159–1165.

[42] Y.-A. Zhu, D.e. Chen, X.-G. Zhou, W.-K. Yuan, DFT studies of dry reforming of methane on Ni catalyst, Catal. Today 148 (3-4) (2009) 260–267.

[43] Q. Liang, G. Brocks, A. Bieberle-Hütter, Oxygen evolution reaction (OER) mechanism under alkaline and acidic conditions, J. Phys. Energy 3 (2) (2021) 026001.

[44] J. Rumble. CRC Handbook of Chemistry and Physics, CRC Press, 2021.

[45] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.

[46] S. Grimes, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132 (2010) 154104.

[47] National Renewable Energy Laboratory, Reference Air Mass 1.5 Spectra. <https://www.nrel.gov/grid/solar-resource/spectra-am1.5.html>.
Supplementary Information

Theoretical proposal of a revolutionary water-splitting photocatalyst:
The monolayer of boron phosphide

Tatsuo Suzuki (鈴木 達夫)

Tokyo Metropolitan College of Industrial Technology

TABLE I. Calculated results: Gibbs free energy $G$, total energy calculated by DFT $E^{\text{DFT}}$, zero-point energy calculated by DFT $E^{\text{ZPE}}$, internal energy change $\Delta U^0(0K \rightarrow T)$, enthalpy change $\Delta H^0(0K \rightarrow T)$, standard entropy $S^0$, and Gibbs free energy at standard conditions $G^0$. The unit is eV.

|          | $G$   | $E^{\text{DFT}}$ | $E^{\text{ZPE}}$ | $\Delta U^0(0K \rightarrow T) - TS^0$ | $\Delta H^0(0K \rightarrow T) - TS^0$ | $G^0$  |
|----------|-------|------------------|------------------|-------------------------------------|-------------------------------------|--------|
| *        | -49.059 |                  |                  |                                     |                                     |        |
| O*       | -6.403  | -55.545          | 0.094            |                                     | -0.011                              |        |
| OH*      | -9.938  | -59.335          | 0.374            |                                     | -0.036                              |        |
| OOH*     | -15.932 | -65.375          | 0.439            |                                     | -0.055                              |        |
| H*0      | -2.557  | -51.850          | 0.235            |                                     | -0.001                              |        |
| H*1      | -2.703  | -58.494          | 0.247            |                                     | -0.001                              |        |
| H*2      | -3.862  | -63.427          | 0.232            |                                     | -0.002                              |        |
| H*3      | -4.324  | -69.940          | 0.243            |                                     | -0.001                              |        |
| H$_2$(g) | -6.827  | -6.771           | 0.271            |                                     | -0.316                              | -6.816 |
| H$_2$O(g) | -14.219 | 0.572            | -0.481           |                                     | -14.128                             |        |
| H$_2$O(l)| -14.216 |                  |                  |                                     |                                     |        |
| O$_2$(g) | -9.911  |                  |                  |                                     |                                     | -9.883 |
| H$^+$ + e$^-$ | 1.032 − 0.0592 $pH + V_e$ |
### TABLE II. Gibbs free energy change $\Delta G$ and the difference $\eta$ between the threshold potential and the redox potential. The unit is eV.

**HER pathways**

| Pathway | Reaction | $\Delta G$ | $\eta$ |
|---------|----------|------------|--------|
| (a0)    | $H^* + e^- + * \rightarrow H*0$ | $\Delta G = -3.589 + 0.0592 \, pH - V_e$ | $\eta = 0.856$ |
| (b0)    | $H^* + e^- + H*0 \rightarrow H_2(g) + *$ | $\Delta G = -5.302 + 0.0592 \, pH - V_e$ | $\eta = -0.856$ |
| (c0)    | $2 \, H*0 \rightarrow H_2(g) + 2 \,*$ | $\Delta G = -1.713$ | |
| (a1)    | $H^* + e^- + * \rightarrow H*1$ | $\Delta G = -3.735 + 0.0592 \, pH - V_e$ | $\eta = 0.711$ |
| (b1)    | $H^* + e^- + H*1 \rightarrow H_2(g) + *$ | $\Delta G = -5.156 + 0.0592 \, pH - V_e$ | $\eta = -0.711$ |
| (c1)    | $2 \, H*1 \rightarrow H_2(g) + 2 \,*$ | $\Delta G = -1.421$ | |
| (a2)    | $H^* + e^- + * \rightarrow H*2$ | $\Delta G = -4.894 + 0.0592 \, pH - V_e$ | $\eta = -0.448$ |
| (b2)    | $H^* + e^- + H*2 \rightarrow H_2(g) + *$ | $\Delta G = -3.997 + 0.0592 \, pH - V_e$ | $\eta = 0.448$ |
| (c2)    | $2 \, H*2 \rightarrow H_2(g) + 2 \,*$ | $\Delta G = 0.897$ | |
| (a3)    | $H^* + e^- + * \rightarrow H*3$ | $\Delta G = -5.356 + 0.0592 \, pH - V_e$ | $\eta = -0.910$ |
| (b3)    | $H^* + e^- + H*3 \rightarrow H_2(g) + *$ | $\Delta G = -3.535 + 0.0592 \, pH - V_e$ | $\eta = 0.910$ |
| (c3)    | $2 \, H*3 \rightarrow H_2(g) + 2 \,*$ | $\Delta G = 1.821$ | |

**OER pathways**

| Pathway | Reaction | $\Delta G$ | $\eta$ |
|---------|----------|------------|--------|
| (d)     | $H_2O(l) + * \rightarrow OH* + H^* + e^-$ | $\Delta G = 5.309 - 0.0592 \, pH + V_e$ | $\eta = -0.353$ |
| (e)     | $OH* \rightarrow O* + H^* + e^-$ | $\Delta G = 4.568 - 0.0592 \, pH + V_e$ | $\eta = -1.094$ |
| (f)     | $2 \, OH* \rightarrow H_2O(l) + O* + *$ | $\Delta G = -0.741$ | |
| (g)     | $H_2O(l) + O^* \rightarrow OOH* + H^* + e^-$ | $\Delta G = 5.718 - 0.0592 \, pH + V_e$ | $\eta = 0.056$ |
| (h)     | $OOH* \rightarrow O_2(g) + * + H^* + e^-$ | $\Delta G = 7.053 - 0.0592 \, pH + V_e$ | $\eta = 1.391$ |
| (i)     | $2 \, OOH* \rightarrow O_2(g) + 2 \ O^* + 2 \ H^* + 2 \ e^-$ | $\Delta G = 11.211 + 2(-0.0592 \, pH + V_e)$ | $\eta = -0.056$ |