Tunable photocatalytic Water-splitting by the Ferroelectric Switch in 2D AgBiP$_2$Se$_6$ Monolayer

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ABSTRACT: Photocatalytic water-splitting is a promising technology to solve the energy crisis and provide renewable & clean energies. Recently, although numerous 2D materials have been proposed as the photocatalytic candidates, the strategies to effectively modulate photocatalytic reactions and conversion efficiency are still lacking. Herein, based on first principle calculations, we show that the photocatalytic activities and energy conversion efficiency can be well tuned by ferroelectric-paraelectric phase transition of AgBiP$_2$Se$_6$ monolayer. It is found that the AgBiP$_2$Se$_6$ monolayer has a higher potential and driving forces of photogenerated hole for water oxidation in ferroelectric phase, but the higher corresponding values of photogenerated electron for hydrogen reduction reaction in paraelectric phase. Besides, the solar-to-hydrogen energy conversion efficiency is also tunable with the phase transition, it is up to 10.04% at ferroelectric phase due to the better carrier utilization, but only 6.66% at paraelectric phase. Moreover, the exciton binding energy is always smaller in paraelectric state than that in ferroelectric state, indicating that the ferroelectric switch could also make a directional adjustment to the photo-excited carrier separation. Our theoretical investigation not only reveals the importance of ferroelectric polarization on water splitting, but also opens an avenue to modify the photocatalytic properties of 2D ferroelectric materials via ferroelectric switch.

INTRODUCTION

Due to the continuous growth of energy crises and environmental pollutions, photocatalysis which is a promising technology to solve these problems, has attracted significant interest in recent years. With the photocatalysts, the organic pollutants could degrade into H$_2$O and CO$_2$,

\[ \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2 + \text{O}_2 \]

which is a "green" route to convert solar energy into chemical energy. Since the pioneering work of Fujishima and Honda, numerous three-dimensional (3D) semiconductors have been extensively studied as photocatalysts for water splitting. Unfortunately, many of the conventional 3D photocatalysts exhibit a wide band gap, which induces a low utilization of sunlight.\textsuperscript{5,7} Moreover, the low carrier mobilities and long migration distance in them usually causes a high recombination rate of photo-excited electrons and holes, which further shrinks its photocatalytic ability at a large level.\textsuperscript{8}

\[ \text{E}_\text{g} = 3.4 \text{ eV} \]

Compared with traditional 3D bulks, 2D materials have several advantages for photocatalytic applications. They always possess large surface area, which will supply plenty of potential reactive sites. The tunable electronic structures which depend on the layer thickness and strain facilitate the optical adsorption. More importantly, the ultrathin nature and short carrier migration distance could prevent the recombination of photogenerated carriers. Therefore, the 2D materials usually possess a high photocatalytic performance. Up to now, a wide variety of 2D photocatalytic materials that have been experimentally or theoretically studied, such as graphitic carbon nitride, phosphorene, III–VI compounds, IV–VI compounds, IV–IV compounds, and transition-metal dichalcogenides (TMDs), and so forth.\textsuperscript{9–24} Besides searching for new 2D photocatalyst materials, regulating the electron and optical properties of existing 2D photocatalyst materials to improve their photocatalytic efficiency is an alternative method, the feasible approaches include doping/adsorbing heteroatom,\textsuperscript{13, 21, 25–29} applying tensile strain,\textsuperscript{18, 30–32} and designing heterojunctions.\textsuperscript{14–16, 20, 22, 33–34}

Intriguingly, polarization also could significantly affect the photocatalytic activities and water splitting efficiency since the electronic properties can be well tuned by ferroelectric polarization as demonstrated recently.\textsuperscript{35–39} For example, the recently emerged 2D M$_2$X$_3$ (M = Al, Ga, In; X = S, Se,}
Te) family and also Janus transition metal dichalcogenides have been shown to be suitable for overall water splitting due to the vacuum level difference on the two respective surfaces and the shifts of the redox potentials. The intrinsic polarization can lead to the spatial separation of photogenerated carriers. Furthermore, according to the reaction mechanism proposed by Yang et al., the intrinsic dipoles help to relieve the restriction on the band gaps (1.23 eV) for water-splitting, which means that the polar semiconductors with narrow band-gap also have an opportunity to match the redox levels of water, making the photocatalytic water-splitting using visible or even infrared light possible. As analysed, the increased solar-to-hydrogen efficiency is mainly from the intrinsic spontaneous polarization. However, the effects of ferroelectric phase on photocatalysis are still unclear. To solve the issue, we investigate the effects of ferroelectric (FE) and paraelectric (PE) phases on the photocatalytic water splitting based on 2D materials ABP2X6 (A and B can be transition metals or rare earths atoms, and X represents the atoms from VIB group), and propose to tune the photocatalysis via ferroelectric switch. It is worthy to point out that both of the phases have been synthesized, it will be feasible to verify the expectation from direct experimental measurements.

In this work, AgBiP2Se6 monolayer is selected for photocatalytic research due to its proper band gap, efficient light utilization and suitable band alignments relative to the redox potential of water splitting. We systematically investigate and compare their electronic and photocatalytic properties of AgBiP2Se6 under FE and PE phases for water-splitting based on density functional theory combining with G0W0-BSE. The result shows that the monolayer exhibits sufficient redox capacity to split water into H2 and O2. The FE AgBiP2Se6 monolayer is a high-performance photocatalyst for water oxidation while PE phase is more suitable for hydrogen reduction reaction. Remarkably, the ferroelectric switch could adjust the photo-redox capacity and the exciton binding energy. Our work demonstrate that FE-PE phase transition is a new way to modify or improve the 2D ferroelectric materials for using as a photocatalysts.

**COMPUTATIONAL METHODS**

Vienna ab initio simulation package (VASP) is selected to perform our density functional theory (DFT) calculations. The frozen-core projector augmented wave (PAW) and the generalized gradient approximation (GGA) approximation are chosen to describe the interaction between the valence and core electrons. The electronic structures are assessed using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional to avoid the underestimate of the band gap calculated within Perdew–Burke–Ernzerhof (PBE) functional. Normal to the sheets, a 20 Å vacuum space is applied to the layers. The long-range vdW interactions between layers are described within a dispersion correction of total energy (DFT-D3 method) was used to incorporate the long-range vdW interaction. For the asymmetric layer arrangement, the dipole correction is considered. The cutoff energy is 500 eV. For the 2D Brillouin zone sampling, 5 × 5 × 1 Monkhorst–Pack k mesh is chosen. The geometrical structure relaxations are carried out until the residual force and energy difference are, respectively, less than 0.02 eVÅ-1 and 10-5 eV. When calculating the Gibbs free energy of hydrogen reduction and water oxidation reactions, we consider the solvent effect by using the implicit water solvent model implemented in VASPsol.

**RESULTS AND DISCUSSION**

To comprehensively understand the effects of ferroelectric phase on the photocatalytic performance of water splitting, we study and compare the detailed differences of electronic properties, spectrum adsorption, band alignments, water adsorption strength and driving force of photo-exited carriers at different phases.

**Structure, electronic properties and optical adsorption at FE and PE phases.** Before the discussions of photocatalytic properties of AgBiP2Se6, we first compare the corresponding structural, electronic and optical adsorption differences at FE and PE phases respectively, as the foundations to understand different photocatalytic behavior. Monolayer AgBiP2Se6 is constituted by a P–P in a triangular pattern and chalcogenide framework with the octahedral sites filled by Ag and Bi atoms. As illustrated in Figure 1a, Ag and Bi atoms are all located in the middle plane for the PE phase. However, the Ag+ ion is shifted off-center along z direction in the ferroelectric ordering, the displacement is much larger than that of the Bi3+ ion, therefore generating a spontaneous polarization of 0.28 Debye vertical to the monolayer. From the calculated total energy, the FE phase of monolayer AgBiP2Se6 is energetically 33 meV lower than the PE one, which is consistent with the previous reports like that of CuInP2S6 monolayer. It also means that it is relatively easy to achieve the ferroelectric switch from PE to FE phase or vice versa. Due to the presence of structural asymmetry, the lattice parameter is also slightly different as listed in Table 1, the value is 6.714 Å at PE phase, but 6.696 Å at FE phase. These results match well with the previous report (6.69 Å for the FE AgBiP2Se6 monolayer).

The structural difference at two phases will lead to the shift of energy levels and spectrum adsorptions. Based on HSE06 methods, the band structures of the PE and FE phase AgBiP2Se6 monolayer are calculated. Due to the heavy Bi atom, the spin-orbital coupling (SOC) correction is also examined with the HSE06 functional. The effect of SOC on the indirect band gaps of FE and PE phase AgBiP2Se6 monolayers are 0.14 and 0.18 eV, respectively, which is small relative to their own indirect band gaps (displayed in Figure S1). Considering the huge computational cost, we do not apply the SOC correction in the following calculation. As shown in Figure 1c and 1d, the band structures present similar features beside the values of band gaps and the positions of band-edge states. It can be seen that both PE and FE phase AgBiP2Se6 are...
semiconductors with indirect band gap. The conduction band minimum (CBM) and valence band maximum (VBM) of PE AgBiP2Se6 is separately located at Γ and K point, but they are located at Γ point and Γ−K path in FE AgBiP2Se6, respectively. Furthermore, as illustrated in Figure S2, for both phases, the main contributions of the CBM of AgBiP2Se6 are p orbitals of Se and Bi atoms, meanwhile the VBM is dominated by the hybridization of Ag d orbital and Se p orbital. At HSE06 level, the indirect band gaps of FE phase AgBiP2Se6 is 2.25 eV which is in accordance with the previous results (2.31 eV for FE AgBiP2Se6, 52-53). In contrast, the band gap value of AgBiP2Se6 is reduced to 2.20 eV at PE phase. As listed in Table S3, we also calculated the electronic properties of CuBiP2Se6, CuInP2S6 and AgBiP2S6 monolayers, it is found that the E\textsubscript{g\textsubscript{d}}(HSE) of FE phase are generally larger than the one in the PE phase. The decrease of band gap accompanied with FE- to-PE phase transition also has been observed in CuCrP2Se6, CuCrP2S6, CuVP2Se6, and CuVP2S6. In addition, for both phases of AgBiP2Se6 monolayer, the band gaps are larger than 1.23 eV, meeting the basic requirement of water splitting, namely the gap value is larger than the difference between the redox potentials of H\textsuperscript{+}/H\textsubscript{2} and H\textsubscript{2}O/O\textsubscript{2}.

![Figure 1](image-url)

**Figure 1** Crystal structure of (a) paraelectric and (b) ferroelectric AgBiP2Se6 monolayer. Band structures of (c) paraelectric and (d) ferroelectric AgBiP2Se6 monolayers based on HSE06 (black line) and G\textsubscript{0}W\textsubscript{0} (red line) functional. The Fermi levels are set as 0 eV.

We confirmed the band gaps of AgBiP2Se6 monolayers using the G\textsubscript{0}W\textsubscript{0} method, since the calculations for optical adsorption will base on the approach. As shown in Figure 1c and 1d, we can see that the indirect band gaps of PE AgBiP2Se6 monolayers is 2.68 eV, while the FE one is 2.70 eV. Notably, the energy differences between direct and indirect band gaps for the FE AgBiP2Se6 monolayers (80 meV) is larger than the thermal energy at room temperature (KT~30 meV), which can effectively prevent the combination of photo-excited carriers. The VBM is higher than the top valence bands at the Γ point, and the excited electrons could jump from valence band to conduction band at Γ point and then the holes move from Γ point to VBM, realizing the separation of photo-generated carriers.

As an efficient photocatalyst, the optical absorption coefficient should be strong, which gives rise to photo-excited electron–hole pairs. Here, we investigate the optical absorbance \(a(\omega)\) and imaginary parts of dielectric function \(\varepsilon \text{Im}(\omega)\) with G\textsubscript{0}W\textsubscript{0}-BSE method, the results are displayed in Figure 2 and S3. The absorbance is calculated by following equation:

\[
a(\omega) = \sqrt{2} \omega \left(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)\right)^{\frac{1}{2}}
\]

Under visible-light region, the optical absorption spectrum shows that AgBiP2Se6 monolayer exhibit an obviously high optical absorbance, indicating it is a potential photocatalyst with visible light response. Moreover, it is found that although the optical adsorption of FE AgBiP2Se6 at the range of green to red light region was suppressed to some degree, it is significantly increased at the ultraviolet light area when compared with the PE phase. The results imply that the optical adsorption can be also modulated by the ferroelectric switch or phase transition.

**Table 1** Optimized Lattice Constants (a), Band Gaps (direct and indirect) at HSE06 and G\textsubscript{0}W\textsubscript{0} level, the Optical Band Gaps (E\textsubscript{opt}), Exciton Binding Energies (E\textsubscript{b}), Dipole Moments (\(\mu\)), and Difference of Electrostatic Potential (\(\Delta V\)) between Top and Bottom Surfaces for Paraelectric and Ferroelectric AgBiP2Se6 Monolayers.

|                  | a (Å) | \(E_\text{g\textsubscript{d}}\text{(HSE)}\) (eV) | \(E_\text{g\textsubscript{d}}\text{(HSE)}\) (eV) | \(E_\text{g\textsubscript{d}}\text{(GW)}\) (eV) | \(E_\text{g\textsubscript{d}}\text{(GW)}\) (eV) | \(E_\text{opt}\) (eV) | \(E_\text{b}\) (eV) | \(\mu\) (Debye) | \(\Delta V\) (eV) |
|------------------|-------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|---------------------|-----------------|-----------------|----------------|
| AgBiP2Se6 (PE)   | 6.714 | 2.20                                          | 2.25                                          | 2.68                                          | 2.70                                          | 2.23                | 0.47            | 0               | 0              |
| AgBiP2Se6 (FE)   | 6.696 | 2.25                                          | 2.33                                          | 2.70                                          | 2.86                                          | 2.23                | 0.63            | 0.28            | 0.27           |

The binding energy of excitons is an important factor to separate photo-excited carriers, which is defined as:

\[
E_\text{b} = E_\text{g\textsubscript{d}} - E_\text{opt}
\]
where $E_g$ is the quasi-particle band gap obtained based on the GW method (corresponding to $E_g^{\text{al(GW)}}$) and $E_{\text{opt}}$ is the energy corresponding to the initial peaks of the optical absorption. The exciton binding energy is displayed in Table 1, basically following the law of $E_b \approx E_g/4$. It can be seen that the FE AgBiP$_2$Se$_6$ monolayer has a larger exciton binding energy than PE one. In order to confirm the law above, we also calculate the exciton binding energy of monolayer AgBiP$_2$Se$_6$, CuBiP$_2$Se$_6$ and CuInP$_2$Se$_6$. More computational details can be found in Figure S3 and S4. As listed in Table S1, all these three cases also follow the law, indicating that the ferroelectric switch is indeed an effective and universal way to regulate the exciton binding energy of ABP$_2$X$_6$ (A = Ag, Cu; B = Bi, In; X = S, Se) system. In addition, the small exciton binding energy (smaller than the one of most MXene monolayers) is favourable for the separation of photogenerated carriers.

For an overall water splitting photocatalyst, the potential of the CBM should be higher than the reduction level of hydrogen (-4.44 eV at pH = 0), and the potential of the VBM should be lower than the oxidation level of oxygen (-5.67 eV at pH = 0). As shown in Figure 3, for both PE and FE AgBiP$_2$Se$_6$ monolayers, the VBM and CBM surpass the standard oxidation potential of H$_2$O/O$_2$ and the standard reduction potential of H$^+$/H$_2$, indicating their sufficient activity for both OER and HER, respectively. According to the previous literature, we define the potential of photogenerated electrons for hydrogen reduction reaction ($U_e$) as the energy difference between the hydrogen reduction potential and the CBM, while the potential of photogenerated holes for water oxidation ($U_h$) is calculated as the energy difference between the hydrogen reduction potential and the VBM. The reduction potential ($E_{H^+/H_2}^{\text{red}}$) changes with the pH according to:

$$E_{H^+/H_2}^{\text{red}} = -4.44 + \text{pH} \times 0.059 \text{ (eV)}$$ (3)

At pH = 0, $U_e$ is 0.68 eV and $U_h$ is 1.52 eV for PE phase AgBiP$_2$Se$_6$. At the bottom surface of FE phase AgBiP$_2$Se$_6$, $U_e$ is 0.50 eV. According to the Yang’s theory, the top surface of FE phase AgBiP$_2$Se$_6$, the reduction potential ($E_{H^+/H_2\text{-top}}^{\text{red}}$) would rise with the electrostatic potential difference ($\Delta \phi$) as:

$$E_{H^+/H_2\text{-top}}^{\text{red}} = E_{H^+/H_2}^{\text{red}} + \Delta \phi$$ (4)

So, the $U_h$ for the top surface FE phase AgBiP$_2$Se$_6$ is 2.29 eV. In the neutral environment (pH = 7), based on the Equation 3, the $U_e$ and $U_h$ for PE phase AgBiP$_2$Se$_6$ monolayer is 0.27 and 1.93 eV, respectively. In contrast, the $U_e$ at the top surface and $U_h$ at the bottom surface for FE phase AgBiP$_2$Se$_6$ is 0.09 and 2.70 eV, respectively. The positive $U_e$ and $U_h$ indicate both PE and FE phase AgBiP$_2$Se$_6$ monolayers potentially have photocatalytic activity for water-splitting in the neutral environment. For practical application, we also evaluate the stability of photocatalysts in the aqueous solution under illumination. According the method proposed by Chen et al., the thermodynamic oxidation potential ($\phi^{\text{ox}}$) and reduction potential ($\phi^{\text{re}}$) of PE and FE AgBiP$_2$Se$_6$ monolayers are calculated, respectively. More computational details can be found in the Supporting Information. As displayed in Figure 3a and 3b, the $\phi^{\text{ox}}$ of both PE and FE AgBiP$_2$Se$_6$ monolayers (red line) are lower than the oxidation potential for O$_2$/H$_2$O, while both the $\phi^{\text{re}}$ (blue line) are higher than the reduction potential for H$^+$/H$_2$, which reveals that photogenerated carriers prefer to react with water molecule rather than the photocatalysts themselves. Hence both PE and FE phase AgBiP$_2$Se$_6$ monolayers have a good resistance to photoinduced corrosion. Notably, in monolayer AgBiP$_2$Se$_6$, the PE phase

**Figure 2** Optical absorption coefficients of paraelectric and ferroelectric AgBiP$_2$Se$_6$ monolayers. The scale of the visible light region (380~780 nm) is in iridescent color.

**Band Alignment.** Owing to the broken mirror symmetry, there is an intrinsic dipole moment for FE AgBiP$_2$Se$_6$ monolayers, which generate a built-in electric field perpendicular to the layer. The direction of built-in electric field pointing from bottom surface to up surface, and the electrostatic potential difference is 0.27 eV (as illustrated in Figure 3b). To explore the spatial distribution of carriers further, we investigate the partial charge density of CBM and VBM for both FE and PE AgBiP$_2$Se$_6$ monolayers, which are presented in Figure 3c and 3d, respectively. For the PE phase, both VBM and CBM uniformly spread over both surfaces. So, the reactivities of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are the same at both surfaces. In contrast, for the case of FE phase, the VBM mainly distribute at the top surface and the CBM at the bottom surface. Under the action of built-in electric field, the photo-excited electrons incline to distribute at the top surface, while the holes tend to distribute at bottom surface. As a result, HER will probably mainly occur at the bottom surface, while OER at the top surface, which would effectively decrease the carrier recombination and increase the photocatalytic efficiency.
has a stronger reducibility and the FE phase processes a higher oxidizability, which demonstrates that the ferroelectric switch could tune the redox abilities of ferroelectric catalyst.

Energy Conversion Efficiency. We then estimate the energy conversion efficiency of monolayer AgBiP$_2$Se$_6$ for photocatalytic water splitting. The method is presented in the Supporting Information. To check the efficiency of the catalytic reaction, the energy conversion efficiency of light absorption ($\eta_{abs}$), carrier utilization ($\eta_{cu}$), solar-to-hydrogen (STH) ($\eta_{STH}$) and corrected STH ($\eta'_{STH}$) are listed in Table 2. Although light adsorption efficiency $\eta_{abs}$ in PE phase (26.04%) is slightly higher than FE phase (23.12%), FE phase has a much higher carrier utilization efficiency $\eta_{cu}$ (44% vs 25.59%) due to the effective electron-hole separation as a result of intrinsic electric field. Therefore, the STH efficiency ($\eta_{STH}$) which can evaluate the additional energy required to surmount the barriers of the HER and OER is obviously larger at FE phase (10.27%) compared with PE phase (6.66%). With the polarization in consideration, the corrected STH efficiency of FE AgBiP$_2$Se$_6$ monolayer can still reach up to 10.04%, which is the highest among the family of ABP$_2$X$_6$ (A = Ag, Cu; B = Bi, In; X = S, Se) materials we considered (as listed in Table S2). One can see that their energy conversion efficiencies also can be well regulated by ferroelectric-ferroelectric phase switch.

Table 2 Energy conversion efficiency of light absorption ($\eta_{abs}$), carrier utilization ($\eta_{cu}$), STH ($\eta_{STH}$) and corrected STH ($\eta'_{STH}$) of Paraelectric and Ferroelectric AgBiP$_2$Se$_6$ Monolayers.

|                  | $\eta_{abs}$ (%) | $\eta_{cu}$ (%) | $\eta_{STH}$ (%) | $\eta'_{STH}$ (%) |
|------------------|------------------|-----------------|------------------|------------------|
| AgBiP$_2$Se$_6$  | 26.04            | 25.59           | 6.66             | --               |
| (PE)             |                  |                 |                  |                  |
| AgBiP$_2$Se$_6$  | 23.12            | 44.40           | 10.27            | 10.04            |
| (FE)             |                  |                 |                  |                  |

Adsortion of Water Molecule. We then evaluate the effects of FE phase transition on the photocatalytic water-splitting capacity. As the first and key step, the adsorption behavior of H$_2$O on the AgBiP$_2$Se$_6$ monolayer will be studied and compare the differences for FE and PE phases. For PE AgBiP$_2$Se$_6$ monolayer, the two sides are the same, so we only investigate one surface (labeled as PE-H$_2$O). For FE AgBiP$_2$Se$_6$ monolayer, the adsorptions on the top and bottom surfaces are both studied (labeled as FE(top)-H$_2$O and FE(bottom)-H$_2$O, respectively). As displayed in Figure S3, different adsorption sites for H$_2$O are considered to explore the most stable adsorption configuration. After geometrically optimized, the most energetically stable adsorption structures of H$_2$O are identified on the AgBiP$_2$Se$_6$ monolayer. On the PE AgBiP$_2$Se$_6$ monolayer surface, the O atom of the absorbed H$_2$O molecule locates above near the hexagonal center of the lattice and the vertical distance between the H and Se layer is about 1.97 Å. On the top surface of FE AgBiP$_2$Se$_6$ monolayer, the O atom stays above the Ag atom with 2.27 Å between the H and Se layer, while on the bottom surface, it is located above the Bi atom and the vertical distance between the H and Se layer is 2.01 Å. In order to estimate the interaction strength between the H$_2$O molecule and the AgBiP$_2$Se$_6$ monolayer, we defined the adsorption energy ($E_{ads}$) as following equation:

$$E_{ads} = E_{total} - E_{layer} - E_{H_2O}$$

where $E_{total}$ is the total energy of the whole gas-adsorbed system, $E_{layer}$ corresponds to the energy of the pristine AgBiP$_2$Se$_6$ monolayer and $E_{H_2O}$ is the energy of the isolated H$_2$O molecule. We find that all the $E_{ads}$ values for the three case are negative and they are in the order of $E_{ads(PE-H_2O)}(-0.466 eV) > E_{ads(FE-H_2O)}(-0.448 eV) > E_{ads(FE-H_2O)}(-0.480 eV)$. Usually, the adsorbed molecule can be stabilized by the charge transfer. Based on the Bader analysis, as plotted in Figure S6, we find there are a total of 28.42×10$^{-3}$, 28.64×10$^{-3}$ and 44.49×10$^{-3}$ electron transferring from AgBiP$_2$Se$_6$ monolayer to adsorbed H$_2$O molecule, which is consistent with the result of adsorption energy in these three cases. The difference of the electron transferring on the two surfaces of FE AgBiP$_2$Se$_6$ monolayer may be due to the electric potential difference. As
illustrated in Figure 3b, due to the instinct electric filed, the bottom surface has a lower electric potential than the top surface, so the electron could transfer to the adsorbed H₂O molecule more easily. The results of electron transfer also in turn confirm the validity of the direction of the built-in electric field in FE AgBiP₂Se₆ monolayer.

**Driving Force of Photo-exited Carriers for Overall Water Splitting.** In order to explore the effect of ferroelectric switch on the driving force of photogenerated electrons and holes of AgBiP₂Se₆ monolayer, we finally systematically investigated mechanisms of both water oxidation and hydrogen reduction under the PE and FE phases, respectively.

![Proposed photocatalytic pathways of water oxidation (a) and hydrogen reduction (b) half reactions with the most energetically favorable absorbed intermediates (OH*, O*, OOH*, and H*) in paraelectric AgBiP₂Se₆ monolayer. The red and green balls represent O and H atoms, respectively. Free energy diagrams of OER (c) and HER (d) on paraelectric AgBiP₂Se₆ monolayer under different conditions. The CBM and VBM of paraelectric AgBiP₂Se₆ monolayer under different biaxial compression strains (e). ∆G of paraelectric AgBiP₂Se₆ monolayer versus different applied biaxial compression strains and pH (f). The optimal reaction barrier (25 meV) is highlighted in yellow plane.](image)

Figure 4

As illustrated in Figure 4a and 5a, the half reaction of water oxidation follows a four-electron (4e) reaction pathway, accompanied by the intermediate product of OH*, O*, and OOH*. The corresponding free-energy profiles for PE and FE phase AgBiP₂Se₆ monolayers are separately summarized in Figure 4c and 5c, where the black lines represent the situation without any external potential to simulate the condition in the absence of any light irradiation (U = 0 V).

More computational details can be found in the Supporting Information. On the surface of PE AgBiP₂Se₆, the adsorbed water molecule is firstly transformed into a *OH species with a ∆G of 1.19 eV; Secondly, after releasing an electron and a proton, the *OH species is oxidized to O* species, with a ∆G of 0.02 eV; Thirdly, combining with another water molecule, *O species is oxidized to OOH* species with a ∆G of 2.12 eV, which is the highest free energy change in the water oxidation half reaction; Finally, the OOH* species spontaneously liberate a free O₂ molecule, a proton and an electron, releasing the heat of 0.07 eV. The water oxidation half reaction on the top surface of FE phase AgBiP₂Se₆ monolayers is similar to that of PE phase, but with different reaction barriers. The ∆G for 1–4 step is 1.24, -0.07, 2.17 and -0.08 eV, respectively. For both phases, the water oxidation half reactions are not energetically favorable on the surface of AgBiP₂Se₆ monolayer without light irradiation.

As shown in Figure 4c and 5c, when the AgBiP₂Se₆ monolayers under illumination, an external potential will be provided by photogenerated holes (U=1.93 and 2.70 V for PE and FE AgBiP₂Se₆ monolayers, respectively). Remarkably, all the steps are downhill in the FE case, indicating that, FE AgBiP₂Se₆ monolayer has the ability of catalyzing water oxidation in the neutral condition under
illumination. More notably, as shown in Figure S7, under illumination, the ferroelectric AgBiP\textsubscript{2}Se\textsubscript{6} monolayer could oxidize water into oxygen spontaneously even in the acid medium (3 ≤ pH < 7), which can’t be done for most existing photoelectrocatalysts, because of the high overpotential and instability.\textsuperscript{61} As for the case of PE phase, the third step is still uphill (ΔG = 0.19 eV), indicating the O\textsuperscript{*} species cannot be transformed into OOH\textsuperscript{*} species spontaneously, namely the OER reaction can’t be achieved even under the light illumination. Therefore, the ferroelectric switch could adjust the driving force of photogenerated holes of AgBiP\textsubscript{2}Se\textsubscript{6} monolayer to water oxidation and FE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer could be a potential photocatalyst for OER.

![Ferroelectric AgBiP\textsubscript{2}Se\textsubscript{6}](image)

**Figure 5** Proposed photocatalytic pathways of water oxidation (a) and hydrogen reduction (b) half reactions with the most energetically favorable absorbed intermediates (OH\textsuperscript{*}, O\textsuperscript{*}, OOH\textsuperscript{*}, and H\textsuperscript{*}) in ferroelectric AgBiP\textsubscript{2}Se\textsubscript{6} monolayer. The red and green balls represent O and H atoms, respectively. Free energy diagrams of OER (c) and HER (d) on ferroelectric AgBiP\textsubscript{2}Se\textsubscript{6} monolayer under the different conditions.

As for the hydrogen reduction half, there are only two steps, as displayed in Figure 4b and 5b. As plotted in Figure 4b, without light irradiation (U = 0 V), firstly, PE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer combines with a proton and an electron to form an H\textsuperscript{*} species with an unfavorable ΔG of 1.33 eV; Next, the H\textsuperscript{*} specie continues to bond a proton and an electron to release a H\textsubscript{2} molecule, which is exothermic by 0.54 eV. For FE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer, the process of hydrogen reduction half reaction is similar, but also with different reaction barriers. The ΔG for the two steps is 1.71 and -0.88eV, respectively, indicating HER is even less favorable at FE phase. Under the external potential (U=0.27 and 0.09 V for PE and FE AgBiP\textsubscript{2}Se\textsubscript{6} monolayers, respectively) provided by photogenerated electrons, the first step for both cases is still uphill, but the barrier is obviously reduced. For the FE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer, the barrier is 1.62 eV at pH=7, which is more than 1.5 times of the one (1.06 eV at pH=7) for the PE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer, indicating the PE phase is more promising for HER although the barrier is still quite high. Generally speaking, HER prefers to react under the acidic environments. When the pH effect is considered, the reaction barrier can be linearly decreased by pH adjustment according to the Equation S1 while the value of U\textsubscript{e} can be lifted according to Equation 3. Taken pH=0 as an example, the reaction barrier can be significantly reduced to 0.24 eV (PE) and 0.80 eV (FE) respectively. In order to further decrease the HER barrier, we apply biaxial compression strain, which has been proven as an effective and feasible approach to tune the catalytic activity.\textsuperscript{62-64} As illustrated in Figure S8, the formation energy of H\textsuperscript{*} can be reduced with the increase of biaxial compression strain, the value of ΔG\textsubscript{H*}, i.e. the reaction barrier of HER on PE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer can be effectively lowered (The discussion can be found in the Supporting Information). Meanwhile, the value of U\textsubscript{e} also can be raised by the biaxial compression strain, due to the lifted CBM as shown in Figure 4e. Therefore, under illumination, the value of ΔG\textsubscript{H*} drops obviously with the decreasing pH and increasing biaxial compression strain, as displayed in Figure 4f. We set 25 meV as an optimal reaction barrier (the yellow plane),\textsuperscript{65} and satisfactorily, there are a large area within the plane, which means the compressed PE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer could have a high activity for hydrogen production in acid environment. To compare the difference of HER reaction barrier between PE and FE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer under the same condition, we take the case of pH=1 and -4% biaxial compression strain as an example. As illustrated in Figure 4d and 5d, the HER reaction barrier of PE AgBiP\textsubscript{2}Se\textsubscript{6} monolayer has reached almost 0 eV under illumination, while the one of FE phase is up to 0.58 eV, demonstrating the ferroelectric switch could also tune the driving force of photogenerated electron of AgBiP\textsubscript{2}Se\textsubscript{6} monolayer to hydrogen reduction in the acidic environments with aid of strain.

\textbf{CONCLUSIONS}

In summary, we theoretically explored the effect of ferroelectric switch on the photocatalytic water-splitting property of AgBiP\textsubscript{2}Se\textsubscript{6} monolayer by analyzing the difference in structural, electronic, and optical characters between FE and PE phases using comprehensive DFT computations. According to our calculation, the ferroelectric switch could regulate the exciton binding energy, redox abilities and driving force of photogenerated carriers in AgBiP\textsubscript{2}Se\textsubscript{6} monolayer. More specifically, (i) the PE phase has a stronger reducibility, while the FE phase processes a higher oxidizability; (ii) the driving force of
photogenerated holes of FE AgBiP2Se6 is stronger than the one in PE phase, while the driving force of photogenerated electron of PE AgBiP2Se6 is more powerful; (iii) the FE phase has a larger exciton binding energy than PE one, so is monolayer AgBiP2Se6, CuBiP2Se6, and CuInP2Se6. Our results vividly revealed that the ferroelectric switch is an effective way to modify or improve the 2D ferroelectric photocatalyst. Moreover, FE AgBiP2Se6 monolayer with strong optical absorbance in visible light region, well H2O adsorption and oxidation abilities, and adequate driving forces to water oxidation is an ideal photocatalysts for OER. What’s more, under biaxial compression strain, the PE AgBiP2Se6 monolayer could have a high activity for hydrogen production in acid environment.

■ ASSOCIATED CONTENT
Supporting Information
This material is available free of charge via the Internet at http://pubs.acs.org.
Band structures of PE and FE AgBiP2Se6 monolayers based on HSE06 with and without the spin-orbit coupling effect; Total and Projected density of states of PE and FE AgBiP2Se6 monolayers based on HSE06 functional; Imagery parts ε of dielectric functions of PE and FE AgBiP2Se6, AgBiP2S6, CuBiP2Se6 and CuInP2Se6 monolayers based on G0W0-BSE level; Band structures of PE and FE AgBiP2Se6, CuBiP2Se6 and CuInP2Se6 monolayers based on G0W0 functional; The H2O molecule adsorption sites at the PE and FE AgBiP2Se6 surface; Top and side views of the most stable adsorption structures of H2O on the surface of PE and FE AgBiP2Se6 monolayers; The Gibbs free energy changes of OER at different pH on FE AgBiP2Se6 monolayer under illumination; For the PE AgBiP2Se6 monolayer, the formation energy of H* under different biaxial compression strains and ∆Ge without illumination under different pH and biaxial compression strains; The direct band gaps at GaW6 functional level, the optical band gaps, exciton binding energies for PE and FE AgBiP2Se6, CuInP2Se6, and CuBiP2Se6 monolayers; Details for the solar-to-hydrogen efficiency; Details for Free energy difference; Discussion on the reaction barrier of HER on PE AgBiP2Se6 monolayer; Details for the thermodynamic oxidation and reduction potentials of PE and FE AgBiP2Se6 monolayers in aqueous solution. (PDF)

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All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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