Internal Electric Fields in Asymmetric Single-layer Lattices for Enhancing Photocatalytic Solar-to-Hydrogen Efficiency

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Abstract

Two-dimensional materials with intrinsic internal electric field possess promising potential to improve the photocatalytic water-splitting performance. However, the construction of the internal electric field is still a great challenge, which requires that the material itself should exhibit spontaneous symmetry breaking with intrinsic polarization. Herein, we propose using a general intercalation approach to introduce spontaneous polarization electric field into single-layer lattice by constructing the spatially asymmetric configurations. Taking septuple-atomic-layer MoSi$_2$N$_4$ as a model material, following the above design principle, four promising MSi$_2$N$_3$Y (M= Mo, W; Y=P, As) monolayers are theoretically identified, exhibiting excellent stabilities, suitabilities and low reaction barriers for overall water splitting. Importantly, the intrinsic internal electric field of MoSi$_2$N$_3$Y promotes the charge-carrier separation and improves the light absorption capacity simultaneously, thus enabling the high solar-to-hydrogen efficiency of 29.84%−32.93%. This study opens up an avenue to rationally engineer the internal electric field and contributes to enhance the photocatalytic efficiency.

Introduction

Photocatalytic water splitting is a green and renewable avenue to convert solar energy and water sources into hydrogen energy, which is of great significance to alleviate the current energy and environmental problems$^{1-3}$. Since the pioneering work in TiO$_2$ by Fujishima and Honda$^4$, numerous potential photocatalytic materials have been proposed for solar hydrogen production$^5-13$. However, the solar-to-hydrogen (STH) efficiency, a vital index for assessing photocatalytic water splitting, is not yet satisfactory for currently available photocatalysts due to the light absorption limit, low carrier utilization and poor kinetic overpotential$^{14-16}$. Two-dimensional (2D) polar materials are promising to overcome the aforementioned problems. Intrinsic spontaneous polarization in such a specific semiconducting system could induce an internal electric filed, conducive to suppressing the charge-carrier recombination and widening light absorption region$^{17-20}$. According to the recent catalytic mechanism proposed by Yang et al$^{21}$, the theoretically STH efficiency of some predicted 2D polar materials can exceed the conventional upper limit of $\sim 18\%$$^{22-25}$. Despite these valuable advances, at present, the difficulties for this field lie in how we can effectively find more promising candidate materials with desirable properties.

Physically, creating 2D spontaneous polarization is usually accompanied by out-of-plane symmetry breaking, which largely depends on the material's asymmetric configurations and constituents. Much conventional attentions are given to achieving this goal by extrinsic modulation strategies, for example via Z-scheme heterostructure construction, elements doping, defect engineering and adatom decoration$^{26-31}$, but these strategies suffer from material selection limitation and structure deformation, restricting the identification of potential photocatalytic candidate materials. On the other hand, establishing the research on spontaneous polarization generated by single-layer lattices themselves shows great and ever-increasing prospects both from fundamental physical understanding and potential photocatalytic applications. However, because of the lack of out-of-plane asymmetry, the construction of
the internal electric field from single-layer lattice remains a great challenging task. Therefore, it is of great significance to develop a feasible path to break out-of-plane spatial symmetry for introducing spontaneous polarization.

In this work, starting from septuple-atomic-layer configuration of the emerging MoSi$_2$N$_4$, we theoretically identify a general intercalation design principle to construct a series of 2D asymmetric single-layer structures featuring intrinsic dipoles. Through the first-principles calculations, we obtained four stable MSi$_2$N$_3$Y (M = Mo, W; Y = P, As) monolayer, and systemically investigated their photocatalytic properties dependent on intrinsic polarization. Our results show that the presence of internal electric field improves the efficiency of charge separation and driving force of photo-induced carriers, thus boosting the photocatalytic performance. Excitingly, the STH efficiencies of MSi$_2$N$_3$Y monolayers are up to 29.84 - 32.93%. Furthermore, the photocatalytic water-splitting reactions on MSi$_2$N$_3$Y monolayers is predicted to operate spontaneously under solar radiation. These present findings provide important insights into rational design of 2D high-performance polar photocatalysts.

**Methods**

We perform the density functional theory (DFT) calculations by using the Vienna ab initio simulation package (VASP)$^{32-33}$. The exchange-correlation interactions were described by the generalized gradient approximation in the form of the Perdew–Burke–Ernzerhof (PBE)$^{34}$. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional$^{35}$ was adopted for the electronic structure calculations. All geometric structures were fully relaxed until the residual force was less than 0.01 eV Å$^{-1}$. The cutoff energy and convergence criterion of energy were set as 500 eV and 10$^{-5}$ eV, respectively. A Monkhorst-Pack k-point mesh of 10×10×1 was employed for sampling 2D Brillouin zone. To avoid interactions between adjacent periodic images, the vacuum space of 20 Å along the out-of-plane direction was added. Grimme's DFT-D3 method$^{36}$ was applied to take van der Waals interactions into account. Ab initio molecular dynamics (AIMD) simulation were carried out to examine the thermal stability at 300K for 5ps with a time step of 2 fs. The phonon dispersion was calculated based on the density functional perturbation theory using the PHONOPY code$^{37}$.

**Results**

**Screening of promising candidates.** Figure 1(a) shows the top and side views of primitive cell of the MoSi$_2$N$_4$ monolayer with a septuple-atomic-layer structure, where the MN$_2$ layer is sandwiched by the top and down Si-N bilayers. The optimized lattice constant of MoSi$_2$N$_4$ monolayer is 2.90 Å, consistent with the value reported by the previous experiments. Based on the sandwich architecture of MoSi$_2$N$_4$ monolayer, we construct 2D MSi$_2$N$_2$XY (M = Mo, W; X/Y = N, P, As, S, Se, Te; X ≠ Y) compounds by a intercalation design principle, that is, inserting a Janus MXY layer into the Si$_2$N$_2$ layer. The atomic arrangements and our studied element compositions of MSi$_2$N$_2$XY monolayers are shown in Fig. 1(b),
where \( M \) represents group-VI transition-metal elements (\( M = Mo, W \)), \( X \) and \( Y \) correspond to group-V and -VI elements (\( X, Y = N, P, As, S, Se, Te; X \neq Y \)). The asymmetric geometry of \( MXY \) layer results in the crystalline symmetry breaking of \( MSi_2N_2XY \) monolayers, which leads to spontaneous polarization along the out-of-plane direction. Through the stochastic combination of element compositions, 30 possible configurations for 2D \( MSi_2N_2XY \) materials are initially identified. Then, all these predicted structures are fully relaxed to obtain their corresponding stable configurations.

To explore the potential application of \( MSi_2N_2XY \) monolayers in water splitting, we present a multilevel workflow combining several key criteria to screen stable, and highly efficient candidate photocatalysts, as shown in Fig. 1(c). In general, the external potential provided by photogenerated electrons (and holes) should be large enough to overcome the overpotential of HER (and OER), so that the whole process of water splitting can proceed spontaneously. Moreover, the STH efficiency can be used to evaluate the energy conversion efficiency of photocatalytic materials quantitatively. Therefore, we introduced the energy cost and STH efficiency as determining descriptors to characterize the photocatalytic activity of \( MSi_2N_2XY \) monolayers.

Following this screening strategy, the structural properties of \( MSi_2N_2XY \) monolayers are studied first. Detailed structural parameters are listed in Tables S1. It is found that some predicted structures display a lattice stretching along the \( z \)-direction after geometry optimizations due to the enlarged bond length between Si and X (Y) atoms \( d_{Si-X} (d_{Si-Y}) \). Excessive distance stretching between \( MXY \) layer and SiN layer means the structural distortions of \( MSi_2N_2XY \) monolayers. We define a threshold value of 3.0 Å for \( d_{Si-X} (d_{Si-Y}) \) to assess the distortion degree of \( MSi_2N_2XY \) monolayers, and find that 22 candidates are within this threshold range, indicating that these structures possess good structural strength.

After that, we perform a series of stability confirmation calculations to further screen stable and synthesizable candidates, as shown in Fig. S1. First, we calculated the enthalpies of formation of \( MSi_2N_2XY \) monolayers by:

\[
E_f = \left\{ E_{tot} - (E_M + 2E_{Si} + 2E_N + E_X + E_Y) \right\} / 27,
\]

where \( E_{tot} \) represents the total energy of the system, and \( E_M, E_{Si}, E_N, E_X \) and \( E_Y \) are the energies of separate M, Si, N, X and Y atoms, respectively. As shown in Fig. S2, we found that the enthalpies of formation of 22 selected \( MSi_2N_2XY \) monolayers are within the range of -0.73 eV to -2.74 eV, demonstrating the energetics. Then, we explore their dynamical stability by calculating the phonon dispersion, for which the results are shown in Fig. 2 and S3. Our calculations suggest that only four candidates, that is, \( MoSi_2N_3P \), \( MoSi_2N_3As \), \( WSi_2N_3P \) and \( WSi_2N_3As \) are dynamically stable, while the others 18 compounds are discarded since they exhibit imaginary frequencies. The AIMD simulations are conducted to further confirm the thermal stabilities of four selected structures (Fig. 2). After 5ps of heating at room temperature, the fluctuation range of energy and temperature is small, and no large structural deformation occurs, attesting high thermal stability. Additionally, four independent elastic constants \( C_{11}, C_{22}, C_{12} \) and \( C_{66} \) of \( MSi_2N_2XY \) monolayers are obtained, which fulfills the Born-Huang criteria\( ^{38} \) for mechanically stable 2D systems. (see the details in the Supporting Information and Table S2). Furthermore, Young’s modulus \( Y(\theta) \) and Poisson’s ratio \( \nu(\theta) \) demonstrate their isotropic mechanical behaviors (Fig. S4). Especially, the calculated

\[
C_{11} = \frac{1}{7} \left\{ E_{tot} - (E_M + 2E_{Si} + 2E_N + E_X + E_Y) \right\} / 27
\]

\[
C_{22} = \frac{1}{7} \left\{ E_{tot} - (E_M + 2E_{Si} + 2E_N + E_X + E_Y) \right\} / 27
\]

\[
C_{12} = \frac{1}{7} \left\{ E_{tot} - (E_M + 2E_{Si} + 2E_N + E_X + E_Y) \right\} / 27
\]

\[
C_{66} = \frac{1}{7} \left\{ E_{tot} - (E_M + 2E_{Si} + 2E_N + E_X + E_Y) \right\} / 27
\]
\( Y(\theta) \) for MoSi\(_2\)N\(_3\)P and WSi\(_2\)N\(_3\)P reach to 312.8 N/m and 324.6, respectively, which is comparable to graphene (342.2 N/m)\(^{39}\) and MoS\(_2\) (330.0 N/m)\(^{40}\).

On the basis of the stability evaluation, four kinds of MSi\(_2\)N\(_2\)XY monolayers, namely, MoSi\(_2\)N\(_3\)P, MoSi\(_2\)N\(_3\)As, WSi\(_2\)N\(_3\)P and WSi\(_2\)N\(_3\)As, are screened out with excellent stabilities. Their band structures predicted by HSE06 functional are shown in the left column of Fig. 3. It can be seen that all the four candidates exhibit semiconducting characters with the band gaps of 0.96 eV, 0.46 eV, 0.79 eV and 0.45 eV for MoSi\(_2\)N\(_3\)P, MoSi\(_2\)N\(_3\)As, WSi\(_2\)N\(_3\)P and WSi\(_2\)N\(_3\)As, respectively. Intriguingly, MSi\(_2\)N\(_3\)Y monolayers can transform from indirect to direct band gap semiconductors, when the Y component varies from P to As because the valence band maximum (VBM) moves from K to the \( \Gamma \) point. Consequently, the narrow band gaps of 2D MSi\(_2\)N\(_3\)Y in the range of 0.45–0.96 eV means that they can expand the light absorption into visible or even infrared regions, implying efficient utilization of solar energy.

**Photocatalytic performance of MSi\(_2\)N\(_2\)Y.** As is well-known, a prerequisite for water splitting of semiconducting materials is that the band edges enclose the hydrogen reduction potential (-4.44 eV at pH = 0) and water oxidation potential (-5.67 eV at pH = 0)\(^{41}\). For conventional photocatalysts without intrinsic polarization, the reduction/oxidation potential is aligned with respect to the conduction/valence band edge according to the same vacuum level, and thus, the band gap required for water splitting should be larger than 1.23 eV. Owing to the broken out-of-plane symmetry, the intrinsic dipoles are introduced into MSi\(_2\)N\(_3\)Y monolayers (Table 1), which generates an internal electric field perpendicular to the layer. The presence of internal electric field results in a vacuum level difference between the two sides of MSi\(_2\)N\(_3\)Y monolayers, which is characterized by the electrostatic potential curves in the middle column of Fig. 3. The internal electric field points from the bottom surface near Y component to the top surface, and the potential differences between the two surfaces are 2.12 eV, 2.55 eV, 2.00 eV and 2.46 eV for MoSi\(_2\)N\(_3\)P, MoSi\(_2\)N\(_3\)As, WSi\(_2\)N\(_3\)P and WSi\(_2\)N\(_3\)As, respectively. Driven by the internal electric field, the photogenerated electrons and holes aggregate on the bottom and top surfaces of MSi\(_2\)N\(_3\)Y monolayers respectively, ensuring that the HER and OER occurs on the two respective regions. In this case, the water redox potentials of MSi\(_2\)N\(_3\)Y monolayers are determined with respect to the vacuum energy levels of the bottom and top surfaces respectively, thus breaking the band gap limitation (1.23 eV) for overall water splitting.

Considering the different vacuum levels, the band edge positions of MSi\(_2\)N\(_3\)Y monolayers are shown in the right column of Fig. 3. Obviously, the conduction band maximum (CBM) of all four candidates lies above the hydrogen reduction potential (\( E_{\text{H}^+/\text{H}_2}\)) and the VBM lies below the water oxidation potential (\( E_{\text{O}_2/\text{H}_2O}\)), fulfilling the band edge requirements for water splitting. Importantly, the energy difference between the \( E_{\text{H}^+/\text{H}_2}^{\text{red}} \) and the CBM (or VBM) represent the redox capacities of photogenerated electrons (or holes), which is denoted as \( U_e \) (\( U_h \)) (Fig. 3). The detailed \( U_e \) at the bottom surface and \( U_h \) at the top surface for MSi\(_2\)N\(_3\)Y monolayers are listed in Table 1. It is found that all four structures satisfy the screening criterion: \( U_e > 0 \) eV and \( U_h > 1.23 \) eV, suggesting their sufficient redox capacities for both HER
and OER. As a result, MSi$_2$N$_3$Y monolayers are preliminarily identified as potential structures for overall water splitting.

In general, the photogenerated electrons and holes distributed at different locations of one material benefits to reducing their recombination probability. To explore the spatial distribution of photogenerated carriers, we examined the partial charge densities at the CBM and VBM for both MSi$_2$N$_3$Y and MSi$_2$N$_4$ monolayers, which is shown in Fig. S5. For the MSi$_2$N$_4$ monolayers, both the charge densities of the CBM and VBM are mainly distributed at the MN$_2$ layer, which is consistent with previous reports. In contrast, for the case of MSi$_2$N$_3$Y monolayers, the charge density of the CBM is mostly localized at the Si-N layer while that of VBM is localized at the MXY layer, resulting in good separation between photogenerated electrons and holes. Such charge distribution can significantly decrease the possibility of recombination of photogenerated electrons and holes, and ensure the high efficiency of photocatalytic reactions.

Above, we have confirmed that MSi$_2$N$_3$Y monolayers possess suitable band edge positions with sufficient redox potentials. Therein, we further investigated the mechanism of the half-reaction of both water oxidation and hydrogen reduction by calculating their reaction free energies at a neutral condition (Computational details can be obtained in supplementary materials). For HER, there are only two reaction steps (reaction (1) and (2)). Therefore, the reaction barrier ($E_{\text{barrier}}$) could be obtained as follows:

\[
E_{\text{barrier-HER}} = \begin{cases} \max (\Delta G_1, \Delta G_2) \max (\Delta G_1, \Delta G_2) > 0 \\ 0 \max (\Delta G_1, \Delta G_2) < 0 \end{cases}
\]

1

While the OER follows four elementary steps (reaction (3), (4), (5) and (6)). The $E_{\text{barrier}}$ of OER is determined by:

\[
E_{\text{barrier-OER}} = \begin{cases} \max (\Delta G_3, \Delta G_4, \Delta G_5, \Delta G_6) \max (\Delta G_3, \Delta G_4, \Delta G_5, \Delta G_6) > 0 \\ 0 \max (\Delta G_3, \Delta G_4, \Delta G_5, \Delta G_6) < 0 \end{cases}
\]

2

When the $E_{\text{barrier}}$ for HER and OER equals to 0, which means that the redox reactions of overall water splitting can proceed spontaneously. The corresponding free-energy profiles for MSi$_2$N$_3$Y monolayers are shown in Fig. 4. In the dark environment, the $E_{\text{barrier}}$s of HER and OER for MoSi$_2$N$_3$P monolayer are calculated to be 0.55 eV and 0.56 eV, respectively, requiring additional energies for photocatalytic reactions. At light irradiation condition, $U_e$ and $U_h$ can act as the driving forces of photogenerated electrons and holes to decrease the $E_{\text{barrier}}$s of HER and OER, respectively, thereby directly promoting the full water-splitting process. Accordingly, we find that the free energies for HER and OER decrease in each step with the external potential of $U_e = 0.96$ V and $U_h = 2.12$ V under illumination, implying that MoSi$_2$N$_3$P monolayer can catalyze water to produce hydrogen and oxygen spontaneously. Similar to the case of
monolayer MoSi$_2$N$_3$P, the other three structures show the different values of $E_{\text{barrier}}$ at the absence of any light irradiation, but they all can satisfy the screening criterion: $E_{\text{barrier-HER}} = E_{\text{barrier-OER}} = 0$ eV under illumination.

**Solar-to-hydrogen efficiency.** Excellent optical response is of great significance to produce more photogenerated carriers under photon absorption. To evaluate the performance of MSi$_2$N$_3$Y monolayers in harvesting sunlight, we calculated their optical absorption spectra by using the HSE06 functional. As shown in Fig. S6, compared with MSi$_2$N$_4$ monolayer, a red-shift of the spectrum is observed for MSi$_2$N$_3$Y monolayers, supporting its utilization of visible light. Moreover, we obtain the peak intensity of up to $2 \times 10^5$ cm$^{-1}$ for MoSi$_2$N$_3$As monolayer, which is higher than that of previously reported 2D MSiGeN$_4$.

Hence, the MSi$_2$N$_3$Y monolayers can effectively harvest sunlight, improving the efficiency of light absorption as a photocatalyst for water splitting. As listed in Table S6, the light absorption efficiency of MSi$_2$N$_3$Y monolayers exceed 90%. Meanwhile, the intrinsic electric field of MSi$_2$N$_3$Y monolayers affects the carrier dynamics, enhancing the carrier utilization efficiency. The improvement of energy conversion efficiency is the ultimate target in the pursuit of solar energy utilization. Supposing that the efficiency of catalytic reaction is 100%, the corrected STH efficiencies of MoSi$_2$N$_3$P, MoSi$_2$N$_3$As, WSi$_2$N$_3$P and WSi$_2$N$_3$As monolayers are predicted to be 30.57%, 29.84%, 32.93% and 30.51%, respectively, which are larger than that of previously reported Janus WSSe (11.68%)$^{43}$, $P_4O_2$ (17.2%)$^{44}$ and AgBiP$_2$Se$_6$ (10.04%)$^{45}$. Note that these predicted values surpass the conventional theoretical limit of 18%$^{22}$. It is thus conclusive that MSi$_2$N$_3$Y monolayers can act as an effective candidate for photocatalytic water splitting with high stability and STH efficiency.

**Discussion**

To summarize, we propose a general intercalated architecture approach to introduce spontaneous polarization electric field into single-layer systems, and further examine the feasibility of this scheme in a real material of MoSi$_2$N$_4$. With the help of a multilevel screening workflow, using first-principles calculations, four candidate materials of MSi$_2$N$_3$Y are theoretically identified. It is found that the internal electric fields of MSi$_2$N$_3$Y monolayers suppress the recombination of photogenerated carriers, improving the efficiency of carrier utilization. Besides, combination of the band alignment, spatial charge distribution and optical absorption intensities and as well as energy cost supports the great potential of MSi$_2$N$_3$Y monolayers in overall water splitting. Especially, the high STH efficiencies of 29.84 – 32.93% enable these four materials to efficiently utilize the solar light for photocatalytic hydrogen production. This work not only demonstrates the importance of intrinsic polarization for boosting photocatalysis, but also provides valuable guidance for further design of 2D polar photocatalysts.

**Declarations**

**Data availability**
The data supporting the findings of this study are available within the article and its Supplementary Information.

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Figures

(a) Top and side views of the MoSi$_2$N$_4$ monolayer (b) Elemental compositions of our proposed MSi$_2$N$_2$XY monolayer. (c) Multilevel workflow for screening potential candidate photocatalysts.
Figure 2

(a)-(d) Phonon dispersion spectra, and AIMD energy fluctuations of MSi$_2$N$_3$Y monolayer at 300K.

Figure 3
(a)-(d) Band alignments of MSi$_2$N$_3$Y monolayers with respect to water redox potential. Cyan and purple bars represent the valence and conduction bands, respectively.

**Figure 4**

(a) Proposed photocatalytic pathways and free energy profiles of OER and HER on (a) MoSi$_2$N$_3$P, (b) MoSi$_2$N$_3$As, (c) WSi$_2$N$_3$P, and (d) WSi$_2$N$_3$As monolayers at different conditions.

**Supplementary Files**

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