Strain engineering of electronic and optical properties of monolayer diboron dinitride

Salih Demirci ^{1,2}, Soheil Ershad Rad ¹, and Seymur Jahangirov ^{1,*}

¹*UNAM-Institute of Materials Science and Nanotechnology, Bilkent University, Ankara 06800, Turkey*

²*Department of Physics, Kırıkkale University, Kırıkkale 71450, Turkey*

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We studied the effect of strain engineering on the electronic, structural, mechanical, and optical properties of orthorhombic diboron dinitride ($\text{o-B}_2\text{N}_2$) through first-principles calculations. The 1.7-eV direct band gap observed in the unstrained $\text{o-B}_2\text{N}_2$ can be tuned up to 3 eV or down to 1 eV by applying 12% tensile strain in armchair and zigzag directions, respectively. Ultimate strain values of $\text{o-B}_2\text{N}_2$ were found to be comparable with that of graphene. Our calculations revealed that the partial alignment of the band edges with the redox potentials of water in pristine $\text{o-B}_2\text{N}_2$ can be tuned into a full alignment under the armchair and biaxial tensile strains. The anisotropic charge carrier mobility found in $\text{o-B}_2\text{N}_2$ prolongs the average lifetime of the carrier drift, creating a suitable condition for photoinduced catalytic reactions on its surface. Finally, we found that even in extreme straining regimes, the highly anisotropic optical absorption of $\text{o-B}_2\text{N}_2$ with strong absorption in the visible range is preserved. Having strong visible light absorption and prolonged carrier migration time, we propose that strain engineering is an effective route to tune the band gap energy and band alignment of $\text{o-B}_2\text{N}_2$ and turn this two-dimensional material into a promising photocatalyst for efficient hydrogen production from water splitting.

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I. INTRODUCTION

Since the revolutionary advent of graphene [1–4] in 2004, two-dimensional (2D) materials have attracted intensive interest from researchers. In 2D structures, the out-of-plane quantum confinement gives rise to a plethora of exotic properties, unprecedented in their bulk counterparts. In graphene, the presence of Dirac cones at corners of the Brillouin zone induces semimetallic charge transport behavior [5], making graphene inapplicable in semiconductor devices. Moreover, very poor light absorption in a single sheet of graphene deteriorates its functionality in optoelectronic applications [6]. These deficiencies have motivated scientists to systematically search for new 2D materials and employ a variety of approaches to tailor their undesired properties. In the case of graphene, for instance, techniques such as doping [7], charging [8], making heterostructures [9], or even changing the chemistry by hydrogenation [10] are widely employed to create superior features.

Strain engineering is another conventional method to manipulate the structural, electronic, and optical properties of 2D materials. Several experimental approaches are available to apply tensile and compressive strains to 2D structures. The monolayer can be transferred on top of a flexible substrate, and uniaxial strain can be induced by bending the substrate [11]. In addition to bending, the substrate can also be stretched to induce a homogeneous uniaxial tensile strain [12]. Another approach is to exploit the thermal expansion mismatch between the substrate and the monolayer to induce a uniform biaxial strain [13]. Finally, a clever approach is to exploit

substrates with the piezoelectric feature, which enables fine control over the scope of strain through applying a precise electric potential to the piezoelectric material, making both tensile and compressive strains achievable [14,15]. The strain tunability of many 2D systems, such as graphene [11,16] and transition metal dichalcogenides (TMDs) [12–14,17], was studied with these approaches. The maximum strain that can be applied using these methods is less than 5% [18]. However, by employing modern approaches, such as fabrication of microelectromechanical system (MEMS) devices, strains of more than 10% can be applied to 2D structures [19]. Motivated by the development of experimental techniques employed in strain engineering, first-principles approaches were widely utilized to predict the strain-induced response of many 2D systems, including graphene [20], graphene [21], transition metal dichalcogenides [22], etc.

The abundance and thermal stability of 2D boron nitride compounds have turned them into suitable candidates for many applications. Hexagonal boron nitride (h-BN) is the most conventional and stable 2D form of the boron nitride compounds [23]. A large band gap makes h-BN an insulator [24]. In addition, h-BN light absorption mainly takes place in the range of 5–6 eV [25], which is far out of the visible region, making it highly transparent. These drawbacks provide room for the investigation of other 2D polymorphs of boron nitride. Recently, another stable 2D boron nitride compound, known as $\text{o-B}_2\text{N}_2$ [26], was predicted through first-principles calculations, where B-B and N-N pairs connect to create an orthorhombic unit cell with a space group symmetry of $Pmmm$ (No. 47), a direct band gap of 1.7 eV, and highly anisotropic optical absorption in the visible range of the light spectrum, suitable for optoelectronic applications.

*seymur@unam.bilkent.edu.tr

In this paper, inspired by the strong visible light absorption in o-B₂N₂ and its suitability for optoelectronic applications, we studied the effect of uniaxial and biaxial strain engineering on the electronic and optical properties of o-B₂N₂. To make sure that this structure can tolerate extreme strains without losing its integrity, the ultimate tensile strength and its corresponding ultimate strain were calculated. The strain-induced response of the structural properties, including bond lengths and lattice parameters, was probed. We found that the 1.7-eV band gap in the pristine condition can be modified broadly to create a suitable condition for photocatalytic applications [27–33]. Finally, the optical absorption response under strain was studied. We found that the anisotropic optical absorption of o-B₂N₂ in the visible range remains intact under a wide range of strain conditions.

II. METHODS

We performed first-principles calculations based on density functional theory (DFT) using a plane-wave basis set with an energy cutoff of 520 eV. We utilized projector-augmented wave potentials [34], and the exchange-correlation potential is approximated by generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) functional [35]. The Brillouin zone (BZ) is represented by an $8 \times 16 \times 1$ k-point grid in the Monkhorst-Pack scheme [36]. The equilibrium configuration of atoms is determined by minimizing the total energy of the system using the conjugate gradient method. The energy convergence criteria between the two consecutive electronic and ionic steps are taken to be 10^{-5} and 10^{-4} eV, respectively. In addition, the maximum pressure on the lattice has been lowered down to 0.1 kbar. To avoid interaction between periodic images in adjacent cells, a vacuum spacing of at least 20 Å was used. All calculations were performed using the Vienna *ab initio* simulation package (VASP) [37]. Electronic structure calculations were corrected via Heyd-Scuseria-Ernzerhof (HSE06) hybrid functionals [38]. The stress-strain curves are calculated, using a $3 \times 3 \times 1$ supercell. To calculate the optical response of the structure to strain, the imaginary part of the frequency-dependent dielectric function, which corresponds to optical absorption, is calculated using the random phase approximation (RPA) with $112 \times 224 \times 1$ k points and 56 bands. The local field effects are included at the Hartree level only [39]. Results obtained at the PBE level are then corrected using the scissors operation based on the difference between the PBE and HSE band gaps.

III. RESULTS AND DISCUSSION

o-B₂N₂ has an orthorhombic unit cell, with two inequivalent lattice constants of $a = 4.57$ Å and $b = 2.50$ Å. The atomic configuration of o-B₂N₂ is shown in Fig. 1(a). The structure is made of B-B and N-N dimers which are connected to each other to create an orthorhombic honeycomb structure. In an unstrained structure, B-N, B-B, and N-N bond lengths are 1.44, 1.44, and 1.70 Å, respectively, where the B-N length is equivalent to the conventional h-BN counterpart. In the pristine condition, o-B₂N₂ is a semiconductor with a direct band gap of 1.70 eV, according to HSE06 calculations, as can be seen in Fig. 1(b) [26].

FIG. 1. (a) Ball-and-stick model of o-B₂N₂, where gray and green balls denote nitrogen and boron atoms, respectively. The unit cell is depicted in a yellow shade. (b) Electronic band structure of o-B₂N₂ in the pristine condition (calculated using the HSE06 hybrid functional). The orange inset shows the high-symmetry lines of the BZ. (c) Stress-strain curves of o-B₂N₂ for armchair (red), zigzag (green), and biaxial (blue) strains, where the vertical dashed lines show the percentage of ultimate strain. (d) Tunability of the direct band gap of o-B₂N₂ with respect to the applied strain. (e) Same as (b) for various strain conditions.

In 2D materials, an applied strain can be described by the following expression:

$$\varepsilon = (l - l_0)/l_0, \quad (1)$$

where l and l_0 are strained and equilibrium unit-cell lengths along the strain direction, respectively. Based on Eq. (1), uniaxial- x (armchair), uniaxial- y (zigzag), and biaxial strains were applied to o-B₂N₂. The stress-strain curve of o-B₂N₂

TABLE I. The evolution of band gap, bond lengths, electron affinity EA under armchair, zigzag, and biaxial strained conditions.

ε	Unstrained	Armchair		Zigzag		Biaxial	
	0	-0.12	+0.12	-0.12	+0.12	-0.12	+0.12
Band gap (eV)	1.70	0.20	2.92	2.07	0.97	0.61	2.41
a (Å)	4.57	4.02	5.12	4.68	4.50	4.02	5.12
b (Å)	2.50	2.57	2.48	2.20	2.80	2.20	2.80
B-B (Å)	1.70	1.50	2.02	1.69	1.70	1.42	2.03
N-N (Å)	1.44	1.34	1.57	1.38	1.46	1.26	1.65
B-N (Å)	1.44	1.41	1.46	1.36	1.55	1.28	1.57
Second B-B (Å)	2.87	2.52	3.10	2.99	2.80	2.60	3.09
Second N-N (Å)	3.13	2.68	3.56	3.29	3.04	2.76	3.47
EA (eV)	3.05	3.77	2.54	1.92	3.90	2.59	3.42

under various types of strain is depicted in Fig. 1(c). We found the ultimate tensile strength (UTS) of o-B₂N₂ under biaxial strain to be 14.3 N/m, which is nearly half of the UTS value that we found for graphene (32.0 N/m) and h-BN (27.8 N/m) in agreement with the literature [40,41]. This places o-B₂N₂ among the 2D materials with relatively high UTS. The strength of a 2D material has a close relation with the charge transfer among its bonding atoms. Our Bader charge analysis shows that the charge transfer between boron and nitrogen atoms in o-B₂N₂ is half that in h-BN, which justifies the inferior UTS and ultimate strain of o-B₂N₂. However, with ultimate strains of 15, 16, and 28% for biaxial, armchair, and zigzag strain regimes, o-B₂N₂ is still among the 2D materials that can tolerate extreme strains. The lower ultimate strain under the armchair and biaxial strains is mainly due to the weakness of B-B bonds compared with the B-N bonds, where after the UTS point B-B bonds get detached. Nonetheless, these ultimate strain values are comparable with that of graphene (22% for biaxial) and h-BN (24% for biaxial) [40,41]. During the strain-engineering process of a 2D material, extreme strains can be imposed on the structure. A suitable candidate for strain engineering should be able to maintain its integrity under severe deformation. Although due to the technical constraints the maximum strain that has been applied to 2D materials is around 10%, the high ultimate strains found in o-B₂N₂ satisfy the prerequisites of strain engineering beyond this threshold in the future.

Assuring that o-B₂N₂ is a suitable candidate for strain engineering of its properties, we further analyzed the effect of the strain on its electronic properties. For the sake of comparison, the band structure of o-B₂N₂ in the pristine condition is presented in Fig. 1(b), and the strain-engineered band structures for the two exemplary cases of $\varepsilon = -0.08$ and $\varepsilon = +0.08$ are presented in Fig. 1(e). The direct band gap of o-B₂N₂ is created by the dispersion in both valence and conduction band edges along the *S*-*Y* direction. Our tight-binding analyses reveal that the dispersion in the conduction and valence is created by the interaction between the second-neighbor B-B and N-N atoms along the armchair direction, respectively [26]. Applying tensile strain along the armchair direction diminishes these interactions and results in less dispersive bands and a larger band gap, while compressive strain has the opposite effect. The reverse trend is observed in the case of the uniaxial compressive and tensile strain along the zigzag direction. This is because o-B₂N₂ has a positive

Poisson's ratio: Applying uniaxial tensile strain in the zigzag direction lowers the distance while increasing the interaction between the second-neighbor B-B and N-N atoms along the armchair direction. Biaxial strain creates behavior similar to the armchair case although the variation is less pronounced. This can be corroborated by the fact that under biaxial tensile (compressive) strain the distances of second-neighbor B-B and N-N atoms increase (decrease), but not as much as they do in uniaxial tensile (compressive) strain along the armchair direction (see Table I).

The variation in the band gap for all cases of compressive and tensile strain is shown in Fig. 1(d). Note that in all strain regimes the band gap can be tuned over a broad energy span. The most prominent tunability occurs under armchair strain, where the band gap variation covers a 3-eV zone. This scope of strain tunability is one of the exotic features of o-B₂N₂, which is rare among conventional 2D materials. For instance, in graphene, which is a semimetal in its unstrained condition, the band gap can be opened up to 0.5 eV by applying up to 15% uniform tensile strain along the armchair direction, while zigzag tunability is much lower [20]. The band gap of silicene and germanene cannot be tuned significantly through uniform strain, where the band gap increases (decreases) on the order of meV upon applying tensile (compressive) strain [42–44]. Unstrained antimonene has a band gap around 0.8 eV, while up to 4% armchair strain can widen this band gap to 1.1 eV; further straining decreases the band gap energy and limits the scope of tunability [45]. TMDs have a direct band gap with the gap located at the *K* point of the BZ, where the band gap varies depending on types of elements around 1–2 eV. Uniaxial or biaxial tensile strains linearly decrease the gap, while inducing a direct to indirect transition in small strains [22,46]. At high tensile strains of more than 12%, the band gap eventually closes, without breaking the bonds [47]. TMDs exhibit the same behavior upon the compressive strain, but the tunability is much lower than the tensile strain [48]. First-principles studies of phosphorene show that the electronic and optical gap increases by 0.2 eV upon applying uniaxial tensile strain up to 5% and decreases by 0.5 eV in the case of uniaxial compressive strain up to 10% and that a direct to indirect transition takes place around 5% uniaxial tensile strain [49–51]. A monolayer of h-BN has an insulator nature with a wide band gap of 4.7 eV; through biaxial tensile strain, the gap can be reduced to less than 2 eV [52], but this is only achievable in extreme strains that are higher than 25%. In

comparison to the aforementioned 2D materials, o-B₂N₂ has a promising band gap tunability. To accentuate this feature of o-B₂N₂, we extracted the slope of the band-gap-vs-strain curve for various conventional 2D materials, assuming a linear band gap variation around the equilibrium. While in o-B₂N₂ this slope is around 100 meV per armchair strain percentage, in graphene the maximum of this slope is around 25 meV per armchair strain percentage, in silicene this slope is less than 5 meV per armchair strain percentage, and in antimonene and h-BN this value is around 75 meV per biaxial strain percentage. In TMDs, such as MoSe₂ the slope is close to that of o-B₂N₂, and in WS₂ and MoS₂ this slope is even higher than that of o-B₂N₂; however, in these compounds, the direct to indirect transition occurring around 2% biaxial tensile strain deteriorates the effectiveness of strain manipulation for optoelectronic applications. Moreover, deformation potentials found in o-B₂N₂, which based on Eq. (4) have a direct relation to the slope of the band gap variation near the equilibrium point, show higher values compared with graphene, h-BN, phosphorene, arsenene, antimonene, and silicene [53–55].

Another important feature that appears in o-B₂N₂ upon strain engineering, is its anisotropic band tunability. In comparison to compressive strain, it is easier to apply tensile strain to a 2D material, and one can go higher in the percentage of applied strain. Thus direction-dependent tunability of o-B₂N₂ enables both widening and narrowing of band gap energy over a wide range (0.97–2.92 eV) only through applying tensile strain. Although direction-dependent band gap tunability has already been reported in several 2D materials with intrinsic structural anisotropy such as tetrahex structures (for instance, tetrahex-carbon, tetrahex-SiC, and tetrahex-BN all exhibit this feature with less than 1.0-, 0.5-, and 0.8-eV tunability over 10% tensile strain, respectively [56–58]), the ~2-eV anisotropic tunability found in o-B₂N₂ makes it outstanding.

The response of the bond lengths and lattice parameters to strain is demonstrated in Table I. Since o-B₂N₂ has a positive Poisson's ratio, in the case of uniaxial strain, the lattice constant transverse to the axis of strain always changes inversely compared with the axial lattice constant. In o-B₂N₂, B-B and N-N bonds are aligned in the armchair direction. Therefore the B-B and N-N bond lengths increase to compensate for the strain in this direction, while the B-N bond length is almost unaffected during the armchair strain. In addition, the increase in the second-neighbor B-B and N-N distances along the armchair direction shows that a part of the elongation is compensated by the rotation of B-N bonds in a way that the B-N-B and N-B-N angles increase along the armchair direction. The B-N bonding energy is around 500 kJ/mol, which is significantly higher than that of B-B (310 kJ/mol) and N-N (160 kJ/mol); consequently, the stiffer B-N bonds are less prone to elongation. On the other hand, none of the bonds is oriented along the zigzag direction; there are only zigzag chains of B-N bonds aligned in this direction that need to compensate for the strain. Hence the length of B-B and N-N bonds remains almost unchanged during uniaxial strain along the zigzag direction, while B-N bond lengths increase. The second-neighbor B-B and N-N distances (along the armchair direction) show a decreasing trend that indicates the widening of angles to neutralize the zigzag strain. Finally, in the case of biaxial strain, the lattice expands in a way that all

bonds get stretched, and the second-neighbor distances also increase.

Excitonic average lifetime plays a crucial role in photocatalytic efficiency. To achieve better insight into the electron-hole separation in o-B₂N₂, we investigated the charge carriers' effective masses and mobilities. To study the effective mass, we fit the following equation to the conduction band minimum (CBM) for electrons and valence band maximum (VBM) for holes, calculated by the HSE06 hybrid functional:

$$m^* = \hbar^2 \left(\frac{d^2 E(k)}{dk^2} \right)^{-1}. \quad (2)$$

The calculated effective masses of electrons and holes, along the *YS* (m_x) and *YΓ* (m_y) edges of the BZ, are reported in Table II. One can see that the effective mass values are highly anisotropic in o-B₂N₂. Having the effective masses, we further calculated the charge carrier mobilities along the *YS* (denoted by μ_x^{2D}) and *YΓ* (denoted by μ_y^{2D}) directions via the following expression [59]:

$$\mu_i = \frac{eh^3 \left(\frac{5C_i + 3C_j}{8} \right)}{K_B T (m_i)^{\frac{3}{2}} (m_j)^{\frac{1}{2}} \left(\frac{9E_{li}^2 + 7E_{li}E_{lj} + 4E_{lj}^2}{20} \right)}, \quad (3)$$

where i determines the transport direction and m_i is the effective mass along direction i . The temperature is assumed to be $T = 300$ K. The E_{li} is the deformation potential constant of the charge carrier, obtained from the following expression:

$$E_{li} = \frac{\Delta E}{\left(\frac{\Delta l}{l_0} \right)}, \quad (4)$$

where ΔE is the variation in the energy of the CBM and VBM bands under small strains ($\epsilon = 0.5\%$ was considered). The calculated values for E_{li} are listed in Table II. The C_i is the in-plane stiffness constant, calculated using the following formula and presented in Table II:

$$C_i = 2 \left(\frac{E_i - E_0}{A_0} \right) \left(\frac{\Delta l}{l_0} \right)^{-2}, \quad (5)$$

where E_i is the total energy of one unit cell after deformation, E_0 is the equilibrium total energy, and A_0 is the area of one unit cell. Previous studies showed that Eq. (3) tends to underestimate the absolute value of charge carrier mobility. Regarding the mobility ratio, however, Eq. (3) yields values close to experimental results [60]. Recently, Zhao *et al.* [61] calculated the mobility values for o-B₂N₂, using the modified Bardeen-Shockley formula. That formula tends to overestimate both the mobility values and the mobility ratios, which accounts for the differences in our results. We expect the experimental values for mobility to be higher than our results, and the mobility ratio to be close to our calculations. Our analysis shows that the charge carrier mobilities found in o-B₂N₂ are highly anisotropic. This feature prolongs the excitonic separation and creates a suitable condition for photocatalytic applications.

We further investigated the effect of strain engineering on the electron affinity (EA) of o-B₂N₂. In practice, EA is of crucial importance in electron-emitting and photosensitive applications. In the semiconductor materials, the electron affinity is defined as the energy required to take an electron

TABLE II. Charge carrier properties based on HSE06 calculations. Here, m_i is the effective mass, C_i is the elastic constant in N/m, E_1^i is the deformation potential constant in eV, and μ_i^{2D} is the carrier mobility at $T = 300$ K in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, while $i = x$ and $i = y$ correspond to armchair and zigzag directions, respectively.

Carrier type	m_x	m_y	C_x	C_y	E_1^x	E_1^y	μ_x^{2D}	μ_y^{2D}
Electron	1.53	0.49	240	273	4.22	8.56	114	265
Hole	1.77	0.47	240	273	6.34	3.80	113	567

from the conduction band edge into the vacuum [62],

$$EA = E_{\text{vac}} - E_{\text{cbe}}, \quad (6)$$

where the vacuum energy E_{vac} is extracted from the asymptotic value of the electrostatic potential as one moves far away in the z direction. The response of EA to strain is reported in Table I. One can see that strain engineering offers tunability of the electron affinity in a wide range from 1.92 eV up to 3.90 eV.

In the pristine condition, o-B₂N₂ offers a polarized optical absorption in the visible range where the peak is located at 2.70 eV in the zigzag direction and the absorption in the armchair direction is very low [26]. The effect of strain on this anisotropic absorption is demonstrated in Figs. 2(a), 2(b), and 2(c), for uniaxial-armchair, uniaxial-zigzag, and biaxial strain, respectively, where red and green lines specify strains along the armchair and zigzag edges, respectively. It can be seen that the absorption peak shifts mimic the band gap behavior under strain. Therefore, in cases of the armchair and biaxial tensile strain, the absorption peaks shift towards the ultraviolet region of the spectrum with a gradual decrease in the absorption rate, and inversely, compressive strain tends to push the peaks into the infrared zone, while increasing the absorption rates. On the other hand, the strain along the zigzag direction induces an exactly opposite trend, where the tensile strain intensifies the absorption and shifts the peak towards lower energies. As the absorption peak moves towards the infrared region, alongside the initial peak in the visible range, a secondary peak in the infrared region appears.

A comparison between o-B₂N₂ and other 2D materials with strong optical response highlights the special behavior of o-B₂N₂ upon strain engineering. Black phosphorus, which has a significant absorption in the UV region, shows a considerable shift towards the visible range coupled with flattening of the absorption peaks under strained conditions [49]. It was also found that H-MoS₂, as one of the best candidates for absorption in the visible region, is highly sensitive to strain, showing a redshift in response to strain, a common feature among TMDs [63,64]. In contrast, o-B₂N₂ offers a flexible band gap tunability, while the peak of light absorption lies in the visible range in a wide range of uniaxial and biaxial strains. In addition, it preserves its anisotropic absorption behavior independent of the type and scope of the applied strain. Moreover, in comparison to o-B₂N₂, the optical absorption in o-B₂P₂, o-Al₂N₂, and o-Ga₂N₂ is weaker, and less anisotropic in the visible range [61].

An efficient photocatalyst for water splitting needs to possess several features simultaneously. First, to have optimum solar light absorption, the band gap energy must be less than 3 eV. Second, the band gap width must exceed the free energy of water splitting, equivalent to 1.23 eV, to provide sufficient

energy to break covalent bonds in water. Third, it needs to have a suitable band edge alignment with the reduction and oxidation potentials of water splitting. In this respect, the VBM location in the energy frame must be lower than the oxidation potential of water ($\text{O}_2/\text{H}_2\text{O}$, $-5.67 \text{ eV} + \text{pH} \times 0.059 \text{ eV}$), and the CBM position must be higher than the reduction potential of water (H^+/H_2 , $-4.44 \text{ eV} + \text{pH} \times 0.059 \text{ eV}$). The photoinduced electron-hole pair drift for an average lifetime of τ before annihilation. To have an efficient photocatalyst, the fourth essential requirement is a prolonged τ . To achieve this final requirement, the photogenerated electron-hole pairs must get separated to prevent their rapid recombination. Semiconductors with anisotropic electron and hole mobilities possess a prolonged charge carrier lifetime.

It can be seen that, in the pristine condition, the 1.7 eV band gap energy of o-B₂N₂ lies within the energy range suitable for the splitting of water. Moreover, due to its intrinsic structural anisotropy, this 2D material offers anisotropic charge carrier mobilities, which increase the charge carrier lifetime. It also has a very promising optical absorption in the visible range of the light spectrum, which covers 43% of the incident beams, reaching the Earth's surface. The only drawback of o-B₂N₂ is its partial band edge alignment with the redox potential of water splitting. This final deficiency of o-B₂N₂ can also be cured through strain engineering. As is shown in Fig. 3, the required band edge alignment occurs under the tensile armchair and biaxial strain. In these two regimes, as the percentage of strain increases, a better band alignment can be achieved. Ultimately, with around 12 and 8% tensile armchair and biaxial strains, respectively, a perfect band alignment can be obtained. It should be mentioned that tensile zigzag strain and all forms of compressive strains deteriorate the compatibility of band edges with the redox potential of water splitting.

IV. CONCLUSION

We performed first-principles calculations to investigate the effect of strain on the electronic, structural, and optical properties of o-B₂N₂. Boron and nitrogen are abundant and cheaply accessible on Earth, and their compounds are highly noble and thermally stable. The well-known h-BN has already dominated the 2D realm, as the best 2D insulator option. With a band gap of 1.7 eV, o-B₂N₂ can offer both the desired features of h-BN and a semiconductor crystal. Here, we demonstrated that o-B₂N₂ possesses high ultimate strain, comparable to that of graphene, which makes strain engineering of this material feasible even in extreme straining regimes. We found that besides exhibiting excellent electronic and optical properties in its pristine condition, o-B₂N₂ can also be an ideal option to achieve any desired band gap up to

FIG. 2. Direction-dependent optical absorption spectra of $o\text{-B}_2\text{N}_2$ upon (a) armchair, (b) zigzag, and (c) biaxial strain engineering. Red and green lines show the light absorption along armchair and zigzag directions, respectively. In (a), the -0.04 case is provided instead of the -0.08 case, since the latter offers much less absorption in the visible range.

FIG. 3. Location of the band edges (CBM and VBM) in $o\text{-B}_2\text{N}_2$ with respect to the vacuum level obtained from the HSE06 functional, where (a), (b), and (c) are related to armchair, zigzag, and biaxial strain, respectively. Strain values are denoted in percent. The dash-dotted lines are aligned with the oxidation and reduction potentials of water splitting, where $\text{pH} = 7$.

2.92 eV while preserving the optimal optical absorption rate, through strain engineering. In fact, the scope of strain tunability and anisotropic tunability found in $o\text{-B}_2\text{N}_2$ is rare among 2D materials. Although, in the pristine condition, $o\text{-B}_2\text{N}_2$ has a wide enough band gap for application in photocatalytic water splitting, its band edges are only partially aligned with the redox potential of water splitting. Via strain engineering, however, the position of band edges can be tailored to become perfectly aligned with the redox potential. Having a suitable band gap, excellent optical absorption in the visible range, and anisotropic carrier mobilities which prolong the average

excitonic lifetime, upon strain engineering of the band edges, o-B₂N₂ can turn into a promising candidate for applications as a photocatalyst in the water-splitting process.

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- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 1102896 (2004).
- [2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature (London)* **438**, 197 (2005).
- [3] Y. Zhang, Y. Tan, H. L. Stromer, and P. Kim, *Nature (London)* **438**, 201 (2005).
- [4] A. K. Geim and K. S. Novoselov, *Nat. Mater.* **6**, 183 (2007).
- [5] F. Schwierz, *Nat. Nanotechnol.* **5**, 487 (2010).
- [6] K. F. Mak, M. Y. Sfeir, Y. Wu, C. H. Lui, J. A. Misewich, and T. F. Heinz, *Phys. Rev. Lett.* **101**, 196405 (2008).
- [7] H. Liu, Y. Liu, and D. Zhu, *J. Mater. Chem.* **21**, 3335 (2011).
- [8] M. Topsakal and S. Ciraci, *Appl. Phys. Lett.* **98**, 131908 (2011).
- [9] J. Wang, F. Ma, W. Liang, and M. Sun, *Mater. Today Phys.* **2**, 6 (2017).
- [10] J. O. Sofo, A. S. Chaudhari, and G. D. Barber, *Phys. Rev. B* **75**, 153401 (2007).
- [11] T. M. G. Mohiuddin, A. Lombardo, R. R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. M. Basko, C. Galiotis, N. Marzari, K. S. Novoselov, A. K. Geim, and A. C. Ferrari, *Phys. Rev. B* **79**, 205433 (2009).
- [12] Y. Wang, C. Cong, W. Yang, J. Shang, N. Peimyo, Y. Chen, J. Kang, J. Wang, W. Huang, and T. Yu, *Nano Res.* **8**, 2562 (2015).
- [13] G. Plechinger, F. X. Schrettenbrunner, J. Eroms, D. Weiss, C. Schüller, and T. Korn, *Phys. Status Solidi RRL* **6**, 126 (2012).
- [14] Y. Y. Hui, X. Liu, W. Jie, N. Y. Chan, J. Hao, Y. Hsu, L. Li, W. Guo, and S. P. Lau, *ACS Nano* **7**, 7126 (2013).
- [15] F. Li, T. Shen, C. Wang, Y. Zhang, J. Qi, and H. Zhang, *Nano-Micro Lett.* **12**, 106 (2020).
- [16] T. Yu, Z. Ni, C. Du, Y. You, Y. Wang, and Z. Shen, *J. Phys. Chem. C* **112**, 12602 (2008).
- [17] W. H. Chae, J. D. Cain, E. D. Hanson, A. A. Murthy, and V. P. Dravid, *Appl. Phys. Lett.* **111**, 143106 (2017).
- [18] S. Yang, Y. Chen, and C. Jiang, *InfoMat* **3**, 397 (2021).
- [19] H. H. Perez Garza, E. W. Kievit, G. F. Schneider, and U. Staufer, *Nano Lett.* **14**, 4107 (2014).
- [20] G. Gui, J. Li, and J. Zhong, *Phys. Rev. B* **78**, 075435 (2008).
- [21] M. Topsakal, S. Cahangirov, and S. Ciraci, *Appl. Phys. Lett.* **96**, 091912 (2010).
- [22] S. Horzum, H. Sahin, S. Cahangirov, P. Cudazzo, A. Rubio, T. Serin, and F. M. Peeters, *Phys. Rev. B* **87**, 125415 (2013).
- [23] L. Liu, Y. P. Feng, and Z. X. Shen, *Phys. Rev. B* **68**, 104102 (2003).
- [24] K. Watanabe, T. Taniguchi, and H. Kanda, *Nat. Mater.* **3**, 404 (2004).
- [25] L. Wirtz, A. Marini, and A. Rubio, in *Electronic Properties of Novel Nanostructures: XIX International Winterschool/Euroconference on Electronic Properties of Novel Materials*, AIP Conference Proceedings Vol. 786 (American Institute of Physics, Melville, NY, 2005), p. 391.
- [26] S. Demirci, S. E. Rad, S. Kazak, S. Nezir, and S. Jahangirov, *Phys. Rev. B* **101**, 125408 (2020).
- [27] Z. Guo, J. Zhou, and L. Zhu, *J. Mater. Chem. A* **4**, 11446 (2016).
- [28] A. K. Singh, K. Mathew, H. L. Zhuang, and R. G. Hennig, *J. Phys. Chem. Lett.* **6**, 1087 (2015).
- [29] B. Luo, G. Liu, and L. Wang, *Nanoscale* **8**, 6904 (2016).
- [30] Y. Sun, Z. Sun, S. Gao, H. Cheng, Q. Liu, J. Piao, T. Yao, C. Wu, S. Hu, S. Wei, and Y. Xie, *Nat. Commun.* **3**, 1057 (2012).
- [31] Y. Sun, H. Cheng, S. Gao, Z. Sun, Q. Liu, Q. Liu, F. Lei, T. Yao, J. He, S. Wei, and Y. Xie, *Angew. Chem.* **51**, 8727 (2012).
- [32] Y. Xu, W. Zhao, R. Xu, Y. Shia, and B. Zhang, *Chem. Commun.* **49**, 9803 (2013).
- [33] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. B. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, and M. Chhowalla, *Nat. Mater.* **12**, 850 (2012).
- [34] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [35] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [36] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [37] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [38] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *J. Chem. Phys.* **125**, 224106 (2006).
- [39] H. Ehrenreich and M. H. Cohen, *Phys. Rev.* **115**, 786 (1959).
- [40] H. Sun, S. Mukherjee, and C. V. Singh, *Phys. Chem. Chem. Phys.* **18**, 26736 (2016).
- [41] Q. Peng, W. Ji, and S. De, *Comput. Mater. Sci.* **56**, 11 (2012).
- [42] C. C. Liu, W. Feng, and Y. Yao, *Phys. Rev. Lett.* **107**, 076802 (2011).
- [43] Y. Cai, C. P. Chuu, C. M. Wei, and M. Y. Chou, *Phys. Rev. B* **88**, 245408 (2013).
- [44] T. Kaloni and U. Schwingenschlogl, *Chem. Phys. Lett.* **583**, 137 (2013).
- [45] D. R. Kripalani, A. A. Kistanov, Y. Cai, M. Xue, and K. Zhou, *Phys. Rev. B* **98**, 085410 (2018).
- [46] L. Wang, A. Kutana, and B. I. Yakobson, *Ann. Phys. (Berlin)* **526**, 9 (2014).
- [47] M. Ghorbani-Asl, S. Borini, A. Kuc, and T. Heine, *Phys. Rev. B* **87**, 235434 (2013).
- [48] E. Scalise, M. Houssa, G. Pourtois, V. Afanasev, and A. Stesmans, *Nano Res.* **5**, 43 (2011).
- [49] D. Cakir, H. Sahin, and F. M. Peeters, *Phys. Rev. B* **90**, 205421 (2014).
- [50] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tomnek, and P. D. Ye, *ACS Nano* **8**, 4033 (2014).

- [51] X. Peng, Q. Wei, and A. Copple, *Phys. Rev. B* **90**, 085402 (2014).
- [52] J. Wu, B. Wang, Y. Wei, R. Yang, and M. Dresselhaus, *Mater. Res. Lett.* **1**, 200 (2013).
- [53] Z. G. Shao, X. S. Ye, L. Yang, and C. L. Wang, *J. Appl. Phys. (Melville, NY)* **114**, 093712 (2013).
- [54] J. Wiktor and A. Pasquarello, *Phys. Rev. B* **94**, 245411 (2016).
- [55] Y. Wang and Y. Ding, *Nanoscale Res. Lett.* **10**, 254 (2015).
- [56] Q. Wei, G. Yang, and X. Peng, *Phys. Rev. Appl.* **13**, 034065 (2020).
- [57] M. E. Kilic and K. Lee, *Carbon* **174**, 368 (2021).
- [58] M. E. Kilic and K. Lee, *Nanoscale* **13**, 9303 (2021).
- [59] H. Lang, S. Zhang, and Z. Liu, *Phys. Rev. B* **94**, 235306 (2016).
- [60] A. Rawat, N. Jena, Dimple, and A. De Sarkar, *J. Mater. Chem. A* **6**, 8693 (2018).
- [61] J. Zhao, H. Zeng, and G. Yao, *Phys. Chem. Chem. Phys.* **23**, 3771 (2021).
- [62] S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
- [63] H. J. Conley, B. Wang, J. I. Ziegler, R. F. Haglund, S. T. Pantelides, and K. I. Bolotin, *Nano Lett.* **13**, 3626 (2013).
- [64] K. He, C. Poole, K. F. Mak, and J. Shan, *Nano Lett.* **13**, 2931 (2013).