Prediction and Characterization of Two-Dimensional Zn₂VN₃

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Abstract

A two-dimensional (2D) monolayer of a novel ternary nitride Zn_2VN_3 is computationally designed, and its dynamical and thermal stability is demonstrated. A synthesis strategy is proposed based on experimental works on production of ternary nitride thin films, calculations of formation and exfoliation energies, and *ab initio* molecular dynamics simulations. A comprehensive characterization of 2D Zn_2VN_3 , including investigation of its opto-electronic and mechanical properties, is conducted. It is shown that 2D Zn_2VN_3 is a semiconductor with an indirect band gap of 2.75 eV and a high work function of 5.27 eV. Its light absorption covers visible and ultraviolet regions. The band gap of 2D Zn_2VN_3 is found to be well tunable by applied strain. At the same time 2D Zn_2VN_3 possesses high stability against mechanical loads, point defects, and environmental impacts. Considering the unique properties found for 2D Zn_2VN_3 , it can be used for application in opto-electronic and straintronic nanodevices.

TOC



Two-dimensional (2D) materials remain an active field of research in science and engineering over the last 15 years. During that time countless 2D structures with unique superconducting (1), opto-electronic (2,3), magnetic (4), mechanical (5,6), and topological (7) properties have been found. For the most part, the research effort has been directed to the exploration of 2D materials which have bulk counterparts representing anisotropic crystals with layers folded together by van der Waals (vdW) forces (8). Weak vdW interaction between the layers of such 2D materials supports a natural structural separation of the 2D subcells in the crystals via mechanical (9) or liquid-phase (10) exfoliation. Although the deposition and growth technologies are generally available for of 2D materials, control of defects and contamination is not yet compliant with the specifications defined for production (11). High processing temperatures are typically required for high quality 2D materials, complicating their production. Despite these challenges, existing and newly developed 2D materials carry the promise of successful integration into technology and commercial devices during the next decade (11).

Various methods to predict and fabricate novel bulk and 2D materials, including experimental, ab initio, and machine learning approaches, are currently in use. To facilitate experimental realization of unexplored structures their proper characterization is needed. It can be successfully realized in computational simulations that have become an effective tool in the prediction and characterization of unknown compounds (12,13). A combination of density functional theory (DFT) calculations and machine learning algorisms allows one to discover exotic low-dimensional structures. A broad range of computational techniques has been utilized to describe the crystal structure of potentially superhard boron-rich MoB_x phases (14). Later, using the evolutionary algorithm, five new superhard ternary compounds in the W-Mo-B system have been predicted at different temperatures, and the composition-temperature phase diagrams have been plotted (15). A thin film of NaCl on the (110) diamond surface has been crystallized in the experiment based on a theoretical guidance provided by the *ab initio* calculations combined with an evolutionary algorithm (16). Data-driven high-throughput investigations have led to identification of 8 binary and 20 ternary non-vdW potentially synthesizable candidates with the hematite and ilmenite type structures (8). Recently, computationally guided high-throughput synthesis has been used to explore the Zn–V–N phase space, resulting in the synthesis of a novel ternary nitride Zn₂VN₃ film (17).

Wide band gap wurtzite Zn_2VN_3 thin films exhibit *p*-type conductivity, charge carrier concentration of ~10¹⁷ cm⁻³, and promising Hall mobility of about 80 cm²/V·s (17). Furthermore, charge carrier concentration in Zn_2VN_3 is controlled by Zn/V ratio. The favorable set of optical and electronic properties makes Zn_2VN_3 thin films an interesting candidate for hole-selective contacts and hole transport layer applications in solar cells. Tunability of carrier concentration in Zn_2VN_3 may also be used to fabricate solar cells with back surface field to facilitate charge transport. Demonstration of epitaxial stabilization of sputter-deposited Zn_2VN_3 thin films at low synthesis temperatures (<200°C) and chemical stability of the nitride material may be suitable for application in tandem perovskite-Si solar cells, in which a diffusion barrier is desired to protect the bottom cell (18). However, the synthesized thin films are characterized by cation disorder. Potentially this can be avoided in 2D Zn_2VN_3 , which may open up additional functionalities for this novel semiconductor material.

In this work, following the recent prediction and synthesis of wurtzite Zn_2VN_3 thin films, the existence of 2D Zn_2VN_3 is investigated. A comprehensive study of its dynamic and thermal stability as well as the grows mechanism is reported. A thorough characterization of 2D Zn_2VN_3 is conducted, including identification of its opto-electronic and mechanical properties. In addition, structural defects in 2D Zn_2VN_3 and its environmental stability are explored. The reported study both predicts a new 2D material and offers its characterization and possible applications.

A monolayer of 2D Zn₂VN₃ is obtained from the recently predicted and synthesized bulk Zn₂VN₃ (17) by cutting it along the (001) direction, as shown in Figure 1a. The top and side views of the 2D Zn₂VN₃ unit cell are also presented in Figure 1a, and the conventional cell is shown in Figure S1a. The unit cell of 2D Zn₂VN₃ consisting of 24 atoms (8 Zn atoms, 12 N atoms and 4 V atoms) stabilizes in a 2D orthorhombic lattice with the space group 36 $\text{Cmc}2_1$ and the lattice parameters are a = 5.72 and b = 5.63 Å (see cif file in SI). The electronic localization function (ELF) reflects the degree of charge localization in the real space, where 0 represents a free electronic state while 1 represents a perfect localization. The calculated ELF for 2D Zn₂VN₃ with the isosurface value of 0.2 (Figure 1a) reflects electron density. The electron localization basin is spherical and completely migrates to the Zn atom. All basins surround the respective cores, suggesting an ionic bond in 2D Zn₂VN₃. The existence of strong ionic bonds in 2D Zn₂VN₃ suggests its high stability against formation of most point defects (19). The calculated phonon dispersion spectra of 2D Zn₂VN₃ along the high symmetry path of the Brillouin zone (Figure 1b) shows its kinetic stability, as the transverse, longitudinal and out-of-plane z-direction acoustic modes have real frequencies and display normal linear dispersion around the Γ point. Thermal stability of 2D Zn₂VN₃ is confirmed via AIMD simulations showing that the structure remains stable after 5 ps at 300 K (Figure S1b and Movie 1)

The majority of 2D materials are exfoliated from powders/thin films or designed via special methods such as chemical vapor deposition (20). Feasibility of exfoliation of 2D Zn₂VN₃ needs to be evaluated. The calculated binding energy that needs to be overcome to achieve exfoliation of a 2D Zn₂VN₃ monolayer from bulk Zn₂VN₃ is 2.83 eV, which is ~20 times higher than that of graphene (Figure S2). The exfoliation energy ΔE_{exf} for 2D Zn₂VN₃, that is, the binding energy between layers in the bulk, is computed as the energy difference between the relaxed 2D and bulk systems (21),

$$\Delta E_{\text{exf}} = \frac{E_{2D} - E_{bulk}}{A} \,. \tag{1}$$

Here, E_{2D} and E_{bulk} correspond to the total energies of the optimized 2D and bulk Zn_2VN_3 , respectively, and A is the in-plane surface area according to the optimized bulk Zn_2VN_3 . ΔE_{exf} of 2D Zn₂VN₃ is found to be 105 meV/Å². This value is ~5 times higher than the ΔE_{exf} value of graphene (~20 meV/Å²) (21,22), while it is below the 130-200 meV/Å² limit proposed for "potentially exfoliable" systems (22,24). Therefore, exfoliation of the 2D Zn₂VN₃ monolayer should be possible at certain conditions. The recently reported approach for deposition of bulk Zn₂VN₃ suggests that it can be formed from evaporation of Zn₃N₂ and VN at a temperature of 390-490 K and in the presence of ionized nitrogen, roughly following the reaction $Zn_3N_2 + VN \rightarrow (N^+)$ $Zn_2VN_3 + Zn$ (evaporation) (17). AIMD simulations conducted in this work show that a Zn_2VN_3 structure containing an extra (unevaporated) Zn atom can be formed at 180 K within ~1.3 ps (Movie 2). Therefore, by controlling the Zn evaporation rate and the ionized nitrogen rate it can be possible to utilize chemical vapor deposition for 2D Zn₂VN₃ synthesis. During the manufacturing, the thickness of sputter-deposited thin films is increased with sputtering power (for constant deposition time). For example, the thickness of the Mo-incorporated Cu₂ZnSnS₄ absorber layer increased with Mo co-sputtering power, as shown in the cross-section scanning transmission electron microscope study (25). More recently, the ternary metal-zinc-nitride thin films of about 235 nm thickness were demonstrated experimentally and implemented in a photodetector device

(26). Proper choice of a substrate is an important step for production of 2D Zn_2VN_3 . For instance, bulk Zn_2VN_3 deposited on glass and sapphire substrates appears to be phase-pure, while the epitaxial stabilization on Al₂O₃ (0001) increases its crystallinity and texture (25).



Figure 1. (a) Schematic representation of Zn_2VN_3 transformation from bulk to 2D, and the 2D Zn_2VN_3 unit cell combined with ELF. The Zn, V, and N atoms are colored in gray, red and violet, respectively. (b) Phonon dispersion curves of 2D Zn_2VN_3 .

Figure 2a shows the band structure of 2D Zn₂VN₃ obtained using the Heyd–Scuseria– Ernzerhof (HSE06) exchange-correlation functional. For the comparison, the band structure of 2D Zn₂VN₃ obtained via the Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation is plotted in Figure S3a. Based on the HSE06 calculations, it is found that 2D Zn₂VN₃ is a semiconductor with an indirect band gap of 2.75 eV and a direct band gap of 2.85 eV. Both gaps are slightly higher than in bulk Zn_2VN_3 (17). Similarly to its bulk counterpart, 2D Zn_2VN_3 is a *p*-type semiconductor with the Fermi level located slightly above the valence band edge. For the indirect gap, the conduction band minimum (CBM) is located in the vicinity of the Γ point, while the valence band maximum (VBM) is located at the S point. In the case of the direct gap, both CBM and VBM are located at the S point. The partial density of states (PDOS) of 2D Zn₂VN₃ (Figure S3b) demonstrates that d states of V atoms give the main contribution to the CBM, while the VBM is formed by p states of N atoms. From the band structure and PDOS plots the CBM localization is noticed. Such localization of states around the CBM is commonly observed in materials due to cation disorder (27, 28). Localization on the d states of V atoms has been found in bulk Zn_2VN_3 (17). It is also supposed that the origin of the CBM localization in 2D Zn_2VN_3 , as reflected in the PDOS plot (Figure S3), is due to the cation disordering.

The optical response of a material at a given frequency can be determined via its frequency-dependent complex dielectric function that can be defined as a function of incident photon energy having real and imaginary parts (29). This function describes the process of light propagation through the material. Light absorption of a material at a given frequency ω can be

simply realized by the positive value of the real part of the dielectric function. Therefore, the real part refers to the ability of a material to store the electric energy. The imaginary part of the dielectric function refers to the ohmic resistance of the material. For instance, the imaginary part of the dielectric function of a pure dielectric has a zero value. The real and imaginary parts of the complex dielectric function for 2D Zn_2VN_3 are presented in Figure 2b. The real part of the dielectric function for the incident electromagnetic field normal to the 2D Zn_2VN_3 surface is positive in the considered region of the electric field, is found to be 1.28. The real dielectric constant has a considerable peak at 4.9 eV with the maximum value of 1.55, and it exhibits a few peaks at higher energies. The imaginary part of the dielectric function shows that 2D Zn_2VN_3 absorbs light in the visible and ultraviolet regions. Considering the electric and optical properties of the predicted 2D Zn_2VN_3 , it can be regarded as a transparent material for the visible lights and a useful shielding material in ultraviolet region.

Figure 2c shows the diagram of the 2D Zn_2VN_3 work function in comparison with other 2D materials and bulk metals possessing the highest known work function values. The work function of 2D Zn_2VN_3 is high, 5.27 eV, comparable to that of borophene (30). The high work function of 2D Zn_2VN_3 can be attributed to the nature of its atomic states around the Fermi level consisting of not only the out-of-plane p_z states but also the in-plane p hybridized states (Figure S4). Thus, the ionization of 2D Zn_2VN_3 requires significant energy and is comparable to that of, for example, borophene.



Figure 2. (a) Band structure of 2D Zn_2VN_3 calculated by the HSE approach. (b) Real and imaginary parts of dielectric function versus energy for 2D Zn_2VN_3 . (c) Comparison of the work function of 2D Zn_2VN_3 with those of common 2D materials and bulk metals.

Mazdziarz formulated the mechanical stability of 2D materials acquired in rectangular lattices as follows (31):

$$\frac{1}{2}(C_{11} + C_{22} + \sqrt{4C_{12}^2 - (C_{11} - C_{22})^2}) > 0$$

$$\frac{1}{2}(C_{11} + C_{22} - \sqrt{4C_{12}^2 - (C_{11} - C_{22})^2}) > 0$$

$$C_{66} > 0$$
(2)

The above presented criteria are met in the case of $2D Zn_2VN_3$ confirming its mechanical stability. The calculated elastic constants C_{ij} for $2D Zn_2VN_3$ are collected in Table S1.

Mechanical properties of 2D Zn_2VN_3 such as Young's modulus, Poisson's ratio and shear modulus are also considered. Young's modulus of 2D Zn_2VN_3 in the x and y directions is calculated as (32,33):

$$E_{[x]} = \frac{c_{11}c_{22} - c_{12}^2}{c_{11}}$$
, and $E_{[y]} = \frac{c_{11}c_{22} - c_{12}^2}{c_{22}}$ (3)

Shear modulus of 2D Zn_2VN_3 is calculated as (30,31):

$$G = C_{66} \tag{4}$$

Poisson's ratio of 2D Zn_2VN_3 in the x and y directions is calculated as (30,31):

$$v_{[x]} = \frac{c_{12}}{c_{11}}, \text{ and } v_{[y]} = \frac{c_{12}}{c_{22}}$$
 (5)

Figure 3 presents the spatial dependence of Young's modulus, shear modulus and Poisson's ratio for 2D Zn_2VN_3 . These parameters are almost direction independent. The values of Young's modulus of 2D Zn_2VN_3 in the x and y directions are found to be ~99.7 N/m. Shear modulus of 2D Zn_2VN_3 is found to be 37.6 N/m. Poisson's ratio of 2D Zn_2VN_3 in both x and y directions is found to be 0.375. For comparison, 2D Zn_2VN_3 has lower stiffness and higher elasticity relative to graphene (34).



Figure 3. Spatial dependencies of (**a**) Young's modulus (N/m), (**b**) shear modulus (N/m), and (**c**) Poisson's ratio for 2D Zn₂VN₃.

 $2D Zn_2VN_3$ can be switched from a direct band gap semiconductor to an indirect band gap semiconductor and its band gap size can be increased/decreased up to ~50% via strain engineering. Although the PBE functional underestimates the band gap compared to the HSE functional, PBE (Figure S3a) and HSE (Figure 2a) display similar trends in the band alignment in the band structure plots. Thus, the effect of strain engineering on the band structure of $2D Zn_2VN_3$ can be studied using the PBE approach. Figure 4a shows changes in the band gap of $2D Zn_2VN_3$ under strain applied along the surface plane. The applied strain is in the range from -10% (compressive strain) to 10% (tensile strain) that can be realized experimentally (35-40). The band gap of $2D Zn_2VN_3$ decreases rapidly from 1.57 eV to 0.76 eV when the compressive strain increases from 0 to 10%. As the VBM shifts from the S point to the Γ point (Figure S5), an indirect-direct band gap transition is observed in $2D Zn_2VN_3$ under the compressive strain higher than 6%. A rapid decrease of the $2D Zn_2VN_3$ band gap from 1.57 eV to 1.07 eV is observed with the increase of the tensile strain from 0% to 8%. The applied tensile strain in the range from 8% to 10% leads to a slight increase of the band gap from 1.07 eV to 1.19 eV (indirect band gap) and 1.22 eV (direct band gap) (Figure S5).

As 2D materials always contain surface defects that may affect their structure stability and performance (41-45), it is necessary to investigate point defects in 2D Zn₂VN₃. Several common point defects are found to be stable in 2D Zn₂VN₃: a single vacancy of a N atom (SV_N); a single vacancy of a Zn atom (SV_{Zn}); a single vacancy of a V atom (SV_V); in-plane and out-of-plane double vacancies of one V atom and one N atom (DV_{V-N}); and in-plane and out-of-plane double vacancies of one Zn atom and one N atom (DV_{Zn-N}). SV defects can be created by removing one Zn, V or N atom from the 2D Zn₂VN₃ surface. The DV_{V-N} and DV_{Zn-N} defects in the 2D Zn₂VN₃ surface are formed when V and N or Zn and N atoms are removed from the surface (in-plane DV) or from the plane perpendicular to the surface (out-of-plane DV) of 2D Zn₂VN₃. The stability of point defects in 2D Zn_2VN_3 is evaluated based on their formation energy, E_{form} . E_{form} of the considered stable defects in 2D Zn₂VN₃ are collected in Table 1. According to Table 1, the SV_{Zn} and SV_N defects have the lowest E_{form} of 4.27 eV and 5.27 eV, respectively. The out-of-plane DV_{Zn-N}, in-plane DV_{Zn-N}, SV_V, in-plane DV_{V-N}, and out-of-plane DV_{V-N} defects have comparably high formation energies of 7.83 eV, 8.54 eV, 10.25 eV, 10.96 eV, and 11.92 eV, respectively. Eform of SVs in 2D Zn₂VN₃ is comparable to that in graphene (~7.50 eV) (46) and MoS₂ (2.10-6.20 eV) (47), while the formation of the DVs in 2D Zn_2VN_3 is less favorable than in graphene (~8.0 eV) (46) and MoS₂ (~4.0 eV) (47).

SV_N	SV_{Zn}	SV_V	in-plane	out-of-plane	in-plane	out-of-plane
			$\mathrm{DV}_{\mathrm{V-N}}$	$\mathrm{DV}_{\mathrm{V-N}}$	$\mathrm{DV}_{\mathrm{Zn-N}}$	$\mathrm{DV}_{\mathrm{Zn-N}}$
5.27	4.27	10.25	10.96	11.92	8.54	7.83

Table 1. E_{form} (eV) of point defects in 2D Zn₂VN₃.

Proper identification and classification of defects is a key capability of atomically resolved scanning tunneling microscopy (STM) (48,49). To facilitate experimental needs it is possible to utilize DFT simulated STM images for the differentiation of point defects in 2D Zn₂VN₃. The atomic structures and corresponding STM images of the pristine and defect-containing 2D Zn₂VN₃ are presented in Figures S6a-d and S7a-d. The STM images of 2D Zn₂VN₃ containing the considered defects correlate with the corresponding atomic structures, and the defects are easily identified. The STM image in Figure S6b (right panel) shows that the SV_N defect in 2D Zn₂VN₃ can be identified by the triangle formed with two bright spots and one dark spot, arising from two Zn atoms and one V atom, with one N atom missing inside the triangle. Similarly, according to

Figures S6c and d (right panels), the SV_V and SV_{Zn} defects in 2D Zn₂VN₃ appear as triangles formed of three small dark spots characterizing three N atoms, with V or Zn atoms missing inside the triangles. The in-plane DV_{V-N} defect in 2D Zn₂VN₃ is presented in Figure S7a. Here, two semihexagons, formed of two bright spots (Zn atoms) and two dark spots (N atoms) each, have two missing atoms (one V atom and one N atom) at their border. The out-of-plane DV_{V-N} defect in 2D Zn₂VN₃ (Figure S7b) is characterized by missing V and Zn atoms in-between five big bright spots (Zn atoms) and one dark spots (N atom) slightly shifted from their positions compared to the perfect case. The in-plane DV_{Zn-N} defect in 2D Zn₂VN₃ is seen in Figure S7c as two missing atoms (Zn and N) inside a square formed of three dark spots (two N atoms and one V atom). The out-ofplane DV_{Zn-N} defect in 2D Zn₂VN₃ (Figure S7d) may be identified as missing atoms within a triangle formed of two bright spots and one dark spot due to two Zn atoms and one V atoms. This pattern is similar to the STM image the SV_N defect. To deeper understand the changes in the electronic structure of 2D Zn₂VN₃ induced by the defects, the density of states resolved in space, known as local density of states (LDOS), calculated for peripheral atoms in the defect core and for atoms far from the defect core, are shown in Figures S8 and S9. It is found that the defects induce significant changes in the electronic structure of 2D Zn₂VN₃. Such changes facilitate defect identification via photoemission spectroscopy techniques.

Figure 4b presents the temperature-depended surface density of point defects in 2D Zn_2VN_3 . The SV_N and SV_{Zn} defects possess significantly higher surface densities compared to the other defects found to be stable in 2D Zn_2VN_3 . The surface density of the SV_V , out-of-plane DV_{Zn-N} , in-plane DV_{V-N} , and out-of-plane DV_{V-N} defects in 2D Zn_2VN_3 is slightly lower than that in graphene (50) and MoS_2 (51), making their formation less energetically favorable. On the other hand, the surface density of the SV_N and SV_{Zn} defects in 2D Zn_2VN_3 is comparable to that of the SV defects in graphene (50) and MoS_2 (51).

Structural degradation of 2D materials can also be caused by their interaction with the humid environment, particularly, with H₂O and O₂ molecules contained in the air. Therefore, the interaction of the H₂O and O₂ molecules with the 2D Zn₂VN₃ surface is further evaluated. As it has been shown previously, for most of 2D materials, oxidation is the most dangerous process that can lead to degradation of their surface (52-54), while H₂O-saturated surfaces can exhibit higher stability as such saturation prevents the oxidation (55,56). It is found that the adsorption energy, E_{ads} , of O₂ on the 2D Zn₂VN₃ surface is as high as -0.14 eV, while E_{ads} of H₂O (-0.49 eV) is ~3.5 lower (Figure S10). Hence, the adsorption of H₂O on 2D Zn₂VN₃ is more favorable compared to O₂. It should be noted, that according to the LDOS plots (Figure S11) remarkable changes in H₂O and O₂ molecular states upon their interaction with the 2D Zn₂VN₃ surface are observed. Therefore, the kinetic analysis of H₂O and O₂ splitting on the 2D Zn₂VN₃ surface is further conducted. Figure 4c presents the result from the CI-NEB calculation. The energy barrier, E_b, for the H₂O and O₂ molecule dissociation on 2D Zn₂VN₃ is found to be 2.82 eV and 2.04 eV, respectively. Considering the obtained high values of E_b for the dissociation of H₂O and O₂ on the 2D Zn₂VN₃ surface, which are comparable to those of the H₂O and O₂ molecule dissociation on InSe (57), and based of the Eads analysis, it can be concluded that 2D Zn₂VN₃ possesses high structural integrity under environmental conditions. A discussion on the potential application of 2D Zn₂VN₃ to water splitting is presented in Supporting Information, and the calculated VBM and CBM positions of 2D Zn₂VN₃ with the redox potential of H₂O and oxidation levels are shown in Figure S12.



Figure 4. (a) Band gap of 2D Zn_2VN_3 as a function of strain. (b) Surface density of point defects in 2D Zn_2VN_3 as a function of temperature. (c) Activation barriers for H₂O and O₂ molecule splitting on 2D Zn_2VN_3 .

In summary, a new material, a 2D analog of the recently predicted and synthesized ternary nitride semiconductor Zn_2VN_3 (17), is predicted computationally. The fabrication of 2D Zn_2VN_3 is highly possible due to is relatively low exfoliation energy of 105 meV/Å². It is also proposed that the chemical vapor deposition approach can be utilized for the synthesis of 2D Zn_2VN_3 similarly to the bulk Zn_2VN_3 (17) and Cu_2ZnSnS_4 thin film (25) manufacturing. The environmental stability of 2D Zn_2VN_3 should be high due to resistivity of its surface to oxygen and defect formation. 2D Zn_2VN_3 has an indirect band gap of 2.75 eV, which can be tuned up to 50% under applied stains. 2D Zn_2VN_3 possesses a high work function of 5.27 eV, absorbs visible and ultraviolet light, and exhibits moderate mechanical properties. All this makes 2D Zn_2VN_3 a good candidate for application in opto-electronic and straintronic devices.

Computational Methods

The spin-polarized first-principles calculations were performed within the framework of density functional theory as implemented in the plane-wave the Vienna Ab initio Simulation Package (VASP) (58). The Perdew-Burke-Ernzerhof functional (PBE) (59) under the generalized gradient approximation and the HSE06 hybrid exchange-correlation functional (60) were used. Dispersive interactions were included using the van der Waals corrected functional (61). The geometry optimization was stopped once the atomic forces and total energy values were smaller than 10^{-4} eV/Å and 10^{-8} eV, respectively. The plane-wave cut-off energy was set to 520 eV. The periodic boundary conditions were applied for the two in-plane transverse directions. A vacuum space of 25 Å was introduced to the direction perpendicular to the surface plane.

The electron localization function (ELF) was calculated to obtain the distribution of electrons in 2D Zn₂VN₃. The Phonopy code associated with VASP was used for the simulation of the phonon spectrum (62). The $3\times3\times1$ supercell of 2D Zn₂VN₃ was used to perform the calculations based on finite displacement methods with the atomic displacement distance of 0.01 Å. The dielectric function of 2D Zn₂VN₃ was calculated based on the TD-HSE06 approach (63). Ab initio molecular dynamics simulations controlled by the Nose–Hoover thermostat were performed for 5 ps at the temperature of 300 K and with a time step of 1.0 fs (64).

The stress-strain relation (65) was used to calculate the components of the stiffness matrix from which the Young's modulus, shear modulus, and Poisson's ratio were obtained and directional dependencies of these quantities were defined using the ELATE software for analysis of elastic tensors (66).

To consider point defects in 2D Zn_2VN_3 a supercell composed of $3\times3\times1$ unit cells (36 Zn, 18 V and 54 N atoms) was created to avoid non-physical interactions between periodic images while keeping affordable computational demand. Under such conditions, the concentration of MV defects was 0.93% and the concentration of DV defects was 1.85%. The Tersoff-Hamann approach was implemented to simulate Scanning Tunneling Microscope (STM) images of pure and defect-containing 2D Zn_2VN_3 (67).

The formation energy E_{form} of point defects in 2D Zn₂VN₃ was calculated as

$$E_{\text{form}} = E_{\text{defect}} - E_{\text{pure}} + N_{\text{Zn}} \cdot E_{\text{Zn}} + N_{\text{V}} \cdot E_{\text{V}} + N_{\text{N}} \cdot E_{\text{N}}, \tag{6}$$

where E_{defect} and E_{pure} are the total energies of pure and defect-containing 2D Zn₂VN₃, E_{Zn} , E_V and E_N are the energies of single Zn, V and N atoms, and N_{Zn} , N_V and N_N correspond to the number of the removed Zn, V and N atoms.

The surface density of defects N_d in 2D Zn₂VN₃, at a finite temperature, was calculated according to the Arrhenius equation:

$$N_d = N_{pure} \ e^{-Eform/(k_B T)},\tag{7}$$

where N_{pure} is the surface density of atoms in pure 2D Zn₂VN₃, k_{B} is the Boltzmann constant, and *T* is temperature. Note that only defects presented at the surface were shown.

The climbing image–nudged elastic band (CI-NEB) method was used to obtain the reaction pathway of the H_2O and O_2 molecules on the 2D Zn_2VN_3 surface (68).

ASSOCIATED CONTENT

Notes

The authors declare no competing financial interest.

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Supporting Information





Figure S1. (a) Conventional cell of 2D Zn_2VN_3 . (b) Energy fluctuation of the 2D Zn_2VN_3 system from AIMD calculations at 300 K.

Section 2. Binding energy of 2D Zn₂VN₃



Figure S2. Binding energy required for exfoliation of (a) 2D Zn₂VN₃ and (b) graphene.



Figure S3. (a) Band structure and (b) PDOS of 2D Zn_2VN_3 obtained via the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.



Figure S4. PDOS of 2D Zn₂VN₃.



Figure S5. Band structure of $2D Zn_2VN_3$ under compressive (upper row) and tensile (lower row) strain obtained via the PBE approach.

Section 4. The calculated elastic constants C_{ij} for 2D Zn₂VN₃

<i>C</i> ₁₁ , N/m	117	
<i>C</i> ₂₂ , N/m	117	
<i>C</i> ₁₂ , N/m	44.5	
<i>C</i> ₄₄ , N/m	37.6	

Table S1. The calculated elastic constants C_{ij} for 2D Zn_2VN_3 .



Figure S6. Atomic stricture (left) and STM image (right) of (a) pure, (b) SV_N , (c) SV_V , and (d) SV_{Zn} defect-containing 2D Zn_2VN_3 .



Figure S7. Atomic stricture (left) and STM image (right) of (**a**) in-plane DV_{V_N} , (**b**) out-of-plane DV_{V_N} , (**c**) in-plane DV_{Zn_N} , and (**d**) out-of-plane DV_{Zn_N} defect-containing $2D Zn_2VN_3$.

To deeper understand the changes in the electronic structure of 2D Zn₂VN₃ induced by the defects, the density of states resolved in space, known as local density of states (LDOS), is calculated for peripheral atoms in the defect core and for atoms far from the defect core, as shown in Figures S8 and S9. The states introduced by the SV_N defect are mainly contributed by the V atom (Figure S8a). The changes in the CBM and the VBM depicted in the LDOS plot for the defect (Figure S8b) arise mainly from the N₁ and N₂ atoms and N₃, respectively. The defect-induced states in the vicinity of the VBM in the LDOS plot of the SV_{Zn} system (Figure S8c) mainly originate from the N₁, N₂ and N₃ atoms. In the case of the in-plane DV_{V_N} defect in 2D Zn₂VN₃ (Figure S9a), mainly the N₁ and N₂ atoms surrounding the defect have partially occupied/unoccupied states contributing into the valence/conduction bands of 2D Zn₂VN₃. The N₁ atom (Figure S9b) is responsible for the in-gap states appearing in 2D Zn₂VN₃ in-gap states appear mainly due to the V atom located in the vicinity of the defect core (Figure S9c). In-gap states in 2D Zn₂VN₃, appearing due to the out-of-plane DV_{Zn_N}, are formed by the V, Zn₂, and N₂ atoms, as shown in Figure S9d.



Figure S8. Atomic stricture (left) and LDOS (right) of (a) SV_N , (b) SV_V , and (c) SV_{Zn} defectcontaining 2D Zn_2VN_3 .



Figure S9. Atomic stricture (left) and LDOS (right) of (a) in-plane DV_{V_N} , (b) out-of-plane DV_{V_N} , (c) in-plane DV_{Zn_N} , and (d) out-of-plane DV_{Zn_N} defect-containing 2D Zn_2VN_3 .

Section 6. H₂O and O₂ on 2D Zn₂VN₃

According to Figure S10a, the most favorable adsorption position of H_2O on 2D Zn_2VN_3 corresponds to the position of the molecule above the Zn-V bond on the side of the hexagon at the distance of 2.01 Å above the surface of 2D Zn_2VN_3 , and the lowest E_{ads} of H_2O on 2D Zn_2VN_3 is -0.49 eV. Figure S10b shows the most favorable adsorption position of O_2 on 2D Zn_2VN_3 . In that case, O_2 is in the ring of the hexagon at the distance of 2.73 Å, and the lowest E_{ads} of O_2 on 2D Zn_2VN_3 .



Figure S10. Atomic configurations of (a) H₂O and (b) O₂ on 2D Zn₂VN₃.

The three highest occupied molecular orbitals (HOMO) of the H₂O molecule, named according to the irreducible representation of the point group of H₂O, are 1b₁ (HOMO), 3a₁ (HOMO-1), and 1b₂ (HOMO-2). According to the LDOS plot (Figure S10a) the 3a₁ orbital is most broadened due to its favored orbital mixing with the N atoms, confirming the interaction ability of 2D Zn₂VN₃ with H₂O. The LDOS plot for the O₂ molecule on 2D Zn₂VN₃ (Figure S10b) reflects additional O₂-induced states within the band gap. The half-filled 2π HOMO state aligns within the valence band maximum and allows the electrons to be excited to the O₂ molecule, thereby creating holes in 2D Zn₂VN₃. The 2π * LUMO state is located above the Fermi level at ~0.90 eV. The presence of the O₂-induced states within the band gap of 2D Zn₂VN₃ and the non-trivial adsorption/oxidation ability of O₂ to 2D Zn₂VN₃ can alter its optical and electronic properties.



Figure S11. LDOS of (a) H₂O and (b) O₂ on 2D Zn₂VN₃.

Section 7. Water splitting application of 2D Zn₂VN₃

Figure S12 shows the calculated VBM and CBM positions of 2D Zn_2VN_3 with the redox potential of H₂O and oxidation levels. It is found that the VBM of 2D Zn_2VN_3 is below the oxidation potential of O₂/H₂O, while the CBM is also lower than the reduction potential of H₂/H₂O, which indicates that 2D Zn_2VN_3 is suitable only for oxygen production.



Figure S12. The calculated VBM and CBM positions of 2D Zn_2VN_3 with respect to the water redox potentials.