Rational Design of Two-Dimensional Buckled-Hexagonal Nb₂S₂ Monolayer as an Efficient Anode Material for Ca-ion Batteries: A First-Principles Study

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ABSTRACT

Presently, great attention is being paid to the search for promising anode materials for metalion batteries due to the rapid evolution of numerous modern electronic gadgets. In this investigation, we have predicted for the first time that the buckled-hexagonal Nb₂S₂ monolayer that may be an efficient anode material for calcium-ion batteries (CIBs). To that objective, we have explored the pristine monolayer system's energetical, dynamical, and thermal stability. The inherent metallicity of the pristine monolayer facilitates its electrical conductivity as an electrode material. Our study also reveals the structural and electrical properties of the Caadsorbed Nb₂S₂ monolayer. It is observed that Ca-atoms prefer to get intercalated on top of the buckled hexagon of the pristine monolayer, and the metallicity of the 2D nanosheet remains preserved. In the adsorption process, bader charge analysis is used to determine the amount of charge transfer from the Ca atom to the Nb₂S₂ monolayer. Furthermore, this system exhibits a high storage capacity of 1288.86 mAh/g and a moderately low diffusion energy barrier of 0.76 eV. The calculated open-circuit voltage of 0.49 V and the other results suggest that the Nb₂S₂ monolayer may be a potential candidate for anode material for rechargeable Ca-ion batteries.

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INTRODUCTION

Energy is the backbone for the overall technological and economic growth of humankind. Consequently, the energy requirement is increasing exponentially with time. The substantial necessity of energy has created an imbalance between the demand and the supply. To meet the demand, energy is generated incessantly by the combustion of fossil fuels (oil, natural gas, coal, etc.) which has adversely affected the global climate. It may be avoided by exploiting renewable and environmentally benign energy sources such as solar, tide, biomass, wind, and geothermal. Standing at this point, efficient energy storage systems are highly desirable for continuous energy storage and supply without disruption. However, energy storage is getting more challenging day by day, from lightweight electronic devices to multifunctional electric networks, day by day. In the last few years of redesign and continuous modification of secondary storage systems, the scientific community has been interested in metal-ion batteries (MIBs) as a promising solution for energy storage for their high energy density, ultrafast charging-discharging rate, significant efficiency, and structural firmness.

Researchers are putting consistent effort into developing efficient metal-ion batteries. This genre of research is primarily focused on two types of metal-ion batteries: monovalent (Li, Na, and K)[1-3] and multivalent (Mg, Ca, and Zn)[4-6] MIBs. Since 1991, Li-ion batteries have played an essential role in the consumer market due to their high energy density, enhanced life cycles, and high-rate capabilities. However, the continuous depletion of Li-based minerals is bound to restrict the abundance of natural Li-source shortly. The discharge capacity of lithiumion batteries tends to deteriorate faster than the batteries made with other metals due to corrosion, overheating, and dendrite growth. The lithium-ion batteries also pose some serious health and safety concerns as they have exploded without warning. Additionally, due to Li's toxicity and high reactivity, the 'beyond Li-ion technologies' are essential to meet the current and future energy requirements. The first appealing alternative is a Na-ion battery. Although the mechanism is analogous, the sodium ions face severe dimerization issues during the charging-discharging period. Due to the reactivity problem and dimerization of the Na-metal ions, the MIB research has progressed towards another alternative: the potassium ion battery (KIB). But, the relatively higher atomic radius of potassium, compared to the other alkali metals, inhibits the intercalation of a sufficient number of K-ions inside the host material which may compromise the efficiency. Furthermore, numerous multivalent ions (viz. Mg, Ca, Zn, and Al) have been proposed to replace alkali metal ions in MIBs. Recently, Ca-ion batteries (CIBs) have drawn tremendous attention in multivalent metal ion battery research. In the earth's crust, Ca is the fifth most abundant element and 2500 times more than Li. From the environmental perspective, the nontoxic nature of the bivalent Ca-metal makes it a promising candidate for its use in bulk production. Thus, the advent of Ca-ion batteries may help meet the demand for environment-friendly and cost-effective metal ion batteries.

Two-dimensional (2D) materials, alternatively called 'atomic layer thickness crystals,' are distinct from their bulk counterparts due to their unique electrical and mechanical properties, ultrahigh surface-to-volume ratio, and enhanced surface activity. In addition, 2D heterostructures, connected via van der Waals (vdW) interactions, are expected to reduce defects which are originated due to lattice mismatching. The revolutionary discovery of graphene[7] has generated tremendous interest among the scientific community for numerous 2D materials in understanding various properties. Consequently, it has been noticed that several 2D materials exhibit numerous unique applications in advanced electronic devices[8-

12] and energy storage applications [13-15], such as metal-ion batteries (MIBs) [16, 17]. For the advancement of metal-ion batteries, it is essential to design appropriate electrode materials with superior electrochemical performance. Among the 2D materials, graphene emerges as an excellent anode material having a specific capacity of 540 mAh/g, whereas that of modified graphene ranges between 1071 to 1450 mAh/g. Various two-dimensional materials viz. transition metal dichalcogenides (MoS₂, WS₂, VS₂, etc.)[18-20], transition metal carbides (MXenes; Mo₂C, Ti₃C₂, V₂C, etc.)[21-23], metal nitrides (TiN, VN, etc.)[24, 25], metal oxides [26, 27], and BP₂ monolayers [28] have shown favorable properties for their use as anode or cathode materials for various metal-ion batteries. The electrochemical properties of α -V₂O₅ has been identified using density functional study[29]. It is always convenient and costeffective if we know the gross properties of the materials before their use for making any device of desired functionality. Theoretical calculations may play an important role in the search for suitable materials with selected properties. For instance, Searles et al.[30] conducted a theoretical study based on density functional theory and concluded that hydrogenated graphene may be an excellent anode material for Na and Ca-ion batteries. Recently, Ghosh et al.[31] investigated the properties of 2D porous boron phosphide and proposed that it may act as an efficient cathode material for Li and Na-ion batteries. In another work[32], this research group has shown 2D homogenous holey carbon nitride as an efficient anode material for Li-ion batteries with ultrahigh capacity. Ball et al.[33] found the 2D covalent triazine framework to be an excellent anode material for Li-ion batteries. Besides these, two-dimensional porous covalent organic frameworks (COFs) have been investigated extensively for suitable electrode materials in metal-ion batteries[34-36]. Recently, the dihafnium sulfide (Hf₂S) has been calculated for Li/Na-ion batteries[37]. Yang et al. explored pillared MnO₂ and the transition metal oxychalcogenide monolayers Li-ion batteries[38] and K-ion batteries[39] respectively. In addition, graphene, defective graphene[40], hetero-atom-doped graphene[41], and its allotropes[42] are typical carbon electrode materials for various metal-ion batteries. In 2019, Li et al.[43] theoretically reported metallic Nb₂S₂C monolayer as a promising 2D anode material for the metal-ions (Li, Na, K, and Mg) batteries with the high power density and good rate capacity. These studies on 2D-monolayers reported maximum capacity in the range of 190-690 mAh/g for the various metal-ion batteries. As there are ongoing attempts to develop advanced two-dimensional materials with high storage capacity, herein we first report computationally a new 2D material (di-niobium di-sulfide; Nb₂S₂) with contemporary interest.

We have herein carried out the first-principles calculations to find the possibility of di-niobium di-sulfide (Nb₂S₂) monolayer as potential anode material in Ca-ion batteries. Computationally, we have employed energetical, dynamical, and thermal stability to find the possibility of the formation of the monolayer practically. Firstly, we optimized the Nb₂S₂ monolayer by having stoichiometry Nb₁₈S₁₈ ($3 \times 3 \times 1$ supercell of Nb₂S₂ monolayer). To understand its dynamical stability and elementary vibrational motion, we opt for quasi-particle phonon calculations, using density functional perturbation theory (DFPT). We have also determined some crucial thermodynamical properties like free energy, entropy, and molar heat capacity at constant volume (C_v). A further important aspect to examine the thermal stability of the monolayer, abilito molecular dynamics (AIMD) simulation, has been performed in canonical ensemble (NVT) at 300K and 500K for 15 picoseconds (ps) at a time step of 1 femtosecond (fs). While calculating the electronic structure, we have found the monolayer exhibits inherent metallicity. Furthermore, we have identified the efficient adsorption sites for Ca-atom adsorption and estimated the charge accumulation and depletion. Thereafter, we measured the feasibility of

adsorption by calculating the adsorption energy of the Ca-atom over the monolayer. The intrinsic metallic nature remains intact in the Ca-adsorbed system, which can be evidenced by the electronic structure. The diffusion energy barriers between the most favored adsorption sites are determined as 0.76 eV, which is moderately low. We have obtained the maximum theoretical storage capacity (C) for the Ca-adsorbed composite system as 1286.88 mAh/g. Furthermore, the open-circuit voltage (OCV) is found at 0.49 V; hence, we suggest the two-dimensional Nb₂S₂ monolayer is an excellent anode material for Ca-ion batteries.

DETAILS OF COMPUTATION

The density functional theory-based first-principles calculations were carried out using generalized gradient approximation (GGA) in conjugation with the Perdew-Burke-Ernzerhof (PBE)[44, 45] exchange-correlation functional $E_{xc}[\rho]$, implemented in the Vienna Ab Initio Simulation Package (VASP) code[46, 47]. The mutual interactions between the electrons and ions were accounted for using projector-augmented-wave (PAW) pseudopotentials[48]. For the calculation of wave functions, the plane-wave cut-off energy was fixed at 400 eV. We considered a gap of 20 Å along the z-axis to avoid any interaction between the monolayer system and its image. The Brillouin zone (BZ) sampling was done using a $(3\times3\times1)$ k-point grid according to the Monkhrost-Pack scheme [49]. A screen hybrid functional (HSE06), introduced by Heyd-Scuseria-Ernzerhof[50], was used with a denser k-point grid $(15 \times 15 \times 1)$ to calculate more accurate band structures, as PBE functional underestimates the band energy gap due to its self-iteration error. The input k-path of the selected Brillouin zone for the HSE06 calculation was created using the vaspkit code[51, 52]. The criterion for the threshold energy convergence was set to 10⁻⁶ eV, and the relaxation procedure was carried out till the force on every atom becomes less than 0.02 eV/Å. For the ab-initio molecular dynamics (AIMD) simulation[53], we considered the $(3 \times 3 \times 1)$ supercell of the 2D-sheet with the Nb₁₈S₁₈ stoichiometry with the canonical ensemble (N, V, T) using Nöse-Hoover thermostat at 300 K and 500 K for 15 ps with a time step of 1 fs. Using density functional perturbation theory, the real-space force constants were calculated, as implemented in the VASP code and the phonon bands were extracted using phonopy code[54]. The van der Waals (vdW) interactions were considered by using Grimme's DFT-D3 dispersion correction[55] for a better understanding of the adsorption process of the Ca-metal atom. The Bader charge analysis [56] and charge-density difference (CDD) plot were adopted to understand the charge-transfer process in the system.

To understand the adsorption strength of Ca atoms on the di-niobium di-sulfide monolayer, the adsorption energy per Ca atom (E_{ad}) was obtained by using the formula [31, 32]

$$E_{ad} = (E_{Nb_2S_2 + Ca} - E_{Nb_2S_2} - nE_{Ca})/n \tag{1}$$

where $E_{Nb_2S_2+Ca}$ and $E_{Nb_2S_2}$ were the total energies of the Nb₂S₂ monolayer with and without adsorption of the Ca-atom, E_{Ca} was the energy of a single Ca atom in bulk phase, and *n* represent the number of Ca-atoms adsorbed at the respective sites of the Nb₂S₂ monolayer surface. The diffusion energy barrier of Ca from one most favored site to another was obtained using the climbing image nudged elastic band (CI-NEB) method[57] with ten images. Further, the post-processing calculations were performed using the VTST tools[58].

RESULTS AND DISCUSSION

The two-dimensional (2D) di-niobium di-sulfide (Nb₂S₂) monolayer has a buckled hexagonal unit cell with excellent symmetrical geometry, as shown in Figures 1a and 1b. This 2D monolayer structure belongs to the P-3m1 space group. For the modeling of the Nb₂S₂ sheet



Figure 1. Optimized structure of $(3\times3\times1)$ Nb₂S₂ monolayer: (a) top view (b) side view. (The green and yellow balls represent Nb and S atoms, respectively), (c) electron localization function of the Nb₂S₂ monolayer. potential energy evolution during AIMD simulations of the Nb₂S₂ monolayer for 15 ps with temperature (d) 300 K and (e) 500 K along with final geometry (top and side).

structure, we have considered the $(3\times3\times1)$ supercell which contains eighteen Nb and eighteen S atoms. The optimized lattice constants of the supercell are found to have a = b = 11.85 Å and c = 20 Å; $a = \beta = 90^{\circ}$ and $\gamma = 119.99^{\circ}$. In the hexagonal 2D structure there are two types of Nb-S bonds: one along the zigzag direction having an optimized bond length of 2.46 Å and another vertical Nb-S along the z-axis with an optimized bond length of 2.53 Å. The bond lengths are comparable with 2D-InAs (2.55 Å) and quite larger than BP monolayer (1.83 Å), p-BP monolayer (1.87), and graphene (1.42 Å). We have also determined the bond angles of the monolayer: the Nb-S-Nb, and S-Nb-S average bond angle in the buckled hexagon is 106.76°; the vertical Nb-S-Nb and S-Nb-S average bond angles are 67.95° and 112°, respectively. The width of Nb₂S₂ monolayer have been found to be 2.53 Å.

It is the fact that the NbS crystal is not a layered structure and is not related to the Nb₂S₂ monolayer. The Nb₂S₂ monolayer belongs to the P-3m1 space group. Having the same space group (P-3m1) and analogous structure with Nb₂S₂, the Fe₂Se₂ monolayer has been successfully synthesized earlier[59]. This motivated us to model and study the Nb₂S₂ monolayer as an anode material in Ca-ion batteries. However, the bulk structure of Nb₂S₂ is not synthesized yet, but the bulk Fe₂Se₂ is a well-established material. Thus, we can expect the Nb₂S₂ monolayer might be obtained as the Fe₂Se₂ monolayer obtained from its bulk counterpart. Moreover, the exfoliation technique can be a possible experimental synthetic route

for obtaining the Nb_2S_2 monolayer. To empower this expectation, we have determined the exfoliation energy by stacking eight monolayers over one another to create a bulk-like Nb_2S_2 environment. Here, we have calculated the energy per NbS-pair in all the systems and compared them for the calculation of exfoliation energy. Starting from the eight-layer stacked structure considered as bulk moiety, if we think in the reverse direction, we can compare the energy per Nb-S pair of the bulk system ($E_8 = -31.48$ eV), the system where four layers are exfoliated from the bulk ($E_4 = -31.44 \text{ eV}$), the system where six layers are exfoliated from the bulk ($E_2 = -31.42$ eV), and finally the monolayers ($E_1 = -31.41$ eV). We have found a very small energy difference during this process. In 2018, Jison et al. developed an efficient computational method to determine exfoliation energy per unit area, $E_{exf}[n]$, as follows[60], (2)

$$E_{exf}[n] = \frac{E_{iso}[n] - E_{bulk}/m}{\mathcal{A}}$$

where $E_{iso}[n]$ represents the energy of the unit cell of an isolated n-layer slab in vacuum; E_{bulk} be the energy of the unit cell of a bulk material composed of m number of layers (m= 2-8); hence, E_{bulk}/m corresponds to the energy of the bulk per layer, and \mathcal{A} be the in-plane area of the unit cell (expressed in $Å^2$). We have utilized this equation to calculate the exfoliation energy of the bulk Nb₂S₂ slab (eight-layer stacked Nb₂S₂ to bilayer stacked Nb₂S₂), for instances, $E_{exf}[8] = 0.48 \text{ meV/Å}^2$; $E_{exf}[4] = 0.20 \text{ meV/Å}^2$ and $E_{exf}[2] = 0.12 \text{ meV/Å}^2$. Moreover, the E_{exf} decreases from the eight-layer to the two-layer stacked moiety. Our calculated E_{exf} values are extremely lower than the graphene, h-BN, MoS₂, and phosphorene reported by Jisoon et al. [60]. Hence, the low computational exfoliation energies suggest that the Nb_2S_2 monolayer can possibly be obtained via the exfoliation method. In terms of the stability of the Nb_2S_2 monolayer, the formation energy per atom (E_f) of the Nb₂S₂ monolayer has also been calculated by the following equation[61],

$$E_f = \frac{E_{Nb_2S_2} - x_{Nb}\mu_{Nb} - x_S\mu_S}{x}$$
(3)

where $E_{Nb_2S_2}$ be the total energy of the (1×1×1) Nb₂S₂ monolayer; μ_{Nb} and μ_S are the chemical potentials of Nb and S respectively (referred to the energies of bulk Nb and S₈ respectively); x_{Nb} and x_S represent the number of Nb and S atoms require to form the unit cell of Nb₂S₂ monolayer ($x_{Nb}=x_S=2$); x is the total number of atoms present in the unit cell of the monolayer (x=2). We obtain the E_f value of -0.87 eV/atom which indicates the possible formation of the 2D Nb₂S₂ monolayer. Hence, the low exfoliation energy and favorable formation energy strongly indicate the stability of the Nb₂S₂ monolayer.

Further, we have plotted the electron localization function (ELF) as shown in Figures 1(c). The ELF was at first defined by Becke and Edgecombe [62] which provides a technique for mapping the extent of electron pair probability and spatial localization of electrons in multielectronic systems. We have visualized the ELF in our study from $(0 \ 0 \ 1)$ lattice plane. Our calculated ELF indicates some presence of pi-electron density and low covalent character in Nb-S bonding (the ELF scaling at 0.5 resides over the Nb-S bond). In addition, the electron density at the hexagon's interstitial site suggests that metalloid bonds are present within the monolayer[63]. With the help of the ELF plots, we have identified the probable electron-deficient sites on the pristine monolayer which helps to locate the probable adsorption sites for Ca intercalation.

Following the structural integrity and symmetry parameters, here we intend to estimate the thermo-dynamical stability of Nb₂S₂ monolayer. The atoms in crystalline solids are arranged into a three-dimensional (3D) periodic array as if the adjacent atoms are connected via tiny springs. Due to the appliance of external force or internal thermal energy, the vibration spreads the whole lattice. This lattice vibration produces mechanical waves in form of heat and sound throughout the periodic 3D array. The quantum of these mechanical waves that move all over the lattice, has a specific energy and momentum. These quanta can be considered as particles, namely phonons, the quantum of vibrational mechanical energy. To check the dynamical stability, firstly, we have calculated the phonon frequencies using the $(3\times3\times1)$ supercell of the Nb₂S₂ unit cell as displayed in Figures S1a and S1b (Supporting Information). In a periodic lattice, we can anticipate two kinds of vibration patterns during the phonon movement: in-plane and out-of-plane vibration[63, 64]. However, in a phonon band structure, the lowest optical modes refer to the out-of-plane vibration, whereas the highest optical modes correspond to the in-plane vibrations[63, 64]. Our calculated phonon band structure for the $(3\times3\times1)$ supercell consists of one band in the imaginary frequency range which originates from the out-of-plane



Figure 2. Electronic properties of the pristine Nb_2S_2 monolayer: (a) Band structures and (b) Density of States (DOS). Fermi levels are set to zero. [HSE06 level of calculation]

calculated (Figure S1d) that the monolayer possesses positive entropy and heat capacity at constant volume (C_v) along with decreasing free energy with increasing temperature. All these facts suggest excellent dynamical and thermodynamical stability of the buckled-hexagonal monolayer. Furthermore, for the practical feasibility of the monolayer, we have checked its thermal stability at room temperature (300K) and elevated temperature (500K). For that, we have carried out an ab-initio molecular dynamics (AIMD) simulation for the (3×3×1) supercell

breathing mode of the lattice. To overcome this issue, we have extended the $(3 \times 3 \times 1)$ supercell to the $(5 \times 5 \times 1)$ supercell and by calculating the phonon band (Figure S1c) we observe that the band in the imaginary frequency gets folded towards the positive frequency range. Hence, we can expect that the monolayer will get rid of the imaginary frequency (out-of-plane vibration) after the calculation of phonon vibration mode using a higher $(7 \times 7 \times 1)$ or $(9 \times 9 \times 1)$ supercell of the Nb₂S₂ unit cell. But we could not proceed further due to the computational limitation. In terms of thermodynamics, material stability depends upon the sufficiently large positive value of entropy and heat capacity at constant volume (C_v) along with sufficient negative free with increasing energy temperature[63]. Herein, we have

within the framework of the canonical ensemble (NVT) for the 15 ps with a molecular dynamic time step of 1 fs at 300 K and 500 K. The fluctuation of potential energy with time (in fs) has been displayed in Figure 1e and Figure 1f. The simulation results evidence that initially there is a small fluctuation of potential energy with respect to the initial ground state energy of the relaxed structure of the pristine monolayer, but the system equilibrated at around 3 ps for both 300 K and 500 K. We observe a negligible structural deformation which ensures the thermal stability of the nanosheet upto 500 K. Hence, it may practically be used at a wide range of temperature.

The high electronic conductivity of an electrode material plays a pivotal role in the fast

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Figure 3. Possible Ca metal atom adsorption sites Nb_2S_2 monolayer [The green and yellow balls represent Nb and S atoms]

behavior of the hexagonal monolayer. Interestingly, here are some Dirac cones present in the band structure. In presence of Dirac cones, the electrical conduction is attributed to the



Figure 4. Electronic properties of the single Ca adsorbed at most favored T_h -site of Nb_2S_2 monolayer: (a) Band structures and (b) Density of States (DOS). Fermi levels are set to zero.

movement of the massless charge carriers (fermions) and the phenomenon is theoretically governed by the relativistic Dirac equation.[65] Thus, the presence of Dirac cone in band structure promotes electron transfer more prominently. In this context, the hexagonal monolayer turns out to be an excellent electron transport The constant flow material. of electrons, at the closed circuit of cathode and anode, can only be efficiently handled by the metallic nature of the electrode. In some cases, the pristine material is either a smallgap or large-gap semiconductor but metallicity appears after metal-ion adsorption[33, 34, 66]. Herein, our monolayer proposed system is inherently metallic which sounds appealing in electrode utility.

charging-discharging process and the larger lifetime of any rechargeable cell.

conductivity of the two-dimensional material, we extract the electronic band structure of the buckled hexagonal Nb₂S₂ monolayer. Since PBE functional

underestimates the band gap value due to the self-iteration error, we have

calculation for better accuracy. The band structure and the projected density

of states are shown in Figure 2a and

Figure 2b which reflect the metallic

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To study the adsorption performance of the Nb_2S_2 monolayer comprehensively, at first, we have identified the adsorption sites for Ca atoms in the nanosheet and thereby examined the nature of Ca and Nb₂S₂ monolayer interaction. From the electron localization function (ELF) plot in Figure 1c, we have located the electron-deficient zones which correspond to the possible adsorption sites. There are four possible sites observed for the monolayer: (i) hexagonal-site $(T_h, over the top of the hexagons), (ii) Nb-site (T_{Nb}, top of Nb atoms), (iii) S-site (T_S, top of S)$ atoms), and (iv) NbS-site (T_{NbS}, over the top of the Nb-S bonds), as shown in Figure 3. To implement the van-der Waals interaction between the Ca metals and the two-dimensional monolayer, the DFT-D3 dispersion (Grimme's correction) are considered for the calculations of ground state energies of the monocalciated systems and further, we have determined the adsorption energy using Equation 1. Among all four adsorption sites, T_h-site is energetically the most favored site ($E_{ad} = -0.78 \text{ eV}$) for the Ca atom adsorption on the Nb₂S₂ monolayer. The single Ca intercalation is an exothermic process with respect to the energetic aspects. However, after geometrical optimization, the Ca atoms on the T_{Nb}-site and T_s-site move to their nearest neighboring buckled hexagon with the same adsorption energy as the T_h-site (-0.78 eV). However, the Ca atom, initially placed at T_{NbS}-site tends to move towards the hexagon, but cannot reach the most favorable T_h-site. This is the reason for which the adsorption energy is comparatively lesser with E_{ad} of -0.24 eV. Hence, our results suggest that the Nb₂S₂ monolayer is associated with the single adsorption sites, namely, T_h-site for Ca intercalation. The relaxed structures are shown in Figures S2(a-d) in the Supporting Information. To explore the electronic property of the calciated monolayers, we have calculated the band structure and total density of states (TDOS) for the Ca adsorbed Nb₂S₂ monolayer. From the band structure and TDOS plots of the system, displayed in Figure 4a and Figure 4b, we note that bands cross the fermi level and it shows a finite density of states around the fermi level, which indicates that the composite system is metallic in nature. Thus, this system meets one of the requirements for making an efficient calcium-ion battery (CIB).

To understand the charge transfer process in the system, we have performed bader charge



Figure 5. CDD plots for single Ca-adsorbed at the most favored site (T_h -site) of Nb_2S_2 monolayer at fixed isosurfaces value of 0.002e/ Bohr³ : (a) Top view (b) Side view

following expression,[67]

analysis. A significant amount of charge (0.76 e) is transferred from the Ca to the monolayer which validates the adsorption of Ca over the nanosheet. This charge transfer suggests the cationic state of the alkaline earth metal, which is essential for efficient intercalation. For a clear picture of the chargetransfer of the alkaline earth metal adsorbed hexagonal Nb₂S₂ system, we have obtained the charge-density difference (CDD) using the

$$\Delta \rho = \rho_{Nb_2S_2 + Ca} - \rho_{Nb_2S_2} - \rho_{Ca} \tag{4}$$

where $\rho_{Nb_2S_2+Ca}$, $\rho_{Nb_2S_2}$, and ρ_{Ca} are the charge densities of the Ca-adsorbed Nb₂S₂ monolayer, pristine Nb₂S₂ monolayer, and isolated Ca atom, respectively, and plotted in Figure 5. The blue isosurfaces signify the charge depletion region, whereas the yellow isosurfaces indicate the

charge accumulation region. The sharp distinction between the two isosurfaces in Figure 5 indicates the charge is transferred from the alkaline earth metal atom to the Nb_2S_2 monolayer.

The performance of a metal-ion battery is largely influenced by the diffusion of the corresponding metal ions in between the favored sites of the monolayer. To exhibit electrode



Figure 6. (a) Possible diffusion pathway of single Ca atom from one T_h -site to another T_h -site of Nb₂S₂ monolayer. There are ten intermediate images have been considered. (b) Energy profile diagram for the diffusion of single Ca atom from one T_h -site to another T_h -site of Nb₂S₂ monolayer. [The green, yellow, and blue balls represent Nb, S, and Ca atoms]

behavior in MIB, a material must possess a low diffusion energy barrier (ΔE_{diff}) as well as sufficiently large metal-ion mobility to manifest efficient charging-discharging rates. However, this energy barrier depends upon the mutual interaction between the metal ions and the monolayer system which decides the activation energy. The nudged elastic band (NEB) is a computational technique to locate the saddle points and probable minimum energy paths (MEP) between the initial and final state of any system. In this method, several intermediate images (structures) are optimized across the path of the transformation. The climbing image (CI) is the modified NEB method where the image with the highest energy is moved to the saddle point. In our findings, we have determined diffusion energy barrier and minimum energy path by implementing the climbing image nudged elastic band (CI-NEB) technique. Thus, we have calculated the energy barrier for the diffusion of a Ca atom from one Th-site to another (see Figure 6b). The minimum energy path (MEP) has been identified for the diffusion process across the Nb-S bond. We have considered ten intermediate images between the initial and final configurations. It is expected that the initial and final configuration of diffusion should have same energy. Here we can observe that there is energy difference of about 0.13 eV between the initial and final states. However, all the T_h-sites are completely hexagonal and physically equivalent in its pristine state (Figure 1a). But after the single Ca-adsorption, several Th-sites become slightly deformed (Figure S2a). Now, when the structure of the initial and final states of diffusion is compared (Figure 6a), the initial T_h-site resembles a hexagonal shape, whereas the final T_h-site exhibits some distortion. As a result, there is little structural change between the diffusion's initial and final states, which may account for the 0.13 eV energy difference between them. As displayed in Figure 6a, the computed diffusion energy barrier is 0.76 eV. This diffusion barrier value is the same as the phosphorene as anode material in Liion battery[68]. The calciated monolayer is expected to have the comparable potentiality as the other promising electrodes like MoN₂ (0.78 eV)[69], vacancy defect induced MoS₂ (0.47-0.74 eV)[70], β_0 -PC (0.66 eV)[71], borophene (0.60-0.66 eV)[72, 73], etc. Thus, the Ca-migration barrier signifies that the Nb₂S₂ monolayer may be used as efficient electrode material in a Ca-ion battery.

For the realistic utilization of any metal-ion batteries, the maximum theoretical storage capacities (C) and the open-circuit voltages (OCV) are relevant parameters apart from the electronic structure, adsorption processes, and diffusion barriers. From the viewpoint of electrode utility of any material, the open-circuit voltage (OCV) is considered to be the key parameter for recognizing the system as cathode or anode material. The cell potential is defined as, $E_{cell} = E_{cathode} - E_{anode}$. The functionality of material as anode or cathode may be decided based on its OCV value. Materials with low OCV values (0.1-1 eV) behave as anode while materials with higher OCV values (>1 eV) exhibit cathodic behavior [31, 32, 74, 75]. To this end, the average OCV for the calciated Nb₂S₂ monolayer (we have considered 3×3×1 supercell) is estimated by considering the charging-discharging half-reaction,[76]

$$Nb_{18}S_{18} + xCa^{+2} + 2xe(-) \leftrightarrow Nb_{18}S_{18}Ca_x$$
 (5)

For an electrode, the OCV does depend upon the change in Gibbs free energy during the Ca adsorption process (ΔG_f) ; $OCV = -(\Delta G_f / 2xe)$, where x and e are the numbers of Ca atoms adsorbed on the pristine monolayer and elementary transferred charge, respectively. The factor '2' stands for the bivalent Ca-metal ion. This ΔG_f can be defined as $\Delta G_f = \Delta E_f + P\Delta V - T\Delta S$. By neglecting both the volume (ΔV) and the entropy effect (ΔS), we obtain the $OCV = -(\Delta E_f / 2xe)$ which is calculated by using the following equation,[76]

$$OCV = \frac{E_{Nb_{18}S_{18}} + xE_{Ca} - E_{Nb_{18}S_{18} + xCa}}{2x} \tag{6}$$

where $E_{Nb_{18}S_{18}+xC}$, $E_{Nb_{18}S_{18}}$, and E_{Ca} are the ground state energies of Ca adsorbed Nb₁₈S₁₈ monolayer, pristine Nb₁₈S₁₈ monolayer, and single Ca atom in its bulk crystal form, respectively. The *x* and *e* indicate the Ca concentration and charge of an electron, respectively. Herein, the OCV value decreases from 0.85 to 0.07 V as the Ca concentration (*x*) increases layer-by-layer from nine to fifty-four (within a 3×3×1 supercell), as shown in Figure 7a. At low concentrations of Ca, the fall of OCV is relatively smaller but, at higher concentrations



Figure 7. (a) Voltage profile diagram due to gradual increase of Ca atoms in the Nb_2S_2 monolayer and (b) Maximum Theoretical Storage capacity (C)

(tetralayer to hexalayer) the drop is quite drastic. The voltage drop at the higher concentrations may be explained due to the increased metal-metal repulsion over the Nb₂S₂ monolayer. The plateaus in the voltage profile (Figure 7a) stand for a stable and effective secondary battery system. Herein, we report the average OCV for the calciated Nb₂S₂ composite system as 0.49 V. Our calculated OCV value is quite analogous to the recently reported graphene-like SiC monolayer (0.45 V)[77] as anode materials for Ca-ion batteries. This OCV value is also similar or comparable with some previously explored anode materials for different metal-ion batteries by various research groups, for instance, homogenous holey-C_xN₃ monolayer for Li-ion battery (0.45 V)[32], FeSe monolayer for Na-ion battery (0.49 V)[78], 2D-bismuthine for K-ion battery (0.5 V)[79], etc. Hence, we expect the 2D-monolayer system as an emerging candidate to exhibit outstanding anodic character for the Ca-ion batteries.

To find the maximum storage capacity, we have calculated the adsorption energy (E_{ad}) of Ca atoms layer-by-layer on the surface of the $(3 \times 3 \times 1)$ Nb₂S₂ system,

$$E_{ad} = \frac{E_{Nb_{18}S_{18} + nCa} - E_{Nb_{18}S_{18}} - nE_{Ca}}{n}$$
(7)

where, $E_{Nb_{18}S_{18}+nCa}$, $E_{Nb_{18}S_{18}}$ and E_{Ca} be the energies of the calciated sheet, pristine sheet and single Ca atom in the bulk system respectively; *n* represents the number of Ca atoms adsorbed. First, we have adsorbed Ca atoms on the most favored sites of the 2D sheet. It is observed that the first layer of the adsorbed system can hold nine Ca atoms and it is designated as a monolayer calciated system. The monolayer is found to be stable enough with an adsorption energy of -1.71 eV. We add nine more Ca atoms at the bottom of the monolayer-calciated system and let it relax, the relaxed bilayer system shows a significant amount of adsorption energy (-1.26 eV). In the monolayer and bilayer calciated systems, the metal ions adsorb directly to the Nb₂S₂ sheet. Similarly, we obtain tetralayer and hexalayer calciated Nb₂S₂ systems with adsorption energies of -0.83 eV and -0.14 eV respectively. However, further adsorption of Ca layers on



Figure 8. Potential energy evolution during AIMD simulations of the (a) monolayer (b) bilayer (c) tetralayer (d) hexalayer Ca-intercalated Nb_2S_2 nanosheet for 5 ps with temperature 300 K along with final geometry (Top and Side).

this system is not energetically allowed. Thus, the hexalayer calciated Nb_2S_2 system is the maximum adsorbed configuration. We observe that the Ca atoms at alternative layers are preferably adsorbed on the top of hexagonal and T_s -sites respectively.

We have shown the optimized geometries of the monolayer to hexalayer calciated systems in Figure S3. For experimental feasibilities, the thermal stability of the Ca-adsorbed layered geometry is a very crucial factor. Thus, we have carried out the AIMD simulation of the monolayer, bilayer, tetralayer, and hexalayer calciated Nb_2S_2 system at 300K for 5 ps with a time step of 1 fs. The fluctuation of potential energy with time and the final geometry after AIMD simulation have been presented in Figure 8 which clearly suggest the high thermal stability of these calciated monolayers which may have practical utilization as anode material in CIB.

Furthermore, we have calculated the maximum theoretical storage capacities (C) by using the following equation,[80]

$$C = \left[\frac{1}{M_{Nb_{18}S_{18}}}\right] \left(z \times x_{max} \times F \times 10^3\right) \tag{8}$$

where $M_{Nb_{18}S_{18}}$ is the atomic mass of pristine Nb₁₈S₁₈ sheet, *z* is the valence number (*z* = 2 for Ca), x_{max} is the highest concentration of Ca on the Nb₂S₂ monolayer, and *F* is the Faraday constant (26.810 A h mol⁻¹). Herein, we report the high theoretical storage capacity (C) for Caion battery (CIB) and the value is 1286.88 mAh/g which is quite larger than some previously reported anode materials viz., Ti₂PX₂-Na (X = S, Se, and Te): 421 - 842 mAh/g[81]; V₃C₂ MXene for Li, Na, K, and Ca metal ions: 269.86 - 606.42 mAh/g[82]; Mo₂CrC₂ MXene for Li, Na, K, and Mg metal ions: 154.88 - 927.51 mAh/g[83]. Thus, the Nb₂S₂ monolayer is expected to have a greater amount of energy in a single discharge.

However, volume expansion is a burning issue of storage devices in practical daily life uses. Thus, we have to consider this point while modeling an anode material for an electrochemical cell. Keeping this in mind, we have calculated the volume change of the calciated and decalciated monolayer. The optimized lattice constant of the pristine 2D-Nb₁₈S₁₈ monolayer is found to be 11.84 Å (a = b), whereas, in the maximum Ca intercalated system, it is found to be 11.87 Å. The net increases of lattice constants are significantly lower (0.25%) than in 2D $Ti_3C_2O_2$ MXene anode material for Na-ion batteries (0.75%)[84] and 2D V₂S₂O for K-ion batteries (4.1%)[39]. This result suggests robust calciation of the monolayer by excluding the volume-expansion issue from the computationally designed anode material in practical utilization. Furthermore, the charging-discharging process is largely influenced by the coalition of the Ca atoms at the highest intercalated geometry. The average Ca-Ca bond length at maximum intercalated geometry is calculated as 3.99 Å. After the AIMD simulation (at 300K for 5ps) of this configuration, the average Ca-Ca bond length increases to 4.1 Å. Both the average bond length is considerably larger than the average Ca-Ca bond length in Ca₂ dimers (3.89 Å). Hence, it rules out the possibility of cluster formation among the Ca atoms during intercalation at the monolayer which stands for the unique anodic nature of the buckled hexagonal Nb₂S₂ nanosheet with sufficiently high capacity.

CONCLUSION

In conclusion, we have used state-of-the-art density functional formalism to investigate the possibility of using the inherently metallic Nb₂S₂ monolayer as an anode material for Ca-ion batteries (CIBs) for the first time. We have calculated the phonon thermodynamic properties like free energy, entropy, and heat capacity at constant volume (C_v) to establish the buckledhexagonal Nb₂S₂ monolayer is energetically, dynamically, and thermally stable for its realistic use. Our study shows that the adsorption of Ca atoms on the monolayer is an energetically favored process with a considerable amount of negative adsorption energy. The calciated Nb_2S_2 monolayer exhibits metallic behavior, which manifests high electrical conductivity for the anode material. We have explored the Ca diffusion barrier, open-circuit voltage (OCV), and maximum theoretical storage capacity (C) of the Ca-intercalated Nb₂S₂ monolayer. The moderately low energy barrier (0.76 eV) in between the adsorption sites suggests the easy diffusion of Ca ions in this system. The significantly low OCV value (0.49 V) suggests the composite system to be an efficient anode material for CIB. The calculated theoretical capacity (1286.88 mAh/g) is found to have quite enriched value than the many reported anode materials for CIBs to date. Hence, we note here that the novel Nb₂S₂ monolayer can unfold a new horizon as an anode material for Ca-ion batteries with contemporary interests.

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SUPPORTING INFORMATION

Phonon band structure, phonon DOS for pristine $(3\times3\times1)$ Nb₂S₂ monolayer, phonon dependent thermodynamic parameter for Nb₂S₂ monolayer; relaxed structures for the single Ca adsorbed Nb₂S₂ monolayer: adsorption at T_h-site and adsorption at T_{NbS}-site (top and side view); relaxed structures of: monolayer, bilayer, tetralayer, and hexalayer calciated Nb₂S₂ system.

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