High-Throughput Computational Characterization of 2D Compositionally Complex Transition-Metal Chalcogenide Alloys

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2D binary transition-metal chalcogenides (TMCs) such as molybdenum disulfide exhibit excellent properties required for energy conversion applications. Alloying binary TMCs can form 2D compositionally complex TMC alloys (CCTMCAs) that possess remarkable properties from the constituent TMCs. High-throughput workflow performing density functional theory (DFT) calculations based on the virtual crystal approximation (VCA) model (VCA-DFT) is designed. The workflow is tested by predicting properties including in-plane lattice constants, band gaps, effective masses, spin–orbit coupling, and band alignments of the Mo–W–S–Se, Mo–W–S–Te, and Mo–W–Se–Te 2D CCTMCAs. The VCA-DFT results are validated by computing the same properties using unit cells and supercells of selected compositions. The VCA-DFT results of the abovementioned five properties are comparable to that of DFT calculations, with some inaccuracies in several properties of MoSTe and WSTe. Moreover, 2D CCTMCAs can form type II heterostructures as used in photovoltaics. Finally, Mo$_0.5$W$_0.5$Se, Mo$_0.5$W$_0.5$STe, and Mo$_0.5$W$_0.5$SeTe 2D CCTMCAs are used to demonstrate the room-temperature entropy-stabilized alloys. They also exhibit high electrical conductivities at 300 K, promising for light adsorption devices. This work shows that the high-throughput workflow using VCA-DFT calculations provides a tradeoff between efficiency and accuracy, opening up opportunities in the computational design of other 2D CCTMCAs for various applications.

1. Introduction

Binary 2D transition metal chalcogenides (TMCs) exhibit strong in-plane chemical bonds and weak out-of-plane interactions, allowing for stable monolayers.[1] The properties of 2D TMCs such as MX$_2$ have been investigated from both computational simulation and the experimental works.[2,3] Monolayer MX$_2$ have direct band gaps ranging from 1.0 to 2.0 eV.[2] They also display thickness-dependent electronic properties of band gap,[4] which transitions from indirect in multiple layers and bulk MX$_2$ to direct in monolayer MX$_2$. Owing to these excellent properties, binary 2D TMCs have recently grown in prominence with their promising applications such as photovoltaics, photodetectors, and field-effect transistors.[5,6]

However, a general problem of binary 2D TMCs is their fixed properties such as band gaps, which limit their applications in fields such as optoelectronics and photovoltaics where adjustable band gaps are needed to accommodate different wavelength ranges.[7] Different modification processes such as alloying,[5] mechanical straining,[8] and forming heterostructures[9] have been applied for achieving the maximized efficiency in light-electricity energy conversion. One of these methods is to obtain van der Waals (vdW) heterostructures by stacking together two different binary monolayers.[10] Different vdW heterostructures have many applications such as field-effect tunneling transistors,[11] photovoltaics,[12] and other optoelectronic devices.[13] 2D TMCs-based vdW heterostructures have been used in heterojunction photovoltaics. For example, the WS$_2$/WSe$_2$ vdW heterostructure has been investigated via density functional theory (DFT) calculations and experiment and shown to be a promising candidate for photovoltaics because of the high light adsorption efficiency and high carrier mobility.[14]

Apart from forming heterostructures, alloying multiple materials of different elements together to form bulk compositionally complex alloys (CCAs) such as CoCrFeMnNi and Al$_x$CoCrFeNi[15,16] has been shown to allow for a high tunability in band structures. In contrast to conventional alloys that are comprised of one or two principal elements and of much lower percentages of other elements,[17] CCAs encompass not only conventional alloys but also high-entropy alloys (HEAs) that have more than five principal elements of equal or near-equal molar ratios.[18] In CCAs, the composition consisting of multiple elements has fundamental effects on configurational entropy, free energy, phase selection, and stability.[18] For example, the increasing of temperature will cause the decrease of Gibbs
free energy in the system of high configurational entropy, thus increasing the stability of CCAs.\[^{[19]}\] Moreover, despite the complexity in local atomic structures caused by random distribution of elements in a multinary alloy,\[^{[20]}\] CCAs with a single solid solution phase and the atoms on the sites of a specific Bravais lattice (e.g., face-centered cubic or body-centered cubic) exhibit many attractive functional properties.\[^{[18]}\] For example, the high electrical conductivity and low thermal conductivity in CCAs such as Al\(_x\)CoCrFeNi and Pb-Sn-Te-Se, makes them promising for thermoelectric applications.\[^{[21]}\] In addition, due to their multi-component nature, CCAs such as FeCoNiCuMn of some stoichiometries have been shown to have a tunable Curie temperature \(T_C\) that reaches room temperature,\[^{[22]}\] and the combination of tunable \(T_C\) and enhanced MCE makes these CCAs attractive as magnetic refrigerant materials.\[^{[22,23]}\]

More recently, research has emerged focusing on using 2D CCAs such as Mo\(_{1-x}\)W\(_x\)S\(_2\) and (Al\(_y\)Ga\(_{1-y}\))\(_{0.5}\)In\(_{0.5}\)P in energy conversion applications, such as photovoltaics, photocatalysts, and optoelectronic devices.\[^{[24]}\] The entropic effect benefits the design and fabrication of multiple-component 2D CCAs with similar concentrations of the constituent elements. Instead of conventional 2D materials with fixed structural and electronic properties, this multi-component design opens up opportunities for tunable properties such as lattice constants and band gaps.\[^{[24]}\] Desired phases and stoichiometries can be achieved through adjusting the contents of each element to enhance materials properties such as catalytic activity and light conversion efficiency.\[^{[25]}\] For example, in order to acquire an optimal range of band gaps and thus optimized absorption coefficients, ternary,\[^{[26]}\] quaternary,\[^{[27]}\] and even penternary\[^{[28]}\] CCAs have been computationally simulated and fabricated for photovoltaic applications. Moreover, the alloying method is able to modify the lattice constant of CCAs based on their constituent elements. For example, lattice strain can occur in vdW heterostructures due to lattice mismatch. The 2D CCAs from alloying with the components of similar crystal structures and in-plane lattice constants can bring in heterostructures and multijunction of the materials with small lattice mismatch, which lowers the interface strain in a heterostructure.\[^{[29]}\]

Quaternary 2D TMC alloys present themselves as potential CCAs due to their multi-elemental composition and high configurational entropy induced by alloying from binary TMCs. Because of tunable structural and electronic properties of multinary TMCs, it is important to investigate the thermodynamically favorable 2D compositionally complex transitional metal chalcogenide alloys (CCTMCAs) for high efficiency energy conversion applications such as photovoltaics, photocatalysts, and optoelectronics, as well as the spintronic applications of random-access memory (RAM).\[^{[7,30,31]}\] For example, quaternary 2D CCTMCAs such as Cd\(_{1-x}\)Zn\(_x\)O\(_{1-y}\)S\(_{1+y}\) are found suitable in photovoltaics applications because of their high carrier mobilities and suitable range of direct band gaps.\[^{[32]}\] In photovoltaics, the efficiency of a device is limited to effective carrier masses, which relate to the charger extraction and recombination dynamics and control the open-circuit voltage.\[^{[33]}\] The carrier mobility, as one of the key properties of photovoltaics, depends on both the momentum relaxation time and effective mass, where the momentum relaxation time is inversely linked to the effective mass in lattice scattering.\[^{[34]}\] It is shown that a large effective mass results in a decreased charge carrier mobility, which therefore lowers the efficiency of light conversion in photovoltaics.\[^{[35]}\] Moreover, quaternary 2D CCTMCAs such as Cu\(_x\)Mo\(_{1-x}\)(Se\(_{1-y}\)S\(_y\))\(_2\) are proposed as potential photocatalysts.\[^{[36]}\] In the process of electrochemical water splitting, the band gap of a 2D CCTMA determines the acceptable photon frequency during light adsorption, whereas the band alignments of conduction band minimum (CBM) and valence band maximum (VBM) are also considered essential in matching potentials of hydrogen/oxygen evolution reactions (H\(^+\)/H\(_2\), H\(_2\)/O\(_2\)) energy at different pH levels.\[^{[10]}\] Additionally, 2D CCTMCAs are also found as potential spintronic applications in spin-logic devices such as RAM for their strong spin–orbit coupling (SOC). These functions rely on the controlling of the electron/hole spins, which comes from the metal d-orbital states in the heavy metal atoms in 2D CCTMCAs.\[^{[31]}\] To sum up, 2D CCTMCAs play significant roles in the applications of energy conversion and spintronics. In order to understand the dependency of various properties of 2D CCTMCAs and their effects in those applications, it is essential to characterize the properties of 2D CCTMCAs such as lattice constants, band alignment, effective carrier masses, spin–orbit splitting, and so on.

Different methods such as Korringa–Kohn–Rostoker coherent-potential-approximation (KKR-CPA) method and DFT calculation have been used to study various properties such as lattice parameters, band gap, and band alignment in CCAs.\[^{[15,9,37]}\] Reports using the KKR-CPA method to study bulk CCAs have confirmed a reduction in electron mean free path and subsequent decrease in electrical and thermal (from electronic contributions) conductivities with increasing principal elements.\[^{[19]}\] Similarly, the KKR-CPA method has been used to study the electronic, magnetic, and transport properties of the Fe-intercalated bulk TaS\(_2\) TMC alloys.\[^{[38]}\] DFT calculations, on the other hand, have been widely used in studying the properties of 2D CCTMCAs such as band gaps and phase stability. During DFT calculation, models of random alloy and special quasi-random structure (SQS) are proposed in order to simulate the disorder CCAs. For example, the DFT calculations using a random alloy model have shown tunable band gaps of quaternary Mo\(_{1-x}\)W\(_x\)Se\(_2\)S\(_2\)Se\(_{2(1-y)}\) 2D CCTMCAs dependent on the composition, which are consistent with the experiment.\[^{[35]}\] Moreover, the combination of DFT using SQS models to study the formation enthalpies of ternary TMC alloys has shown that MoSe\(_{2(I-x)}\)Te\(_{2x}\), WSe\(_{2(I-x)}Te\(_2x\), MoS\(_{2(I-x)}\)Te\(_{2x}\), and WS\(_{2(I-x)}\)Te\(_{2x}\) alloy systems are unstable at 0 K.\[^{[37]}\] Comparing to the KKR-CPA method, DFT calculations can predict more accurate structural and electronic properties such as lattice parameters, electronic density of states, and band gaps.\[^{[19,40]}\] However, when dealing with quaternary 2D CCTMCAs with different compositions, supercells with a number of atoms are required, which makes the DFT calculations very time-consuming. Therefore, alternative methods are desired in efficiently characterizing structural and electronic properties.

Virtual crystal approximation (VCA), as an alternative method to investigate the CCAs of different compositions, has been applied to reduce computational cost while achieving a comparative accuracy to supercell-DFT calculations using an averaged potential from mixing elemental potentials.\[^{[41]}\] Specifically, the VCA method provides a convenient and efficient way to model
CCAs by generalizing their multi-elemental composition into the weighted average of the individual alloying elements. In comparing to regular DFT calculations of large supercells in investigating multinary CCAs, DFT calculation using VCA method (VCA-DFT) is performed significantly smaller unit cells, offering much greater simplicity and lower computational cost. Namely, calculations using the VCA model is much faster than the using the SQS model. For example, optimizing the MoWSSe (see below) with the former model and 64 computer cores costs about 35 s whereas with the latter costs about 5600 s. Note that, as a result of this simplification, VCA neglects any short-range order and local distortions and therefore cannot replicate the fine details of an alloy. The VCA-DFT method as implemented in the Vienna Ab initio Simulation Package (VASP) has found successful applications in studying TMC systems such as WSe$_2$(1-3)(2). The VCA-DFT method has also been used to obtain structural properties, phase determination, and electronic properties such as band gaps and effective masses of carriers, the results of which are all comparable to experiments. Therefore, utilizing the VCA-DFT method is helpful in characterizing the CCAs of different compositions, facilitating materials screening and selection for different applications.

In this work, we propose a high-throughput workflow to investigate the properties of 2D CCTMCs as candidates for various energy and information technology applications such as light conversion and computer logic systems. We use the Mo-W-S-Se, Mo-W-S-Te, and Mo-W-Se-Te 2D CCTMCs as examples to illustrate the search and selection of 2D CCTMCs with different structural and electrical properties via VCA-DFT calculations. Meanwhile, we adopt the unit cell and SQS models to benchmark the accuracy of the results from using the VCA-DFT method. We show that the structural and electronic properties of 2D CCTMCs including in-plane lattice constants, band gaps, effective carrier masses, spin–orbit splitting, and band alignment are in good agreement with the DFT calculations based on the unit-cell (unit-cell-DFT) and SQS (SQS-DFT) models. We then select nine ternary and three quaternary 2D CCTMCs to investigate the stability using the metrics of formation energy and Gibbs free energy. We then focus on the three quaternary 2D CCTMCs, Mo$_{0.5}$W$_{0.5}$SSe, Mo$_{0.5}$W$_{0.5}$STe, and Mo$_{0.5}$W$_{0.5}$SeTe, which are found to be able to form type II band alignments with other quaternary 2D CCTMCs, owing to their high configuration entropy. These three quaternary 2D CCTMCs have negative Gibbs free energies at 300 K, serving as good examples as entropy-stabilized multinary 2D alloys. Additionally, Mo$_{0.5}$W$_{0.5}$SSe, Mo$_{0.5}$W$_{0.5}$STe, and Mo$_{0.5}$W$_{0.5}$SeTe show high electrical conductivity at room temperature (300 K), making them possible to be utilized in energy conversion applications. We therefore suggest the VCA-DFT-based workflow as a potential high-throughput framework in searching for 2D CCTMCs for various applications. Given that many multinary 2D materials are being successfully synthesized, our work serves as an example of placing these 2D materials in the context of 2D HEAs. In doing so, one gains not only novel perspectives but also an extra degree to freedom (entropy) to control the stability. Furthermore, we show in this work that the VCA model is suitable for modeling multinary 2D alloys with a balanced tradeoff between accuracy and efficiency, opening up a wide range of opportunities for studying other multinary 2D alloys.

2. Experimental Section

The VCA-DFT method is applied in the Vienna Ab initio Package (VASP) to study the Mo-W-S-Se, Mo-W-S-Te, and Mo-W-Se-Te 2D CCTMCAs, Mo$_{1-x}$W$_x$S$_y$Te$_{2-2y}$, Mo$_{1-x}$W$_x$S$_y$Se$_{2-2y}$, and Mo$_{1-x}$W$_x$Se$_y$Te$_{2-2y}$, with $x$ and $y$ ranging from 0 to 1 at an incremental step of 0.05. The range of $x$ and $y$ was resulted in three sets of 441 quaternary 2D CCTMCAs. Figure 1a illustrates the structure model from the VCA method, and Figure 1b,c displays a 4 × 4 × 1 SQS supercell obtained from the ATAT package. All the calculations were performed using VASP, and the plane waves of kinetic energies smaller than 500 eV were included in the basis sets. The standard projector augmented wave (PAW) potential files for Mo, W, S, Se, and Te were used. The Perdew–Burke–Ernzerhof (PBE) functional in DFT was well known to underestimate band gaps. All the calculations were performed using VASP, and the plane waves of kinetic energies smaller than 500 eV were included in the basis sets. The standard projector augmented wave (PAW) potential files for Mo, W, S, Se, and Te were used. The Perdew–Burke–Ernzerhof (PBE) functional in DFT was well known to underestimate band gaps. If more advanced theories accounting for many-body effects that were missing in the PBE functional were used, the theoretical band gaps would generally be higher. The PBE-calculated optical band gaps of WSSe and MoSSe agreed well with the experimental band gaps. A Monkhorst–Pack $15 \times 15 \times 1$ k-point grid was used. The in-plane lattice constants and atomic coordinates of all systems were fully optimized using a quasi-Newton algorithm with the force convergence criterion of 0.01 eV Å$^{-1}$. The band structures were calculated along the $\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma$ special k-point path (each line segment had 40 k points), where the band gaps and effective carrier masses were extracted. Effective electron and hole masses were also calculated.
using the Sumo package\textsuperscript{[57]} and the averaged effective masses reported in the K-M and K'-I directions. To calculate the spin–orbit splitting magnitude, SOC was included in the calculations. The electrical conductivities of three quaternary 2D CCTMC\textsubscript{As} were reported in the literature\textsuperscript{[7,30,31]} However, a systematic workflow that could be applied to search for materials with various applications in an efficient manner was lacking. In order to efficiently discover those materials from 2D TMC\textsubscript{As}, a workflow was proposed (see Figure 2) that utilized VCA-DFT to obtain essential structural and electronic properties. The workflow was consisted of first proposing several simple binary TMC compounds. Different alloying 2D CCTMC\textsubscript{As} could thus be generated by the combination of the binary compounds. Then the workflow applied DFT calculations using the averaged pseudopotential of corresponding elements to characterize the VCA model. Five essential properties were computed for selecting materials in various applications, which were in-plane lattice constant, band gap, hole and electron effective masses, spin–orbit splitting, and band alignment of CBM and VBM. Due to lack of Bloch bands, the effective masses reported here were meant to be comparable to the effective masses originated from the effect band structure that could be obtained from calculations using periodic supercells. Therefore, at the same time, the reliability and accuracy of the calculation process were cross-examined by benchmarking DFT calculations using unit-cell and SQS models. Three-atom unit cells were used to model the binary MX\textsubscript{2} and Janus MX\textsubscript{Y} (X ≠ Y = S, Se, or Te) structures of TMC\textsubscript{As}, whereas for the complex ternary and quaternary 2D CCTMC\textsubscript{As}, SQS supercells were created to simulate the disordered structures. Specifically, these VCA-DFT calculations were validated using six binary TMC unit cells and six Janus unit cells, as well as three ternary SQS supercells and three quaternary SQS supercells with special stoichiometries that were Mo\textsubscript{0.5}W\textsubscript{0.5}S\textsubscript{2}, Mo\textsubscript{0.5}W\textsubscript{0.5}Se\textsubscript{2}, Mo\textsubscript{0.5}W\textsubscript{0.5}Te\textsubscript{2}, Mo\textsubscript{0.5}W\textsubscript{0.5}S\textsubscript{Se}, Mo\textsubscript{0.5}W\textsubscript{0.5}S\textsubscript{Te}, and Mo\textsubscript{0.5}W\textsubscript{0.5}S\textsubscript{SeTe}.

### 3. Results and Discussion

#### 3.1. Benchmark Calculations of the VCA-DFT Model

We perform VCA-DFT calculations to obtain five essential structural and electronic properties including the in-plane lattice constant, band gap, hole and electron effective masses, spin–orbit splitting, and band alignment, in order to search for suitable 2D CCTMC\textsubscript{As} in potential applications of energy conversion and spin-logic devices. First of all, the in-plane lattice constant of a 2D material is a fundamental parameter in describing the monolayer geometry. Besides, the lattice constants of 2D CCTMC\textsubscript{As} are helpful to understand the composition-dependent lattice change, which is important in considering the lattice matching
of two different 2D CCTMCAs during designing the 2D stacked heterostructure, in order to avoid the misfit and change of the crystal structure. Second, it is essential to tune band gaps to fit in the range of photonic frequency of different light sources in light adsorption devices in photovoltaics and photocatalysts. An appropriate band gap range matching photonic frequency increases the efficiency of harvesting light energy. Third, effective masses of electrons and holes are critical in predicting carrier optical response and transport property of semiconductors.[60] The effective masses also determine the effective density of states, which further impacts the open circuit voltage.[35] Fourth, 2D Group-VI TMCs, such as MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$, have been heavily investigated as potential materials in the field of spintronics and valleytronics due to their broken inversion symmetry.[61–63] These 2D materials contain two inequivalent valleys that occur at opposite spin signs at the K points of the Brillouin zone, and time reversal symmetry in TMCs causes spin splitting with strong SOC in TMCs.[61] Due to the broken inversion symmetry in TMCs, this coupling between spin and valley pseudospin leads to identical results compared to the DFT results using a three-atom unit cell. We also notice that the in-plane lattice constants of the six binary TMCs share three values, 3.18 Å, 3.32 Å, and 3.55 Å, where the binary TMCs of same chalcogen element have the same lattice constants. This is understood by the large difference in the anion radii of S$^{2-}$ (1.70 Å), Se$^{2-}$ (1.84 Å), and Te$^{2-}$ (2.07 Å), whereas the cations of Mo$^{6+}$ and W$^{6+}$ possess similar ionic radii of 0.79 Å and 0.80 Å, respectively.[65] Moreover, the discrepancy in the covalent radii between Mo (1.54 Å) and W (1.62 Å) is also smaller than that among S (1.05 Å), Se (1.20 Å), and Te (1.38 Å).[65] For the CBM and VBM, the VCA-DFT results match well with other DFT calculation results at the PBE level. Additionally, the CBM values of Mo$_{0.5}$W$_{0.5}$Te$_2$, W$_{0.5}$S$_2$, and W$_{0.5}$Se$_2$ are closer to the DFT calculation results in ref.[71] using the PBE functional including SOC.

| Table 2. In-plane lattice constant $a_0$, band gap $E_g$, hole and electron effective masses $m^*_h$, spin–orbit splitting $\Delta E_{SO}$, CBM, and VBM with reference to the vacuum level of Janus MX$_2$ with the 2H structure. The first row of each property is obtained from using the VCA-DFT method, whereas the second row is from using three-atom unit cells to simulate monolayer Janus structures. |
|---|
| **Property** | MoSSe | WSSe | MoSTe | WSTe | MoSeTe | WSeTe |
| $a_0$ (Å) | 3.26 | 3.26 | 3.40 | 3.39 | 3.45 | 3.47 |
| $E_g$ (eV) | 1.54 | 1.66 | 1.31 | 1.40 | 1.23 | 1.29 |
| $m^*_h$ ($m_0$) | 0.64 | 0.45 | 0.73 | 0.49 | 0.73 | 0.49 |
| $\Delta E_{SO}$ | 0.17 | 0.45 | 0.21 | 0.49 | 0.21 | 0.49 |
| CBM | $-3.94$ | $-3.59$ | $-3.79$ | $-3.49$ | $-3.86$ | $-3.59$ |
| VBM | $-5.48$ | $-5.25$ | $-5.10$ | $-4.88$ | $-5.09$ | $-4.88$ |

Following the above high-throughput procedure, we begin with computing the five properties of MX$_2$ ($M =$ Mo, W; $X =$ S, Se, or Te) using unit-cell-DFT calculation as a benchmark to the corresponding VCA-DFT results. All 2D MX$_2$ in this work are assumed to adopt the 2H phase. Table 3 lists these calculated properties for the six MX$_2$. We can see that the VCA-DFT method leads to identical results compared to the DFT results using a three-atom unit cell. We also include the results from the literature for comparison. The VCA-DFT values for the five properties also agree well with previous studies. For example, the in-plane lattice constants and band gaps of MoS$_2$ (WS$_2$) 3.18 Å (3.2 Å) and 1.67 eV (1.55 eV) from our VCA-DFT calculations, are nearly identical to 3.18 Å (3.32 Å) and 1.68 eV (1.53 eV) in refs. [67,68]. We also notice that the in-plane lattice constants of the six binary TMCs share three values, 3.18, 3.32, and 3.55 Å, where the binary TMCs of same chalcogen element have the same lattice constants. This is understood by the large difference in the anion radii of S$^{2-}$ (1.70 Å), Se$^{2-}$ (1.84 Å), and Te$^{2-}$ (2.07 Å), whereas the cations of Mo$^{6+}$ and W$^{6+}$ possess similar ionic radii of 0.79 Å and 0.80 Å, respectively.[65] Moreover, the discrepancy in the covalent radii between Mo (1.54 Å) and W (1.62 Å) is also smaller than that among S (1.05 Å), Se (1.20 Å), and Te (1.38 Å).[65] For the CBM and VBM, the VCA-DFT results match well with other DFT calculation results at the PBE level. Additionally, the CBM values of Mo$_{0.5}$W$_{0.5}$Te$_2$, W$_{0.5}$S$_2$, and W$_{0.5}$Se$_2$ are closer to the DFT calculation results in ref.[71] using the PBE functional including SOC.

| Table 3. In-plane lattice constant $a_0$, band gap $E_g$, hole and electron effective masses $m^*_h$, spin–orbit splitting $\Delta E_{SO}$, CBM, and VBM with reference to the vacuum level of ternary 2D CCTMCAs with the 2H structure. The first row of each property is obtained from using the VCA-DFT method, whereas the second row is from using 48-atom SQS supercells of monolayer ternary structures. |
|---|
| **Property** | Mo$_{0.5}$W$_{0.5}$S$_2$ | Mo$_{0.5}$W$_{0.5}$Se$_2$ | Mo$_{0.5}$W$_{0.5}$Te$_2$ |
| $a_0$ (Å) | 3.18 | 3.32 | 3.55 |
| $E_g$ (eV) | 1.74 | 1.50 | 1.09 |
| $m^*_h$ ($m_0$) | 0.51 | 0.56 | 0.57 |
| $\Delta E_{SO}$ | 0.29 | 0.33 | 0.35 |
| CBM | $-4.11$ | $-3.73$ | $-3.72$ |
| VBM | $-5.84$ | $-5.23$ | $-4.81$ |
consistent. Based on our results of VCA-DFT versus unit-cell-DFT and SQS-DFT calculations, the VCA-DFT method leads to comparable results such as lattice constants, band gaps, spin-orbital splitting, and band alignments with the unit-cell-DFT and SQS-DFT results. The results from VCA-DFT calculations of binary and ternary CCTMCAs are also comparable to those recorded in the Computational 2D Materials Database (C2DB).[82] Some exceptions happen during validating the band gap and effective hole mass in the Janus MoS\textsubscript{2}Te and WSe\textsubscript{2}Te structures, where the VCA-DFT calculations lead to the inconsistent conduction band as CBM, effective hole mass, and band gap compared to the DFT calculation using the unit cell models. Because its use of the averaged potential, the VCA-DFT is not always capable of predicting the local atomic environment,[45,83] where a large difference in ionicity could result in low accuracy in predicting the local atomic environment, where a large difference in ionicity could result in low accuracy in predicting the formation energy of 2D CCTMCAs shows the discrepancy from the SQS-DFT calculated result. Therefore, it is essential to use the unit-cell and SQS models to benchmark the VCA-DFT results. This not only validates the accuracy of VCA-DFT calculations on 2D CCTMCAs but also provides an indication when there is deviation in VCA-DFT results.

### 3.2. Structural and Electrical Properties of General CCTMCAs

Table 4. In-plane lattice constant \(a_{0}\), band gap \(E_{g}\), hole and electron effective masses \(m_{h}^{*}\) and \(m_{e}^{*}\), spin–orbit splitting \(\Delta E_{SO}\), CBM, and VBM with reference to the vacuum level of quaternary 2D CCTMCAs with the 2H structure. The first row of each property is obtained from using the VCA-DFT method, whereas the second row is from using 48-atom SQS supercells of monolayer quaternary structures.

|                        | \(\text{Mo}_{y}\text{W}_{1−y}\text{S}_{2x}\text{Se}_{2(1−x)}\) | \(\text{Mo}_{y}\text{W}_{1−y}\text{S}_{2x}\text{Te}_{2(1−x)}\) | \(\text{Mo}_{y}\text{W}_{1−y}\text{S}_{2x}\text{Te}_{2(1−x)}\) |
|-----------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| \(a_{0}\) (\(\text{Å}\)) | 3.26                                            | 3.40                                            | 3.45                                            |
| \(E_{g}\) (\(\text{eV}\)) | 1.60                                            | 1.57                                            | 1.26                                            |
| \(m_{h}^{*}\) (\(\text{m}_{0}\)) | 0.54                                            | 0.52                                            | 0.55                                            |
| \(m_{e}^{*}\) (\(\text{m}_{0}\)) | 0.44                                            | 0.49                                            | 0.48                                            |
| \(\Delta E_{SO}\) (\(\text{eV}\)) | −5.37                                           | −5.48                                           | −5.49                                           |
| CBM (\(\text{eV}\)) | −3.76                                           | −3.72                                           | −3.79                                           |
| VBM (\(\text{eV}\)) | −3.90                                           | −3.75                                           | −3.69                                           |

Table 5. Ranges of in-plane lattice constant \(a_{0}\), band gap \(E_{g}\), hole and electron effective masses \(m_{h}^{*}\) and \(m_{e}^{*}\), spin–orbit splitting \(\Delta E_{SO}\), CBM, and VBM with reference to the vacuum level of quaternary 2D CCTMCAs with the 2H structure.

|                        | \(\text{Mo}_{y}\text{W}_{1−y}\text{S}_{2x}\text{Se}_{2(1−x)}\) | \(\text{Mo}_{y}\text{W}_{1−y}\text{S}_{2x}\text{Te}_{2(1−x)}\) | \(\text{Mo}_{y}\text{W}_{1−y}\text{S}_{2x}\text{Te}_{2(1−x)}\) |
|-----------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| \(a_{0}\) (\(\text{Å}\)) | 3.18–3.32                                       | 3.18–3.55                                       | 3.32–3.55                                       |
| \(E_{g}\) (\(\text{eV}\)) | 1.44–1.81                                       | 1.06–1.81                                       | 1.06–1.55                                       |
| \(m_{h}^{*}\) (\(\text{m}_{0}\)) | 0.43–0.67                                       | 0.43–0.73                                       | 0.44–0.73                                       |
| \(m_{e}^{*}\) (\(\text{m}_{0}\)) | 0.32–0.57                                       | 0.32–0.62                                       | 0.32–0.61                                       |
| \(\Delta E_{SO}\) (\(\text{eV}\)) | 0.15–0.47                                       | 0.15–0.49                                       | 0.19–0.49                                       |
| CBM (\(\text{eV}\)) | −4.27 to −3.55                                 | −4.32 to −3.46                                 | −3.94 to −3.56                                 |
| VBM (\(\text{eV}\)) | −5.94 to −5.10                                 | −5.94 to −4.68                                 | −5.33 to −4.70                                 |

We then adopt Vegard’s law[81] to link the 2D CCTMCAs with binary TMCs in Equation (1) and summarize the relationship between lattice constants \(\hat{a}\) of quaternary 2D CCTMCAs and binary TMCs (e.g., MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, or WSe\textsubscript{2}). As an example, the lattice constant of a quaternary compound, \(\text{Mo}_{y}\text{W}_{1−y}\text{S}_{2x}\text{Se}_{2(1−x)}\), following Equation (1) is written as

\[
\hat{a} = xy a_{\text{MoS}_{2}} + (1-x)y a_{\text{MoSe}_{2}} + x(1-y) a_{\text{WS}_{2}} + (1-x)(1-y) a_{\text{WSe}_{2}} \tag{2}
\]

That is, the lattice constants of quaternary 2D CCTMCAs can be approximated as the combination of compositionally dependent lattice constants of the binary TMCs. Figure 3d compares \(\hat{a}\) from VCA-DFT calculations and \(\hat{a}\) from Equation (2). In the inset, we show the distribution of the deviation between two sets of data. The results from these two methods agree well with each other, with average deviations of 0.006, 0.020, and 0.010 Å for these three 2D CCTMCAs, respectively.

Figure 4a–c displays the band gaps of 2D CCTMCAs Mo-W-S-Se, Mo-W-S-Te, and Mo-W-Se-Te, which show that the band gaps range from 1.44 to 1.81, 1.06 to 1.81, and 1.06 to 1.55 eV, for the Mo-W-S-Se, Mo-W-S-Te, and Mo-W-Se-Te 2D CCTMCAs, respectively. We again apply Vegard’s law[81] to estimate the band gaps of 2D CCTMCAs by using the band gaps of binary TMCs (see Table 1). Similar to Equation (2), we can write the formula for the band gap using the binary TMCs. For example, for the quaternary Mo-W-S-Se 2D CCTMCAs, their band gaps can be written as

\[
\hat{E}_{g} = xy E_{g,\text{MoS}_{2}} + (1-x)y E_{g,\text{MoSe}_{2}} + x(1-y) E_{g,\text{WS}_{2}} + (1-x)(1-y) E_{g,\text{WSe}_{2}} \tag{3}
\]

and the other two 2D CCTMCA systems have the similar formulas. Figure 4d compares the band gaps resulted from VCA-DFT calculations and from Equation (3). As can be seen, the
Figure 3. In-plane lattice constants of a) Mo$_{y}$W$_{1-y}$S$_{2x}$Se$_{2(1-x)}$, b) Mo$_{y}$W$_{1-y}$S$_{2x}$Te$_{2(1-x)}$, and c) Mo$_{y}$W$_{1-y}$Se$_{2x}$Te$_{2(1-x)}$ 2D CCTMCAs calculated with the PBE functional. d) Comparison between the in-plane lattice constants from the VCA-DFT method and from the estimation in Equation (2).

calculated band gaps of the Mo-W-S-Se, Mo-W-S-Te, and Mo-W-Se-Te 2D CCTMCAs from the two methods are nearly identical, with the average deviations of merely 0.007, 0.039, and 0.011 eV, respectively. This consistency indicates that using VCA-DFT can lead to reliable lattice constants and band gaps of 2D CCTMCAs in an efficient way.

The diverse lattice constants and band gaps of 2D CCTMCAs are essential for various applications such as in the design of heterostructures for light harvesting.\cite{26} For example, the growth of heterostructures requires a lattice match between a 2D CCTMCA as the substrate layer and another 2D CCTMCA grown on the substrate. The matching in lattice constants of two monolayers of 2D CCTMCAs is beneficial for reducing the bilayer strain, whereas the wide band gap ranges of 2D CCMTCAAs could also be helpful in maximizing the light conversion efficiency for many applications.\cite{37} Figure 5 depicts the relationship between lattice constants and band gaps of the three 2D CCTMCAs. We know from the plot that there are majorly two regions based on heterostructure lattice matching, bounded by three edges of MoS$_2$/WS$_2$, MoSe$_2$/WSe$_2$, and MoTe$_2$/WTe$_2$ to the left, middle, and right edges. The two regions correspond to Mo$_{y}$W$_{1-y}$S$_{2x}$Se$_{2(1-x)}$/Mo$_{y}$W$_{1-y}$S$_{2x}$Te$_{2(1-x)}$, and Mo$_{y}$W$_{1-y}$S$_{2x}$Se$_{2(1-x)}$/Mo$_{y}$W$_{1-y}$S$_{2x}$Te$_{2(1-x)}$ heterostructures, respectively. The lattice constant and band gap distributions of three 2D CCTMCAs in Figure 5 therefore provide guidance in designing heterostructures (see below) from a pair of 2D CCTMCA monolayers in order to minimize the lattice mismatch as well as to maintain the desired band offset value.

Figure 6 displays the hole and electron effective masses of 2D CCTMCAs. The four corners of Figure 6a stand for the effective carrier masses of MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$. We observe that increasing the W content (i.e., decreasing y while x is fixed) generally reduces the effective masses. For the Mo-W-S-Se 2D CCTMCAs, increasing the Se content lowers the effective masses of both electrons and holes. The relationship between the effective masses and two anion contents (x and 1–x value) is complicated in the other two 2D CCTMCAs. The lower effective carrier mass is found at the two regions of x close to 0 and x close to 1, where one of the chalcogens dominates in the 2D CCTMCAs. For example, in the Mo-W-S-Te 2D CCTMCAs, the effective carrier mass first increases as the content of S increases from 0 to 0.6, and then decreases as the content of S further increases up to 1.0. In designing heterostructures, low effective masses are beneficial to enhance the carrier transport and thus
improve the collected photocurrent during the light harvesting process.\cite{35} However, too small effective carrier masses are associated with a large curvature of electronic dispersion and thus sharp band edges, affecting the local density of states. As a result, the overall collected photocurrent will decrease, thus degrading the efficiency of light conversion.\cite{85} Therefore, small effective carrier masses and local carrier concentration are competing with each other to maintain an optimal light conversion of photovoltaics and photocatalysts. The compositional variation of 2D CCTMCAs results in the tunable effective mass ranges for both electrons and holes. The design using compositionally complex systems offers a promising method in adjusting the effective carrier mass for efficient light adsorption devices.

**Figure 7** shows the calculated spin–orbit splitting of 2D CCTMCAs. Compared to monolayer MoS$_2$, which has a $\Delta E_{SO}$ of 0.15 eV,\cite{77} the 2D CCTMCAs generally can have higher values of $\Delta E_{SO}$ and up to more than three times of the value of MoS$_2$. As a proposed candidate for spintronics devices, graphene shows a $\Delta E_{SO}$ of about 0.01 eV\cite{86} which is much lower than those of the 2D CCTMCAs, suggesting that the 2D CCTMCAs has the potential in spintronic applications for spin-logic devices such as RAM.\cite{87} Strong spin–orbit splitting and its insensitivity to anion species in 2D CCTMCAs result from the presence of out-of-plane mirror symmetry and absence of inversion symmetry.\cite{88} As a consequence, the resulting electric field is generated in the plane of cations causing electrons to move in the same plane. The SOC interactions split the energy degeneracy of these electrons and the splitting magnitude depends on only the atomic numbers of
the cation species (Mo and W, and the latter is much heavier, so is the stronger SOC and $\Delta E_{SO}$). Figure 7 also reveals that $\Delta E_{SO}$ is more dependent on the content of cations than that of anions. By increasing the content of the cations, e.g., reducing $y$, the $\Delta E_{SO}$ increases rapidly from 0.15 eV to nearly 0.50 eV. By contrast, increasing $x$ does not alter $\Delta E_{SO}$ as much as change $y$. The strong spin–orbit splittings of 2D CCTMCAs suggest the possibility of utilizing them for spintronic applications. This is understood from the source of SOC from the interaction between electron and magnetic field induced by the nucleus spin. Because the magnetic field is directly related to the charge from the nucleus, a larger atomic number will have a stronger SOC. 

Figure 8 shows the CBM and VBM of 2D CCTMCAs with reference to the vacuum level. Because VCA cannot capture the effect
of an out-of-plane dipole moment, the difference in the vacuum levels on the two chalcogen sides of a monolayer CCTMCA is not taken into account. The conduction band offset (CBO) and valence band offset (VBO) are calculated, respectively, as the differences in the CBMs and VBMs of two 2D CCTMCAs. From the maximum and minimum values of CBM and VBM in the three sets of 2D CCTMCAs, we determine the ranges for CBO as from 0.049 to 0.861 eV and VBO as from 0.001 to 1.265 eV. Previous studies have shown that the stacking bilayer structure of TMCs can achieve ranges of CBO from 0.76 ± 0.12 eV and VBO from 0.83 ± 0.07 eV.[89,90] Because of the wide range of band offsets, it is possible to obtain different types of heterostructures using one 2D CCTMCA and pairing it with another 2D CCTMCA. Additionally, the band gap ranges between the CBOs and VBOs correspond to the photon frequencies within the near-infrared region of the solar spectrum, endowing the potential of employing 2D CCTMCAs for the applications of high-efficiency photovoltaics.[91] Figure 9a displays 27 selected CBM and VBM of 2D CCTMCAs that can form type II heterostructures with the selected reference ternary and quaternary 2D CCTMCAs. For example, the CBO and VBO of the Mo$_{y}$W$_{(1-y)}$S$_2$/Mo$_{y}$W$_{(1-y)}$Te$_2$ heterostructure are 0.27 and 0.39 eV, respectively.

At the same time, in the design of heterostructure 2D CCTMCAs, because of the composition-dependent wide range of CBO and VBO, versatile heterostructures are achievable by stacking different composition/type of 2D CCTMCAs together. The search of pairing 2D CCTMCAs to form stacked heterostructures should also account for the relationship between lattice constants and band gaps (see Figure 5). Specifically, in designing the heterostructure, to minimize the lattice mismatch, two systems with small difference in lattice constants are preferred. We here investigate two sets of 2D CCTMCAs of Mo-W-S-Se and Mo-W-S-Te, and Mo-W-S-Se and Mo-W-Se-Te, as shown in Figure 5, where the range of lattice constants of two 2D CCTMCAs in each set overlaps with each other. Figure 9b and c show the band alignments between some selected 2D CCTMCAs (in red color) that can match with the reference 2D CCTMCA (in blue color) in ternary and quaternary systems. From the results of both ternary and quaternary 2D CCTMCAs, we find many of them can form type II heterostructures with a small lattice mismatch from the reference material, indicating the potential of 2D CCTMCAs as building blocks for light harvesting heterostructures. Because the Mo-W-S-Se 2D CCTMCAs have a relatively small range of in-plane lattice constants (see Figure 3), Figure 9b shows that there is no ternary Mo/W-Se-Te 2D CCTMCA that satisfy both small lattice mismatch and type II band alignment with the reference of ternary Mo/W-S-Se 2D CCTMCA. The ternary Mo-W-S/Se and Mo-W-S/Te 2D CCTMCAs heterostructure shows that the largest lattice mismatch can reach to 10% between Mo$_{0.25}$W$_{0.75}$S$_2$/Mo$_{0.15}$W$_{0.85}$Te$_2$ (e.g., the lattice mismatch in the Mo$_{0.25}$W$_{0.75}$S$_2$/Mo$_{0.15}$W$_{0.85}$Te$_2$ heterostructure is 11.9%). The

![Figure 8. Conduction band minima of a) Mo$_{y}$W$_{(1-y)}$Se$_2$S$_{2(1-x)}$, b) Mo$_{y}$W$_{(1-y)}$Se$_2$Te$_{2(1-x)}$, and c) Mo$_{y}$W$_{(1-y)}$Se$_2$Te$_{2(1-x)}$ 2D CCTMCAs. The corresponding valence band maxima are shown in (d), (e), and (f), calculated with the PBE functional.](image-url)
Figure 9. Band alignment of ternary and quaternary 2D CCTMCAs. The red bars are selected to compare to the reference blue bars with (a) or (b) the same elements and c) different elements. The stoichiometry of each 2D CCTMCA is shown above the bars and the number at the bottom of each bar denotes the corresponding in-plane lattice constant.
3.3. Energetic Stability of High-Entropy CCTMCAs

One concern in designing 2D CCTMCAs is their thermodynamic stability. Here, we address this concern by focusing on the Gibbs free energy in nine ternary and three quaternary 2D CCTMCAs with equal x and y. The three quaternary 2D CCTMCAs are modeled using the SQS method. We compute the Gibbs free energy, a combination of the ground-state energy of mixing at 0 K and the temperature-dependent energy from configurational entropy, to evaluate the stability of 2D CCTMCAs at different temperatures. We first compute the energy reference in the 2D CCTMCAs of quaternary 2D CCTMCAs such as MoW1−xSxSyTe2−x by assuming the 2D CCTMCAs is made from four parent binary alloys of MoS2, MoSe2, WSe2, and WTe2. Therefore, based on Vegard’s law,[84] the reference formation energy \( E_{\text{ref}} \) is represented as a function of the ground state energies \( E_x \) of the four binary TMCs and the coefficients from the content of each element, which can be written as:

\[
E_{\text{ref}},(x,y) = xyE_{f,MoS_2} + y(1-x)E_{f,MoSe_2} + x(1-y)E_{f,WSe_2} + (1-x)(1-y)E_{f,WTe_2}
\]

Similarly, we have reference formation energies for the other two systems written as:

\[
E_{\text{ref}},(x,y) = xyE_{f,MoS_2} + y(1-x)E_{f,MoTe_2} + x(1-y)E_{f,WTe_2} + (1-x)(1-y)E_{f,WSe_2}
\]

\[
E_{\text{ref}},(x,y) = xyE_{f,MoSe_2} + y(1-x)E_{f,MoTe_2} + x(1-y)E_{f,WSe_2} + (1-x)(1-y)E_{f,WTe_2}
\]

\[
E_{\text{ref}},(x,y) = xyE_{f,MoSe_2} + y(1-x)E_{f,MoTe_2} + x(1-y)E_{f,WTe_2} + (1-x)(1-y)E_{f,WSe_2}
\]



Table 6. The formation energies, Gibbs free energies of mixing (at temperatures of 300 and 600 K) of nine ternary monolayer 2D CCTMCAs with the 2H structure.

|                  | MoWS₂   | MoWSe₂ | MoWTe₂ |
|------------------|---------|--------|--------|
| \( E_{\text{mix}} \) (eV) | −0.005  | −0.004 | −0.020 |
| \( G^0_{\text{mix}} \) (eV) | −0.023  | −0.022 | −0.020 |
| \( G^T_{\text{mix}} \) (eV) | −0.041  | −0.040 | −0.038 |

We define the enthalpy of mixing \( (E_{\text{mix}}) \) by subtracting the reference energy from the enthalpy based on the DFT calculation of the quaternary system as:

\[
E_{\text{mix}} = E_f(x,y) - E_{\text{ref}}(x,y)
\]

In the calculation of energy of mixing for ternary 2D CCTMCAs such as MoS₂ or MoWS₂, we use two binary alloys of MoS₂/MoSe₂ and MoS₂/WSe₂, as the reference.

The configurational entropy of mixing of the system can be written as[92]

\[
S_{\text{mix}}(x,y) = -k_B N [x \ln x + (1-x) \ln(1-x) + y \ln y + (1-y) \ln(1-y)]
\]

Based on Equation (8), we know that the nine ternary and three quaternary 2D CCTMCAs with \( x = y = 0.5 \) have the highest configurational entropy among all the 2D CCTMCAs. The Gibbs free energy of mixing \( (G^T_{\text{mix}}) \) for the 2D CCTMCAs system equals the energy of mixing \( (E_{\text{mix}}) \) subtracted by the multiplication of temperature \( (T) \) and configurational entropy \( (S_{\text{mix}}) \), i.e.,

\[
G^T_{\text{mix}}(x,y) = E_{\text{mix}}(x,y) - TS_{\text{mix}}(x,y)
\]

In order to demonstrate the stability of the ternary 2D CCTMCAs, Table 6 lists the energies of mixing and Gibbs free energies of nine 2D CCTMCAs. Based on the relative contents of each element, the configuration entropy for those selected ternary and Janus 2D CCTMCAs is \( S = k_B \ln 2 \). For the nine ternary 2D CCTMCAs, the negative energy of mixing \( E_{\text{mix}} \) and the Gibbs free energy of MoWS₂, MoWSe₂, and MoWTe₂ indicate that these three ternary alloys are stable at 0, 300, and 600 K. For the six Janus structures, on the other hand, the energy of mixing at 0 and 300 K are all positive, implying the unstable structures at 0 and 300 K. MoS₂ and WSe₂ become stable and have negative Gibbs free energies at 600 K. The Gibbs free energies of the Mo/W-S-Te and Mo/W-Se-Te-based 2D CCTMCAs at 600 K remain positive, suggesting that even at high temperature, these four Janus structures are still unstable and likely to suffer from decomposition.

Table 7 summarizes the energy of mixing and Gibbs free energy of three quaternary 2D CCTMCAs at 0, 300, and 600 K. We can observe that the calculated formation energy of MoW₀.₅₀S₀.₅₀Se₂ is negative, indicating this quaternary 2D CCTMCA is stable at...
0 K. Indeed, monolayer Mo$_{0.5}$W$_{0.5}$SSe has also been experimentally synthesized.\cite{91} By contrast, for the other two 2D CCTMCAs, Mo$_{0.5}$W$_{0.5}$STe and Mo$_{0.5}$W$_{0.5}$SeTe, the formation energies are positive, which is related to the large lattice difference among the four corresponding binary TMCs of each quaternary 2D CCTMCA system.\cite{37} The difference in the atomic radii of S and Te is larger than that between the atomic radii of Se and Te, which also explains the higher formation energy of Mo$_{0.5}$W$_{0.5}$STe than Mo$_{0.5}$W$_{0.5}$SeTe.

However, it is possible to stabilize the quaternary systems by considering the temperature effect in the Gibbs free energy. For each of the three quaternary 2D CCTMCAs we choose, the configurational entropy is 3$k_B$log2. Table 7 shows that the Gibbs free energies of mixing ($G_{\text{mix}}$) for all the three 2D CCTMCAs are negative at room temperature, indicating the stable structures of three quaternary systems at the temperature of 300 and 600 K. We can see that the temperature-dependent entropy term contributes to the lowering of Gibbs free energy in a great deal, and both Mo$_{0.5}$W$_{0.5}$STe and Mo$_{0.5}$W$_{0.5}$SeTe, which show the positive energy of mixing, having negative Gibbs free energies at 300 K. Compared to the Janus structure 2D CCTMCAs of Mo-W-S-Se and Mo-W-S-Te, whose Gibbs free energies remain positive even at 600 K, we can conclude that the entropy effect is beneficial for stabilizing quaternary 2D CCTMCAs. Therefore, the method of designing multinary 2D CCTMCA not only result in the tunable properties, but also lead to stable alloying phase by taking the advantage of the entropy effect.

From Table 7 and the above discussion, we know that the positive formation energy of both Mo$_{0.5}$W$_{0.5}$STe and Mo$_{0.5}$W$_{0.5}$SeTe can be stabilized at high temperature. However, these two quaternary 2D CCTMCAs still show the unstable phase at low temperature, which could result in the phase separation. Even though the process of phase separation in quaternary 2D CCTMCAs is complicated, we can predict the direction where the quaternary 2D CCTMCAs will undergo a phase separation into a group from two dissimilar binary TMCs. We assume that a quaternary 2D CCTMCA (Mo$_{0.5}$W$_{0.5}$STe, e.g.) can be made up from four different binary TMCs with different cation anion pairs (MoS$_2$, WTe$_2$, MoTe$_2$, and WS$_2$), which can further be categorized into two groups (MoS$_2$-WTe$_2$) and (MoTe$_2$-WS$_2$). We then calculate the energy difference between these groups to predict the phase separation from quaternary 2D CCTMCA to binary TMCs group. As an example of the Mo$_{0.5}$W$_{0.5}$STe phase transformation, by taking two groups of binary TMCs (MoS$_2$-WTe$_2$) and (MoTe$_2$-WS$_2$) as reference, we can predict the stable group when phase separation happens using the nonideality of the solution. The nonideality $\Delta \mu$ is calculated via the chemical potential difference between two groups of binary TMCs, such as MoS$_2$-WTe$_2$ and MoTe$_2$-WS$_2$\cite{9}

\[
\Delta \mu = \left( \mu_{\text{MoS}_2} + \mu_{\text{WTe}_2} \right) - \left( \mu_{\text{MoTe}_2} + \mu_{\text{WS}_2} \right)
\]

Similarly, we write $\Delta \mu$ for the other two 2D CCTMCAs as

\[
\Delta \mu = \left( \mu_{\text{MoS}_2} + \mu_{\text{WSe}_2} \right) - \left( \mu_{\text{MoSe}_2} + \mu_{\text{WS}_2} \right)
\]

\[
\Delta \mu = \left( \mu_{\text{MoSe}_2} + \mu_{\text{WTe}_2} \right) - \left( \mu_{\text{MoTe}_2} + \mu_{\text{WS}_2} \right)
\]

The calculated nonideality results for the three 2D CCTMCAs are shown in Table 7, where the $\Delta \mu$ is in agreement with the previous work.\cite{9} The positive $\Delta \mu$ of Mo$_{0.5}$W$_{0.5}$STe indicates that the latter binary group of (MoTe$_2$-WS$_2$) is more stable, into which the quaternary 2D CCTMCA would decompose. We can see from the results that for the three quaternary 2D CCTMCAs systems of Mo-W-S-Se, Mo-W-S-Te, and Mo-W-Se-Te, the most stable binary TMC groups are MoSe$_2$-WS$_2$, MoTe$_2$-WS$_2$, and MoTe$_2$-WSe$_2$, respectively. Previous experimental result has shown one example of the phase separation in Mo-W-S-Se quaternary 2D CCTMCAs in ref.\cite{9} as the spinodal decomposition of quaternary 2D CCTMCAs Mo-W-S-Se into two ternary 2D CCTMCAs within the miscibility gap.

According to the calculated Gibbs free energies, we find that the three quaternary 2D CCTMCAs from SQS supercell are stable at room temperature. We henceforth focus on these three quaternary 2D CCTMCAs in discussing their electronic properties such as band structure and electrical conductivity, for the purpose of applying them as the potential materials in energy conversion applications. Figure 10 displays the band structures of three quaternary 2D CCTMCAs calculated with the PBE functional without and with considering the SOC. We can see that the calculations with or without considering SOC show the direct band gap of these three 2D CCTMCAs at K point. The SO splitting energies at the K point for Mo$_{0.5}$W$_{0.5}$SSe, Mo$_{0.5}$W$_{0.5}$STe, and Mo$_{0.5}$W$_{0.5}$SeTe are 0.31, 0.35, and 0.36 eV, respectively.

### 3.4. Electrical Conductivity of High-Entropy CCTMCAs

Figure 11 displays the electrical conductivity of Mo$_{0.5}$W$_{0.5}$SSe, Mo$_{0.5}$W$_{0.5}$STe, and Mo$_{0.5}$W$_{0.5}$SeTe at 300 K. We also compute the electrical conductivity of monolayer MoS$_2$ and benchmark the results with the literature.\cite{94} The relaxation time used in these calculations is taken as an approximated constant value of 10.0 fs, which has been used in the calculations of electrical conductivity for other monolayer semiconductors such as SnSe, Sc$_2$C, and TiSe$_2$.\cite{95-97} We first observe that the band gaps of these three 2D CCTMCAs, corresponding to the regions where the conductivity equals to zero, are in agreement with the VCA-DFT results (see Figure 5). These band gaps lie from the visible light range to the near-infrared region, which enables the photovoltaic effect in a wider region to enhance the photovoltaic conversion efficiency.\cite{98} In Figure 11, the negative (left) side of the chemical potential illustrates the holes conductivity (p-type), and the positive (right) side is for the conductivity from electrons (n-type). By
Figure 10. Band structures of three quaternary 2D CCTMCAs, Mo$_{0.5}$W$_{0.5}$SSe, Mo$_{0.5}$W$_{0.5}$STe, and Mo$_{0.5}$W$_{0.5}$SeTe. SOC is not considered in the panels (a), (b), and (c), whereas it is accounted for in panels (d), (e), and (f).

Figure 11. Electrical conductivity of Mo$_{0.5}$W$_{0.5}$SSe, Mo$_{0.5}$W$_{0.5}$STe, and Mo$_{0.5}$W$_{0.5}$SeTe at 300 K as a function of the chemical potential. Electrical conductivity of MoS$_2$ is also plotted as benchmark.
changing the chemical potential that can be realized by different methods such as doping or applied gate voltage.\textsuperscript{[99]} 2D CCTMCAs can reach a high conductivity of \(1.7 \times 10^6\) S m, which guarantees the high carrier transport within the single layer. Moreover, the three quaternary 2D CCTMCAs exhibit higher electron conductivity comparing to pristine MoS\(_2\) monolayer. The high conductivity of three examples shows their potential in the energy conversion applications such as photovoltaics.

4. Conclusions
In summary, we propose a workflow using the DFT calculation from VCA models in search of suitable multinary 2D CCTMCAs in different applications in energy conversion and spintronics. We have computationally characterized five critical structural and electrical properties of 2D CCTMCAs and also benchmarked DFT results using unit cell and SQS models to validate the accuracy of calculation from VCA method. We find that VCA-DFT calculations lead to comparable results of lattice constants, band gap, electron and hole effective masses, spin–orbit splitting, and band alignment with the unit-cell-DFT and SQS-DFT results, with some exceptions in the CBM, effective hole masses, and band gaps of Mo\(_6\)Te and W\(_6\)Te, which are caused by the inaccurate prediction of the location of CBM in VCA-DFT calculations. Our results show that the multinary 2D CCTMCAs exhibit tunable properties such as band gaps, lattice constants, effective masses, and band alignments. These tunable properties are helpful in designing the lattice matching type II heterostructures for the applications of light absorption and conversion devices. The strong SOC of 2D CCTMCAs also suggest the possibility of utilizing the multinary 2D CCTMCAs in spintronics. In addition to the high-throughput computational characterization of 2D CCTMCAs workflow, we propose three quaternary 2D CCTMCAs, Mo\(_{0.5}\)W\(_{0.5}\)Se\(_2\), Mo\(_{0.5}\)W\(_{0.5}\)Te\(_2\), and Mo\(_{0.5}\)W\(_{0.5}\)Se\(_2\)Te at room temperature, serving as excellent examples to illustrate the entropy-stabilized alloys from multiple component design of 2D CCTMCAs. In addition, they also show high electrical conductivity as promising materials for energy conversion applications. Although currently most research on quaternary TMC alloys centers on Mo/W-based alloys, 2D nanosheets of TaSe\(_2\), NbSe\(_2\), and NiTe, have been obtained in experiments, indicating that alloying of these TMCs may be used to develop 2D CCTMCAs.\textsuperscript{[100]} The high-throughput workflow we proposed enables the extension of the research on the 2D CCTMCAs consisting of other transition metal, metal, and chalcogen elements.

Acknowledgements
This work was supported by the National Science Foundation (NSF) (Grant No. DMR-2020277). The authors also thank the start-up funds from Arizona State University (ASU). N.B. thanks the Science and Engineering Experience (SCENE) program at ASU. This research used computational resources of the Texas Advanced Computing Center under Contracts No. TG-DMR170070 and the Agave cluster at ASU.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
2D high-entropy alloys, 2D transition-metal chalcogenides, density functional theory, energy harvesting

Received: August 17, 2020
Revised: September 10, 2020
Published online: October 7, 2020

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