

RESEARCH PAPER

## Design of Biosensors Based Transition-Metal Dichalcogenide for DNA-base Detection: A First-Principles Density Functional Theory Study

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### ABSTRACT

A biosensor can be defined as a device that sense a biologically specific material and response. The main function of sensing platform, as a one of the hottest topic attracting scientific minds, playing an important role in biosensors. In this paper, we theoretically reveal the electronic structures of  $m\text{MoS}_2$  doped by 3d transition metals. Furthermore, adsorption of nucleic acids (Adenine (A), Cytosine (C), Guanine (G), Thymine (T) and Uracil (U)) on monolayers of modified transition-metal dichalcogenides (mTMDs) such as molybdenum disulfide ( $\text{MoS}_2$ ) and tungsten disulfide ( $\text{WS}_2$ ) as a sensing platform is compared using first-principles density functional theory (DFT). We found that all nucleobases are physisorbed on TMDs due to van der Waals (vdW) interactions demonstrating that  $\text{MoS}_2$  is better than other TMDs and may also be used to detect nucleic acid sequence for medical science. Interestingly, the adsorption energies, band structures, electronic properties and magnetic behavior of the transition metal (TM) atom adsorbed  $m\text{MoS}_2$  have been systematically investigated. The theoretical results show that structures of  $m\text{MoS}_2$  efficiently modified by absorbing different TM atoms which related to their number of d electrons. The order of binding energies of the nucleobases adsorbed on  $\text{MoS}_2$  and  $\text{WS}_2$  is  $G > A > T > C > U$  using DFT-D3 method.

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### INTRODUCTION

The role of nucleic acid is vital in life science and its sequence detection is very important in the field of diagnosis of disease, forensic sciences, and genomics systems. Electrochemical biosensors have many advantages, including simplicity, high selectivity, and sensitivity and low-cost in nucleic acid sequence detection [1]. Nucleic acid molecules sequences are identified based on calorimetric and fluorescent assays [2], using nanomaterials such as carbon nanotube [3], quantum dots [4] and graphene [5]. The unusual properties of layered graphene and its successful applications in electronics, sensors, and energy devices have inspired and renewed interest in other monolayer materials [6].

To this end, alternative 2D materials [7] were

developed in electrochemical sensors based on exceptional physical and electrochemical properties. Because of the poor ON/OFF current ratio in graphene [8], a semiconducting analog of graphene, particularly,  $\text{MoS}_2$  has attracted huge attention in the last few years. TMDs constitute a class of 2D materials with intrinsic band gaps of 1-2 eV used for various applications and increasingly becoming a popular material for biosensing applications. A significant number of publications have emerged about incorporation of TMDs into biosensors in recent years [9-12].

As already discussed in detail, high surface-to-volume ratio and layered structure of this materials can accommodate a large capacity of chemical biospecies. TMD materials have been widely used as effective assay methods for environmental

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monitoring, food safety, and clinical diagnosis in the past few decades due to their simplicity, low-cost, high sensitivity, and selectivity [13, 14].

MoS<sub>2</sub> is one of the well-known metal dichalcogenides used in nanoelectronics, catalysis process, optoelectronics, and energy harvesting [15-18]. MoS<sub>2</sub> is a semiconducting material with a hexagonal arrangement of S atoms on the surface and Mo atoms in the middle surfaces of S atoms. Mo and S atoms are covalently bonded with a typical distance of about 2.40 Å and the S-Mo-S angle of 80.6°.26 [19, 20]. Also, WS<sub>2</sub> nanosheets are applied in solid lubricants, catalysis, tips in the scanning microscopy, and nucleic acid detection as nano-quenchers. Electronic and mechanical properties of WS<sub>2</sub> have been studied theoretically by several groups [21-23].

TMDs (MoS<sub>2</sub> and WS<sub>2</sub>) are used in electronics, catalysis and vapor molecule detection as a sensing platform [24-26]. With distinctive performances, mMoS<sub>2</sub> has been a potential candidate as the complement or substitute to graphene [27]. Many methods were developed to explore the applications of mMoS<sub>2</sub> for nanoscale electronics and spintronic devices and modulate the magnetic properties of mMoS<sub>2</sub>, such as defect, chemical doping, elastic strain, alloy, and chemical adsorption [28-32].

Our results present and discuss the relationships between the sensing performances and the special nanostructures within the MoS<sub>2</sub> nanocomposites. It is well-known that adsorption of TM atoms is a promising and effective method for modulating the electronic and magnetic properties of materials which demonstrated a great potential in many materials [33]. Based on our results, variation in adsorption energy obtained from different TM atoms adsorbed on mMoS<sub>2</sub> can effectively modulate the band structures and the magnetic properties of the mMoS<sub>2</sub> due to their number of d electron.

Furthermore, understanding biomolecular interactions between the organic molecules and surfaces is important for designing better sensors with a higher selectivity [34, 35]. Hence, many theoretical studies have been carried out to find out nucleic acid interactions with 2D surfaces of MoS<sub>2</sub> for sensing the biomolecules. In this work, we investigated the adsorption energy, stable geometry, magnetic and electronic properties of TM atoms adsorbed on mMoS<sub>2</sub>.

## COMPUTATION METHODS

DFT calculations were performed via Xplorer

- OpenMX code simulation package [36]. We used non-local van der Waals density functional (DFT-D3) at the GGA level of theory with the revPBE exchange-correlation functional for the calculations to describe the interactions between bases and substrates [37-39]. The core electrons represented by norm-conserving Morrison, Bylander and Kleinman pseudo-potentials [40]. The kinetic energy cutoff was set on 250 Ryd for integration of charge density in real space.

In order to cut the interaction between the supercell images, a 30 Å spacing was used in the direction perpendicular to the substrate. For all structures, geometry optimization was performed with convergence thresholds of 10<sup>-4</sup> eV for energy and 0.01 eV/Å for Hellmann-Feynman force without any symmetry constraints [41]. Calculations were performed with 12×12×1 lateral supercells of MoS<sub>2</sub> (72 atoms) and WS<sub>2</sub> (108 atoms) [42]. Brillouin zone integrations were performed with a 3×3×1 Monkhorst-Pack k-point mesh to calculate total energies and densities of states. Binding energies of the bases with substrates (MoS<sub>2</sub> or WS<sub>2</sub>) were calculated using the equation:

$$E_{BE} = E_{Sub + Bas} - (E_{Sub} + E_{Bas})$$

Where,  $E_{Sub + Bas}$ ,  $E_{Sub}$ , and  $E_{Bas}$  are total energies of the complex, substrate, and bases [43]. The metal atoms were first placed in three high symmetry positions on the surface of mMoS<sub>2</sub> (T<sub>Mo</sub>, T<sub>S</sub>, and H sites) and then relaxed.

## RESULTS AND DISCUSSION

### Adsorption of nucleobases on to mMoS<sub>2</sub> and mWS<sub>2</sub> surfaces

In this section, we have placed bases on top of MoS<sub>2</sub> and WS<sub>2</sub> as the starting geometries for the calculations; several initial configurations were constructed. All of the starting configurations were relaxed and approached the surface of the MoS<sub>2</sub>/WS<sub>2</sub> sheet with parallel and perpendicular orientation with respect to the molecular axis of MoS<sub>2</sub>/WS<sub>2</sub>. Furthermore, full structural optimization was carried out to evaluate the relative stability of the relaxed configurations. The least vertical distance and energy configuration, for each system, were chosen among the various possibilities. Force minimized structures of MoS<sub>2</sub>-base and WS<sub>2</sub>-base complexes are shown in Fig. 1 and Fig. 2, respectively.

The calculated vertical separations between

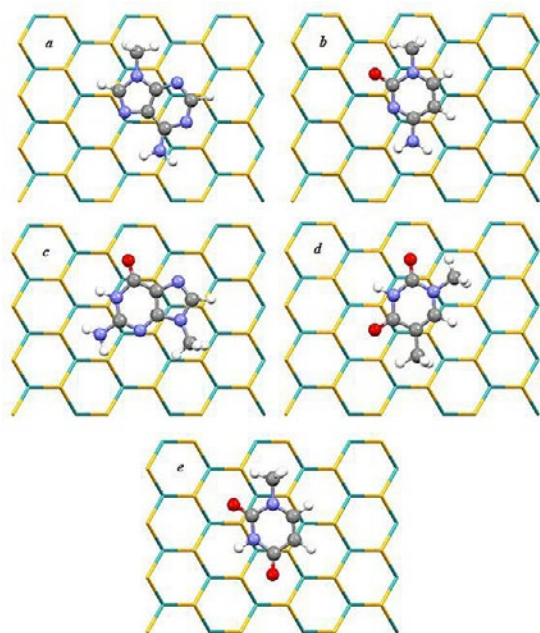


Fig. 1. Optimized structures of nucleobases adsorbed onto monolayer MoS<sub>2</sub>. [(a) Adenine, (b) Cytosine, (c) Guanine, (d) Thymine and (e) Uracil]. (Purple: Mo, Yellow: S, Red: O, Blue: N, Gray: C and White: H).

mTMDs and nucleobases are in the ranges 2.90 - 3.36 Å and 2.96-3.30 Å for MoS<sub>2</sub> and WS<sub>2</sub>, respectively. It is clear that the difference in the vertical distances between the TMDs is very small and bases do not change the surface geometrical parameters such as M-S bond distances and S-M-S angles significantly indicating the physical adsorption (through vdW interactions) of nucleobases on the mMoS<sub>2</sub> surface. In TMDs, heteroatoms like N and O can incline the molecules slightly on MoS<sub>2</sub> and WS<sub>2</sub>. In addition to the heteroatoms, the hydrogen atoms in the tail (-NH<sub>2</sub> and -CH<sub>3</sub> group) of nucleobase interacts with MoS<sub>2</sub> and WS<sub>2</sub> surfaces. For instance, in MoS<sub>2</sub>-A complex, the H atom of CH<sub>3</sub> group in adenine is in close contact with S atom of the surface with a typical distance of about 2.70 Å. In the case of MoS<sub>2</sub>-C, H of a methyl group and O of cytosine are relatively closer to substrates with distances of about 2.69 Å and 3.30 Å, respectively. For MoS<sub>2</sub>-G, H of NH<sub>2</sub> and O of guanine interact stronger than the other atoms and the vertical distance for this close contact is about 3.19 Å. In the case of MoS<sub>2</sub>-T, H atoms of two methyl groups of thymine have a close contact about 3.09 Å with surface, and for MoS<sub>2</sub>-U, similar to other complexes, H of CH<sub>3</sub> of uracil is in closer contact, about 3.12 Å, than other atoms [44-48].

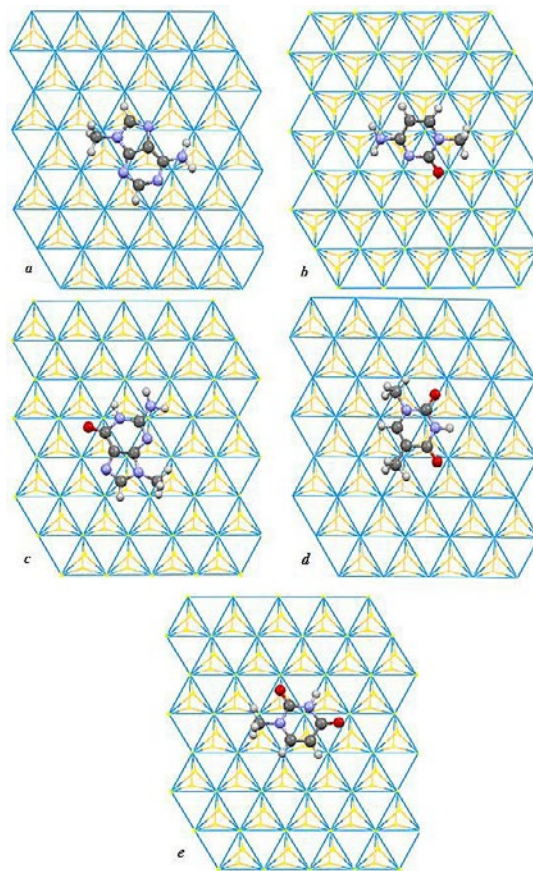


Fig. 2. Optimized structures of nucleobases adsorbed onto monolayer WS<sub>2</sub>. [(a) Adenine, (b) Cytosine, (c) Guanine, (d) Thymine and (e) Uracil]. (Purple: Mo, Yellow: S, Red: O, Blue: N, Gray: C and White: H).

Furthermore, from the energy values, it can be seen that for all the nucleobase molecules, the binding energies for the most stable systems lie within the range of -0.734 eV to -0.816 eV for MoS<sub>2</sub> and -0.760 eV to -0.836 eV for WS<sub>2</sub>. The order of binding affinity of nucleobases with MoS<sub>2</sub> and WS<sub>2</sub> is G > A > T > C > U, which is similar to earlier studies. However, among all bases, G has the highest binding affinity and it may be recognized by substrates similar to silicon carbide or polyaniline. Our calculated geometries match with earlier studies. The structure and energetics of MoS<sub>2</sub>/WS<sub>2</sub> and nucleobases are discussed in Table 1.

Based on the results, the highest difference between the binding energy values for individual nucleobase molecules interacting with MoS<sub>2</sub> and WS<sub>2</sub> was calculated to be 0.082 eV and 0.076 eV, respectively. Consequently, the MoS<sub>2</sub> sheet does seem to be a proper choice to distinguish different the nucleobase molecules based on the obtained

energy profile. In this regards, in the design of biosensors for detection of nucleic acid, we focus on  $m\text{MoS}_2$  as a sensing platform.

*First-principles study of transition and alkali metal atoms adsorption on  $m\text{MoS}_2$*

Researchers demonstrated that DNA- $\text{MoS}_2$  strong binding can be achieved by introducing metal atoms, such as transition and alkali metal atoms on to the  $m\text{MoS}_2$  surface [49]. So, the binding characteristics and adsorption behavior of transition and alkali metal atoms on  $m\text{MoS}_2$  were studied using the DFT calculations. We considered the possible adsorption sites for metal atoms approaching the  $m\text{MoS}_2$  surface. The selected sites are the top site of the S atom ( $T_s$ ), the top site above the Mo atom ( $T_{\text{Mo}}$ ) and the hollow site above the center of the hexagon or pentagon ring (H). The configurations of the metal atoms adsorption systems are shown in Fig. 3.

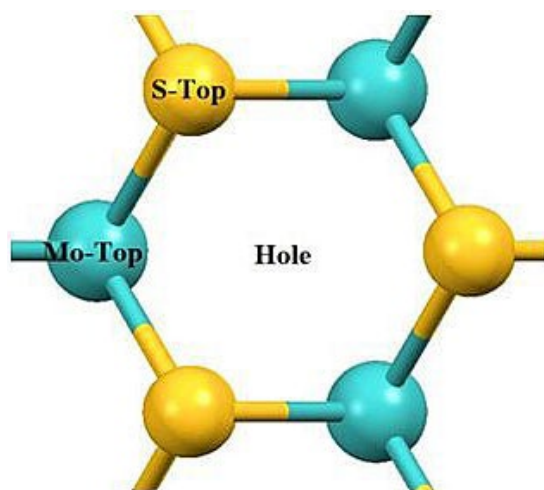


Fig. 3. Three sites of metal atoms adsorbed on  $\text{MoS}_2$ .  $T_s$ ,  $T_{\text{Mo}}$ , and H stand for the sites above the S atom, Mo atom and the center of the hexagonal or pentagonal ring of  $\text{MoS}_2$ , respectively. The yellow, green and white balls represent S, Mo and metal atoms.

To find the most favorable adsorption configurations, the optimized  $m\text{MoS}_2$  surface was employed for metal atoms adsorption. After full structural relaxation of the selected configurations, the binding energy for these three sites is calculated. Table 2 shows the extranuclear electrons arrangement (EEA), adsorption energies ( $E_{\text{ads}}$ ), vertical distance and charge transfer ( $C_T$ ) analysis of the metal atoms (based on Hirschfeld) adsorbed on to  $m\text{MoS}_2$  at the most stable adsorption sites.

It can be seen that the  $T_{\text{Mo}}$  site is the most favorable surface adsorption site for the metal. Also, in all alkali cases, negligible charge transfer occurred between the involving systems while there is obvious electron transfer from transition metal atoms to the  $m\text{MoS}_2$ . Based on Hirschfeld charge analysis, we found that the number of electrons transferred reduces gradually from Fe to Ni.

Furthermore, the results show that the interactions between the transition metal (TM) atoms and the nearest S atoms can be easily qualified as the covalent interactions, and such TM atoms have been chemisorbed on the surface. Consequently, the TM- $m\text{MoS}_2$  sheet seems to be a proper choice to distinguish the base molecules based on the obtained adsorption energies. The variation in adsorption energies with different TM atoms may be related to their d electrons. The Ni with 8 d electrons has the largest adsorption energy, while the adsorption energies of Cu with full filled d orbital are small. The overall variation trend of the adsorption energies for different TM

Table 1. Total energies and vertical distances of nucleobases adsorbed on  $\text{MoS}_2$  and  $\text{WS}_2$ .

System	$E_{\text{ads}}$ (eV)		Distance ( $^{\circ}\text{A}$ )	
Aden+ $\text{MoS}_2$	-0.782	-0.799	2.90	2.96
Cyto+ $\text{MoS}_2$	-0.767	-0.782	3.24	3.25
Guan+ $\text{MoS}_2$	-0.816	-0.836	3.12	3.18
Thym+ $\text{MoS}_2$	-0.752	-0.764	3.19	3.14
Urac+ $\text{MoS}_2$	-0.734	-0.760	3.36	3.30

Table 2. Calculated extra nuclear electrons arrangement (EEA), adsorption energies ( $E_{\text{ads}}$ ), vertical distance ( $\text{A}^{\circ}$ ), and amounts of charge transfer ( $C_T$ ) of the metal atoms adsorbed on  $m\text{MoS}_2$  at the most stable adsorption sites, from the metal atoms to  $m\text{MoS}_2$ .

	Metal	EEA	Site	Distance ( $^{\circ}\text{A}$ )	$C_T$ (e)	$E_{\text{ads}}$ (eV)
Transition Metals	Fe	$3d^64s^2$	$T_{\text{Mo}}$	2.168	0.613	-2.303
	Co	$3d^74s^2$	$T_{\text{Mo}}$	2.142	0.467	-2.764
	Ni	$3d^84s^2$	$T_{\text{Mo}}$	2.148	0.385	-3.514
	Cu	$3d^{10}4s^1$	$T_{\text{Mo}}$	2.328	0.389	-1.307
Alkali Metals	Li	$1s^22s^1$	$T_{\text{Mo}}$	1.451	0.510	-0.980
	Na	$3s^1$	$T_{\text{Mo}}$	2.033	0.364	-0.735
	Mg	$3s^2$	$T_{\text{Mo}}$	2.066	0.282	-0.245
	Ca	$4s^2$	$T_{\text{Mo}}$	2.013	0.286	-0.668



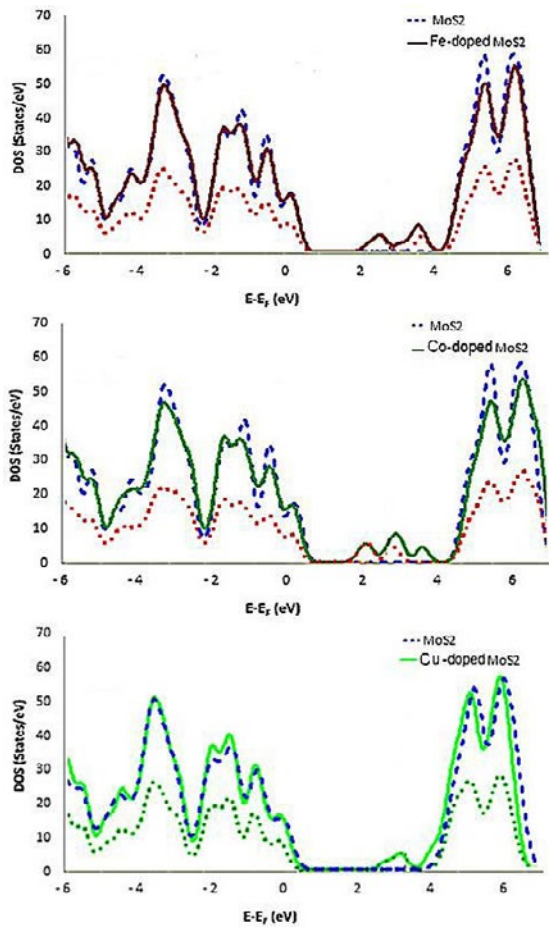


Fig. 4. Total densities of states (DOS) of pristine MoS<sub>2</sub> and TM-MoS<sub>2</sub>. [(a) Fe, (b) Co, (c) Ni, and (d) Cu].

atoms with the number of d electron is consistent with the analysis of the bond length of TM-S (Mo), and hence, we focus on TM-mMoS<sub>2</sub> as a sensing platform in biosensors.

#### Magnetic and electronic properties of TM-mMoS<sub>2</sub>

In addition, the magnetic properties of mMoS<sub>2</sub> can be modulated by the embedded transition metals. The ground state of mMoS<sub>2</sub> is nonmagnetic, while the transition metal-embedded mMoS<sub>2</sub> show total spin magnetic moments of 2.21 μB, 1.01 μB, 0.00 μB, and 1.00 μB for Fe, Co, Ni, and Cu, respectively. To gain a deeper understanding of the interaction between the embedded metal atoms and the defect center of mMoS<sub>2</sub>, among all transition metal elements, we embedded Fe to Cu (except Ni ( $\mu_B=0$ )) in the mMoS<sub>2</sub> and calculated the density of state (DOS) curves of Fe-MoS<sub>2</sub>, Co-MoS<sub>2</sub>, and Cu - MoS<sub>2</sub> systems, as displayed in Fig. 4.

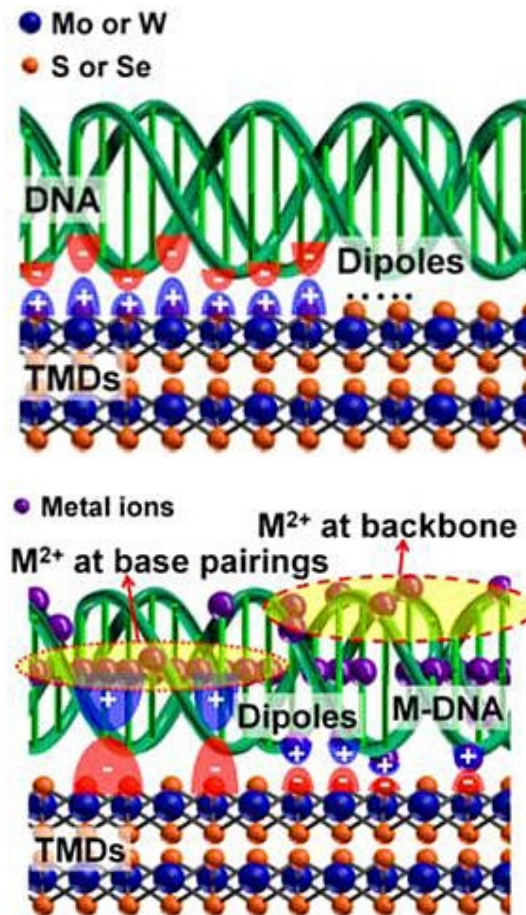


Fig. 5. Schematic representation of basic steps in designing a nanobiosensor for nucleic acid detection.

Fig. 4a-c shows the DOS of Fe-MoS<sub>2</sub>, Co-MoS<sub>2</sub> and Cu-MoS<sub>2</sub> systems. A distinct feature is that asymmetric DOS peaks appear near the Fermi level, which is significantly different from the perfect mMoS<sub>2</sub>.

In a good agreement with experiments and earlier theories, pristine mMoS<sub>2</sub> shows a band gap of 1.68 eV. Changes in the band gap occur when transition metals were adsorbed on MoS<sub>2</sub> surfaces. According to the results, one may conclude from the analysis of geometries and energetics of the above-mentioned systems that Ni-MoS<sub>2</sub> can act as a potential candidate to sense the nucleobases in DNA sequencing and other biomolecules.

With further increase in the number of the adsorbed Ni atoms on one side of mMoS<sub>2</sub>, the binding energies gradually decrease, as shown in Fig. 6.

Although the binding energies slightly depend

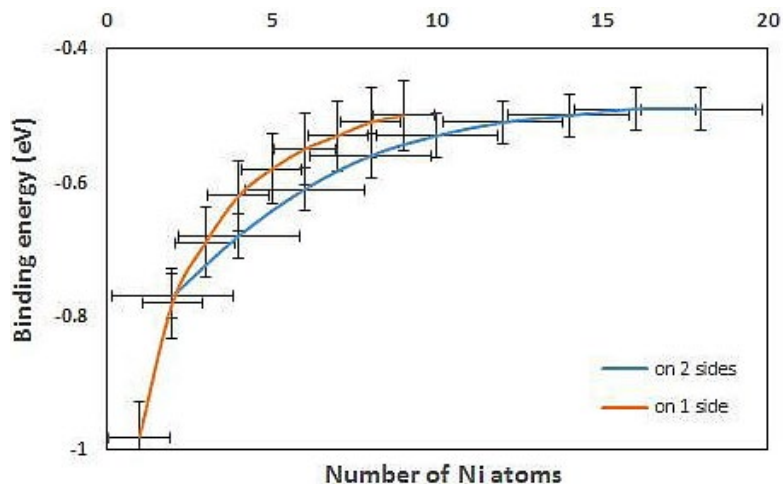


Fig. 6. The binding energy of a single Ni atom as a function of the number of Ni atoms.

on the detailed configurations of the adsorbed Ni atoms for some Ni adsorption concentrations, the decreasing trend of the binding energy still remains for the single Ni. Considering the different possibilities in adsorption configuration for different Ni concentrations, Ni atoms still favor adsorbing at the top sites of Mo atoms even if the Ni concentration is high. Furthermore, with the increase in the number of the adsorbed Ni atoms on the two sides of  $m\text{MoS}_2$ , the binding energies decrease gradually. In addition, with increasing the Ni adsorption concentration, the difference between different adsorption configurations could be decreased due to the repulsive interactions between Ni ions.

## CONCLUSION

Despite their extensive applications in energy storage and optoelectronic devices, the use of  $m\text{MoS}_2$  nanosheets for biosensing is still largely unexplored. In this study, adsorption characteristics of nucleic acid on TMDs ( $\text{MoS}_2$  and  $\text{WS}_2$ ) as a sensing platform were investigated using first-principles DFT-D3. We illustrated the key properties of 2D  $\text{MoS}_2$  offering unique opportunities for biosensing. Results revealed that nucleobases are physisorbed on  $\text{MoS}_2$  and  $\text{WS}_2$  with the order of interactions being  $G > A > T > C > U$ . In general, some new features occur in adsorption of transition metal (TM) atoms (from Fe to Cu) onto TMDs. The results show that the most stable adsorption site is  $T_{\text{Mo}}$ . However, almost all the TM atoms are chemically adsorbed on  $m\text{MoS}_2$ . As these originate from the transition metal atoms at

different energies, a selective detection is possible in the Ni- $\text{MoS}_2$  cases. It is expected that many of new biosensing concepts are discovered and developed in the next decade to offer more opportunities for research activities in relevant areas and for industries via the rapid uptake of this material into biosensing systems [50-53].

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## CONFLICT OF INTEREST

The authors declared to no conflict of interest.

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