Influence of single and double-atom metal doping on the electrocatalytic hydrogen evolution activity of 2D-MoS₂ surface

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Abstract— The Hydrogen evolution reaction (HER) is an important process during electrocatalytic water splitting for hydrogen energy generation. Two dimensional (2D) MoS₂ has been considered as a promising alternative to Pt-based catalysts in the hydrogen evolution reaction. However, the highest contribution for the catalytic activity of 2D-MoS₂ is from its edge sites, this in turn leaves many in-plane domains useless. In this study, the effect of single atom metal (Pt, Ni and Pt-Ni) doping on HER catalytic activity of in-plane atoms was investigated using density functional theory calculations. The Gibbs free energy of adsorbed hydrogen on pristine MoS₂ decreased from 1.86eV to -0.08eV in PtNi co-doped MoS₂. This demonstrates enhanced catalytic activity of MoS₂ due to atomic doping. The enhanced catalytic activity may also be attributed to the observed changes and increase in the density of electronic states near the Fermi energy level.

Keywords-Atomic doping, Density functional theory, Hydrogen evolution reaction, Molydenum disulphide, Nickel, Platinum styling.

I. INTRODUCTION

Global energy demands show an increasing trend, with annual consumption forecasted to hit about 778 Etta Joule by 2035[1]. As this energy demand rises, its impact on the environment and global economics has been a major topic of discussion[2]. In general, energy is the driver of global economics. As a result, it has been a challenge to fully switch over to renewable energy due to sustainability issues, although it has the potential of meeting the energy demand in the future. Fossil fuels account for more than 80 percent of current primary energy consumption. This does not only put much strain on the oil and gas reserves but also comes with attendant effects such as climate change which has resulted to global warming[3]. The United Nations Framework Convention on Climate Change (UNFCCC) was established in 1992 as a part of a collective agreement by countries to collectively find solutions to reduce increasing global average temperature. Several scholars are of the opinion that this can be addressed using renewable energy.

In today's world, renewable energies are becoming an increasingly important issue. In addition to the rising cost of fossil fuels and the threat of climate change, there have also been positive developments in this area that include efficiency improvements as well as falling prices. All this has increased demand for alternative energy, and has facilitated the transition to cleaner, more efficient electrical power methods[4] like hydrogen which is a possible replacement for fossil fuels because it is an environmentally friendly source of energy.

Hydrogen is a crucial and necessary element of a decarbonised, sustainable energy system capable of delivering stable, cost-effective and non-polluting energy[5]. Hydrogen-based fuel cells are among the various technologies correlated with renewable energy and constitute one of the most important technological advances to curb the situation[6]. Noble metals such as platinum (Pt) and iridium are commonly selected for their high performance, yet their availability on Earth's crust and high price render them impractical for potential use and mostly unfavoured[7]. Molybdenum disulphide (MoS_2), has recently attracted attention in hydrogen generation due to its novel electronic, optical, optoelectronic, and catalytic properties. The bulk MoS_2 crystal is an indirect semiconductor band gap with an energy gap of 1.29 eV[8]. Molybdenum disulphide (MoS_2) promises catalytic activity in the hydrogen evolution reaction (HER) due to the active sites located at the edges of the crystal two-dimensional layered structure however the efficiency is limited by the reactivity of active sites and density, weak electrical transport and inefficient electrical

interaction with the catalyst[9]. This work seeks to study the catalytic activity of pristine and doped 2D-MoS$_2$ towards HER using density functional theory.

II. COMPUTATIONAL METHOD

Density functional theory was employed to investigate the effect of metal doping on the catalytic behaviour of MoS$_2$ for the hydrogen evolution reaction (HER). All spin polarized DFT calculations were performed using Dmol3 in materials studio developed by Accelrys Software Inc. The generalized gradient approximation by Perdew-Burke-Ernzerhof (GGA-PPE) [11] was used to address the exchange-correlation energy. Double numerical polarized (DNP) was chosen as the basis set for the system. Self-consistent field (SCF) tolerance was set at 2×10^{-6} eV threshold to ensure accuracy. The interactions between ionic and valance electron described using the DFT semi-core pseudopotential (DSPP). The MoS$_2$ monolayer was represented by a 5 X 5 supercell as shown in Figure 1. The k-points of the reciprocal space were sampled with 3x3x1 Monkhorst-Pack scheme. The monolayer was doped by Pt, Ni and PtNi to enhance HER catalytic activity. For metal doped MoS$_2$ monolayer, a single Mo atom was replaced with a either a Pt or Ni metal atom. Figure 1 shows the structure of pristine and doped-MoS$_2$.
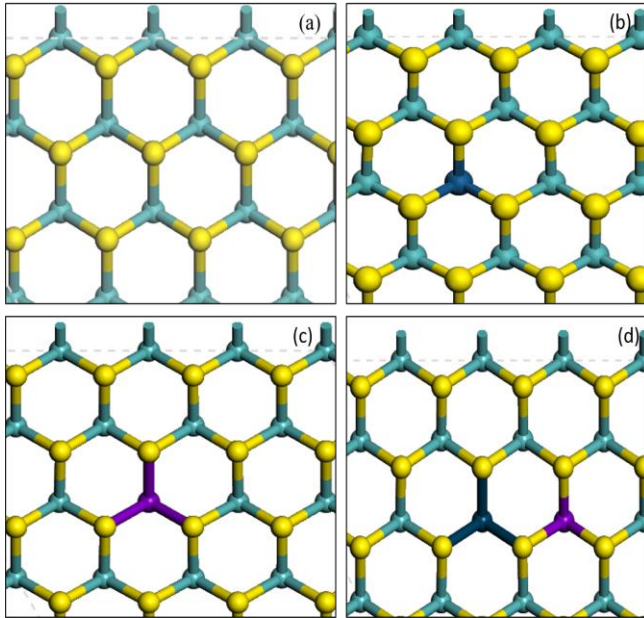

Figure 1: structure of MoS2 (a) pristine-MoS$_2$, (b) Pt-MoS$_2$, (c) Ni-MoS2 and (d) PtNi-MoS2. The glaucous, yellow, blue and purple represent Mo, S, Ni and Pt atoms, respectively.

The metal atom (Pt or Ni) binding energy in the was calculated from:

$$E_b = E_{M-MoS_2} - E_M - nE_{MoS_2} \qquad (1)$$

Where, E_{M+MoS_2} represents the total energy of the Metal atom and MoS$_2$ monolayer, E_M and E_{MoS_2} are the total energies of the Metal atom and MoS$_2$ monolayer, respectively. n represent the number of substituted Mo atoms

The methodology used in this study was adopted from Shi et.al [12]. The Gibbs free energy G, which can be used to characterize the catalytic behaviour of materials towards HER was calculated from the following reaction.

$$\Delta G_H = \Delta E_H - \Delta E_{ZPE} - T\Delta S_H \qquad (2)$$

Where ΔE_{ZPE} represents the zero-point energy difference and ΔS_H is the entropy difference (@ 300K and 1 bar). ΔE_H represents the hydrogen chemisorption energy, which can be calculated from:

$$\Delta E_H = \Delta E_{MoS_2+H_2} - \Delta E_{MoS_2} - \Delta E_{H_2} \qquad (3)$$

where $\Delta E_{MoS_2+H_2}$ and ΔE_{MoS_2} are the total energy of MoS$_2$ with and without hydrogen adsorption, respectively. ΔE_{H_2} is the total energy of a molecule hydrogen under the gas phase. The value of $\Delta E_{ZPE} - T\Delta S_H$ was reported to be about 0.24 eV. Therefore, the Gibbs free energy of hydrogen adsorption can be calculated from [12, 13]:

$$\Delta G_H = \Delta E_H + 0.24 \qquad (4)$$

III. RESULTS AND DISCUSSION

A. Structural and electronic properties

The structures were first optimized in order to analyze the influence of metal substitution on the structures and electronic properties of MoS$_2$ monolayer. The lattice constant after optimization was 3.18 Å, which correlates with other reported values. The binding energy which describes the formation energy associated with replacing Mo with Ni or Pt was calculated using equation 1. The binding energies were calculated to be -0.02 eV, -0.04 eV and -3.08 eV for Ni, Pt and Pt-Ni, respectively. The negative values of the binging energy represent an endothermic process and also suggest that all proposed metal doping is energetically favourable. It should also be noted that the smaller binding energy demonstrates weaker thermodynamic stability. The stability of the catalysts has been proven to improve with hydrogen adsorption [14]. On the other hand, the larger binding energy when doping with both Pt-Ni shows stronger chemical interactions between the metal atoms and the MoS$_2$ monolayer.

The effect of metal doping on electronic properties and local geometry can be understood by evaluating electronic density of states (DOS) of the structures. Furthermore, the DOS of these catalysts can provide insights on the chemical origins of HER activity in doped MoS_2 [15-18]. Figure 2 shows the total DOS of pristine and doped MoS_2 catalyst.
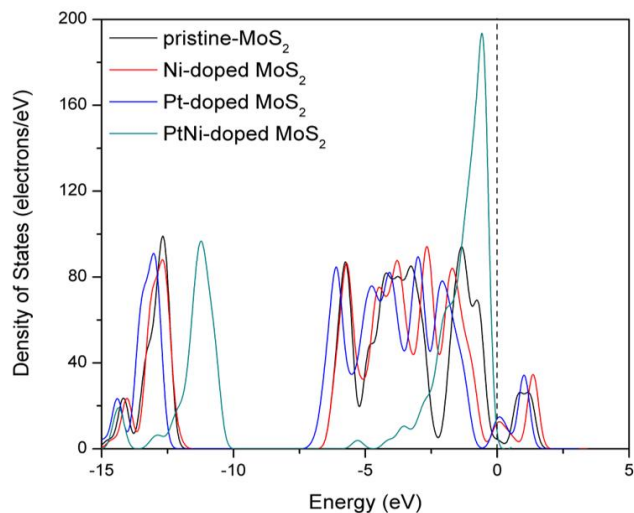

Figure 2: DOS of pristine and doped MoS2 before. The black dotted line represents the fermi level, which is set at zero.

There is a noticeable difference in the density states when MoS_2 is doped with the metal atoms as observed in Figure 2. The changes observed near the fermi level in can be attributed to the formation of bonds between the metal dopants and S atoms. The gap states which resulted in a slight increase near the fermi level can be attributed to the 3d orbitals of the Ni atom, the 5d states of the Pt atom and 3p orbitals of the S atoms that are bonded to the substituting metal atom. The double doped MoS_2 monolayer shows a sharp increase near the fermi level which may be due stronger chemical bonding between Pt-S, as well as between Ni-S. The increased electronic states due to the introduction of dopants may facilitate electron supply [18] to the adjacent S-adsorption sites, thus resulting in the enhanced H adsorption ability of in-plane S atoms and thereby improved HER activity.

B. Effect of doping on hydrogen adsorption

Generally, the hydrogen evolution reaction (HER) will proceed through two main steps. The first step, commonly referred to as the Volmer step include the adsorption of hydrogen atoms on the catalyst site. The second step, Heyrovsky or Tafel step, includes the desorption and release of molecular hydrogen from the catalyst site [12,19]. The Volmer step, is considered the rate determining step as it has a relatively higher energy barrier in comparison with the second step. Therefore, in order to understand the HER, hydrogen adsorption behaviour must be investigated.
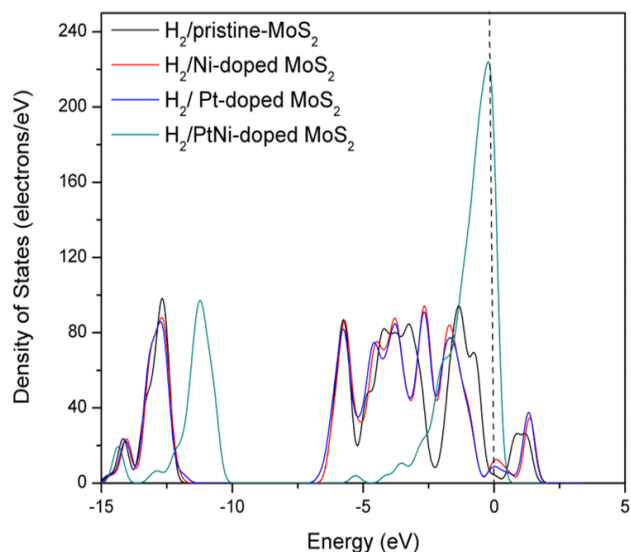

Figure 3: DOS of pristine and doped MoS2 after hydrogen adsorption. The black dotted line represents the fermi level, which is set at zero.

To investigate the effect of metal doping on the hydrogen adsorption behaviour of in-plane S domains of MoS_2 monolayer, the Mo atom is substituted with Pt, Ni and Pt-Ni co-doping, respectively. Only the neighbouring S atoms, where Mo was either substituted with Pt or Ni were investigated as adsorption sites. The influence of metal doping on hydrogen adsorption is first demonstrated using the density of states after hydrogen adsorption, as presented in Figure 3. Figure 2 shows the DOS plots before hydrogen adsorption. In comparison with pristine MoS_2, the density of states for all metal doped MoS_2 monolayer changed following adsorption of H_2 molecule of Sulfur atoms. This demonstrates that the inert in-plane S atoms become more reactive towards hydrogen when MoS_2 is doped with Ni and Pt. The Ni-doped MoS_2 and the Pt-doped MoS_2 appear to have similar peaks and behavior when hydrogen adsorbs. However, at the fermi level the Ni-doped MoS_2 has a higher peak which shows better activity than the Pt-doped MoS_2. When MoS_2 is doped with both Pt and Ni, there is a shift towards the fermi level and increased density states. This shows that the double metal doping significantly improves the reactivity of in-plane S atoms of the MoS2 monolayer

To further analyze the influence of metal doping on hydrogen adsorption, the Gibbs free energy ΔG_H of adsorbed hydrogen molecule on pristine MoS_2 and doped MoS_2 is reported in Table 1. The negative near-zero value of ΔG_H for all doped MoS2 monolayers substantiates the improved hydrogen adsorption which were observed from the DOS plots. The Gibbs free energy (ΔG) is commonly used to characterize the HER activity of materials. According to thermodynamics, if $\Delta G > 0$, it will be difficult for the hydrogen atom to bind to the catalyst site. This consequently affects the, rate determining Volmer step as discussed above.

In addition, when ΔG< 0, the hydrogen is strongly adsorbed on the catalyst which can affect the desorption process and thus hindering the release of the molecular hydrogen. As a result, the materials exhibit their best catalytic behaviour when ΔG =0 [12]. The improvement in catalytic activity clearly show a strong dependence on both Ni and Pt metal doping, as reported by previous studies. The presence of all three dopants Pt, Ni and Pt-Ni atoms shows significant improvement in HER catalytic activity of MoS_2.

TABLE I.   GIBBS FREE ENERGY OF PRISTINE AND DOPED MoS_2

HER MoS_2 catalyst	Gibbs free energy, ΔG (eV)
Pristine MoS_2-Mo site	2.42
Pristine MoS_2-S site	1.86
Pt-doped	-0.03
Ni-doped	-0.06
Pt-Ni co-doping	-0.08

The effect of distance on adsorbed Gibbs free energy is presented in Figure 3. The result reveal weakened hydrogen adsorption as distance of hydrogen to dopant increases. This further demonstrates that the hydrogen adsorption is dependent on atomic doping [17]. Moreover, these results indicate that the in-plane S atoms, in the presence of Pt and Ni dopants, can exhibit HER catalytic activity comparable to that of the highly active edge S- atoms.
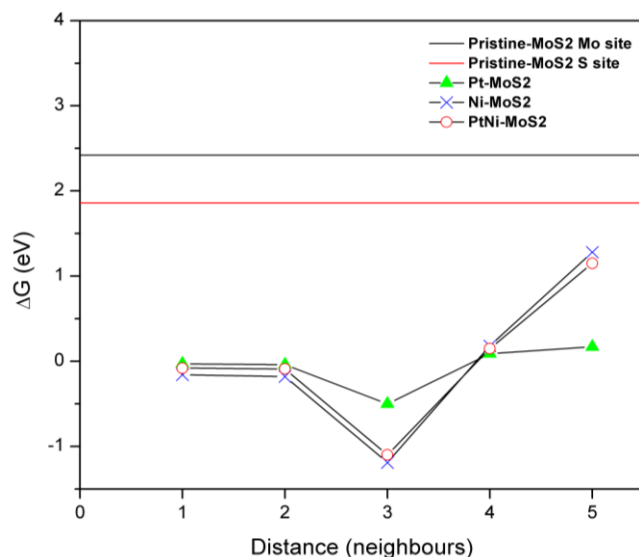

Figure 3: Hydrogen adsorption free energy ΔGH on MoS2 edges as a function of distance of hydrogen to the dopant atom. The distance is given as the nth nearest-neighbour Sulfur position relative to the site of the dopant atom.

IV.   CONCLUSION

DFT was used to investigate the hydrogen adsorption behavior on pristine and Pt-Ni doped 2D-MoS_2 monolayer. The DOS plots revealed that doping MoS2 monolayer with Ni and Pt can significantly improve hydrogen adsorption on in-plane S atoms. This may be attributed to the increased the electronic states near fermi level due to hybridization caused by atomic metal doping. The negative near-zero values of Gibbs free energy ($ΔG_H$) for all doped MoS_2 monolayers further substantiates the improved hydrogen adsorption. Overall, the findings demonstrate that atomic Pt metal co-doping with cheaper metals such as Ni can significantly improve hydrogen adsorption and therefore HER activity of MoS_2. The approaches of the present study can pave a pathway and provide useful insights on strategies to trigger the activity of inert 2D-MoS_2 in-plane S atoms towards HER and other energy-related catalytic processes

REFERENCES

[1]   A. Rafiee and K. R. Khalilpour, "Renewable Hybridization of Oil and Gas Supply Chains," in Polygeneration with Polystorage for Chemical and Energy Hubs, 2019.

[2]   J. Karnaz, "Compressor and system energy efficiency improvements through lubricant optimization," in Institution of Mechanical Engineers - 8th International Conference on Compressors and Their Systems, 2013.

[3]   J. Yoon, Y. Sun, and J. A. Rogers, "Flexible Solar Cells Made of Nanowires/Microwires," in Semiconductor Nanomaterials for Flexible Technologies: From Photovoltaics and Electronics to Sensors and Energy Storage, 2010.

[4]   B. Zohuri and B. Zohuri, "Types of Renewable Energy," in Hybrid Energy Systems, 2018.

[5]   I. Staffell et al., "The role of hydrogen and fuel cells in the global energy system," Energy and Environmental Science. 2019.

[6]   T. Wilberforce, A. Alaswad, A. Palumbo, M. Dassisti, and A. G. Olabi, "Advances in stationary and portable fuel cell applications," Int. J. Hydrogen Energy, 2016.

[7]   T. Corrales-Sánchez, J. Ampurdanés, and A. Urakawa, "MoS2-based materials as alternative cathode catalyst for PEM electrolysis," in International Journal of Hydrogen Energy, 2014.

[8]   D. Voiry et al., "Conducting MoS_2 nanosheets as catalysts for hydrogen evolution reaction," Nano Lett., 2013.

[9]   M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li, and S. Jin, "Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS_2 nanosheets," J. Am. Chem. Soc., 2013.

[10] X. Li and H. Zhu, "Two-dimensional MoS_2: Properties, preparation, and applications," J. Mater., 2015.

[11] Perdew, J. P., Burke, K. and Ernzerhof, M. Generalized gradient approximation made simple. Physical review letter, 77 (1996), 3865.

[12] [2] Shi, W., Wang, Z. and Fu, Y. Mechanical bending induced catalytic activity enhancement of monolayer 1 T'-MoS$_2$ for hydrogen evolution reaction. Journal of Nanoparticle Research, 19, 9 (2017), 296.

[13] Greeley, J., Jaramillo, T. F., Bonde, J., Chorkendorff, I. and Nørskov, J. K. Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. Nature Materials, 5, 11 (2006/11/01 2006), 909-913.

[14] Cao, J., Zhou, J., Zhang, Y. and Liu, X. Theoretical study of H2 adsorbed on monolayer MoS2 doped with N, Si, P. Microelectronic Engineering, 190 (2018), 63-67.

[15] Hao, Y., Wang, Y.-T., Xu, L.-C., Yang, Z., Liu, R.-p. and Li, X.-y. 1T-MoS2 monolayer doped with isolated Ni atoms as highly active hydrogen evolution catalysts: A density functional study. Applied Surface Science, 469 (2019), 292-297.

[16] Tsai, C., Abild-Pedersen, F. and Nørskov, J. K. Tuning the MoS2 Edge-Site Activity for Hydrogen Evolution via Support Interactions. Nano Letters, 14, 3 (2014), 1381-1387.

[17] Deng, J., Li, H., Xiao, J., Tu, Y., Deng, D., Yang, H., Tian, H., Li, J., Ren, P. and Bao, X. Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS2 surface via single-atom metal doping. Energy & Environmental Science, 8, 5 (2015), 1594-1601.

[18] Hakala, M., Kronberg, R. and Laasonen, K. Hydrogen adsorption on doped MoS2 nanostructures. Scientific Reports, 7, 1 (2017), 15243.

[19] Shi, W. and Wang, Z. Effect of oxygen doping on the hydrogen evolution reaction in MoS2 monolayer. Journal of the Taiwan Institute of Chemical Engineers, 82 (2018), 163-168.

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