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Effect of Doping Concentration on Structural Stability and Formation Energy of the Fluorine Doped Hexagonal Molybdenum Dioxide (MoO_2). A First Principle Study

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Abstract

The structural properties of undoped and Fluorine doped Hexagonal Molybdenum dioxide (MoO_2) with different doping concentrations have been calculated using Density Functional Theory (DFT) within Generalized Gradient Approximation (GGA) as implemented in Quantum Espresso (QE). The calculated results were for the formation energy of 4.17%, 8.33%, 12.5%, of F doped MoO_2 are 232.5eV, 463.0eV, and 698.5eV respectively, which show the variation of energy based on the increase in the doping concentration that led to having the breakage of bond in the structure of the compound. The undoped and 4.17% of F doped MoO_2 have three free atoms, which maintain the stability of the structure, but when the doping concentration was increased, the bond breaks simultaneously which led to having four and five free atoms for 8.33%, and 12.5% of F doped MoO_2 respectively. This makes 4.17% of F doped MoO_2 with 17.09Ry more stable. Similarly, the bond length of undoped MoO_2 was 2.2505pm, but when doped with 4.17% of F it changes to 2.3030pm which indicates a greater stability of the structure concentrations of the dopant above 4.17% reduced the bond length, which made the structure less stable.

Keywords: Fluorine; Doped; Density functional theory; generalized gradient approximation; Quantum ESPRESSO

I. INTRODUCTION

Various 2D materials such as graphene, transition metal dichalcogenides, antimony, black phosphorus, have been synthesized [1-6] to illustrate the incredible potential for new type of optoelectronic devices. owing to their unique properties and rich in feasibility for the fabrication of 2D materials technologies [7]. Certainly, some of specific 2D materials have shortcomings such as zero band gap, low absorption efficiency, and instability in open atmosphere which are some of the challenges in fabrication of ideal nanoscale devices. In order to overcome these challenges, the transition metal oxides TMO have been found to be effective 2D materials in terms of possessing high conductivity, piezoelectricity, colossal magnetoresistance, better stability in

open environment and superconductivity, etc. [8-10]. Molybdenum dioxide is a typical TMO material having three crystalline polymorphic forms; hexagonal phase ($P6_3/mmc$) [11], tetragonal phase ($P4_2/mnm$) [12] and monoclinic ($P2_1/c$) [13], and also possesses a partially rutile configuration [14] containing MoO_6, octahedrally linked Mo through oxygen atoms in the edges of unit cell involves four MoO_2 units which is opposite to two-unit cells [15-16], It is well known that the properties of molybdenum oxides are strongly dependent on their crystalline structures; in particular, the rutile structure of MoO_2 is interesting due to possession of superb metallic-like electrical conductivity, low electrical resistivity, high melting point [17-18], facile ion transport [19], and excellent chemical stability [20]. It has been interrelated to various interatomic bonding and comparatively over the top density of states at the Fermi level. The presence of free electrons generates Mo^{4+} in MoO_2 in contrast to generation of Mo^{6+} from MoO_3; hence, all the valence electrons in molybdenum metal are covalently bonded to nearest oxygen atoms [21]. A small variation in Mo valence may cause significant fluctuations in physical properties of the molybdenum oxides. For instance, it is possible to obtain compounds of other oxides with diverse physical properties [22-23].

The main difference of transition metals (TM) from other metals is that their valence electrons may be present in more than one shell. Hence, most TM have more than one oxidation states. The oxides of TM show a rich variety of electronic properties, ranging from insulating to metallic and even superconducting behavior. The same applies to their magnetic properties, where everything is found from Pauli Paramagnetic to local moment behavior including the occurrence of ferromagnetism and anti-ferromagnetism. Additionally, these materials can often be tuned from one electronic or magnetic phase to another by varying the temperature, pressure, or by doping. Therefore, the transition metal oxides TMO have been for a long time the subject of intense experimental and theoretical study. Especially d-band TMO are of interest because of their catalytic properties. Transition metal oxides are used in a wide variety of technologically important catalytic processes. For example, they are used in selective oxidation, selective reduction and dehydrogenation [24]. Understanding surface structure and reactions is important for understanding these catalytic processes.

Theoretically and experimentally, Hexagonal MoO_2 has received less attention than other structural phases of MoO_2, with only a handful of studies in the literature [25-27]..This is because the Hexagonal phase has major problem of metallic character and weak paramagnetic properties at room temperature [28], Recently two studies by Eyert and co-workers used LDA within the augmented spherical wave (ASW) method to investigate the instability in the Hexagonal MoO_2 and also to study the Fermi surface of MoO_2 in comparison with angle-resolved photoemission spectroscopy.

Over the past few decades, other crystal phases of MoO_2 have been utilized in electrocatalysts application, these studies have indicated that the activity of crystal size in Hexagonal MoO_2 correlates with the number of the unsaturated Mo and O sites along the edges, where as their basal planes are catalytically passive.

Therefore, exposing the maximum number of edge sites and improving the intrinsic activity of the edge sites of the hexagonal MoO_2 by chemical doping have become main strategies to enhance the activity.

II. COMPUTATIONAL DETAILS

DFT calculations were performed using the project augmented wave basis set as implemented in Quantum ESPRESSO. [29] A plane wave cut-off energy was used as 160eV was used, and the exchange correlation function was treated using the PBE for the GGA [30]. The valence electrons of Molybdenum (Mo) and Oxygen were $4d^5 5s^1$ and $2s^2 2p^6$ respectively [31] with hexagonal structure, space group $p6_3$/mmc {194}, and point group 6/mmm. A simple conventional unit cell with lattice parameters of: a = b = 2.859Å, c =10.460Å, $\propto = 90^{\circ} = \beta$ and $\gamma = 120.001^{\circ}$ contains only two Molybdenum (Mo) and four Oxygen atoms (O), a supercell of $2 \times 2 \times 1$ is used in order to increase the number of atoms relative to the standard conventional unit cell for both the pure and doped Molybdenum dioxide. The supercell consists of twenty-four (24) atoms with eight (8) Molybdenum and sixteen (16) Oxygen satom, the new lattice parameters for the supercells of Molybdenum dioxide are $a = 4.951119\hat{A} = b$, and $c = 10.460316\hat{A}$. The supercell dimensions are kept fixed throughout the calculations, while the atomic positions are fully relaxed for all calculations using Broyden Fletcher-Goldfarb-Shannon (BFGS) algorithm, until the forces acting on the atoms are below 0:001 eV/Å.

III. RESULT AND DISCUSSION

A. Structural Properties

Define Table I is the Substitutional configuration of 4.17% of fluorine doped Hexagonal Molybdenum dioxide, there are sixteen (16) different symmetrical approach in which one

oxygen can be replaced by one fluorine in different doping concentrations [32]. in present study $D_{16}0.0417$ was considered. The structure is more stable than the pure Molybdenum dioxide which both have three free atoms, and there is no transition between the structures and the crystals parameters remain the same as that of the pure (undoped) Molybdenum dioxide [33].

TABLE I CONFIGURATION FOR SUBSTITUTIONAL DOPING OF 4.17 % OF FLUORINE ON OXYGEN IN MOLYBDENUM DIOXIDE

Undoped	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
$D_1$0.0417	F	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
$D_2$0.0417	O	F	O	O	O	O	O	O	O	O	O	O	O	O	O	O
$D_3$0.0417	O	O	F	O	O	O	O	O	O	O	O	O	O	O	O	O
$D_4$0.0417	O	O	O	F	O	O	O	O	O	O	O	O	O	O	O	O
$D_5$0.0417	O	O	O	O	F	O	O	O	O	O	O	O	O	O	O	O
$D_6$0.0417	O	O	O	O	O	F	O	O	O	O	O	O	O	O	O	O
$D_7$0.0417	O	O	O	O	O	O	F	O	O	O	O	O	O	O	O	O
$D_8$0.0417	O	O	O	O	O	O	O	F	O	O	O	O	O	O	O	O
$D_9$0.0417	O	O	O	O	O	O	O	O	F	O	O	O	O	O	O	O
D_{10}0.0417	O	O	O	O	O	O	O	O	O	F	O	O	O	O	O	O
D_{11}0.0417	O	O	O	O	O	O	O	O	O	O	F	O	O	O	O	O
D_{12}0.0417	O	O	O	O	O	O	O	O	O	O	O	F	O	O	O	O
D_{14}0.0417	O	O	O	O	O	O	O	O	O	O	O	O	F	O	O	O
D_{15}0.0417	O	O	O	O	O	O	O	O	O	O	O	O	O	F	O	O
D_{16}0.0417	O	O	O	O	O	O	O	O	O	O	O	O	O	O	F	F

Similarly, table II is the Substitutional configuration of 8.33% of fluorine doped Hexagonal Molybdenum dioxide, there are eight (8) different symmetrical approach in which two oxygen can be replaced by two fluorine in different doping concentrations. in present study $D_1$0.0833 was considered [32]. The structure is not stable and there are four free atoms in the structure, but the crystals parameters remain the same as that of the pure (undoped) Molybdenum dioxide [33].

TABLE II CONFIGURATION FOR SUBSTITUTIONAL DOPING OF 8.33% OF FLUORINE ON OXYGEN IN MOLYBDENUM DIOXIDE

Undoped	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
$D_1$0.0833	F	O	O	O	O	O	O	O	O	O	O	O	O	O	O	F
$D_2$0.0833	O	F	O	O	O	O	O	O	O	O	O	O	O	O	F	O
$D_3$0.0833	O	O	F	O	O	O	O	O	O	O	O	O	O	F	O	O
$D_4$0.0833	O	O	O	F	O	O	O	O	O	O	O	O	F	O	O	O
$D_5$0.0833	O	O	O	O	F	O	O	O	O	O	O	F	O	O	O	O
$D_6$0.0833	O	O	O	O	O	F	O	O	O	O	F	O	O	O	O	O
$D_7$0.0833	O	O	O	O	O	O	F	O	O	F	O	O	O	O	O	O
$D_8$0.0833	O	O	O	O	O	O	O	F	F	O	O	O	O	O	O	O

Also, table III is the Substitutional configuration of 12.5% of fluorine doped Hexagonal Molybdenum dioxide, there are fourteen (14) different symmetrical approach in which three oxygen can be replaced by three fluorine in different doping concentrations. in present study $D_8$0.125 configuration was considered [32]. The structure is not stable and there are five free atoms in the structure, but the crystals parameters remain the same as that of the pure (undoped) Molybdenum dioxide [33].

TABLE III CONFIGURATION FOR SUBSTITUTIONAL DOPING OF 12.5% OF FLUORINE ON OXYGEN IN MOLYBDENUM DIOXIDE

Undoped	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
$D_1$0.125	F	F	O	O	O	O	O	O	O	O	O	O	O	O	O	F
$D_2$0.125	F	O	F	O	O	O	O	O	O	O	O	O	O	O	O	F
$D_3$0.125	F	O	O	F	O	O	O	O	O	O	O	O	O	O	O	F
$D_4$0.125	F	O	O	O	F	O	O	O	O	O	O	O	O	O	O	F
$D_5$0.125	F	O	O	O	O	F	O	O	O	O	O	O	O	O	O	F
$D_6$0.125	F	O	O	O	O	O	F	O	O	O	O	O	O	O	O	F
$D_7$0.125	F	O	O	O	O	O	O	F	O	O	O	O	O	O	O	F
$D_8$0.125	F	O	O	O	O	O	O	O	F	O	O	O	O	O	O	F
$D_9$0.125	F	O	O	O	O	O	O	O	O	F	O	O	O	O	O	F
D_{10}0.125	F	O	O	O	O	O	O	O	O	O	F	O	O	O	O	F
D_{11}0.125	F	O	O	O	O	O	O	O	O	O	O	F	O	O	O	F
D_{12}0.125	F	O	O	O	O	O	O	O	O	O	O	O	F	O	O	F
D_{13}0.125	F	O	O	O	O	O	O	O	O	O	O	O	O	F	O	F
D_{14}0.125	F	O	O	O	O	O	O	O	O	O	O	O	O	O	F	F

Generally, in order to find the stability of the structure after doping, the dopant formation energy (E_f) simply refers to the energy needed to insert one or more fluorine atom into the supercell with a chemical potential μ_F after removing one or more Oxygen atom with a chemical potential μ_O from the same position, the formation energy was calculated using equation (1) [34].

$$E_f = E_{total}\,(MoO_2 + F) - E_{total}(MoO_2) + \mu_O - \mu_F \qquad (1)$$

Where E_f= formation energy (eV), $E_{total}\,(MoO_2 + F)$= total energy of Hexagonal Molybdenum dioxide doped fluorine (eV), $E_{total}(MoO_2)$= total energy of pure molybdenum dioxide, μ_O= chemical potential per atom of oxygen, μ_F= chemical potential per atom of fluorine. The chemical potentials were numerically calculated as the total energy per atom in the bulk system. All the calculated formation energies were tabulated in the Table IV below.

TABLE IV FORMATION ENERGY OF PURE AND DOPED MOLYBDENUM DIOXIDE

Compound	Total Energy (eV)	Chemical potential	Free Atom	Formation Energy (eV)
Pure MoO_2	-1631.024	-67.959	3	Nil
4.17% of Fluorine	-1647.430	-68.643	3	232.5
8.33% of Fluorine	-1663.530	-69.326	4	463.0
12.5% of Fluorine	-1680.306	-70.013	5	698.5

Table IV is the calculated formation energies of 4.17%, 8.33%, and 12.5% of fluorine on Hexagonal Molybdenum dioxide which are 232.5eV, 463.0eV, and 698.5eV respectively. The table shows the variation of energy based on the increase in the doping concentration, the formation energy increases with the increase in the doping concentration which led to having the breakage of bond on structure. It was observed from Fig. 1(a and b) that the structure of pure Hexagonal Molybdenum dioxide and 4.17% of fluorine on Hexagonal Molybdenum dioxide has three (3) free atoms,

which maintain the stability of the structure, but when the doping concentration were increased, the number of free atoms increases from three (3) to four (4) in Fig. 1c for 8.33% of fluorine and five (5) free atoms in Fig. 1d for 12.5% of fluorine. The formation energy of the doped compound of 4.17% of fluorine is 232.5 eV which is more stable than 8.33%, and 12.5% of fluorine with four (4), and five (5), free atoms respectively.

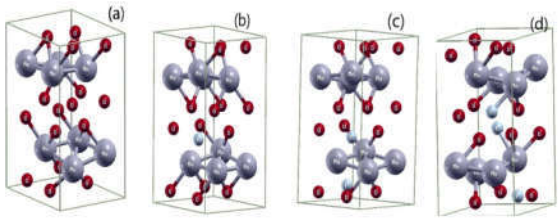

Fig. 1 (a) pure Molybdenum dioxide (MoO_2) (b) 4.17% of fluorine doped molybdenum dioxide ($F.MoO_2$) (c) 8.33% of fluorine doped molybdenum dioxide ($F.MoO_2$) (d) 12.5% of fluorine doped molybdenum dioxide ($F.MoO_2$).

Table V shows the bond length of pure Hexagonal Molybdenum dioxide and Fluorine doped Hexagonal Molybdenum dioxide with different doping concentration. It was observed that 4.17% of fluorine increases in bond length when doped with pure Hexagonal molybdenum dioxide from 2.2505 - 2.3030pm which indicates a greater stability of the compound, because the bond length increases across a period and decreases down a group, similarly when doped with 8.33% and 12.5% of fluorine doped Hexagonal Molybdenum dioxide shows a decrease in bond length from 2.2698 - 2.2099pm respectively, which shows the instability in the compound. The more atom holding together the greater the stability of the compounds and the bond length is inversely related to the bond energy. in this case, the four (4) and five (5) free atoms of 8.33 %, and 12.5 % clearly shows the instability of the structures, and make 4.17% of fluorine on Hexagonal molybdenum dioxide be more stable.

TABLE V BOND LENGTH OF PURE AND DOPED MOLYBDENUM DIOXIDE

Compound	% of Dopant	Bond Length ($\AA$)
MoO_2	Nil	2.2505
MoO_2	4.17%	2.3030
MoO_2	8.33%	2.2698
MoO_2	12.5%	2.2099

IV. Conclusion

In conclusion, using the first-principles calculations, we have studied the effect of doping concentration on structural stability of the fluorine doped Hexagonal MoO_2. The Doped structures with F replacing several distinct Oxygen at different doping concentrations (4.17%, 8.33% and 12.5%) sites were looked into. From the calculated formation energies, the most stable structure among the F doped system is found to be at 4.17% doping concentration. The formations energies for doping $H - MoO_2$ with F are 17.09, 34.173and 51.336 eV at 4.17%, 8.33% and 12.5% doping concentration. respectively. Confirming for stability at 4.17% due to a less formation energies value.

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