

# Investigation of structural stability and electronic properties of MnO<sub>2</sub> Nanostructure with Incorporation of Ti and Cr Atom- Using DFT

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## ABSTRACT

The realistic structures of pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures are optimized and simulated precisely with the help of density functional theory method along with the selection of B3LYP/LanL2DZ basis set. Using chemical hardness, formation energy and chemical potential, structural stability of  $\beta$ -MnO<sub>2</sub> nanostructures are discussed. Dipole moment and point symmetry of pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures are investigated. The electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructures are studied in terms of electron affinity, ionization potential and HOMO-LUMO gap. The present work improves the electronic properties and structural stability of  $\beta$ -MnO<sub>2</sub> nanostructure with the influence of Ti and Cr atom.

**KEY WORDS:**  $\beta$ -MnO<sub>2</sub>, HOMO, LUMO, dipole moment, chemical potential.

## 1. INTRODUCTION

Manganese dioxide (MnO<sub>2</sub>) has taken a great interest due to its low cost, abundant storage in earth and high theoretical capacity (Huang, 2015; Liu, 2005). Until now, numerous reports have been focused on synthesis of MnO<sub>2</sub> with realistic structures for use in active points (Li, 2015). Various morphologies and nanostructures including hierarchical (Dubal, 2015), hollow and arrayed ones (Li, 2015) have been enhanced to calculate their prominent electrochemical properties for energy storage application. As a matter of fact the excellent permeation and high specific surface area influence the deep contact of active surface with electrolyte ions of MnO<sub>2</sub>.

Nano materials have been subjected to intensive research in entire world owing to their potential applications in photonics, electronics and catalysis (Xi, 2004). MnO<sub>2</sub> exists in different oxidation states of manganese (II, III and IV). Utmost, the general known manganese oxides Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, MnO and Mn<sub>3</sub>O<sub>4</sub> have an extensive range of applications such as molecular-sieves (Yuan, 2005), redox catalysts (Yang, 2006), ion exchange, electrode materials for lithium batteries and biosensor (Minakshi, 2009) and magnetic materials (Liu, 2005), due to their extensive structural diversity with unique physical and chemical properties. MnO<sub>2</sub> exhibits in various crystallographic structures including  $\delta$ ,  $\alpha$ ,  $\beta$  and  $\nu$  type. Cao (2010) reported the synthesis of  $\alpha$ -MnO<sub>2</sub> nanorods utilizing manganese sulfate as a beginning material. Tsang (1998) have studied the reduction of potassium borohydride with potassium permanganate in an aqueous solutions to get ternary and binary manganese oxides. Ahmad (2004) have proposed the synthesis of different manganese oxides through thermal decomposition of manganese found utilizing cetyltrimethyl-ammonium-bromide as surfactant and manganese acetate as precursor. Wang (2008), have synthesis  $\alpha$ -MnO<sub>2</sub> microspheres with the help of low-temperature hydrothermal method using potassium persulfate as oxidizing agent and manganese sulfate as base material. Moreover by hydrothermal routes, MnO<sub>2</sub> have been synthesized by numerous other methods, including sol-gel process, precipitation/ion-exchange, sol-process, microwave heating and high-temperature solid-state routes (Rao, 2007). Kim (2007), have proposed to synthesis  $\beta$ -MnO<sub>2</sub> nanorods and investigate the magnetic and structural properties of manganese dioxides. The calculated band gap value of  $\alpha$ - and  $\beta$ - is 2.7 and 1.6 eV respectively. The motivation behind the present work is to investigate the structural and electronic properties of rutile  $\beta$ -MnO<sub>2</sub> nanostructure using DFT method. The literature survey was done with the help of SCOPUS and Cross Ref database, few work only published about the MnO<sub>2</sub> nanostructure. Density functional theory reveals the structural and electronic properties of MnO<sub>2</sub> nanostructures (Nagarajan, 2015). From the literature survey, we come to know that there are numerous works have been carried out with DFT on both experimentally and theoretically (Nagarajan, 2014). In the present work, rutile  $\beta$ -MnO<sub>2</sub> nanostructures are optimized and improved the structural and electronic properties with the incorporation of Ti and Cr atom as dopant.

## 2. MATERIAL AND METHOD

**Computational Methods:** The realistic rutile  $\beta$ -MnO<sub>2</sub> nanostructures are optimized and simulated precisely with facilitate Gaussian 09 package. In the present work, Becke's three-parameter hybrid functional in combination with Lee-Yang-Parr correlation functional (B3LYP), LanL2DZ basis set has been used in DFT method. The atomic number of manganese and oxygen is twenty five and eight respectively. Selection of prominent basis set is a most significant criteria for simulating  $\beta$ -MnO<sub>2</sub> nanostructure. LanL2DZ basis set is a perfect choice among others which gives good output with pseudo potential approximation for  $\beta$ -MnO<sub>2</sub> nanostructure (Becke, 1988; Hay, 1985). The HOMO-LUMO gap and density of states (DOS) spectrum of pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructure can be analyzed via Gauss Sum 3.0 package (Boyle, 2007). While optimizing  $\beta$ -MnO<sub>2</sub> nanostructures, the convergence range is observed in the range of 10<sup>-5</sup> eV.

### 3. RESULTS AND DISCUSSION

The present work is deals with ionization potential (IP), dipole moment (DM), chemical hardness (CH), electron affinity (EA), point group chemical potential (CP) and HOMO-LUMO gap of  $\beta$ -MnO<sub>2</sub> nanostructures and the electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructure are fine-tuned with the substitution of titanium and chromium element. Figures 1, 2 and 3 represents the pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures respectively. The pristine  $\beta$ -MnO<sub>2</sub> nanostructure has twenty four Mn atoms and eight oxygen atoms to form rutile structure. Ti substituted  $\beta$ -MnO<sub>2</sub> nanostructure consist of eleven Mn atoms, eight oxygen atoms and one Mn atom is replaced with one Ti atom. Similarly, Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructure contains eight oxygen atoms, eleven Mn atoms and one Mn atom is replaced with one Cr atom to maintain the stoichiometry structure.

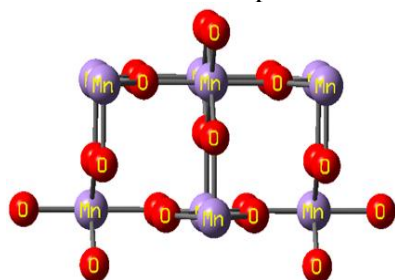


Figure.1. Pristine  $\beta$ -MnO<sub>2</sub> nanostructure

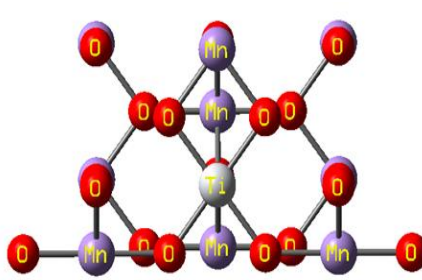


Figure.2. Ti substituted  $\beta$ -MnO<sub>2</sub> nanostructure

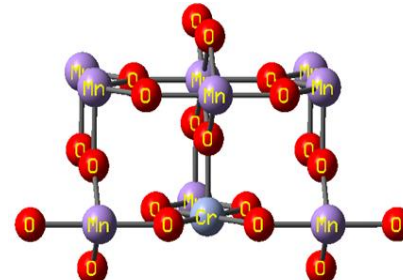


Figure.3. Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructure

**Structural stability and electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructures:** The structural stability of pristine  $\beta$ -MnO<sub>2</sub> nanostructures is described in the terms of formation energy,

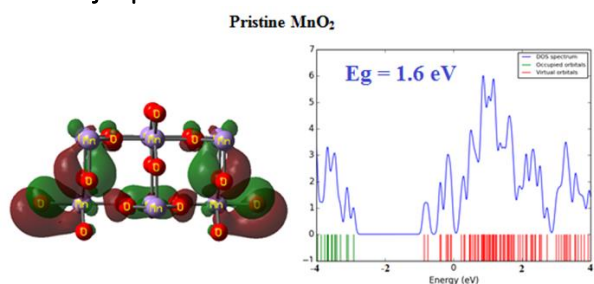
$$E_{\text{form}} = 1/n[E(\beta\text{-MnO}_2 \text{ nanostructure}) - p E(\text{Mn}) - q E(\text{O}) - r E(\text{dopant})]$$

Where  $E(\beta\text{-MnO}_2 \text{ nanostructures})$  refers to the total energy of  $\beta$ -MnO<sub>2</sub> nanostructures,  $E(\text{Mn})$ ,  $E(\text{O})$  and  $E(\text{dopant})$  represent the corresponding energies of isolated manganese, oxygen and impurity atoms. The  $p$ ,  $q$  and  $r$  represents the number of manganese, oxygen and impurity atoms respectively,  $n$  refers the total number of atoms in  $\beta$ -MnO<sub>2</sub> nanostructure. The dipole moment, point group and formation energy of pristine, Ti and Cr incorporated  $\beta$ -MnO<sub>2</sub> nanostructure are tabulated in Table.1. The formation energy of pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures are -2.03, -2.84 and -3.44 eV respectively. The stability of  $\beta$ -MnO<sub>2</sub> nanostructure is mainly related to formation energy. The structural stability of  $\beta$ -MnO<sub>2</sub> nanostructure is directly proportional to formation energy. The structural stability of  $\beta$ -MnO<sub>2</sub> nanostructure is enhanced with the incorporation of Ti and Cr element owing to the increasing of formation energy. The dipole moment of pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures is 9.64, 13.06 and 19.2 Debye respectively. The uniform distribution of charge is takes place in pristine  $\beta$ -MnO<sub>2</sub> nanostructure. Due to the substitution of Ti and Cr atom in pure  $\beta$ -MnO<sub>2</sub> nanostructure, small disturbance may occur while the distribution of charge takes place inside the  $\beta$ -MnO<sub>2</sub> base material. Apart from this, the structural stability and electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructure is improved with the incorporation of Ti and Cr dopant atom. The point symmetry group of  $\beta$ -MnO<sub>2</sub> nanostructure is observed to be  $C_s$  which exhibits identity (E) and reflection through the mirror plane symmetry operation.

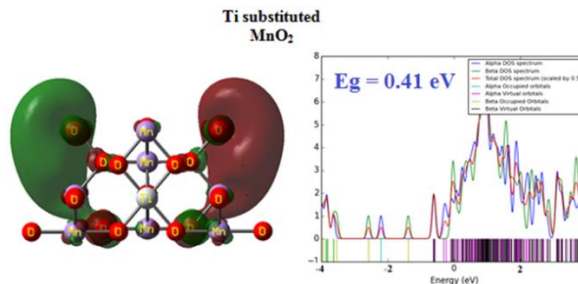
**Table.1. Formation energy, point symmetry and dipole moment of  $\beta$ -MnO<sub>2</sub> nanostructures**

MnO <sub>2</sub> Nanostructures	Formation energy (eV)	Dipole moment (Debye)	Point group
Pristine MnO <sub>2</sub>	-2.03	9.64	$C_s$
Ti substituted MnO <sub>2</sub>	-2.84	13.06	$C_s$
Cr substituted MnO <sub>2</sub>	-3.44	19.2	$C_s$

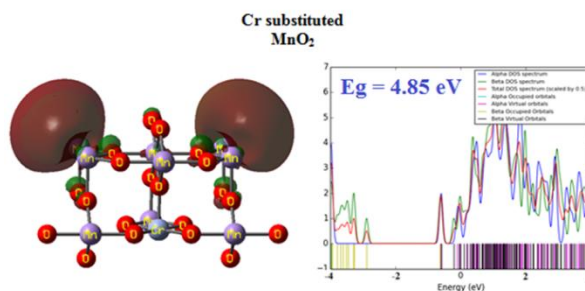
The electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructure can be described in terms of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) (Nagarajan, 2014). The HOMO-LUMO gap value for pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures are 1.6, 0.41 and 4.85 eV respectively. This infers that the conductivity of  $\beta$ -MnO<sub>2</sub> nanostructure is increases with the substitution of Ti atom. In contrast, the conductivity of  $\beta$ -MnO<sub>2</sub> nanostructure rapidly decreases owing to the substitution of Cr atom in  $\beta$ -MnO<sub>2</sub> nanostructure. Since the electronic configuration of Mn, Ti and Cr are differs. Thus, the electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructure can be fine-tuned with the substitution of Ti and Cr element. Visualization of density of states spectrum and HOMO-LUMO gap for pristine, Ti and Cr incorporation  $\beta$ -MnO<sub>2</sub> nanostructures are shown in Figure 4, 5 and 6 respectively.



**Figure.4. Visualization of density of states spectrum and HOMO-LUMO gap for pristine MnO<sub>2</sub> nanostructure**



**Figure.5. Visualization of density of states spectrum and HOMO-LUMO gap for Ti substituted MnO<sub>2</sub> nanostructure**

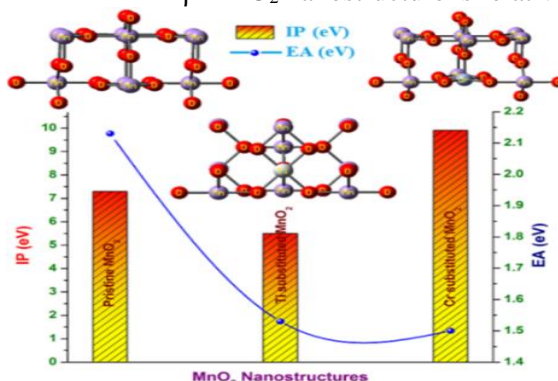


**Figure.6. Visualization of density of states spectrum and HOMO-LUMO gap for Cr substituted MnO<sub>2</sub> nanostructure**

In particularly,  $\beta$ -MnO<sub>2</sub> exhibit narrow band gap semiconductor. Therefore, less energy is enough to transfer electron from HOMO level to LUMO level. As a result in DOS spectrum, the localization of charges is observed to be less in HOMO level rather than LUMO level. With the influence of Ti and Cr impurity, the densities of charges in LUMO level as well as HOMO levels are enhanced. Thus, the electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructures can be fine-tuned with the support of Ti and Cr atom.

#### **Ionization potential, electron affinity, chemical hardness and chemical potential of $\beta$ -MnO<sub>2</sub> nanostructures:**

The electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructure can also be illustrated in terms of ionization potential (IP) and electron affinity (EA) (Sriram, 2013; Nagarajan, 2014b). Figure 4 implies the IP and EA of  $\beta$ -MnO<sub>2</sub> nanostructures. The variation of energy is recorded due to the addition of electron in  $\beta$ -MnO<sub>2</sub> nanostructure is called as EA and the average energy is needed to remove the electron from  $\beta$ -MnO<sub>2</sub> nanostructure is known as IP. Different trends are observed for both ionization potential and electron affinity as shown in Figure 2. EA plays a vital role in the specialization of chemical sensors and plasma physics. The electron affinity for pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructure is 2.13, 1.53 and 1.5 eV respectively. Therefore, the adding of electron in pristine  $\beta$ -MnO<sub>2</sub> nanostructure results more energy fluctuation is recorded. Similar trends are recorded in IP as like electron affinity. It is inferred that the average energy is required more to remove electron from Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructure. Since the HOMO-LUMO gap for Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructure is relatively high.



**Figure.7. IP and EA of  $\beta$ -MnO<sub>2</sub> nanostructures**

The structural stability of  $\beta$ -MnO<sub>2</sub> nanostructures can also be described in terms of chemical hardness (CH) and chemical potential (CP) (Chandiramouli, 2014; Nagarajan, 2014; Sriram, 2014). The chemical potential and chemical hardness can be calculated utilizing the equation  $\mu = -(\text{IP} + \text{EA})/2$  and  $\eta = (\text{IP} - \text{EA})/2$  respectively as shown in Table.2. The effect of CP and CH can also be studied with the help of effective fragment potential model. Chemical hardness always represented as electronegativity, which is one of the best factors in semiconductor physics.

**Table.2. Chemical potential and chemical hardness of  $\beta$ -MnO<sub>2</sub> nanostructures**

Nanostructures	Chemical potential (eV)	Chemical hardness (eV)
Pristine MnO <sub>2</sub>	-4.71	2.58
Ti substituted MnO <sub>2</sub>	-3.515	1.985
Cr substituted MnO <sub>2</sub>	-5.705	4.205

Various trends are recorded on both chemical potential and chemical hardness. Owing to the charge states, CH as well as CP gets fine-tuned. The pristine and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures observed high value of chemical potential and chemical hardness. Thus, the structural stability of  $\beta$ -MnO<sub>2</sub> nanostructure is enhanced with the substitution of Cr atom.

#### 4. CONCLUSION

The realistic structures for pristine, Ti and Cr substituted  $\beta$ -MnO<sub>2</sub> nanostructures are simulated successfully with facilitated B3LYP and LanL2DZ basis set. The structural stability of  $\beta$ -MnO<sub>2</sub> nanostructure are studied with the influence of chemical potential, formation energy and chemical hardness. Dipole moment of pristine, Ti and Cr incorporation  $\beta$ -MnO<sub>2</sub> nanostructures are also reported. Using DOS, HOMO-LUMO gap, electron affinity and ionization potential, electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructures are investigated. From the observation of the present work,  $\beta$ -MnO<sub>2</sub> nanostructure can be fine-tuned with the substitution of Ti and Cr atoms as dopants. Moreover, structural stability and electronic properties of  $\beta$ -MnO<sub>2</sub> nanostructure can be tailored, which find its potential applications in photonics, electronics and catalysis.

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