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Theoretical investigation on the effect of Mn/F composition on open circuit voltage of Cu₂O-ZnO heterojunction solar cell

Saravanakannan V.*¹ and Radhakrishnan T.²

¹School of Electrical & Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur, India

²Department of Physics, SrinivasaRamanujan Center, SASTRA University, Kumbakonam, India

ABSTRACT

The electronic properties and structural stability of Copper Aluminum Oxide and Zinc Oxide, anionic substituted zinc oxide and cationic substituted zinc oxide were studied in the form of two dimensional structure using Gaussian 09 program package with a B3LYP/LANL2DZ basis set. The HOMO-LUMO, chemical hardness of different structures are calculated and reported. The effects of pure ZnO, Mn substituted ZnO and F substituted ZnO on Cu₂O investigated along with HOMO-LUMO gap. The HOMO-LUMO band alignment between Cu₂O and ZnO, ZnO:Mn and ZnO:F was demonstrated and to understand how V_{OC} increases with anionic and cationic substitution of ZnO on Cu₂O. The result shows that the ZnO:F conduction band moves closer to the vacuum level, which exhibit that the decreases of the conduction band offset between ZnO:F and Cu₂O and hence an enhancement of theoretical V_{OC} . The cationic substitution of ZnO was observed that the escalation of the open circuit voltage (V_{OC}). With the improved V_{OC} relatively high solar power conversion efficiency.

Keywords: Cu₂O-ZnO, nanostructure, HOMO-LUMO, open circuit voltage.

INTRODUCTION

The conjugated organic molecules exhibit good properties such as electrical, thermal, photochemical stability and high charge mobility, which as a result of their broad range of electronic applications such as Field effect transistors [1], electroluminescent devices [2] photovoltaic [3] and batteries [4]. Therefore, the interesting properties of conjugated molecules play an important role in technology and to understand molecular structure and the electronic properties to provide guidelines for the development of new materials. These properties depend on the degree of electronic delocalization. To control the band gap is one of the most important physical properties which are a current research topic. The relationships between molecular structure and electronic properties can establish by theoretical analysis of the electronic structure of conjugated systems [5]. The propitious photovoltaic material has been demonstrated that the hetero-junction conjugated molecule n-type ZnO and P-type Cu₂O form a solar cell with the photon absorber as Cu₂O. [6,7]. In this paper, we report to increase the efficiency of Cu₂O-ZnO heterojunction using the ternary conjugated structures such as Mn substituted ZnO, (ZnO:Mn) and F substituted Mn (ZnO:F), thus increasing the open circuit voltage V_{OC} [8].

COMPUTATIONAL METHODS

The Cu₂O-ZnO/ZnO: Mn/ZnO: F nano structure calculation has been performed on the theoretical account of the density functional theory [9]. The different structure of Cu₂O, ZnO, ZnO:Mn and ZnO:F are geometrically

optimized through Gaussian 09 package [10] employing Becke's three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP) method optimized with LANL2DZ basic set [11,12]. The different optimized clusters HOMO-LUMO gap and Density of state (DOS) spectrum of different structure calculations are carried out using Gauss sum 3.0 packages [13].

RESULTS AND DISCUSSION

Structural properties of Cu₂O, pure and doped ZnO nanostructures

The present work focused on HOMO-LUMO gap, formation energy and structural stability and electronic properties of the Cu₂O, ZnO, ZnO:Mn and ZnO:F nanostructures. From the HOMO-LUMO gap we can observe the conduction band offset (CBO) and valence band offset (VBO) and to study the closer the vacuum level. Figure.1 (a) represents Cu₂O nanostructure and Figure.1 (b) represents the pure ZnO nanostructure have eight Zn atoms, eight O atoms. Figure.1(c) and Figure.1(d) denotes that four Mn atoms are replaced for Zn atoms and four F atoms are replaced for O atoms in the pure ZnO nanostructures respectively. For all the nanostructures the bond length is kept as 1.7Å°. All the molecular geometries have been calculated with the hybrid B3LYP function combination with LANL2DZ basis sets using Gaussian 03 program.

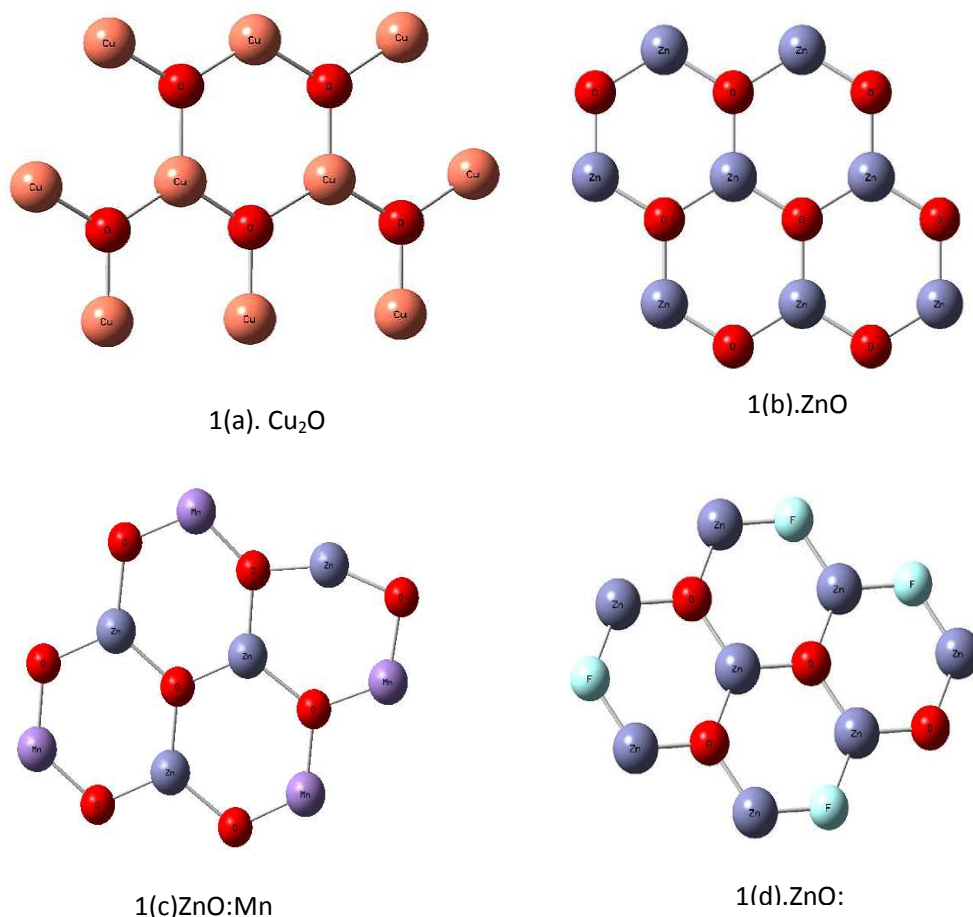


Figure.1 The optimized structures of (a) Cu₂O, (b) ZnO, (c) ZnO:Mn, (d) ZnO:F

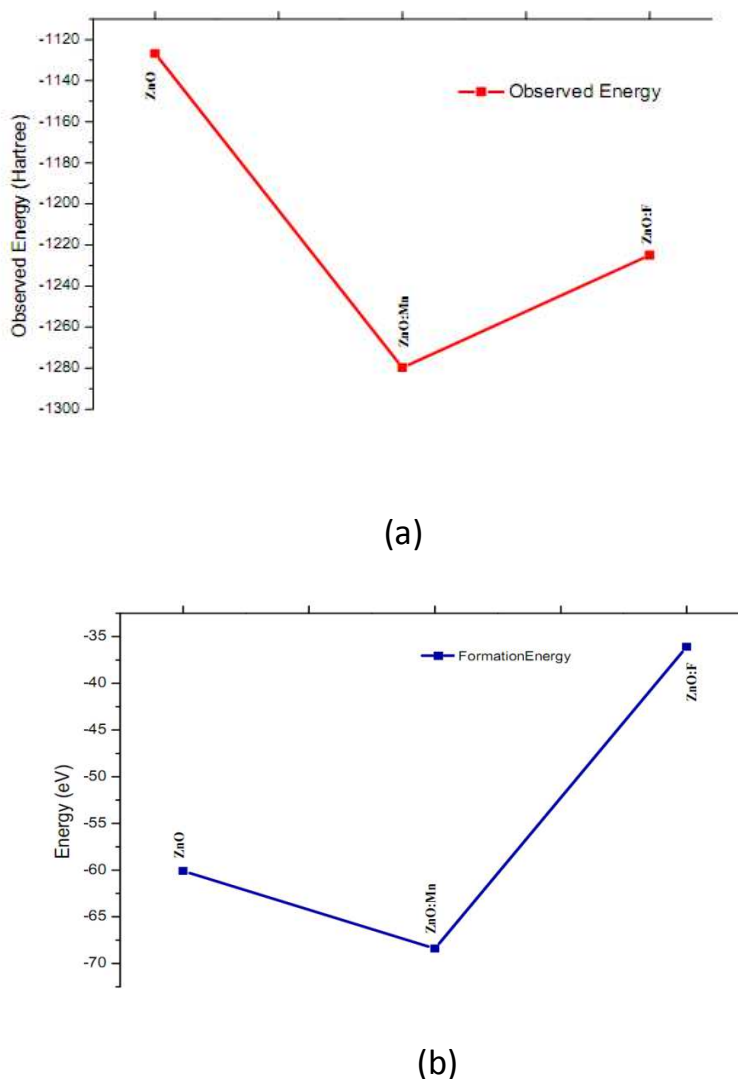


Figure.2 (a) The observed energy (b) formation energy of an optimized structure of pure and doped ZnO nanostructures

The calculated energy of optimized structures of pure and doped ZnO structures is shown Figure.2. The energy observed for pure ZnO is -1126.8 Hartrees and ZnO:Mn and ZnO:F energies are -1279.74 and -1225 Hartrees respectively. The energy value decreases with doped Mn and F substituted to Zn and O respectively. The structural stability of Cu₂O, ZnO, ZnO: Mn and ZnO: F nano structures can be calculated using the formation energy from equation 1.[14]

$$E_{\text{form}} = E(\text{Cu}_2\text{O nanostructure}) - xE(\text{Cu}) - yE(\text{O}) - zE(\text{dopant});$$

$$E_{\text{form}} = E(\text{ZnO nanostructure}) - xE(\text{Zn}) - yE(\text{O}) - zE(\text{dopant}) \text{ ----- (1)}$$

where E (Cu₂O nanostructure), E (ZnO nanostructure) represents the total energy of Cu₂O and ZnO respectively. E(Cu), E(Zn), E(O) is representing the corresponding energy of isolated Cu, Zn, O and E(dopant) represents the dopant atom namely Mn and F. Moreover x, y and z represent the to the Cu or Zn, O and dopant atom respectively. The formation energy of Cu₂O, ZnO, ZnO:Mn and ZnO:F nanostructures are -44.43eV, -60.10eV, -68.46eV and -

36.14eV respectively. From the observation the stability of anionic substitution ZnO has low compared with pure and cationic substitution.

Electronic properties of Cu₂O, pure and doped ZnO nanostructures

The electronic properties of Cu₂O and ZnO, ZnO: Mn and ZnO: F nanostructures debated in terms of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) [15]. Figure.3 shows the range of Density of States (DOS) values provides insight to density of charge along the Fermi level. The HOMO-LUMO gap varies arbitrarily because of overlapping of 3d orbits of Copper and Oxygen 2d orbits for Cu₂O. Similarly for ZnO structures, the gap varies with overlapping of 3d orbits of Zinc and 2d orbits of Oxygen.

The energy gap value for Cu₂O and pure ZnO is 1.18eV and 0.43 respectively. Depending upon the geometry of the structure, the band gap increases or decreases for doped with F or Mn to ZnO nanostructures respectively. When the energy gap increases, it leads to decrease in conductivity of ZnO nanostructures. For F substituted ZnO nanostructures, the energy gap further increases to 0.53eV and the energy gap decreases to 0.43eV for Mn substituted ZnO nanostructures. The resistivity of ZnO nanostructures increased due to substitution of fluorine atoms. Finally the electronic properties of ZnO nanostructures can be fine-tuned by increasing the number of atoms, substitution of proper impurities and by the creation of a defect. The tuning of the band gap in Cu₂O and ZnO leads to many applications like photo catalysis, photovoltaic cells and in lithium batteries etc., [15]

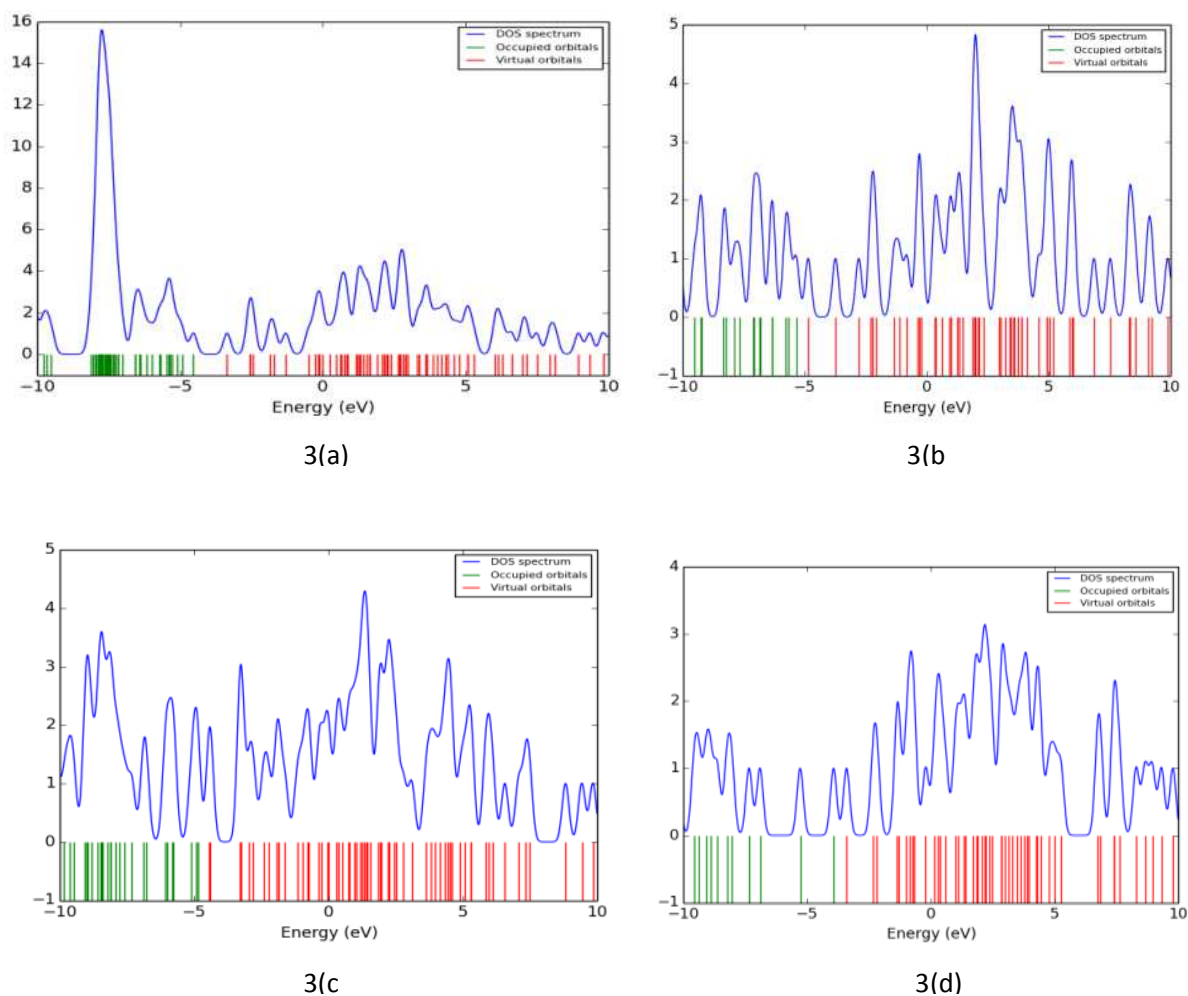


Fig. 3 The Density of state diagram for optimized structures of (a) Cu₂O, (b) ZnO, (c) ZnO:Mn (d) ZnO:F

Figure.4 shows HOMO- LUMO visualization clearly exposes that the electron cloud is an occupied orbital (green color) and in contrast the electron cloud is more in virtual orbit (red color) for defect structured nanostructure due to band gap.

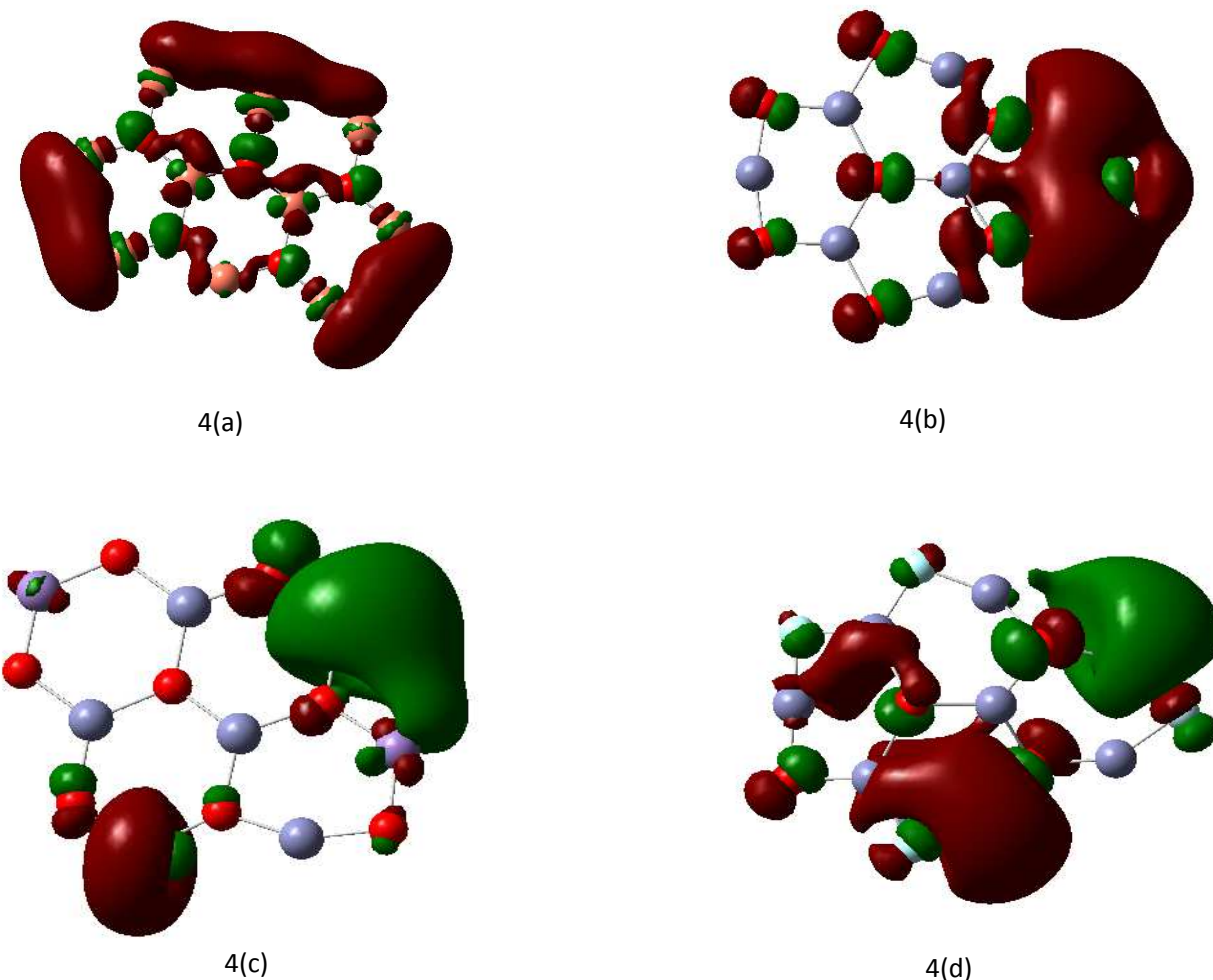


Fig. 4 HOMO-LUMO visualization band gap diagram of optimized structures of

(a) Cu_2O , (b) ZnO , (c) ZnO:Mn (d) ZnO:F

The band alignments of $\text{Cu}_2\text{O-ZnO}$, $\text{Cu}_2\text{O-ZnO:Mn}$ and $\text{Cu}_2\text{O-ZnO:F}$ heterojunctions are schematically drawn as Figure.5. From that, we can see the conduction band offsets (CBOs) for $\text{Cu}_2\text{O-ZnO}$, $\text{Cu}_2\text{O-ZnO:Mn}$ and $\text{Cu}_2\text{O-ZnO:F}$ are 1.5eV, 1.09eV and 0.04eV respectively. The Valance band offsets (VBOs) are determined to be 0.81eV for $\text{Cu}_2\text{O-ZnO}$ and 0.3eV for $\text{Cu}_2\text{O-ZnO:Mn}$. Interestingly, we can observe that the CBOs for $\text{Cu}_2\text{O-ZnO:F}$ is obtained within the Cu_2O band gap region. The 1.14eV difference moves the conduction band of ZnO:F closer to the vacuum level compared to ZnO ; we assumed that was changed in conduction band edge is responsible for the enhancement of open circuit voltage (V_{oc}) [8].

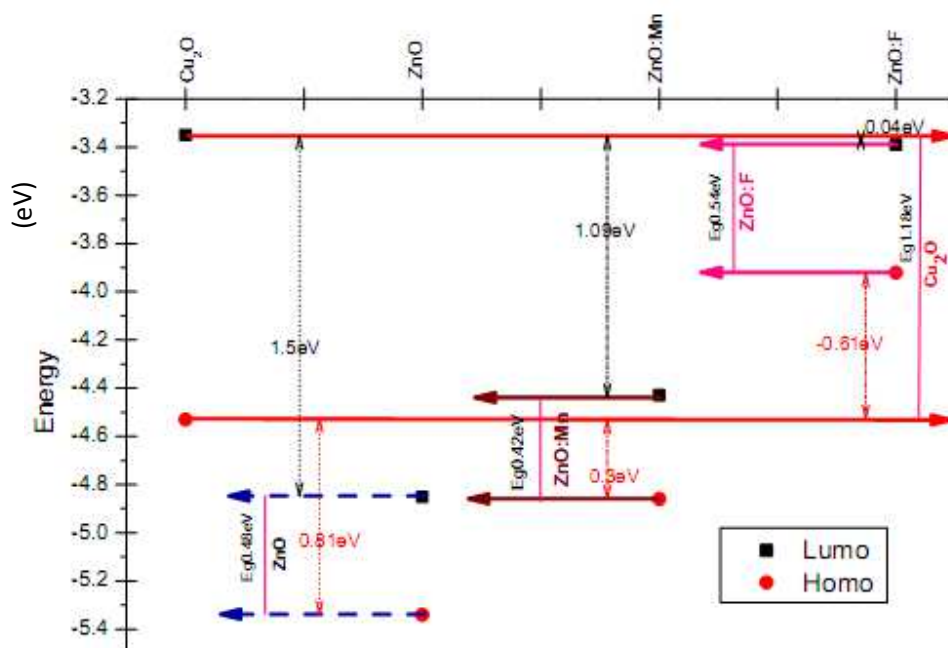


Fig.5. Schematic of the flat-band diagrams at the heterojunction for the $\text{Cu}_2\text{O-ZnO}$, $\text{Cu}_2\text{O-ZnO:Mn}$ and $\text{Cu}_2\text{O-ZnO:F}$

CONCLUSION

Using DFT, pure cupric oxide, pure zinc oxide and manganese substituted zinc oxide, fluorine substituted zinc oxide nanostructures are optimized with B3LYP/LanL2DZ basis set and simulated successfully. The structural stability of all nanostructures is discussed using formation energy and it was compared with observed energy. With the help of HOMO-LUMO gap, the influence of substituted nanostructures is discussed. $\text{Cu}_2\text{O-ZnO: X}$ ($X=\text{F}$ or Mn) heterojunction solar cell was simulated with HOMO-LUMO energy levels. The effect of $\text{Cu}_2\text{O-Fluorine}$ substituted ZnO heterojunction conduction band offset is closer to the vacuum level compare to other heterojunction nanostructures. We suspect that this change in conduction band edge is responsible for the enhancement of V_{oc} . In this study, the quantum chemical investigation of the geometries and electronic properties of cupric oxide, zinc oxide, manganese substituted zinc oxide and fluorine substituted zinc oxide nanostructure of these materials and to study the possibility to suggest these materials for solar cell application.

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