Density Functional Theory Study of surface properties of SnO_2 doped with nitrogen and chlorine for application in solar cells.

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INTRODUCTION

- DSSCs are composed of four major components: a wide band gap SnO_2 semiconductor, a dye-sensitizer to absorb photons from the sun, an electrolyte that creates the interface with the semiconductor and a counter electrode carrying an electro-catalyst, which facilitates transfer of electrons to the electrolyte [1,2].
- In DSSCs, a semiconductor absorb and facilitate transport of election into the cathode material. Due to optical band gap slightly above 3 eV SnO_2 is only photoactive in the UV region of electromagnetic spectrum and an inefficient active in DSSC.
- Introduction of the impurities reduces the band gap of semiconductor and shift the absorption from UV to Vis and near infrared

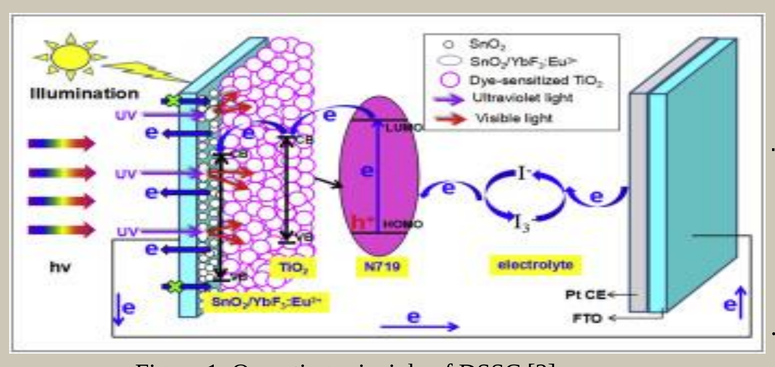
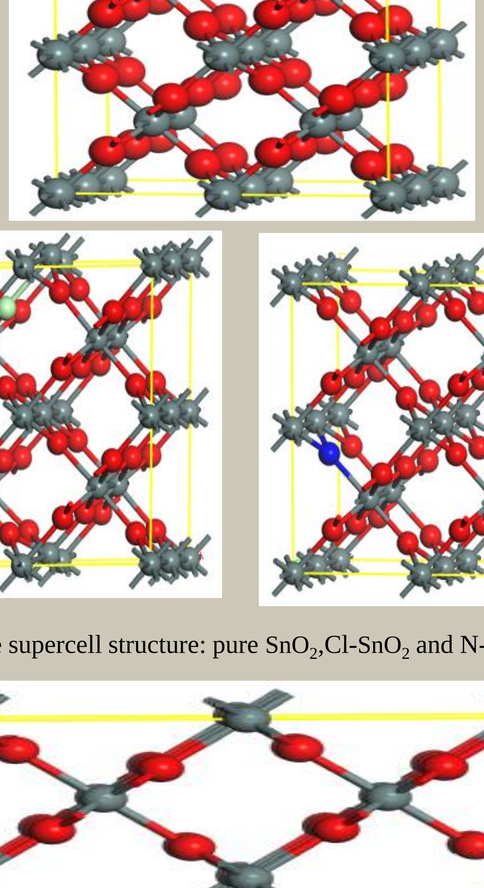
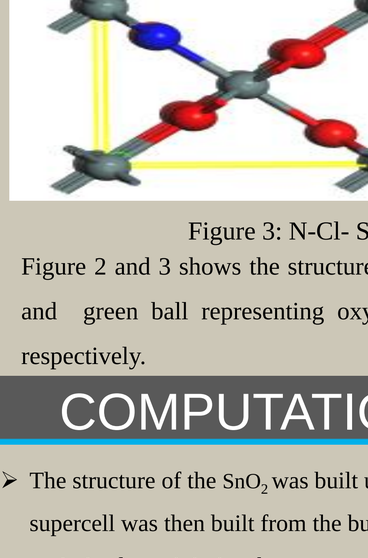


Figure 1: Operating principle of DSSC [3]

In this study, we carried out DFT study on the doped 2x2x2 supercell structure doped with Nitrogen and Chlorine .To understand the electronic and optical properties particularly the band structured ,DOS and absorption of $NaSnO_2$, $ClSnO_2$ and $CL\text{-}NSnO_2$.

STRUCTURES





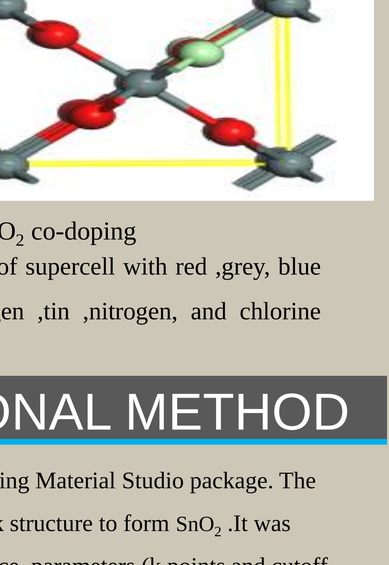


Figure 2:The supercell structure: pure SnO_2,$Cl\text{-}SnO_2$ and $N\text{-}SnO_2$ doped.

Figure 3: N-Cl- SnO_2 co-doping

Figure 2 and 3 shows the structure of supercell with red ,grey, blue and green ball representing oxygen ,tin ,nitrogen, and chlorine respectively.

COMPUTATIONAL METHOD

- The structure of the SnO_2 was built using Material Studio package. The supercell was then built from the bulk structure to form SnO_2 .It was optimized to minimize the convergence parameters (k points and cutoff energy) ,which were 4x4x6 and 650 eV respectively.
- The SnO_2 2x2x2 supercell was optimized using the CASTEP module in BIOVA Materials Studio [4], and the electronic and optical properties were calculated using CASTEP code.

RESULTS AND DISCUSSIONS

Band structure and density of state

The band structure and density of state are illustrated in figure 5 to figure7. In these figures it can be seen that the bottom of conduction band and the top valence band are located at the G point in the brollouin zone. There is a high peak in the conduction band which is near the fermi level and is contributed by the orbital electrons of nitrogen and chlorine atom. The valence band is controlled by O-2p,and some few Cl-2p and Sn-5s state. We have some states of Cl-2p and Sn-5s which are dominant in the conduction band minimum. Few p-state of N atom can be seen in the conduction band, but far from the fermi level hence ignored. The introduction of the new state contrast the band gap of the system

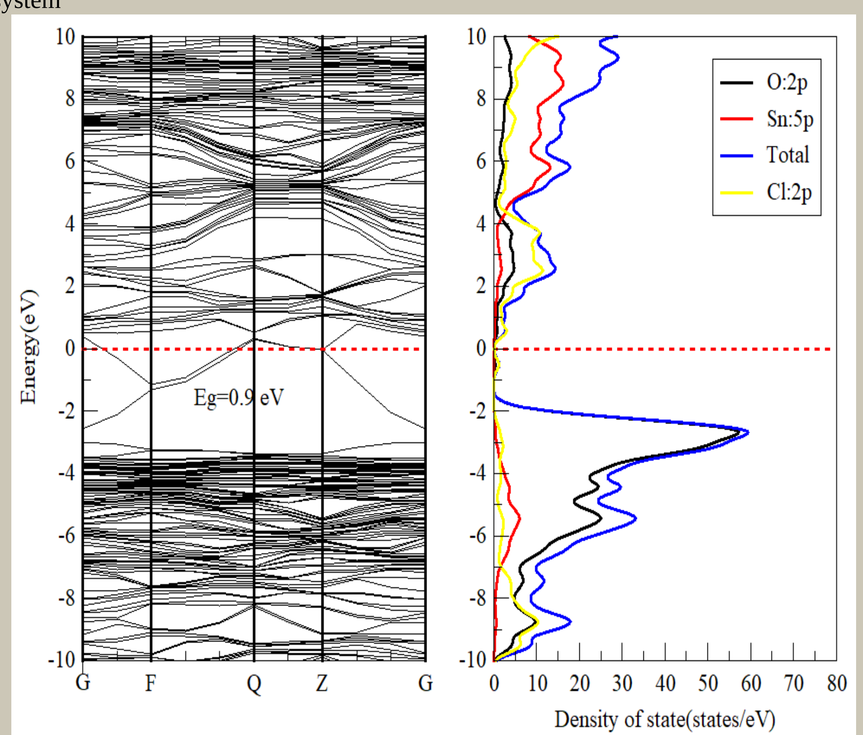


Figure 5: band structure and density of state of $Cl\text{-}SnO_2$

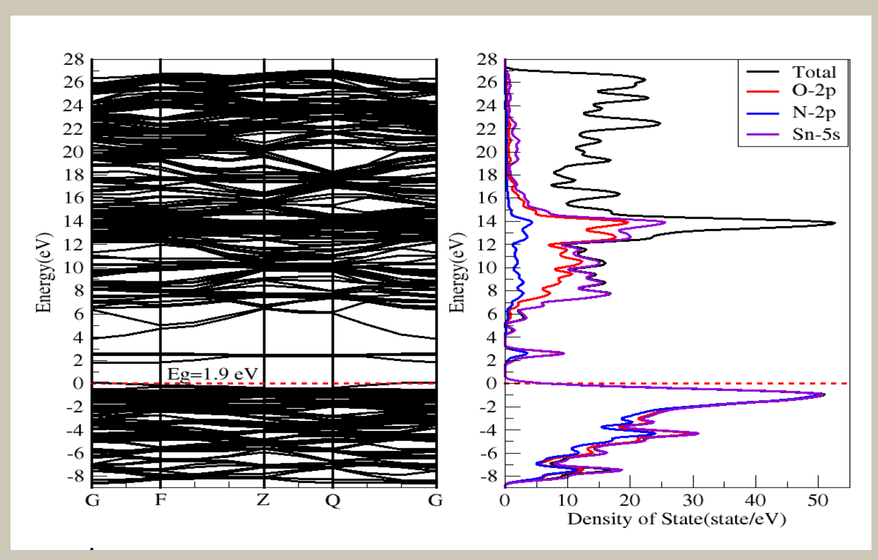


Figure 6: Band structure and density of state of $N\text{-}SnO_2$.

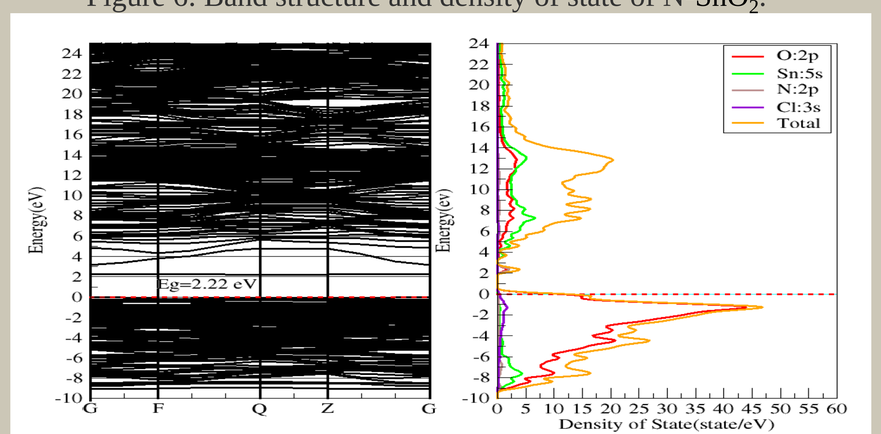


Figure 7: Band structure and density of state of $Cl,N\text{-}SnO_2$

Table 1: The lattice parameter of pure and doped SnO_2

Lattice parameter(Å)	a	b	c
Bulk	9.055	9.055	6.016
N	9.718	9.718	6.481
Cl	9.775	9.775	6.017
N-Cl	9.269	9.269	6.018
Literature[5]	9.349	9.349	6.299

The calculated equilibrium lattice parameters of pure ad doped structure are shown in the table .From the results we know that the lattice parameter of the doped structure will increase due to the difference in atomic radius of different elements. This results in the expansion of the parameter a and c.

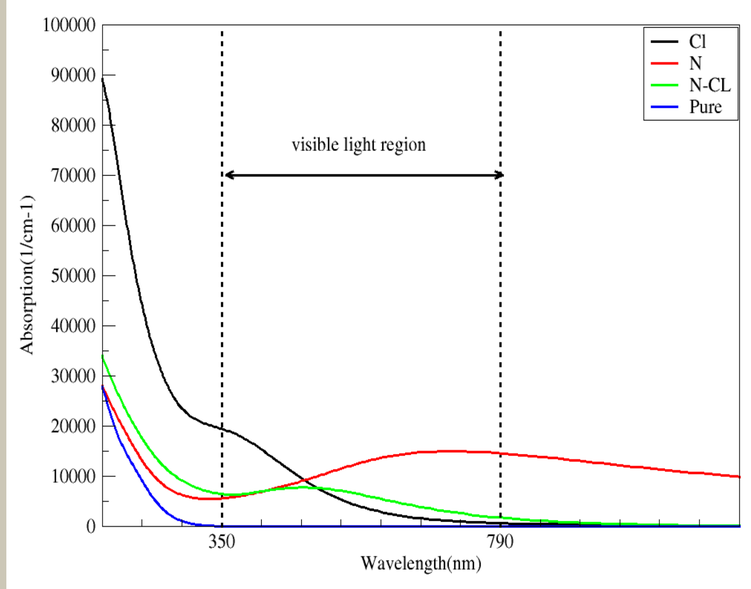


Figure 8: The absorption spectrum of pure and doped structure

The absorption of both doped and pure structure ,it follows from these figures that pure SnO_2 shows no activity in the visible region and the doped SnO_2 shows higher absorption coefficient in the visible and in the infrared. When a narrow-band semiconductor material is added to the meso-porous SnO_2 electrode the light absorption in the visible increases and hence the light harvesting efficiency increases of the DSSC[3].

CONCLUSION

In this work, we have studied the effect of nitrogen and chlorine on electronic and optical properties of SnO_2. The electronic properties particularly the band gap and density of state was calculated, Undoped SnO_2 shows intense absorbance in the wavelength range below 390nm exhibiting a band gap of 3.57 eV. The band gap was found to decrease from 3.57 eV to 0.9,1.9,2.2 eV for chlorine doped, nitrogen doped and for co doping of nitrogen and chlorine respectively.

Our findings generally suggests that doping and co-doping SnO_2 with in nitrogen and chlorine introduces new state and contrast the band gap which results in shifting the absorption from UV to Vis and near infrared and is preferable for SnO_2 semiconductors having this features for application in DSSCs.

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