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Electronic gap reduction in co-doped (Cu-N) anatase TiO₂ semiconductor: A DFT study

A.Suresh¹, N.Soundararajan¹, A.B.M. Ahmed¹*

¹School of Physics, Madurai Kamaraj University, Madurai. India

*Corres.author: abmahmed@gmail.com

Abstract: TiO_2 doped with metal atoms shows better photoconversion efficiency compared with undoped TiO_2 . In this work, we have calculated the electronic structure of monodoped and co-doped anatase TiO_2 . The calculations were carried out using Quantum ESPRESSO package which implements density functional theory and pseudopotential method. Our results show that band gap reduction in doped anatase titania and it is compared with the previous work. The chosen GGA and ultrasoft pseudopotential provides better band gap reduction. In dopant case, Cu creates acceptor levels just above the valence band and shifts conduction band to 1.9eV from 2.05eV and N substitution creates donor level just below to the conduction band. The PDOS explains the impurity states created by dopants.

Keywords: Semiconductors; Electronic Band Structure; Density Functional Theory; Band gap reduction.

Introduction

Among transition metal oxides, TiO_2 plays pivotal role in semiconductor energy industry due to its desirable properties such as chemical inertness, non-toxic nature and stability against corrosion[1-3]. However, because of its wide band gap (3.2 eV for anatase and 3.0 eV for rutile) its ability to harness the energy from solar radiation is limited. This shortcoming can be overcome by several methods such as structural modification, doping etc., [4-7]. Doping an element with TiO_2 is considered as the feasible and effective way of restructuring the bandgap of TiO_2 . Various dopants have been substituted in TiO_2 in which nitrogen(N) is considered as the favourable dopant which can reduce the bandgap of TiO_2 [8]. Though nitrogen doping may cause high recombination probability, the co-doping of metal atoms and nitrogen in TiO_2 [9-10] provides an effective way to reduce the recombination rate. This in turn leads to enhancement of photocatalytic activity. Various studies have been reported for co-doping of metal and non-metal atoms with TiO_2 . In this work, effects of co-doping of Cu and N in substitution positions in TiO_2 are investigated.

This paper is organised as follows. The Section II gives the computational details employed in this work. In Section III, the band structure, density of states and charge density results are discussed for undoped and co-doped TiO_2 cases. In Section IV, conclusions are drawn from the results.

In this present work, Quantum ESPRESSO computer simulation package used for calculations, which is based on density functional theory, the plane waves and pseudopotential method[11]. The electron-ion interaction and Exchange correlation term were treated by PW91 GGA functional type pseudopotential using Vanderbilt ultra soft method [12]. The convergence achieved at 4X4X2 mesh[13] for k-point sampling and 30Ry for energy cutoff of plane wave expansion. The equilibrium volume was obtained by volume

optimisation. Final forces on atoms were less than 0.003 Ry/a.u. Supercell comprising of 48 atoms of anatase was constructed. The pure supercell was monodoped with nitrogen in place of oxygen and copper in place of titanium separately and then co-doped with Cu and N constructed for band structure calculations. All structures pure, monodoped and co-doped were optimized using BFGS quasi Newton algorithm. Brillouin zone integration was carried out by gaussian smearing methods.

Computational details



Fig.1 (a) Anatase Supercell with 48 atoms where red ball indicates O atom and large sized ball indicates Ti atom (b) High Symmetry k-points along Irreducible brillouin zone

Anatase TiO₂ has a tetragonal structure and its experimental lattice parameters are a = b = 3.785 Å and c = 9.514 Å[14]. First anatase unit cell was optimized and its lattice parameter are a = b = 3.791 Å and c = 9.63Å. Then 2x2x1 structure is created by using optimized single unit cell structure and optimized successively and their values are a = b = 7.582 Å and c = 9.634 Å. After Cu dopant introduced into the structure, once again the structure was optimized. Cu atom is substituted into anatase structure in Ti lattice site with the atomic ratio of 0.0625. After geometry optimisation the lattice parameters are a = b = 7.593 Å and c = 9.621 Å. Then N atom is substituted into the lattice by removing one oxygen atom and the optimized lattice parameter were a = b = 7.615 Å and c = 9.62186 Å. And lattice parameter of co-doped structure were a = b = 7.629 Å and c = 9.589 Å. Optimized lattice parameter of all structures showed slight changes indicating stability of doped system. Total energy of both monodoped and co-doped structures shows that they are energetically favourable.

Results and Discussion

Among three mineral forms of titanium dioxide, the anatase shows the strongest photocatalytically activity than other two. It has indirect band gap of value 3.2 eV. Anatase has tetragonal structure with four formula units in its structure. In order to study the photocatalytic activity of both mono doped and co-doped anatase, we have constructed an anatase supercell and substituted dopants into the anatase structure.

. Along high-symmetry directions of irreducible brillouin zone the self-consistent band structure has been calculated. Fig.2 shows the calculated band structure diagram for anatase and its doped structures. The valence band maximum of pure anatase supercell has been set as reference for all other doped structures. The calculated electronic band gap for pure anatase supercell was 2.05eV. This band gap value is smaller than experimental value and 0.14eV higher than previous theoretical work ¹⁰. We got indirect transitions from valence band at M to conduction band at G as the minimum gap which is consistent with the previous electronic structure studies by LMTO and OLCAO methods ^{15,16,17}.



(a) (b) (c) (d) Fig. 2 Band structure of (a) anatase supercell, (b) N-doped (c) Cu-doped, (d) Cu-N doped supercells

The substitutional dopants (both Cu and N) created impurity states in electronic band structure of anatase. The Cu introduced two lone pair states just above to the valence band minimum thus reduced the band gap of TiO_2 . In Cu doped case, the band gap value is reduced to 1.95 eV from 2.05 eV. The N doped structure exhibits impurity states right below to the conduction band minimum. Both Cu-N co-doped structures further reduce band gap value to 1.8 eV. In all cases, valence band minimum predominantly made by O-2p orbital. Lower valence bands show hybridisation between O-2p and Ti-3d orbital and they are covalent bond in nature. Bottom of conduction band consists of mostly by Ti 3d orbital and rest of the bands are non- bonding states with oxygen atom ¹⁸. Doping and co-doping of Cu-N in anatase structure slightly modify the local bond length around their positions. And all their volumes are almost same.

Density of States

The projected density of states (PDOS) is calculated using linear tetrahedra method. The bond length between Cu - O is reduced by 0.05Å than pure relaxed supercell. Fig. 3 show total PDOS of anatase and doped structures and Fig. 4 show PDOS of individual atoms contribution to band structure. PDOS supports the calculated band structure in which oxygen O-2s orbital mainly contributes to the band which is lower to the valence band. And the upper valence band is made up of O-2p orbitals. As discussed in band structure PDOS shows hybridization of oxygen p-orbital's with Ti-3d orbital.



Fig. 3 Total Density of States of (a) Anatase (b) N-Doped (c) Cu-Doped (d) Cu-N-Doped supercells



Fig. 4 PDOS of pure and co-doped structures

One new band occurs between valence band and conduction band due to N introduction in the anatase structure which is clearly shown in Figure 3. Nitrogen p orbital contributes to valence band and introduces one impurity state right below to the conduction band minimum. In Cu doped structure oxygen occupies valence bands as in pure supercell but Cu reduces band gap by extending valence band's maximum to upper level. PDOS clearly shows oxygen 2p orbital contributes to valence band maximum and there is hybridization with Cu 3d orbital. Cu atom does not contribute to conduction bands. Over all band gap is reduced by both Cu-N co-doping which is clearly shown in PDOS.



Fig. 5. Charge density plot for pure anatase supercell (a) lowest valence band (b) upper valence band (c) upper conduction band



Fig. 6. Charge density plot for Nitrogen doped anatase supercell (a) lowest valence band (b) upper valence band (c) upper conduction band



Fig. 7. Charge density plot for Copper doped anatase supercell (a) lowest valence band (b) upper valence band (c) upper conduction band



(a) (b) (c) (d) (e) (f)
Fig. 8. Charge density plot for Cu-N co-doped anatase supercell (a) lowest valence band around N atom
(b) lowest valence band around Cu atom upper valence band (c) upper valence band around N atom (d) upper valence band around Cu atom (e) conduction band around n atom (f) conduction band around Cuatom

Charge Density

To show the chemical bonding nature and to support PDOS features of both doped and pure supercell, charge density plot has been drawn with the help of Xcrysden software[18]. Charge plot has been calculated at k-point which is intermediate point between gamma and M point. The 2D charge density plots from Fig. 5-8 clearly describe the bonding nature of valence and conduction bands in which bands are divided into three main regions. The most stable bonding occurs between O-2p and Ti-3d orbital which is located at lower valence bands. In middle and upper valence bands O-2p and Ti-3d hybridisation occurs but their charge plot shows non-covalent bonding in nature. The bottom of conduction bands is made up of mainly by Ti-3d orbital and there is overlap between O-2p and Ti-3d orbital. All other bands are of 3D orbital are non-bonding states with the O-2p orbital which is clearly shown by charge plot[19].

The new bands introduced into the band structure by Cu are made up of 3D orbital. These orbital shows non-bonding states with O-2p orbital. In valence band, oxygen O-2p orbital making bonding with Ti-3d orbital where this is not happened at pure supercell. The top most valence band of Cu doped system is purely made by Cu-3d (d_{z2}) orbital which also shows non-bonding character with O-2p orbital and this feature shown in Fig. 5-8. The whole conduction band is contributed by Ti-3d orbital in all doped structures. Nitrogen atom makes bond with surrounding Ti atom at valence band and shows non-bonding states with Ti atom at conduction band. While in co-doped case dopant's monodoping features reflects at co-doped system.

Conclusion

Density functional theory studies have been carried out for anatase supercell and Cu and N co-doped supercell consisting of four unit cell in its structure. The optimized structure and its unit cell parameters compared with the previous and experimental work and they are in good agreement with the existing results.

Electronic band structure shows reduction by Cu doping which is higher than the previous simulation work. Similarly N and co-doping considerably reduced the band gap. The PDOS explains bonding nature between pure and doped system and the charge plot supports band structure and PDOS.

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