First-Principles Study on Anatase Co/TiO$_2$: Effect of Co Concentration

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Abstract This study was performed to comprehend the systematic analysis of the cobalt impurity states in different concentrations as well as their influence on the TiO2 band structure and density of states. For thisporpuse, first principle plane wave pseudo-potential technique based on density functional theory with CASTEP module were used. The calculations showed that band gap of Co-doped TiO2 decreases with an optimal doping concentration of 20% as a result of the overlap among the Co 3d, Ti 3d, and O 2p states, which enhances photocatalytic activity in the visible light region.

Keywords Molecular simulation, Castep, Band stracture, Density of states

1. Introduction

Anatase TiO$_2$ became the most widely investigated semiconductor in many fields such as solar cells, air and water pollution controlling. The anatase phase TiO$_2$ has been employed the photocatalytic activity only under the ultraviolet (UV) light illumination due to its large indirect band gap ca 3.2 eV. Considerable research has gone into modifying the band gap of TiO$_2$. One of the most effective methods involves Dopping of transition metal ions into TiO$_2$ [1-9].

Since then, different metals have been doped into TiO$_2$ nanomaterials. Commonly assumed knowledge says that the noble metal ion acts as a sink for photoinduced charge carriers, and this promotes interfacial charge-transfer processes. Li et al. developed La^{3+}-doped TiO$_2$ via sol–gel and found that lanthanum doping inhibits phase transformation of TiO$_2$, enhances its thermal stability, reduces its crystallite size, and increases Ti^{3+} surface content [10]. Bessekhouad et al. investigated Li, Na and K doped TiO$_2$ nanoparticles and found that the crystalline levels were largely dependent on both the nature and the concentration of the alkaline. [11].

Doping an element with TiO$_2$ is considered as the feasible and effective way of restructuring the bandgap of TiO$_2$. The doping of semiconductors changes the probabilities for charge carriers to participate in conduction. This probability were quantified by the density of states within the semiconductor as a function of electron energy. This density of states combined with the probability distribution of a state at a particular energy being occupied will determine the overall density of charge carriers as a function of energy. In order to quantify the possible energy states available in a quantum mechanical system we need solutions to Shrodinger's equation.

However, the theoretical analysis by computer simulation could clarify the ion doping effects on crystal and electronic structure. The use of quantum mechanical calculations to accurately predict the structure and properties of crystals is going to have significant implications for the studies of semiconductors.

CASTEP is a first principles electronic structure code for predicting properties of materials. It employs the density functional theory plane-wave pseudopotential method, which allows to perform first-principles quantum mechanics calculations that explore the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites [12-14].

Ashahi et al have performed first-principles calculations using the full-potential linearized augmented plane-wave method to investigate detailed electronic and optical properties of TiO$_2$ in the anatase structure [15].

Segall et al have studied the band structures and charge densities of nitrogen, carbon and boron doped TiO$_2$ by first-principles simulation with the CASTEP code [16].

Andriyevsky et al have studied Electronic band structure, density of states and complex dielectric function of KDP crystal at Fdd2 and space groups of symmetry corresponding to the ferroelectric and paraelectric phases, have been calculated within the density functional theory using the VASP code. The experimental data and theoretically calculated dielectric functions have demonstrated a good agreement [17].

To obtain insight into this issue, we have performed a careful and systematic analysis of the cobalt impurity states in different concentrations as well as their influence on the TiO$_2$ band structure and density of states.
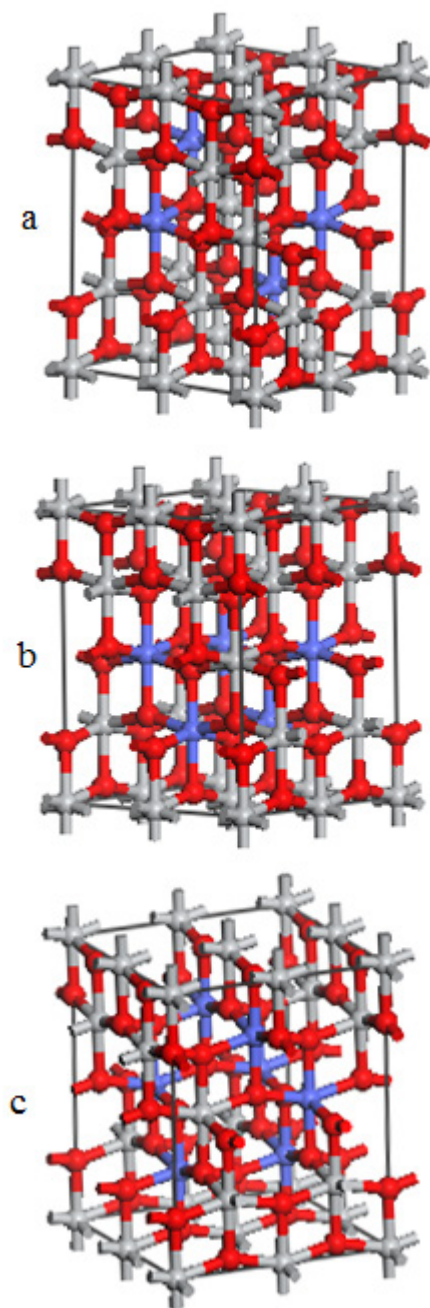
Figure 1 shows the supercell structures of crystalline Co-doped TiO$_2$. The pure supercell was monodoped with cobalt in place of titanium.
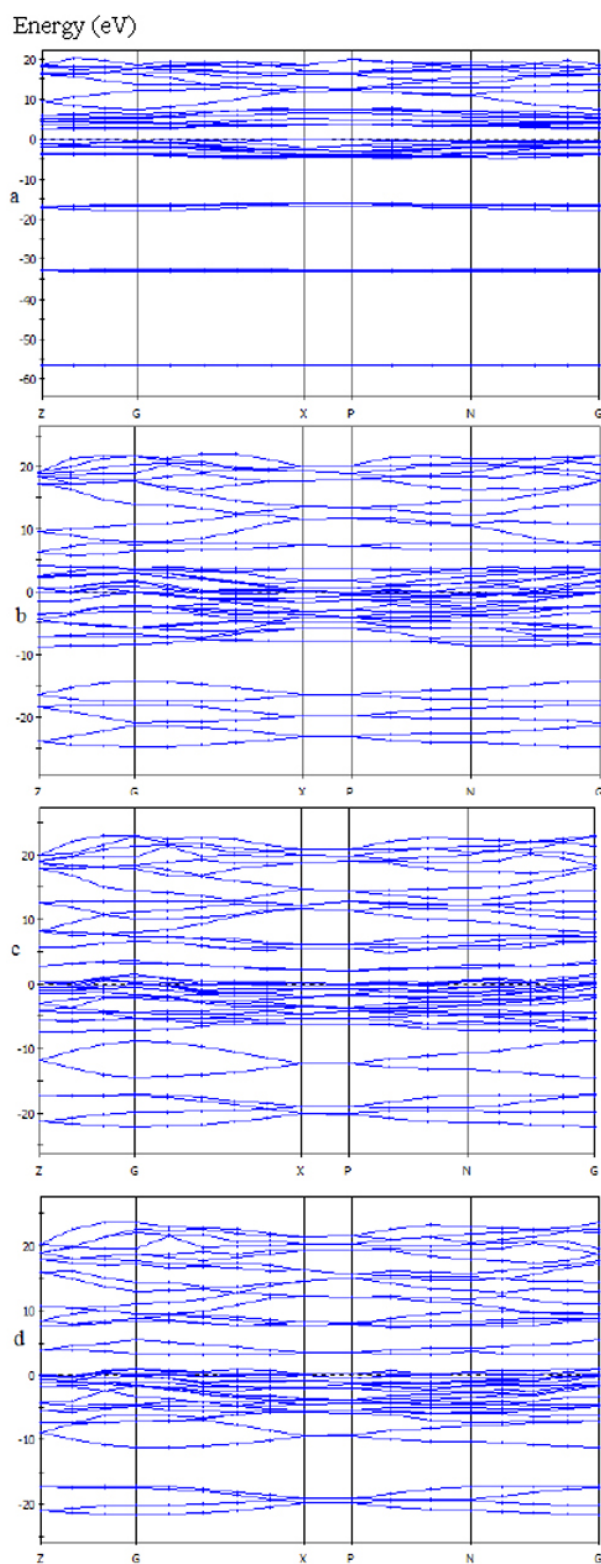

Figure 1. $2 \times 2 \times 1$ supercell models with various concentrations of Co: (a) 15%, (b) 20%, (c) 25%

2. Computational Details

All presented calculations were performed using a first principle plane wave pseudo-potential technique based on density functional theory with CASTEP module [13] of Materials Studio. The density functional is treated by GGA with the exchange correlation potential parameterization.

Figure 2. Band stracture of undoped TiO$_2$ (a) and TiO$_2$ doped with Co 15% (b), 20% (c), 25% (d). The horizontal dotted line is the Fermi energy level

To calculate various concentrations of Co, a $2 \times 2 \times 1$ supercell was constructed with 16 Ti and 32 O atoms, as shown in Figure 1. The calculations for the doping system were conducted for the $2 \times 2 \times 1$ supercell containing 4, 5, and 7, Co atoms in the substitutional sites of the Ti atoms, as shown in Figures 1a-c.

Figure 3. Density of states (DOS) of undoped TiO$_2$ (a) and TiO$_2$ doped with Co 15 % (b), 20 % (c), 25 % (d). The vertical dotted line is the Fermi energy level

3. Result and Discussion

Anatase TiO_2 has a tetragonal structure with two lattice parameters a = b = 3.785 Å and c = 9.514 Å[14] and belongs to the space group 141/amd.

In this study, first anatase unit cell was optimized and its lattice parameter are a = b = 3.791 Å and c= 9.63Å. The energy band structure and density of states (DOS) for pure anataseTiO_2 is obtained within the GGA approximations that are shown in Figures 2a and 3a respectively.

Then, Co dopant is substituted into anatase structure in Ti lattice site in various concentrations(15, 20 and 25%), once again the structure was optimized. Total energy of doped structures shows that they are energetically favourable. The valence configurations of the atoms were $3s^2 3p^6 3d^2 4s^2$ for Ti, $2s^2 2p^4$ for O, and $3d^7 4s^2$ for Co.

Figure 2a shows that the top of valence bands (VBs) appears to be relatively flat and the bottom of conduction bands (CBs) have small dispersion. The Fermi level, indicated by a dotted line, is also valence band maximum and was set to zero. The band structure of pure anatase TiO_2 shows semiconducting behavior because in this case direct energy band gap is 2.29 eV. It is less than the experimental value Eg = 3.23 eV. this underestimation is an intrinsic feature of the generalized-gradient approximation (GGA).

In figure 3a, we can also clearly see the conduction bands, are mostly formed by Ti-4d state, with a contribution of the O-3 p states, while the valance bands are mainly consist of the hybridizations of Ti-3d states and O-2p states.

Using the first-principle calculations the electronic structures and band parameters for Co/TiO_2 in varius concentration (15, 20 and 25%) are obtained within the same approximations. The energy band structure and density of states (DOS) of Co/TiO_2 in concentration 15, 20 and 25% are shown in Figures. 2b-d and 3b-d respectively.

Figure 2 and 3 shows the substitutional Co dopant created impurity states in electronic band structure of anatase. The Co introduced two lone pair states just above to the valence band maximum thus reduced the band gap of TiO_2 with an optimal doping concentration of 20%.

The band gap values are reported in table 1. As presented in table 1, the band gap is decreased to1.88 and 1.59 for cobalt content 15 and 20% respectively, while an increased band gap is observed in cobalt concentration 25%.

Table 1. Experimental and calculated band gaps of TiO_2 and Co/TiO_2

sample	Band gap (eV)	
	calculated	Experimental
TiO_2	2.29	3.23
Co/TiO_2 15%	1.88	-
Co/TiO_2 20%	1.59	1.64
Co/TiO_2 25%	2.22	-

4. Conclusions

The DOS and band structure of cobalt doped TiO_2 indicated that the cobalt dopant induced the band gap narrowing. Thus the performance of TiO_2 can be enhanced by shifting the absorption spectrum into the visible region. It is apparent that the band gap shifts towards lower values with the increase in Co concentrations. The decreasing trend of band gap with the increasing dopant level indicates that more number of free electrons is available for charge conduction.

In addition, the variation of the band gap showed the band gap is greatly sensitive to the dopant concentration. It is observed that, higher concentrations of cobalt facilitate conductivity of TiO_2. It is important to note that, at moderate level of doping (20%) exhibits the lowest band gap. Further increase in dopant concentration until 25% results in larger band gap. Therefore the best concentration of cobalt dopant was 20% based on the first-principles calculations.

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