International Journal of Optics and Applications 2015, 5(5): 147-150
DOI: 10.5923/j.optics.20150505.01

Optical and Dielectric Properties of Co Doped TiO_2 as Judged by Simulation Analysis

Yasaman Abed[1], Fatemeh Mostaghni[2,*], Mostafa Khosravi[1]

[1]Department of Physic, Payam Noor University, Iran
[2]Department of Chemistry, Payam Noor University, Iran

Abstract In this paper, anatase TiO_2 has been doped with three different concentrations of cobalt. Absorption, dielectric and the consequent optical nano-composite refraction constants have been calculated according to density function theory (DFT) and by using castep calculation method. LDA+U approximation has been used for correlation and exchange effects and results have been compared by experimental method. The calculations showed that by increasing Co concentration, dielectric constant will increase and structure of the main spectrum goes toward less energy which satisfies the corresponding experimental data result. Also the results showed that band gap of Co-doped TiO_2 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, Elastic, Dielectric constant, Optical properties

1. Introduction

Titanium dioxide is an important member of the II-VI semiconductor family, with a band gap of 3.23 eV. Titanium dioxide has attracted the attention of many researchers because of its unique physical properties for electrical and photoelectrical applications. Under UV light illumination, TiO_2 undergoes charge-transfer processes and produces electron-hole pairs on the surface. Nowadays solar cells are produced based on titanium dioxide, which can be named as the new generation of photovoltaic cells. It can be proposed as an alternative to solar cells due to its low cost [1-2].

To improve its efficiency, great efforts have been made to reduce the band gap of TiO_2, most of those are through doping of foreign elements such as Cr, Fe, Co, Mo, N, and C [3-5].

The titanium dioxide has three different structures, anatase rutile and brookite. It should be noted that the shapes of the crystallites vary with preparation techniques [6]. TiO_2 will be usually crystallized in anatase form at low temperature. As temperature goes up, the metastable anatase phase will be changed to a stable rutile phase in a transformation. Size and morphology are two important parameters for measuring and identifying physical properties of nanoparticles which are affected by the production method.

* Corresponding author:
mostaghnif@yahoo.com (Fatemeh Mostaghni)
Published online at http://journal.sapub.org/optics

Nowadays, the development of ab initio molecular dynamics methods 1–3 within the density functional local density approximation has lead to a significant improvement in the understanding of material properties on an atomistic level [7, 8].

In this study, the effect of increasing of cobalt to titanium dioxide anatase and the impact of dopant concentration have been investigated by using molecular simulations on optical and dielectric properties of nanocomposites. To investigate these properties, we performed ab-initio pseudopotential calculations with the local density approximation (LDA+U) of the density functional theory (DFT).

2. Computational Details

Castep software has been used in this study and the calculations have been done based on density functional theory [9, 10]. To calculate the exchange-correlation energy in the Cohen-Sham equations, LDA+U approximation has been used [11]. The number of K points used to study of the optical properties is 3,000 points. TiO_2 anatase has space group of 141/AMD and a tetragonal form. Titanium and oxygen atom coordinates in this crystal was at (0,0,0) and (0,0,0.23) respectively. The orbital atom structures in compounds are for titanium: $3S^2 3P^6 3d^2 4S^2$, oxygen: $2S^2 2P^4$ and cobalt: $3d^7 4S^2$. Lattice parameters used for this cell were a = b = 3.7834 and c = 9.4841. The super cell 4 × 4 × 2 has been used in this study.

3. Results and Discussion

3.1. Optical Properties

One of the optical quantities which is greatly affected by impurities is energy gap. The energy gap determines the threshold for absorption of photons in semiconductors. Here, the effect of different concentrations of cobalt dopant on energy gap has been examined. For this purpose, the absorption spectrum of cobalt doped titanium dioxide with three concentrations (15-20-25) has been simulated in the UV-Vis wavelength range, 200-800 nm. To calculate the energy gap, we use following equation [12]:

$$(\alpha h\vartheta)^{1/2} = B(h\vartheta - E_g) \quad (1)$$

Where hν is the photon energy, Eg is the energy gap and B is an interconstant (between10^5-10^6). To calculate the optical band gap, we draw $(\alpha h\nu)^{1/2}$ in terms of hν and extend the linear part of the chart to cut the hν axis (extrapolation). The cut place of the graph is the energy gap (Figure 1), and the results are listed in Table 1.

Table 1. Band gap values for pure and cobalt doped TiO_2

Compound	E_g	
	computational	experimental
TiO_2	2.86	3.08 [13]
$Co_{15}Ti_{85}O_2$	2.72	-
$Co_{20}Ti_{80}O_2$	1.66	1.66 [14]
$Co_{25}Ti_{75}O_2$	2.17	-

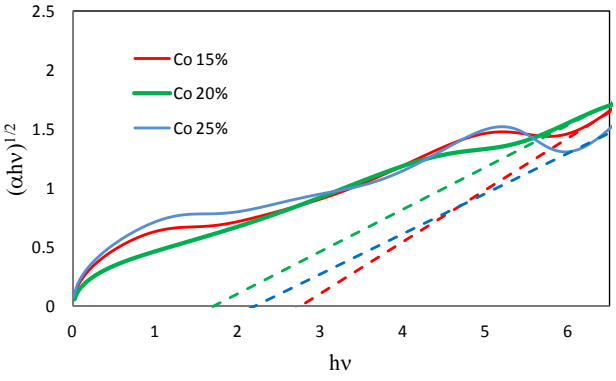

Figure 1. UV-Vis diffuse reflectance spectra and plot $(\alpha h\nu)^{1/2}$ vs. photon energy of Co/TiO_2 15% , 20% and 25%

As can be seen the energy gap of doped samples is less than that of a pure form. Increasing the cobalt will result in the enhancement of the magnetic properties of the sample. As a result, the interactional potential becomes stronger and the energy gap is reduced in relation to pure form.

According to the energy gap, we find that at first energy gap decreases by increasing cobalt until it reaches 20% concentration, its best rate, and the energy gap increases by increasing the concentration.

3.2. Dielectric Constant

Complex dielectric function describes optical properties of a compound. These dielectric functions have contributions from interband (inter) and intraband (intra) electron transitions, which can be written as below [15]:

$$\varepsilon_{exp}(\omega) = \varepsilon_{inter}(\omega) + \varepsilon_{intra}(\omega) \quad (2)$$

The interband electron transitions is calculated by real part Re (ε) of dielectric function. Interband contributions are due to electron transitions from occupied to empty bulk bands separated by an energy gap. The intraband is calculated by the imaginary part Im(ε) of dielectric function. Intraband contributions come from electron transitions at the Fermi level in incompletely filled bands, or when a filled band overlaps in energy with an empty band.

Dielectric function is used to describe the response of the crystal to the electromagnetic field; it depends on the electron band structure of the crystals. Studies of the dielectric function, using optical spectroscopy, to determine the entire band structure are very useful.

Imaginary part of dielectric function is shown by the following equation [16].

$$Im(\varepsilon(\omega)) = \left(\frac{4\pi^2 e^2}{m^2\omega^2}\right)\sum\int \langle i|M|j\rangle^2 f_i(1-f_i) * \delta(E_f - E_i - \omega)d^3 \quad (3)$$

Where i, j are the initial and final states respectively, M is a bipolar matrix, Fi is the distribution form function for i state and Ei is the electron energy in the i-th state. The real part of the dielectric function Re(ε) is calculated by following equation in which P is the principal amount of integration [17].

$$Re(\varepsilon(\omega)) = 1 + \frac{2}{\pi}P\int_0^\infty \frac{\omega\acute{\varepsilon}_2(\acute{\omega})}{\acute{\omega}^2-\omega^2}\, d\acute{\omega} \quad (4)$$

In Figure 2, the real part of the dielectric function and refractive index has been shown for Co/TiO_2 samples.

In Re(ε) minimum area, the function is negative, i. e.; the waves will not be published in these areas. In these areas, called unauthorized areas, we have the processes of absorption and dissipation.

According to the Re(ε) chart, we found that by increasing cobalt concentration, the main structure of the spectral shifted to the lower energies, i. e., the roots of the real part of the dielectric function occurs at lower energies.

One of the main values in investigating Re(ε) spectrum, is the static dielectric constant, which is the real value of Re(ε) in zero energy, which has been calculated here by LDA+U for different concentrations and have been reported in Table 2.

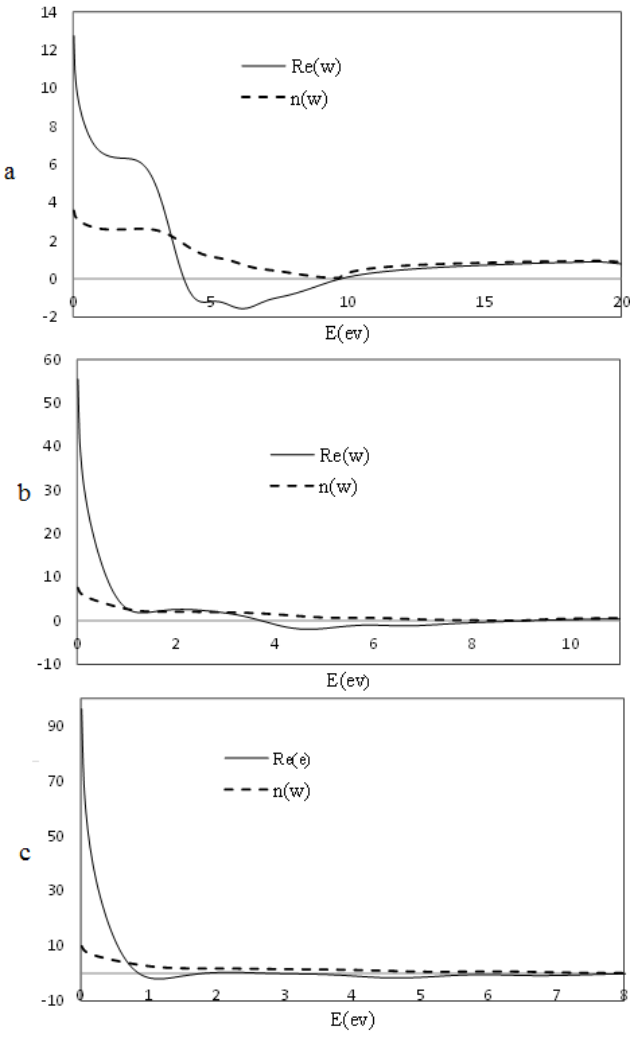

Figure 2. The real part of the dielectric function and refractive index of Co/TiO_2 15% (a), 20% (b) and 25% (c)

Table 2. The computational results of static dielectric constant and static refractive index

Sample	static dielectric constant	static refractive index
TiO_2	6.14	2.47
Co/TiO_2 15%	12.7	3.56
Co/TiO_2 20%	27.9	5.29
Co/TiO_2 25%	55.5	7.45

The relationship between the real and imaginary parts of the dielectric function is shown below [18].

$$Re(\varepsilon(\omega)) = n^2(\omega) + K^2(\omega) \quad (5)$$

$$Im(\varepsilon(\omega)) = 2n(\omega)K(\omega) \quad (6)$$

Where n(w) is a real part of the refractive index. The static refractive index is the root Re(ε) in zero energy. K(w) is the refractive index of the imaginary part, which is also called extinction coefficient.

Extinction coefficient for a substance is measuring the amount of absorption of electromagnetic radiation by that substance. If the electromagnetic wave passes easily through it, the substance has a low extinction coefficient and vice versa, if the radiation penetrates the substance barely, it has a high extinction coefficient. Real part of the refractive index has been shown in Figure 2.

The results showed that dielectric constants increases with increasing Co concentrations. This is the expected result, since the dielectric constant changes are inversely related with the threshold optical transitions, i. e., the trend of gap change.

4. Conclusions

According to the energy gap, we find that at first energy gap decreases by increasing cobalt until it reaches 20% concentration, its best rate, and the energy gap increases by increasing the concentration. Also, as cobalt increases, dielectric constant increases and structure of the main spectrum goes toward less energy. In addition, our calculations showed that the most absorption in visible region belong to Co doped TiO_2 20%.

ACKNOWLEDGEMENTS

We are thankful to the Payam Noor University for their support and encouragements.

REFERENCES

[1] Henderson, M. A., 2011, A surface science perspective on TiO_2 photocatalysis, Surface Science Reports, 66, 185–297.

[2] Fujishima, A., Zhang, X., and Tryk, D. A., 2008, TiO_2 photocatalysis and related surface phenomena, Surface Science Reports, 63, 515–582.

[3] You, M., Kim, T. G., Sung, Y., 2010, Synthesis of Cu-doped TiO_2 nanorods with various aspect ratios and dopant concentrations, Crystal Growth and Design, 10, 983-987.

[4] Liu, Y., Zhou, H., Li, J., Chen, H., Li, D., Zhou, B., and Cai, W., 2010, Enhanced photoelectrochemical properties of Cu_2O-loaded short TiO_2 nanotube array electrode prepared by sonoelectrochemical deposition, Nano-Micro Letter, 2(4), 277-284.

[5] Zhu, S., Shi, T., and Liu, W., 2007, Direct determination of local structure around Fe in anatase TiO_2, Physica B, 396(1-2), 177–180.

[6] Asahi, R., Taga, Y., Mannstadt, W., and Freeman, A.J., 2000, Electronic and optical properties of anatase TiO_2, Physics Review B, 61, 7459–7465.

[7] Trani, F., Vidal, J., Botti, S., Marques, M. A. L., 2010, Band structures of delafossite transparent conductive oxides from a self-consistent GW approach, Physics Review B, 82, 085115.

[8] Bhatt, R., Bhaumik, I., Ganesamoorthy, S., Karnal, A. K., Swami, M. K., Patel, H. S., Gupta, P., and Operties K., 2014, Urbach tail and bandgap analysis in near stoichiometric $LiNbO_3$ crystals, Physics Status Solidi A, 6(4), 17-22.

[9] Materials Studio 6.0 software manual (2011).

[10] Milman, V., Winkler, B., White, J. A., Packard, C. J., Payne, M. C., Akhmatskaya, E. V., and Nobes, R. H., 2000, International Journal of Quantum Chemistry, 77, 895910.

[11] First, Noor, N. A., Ikram, N., Ali, S., Nazir, S., Alay-e-Abbas, S. M., and Shaukat, A., 2010, principles calculations of structural, electronic and optical properties of $Cd_x Zn_{1-x} S$ alloys, Journal of Alloys and Compounds, 507 (2), 356-363.

[12] Mai, W., Wen, F., Xie, D., Leng, Y., Mu, Z., 2014, Structure and composition study of carbon-doped titanium oxide film combined with first principles, Journal of Advanced Ceramics, 3(1), 49–55.

[13] Kernazhitsky, L., Shymanovska, V., Gavrilko, T., Naumov, V., Kshnyakin, V., 2013, Optical absorption of polydisperse TiO2: Effect of surface doping by transition metal cations, Ukrainian Journal of Physical optics. 14(1), 15-23.

[14] Mostaghni, F., Abed, Y., 2015, First-Principles Study on Anatase Co/TiO_2: Effect of Co Concentration, Physical Chemistry, 5(2), 34-38.

[15] Amrosch-Draxl, C., and Sofo, J. O., 2006, Linear optical properties of solids within the full-potential linearized augmented planewave method, Computer Physics Communications, 175, 1-14.

[16] Fang, R. C., 2003, Solid Spectroscopy, Chinese Science Technology University Press, Hefei.

[17] Okoye, C. M. I., 2003, Theoretical study of the electronic structure, chemical bonding and optical properties of $KNbO_3$ in the paraelectric cubic phase, Journal of Physics Condensed Matter, 15, 5945-5958.

[18] Zhang, Y., and Shen, W. M., 2005, Basic of Solid Electronics, Zhe Jiang University Press, Hangzhou.