Int. J. Nanosci. Nanotechnol., Vol. 19, No. 1, March 2023, pp. 43-50
DOI: 10.22034/ijnn.2023.130520.1920

Short Communication

Structural and Optical Properties Study of Ag and Mg co-Doped TiO_2 by Comparison between DFT Calculation with Experimental Results

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(Received: 7 July 2020 and Accepted: 15 January 2023)

Abstract

This work aims to study the structure and optical properties of TiO_2 nanoparticles co-doped with Ag and Mg. Density functional theory (DFT) calculations are performed to study the influence of Ag and Mg doping on the geometry, electronic structure, and photophysical properties of TiO_2. The calculated band gap of TiO_2 doped with AgMg is 2.955 eV, which is in good agreement with the experiment. In addition, an almost good correlation was found between the calculated optical properties (such as the band structure) and the experimental UV absorption. The results of this comparative study can be used to develop TiO_2-based photocatalysts and analyze microscopic information about the electronic structure of activated TiO_2 nanoparticles.

Keywords: *TiO_2, Band Structure, UV absorption, Photocatalyst.*

1. INTRODUCTION

Semiconductor photocatalysts are materials suitable for power generation and environmental protection. These applications include hydrogen production, and air and water purification [1-7]. Unfortunately, the bandgap of anatase TiO_2 is very wide (approximately 3.2 eV). It only responds to ultraviolet light, which accounts for only a small part of sunlight, while visible light, which absorbs most of the sunlight, can't be used [8-11].

Several techniques have been used to improve the photoreaction of TiO_2 to visible light radiation, such as structural modification, [12, 13, 14] formation of semiconductor composites, [15, 16] sensitization of quantum dots, [13, 17, 18, 19,20], and doping mixed elements, [21, 22, 23, 24, 25]. Some methods include ion implantation, hydrothermal reaction, sol-gel reaction, solid-phase reaction, etc., for doping TiO_2. Sol-gel technology is undoubtedly the simplest, cheapest, and most attractive method to synthesize TiO_2 at low temperatures, and it is easier to use for the doping of metals [26]. Among all these methods, the doping of mixed elements is considered to be one of the most direct and effective methods. There have been multiple regulations regarding the doping of mixed elements, such as non-metal doping [21, 22, 23, 27] and transition metal doping [24, 28, 29] with transition metals can effectively improve the photocatalytic activity of visible light [30]. Yi-nan Wu et.al showed that the (Mn, Ni) co-doped ZnO catalyst was prepared using Stephania abyssinica leaf extract. The photocatalytic activities of the catalysts were also evaluated for the degradation of

Methylene Blue (MB) dye under visible light [31]. In some studies, the high visible-light photoactive nitrogen and sulfur co-doped TiO_2(N, S-TiO_2) nanoparticles and nanosheets were synthesized via facile sol–gel and hydro-thermal methods, respectively. The photocatalytic activities of N, S-TiO_2 catalysts were evaluated by degradation of non-steroidal anti-inflammatory drugs, ibuprofen (IBP) and naproxen (NPX), under simulated solar irradiation [32]. The combination of modeling and experimental methods helps to improve the accurate prediction of material properties. One of the modeling methods and designing engineering systems is the enthalpy-porosity technique, which is used to predict the properties of some hydrocarbons such as paraffin [33]. Finite volume simulations resulted in finding the distribution of velocity, and temperature, of the Linear Fresnel Reflector (LFR) unit, and multi-way twisted tape (MWTT) was applied in engineering nanofluid research such as Al_2O_3-water was employed [34]. One of the other successful methods for resolving the conflict between energy supply and request in space and time is Thermal Energy Storage (TES). Such a technique was proposed as a possible solution to heat shortages and pollution issues. In this work, a novel honeycomb configuration for heat storage has been scrutinized to enhance the performance of the system [35].

K. Hareesh. et.al develop a photocatalyst wherein nitrogen and phosphorus co-doped carbon quantum dots are scaffolded onto TiO_2 nanoparticles (NPCQD/TiO_2), denoted as NPCT henceforth. The first-principles density functional theory (DFT) simulations are carried out which predict the decrease in the work function and band gap, and the increase in the density of states of NPCT as the factors responsible for the observed enhancement in visible light photocatalytic hydrogen production [36]. Improved gas sensors based on pure anatase TiO_2 and Co-doped TiO_2 nanoparticles were evaluated. A cobalt-doped TiO_2 nanoparticle. Based on density functional theory (DFT), the calculated bandgap of Co-doped TiO_2 decreased by 72% compared to pure TiO_2. Structural simulation and mechanism analysis elucidated the good gas-sensing perfor-mance at room temperature and the property enhancement of the Co-doped TiO_2 gas sensor [37]. From the point of view of improving the elements added to the structure of nanomaterials, different experimental conditions, and sample preparation methods make the mechanism of co-doping synergistic effect difficult to understand. Computer modeling can overcome the complexity of the experimental situation and help us analyze the electronic structure of Ag-Mg- co-doped TiO_2, at the micro-level. TiO_2 is co-doped with Ag and Mg to understand how the doping state of Ag and Mg affects the absorption of visible light by TiO_2 [38]. TiO_2 and co-doped TiO_2 are recognized as the most suitable candidates among many photocatalysts because of their low toxicity, excellent biocompatibility, and long-term stability to light and chemical degradation. [39]. In our previous work, we used the sol gel method to produce Ag/Mg/TiO_2 nanoparticles and studied their photocatalytic activity [26]. However, the study of the microstructure and properties of the electronic structure of Ag/Mg/TiO_2 nanoparticles is carried out with the help of computational research. The accuracy of the micro-level description can be confirmed by the correspondence between theoretical research and experimental results. A comparative study of Ag/Mg/TiO_2 nanoparticles was carried out to achieve this goal using the GGA+U method based on density functional theory (DFT). The electronic structure and optical properties of TiO_2 were studied with Mg and Ag.

2. METHOD

2.1. Molecular Simulation

TiO_2 has three crystalline phases, of which the anatase phase is the most photo-catalytically active [40,41,42]. Anatase TiO_2 has a tetragonal structure with I41/AMD symmetry group and lattice parameters a = b = 3.776 Å and c = 9.486 Å [43]. The doped system is created based on a 36-atom anatase supercell, with a repetition number of 2 × 2 × 1. The Ag- Mg-co-doped configurations were made by replacing two Ti atoms with Ag and Mg atoms. The atomic quantitative relation of co-doped metals to Ti was 0.055, which is near the worth utilized in several experimental studies [44, 45, 46]. The supercell with co-doped Ag and Mg is shown in Figure 1. Complete simulations were carried out using the CASTEP module [47] in the Materials Studio 6 Software Package [48]. This module involves a variety of well-certified functions and force fields for quantum mechanics minimization and analysis searches for periodic solids. At first, GGA-PBE functional [49] was used to get the geometry optimization configuration for the $Ag/Mg/TiO_2$. The total crystal energy minimization was conducted by Spin-polarized DFT calculations using ultra-soft pseudo-potentials within the Vanderbilt form [50]. The wave functions of the valence electrons were expanded through a plane wave basis set to a cutoff energy of 340 eV. The Monkhorst-Pack [51] scheme with a 2 ×3 × 3 K-point grid was used to generate k-points for reciprocal space sampling. The convergence threshold for self-consistent iterations was set to 2×10^{-6} eV/atom.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

As shown in Figure 1, the lattice parameters change slightly when Ag and Mg atoms are replaced in a co-doped supercell.

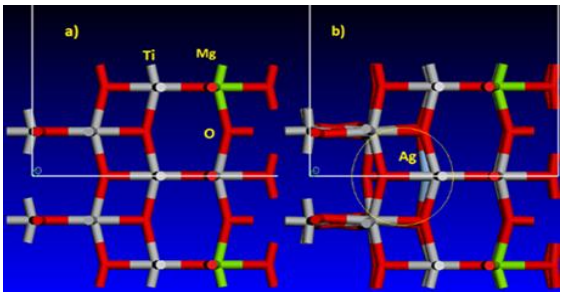

Figure 1. *Structural modeling of before (a) and after (b) geometry optimization of co-doped TiO_2 supercell.*

In TiO_2 co-doped with Ag and Mg, substitutional metal atom doping results in a slight extension of the Ag-O and Mg-O bonds (Table 1).

Table 1. *Bond length(Å) analysis before/ after geometry optimization.*

Ag-O bond lengths before geometry optimization (initial codoped supercell)	Ag-O bond lengths after geometry optimization at a different position
1.973 (XYplane)	2.370,2.150,2150,2.636 (XYplane)
1.930 (Zaxis)	2.338,2.065 (Zaxis)
Mg-O bond lengths before geometry optimization (initial co-doped supercell)	Mg-O bond lengths after geometry optimization at a different position
1.973(XY plane)	2.103,2.170,2.170,1.976 (XY plane)
1.930(Zaxis)	1.989,1989(Z axis)

Figure 2. shows the calculated QM and experimental XRD pattern for $Ag/Mg/TiO_2$.
According to the calculated XRD pattern, calculated picks are in good agreement with the experimental data (2θ=25.2 and 2θ=38).

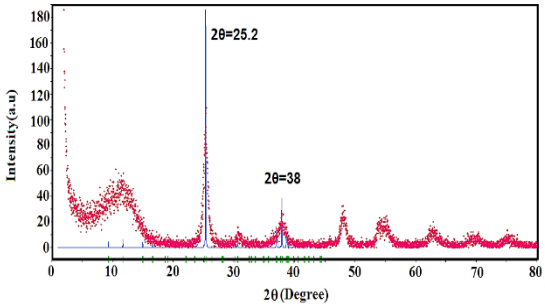

Figure 2. *The calculated (solid line) and*

experimental (dashed line) x-ray diffraction pattern of Ag/Mg/TiO_2.

It is possible to determine the effect of doped metals on the TiO_2 structure based on experimental XRD results combined with molecular simulations. For the above reasons, as can be seen in Figure 2, there is good agreement between the experimental diffraction pattern and the calculated XRD The pattern of Ag/Mg/TiO_2 nanoparticles reveals that the co-doping of anatase TiO_2 by a small number of metals has affected the surface of anatase TiO_2 [26].

3.2. Band Structure

To understand the band structure well and study the influence of the electronic structure of Ag and Mg on the TiO_2 surface, the band gap of the Ag/Mg/TiO_2 was calculated by the GGA- PBE functional. (Figure 3.) The DFT + U method was accepted to describe the strong on-site Coulomb repulsion [52, 53]. Band structure K- point is 5 ×5 × 3.

Figure 3. indicates that the energy gap between the conduction band (CB) and valance band (VB) is 2.955eV which is in good agreement with our prior experimental reported works [26].

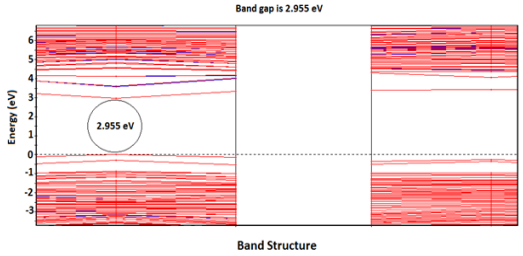

Figure 3. *The plot of the calculated band structure of Ag/Mg/TiO_2.*

3.3. DOS and PDOS Analysis

To systematically understand the electronic structure of Ag / Mg / TiO_2, after band structure analysis, density functional theory (DFT) calculations were conducted for the crystal structure of co-doped supercell TiO_2, both in terms of density of states (DOS) and partial density of states (PDOS).). The total density of states (DOS) and the partial density of states (PDOS) were performed to rearrange the electron density of the atoms participating in the energy transfer system. The DOS and PDOS of Ag and Mg elements of co-doped TiO_2, Ti, and O atoms are shown in Figure 4. (a-d).

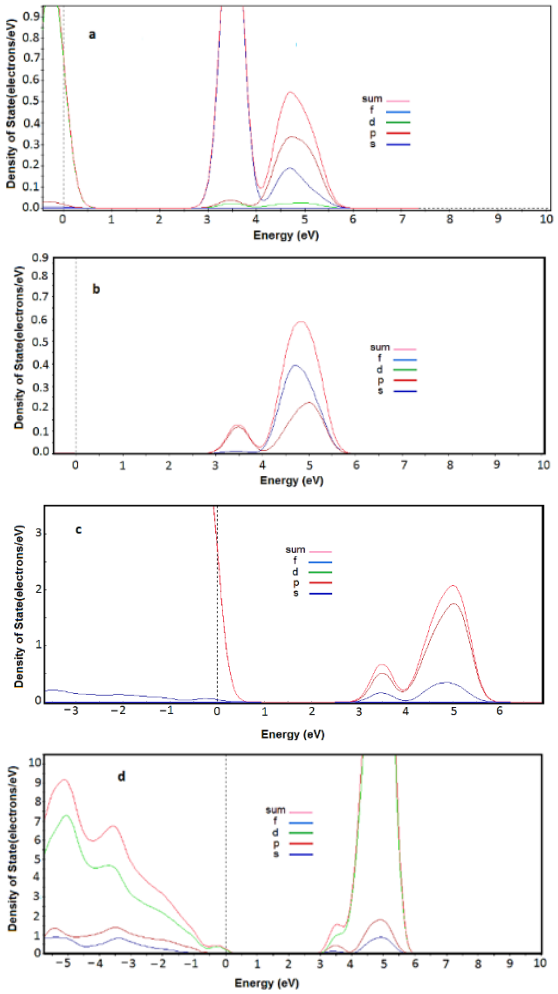

Figure 4. *The plot of the calculated density of states and partial density of states. a-Ag, b-Mg,c-O, and d-Ti atoms*

It can be observed from Figure 3, that for the Ag/Mg/TiO_2, the top of the valence band (TVB) is mainly localized on the conjugated 2p orbitals of Oxygen atoms of TiO_2 and partly 4d orbitals of Ag-doped atoms on the TiO_2 and the bottom of the conducting band (BCB) are mainly located on the conjugated 3d orbitals of Ti atoms of the TiO_2 and partly on the 5s orbital of Ag-doped atoms on the TiO_2. The gap of Ag/Mg/TiO_2 was determined by the energy difference between the LUMO (lowest

unoccupied), 3d orbitals of Ti atoms, and HOMOs (highest occupied), 2p orbitals of O atoms. By reducing the energy gap, electrons move to a higher energy level and the chemical stability of the Ag / Mg / TiO_2 system declines.

3.4. Optical Property

The simulated band gap attributed to the calculated optical absorption spectrum of Ag-Mg/TiO_2 (Figure 5), using quantum mechanics calculations (Band structure) is in relatively good agreement with an experimental gap of Ag/Mg/TiO_2.

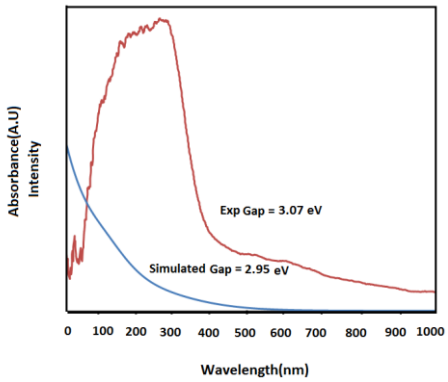

Figure 5. *Comparative UV absorption between experimental and simulated results related to band gaps.*

The experimental gap is attributed to the UV-visible absorption spectrum value at 403 nm via Kubelka–Munk transformed reflectance [54] function spectrum which has been reported from our previous work (sol-gel synthesized of Ag/Mg/TiO_2) [26]. The experimental band gap energy (Eg) of Ag/Mg/TiO_2 was determined by measuring UV-vis-DRS. Determination of Eg for the sample was done using the Kubelka–Munk (K–M) eq (1):

$$a = (1\text{-}R)^2/2R \qquad (1)$$

where R is the reflectance and a is the Kubelka–Munk function, where α is directly related to the absorption intensity of gap energy [55].

4. CONCLUSION

DFT quantum calculations exploiting periodic boundary conditions have reached enough accuracy to predict crystallographic and electronic structure properties of periodic solid materials. During this work, simulation investigation concerning Ag-Mg –TiO_2 indicates that the Mg-doped element has less impact on the crystal parameters division from the pristine catalyst. This result is confirmed by the density of states analysis particularly. Comparison of simulated with calculated XRD pattern shows that co-doped components haven't necessary impact on the structural characterization of the TiO_2 supercell, however, the value of the energy gap in our modeling crystal shows the appropriate number of 2.95 eV, which is suitable for the use of titanium oxide doped derivatives in photocatalytic works. Also, the numerical results of the comparison of experimental and simulation in the sections of the XRD and optical absorption properties according to the energy gap calculations by the Kubelka–Munk (K–M) eq results show a good agreement .Therefore, it can be concluded doping of some transition metals has goodly effects on the optical property of TiO_2 as a traditional semiconductor with a broad variety of applications in environmental chemistry and optical technology, for example, nano photo-catalyst materials and solar cell nanotechnology.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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