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DFT study of TiO₂ brookite (210) surface doped with silver and molybdenum

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Abstract

The most popular semiconductor in dye-sensitized solar cells (DSSCs) is titanium dioxide (TiO₂) because of its low cost, non-toxicity, and good stability. However, the DSSCs still have low efficiency due to the low light absorption of TiO₂ in the visible region. Understanding the properties of TiO₂ can contribute to improving the efficiency of DSSCs. In this study, we use density functional theory to investigate the electronic and optical properties of TiO₂ brookite (210) surface mono-doped and co-doped with 4d transition metals, silver, and molybdenum. Our results show that the band gap energy of brookite (210) surface is 3.514 eV, which reduces to 1.143 eV and 0.183 eV when doped with Ag and Mo, respectively. However, doping with both Ag and Mo yielded a band gap of 0.387 eV. The results suggest the presence of Ag and Mo 4d states below the conduction band minimum, which could be responsible for the narrowing of the band gap on the brookite (210) surface. Both mono-doped and co-doped brookite (210) surfaces have higher visible light absorbance compared to the undoped brookite (210) surface and extend to the near-infrared region.

1. Introduction

The continuous reliance on fossil fuels has been a major global concern in the recent past, particularly with issues concerning global warming and carbon dioxide emissions. These concerns have led researchers to search for alternative sources of energy that are renewable and environmentally friendly. The current global market of renewable energy is dominated by the first-generation solar cells commonly known as silicon solar cells. However, the high cost of silicon solar cells remains a challenge, hence a concerted effort to improve the efficiency of newer low-cost alternatives such as dye-sensitized solar cells (DSSCs) and perovskites solar cells [1–4]. Despite the low cost, the DSSCs still have a low efficiency that is measured at approximately 12% [5, 6]. One of the key areas in the optimization of DSSCs is the preparation of the TiO₂ semiconductor, as it has a major impact on dye molecules, electron transfer, and the separation of charge carriers [7].

Experimental and computational studies have shown that TiO₂ is a good material for solar cells and photocatalytic applications [5]. However, TiO₂ polymorphs have limited absorption edges in the visible region due to the wide band gap of the polymorphs [8]. The most common TiO₂ polymorphs are rutile, anatase, and brookite with band gaps of 3.0 eV, 3.2 eV, and 3.4 eV, respectively [8, 9]. Several band gap modification techniques, such as elemental doping [10–15], semiconductor composite formation [16, 17], quantum dot sensitization [18, 19], and structural modification [20–22] have been shown to be effective in improving the absorption of TiO₂ in the range from the ultraviolet (UV) to the visible light wavelength. Several doping schemes have been proposed, including transition-metal doping and non-metal doping; and a combination of the two schemes to reduce the recombination rate of photogenerated carriers. Recent studies have shown that the
3. Results and discussions

3.1. Structural properties

Figure 1(a) shows the optimized brookite bulk structure containing eight titanium and sixteen oxygen atoms, (b) brookite (210) surface, and (c) brookite (210) surface with the Ag/Mo dopant highlighted in yellow. The lattice parameters of the optimized structure are listed in Table 1 and are compared to the experimental and previous
theoretical results. The calculated lattice parameters are consistent with the experimental and theoretical literature results within percentage errors of 0.196%, 0.202%, and 0.195% for a, b, and c lattice parameters, respectively.

3.2. Electronic properties

Figure 2 shows the band structures of (a) the pure brookite bulk structure and (b) the undoped brookite (210) surface. It can be observed that the calculated band gap energy of the bulk brookite is 2.360 eV, which is less than 3.400 eV obtained experimentally \[8\] and comparable to 2.485 eV obtained computationally using GGA \[51\]. The disparity between the experimental band gap energy and the calculated band gap energy of this work of the bulk brookite is attributable to the functional tendency of GGA to underestimate the band gap energy due to the exchange correlation energy \[52\]. Additionally, the conduction bands minimum (CBM) and valence bands maximum (VBM) are observed to be both located at G; this shows that pure brookite can be regarded as a direct band gap semiconductor. The obtained band gap energy of the brookite (210) surface is 3.514 eV and is also a direct band gap semiconductor.

Figure 3 shows the band structures of the doped brookite (210) surface, doped with (a) Ag, (b) Mo, and (c) co-doped with both Ag and Mo. The calculated energy gap for the Ag-doped surface is 1.143 eV, for the Mo-doped surface is 0.183 eV, and for the co-doped surface is 0.387 eV. The obtained results of the doped brookite (210) surfaces illustrate that there are new energy levels, which are observed at the bottom of the conduction band and top of the valence band, for Ag, Mo, and co-doped, making it easier for electrons to jump from the VB to the CB. When hybridized with O 2p states or Ti 3d states, the transition metal (Ag and Mo) 4d states are somewhat delocalized, resulting in the formation of impurity energy levels (IELs). Such a hybrid effect may shape energy levels in the band gap or form a hybrid with CBM/VBM, allowing electrons and holes to be trapped. It contributes to the separation of photogenerated electron–hole pairs, photoexcited carrier migration, and photocatalysis. Like the brookite bulk structure and the brookite (210) surface, the band structures of the doped brookite (210) surfaces show a direct band gap. Because brookite is difficult to synthesize in a laboratory, there has been no previous experimental work on brookite that was doped with Ag and Mo that correlates to this computational work. However, the structure of the surface of brookite TiO2 (210) has been reported to be similar to that of the most stable anatase TiO2 (101) surface \[31\]. Mogal et al have previously used a single-step sol-gel method to synthesize Ag-doped TiO2 with varying Ag content ranging from 0.75 at % to 3.5 at % \[53\]. The study found that 0.75 at % doping effectively narrows the band gap, with the band gap obtained being 2.34 eV for 0.75 at %. Aini et al previously used the sonochemical method to synthesize Ag-doped anatase TiO2 photocatalysts with silver concentrations of 1,3,5,7, and 9% \[54\]. The band gap energies of undoped and Ag-doped TiO2 were 3.4 eV, 3.0 eV, 3.3 eV, 3.1 eV, 3.25 eV and 2.8 eV, respectively, based on UV–vis Diffuse Reflectance Spectroscopy (DRS) measurements.
Reflectance spectra. The band gap energy decrease is greatest in 9% Ag-doped TiO$_2$ [54]. Wang et al investigated the photocatalytic activities of Mo-doped anatase TiO$_2$ by photodegradation of methyl orange (MO) under irradiation of UV-visible and simulated solar light [55]. According to their findings, Mo doping in anatase TiO$_2$ reduces the band gap from 3.19 eV of TiO$_2$ to 3.05 eV of Ti$_{0.97}$Mo$_{0.03}$O$_2$. Huang J et al conducted an experiment to test the photocatalytic activity of Mo-doped anatase TiO$_2$ by degradation methylene blue under irradiation of a 500 W xenon lamp and natural sunlight outdoor [56]. Their findings show that the band gap decreases from 3.05 eV of TiO$_2$ to 2.73 eV of TiMo$_{0.02}$O. Our results are consistent with the previously mentioned experimental work on Ag and Mo doping of anatase TiO$_2$.

To study the nature of states that contribute to the conduction and valence band edges, the total density of states (TDOS) and the partial density of states (PDOS) were calculated. Figure 4 shows all the atomic orbitals (TDOS) as well as distinct atomic shells (PDOS) in the band edges of the brookite bulk, brookite (210) surface, mono-doped and co-doped brookite (210) surface. For the bulk of brookite and brookite (210) surface, it was observed that the CB is dominated by the Ti 3$d$ states with a small amount of O 2$p$ states, while the VB is dominated by the O 2$p$ states with a small amount of Ti 3$d$ states. After doping the (210) surface, it was observed that there is a delocalization in the Ti 3$d$ and O 2$p$ states, contributing to the formation of energy levels in the band gap.
3.3. Optical properties

To study TiO\textsubscript{2} brookite for application in photocatalysis, the optical properties were calculated. Our calculations of the optical properties cover the dielectric function, conductivity, refractive index, absorption, reflectivity, and loss function. The dielectric function is a complex quantity that describes the dielectric response of the material and is associated with the electronic structure. It is defined by a summation of a real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts as shown in equation (1),

$$\varepsilon = \varepsilon_1(\omega) + \varepsilon_2(\omega)$$

The real and imaginary parts are correlated to the electronic polarizability and electronic absorption of the material, respectively. The calculated dielectric functions of the bulk structure of brookite, and the undoped and doped brookite (210) surfaces are presented in figure 5. Represented in figures 5 (a) and (b) are the real and imaginary parts of the dielectric function, respectively. For the real part, the brookite bulk structure shows high polarizability in the UV-Vis region compared to the undoped and doped brookite (210) surfaces. From figure 5(b), which is the imaginary the dielectric function, it can be observed that the brookite bulk structure shows two absorption peaks. However, for undoped and doped surfaces, only one absorption peak is observed. The undoped surface shows no response after 500 nm, whereas the imaginary parts of dielectric function for the doped surfaces proceed and show an enhanced response in the near-infrared region, which enhanced the light absorption. From the dielectric function, the Kramers-Kronig transformation is used to obtain the real part $n(\omega)$ and the imaginary part $k(\omega)$ (extinction coefficient) of the refractive index as [51]:

$$n(\omega) = \left(\frac{|\varepsilon(\omega)| + \varepsilon_1(\omega)}{2}\right)^{\frac{1}{2}}$$

$$k(\omega) = \left(\frac{|\varepsilon(\omega)| - \varepsilon_1(\omega)}{2}\right)^{\frac{1}{2}}$$

The imaginary part of the refractive index is correlated with light absorption. In figure 6, it is observed that the refractive index is in agreement with the relation between the dielectric function and the refractive index. In figures 7(a) and (b), we show calculated real and imaginary parts of the conductivity function, respectively. The real part of the conductivity is related to resistive joule heating, while the imaginary part is related to the inductive current. It shows that the doped brookite surfaces have enhanced conductivity in the visible region, and thus improved conductivity compared to that of the bulk brookite structure.

The absorption $\alpha(\omega)$, reflectivity $R(\omega)$, and loss function $L(\omega)$ can also be derived from the dielectric function.

$$\alpha(\omega) = \frac{2k\omega}{c}$$

$$R(\omega) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$
The calculated results of the absorption are presented in figure 8. As expected, the bulk brookite structure shows very high absorption in the ultraviolet spectrum and less absorption in the visible region. Compared to the bulk structure of brookite, the undoped brookite (210) surface shows less absorbance in both regions. For the brookite (210) surface, the doping effectively increased the absorbance in the visible region. It can be observed that the Ag-doped brookite (210) surface has a higher absorbance than the bulk structure of brookite between 500 and 600 nm and extends the absorption toward the infrared region. The Mo-doped brookite (210) surface extends the absorption from 600 nm towards the infrared region. When co-doped with Ag and Mo, the structure has a higher absorbance than the other structures beginning at a wavelength of 470 nm and extends its absorption into the infrared region of the spectrum. The behavior of the absorption curves is quite comparable to that of the imaginary parts of the dielectric function and the refractive index, as seen in figures 5 and 6, respectively. The optical absorption calculations agree with the outcome of the laboratory work on anatase TiO$_2$ performed by Mogal et al [53]. They reported a change in the position of the absorption edge, which shifted from 403 nm in pure TiO$_2$ to 414 nm in Ag-doped TiO$_2$. The experimental results of Wang et al reveal that for 2% to 3% Mo-doped TiO$_2$, there is a significant increase in the amount of light absorbed in both the UV and visible spectrums [55]. Similarly, Huang J et al observed a significant red shift of the absorption edge when TiO$_2$ was doped with silver [56].

Figure 9 shows the reflectivity of brookite bulk structure, undoped and doped brookite (210) surfaces when exposed to light photons. The results show that the reflectivity of the bulk brookite structure is significantly
**Figure 8.** Calculated optical absorption of the brookite bulk structure, undoped and doped brookite (210) surfaces.

**Figure 9.** Calculated reflectivity of the brookite bulk structure, undoped and doped (210) surfaces.

**Figure 10.** Calculated loss function of the brookite bulk structure, undoped and doped (210) surfaces.
higher compared to that of the undoped and doped brookite (210) surfaces. The lower reflectivities of the undoped and doped (210) surfaces suggest that these structures can be used as transparent conducting oxide materials. For the Ag and Mo co-doped brookite (210) surfaces, there is an increase in reflectivity from 550 nm extending to the infrared region. The calculated loss functions (i.e., the energy loss of an electron when passing through a medium) are presented in figure 10. Both the bulk structure and the undoped brookite (210) surface show notable activities in the UV region, then show no significant activities in the visible region whereas the doped brookite (210) surfaces show activities in the two regions.

4. Conclusion

The electronic and optical properties of the bulk structure of the, undoped, mono-doped and co-doped brookite (210) surfaces were successfully investigated using density functional theory and compared with other work in the literature. In all cases we found a direct band gap, which is expected for brookite TiO₂. The results suggest the formation of energy levels in the conduction band after doping brookite (210) surface, resulting in a narrowing of the band gap. With the formation of the energy levels, the electrons move from the VB to CB with less probability of charge recombination. Both mono-doped and co-doped brookite (210) surfaces exhibit good visible light absorption due to the narrowed band gap caused by the introduction of Ag and Mo 4d states below the conduction band minimum. When the surface of brookite (210) is doped with Ag and Mo, absorption calculations show a red shift in the visible region that extends to the near-infrared region. These calculations could provide a basis for challenging synthesis and exploration of undiscovered properties of doped brookite and extend the knowledge for developing better photocatalysts for application in DSSCs.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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