Doping effects on catechol functionalized anatase TiO$_2$(101) surface for dye-sensitized solar cells

Jin-Hua Luo$^{1,2}$, Yun-Fei Mo$^{1,3}$, Ze-Sheng Li$^3$ and Fu-You Du$^{1,*}$

$^1$ Hunan Key Laboratory of Applied Environmental Photocatalysis, College of Biological and Environmental Engineering, Changsha University, Hunan Province, Changsha 410022, People’s Republic of China
$^2$ Key Laboratory of Cluster Science of Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 100081, People’s Republic of China
$^3$ School of Electronic and Communication Engineering, Hunan Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Hunan Province, Changsha 410022, People’s Republic of China

* Author to whom any correspondence should be addressed.

E-mail: jhluo@ccsu.cn and dufu2005@126.com

Keywords: dye-sensitized solar cells, catechol, adsorption, density functional theory, metal doped TiO$_2$ surface

Supplementary material for this article is available online

Abstract

Doping effects of Al, Mg and Cr on the structural and photoelectric properties of catechol functionalized anatase TiO$_2$(101) surface (CFAS) have been studied using density-functional theory. The results indicate that the adsorption processes of CFAS and catechol functionalized doped anatase TiO$_2$(101) surfaces (CFDAS) are all exothermic and these adsorption systems are quite stable. The relative lower formation energy of Al-doped TiO$_2$ means that it is energetically favorable structure under Ti-rich conditions. For band structure of catechol-Cr-doped-TiO$_2$, the electron transition energy will be reduced, and visible light absorption will be extended on account of the decreased band gap and widespread impurity states. The positive Fermi energy shift of Cr-doped TiO$_2$ suggests that it is beneficial to increase the open circuit voltage compared with pure TiO$_2$ under the same conditions. When catechol as a model organic sensitizer functionalizing the pure and Al, Mg and Cr doped TiO$_2$ (101) surfaces, a positive shift of the Fermi energies is observed in comparison with those materials without catechol functionalization. Compared with the optical properties of CFDAS, Cr doping has a greater effect on the optical properties of anatase TiO$_2$ (101) surface than that of Al or Mg doping. The results show that Cr doped anatase TiO$_2$ (101) surface is a better photoanode material and can be applied in Dye-Sensitized Solar Cells.

1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn enormous attention because of their low manufacturing cost, high efficiencies, environmental-friendly, and so on [1, 2]. Several efforts have been made to enhance the performance of DSSCs by improving the properties of sensitizers [3–6], counter electrode materials [7, 8], electrolytes [9] and the photoanode materials [10, 11], especially TiO$_2$. To date, various TiO$_2$ modification methods including metal (Al, Mg, Zr, Nb, Cr, W) doping have been utilized to construct DSSCs with high energy-conversion efficiency [10–18]. Recently, Khosravi et al have revealed that Al-doped TiO$_2$ thin films prepared by spray pyrolysis method exhibited potential photovoltaic applications [16]. Janoha et al have demonstrated that Mg-doped nanostructure TiO$_2$ electrode increased the power conversion efficiency from 6.26% to 7.36% [17]. Nguyen et al reported that Cr doped TiO$_2$ nanotubes enhanced the photocurrent intensity to improve performance of DSSCs [18]. Besides, the interaction between dyes and the surface of TiO$_2$ has attracted increasing attention [19–22]. Meanwhile, catechol functionalized TiO$_2$, as a prototypical model for DSSCs has also received much attention [23–25]. The strength of optical absorption in the visible region plays an essential role in photovoltaic efficiency of catechol-TiO$_2$ interfaces [23]. Li et al [24, 25] have studied the
adsorption behaviors of catechol on anatase (101) surface and rutile TiO$_2$ (110) surface. Rispellini et al. [26] have found that the performance of DSSCs employed by catechol as an anchoring group is better than that of isonicotinic acid. Liu et al. [27] have pointed out that bidentate adsorption mode for catechol on the anatase TiO$_2$ (101) surface is essentially immobile. Lin et al. [28] have shown that the thermal fluctuations of catechol on the anatase TiO$_2$ (101) surfaces enhance the absorption spectrum. Li et al. [29, 30] have selected catechol-TiO$_2$ interfac as a research object for electron injection process to investigate the effects of Zn and W dopant in TiO$_2$ by density functional calculations. As far as we know, many studies have been focused on the doped interface as a research object for electron injection process to investigate the effects of Zn and W dopant in TiO$_2$

3. Results and discussion

2. Computational methods

Plane wave DFT calculations were performed within VASP code in MedeA software [33, 34]. The cutoff energy was 400 eV. $2 \times 2 \times 2$ Monkhorst-Pack k-point mesh [35] were used for geometry optimization and 4 × 4 × 4 for electronic and optical properties calculations. Exchange-correlation functional was described by the Perdew–Burke–Ernzerhof (PBE) [36], and a Hubbard U term of 6 eV to both O (2p) and Ti (3d) states [37, 38] was employed. A force convergence tolerance on the atoms of <0.02 eV Å$^{-1}$ was set for geometry optimizations. The calculated anatase bulk lattice parameters are $a = 3.776$ Å and $c = 9.486$ Å, which are consistent with the experimental values ($a = 3.782$ Å and $c = 9.502$ Å) [39]. The anatase TiO$_2$ (101) surface was built from a $3 \times 3$ 108-atom supercell. The slab model included four TiO$_2$ trilayers (O–Ti–O) thick, with a vacuum layer of 15 Å. In order to mimic the bulk effects, atomic positions at the bottom of two O-Ti-O trilayers were fixed.

3. Results and discussion

3.1. Adsorption energy and formation energy of doped configurations

3.1.1. Adsorption energy

Take the factor of stability into account, the bidentate adsorption mode is chosen to study the doping effects on CFAS [27]. The optimized configuration of CFAS is shown in figure 1. To further study the doping effects for adsorption configuration, Ti (1) represents the substitutive Ti atom for Al, Mg and Cr atoms, respectively. To reveal the stability of doped systems, the adsorption energy ($E_{\text{ads}}$) is estimated according to

$$E_{\text{ads}} = E(\text{catechol/surface}) - E(\text{surface}) - E(\text{catechol})$$ (1)

where $E(\text{catechol/surface})$, $E(\text{surface})$ and $E(\text{catechol})$ are the energies of adsorption system, mutually independent TiO$_2$ (101) surface and catechol molecule, respectively. According to this definition, a negative value of $E_{\text{ads}}$ indicates the doped system is stable.

The adsorption energies for adsorption systems are listed in table 1. The calculated adsorption energy for catechol-TiO$_2$ is $-1.24$ eV, and its absolute value is closer to the calculated value of 1.25 eV by Liu et al. [27]. It’s worth noting that our definition of the adsorption energy is contrary to that of Liu et al. The adsorption energy value ($-3.47$ eV) of catechol-Mg-doped-TiO$_2$ in table 1 is the lowest of all adsorption systems. The relative lower adsorption energy means that the adsorption system possesses better structural stability. Table 1 also demonstrates that the adsorption energies of all adsorption systems are negative. The above results reveal that the adsorption processes of catechol on pure and doped TiO$_2$ (101) surfaces are exothermic and the adsorption systems are quite stable.

3.1.2. The formation energy of doped configurations

The concentration $c$ of point defects in thermodynamic equilibrium can be expressed as follows:

$$c = N_{\text{site}}N_{\text{config}} \exp \left( -E_f / KT \right)$$ [40]. Here, $E_f$ is the defect formation energy, and the lower formation energies of defects, the more likely to form. By exploring possibility, stability and optimal growth conditions of doping, one can study the dopant formation energies, according to the following equation [41].
where $E_T$ (doped) and $E_T$ (undoped) are the total energies of doping system and undoping system, respectively. $\mu_M$ and $\mu_T$ are the chemical potentials of doped metal elements and Ti, respectively. $n_M$ and $n_T$ are the numbers of the doped metal atoms and the substituted Ti atoms, respectively. Here, gas O$_2$, bulk metal Ti, Al, Mg and Cr are used to determine the chemical potentials: $\mu_O = \mu (O_2)/2$, $\mu_T = \mu_T^{\text{metal}}$, $\mu_M = \mu_M^{\text{metal}}$, $\mu_M = \mu_M^{\text{metal}}$, and $\mu_Cr = \mu_Cr^{\text{metal}}$. Growth conditions play vital roles in the formation energy. For TiO$_2$, $\mu (TiO_2)$ can be expressed as $2\mu_O + \mu_T = \mu (TiO_2)$. Under Ti-rich conditions, $\mu_O$ can be calculated as follows: $\mu_O = \frac{1}{2} (\mu (TiO_2) - \mu_T)$. And under O-rich conditions, $\mu_T$ can be obtained with the expression $\mu_T = \mu (TiO_2) - 2\mu_O$. Under different growth conditions, the formation energies of doped systems are listed in Table 2.

From the results of Table 2, the following trends are observed: (1) $E_f$ of these doped TiO$_2$ (101) surface systems under Ti-rich conditions are less than those of doped TiO$_2$ (101) surface systems under O-rich conditions. (2) Al-doped TiO$_2$ has lower value of $E_f$ than other doped systems whether under O-rich or Ti-rich conditions. The negative value of $E_f$ ($-1.63$ eV) means that Al-doped TiO$_2$ is energetically feasible under Ti-rich conditions.

### Table 1. Adsorption Energies (eV) of CFDAS

| Configurations       | Adsorption energies (eV) |
|----------------------|--------------------------|
| catechol-TiO$_2$     | $-1.24$                  |
| catechol-Al-doped-TiO$_2$ | $-2.80$           |
| catechol-Mg-doped-TiO$_2$ | $-3.47$              |
| catechol-Cr-doped-TiO$_2$ | $-1.20$              |

### Table 2. Impurity formation energies $E_f$ (in eV) of doped TiO$_2$ (101) surface systems under both Ti-rich and O-rich conditions.

| Configurations       | Ti-rich | O-rich |
|----------------------|---------|--------|
| Al-doped-TiO$_2$     | $-1.63$ | $2.60$ |
| Mg-doped-TiO$_2$     | $2.13$  | $6.35$ |
| Cr-doped-TiO$_2$     | $1.71$  | $5.93$ |

$E_f = E_T$ (doped) $- E_T$ (undoped) $- n_M\mu_M + n_T\mu_T$  \hspace{1cm} (2)
conditions. However, the positive value of $E_f$ (2.60 eV) suggests that Al-doped TiO$_2$ is not conductive to form under O-rich conditions. It is worth mentioning that although the values of $E_f$ of Mg and Cr-doped TiO$_2$ are positive, they can form under certain conditions according to the results of the reported works [17, 18].

3.2. Electronic properties

3.2.1. Band structure

To explore the variations of band gap due to doping and catechol functionalization, the energy bands of pure TiO$_2$, Cr-doped TiO$_2$, Al-doped TiO$_2$ and Mg-doped TiO$_2$ were calculated, and the corresponding results are shown in figures 2–3 and S1–S2 (available online at stacks.iop.org/MRX/8/015906/mmedia). And the energy bands of catechol functionalized pure TiO$_2$ and Al, Mg, and Cr doped TiO$_2$ were also calculated, as shown in figures 4 and S3–S5, respectively. The calculated band gaps are summarized in table 3 for pure and Al, Mg, and Cr doped TiO$_2$ (101) surfaces and catechol adsorbed pure and Al, Mg, and Cr doped TiO$_2$ (101) surfaces.

From the results of table 3, the calculated band gap of pure TiO$_2$ (3.04 eV) is similar with the experimental value (3.2 eV) [42]. From figures S1–S2 and table 3, it can be seen that the band gaps of Al and Mg-doped TiO$_2$ (3.02 eV and 2.95 eV, respectively) are a little bit lower than that of pure TiO$_2$ (3.04 eV). The result reveals doped Al or Mg atoms could reduce the band gaps of pure TiO$_2$, resulting in a small redshift of the optical absorption of TiO$_2$, and the theoretical prediction for the redshift of the optical absorption of Al-doped TiO$_2$ is in accordance
with the experimental report [43]. In addition, compared with pure TiO₂, the Fermi levels for Al and Mg-doped TiO₂ (see figures S1–S2) shift downward to valence band.

Figure 3 gives the band structure of Cr-doped TiO₂. The valence band maximum (VBM), the conduction band minimum (CBM), CBM + 1, CBM + 2 and CBM + 3 are labeled in figure 3. The calculated band gap of Cr-doped TiO₂ (2.06 eV) is narrower than that of pure TiO₂ (3.04 eV, see table 3). The electrons in VBM can also transit to CBM + 1 or CBM + 2 or CBM + 3. The transition energies of \( E_{\text{VBM, CBM}+1} \) (2.08 eV), \( E_{\text{VBM, CBM}+2} \) (2.25 eV) and \( E_{\text{VBM, CBM}+3} \) (2.98 eV) are also lower than the band gap of pure TiO₂. For these results, the appearance of these new energy levels cause Fermi level of Cr-doped TiO₂ to shift upward to conduction band and optical spectrum to red-shift compared with pure TiO₂.

Figure 4 shows the band structure of catechol-TiO₂, and the corresponding VBM-3, VBM-2, VBM-1, VBM, CBM, and CBM + 1 are labeled. Figure 4 demonstrates three impurity energy levels in the energy range are between −2.3 and 0 eV, ascribing to the catechol functionalized. From table 3, it is found that the calculated band gap of catechol-TiO₂ (1.17 eV) is narrower than that of pure TiO₂ (3.04 eV) and Cr-doped TiO₂ (2.06 eV). The electrons in VBM can also transit to CBM or CBM + 1 or CBM + 2 or CBM + 3. The transition energies of \( E_{\text{VBM, CBM}+1} \) (2.08 eV), \( E_{\text{VBM, CBM}+2} \) (2.25 eV) and \( E_{\text{VBM, CBM}+3} \) (2.98 eV) are also lower than the band gap of pure TiO₂. For these results, the appearance of these new energy levels cause Fermi level of Cr-doped TiO₂ to shift upward to conduction band and optical spectrum to red-shift compared with pure TiO₂.

Figures S3–S4 show the band structure of catechol-Al-doped TiO₂ and catechol-Mg-doped TiO₂, respectively. The results of figures S3–S4 show that some impurity energy levels of catechol enter into the valence band. From figures S3–S4 and table 3, the band gaps of catechol-Al-doped TiO₂ and catechol-Mg-doped TiO₂ are 1.69 eV and 0.33 eV, respectively. According to exhibits the band structure of catechol-Cr-doped TiO₂ shown in figure S5, the three impurity energy levels (−2 eV–0 eV) derive from catechol adsorption, and other impurity energy levels (0 eV–1 eV) mainly originate from introduction of Cr. From table 3, the band gap of catechol-Cr-doped TiO₂ is 0.32 eV, which decreases significantly compared with that of pure TiO₂. The reduced

Table 3. The calculated band gaps \( E_g \) (in eV) for pure, doped TiO₂ (101), and catechol adsorbed pure and doped TiO₂ (101) systems.

| Configurations                  | \( E_g \) (eV) |
|--------------------------------|----------------|
| pure TiO₂                      | 3.04           |
| Al-doped TiO₂                  | 3.02           |
| Mg-doped TiO₂                  | 2.95           |
| Cr-doped TiO₂                  | 2.06           |
| catechol-TiO₂                  | 1.17           |
| catechol-Al-doped-TiO₂         | 1.69           |
| catechol-Mg-doped-TiO₂         | 0.33           |
| catechol-Cr-doped-TiO₂         | 0.32           |

Figure 4. Band structure of catechol-TiO₂. The Fermi energy is set to 0 eV.
band gap and widely distributed impurity states lead to reduce electron transition energy and further improve the visible light absorption. Meanwhile, the energy band gaps of catechol-TiO$_2$ and catechol adsorbed doped TiO$_2$ (101) systems (1.17 eV, 1.69 eV, 0.33 eV and 0.32 eV), suggesting these systems are still semiconductors.

3.2.2. Electron injection mechanism

To trace the electron injection mechanism, the partial charge densities of catechol-TiO$_2$ are displayed in figure 5. Figure 5 shows that the electronic density from VBM is predominately located on the catechol adsorbed on the TiO$_2$ (101) surface, while the electronic densities from CBM and CBM$^+$ are basically located on the Ti (3d) orbitals of TiO$_2$ (101) surface. It is found that other partial charge densities from the VBM-1 and VBM-2 are mainly dominated by $\pi$-conjugated orbitals of the catechol and the adsorption interface, and the partial charge densities for VBM-3 mainly reside in TiO$_2$ (101) surface, suggesting that the catechol and TiO$_2$ (101) surface could interact with each other. The electrons are excited from the photoexcited catechol to the conduction band of TiO$_2$ directly, which proves a direct injection mechanism [46]. The partial charge densities of catechol-Al-doped-TiO$_2$, catechol-Mg-doped-TiO$_2$ and catechol-Cr-doped-TiO$_2$ are displayed in figures S6–S8, respectively. Figure S6 shows that the electronic density from VBM mainly consists of $\pi$-conjugated orbitals of the catechol, while the electronic densities from CBM and CBM$^+$ mainly reside in the Ti (3d) orbitals of TiO$_2$ (101) surface. It is obvious that some partial charge density of VBM-2 exists in the nearby doped Al atom. Figure S7 presents that the electronic density from VBM mainly resides in the nearby doped Mg atom of TiO$_2$ (101) surface, while the electronic density from CBM mainly consists of $\pi$-conjugated orbitals of the catechol. Figure S8 shows that the electronic densities from VBM and CBM mainly reside in the nearby doped Cr atom of TiO$_2$ (101) surface, while the electronic densities from VBM-2 and VBM-3 mainly consist of $\pi$-conjugated orbitals of the catechol. From figures S6–S8, it can be seen that the introduction of Al, Mg and Cr have a large impact on the partial charge densities of catechol adsorbed doped TiO$_2$ (101) systems for the $\Gamma$ point of specific bands and optical properties of catechol adsorbed doped TiO$_2$ (101) systems.

3.2.3. The effect of Fermi energy

As we know, TiO$_2$ (101) surface has attracted much interest in DSSCs [47–49]. Figure 6 shows the Fermi energy of pure, doped TiO$_2$ (101), and catechol adsorbed pure and doped TiO$_2$ (101) systems. For DSSCs, $V_{oc}$ is
dependent upon the potential of Fermi level of TiO2 photoelectrode and the standard reduction potential of redox couple \( V_{\text{red}} \) \[50\]. To explore doping effect on CFAS, \( V_{\text{red}} \) is set as the iodine/iodide couple. Assuming that \( V_{\text{red}} \) of I\(^{-}/\)I\(^{3-}\) is a constant, the positive Fermi energy shift may lead to a high \( V_{\text{oc}} \) of DSSCs. Meanwhile, the negative Fermi energy shift increases the driving force of electron injection of DSSCs. Figure 6 presents that the Fermi energy of Cr-doped TiO2 \((101)\) surface shifts positively, while the Al or Mg-doped TiO2 \((101)\) surface shift negatively by comparison to pure TiO2 \((101)\) surface. These results indicate that the Cr doping is beneficial to increase the \( V_{\text{oc}} \) compared with that of pure TiO2 \((101)\) surface under the same conditions. Moreover, Al or Mg-doped TiO2 \((101)\) surface is favored to increase the driving force of electron injection of DSSCs. When catechol as a typical dye functionalizing TiO2 \((101)\) surfaces, the Fermi energies of these materials all shift towards positive.

### 3.2.4. Density of states

The density of states (DOS) for pure and different doped TiO2 \((101)\) surfaces are illustrated in figure 7. For Al- and Mg-doped TiO2 \((101)\) surfaces (figures 7(b), (c)), both the CBM and VBM move into higher energy compared with pure TiO2 \((101)\) surface’s (figure 7(a)). Figure 7(d) shows that the Fermi level moves into the middle of the forbidden region by Cr doping, and reveals that Cr-doped TiO2 \((101)\) surface exhibits semimetallic behaviour. Our theoretical results are in agreement with the findings of Khan \textit{et al}[51]. The substitution of Ti with Cr lowers both VBM and CBM of Cr-doped TiO2 \((101)\) surface, in comparison with those pure TiO2.
remarkably by reason that electrons of the valence band can enter into impurity states. Catechol-Al-doped TiO₂ shift wholly to the higher energy region compared with that of catechol-TiO₂. Mg doping have slight variation of DOS of pure TiO₂. There is an interaction between catechol and pure TiO₂. It can be observed that catechol exerts a key influence on electronic properties of pure TiO₂. As shown in figure 7, it can be also seen that Al and Mg doping have slight variation of DOS of pure TiO₂ (101) surface, but Cr doping has more changes of DOS of pure TiO₂ (101) surface.

In order to investigate the nature of impurity states, the projected density of states (PDOS) of pure and doped TiO₂ (101) surfaces were calculated (figure 8). It is clearly seen from figure 8(a), the valence bands (VBs) are mainly occupied by O 2p orbitals, whereas the conduction bands (CBs) are primarily dominated Ti 3d orbitals. For the PDOS of Al and Mg-doped TiO₂ (101) surfaces are depicted in figures 8(b) and (c). It is obvious that the VBs consist of Al 3p or Mg 3p orbitals and O 2p orbitals. The increase of total electrons doped by the Al and Mg atoms leads to decrease the band gap, which will cause optical absorption edge to red-shift. It is noted that the intensities of Al 3p and Mg 3p states peak are weak (<0.3 states/eV). The PDOS of Cr-doped TiO₂ (101) surface is shown in figure 8(d). The PDOS of Cr 3d states analysis demonstrates that the gap states are mostly composed of the Cr 3d orbitals. Hence, the optical absorption edge of Cr-doped TiO₂ (101) surface has a red-shift for the introduction of Cr.

Then we further analyzed the electronic structures of the TiO₂ (101) surface under the influence of the functionalizing molecules. Figure 9 shows the total density of states (TDOS) of CFAS and catechol, respectively. It can be observed that catechol exerts a key influence on electronic properties of pure TiO₂ (101) surface. The adsorbed catechol gives rise to narrow band gap in the electronic properties of pure TiO₂ (101) surface, hence optical adsorption margin of CFAS moves to longer wavelength. Besides, adsorbed catechol produces three impurity states in the range of −2.5 eV−0 eV in figure 9. It is clear that there are delocalization and strong hybridization between occupied states and the top of the original valence band of CFAS. Therefore, it reveals that there is an interaction between catechol and pure TiO₂ (101) surface. Three impurity states promote charge carriers transition from valence band (or conduction band) to impurity states.

To explore the constituent of the impurity energy levels due to catechol functionalized, the TDOS of catechol functionalized pure and doped TiO₂ (101) systems are illustrated in figure 10. The energy bands of TDOS of catechol-Al-doped-TiO₂ shift wholly to the higher energy region compared with that of catechol-TiO₂ (see figures 10(a) and (b)). From figure 10(b), we can see clearly that only one impurity peak appears near the Fermi energy in TDOS of catechol-Al-doped-TiO₂ and impurity states caused by catechol functionalized mainly overlap with the valence band. As shown in figure 10(c), energy band also moves to the higher energy region and catechol functionalized generates the impurity states which overlapped with the valence band for catechol-Mg-doped-TiO₂. From figure 10(d), it can be seen that for catechol functionalized Cr-doped TiO₂ (101) surface, impurity states mainly contributed by catechol and Cr-doped appear localized between valence band and conduction band in the range from −2 eV−1 eV. Hence, the conductance of this system increases remarkably by reason that electrons of the valence band can enter into impurity states.
3.3. Optical properties
Absorption of photon describes optical properties, which provides detail information about the density of states and electronic band structure of a semiconductor \([51]\). Usually, the optical absorption coefficient is correlated with the imaginary part of the dielectric constant. The optical absorption spectrum of pure TiO\(_2\) (101) surfaces, and catechol adsorbed pure and doped TiO\(_2\) (101) systems are plotted in figure 11. We take visible-light optical absorption into consideration. From figure 11, it is obvious that all doped TiO\(_2\) (101) systems induce the enhancement of visible light absorption, in comparison with that of pure TiO\(_2\). After catechol adsorbed pure and doped TiO\(_2\) (101) systems, the adsorbed systems can harvest longer-wavelength visible-light. For optical absorption spectrum of Mg, Cr, and Al doped TiO\(_2\) (101) surface, the intensity of absorption peak of Mg-doped TiO\(_2\) located at the range of 0–1.5 eV is the largest one. Moreover, the intensity of absorption peak of Cr-doped TiO\(_2\) located at the range of 1.5–3 eV is the largest one. For catechol adsorbed pure and doped TiO\(_2\) (101) systems, the intensity of absorption peak of catechol adsorbed Cr-doped TiO\(_2\) located at the range of 1–3 eV is the largest one. That is because that the impurity energy levels in doped systems benefit the light absorption. As a bridge, the impurity energy levels will benefit the electron transition \([52]\). Therefore, compared with pure TiO\(_2\), the light absorption abilities of catechol-Cr-doped-TiO\(_2\) are enhanced in longer...
wavelengths regions. In brief, Cr-doped TiO₂ exhibits a more efficient material for DSSCs, these results agrees well with the recent experiment [18].

4. Conclusions

In this work, we report a theoretical investigation of doping effects of CFAS. According to our study, the negative adsorption energies of CFDAS reveal that the processes of catechol adsorbed on pure and doped anatase TiO₂(101) surfaces are exothermic. Catechol-Mg-doped-TiO₂ possesses the most stability due to the lowest adsorption energy value (−1.20 eV). The calculations of dopant formation energies show that the configuration of Al-doped TiO₂ is thermodynamically favorable under Ti-rich conditions. The substitution of Al, Mg and Cr for Ti in anatase TiO₂(101) surface would decrease band gap due to the gap states. Catechol functionalization introduces three impurity energy levels in the range of −2.5 − 0 eV. Compared with the Fermi energy of pure TiO₂, Cr-doped TiO₂ moves to the positive direction. The results indicate that Cr-doped TiO₂ is beneficial to increase the open circuit voltage. Furthermore, catechol adsorbed Cr-doped TiO₂ will cause narrow band gap, superior absorption in the visible light region. The results demonstrate that Cr-doped TiO₂ is a potential candidate as a photoanode material of DSSCs field application.

Acknowledgments

We thank the financial supports from the National Natural Science Foundation of China (21964006), the Theoretical Physics Special Project of National Natural Science Foundation of China (11747123), the Natural Science Foundation from Hunan Province (2020JJ4640, 2017JJ3340), and the Scientific Research Projects of Changsha University (Grant No. SF1603, SF1934), respectively.

ORCID iDs

Jin-Hua Luo https://orcid.org/0000-0001-6247-4517

References

[1] O’Regan B and Grätzel M 1991 A low-cost, high–efficiency solar cell based on dye-sensitized colloidal TiO₂ films Nature 353 737–40
[2] Hagfeldt A, Boschloo G, Sun L, Kloo L and Pettersson H 2010 Dye-sensitized solar cells Chem. Rev. 110 6595–663
[3] Sun H, Liu D, Wang T, Lu T, Li W, Ren S, Hu W, Wang L and Zhou X 2017 Enhanced internal quantum efficiency in dye-sensitized solar cells: effect of long-lived charge-separated state of sensitizers ACS Appl. Mater. Interfaces 9 9880–91
[4] Mousavi F, Shamsipur M, Taherpour A, (Arman) and Moghimi A 2021 Feasibility of using two benzo-substituted pyriliium-based compounds in dye-sensitized solar cells Mater. Sci. Semicond. Process. 123 105468
[5] Sreeja S and Pesala B 2020 Plasmonic enhancement of betanin-lawsone co-sensitized solar cells via tailored bimodal size distribution of silver nanoparticles Sci. Rep. 10 8240
[6] Roy J K, Kar S and Leszczynski J 2020 Revealing the photophysical mechanism of N,N’-Diphenyl-aniline based sensitizers with the D−D−π–A framework: theoretical insights ACS Sustainable Chem. Eng. 8 13328–41
[7] Wu M, Lin X, Wang Y, Wang L, Guo Q, Díez P, Peng X, Hagfeldt A, Grätzel M and Ma J 2012 Economical Pt-free catalysts for counter electrodes of dye-sensitized solar cells J. Am. Chem. Soc. 134 3419–28

[8] Hou Y, Wang D, Yang X, Fang W, Zhang B, Wang H F, Lu G Z, Hu P, Zhao J Y and Yang H G 2013 Rational screening low-cost counter electrodes for dye-sensitized solar cells Nat. Commun. 4 1583

[9] Bai Y, Cao Y, Zhang J, Wang M, Li R, Wang P, Zakeeruddin S M and Grätzel M 2008 High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts Nature Mater 7 626–30

[10] Horie Y, Daizaka K, Mukaë H, Guo S and Nomiyama T 2016 Enhancement of photocovery by columnar Nb-doped TiO2 compact layer in dye-sensitized solar cells with low temperature process of dc sputtering Electrochem. Acta 187 348–57

[11] Vafaei M and Mohammadi M R 2017 Impact of chromium doping on physical, optical, electronic and photovoltaic properties of nanoparticle TiO2 photoanodes in dye-sensitized solar cells New J. Chem. 41 14516–27

[12] Moradzaman M, Mohammadi M R and Nourizadeh H 2015 Efficient dye-sensitized solar cells based on CNs and Zr-doped TiO2 nanoparticles Mater. Sci. Semicond. Process. 40 383–90

[13] Matsubara M, Sanui R, Partoens B and Lamoën D 2017 Doping anatase TiO2 with group V-b and VI-b transition metal atoms: a hybrid functional first-principles study Phys. Chem. Chem. Phys. 19 1945–52

[14] Guo Y, Zou T, Cheng Q, Jiao B and Zhang X 2019 Towards improvement of photovoltaic performance of aqueous dye-sensitized solar cells by tungsten-doped mesoporous nanobeads TiO2 working electrode J. Wuhan Univ. Technol.-Mat. Sci. Ed. 34 17–22

[15] Nguyen H H, Gavvali G, Hoon I S, Sekino T and Lee S W 2018 Cr-doped TiO2 nanotubes with a double-layer model: an effective way to improve the efficiency of dye-sensitized solar cells Appl. Surf. Sci. 458 523–8

[16] Khosravi M, Toroghinejad M R, Vaezi M R and Saidi A 2020 Structural, electrical, optical and morphological properties of aluminum-doped TiO2 thin films deposited by spray pyrolysis method J. Mater. Sci. Mater. Electron. 31 7150–63

[17] Manju J and Joseph Jawhar S M 2018 Synthesis of magnesium-doped TiO2 photoelectrodes for dye-sensitized solar cell applications by solvothermal microwave irradiation method J. Mater. Res. 33 1534–42

[18] Nguyen Huy H, Gavvali G, Martinez-Ovieido A, Kshetri Y and Lee S 2020 Physicochemical properties of Cr-doped TiO2 nanotubes and their application in dye-sensitized solar cells J. Photochem. Photobiol. A 397 111816

[19] Mandal S, Kandregula G R and Tokala V N B 2020 A computational investigation of the influence of acceptor moieties on photovoltaic performance and adsorption onto the TiO2 surface in triphenylamine-based dyes for DSCC application J. Photochem. Photobiol. A, 401 112745

[20] Canto-Aguilar E J, Gutiérrez-Moreno D, Sastre-Santos A, Morikawa D, Abe M, Fernández-Lázaro F, Oskam G and Mori S 2020 Electronic structure of F-doped bulk rutile, anatase, and titanium dioxide J. Phys. Chem. C 123 537–46

[21] Liu L-M, Li S-C, Cheng H, Diebold U and Selloni A 2011 Growth and organization of an organic molecular monolayer on TiO2: a theoretical study: enhancing electron injection in dye-sensitized solar cells J. Mater. Chem. 21 11367–78

[22] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations Phys. Rev. B 13 5188–92

[23] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8

[24] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA + U study Phys. Rev. B 57 1505–9

[25] Tossoni S, Lamiel-Garcia O, Fernandez Hevia D, Doña J M and Ibars F 2012 Electronic structure of F-doped bulk rutile, anatase, and brookite polymorphs of TiO2 J. Phys. Chem. C 116 12738–46

[26] Burdett J K, Hughbanks T, Miller G J, Richardson W and Smith J V 1987 Structural-electronic relationships in inorganic solids: powder neutron diffraction studies of the rutile and anatase polymorphs of titanium dioxide at 15 and 295 K J. Am. Chem. Soc. 109 3639–46

[27] Van de Walle C G and Neugebauer J 2004 First-principles calculations for defects and impurities: applications to III-nitrides J. Appl. Phys. 95 3851–79

[28] Ma X, Wu Y, Lu Y, Xu J, Wang Y and Zhu Y 2011 Effect of compensated codoping on the photoelectrochemical properties of anatase TiO2 photocatalyst J. Phys. Chem. C 115 16963–9
[42] Tang H, Prasad K, Sanjines R, Schmid P E and Lévy F 1994 Electrical and optical properties of TiO$_2$ anatase thin films J. Appl. Phys. 75 2042–7
[43] Liu S, Liu G and Feng Q 2010 Al-doped TiO$_2$ mesoporous materials: synthesis and photodegradation properties J. Porous Mater. 17 197–206
[44] Elumalai N K and Uddin A 2016 Open circuit voltage of organic solar cells: an in-depth review Energy Environ. Sci. 9 391–410
[45] Seki K, Furube A and Yoshida Y 2015 Theoretical limit of power conversion efficiency for organic and hybrid halide perovskite photovoltaics J. Appl. Phys. 54 08K104
[46] Persson P, Bergstrom R and Lunell S 2000 Quantum chemical study of photoinjection processes in dye-sensitized TiO$_2$ nanoparticles J. Phys. Chem. B 104 10348–51
[47] Vittadini A, Selloni A, Rotzinger F P and Grätzel M 1998 Structure and energetics of water adsorbed at TiO$_2$ Anatase (101) and (001) Surfaces Phys. Rev. Lett. 81 2954–7
[48] Diebold U 2003 The surface science of titanium dioxide Surf. Sci. Rep. 48 53–229
[49] Moreno M, García-Lastra J M, Barriuso M T and Aramburu J A 2007 Transition metal impurities in wide gap materials: are the electronic properties well described through the ligand field theory? Theor Chem Account 118 665–71
[50] Peter L M 2007 Dye-sensitized nanocrystalline solar cells Phys. Chem. Chem. Phys. 9 2630
[51] Khan M, Cao W, Chen N, Asadullah and Iqbal M Z 2013 Ab-initio calculations of synergistic chromium–nitrogen codoping effects on the electronic and optical properties of anatase TiO$_2$ Vacuum 92 32–8
[52] Wu G, Zheng S K, Wu P, Su J and Liu L. 2013 Electronic and optical properties analysis on Bi/N-codoped anatase TiO$_2$ Solid State Commun. 163 7–10