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A DFT study of the electronic structures and optical properties of (Cr, C) co-doped rutile TiO$_2$

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Abstract

To get an effective doping model of rutile TiO$_2$, we systematically study geometrical parameters, density of states, electron densities, dielectric functions, optical absorption spectra for the pure, C mono-doping, Cr mono-doping and (Cr,C) co-doping rutile TiO$_2$, using density functional calculations. We find that a C doped system presents higher stability under Ti-rich condition, while Cr doped and (Cr,C) co-doped systems are more stable under O-rich condition. For (Cr,C) co-doping situation, the imaginary part of the dielectric function reflects the higher energy absorption efficiency for incident photons. Moreover, co-doping system exhibits much bigger red-shift of optical absorption edge compared with Cr/C single doping systems, because of the great reduction of the direct band gap. The calculated optical absorption spectra show that the (Cr,C) co-doping rutile TiO$_2$ has higher photocatalytic activity in the visible light region.

Keywords: rutile TiO$_2$; co-doping; impurity states; band gap; photocatalytic activity.

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1. Introduction

The most urgent task in the current society is to develop new environmental-friendly materials to replace traditional materials. This trend gives the driving force of TiO$_2$ (rutile and anatase) as photocatalytic materials, since they have great potential to utilize solar energy. Rutile is the most stable phase of titanium dioxide. It is used in photocatalysis, such as hydrogen production by water decomposition, self-cleaning, antimicrobial surfaces, water or air purification [1-5]. However, the intrinsic wide band gap (3.0 eV for rutile [6]) limits these applications. Moreover, the wide band gap restricts rutile to respond only to ultraviolet (UV) irradiation. Since the UV-light region accounts for less than 5% of the total solar spectra, rutile has low efficiency for using sunlight. To overcome these limitations, we have to find a way to reduce the band gap and consequently to enhance the photocatalytic efficiency.

In order to overcome the UV limitation, some scholars use nonmetal ions to dope rutile titanium dioxide. He et al. [7] found that band gap narrows by 0.4 eV after iodine doping, which promotes the photocatalytic activity. Dan et al. [8] found that replacing two O atoms with two N atoms can greatly increase the optical absorption in the visible light region. Pan et al. [9] found that the impurity energy level is introduced due to the coupling between O 2p and C 2p states, leading to the red-shift of optical absorption edge obviously. Moreover, the efficiency of light absorption increases after doping. Other scholars put forward the method of metal ions doping. Yu et al. [10] calculated a substitutional Sn doping at the Ti site, leading to reduce the band gap of rutile TiO$_2$, with a strong red-shift enhancement. Shao et al. [11] performed DFT (density functional theory) on Mn substitutional doping rutile, which can make full use of wide spectral region under solar irradiation.

Recent studies have shown that by using appropriate dopants, rutile TiO$_2$ can be transformed into a superior photocatalyst. M Fittipaldi et al. [12] concentrated on (B,F) co-doping rutile TiO$_2$, finding that the interaction between B and F leads to evidently enhanced performances in pollutant degradation. Liu et al. [13] have synthesized (S,N) co-doping rutile TiO$_2$ photocatalyst, applying a hydrothermal method and subsequent nitridation under NH$_3$ flow. They found that (S,N) co-doping rutile TiO$_2$ has a better photocatalytic activity than S mono-doping or N mono-doping for degradation of methylene blue in the visible light region (wavelength is about 400-760 nm). Han et al. [14] found that N + H co-doping induces obvious band gap reduction without introducing any impurity states in the forbidden gap. Meanwhile, metal ions and nonmetal ions co-doping rutile began to attract the attention of scholars. Dan et al. [8] studied the (N,Co) co-doping rutile TiO$_2$, which extends the optical absorption to the visible light region. Zhu et al. [15] calculated that optical properties of co-doping rutile TiO$_2$ with nitrogen and platinum group metals (Ru,Rh,Pd), showing that an improvement of the absorption efficiency of visible light to some extent.

In this work, we calculate geometry structures, electronic structures and optical properties of Cr/C substitutional mono-doping and (Cr,C) substitutional co-doping
rutile TiO₂, using density functional theory. According to our previous experience, we first use WC (Wu and Cohen) [16] flavored generalized gradient approximation to optimize the geometrical structures, using the plane-wave ultrasoft pseudopotentials method as executed in CASTEP module. To explore electronic structures, we perform the total density of states and partial density of states for pure TiO₂ and doped TiO₂ models with HSE06 hybrid functional calculation on the frame of Gaussian type of orbital. The HSE06 hybrid functional calculation in Gaussian 09 has the advantages of significant time saving in comparison with HSE06 in CASTEP. Therefore, we can use the HSE06 hybrid functional in Gaussian 09 to calculate band gaps rapidly and accurately [22]. To predict the dielectric function and optical absorption spectra, we treat the band gaps by using HSE06/6-31G hybrid functional calculation in Gaussian 09 program as the experimental values. Then we calculate the band gap values using GGA-WC functional in CASTEP. The difference between two different kinds of band gap values is deemed as a correction value, i.e. 'scissors operator'. Finally, we put the 'scissors operator's back in CASTEP to calculate dielectric functions and UV-Vis absorption spectra, because Gaussian 09 lacks the ability to compute these two properties for extended systems. Thus, we can give a relatively reasonable explanation for the modification mechanism of (Cr, C) co-doped rutile TiO₂.

2. Computation

2.1 Models

Rutile TiO₂ belongs to the tetragonal crystal system [17], and the space group is P42/mnm (D144h). Each lattice contains six atoms (two Ti atoms and four O atoms). One Ti⁴⁺ ion is surrounded by 6 O²⁻ ions, and its coordination number is 6; one O²⁻ ion is surrounded by 3 Ti⁴⁺ ions, and its coordination number is 3. We use a 2x2x3 rutile supercell (Ti₂₄O₄₈) as a computational model, containing twelve primitive unit cells of rutile TiO₂. To build the mono-doping models, we substitute the single C and Cr atoms for single O and Ti atoms, respectively. Hence the obtained configuration is Ti₂₄CO₄₇/Ti₂₃CrO₄₈. For the (Cr, C) co-doping rutile TiO₂, we replace O and Ti atoms with C and Cr atoms, as shown in Figure 1. Thus, the configuration of Ti₂₃CCrO₄₇ with 2.08at% C and 4.17at% Cr is formed. The three doping concentrations chosen are relatively reasonable compared with experimental execution [18].
Figure 1. The pure TiO₂ and three doped models for the 2×2×3 rutile TiO₂ supercells are given. (a) the model of pure TiO₂, (b) the model of TiO₂@C, (c) the model of TiO₂@Cr and (d) the model of TiO₂@CrC. The titanium and oxygen atoms are denoted by gray and red balls, respectively. The substitutional carbon and chromium atoms are denoted by black and blue balls, respectively.

2.2 Computing methods

To optimize geometric structure, we do all the calculations with the WC (Wu and Cohen) flavor of GGA, using the plane-wave ultrasoft pseudopotentials method in CASTEP [16,19]. We first use the Visualizer in Materials Studio to realize the model building. Based on the optimized rutile TiO₂ unit cell, we build a 2x2x3 supercell, in which Cr and C atoms replaces Ti atom and O atom, respectively. After atomic substitution, we optimize the doped models. We have performed the optimization calculation with the minimization algorithm using the Broyden-Fletcher-Goldfarb-Shanno scheme [20]. The valence electronic configurations are considered as: 3s²3p⁵3d²4s² for Ti, 2s²2p⁴ for O, 3s²3p⁵3d⁵4s¹ for Cr, 2s²2p² for C. To achieve accurate calculation and fast convergence, the 2x2x2 Monkhorst-park Special K point is used to calculate the integral calculation of the irreducible Brillouin zone [21]. The convergence criteria for geometry relaxations in computational progress are set as: the cutoff energy for the plane wave basis set is 340 eV, the atomic maximal interaction forces are less than 0.3 eV/nm, the maximum displacement distance is less than 1x10⁻⁴ nm, atomic maximum internal pressure is less than 0.05 GPa, and the maximum atomic variational energy is less than 1 x10⁻⁵ eV. In addition, we calculate the TiO₆ dipole moments according to the dipole moment formula: \[ \mu = qd, \] where q denotes the net charge between Ti and O atoms, and d indicates the central distance between Ti and O atoms [22].
To accurately calculate the electronic properties after optimizing geometric structure, we use the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional with the modified 6-31G basis sets under the framework of the Gaussian-type orbital to calculate the density of states (DOS) in Gaussian 09 program. According our previous experience, the GGA-WC optimized geometric structures are very close to the optimized geometric structures in Gaussian 09 [23]. Therefore, we can use the former to save a lot of time. Gaussian 09 is a comprehensive computational quantum program for quantum chemistry, but now it has begun to be applied in solid state physics. For the modified 6-31G basis sets, we can remove the diffuse functions with an exponent less than 0.12, because good-quality molecular basis sets normally include diffuse functions to model tails of wave functions that do not exist in solids [24]. Therefore, the revised Ti and Cr basis sets can be used for TiO$_2$ solid calculation. To get the most satisfactory integration, we choose the ultrafine precision (int=ultrafine) in the energy calculation progress. Gaussian 09 provides a single point energy calculation for each system, and we use 8x8x8 k-mesh and corresponding 256 k-points, which is quite different from plane-wave scheme to adopt much fewer irreducible k-points. This is enough to produce necessary features in the density of states analyses for 2x2x3 rutile supercells. By completing the settings for these parameters, HSE06 hybrid functional in Gaussian 09 has full ability to predict electronic structures of doped models closest to experimental values.

Because Gaussian 09 is unable to calculate some optical absorption spectra for three-dimensional periodic solid systems, we take the band gaps of the doped systems in Gaussian 09 as the experimental values. After calculating band gaps for the same systems using GGA-WC functional, we treat the difference between two different band gap values as a 'scissors operator'. Then we calculate the dielectric functions and UV-Vis optical spectra by using 'scissors operator's in CASTEP.

3. Results and discussion

3.1 Geometrical parameters

To analyze geometrical changes after the dopant entering the lattice, we calculate the optimized cell parameters for the pure and different doped models, as shown in Table 1. The optimized bulk cell parameters for pure TiO$_2$ (a=b=4.593 Å, c=2.940 Å) are in good agreement with experimental values (a=b=4.594 Å, c=2.959 Å) [25,26] and other theoretical values (a=b=4.614 Å, c=2.976 Å) [7]. Clearly, our calculated a and b by GGA-WC are very close to experimental values. The value of c is different from ours. Our result is 0.64 percent less than experimental value, showing the reliability of our method. After doping, we find that the volumes for three doping samples have increased. This indicates that the introduction of dopant causes the volume expansion of supercells. Besides, we also calculate the average bond lengths, total energies, defect formation energies, average net charges, and dipole moments of substituted Ti/O doping, which are shown in Table 2.
Table 1. The calculated cell parameters, crystal volume changes for the pure TiO\textsubscript{2}, TiO\textsubscript{2}@C, TiO\textsubscript{2}@Cr, TiO\textsubscript{2}@CrC, TiO\textsubscript{2}@Cr\textsubscript{1}C\textsubscript{1} far, and the experimental values for pure TiO\textsubscript{2}.

<table>
<thead>
<tr>
<th></th>
<th>Exp</th>
<th>Pure TiO\textsubscript{2}</th>
<th>TiO\textsubscript{2}@C</th>
<th>TiO\textsubscript{2}@Cr</th>
<th>TiO\textsubscript{2}@CrC</th>
<th>TiO\textsubscript{2}@Cr\textsubscript{1}C\textsubscript{1} far</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.( Å)</td>
<td>2.959</td>
<td>2.940</td>
<td>2.955</td>
<td>2.942</td>
<td>2.947</td>
<td>2.948</td>
</tr>
<tr>
<td>V( Å\textsuperscript{3})</td>
<td>62.449</td>
<td>62.021</td>
<td>63.045</td>
<td>62.361</td>
<td>62.739</td>
<td>62.869</td>
</tr>
<tr>
<td>ΔV(Å\textsuperscript{3})</td>
<td>1.024</td>
<td>0.34</td>
<td>0.718</td>
<td>0.848</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. The average bond lengths, total energies, defect formation energies and average net charges for the pure TiO\textsubscript{2}, TiO\textsubscript{2}@C, TiO\textsubscript{2}@Cr, TiO\textsubscript{2}@CrC and TiO\textsubscript{2}@Cr\textsubscript{1}C\textsubscript{1} far.

<table>
<thead>
<tr>
<th>Models</th>
<th>Average bond length (Å)</th>
<th>Total energy (au)</th>
<th>E\textsubscript{f} (eV)</th>
<th>Average net charge (eV)</th>
<th>Dipole moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}</td>
<td>1.961</td>
<td>-23994.507</td>
<td></td>
<td></td>
<td>2.020</td>
</tr>
<tr>
<td>TiO\textsubscript{2}@C</td>
<td>1.978</td>
<td>2.091</td>
<td>-23957.174</td>
<td>2.061</td>
<td>-1.031</td>
</tr>
<tr>
<td>TiO\textsubscript{2}@Cr</td>
<td>1.974</td>
<td>1.909</td>
<td>-24189.271</td>
<td>2.94</td>
<td>-23.98</td>
</tr>
<tr>
<td>TiO\textsubscript{2}@CrC</td>
<td>1.967</td>
<td>2.226</td>
<td>-24152.038</td>
<td>8.65</td>
<td>-22.01</td>
</tr>
<tr>
<td>TiO\textsubscript{2}@Cr\textsubscript{1}C\textsubscript{1} far</td>
<td>1.969</td>
<td>2.104</td>
<td>-24151.944</td>
<td>6.09</td>
<td>-19.46</td>
</tr>
</tbody>
</table>

To explore the relative stability for C and Cr mono-doping/co-doping into the rutile TiO\textsubscript{2} lattice, we calculate the defect formation energies for these doping models under the reduction and oxidation conditions. To make a purposeful comparison, the farthest away configuration (TiO\textsubscript{2}@Cr\textsubscript{1}C\textsubscript{1} far) is also included. Here, we use the following formula to calculate the defect formation energies, which is performed by Yin et al. [27]:

\[
E_{\text{form}} = E(\text{doped}) - E(\text{pure}) + \mu_{\text{Ti}} + \mu_{\text{O}} - \mu_{\text{Cr}} - \mu_{\text{C}}
\]

where E(\text{doped}) and E(\text{pure}) are the total energies of the doping models containing all the impurities, of the pure host supercell, respectively. The \(\mu_{\text{O}}, \mu_{\text{Ti}}, \mu_{\text{C}}, \mu_{\text{Cr}}\) denotes the chemical potentials of the O, Ti, C and Cr, respectively. The chemical potentials depend on growth condition, which is different under Ti-rich or O-rich. Therefore, the difference of chemical potentials leads to the change of formation energy. For pure TiO\textsubscript{2}, \(\mu_{\text{O}}\) and \(\mu_{\text{Ti}}\) satisfy this relationship: \(2\mu_{\text{O}} + \mu_{\text{Ti}} = \mu_{\text{TiO}_2}\). Under oxidation condition, \(2\mu_{\text{O}}\) denotes the total energy of \(\text{O}_2\) molecule, and \(\mu_{\text{O}}\) can be calculated by: \(\mu_{\text{O}} = \mu_{\text{O}_2}/2\); for reduction condition, \(\mu_{\text{Ti}}\) denotes the total energy of the bulk metal Ti, namely \(\mu_{\text{Ti}} = \mu_{\text{Ti-metal}}\). The calculated defect formation energies of different doping models are given in Figure 2.

The calculated results indicate that three doping models have lower formation energies under O-rich condition than Ti-rich condition. Due to the lower formation energy, synthesis of Cr mono-doping or (Cr,C) co-doping TiO\textsubscript{2} has a great advantage...
under O-rich condition. In addition, here are some other features: (1) For C mono-doping situation under Ti-rich condition, the formation energy is less than O-rich condition. (2) The doped TiO$_2$ with Cr have the lowest formation energy under O-rich condition, which is the most stable one in this extreme condition. (3) Under Ti-rich condition, the formation energy of (Cr,C) co-doping TiO$_2$ is lower than Cr mono-doping, partly because of the mutual attraction between Cr and C atoms \[28,29\]. (5) The (Cr,C) adjacent co-doped system has lower defect formation energy than the farthest away system under Ti/O-rich condition.

![Figure 2](image.png)

**Figure 2.** The calculated defect formation energies of different doping models as a function of the difference of oxygen chemical potential.

### 3.2 Density of states and electron density

As mentioned above, we calculate the band gaps by using Gaussian 09 program with HSE06 hybrid functional calculation on the frame of Gaussian type of orbital. To analyze the composition of valence band and conduction band, and further understand the changes of the electronic structures, the total density of states (TDOS) and partial density of states (PDOS) of doping models are calculated in Figure 3. To facilitate comparison, we set the Femi levels as 0 eV in the DOS analysis process. For pure TiO$_2$, our calculation result is 3.06 eV, which is pretty close to experimental values \[26,30\], certifying the reliability of our method. The valence band mainly consists of O 2p states, and Ti 3d states are major composition for the conduction band. The electronic structures will change after Cr/C doping, due to the changes in geometrical structure. We consider the spin polarization of three doped systems in DOS calculation. We find that the spin up DOS is almost identical to the spin down
DOS, because Cr and C have an even number of electrons, and Cr is not a ferromagnetic element (Fe, Co, Ni), unlike the mono-doped TiO₂ with Cr studied by Pieve et al [31]. For C mono-doping TiO₂, there are three impurity states locate in the band gap. One of the impurity states is near the top of valence band, coupling with the valence band edge. This causes the valence band shifting up. Therefore, we can observe that the direct band gap is decreased to 2.74 eV. Our results are more accurate than previous theoretical values (The pure rutile TiO₂ is 2.0 eV, and 1.1 eV for C mono-doping) [32,33]. Other two impurity states are very close to the top of the valence band edge and the bottom of conduction band edge, which can transfer excited electrons with lower energy absorption to the conduction band. These two impurity states belong to shallow impurity levels, which can be used as capture traps for photo-generated electrons or holes, improving the photo-quantum efficiency. For Cr mono-doping TiO₂, the direct band gap value is decreased to 2.64 eV. This is slightly larger in comparison with other theoretical calculation value (2.3 eV), which is calculated by using LDA+U method [34]. For the valence band, the effect of O 2p states is greater than Ti 3d states, while the conduction band is opposite. A shallow impurity states approaches the valence band gap edge, which is a similar case to the C mono-doping. Remarkably, the Cr 3d state has small influence on the valence band. We find that (Cr,C) co-doping yields the best band structure in term of band gap and potential optical catalysis. The impurity states couple with the top of valence band edge and the bottom of conduction band edge. This narrows the direct band gap to 2.3 eV, which is similar to the calculated band gap of (V,N) co-doped rutile TiO₂ (2.52 eV) by using WIEN 2k package [35]. Therefore, (Cr,C) co-doping situation can further extend the optical absorption edge to visible light scope, which is propitious to strongly enhance photocatalytic activity.
Figure 3. The calculated total and partial DOS of pure TiO$_2$, TiO$_2$@C, TiO$_2$@Cr and TiO$_2$@CrC.

To further learn the electronic structure and process of electron-transfer, we plot electron density diagrams of three doping systems, as shown in Figure 4. The electronegativity of the C atom is 2.55, less than that of the O atom (3.44); and the electronegativity of the Cr atom is 1.66, higher than that of the Ti atom (1.54). Due to the existence of electronegativity difference, the charge density of doped plane will be redistributed. Clearly seen from Figure 4 (d), the charge density between Cr and C area in the co-doping situation is much bigger than that between Ti and O in un-doping TiO$_2$. This indicates that more charges transfer from Cr atom to adjacent C atom, and the Cr-C ionic bond is stronger than that of corresponding Ti-O bond in pure TiO$_2$. These two impurity atoms generate local internal electric fields in the doped localized region, which can inhibit the recombination of photo-generated electron-hole pairs, increasing photon-quantum efficiency to a large extent [36,37].

Figure 4. The calculated electron density for (a) pure TiO$_2$, (b) TiO$_2$@C, (c) TiO$_2$@Cr, (d) TiO$_2$@CrC. The color from blue to red indicates the change of electron density from low to high. The central white area of each atom shows that electron density exceeds the upper limit of color scope (0.650).
3.3 Dielectric function

To calculate dielectric functions for pure and doping systems, we first have to obtain their band gaps by using HSE06/6-31G hybrid functional calculation in Gaussian 09 program as the experimental values. Then we calculate the band gaps by using GGA-WC functional. We regard the difference between two different band gap values as a 'scissors operator', which can be seen in Table 3. Finally, we input the 'scissors operator's in CASTEP to calculate the dielectric functions, as shown in Figure 5.

Table 3. The band gap values calculated by HSE06 and GGA-WC, and corresponding 'scissors operator's for different models.

<table>
<thead>
<tr>
<th>Band gap (eV)</th>
<th>Pure TiO$_2$</th>
<th>TiO$_2$@C</th>
<th>TiO$_2$@Cr</th>
<th>TiO$_2$@CrC</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSE06</td>
<td>3.06</td>
<td>2.74</td>
<td>2.64</td>
<td>2.32</td>
</tr>
<tr>
<td>GGA-WC</td>
<td>1.87</td>
<td>1.03</td>
<td>1.54</td>
<td>1.29</td>
</tr>
<tr>
<td>Scissors operator</td>
<td>1.19</td>
<td>1.71</td>
<td>1.10</td>
<td>1.03</td>
</tr>
</tbody>
</table>

When an electromagnetic wave propagates through a medium and takes into account the influence of absorption, we use a complex number to describe the relative dielectric function [38,39]. This complex number can be expressed as $\varepsilon(w)=\varepsilon_1(w)+i\varepsilon_2(w)$, where $\varepsilon_1(w)=n(w)^2-k(w)^2$, $\varepsilon_2(w)=2n(w)k(w)$. The real part reflects the possibility that the electron-releasing energy shifts to the lower energy level. The imaginary part reflects the efficiency for electron absorbing photon energy. Therefore, the electron transition capability from valence band to conduction band depends on the imaginary part size of the dielectric function. Since the energy range of visible light is 1.63 eV-3.10 eV, we compare the change of imaginary part in this range. For C mono-doping system, the imaginary part of the dielectric function is slightly shifted left (about 2.0 eV), which extends the light response range. This is in good agreement with previous report on C anion-doped rutile [40]. After Cr mono-doping, imaginary part of dielectric function shows a trend of decreasing at first and then increasing, which is consistent with previous report (the inflection point appears in the energy= 1.92 eV) [41]. This reveals that the energy absorption efficiency of some incident photons is relatively low in this scope. More importantly, (Cr,C) co-doping system not only increases the values of imaginary part in the high-energy region (around 3.1 eV), but also increases the values in the range of visible light energy, thus improving photocatalytic activity. This is similar to (Cu,N) co-doping anatase TiO$_2$ [42].
Figure 5. The calculated dielectric functions of pure and different doping systems. The black solid line represents the real part, and the red dotted line represents the imaginary part.

3.4 Optical absorption spectra

In addition to the dielectric function analyses, we also systematically calculate the UV-Vis absorption spectra of these systems by using the 'scissors operator's, as shown in Figure 6. According to previous study, because of the intrinsic wide band gap, pure rutile TiO$_2$ can only absorb ultraviolet light, which indicates that the application range of pure TiO$_2$ is very limited. After C/Cr doping, the composition of electronic structure has changed, which makes optical absorption edge extend to visible light region. Beyond that, we discover that slight decrease of absorption coefficient for TiO$_2$@Cr and TiO$_2$@CrC in the ultraviolet region than pure TiO$_2$. For C mono-doping TiO$_2$, the optical absorption edge extends to 450-500 nm (2.49 eV-2.76 eV), leading to an increase of visible light absorption compared with pure TiO$_2$. This change is consistent with previous report (within the 400-575 nm range, C mono-doping TiO$_2$ has obvious red-shift to the absorption of visible light) [43]. Red-shift is attributed to band gap narrowing, which results in reducing the energy requirement for electron transition process. For Cr mono-doping situation, it presents a little stronger visible light absorption, due to slight band gap reduction than C doping. The impurity states are very close to the top of the valence band, which can be used to capture photo-generate holes, thus promoting photocatalytic activity. Therefore, according to the previous experiment [44], Cr mono-doped rutile
TiO$_2$ can be used for decomposing stearic acid when the doping concentration is in specific range. What's more, the red-shift of (Cr,C) co-doping is the most obvious among these doping situations, which is consistent with its satisfactory electronic structure. The impurity states couple with the top of valence band edge and the bottom of conduction band edge simultaneously, producing the narrowest band gap of 2.3 eV. Its optical absorption edge is largely broadened, and even extends to the adjacent infrared region. In summary, (Cr,C) co-doping rutile TiO$_2$ not only extends the optical absorption range to visible light area, but also enhances the capacity for absorbing visible light. This phenomenon is consistent with (Co,N) or (Cu,N) co-doping situation [8,36]. Accordingly, (Cr,C) co-doping system is a feasible scheme for promoting photocatalytic activity of TiO$_2$ in the visible light region.

![Figure 6](image_url)

**Figure 6.** The calculated UV-Vis absorption spectra of pure and three doped situations.

4. Conclusion

In this work, we investigate geometrical parameters, electronic structures and optical properties for C doping, Cr doping and (Cr,C) co-doping rutile TiO$_2$, using density functional theory calculation. The results show that the introduction of dopants causes lattice distortion, which leads to local internal electric field, causing the changes of dipole moments. For analyses of defect formation energy, the C doping system is more favorable under Ti-rich condition, while Cr doping and (Cr,C) co-doping systems are opposite. The doping effects will change the composition of DOS, band gaps, as well as charge distributions in doped planes. Moreover, the effect of dopants on the electronic structures is localized. For (Cr,C) co-doping system,
Impurity states couple with the top of valence band edge and the bottom of conduction band edge, respectively, due to the strong interaction between Cr and C atoms. For the analyses of dielectric function and UV-Vis absorption spectra, co-doping system not only increases efficiency of energy absorption, promoting electron transition, but also strengthens the absorption capacity of visible light, thus largely improving photocatalytic activity of TiO$_2$ under visible light area.

Acknowledgment

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• We calculate (Cr,C) co-doped rutile TiO$_2$ using density functional theory.
• The (Cr,C) co-doping situation is more energetically favorable under oxidation condition.
• The impurity states modify the electronic structures, resulting in band gap narrowing.
• The electron transfer between Cr and C atoms reflects a stronger ionic bond than Ti-O bond in pure TiO$_2$.
• The optimal band gap is found to be about 2.3 eV after (Cr,C) co-doping.