Electronic and optical performances of Si and Fe-codoped TiO₂ nanoparticles: A photocatalyst for the degradation of methylene blue

Yanming Lin, a, b, Zenyi Jiang, a, * Chaoyuan Zhu, b Xiaoyun Hu, c Xiaodong Zhang, d Haiyan Zhu, a, Jun Fan, d, Sheng Hsien Lin, b, e

a Institute of Modern Physics, Northwest University, Xi’an 710069, PR China
b Department of Applied Chemistry, Institute of Molecular Science, National Chiao-Tung University, Hsinchu 30050, Taiwan
c Department of Physics, Northwest University, Xi’an 710069, PR China
d School of Chemical Engineering, Northwest University, Xi’an 710069, PR China
e Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan

A R T I C L E   I N F O
Article history:
Received 26 February 2013
Received in revised form 23 April 2013
Accepted 28 April 2013
Available online 4 May 2013

PACS:
31.15.E-, 71.15.Mb, 71.20.-b

Keywords:
TiO₂
Codoping
Visible-light photocatalyst
Density functional theory

A B S T R A C T
The effect of substitutional Si, Fe, and Si and Fe (co)doping on the electronic structure and optical properties of anatase and rutile TiO₂ have been investigated by the density functional theory. The calculated results indicate that Si doping TiO₂ will induce an obvious band gap narrowing by mixing O 2p with Si 3p states, and a series of impurity energy levels (Fe 3d) appear in edge of the VB and the CB through Fe doping. The synergistic effects of Si and Fe codoping can extend optical absorption edge, which leads to higher visible-light photocatalytic activities than pure and monodoped anatase TiO₂. Si and Fe-codoped TiO₂ nanoparticles was examined by measuring the rate of methylene blue decomposition. The experimental results show that Si and Fe-codoped TiO₂ sample exhibits better optical absorption performance and higher photocatalytic activities for the degradation of methylene blue than pure and monodoped TiO₂, which verifies the reliability of our calculated results.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction
Solar energy is the most noteworthy among renewable and sustainable energy resources because it is a clean and unlimited resource of energy and has the global availability. In order to relieve the energy crises, environment pollution and global warming, utilization of solar energy using photocatalysts has been extensively studied [1–3]. Among all materials developed for photocatalytic applications, titanium dioxide (TiO₂) is shown to be most promising owing to its high efficiency, low cost, photo stability and nontoxicity [4–8]. However, as an important functional semiconductor material, the universal applications of TiO₂ are restricted to ultraviolet (UV) light (λ < 400 nm) due to the wide band gap of TiO₂ (3.2 eV for anatase phase and 3.0 eV for rutile phase). To efficiently utilize solar energy, reducing the band gap of TiO₂ to make it photosensitive to visible light has become one of the most important goals in photocatalytic and photovoltaic applications.

In the past decades, considerable efforts have been devoted to modifying the electronic structure of TiO₂-based materials. For example, doping with transition metals such as Ag, Fe, Cr, and Ni [9–12], for the sake of shifting the absorption edge of TiO₂ to visible light. However, the drawbacks of transition-metal-doped materials are attributed to their thermal instability, increase of carrier-recombination centers and the requirement of an expensive facility (e.g. ion implantation). An alternative method to decrease the band gap of TiO₂ can be achieved by substituting lattice oxygen with nonmetal elements such as C, N, Si, F, and I [13–17]. Among the nonmetal doping systems, Si-doping TiO₂ has been reported to be a good candidate due to its unique properties of high thermal stability, low carrier-recombination centers and narrowing the band gap of TiO₂, as Si 3p states can effectively mix with O 2p states, leading to an acceptor level above the valence band maximum [15,18–21].

A few latest researches show that different ions codoping into TiO₂ can further narrow its band gap and enhance its photocatalytic activity [22–28]. For instance, Li et al. reported the C/H-codoping produces significant band gap narrowing, which leads to higher visible-light photocatalytic efficiency than the C-doped anatase TiO₂ [23]. The research of Su et al. suggested that the codoping

© 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.04.061
of TiO$_2$ with N and Fe leads to the much narrowing of the band gap and greatly improves the photocatalytic activity under visible light irradiation [25]. Lv et al. reported the (Bi, C and N)-codoped TiO$_2$ nanoparticles [26]. It was found that the cation and the anion affect the properties of TiO$_2$ differently, and the order of photoactivity for TiO$_2$ samples is as follows: (Bi,SCN)-TiO$_2$ > Bi-TiO$_2$ > undoped TiO$_2$ > P25 TiO$_2$ under UV- or visible-light illumination. Long et al. investigated systematically the band gap engineering of (N,Si)-codoped TiO$_2$ from hybrid density functional theory calculations [28]. The calculated results show that N and Si codoping can harvest longer-wavelength visible light than either of N and Si monodoping, owing to the contribution from N 2p in the forbidden gap and Si 3p at the tail of the conduction band. These results indicate that codoping is one of the most effective approaches to extend the absorption edge to the visible light range in TiO$_2$. However, to the best of our knowledge, photocatalytic activity and optical absorption properties of Si and Fe-codoped TiO$_2$ for the degradation of methylene blue (MB) solution have no report on the theory and experiment. Therefore, the enhanced absorption of visible-light and photocatalytic activity are expected for Si and Fe-codoped TiO$_2$ material.

In this work, the electronic and optical performances of Si and Fe-codoped TiO$_2$ photocatalyst are studied using the density functional theory (DFT) to reveal the synergistic effects of Si and Fe codoping on the mechanism of band gap reducing and the origin of the enhanced visible-light photocatalytic activity. Nanocrystalline Si and Fe-codoped TiO$_2$ sample was successfully prepared by sol–gel-solvothermal method. It was found that the Si and Fe-codoped TiO$_2$ sample exhibited strong visible-light absorption and outstanding visible-light photocatalytic activity for the degradation of MB solution, which verified the reliability of our calculated results.

2. Calculational methods and experimental details

2.1. Computational details

The spin-polarized calculations were performed using the projector augmented wave (PAW) pseudopotentials as implemented in the VASP code [29,30]. The exchange correlation function was treated by the generalized gradient approximation (GGA) with the Perdew-Wang parameterization (known as GGA-PW91) [31]. The Brillouin-zone integrations were approximated by using the special k-point sampling of the Monkhorst-Pack scheme [32]. A cutoff energy of 500 eV and a mesh size of 5 × 5 × 5 were used for geometry optimization and electronic structure calculations. Using the block Davidson scheme, both the atomic positions and cell parameters were optimized until the residual forces were below 0.01 eV Å$^{-1}$. In order to obtain the band gap that was consistent with the experimental result, the GGA+$U$ method [33] was employed. The Coulombic interaction U and exchange energy J were set to be 10.0 eV and 1.0 eV, respectively. The calculated band gap of pure anatase TiO$_2$ was 2.9 eV, which was in good agreement with the experimental value [34]. The valence electron configurations considered in this study included Ti (3d$^2$4s$^2$), O (2s$^2$2p$^4$), Si (3s$^2$3p$^2$), and Fe (3d$^4$4s$^2$). All the (co)doped systems were constructed from a relaxed (2 × 2 × 1) 48-atom anatase and a relaxed (2 × 2 × 2) 48-atom rutile TiO$_2$ supercell, and shown in Fig. 1. As the position of Fe in the TiO$_2$ lattice was unclear, variety of positions of Fe atoms in the lattice were considered, such as substitutional Fe at the Ti site (Fe@Ti) and O site (Fe@O). In the Si-doped TiO$_2$, an Si atom is substituted by an Si atom (Si@Ti) [6]. Similar substitutions were also considered for codoped systems, as Fe locates at either Ti or O site and Si locates at Ti site, namely, Si@Ti and Fe@Ti and Si@Ti and Fe@O.

2.2. Preparation of the photocatalyst

Nanocrystalline TiO$_2$ codoped with Si and Fe in this work was prepared by a sol–gel-solvothermal method. Tetrabutyl titanate ([CH$_3$][(CH$_2$)$_3$]O)$_4$Ti) was used as a starting material, tetraethyl orthosilicate ([C$_2$H$_5$O]$_4$Si) as a silicon source, and ferric nitrate hexahydrate (Fe(NO$_3$)$_3$·9H$_2$O) as an iron source. All chemicals used in the experiments were of analytical reagent grade. Firstly, a desired amount (0.3367 g) of Fe(NO$_3$)$_3$·9H$_2$O was dissolved in 39.66 ml of glacial acetic acid (CH$_3$COOH) solution under stirring. Then, 5.58 ml of (C$_2$H$_5$O)$_4$Si was dropwise added into the solution with stirring for 1 h. Secondly, 28.36 ml of [CH$_3$][(CH$_2$)$_3$]O)$_4$Ti was also dropwise added into the solution with continuous stirring for 2 h, and the solution was transferred to a Teflon tube and placed in a 300 cm$^3$ stainless steel autoclave and the solution was heated in an oven and kept at 140 °C for 14 h. Thirdly, the precipitate obtained

![Fig. 1. Geometries of doping systems: (a) anatase supercell (Ti$_6$O$_{12}$) and (b) rutile supercell (Ti$_6$O$_{12}$). The atom doping sites are marked with Si and Fe. The gray spheres and red spheres represent the Ti and O atoms, respectively. The purple sphere and cyan sphere represent Si and Fe atom, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)](image-url)
was washed with ethanol and distilled water, respectively. Finally, the precipitate obtained was dried in a vacuum oven at 70 °C for 48 h. For comparison purposes, the samples of pure, Si-doped and Fe-doped TiO2 were also prepared by similar procedures, respectively.

2.3. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2400 diffractometer with Cu Kα radiation with \( \lambda = 0.154178 \) nm. The Brunauer–Emmett–Teller (BET) surface area of the samples was measured through nitrogen adsorption at 77 K (Nova 2000e). All the samples were degassed at 473 K for 4 h before the measurement. The UV–vis absorption spectra were obtained on an UV–vis spectrophotometer (UV-3600) equipped with an integrating sphere assembly, and using BaSO4 as the reference sample. The spectra were recorded at room temperature in air within the range 300–800 nm.

2.4. Photocatalytic measurement

To evaluate the photocatalytic activity of samples, photocatalytic experiments were carried out in an inner-irradiation-type reactor. A cylindrical reaction cell was used to contain the reaction solution and a 500 W long-arc xenon lamp surrounded with a water cooling system was fixed in the center of the reaction cell. 0.2 g of photocatalyst was suspended in 200 mL of a methylene blue solution (20 mg/L) under stirring magnetically. The mixture was kept in the dark for 30 min to establish an adsorption–desorption equilibrium before the light radiation. The amount of MB in the solution was determined on the basis of its characteristic optical absorption at 665 nm using an UV–vis spectrophotometer based on Lambert–Beer’s law.

3. Results and discussion

3.1. Optimized structure and defect formation energy

We performed structure optimization for the pure anatase and rutile TiO2 supercell. For the anatase TiO2, our calculated lattice parameters are \( a = b = 3.774 \AA \) and \( c = 9.409 \AA \), which are in good agreement with the experimental values of \( a = b = 3.782 \AA \) and \( c = 9.502 \AA \) (within an error of 0.98%) [35]. For the rutile TiO2, the calculated parameters of the unit cell are \( a = b = 4.566 \AA \) and \( c = 2.950 \AA \), which are consistent with the experimental values of \( a = b = 4.593 \AA \) and \( c = 2.959 \AA \) (within an error of 0.59%) [35]. These results indicate that our calculation methods are reasonable, and the calculated results are authentic.

To probe the stabilities of the doped systems, we calculated the defect formation energy (\( E_f \)) for the doped and codoped systems according to the formulas

\[
E_f(\text{X@Y}) = E(\text{X@Y}) - E(\text{Pure}) - (\mu_X - \mu_Y)
\]

\[
E_f(\text{Si@Ti} + \text{Fe@Ti}) = E(\text{Si@Ti} + \text{Fe@Ti}) - E(\text{Pure}) - (\mu_{\text{Si}} + \mu_{\text{Fe}} - \mu_{\text{O}} - \mu_{\text{V}})
\]

\( X = \text{Si, Fe; Y = Ti, O} \)

where \( E(\text{Pure}) \) is the total energy of the host pure TiO2 supercell, \( E(\text{X@Y}) \) and \( E(\text{Si@Ti} + \text{Fe@Ti}) \) are the total energies of the supercells containing the impurities. For TiO2, the chemical potentials of O and Ti satisfy the relation ships \( \mu_{\text{Ti}} + 2 \mu_{\text{O}} = \mu_{\text{TiO}_2} \), \( \mu_{\text{O}} \leq \mu_{\text{O}_2} \), and \( \mu_{\text{Ti}} \geq \mu_{\text{metal}} \). The chemical potential \( \mu_{\text{O}} \) is determined by the energy of an O2 molecule, \( \mu_{\text{Ti}} \) is the energy of one Ti atom in the bulk Ti. \( \mu_{\text{Si}} \) and \( \mu_{\text{Fe}} \) are the chemical potentials of the Si and Fe impurities, which are calculated from the bulk Si and Fe, respectively. It should be noted that the smaller the \( E_f \) value, the more easily the impurity ions can be incorporated into the TiO2 supercell. Our calculated formation energies for all doped and codoped TiO2 are listed in Table 1. It can be observed that the formation energy of Fe@Ti and Si@Ti and Fe@Ti are much smaller than that of FeO@Ti and Si@Ti and Fe@O in Fe-doped and Si and Fe-codoped anatase TiO2 under O-rich growth condition, and the formation energy of FeO@Ti and Si@Ti and Fe@O are much smaller than that of Fe@Ti and Si@Ti and Fe@Ti under Ti-rich growth condition, respectively. In particular, the formation energy of Fe@Ti and Si@Ti and Fe@Ti are negative values under O-rich growth condition, which indicates that the Si and Fe impurity are readily incorporated into the crystal. For the rutile TiO2 system, the formation energy of Fe@Ti and Si@Ti and Fe@Ti are much smaller than that of FeO@Ti and Si@Ti and Fe@O in Fe-doped and Si and Fe-codoped systems under both O-rich and Ti-rich growth conditions. These results indicate that Si and Fe impurities are preferred to substitute the Ti ion in anatase and rutile TiO2 systems under both Ti-rich and O-rich growth conditions, and Si@Ti and Fe@Ti/TiO2 photocatalyst has higher stability than other doped systems. Fig. 1(a) and (b) shows the corresponding anatase and rutile TiO2 geometries, respectively.

3.2. Electronic structures

To study the effects of Si or/and Fe doping on the photocatalytic activity and optical absorption properties of anatase and rutile TiO2, the electronic structures of all the (co)doping models are calculated. As the traditional DFT method seriously underestimated the band gap for semiconductors [35–37], we calculated the electronic structure using the DFT+U method, and the calculated band gap is 2.90 eV and 2.67 eV for anatase and rutile TiO2, respectively. This calculated results are consistent with the experimental value of 3.20 eV for anatase structure [38] and 3.00 eV for rutile structure [39,40].

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Defect formation energies of (co)doped anatase and rutile TiO2 systems.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doped</td>
<td>Defect formation energy (eV)</td>
</tr>
<tr>
<td>Anatase</td>
<td>Rutile</td>
</tr>
<tr>
<td>Ti-rich</td>
<td>O-rich</td>
</tr>
<tr>
<td>Si@Ti</td>
<td>1.1112</td>
</tr>
<tr>
<td>SiO@Ti</td>
<td>5.8479</td>
</tr>
<tr>
<td>Fe@Ti</td>
<td>8.2451</td>
</tr>
<tr>
<td>FeO@Ti</td>
<td>7.8023</td>
</tr>
<tr>
<td>Codoped</td>
<td>Si@Ti and Fe@Ti</td>
</tr>
</tbody>
</table>

The total density of states (TDOS) and partial density of states (PDOS) of the (co)doping anatase TiO2 are calculated and plotted in Fig. 2 for all the pure and doping anatase TiO2 models, with up-spin DOS above zero and down-spin DOS below zero. For comparison, the TDOS and PDOS of pure anatase are also calculated, which indicate that the valence band (VB) mainly consists of the O 2p states with a large bandwidth, showing strong delocalization and bonding characteristic among the O 2p electrons, while the conduction band (CB) is mainly contributed by the Ti 3d states. In Si-doped anatase TiO2 (Si@Ti), the VB broaden as the mixing of O 2p and Si 3p states, and the CB bottom has a decline about 0.15 eV, which can lead to a band gap narrowing. For Fe-doped anatase TiO2 (Fe@Ti), it is shown that the band gap decreases by about 0.6 eV and most Fe 3d states are located in the band gap compared with the pure anatase TiO2, which may be due to stronger interactions between the Fe 3d and Ti 3d orbitals. For Si and Fe-codoped anatase TiO2 system (Si@Ti and Fe@Ti), some impurity states (Si 3p and Fe 3d) are
mixed with the VB and CB edge. The top of the VB has an obvious upward shift while the CB bottom has an obvious downward shift, which results in a band gap narrowing of about 1.0 eV compared with the pure anatase TiO2. Thus, synergistic effect of Si and Fe codoping can lead to a decrease of the photon excitation energy and redshift the optical absorption edge to the visible-light range.

As in the case of (co)doping rutile TiO2, the electronic structures of all the pure and doping rutile TiO2 models were also calculated in order to investigate the Si and Fe doping effects on the optical absorption of rutile TiO2. The TDOS and PDOS of all the models are shown in Fig. 3, with up-spin DOS above zero and down-spin DOS below zero. For pure rutile TiO2, the VB is mainly contributed by the O 2p state, while the CB is mainly contributed by the Ti 3d state, as shown in Fig. 3(a) and (a’). The calculated band gap value is 2.67 eV, which is similar to other theoretical results [41,42]. For Si-doped rutile TiO2 (Si@Ti), the VB broadens with the coupling of O 2p and Si 3p states, and the top of the VB has a rise about 0.12 eV compared with pure rutile TiO2. These results lead to a band gap narrowing. For Fe-doped rutile TiO2 (Fe@Ti), the top of the VB has a rise about 0.3 eV with the mixing of Fe 3d and O 2p states. Compared with the pure rutile TiO2, the CB bottom has a decline about 0.11 eV with the coupling of Fe 3d and Ti 3d states. Consequently, Fe doping can further reduce the energy needed for electrons to be excited from the VB to the CB, which may be responsible for the redshift phenomena of optical absorption edge in Fe-doped TiO2. For Si and Fe-codoped rutile TiO2 (Si@Ti and Fe@Ti), the top of the VB also has a rise about 0.48 eV with the coupling of Si 3p, Fe 3d and O 2p states. And the bottom of the CB has a decline about 0.23 eV with the mixing of Fe 3d down-spin state and Ti 3d state. These results may induce an obvious redshift of the optical absorption edge in Si and Fe-codoped TiO2.

Therefore, synergistic effects of Si and Fe codoping lead to a decrease of the photon excitation energy from the VB to the CB, which may induce more significant redshift of the absorption spectrum. The calculated results indicate that Si and Fe codoping may lead to an outstanding photocatalytic activity in TiO2 material.

3.3. Optical properties

According to the obtained electronic structures, we calculated the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$. The dielectric function can be defined in terms of current and field, which is most applicable for conductivity and optical responses. The corresponding absorption spectrum was estimated by the following equation

$$I(\omega) = 2\omega \left( \frac{\varepsilon_2^2(\omega) + \varepsilon_1^2(\omega) - \varepsilon_1(\omega)}{2} \right)^{1/2}$$  \hspace{1cm} (3)

where $I$ is the optical absorption coefficient, $\omega$ is the angular frequency ($\omega = h\omega$).

The absorption spectrum of the pure and doping TiO2 systems are calculated and shown in Fig. 4. In anatase TiO2 (see Fig. 4(a)), it is
Fig. 3. Calculated TDOS and PDOS of different doping rutile TiO$_2$. The top of the valence band of pure rutile TiO$_2$ is taken as the reference level. Curves above and below the horizontal axis refer to the up-spin and down-spin DOS, respectively.

Fig. 4. The optical absorption spectra of pure and doping TiO$_2$ models: (a) anatase phase, and (b) rutile phase.

Fig. 5. XRD patterns for the pure and doping TiO$_2$ samples.

found that pure anatase TiO$_2$ can only respond to the UV-light and show no absorption activity in the visible-light region. For Si-doped system, it is clear that the narrowed band gap induces the increasing optical absorption in the UV-light region. For Fe-doped system, there are a series of impurity states (Fe 3d orbital) appearing in the band gap and the band gap has an obvious narrowing, which leads to a good optical absorption in the visible-light region. For Si and Fe-codoped TiO$_2$ system, synergistic effect of Si and Fe codoping induces a band gap narrowing, which lead to a decrease of the photon excitation energy in the view of electronic structure. It is also found that the pure rutile TiO$_2$ (Fig. 4(b)) can only respond to the UV-light and shows no absorption performance in the visible-light region. For Si doping system, with the coupling of O 2p and Si 3p states, the narrowed band gap induces the increasing optical absorption in the UV-light region. For Fe doping system, there are some impurity states (Fe 3d states) appearing in the edge of the VB and the CB. Thus, the electron transition from these impurity states to the CB would lead to an obvious reduction of absorption energy, which enhances the visible-light absorption for Fe-doped
TiO$_2$. For Si and Fe-codoped system, it is obvious that the Si and Fe-codoped TiO$_2$ has a strong visible-light absorption in the range of 420–680 nm, which is due to decrease energy needed for electrons to be excited from the VB to the CB with synergistic effect of Si and Fe codoping. Therefore, Si and Fe doping may lead to an excellent visible-light photocatalytic activity in TiO$_2$ material.

3.4. Characterization of the samples

Fig. 5 illustrates the XRD patterns for pure anatase TiO$_2$, Si-doped, Fe-doped and Si and Fe-codoped TiO$_2$ samples. It is found that almost all of the diffraction peaks are contributed by the anatase TiO$_2$ phase and no other visible impurity peak can be distinguished in the pattern of pure or doped sample. The BET surface areas for pure, Si-, Fe-, and Si and Fe-codoped TiO$_2$ are 84.21, 252.42, 226.72 and 308.31 m$^2$/g, respectively. It is shown that the surface area of TiO$_2$ powders is increased to 308.31 m$^2$/g with the coexistence of Si and Fe in TiO$_2$, about four times of that of pure TiO$_2$ powders.

The optical absorption spectra of the pure and doping systems are also measured by experiments, and shown in Fig. 6. Compared with the pure TiO$_2$, it is clear that the incorporation of Si into TiO$_2$ lattice induces the enhanced optical absorption in the UV-light region. For Fe-doped system, it exhibits an excellent absorption activity in the visible-light region. For Si and Fe-codoped TiO$_2$, it is obvious that the optical absorption in the UV-Vis region is stronger than that of pure TiO$_2$, especially in the visible-light region.

Therefore, the enhancement of absorption in the visible-light region can promote the utilization of the solar light, which may be responsible for the redshift of optical absorption edge and the outstanding photocatalytic activity in Si and Fe-codoped anatase TiO$_2$. However, there are small misalignments between the experimental and theoretical results, which may be due to neglect of the anisotropy of the absorption coefficient and the well-known limitation of DFT. But, from the perspective of qualitative analysis, the experimental results are consistent with the calculations.

3.5. Photocatalytic activity

The photocatalytic activity of the undoping and doping TiO$_2$ samples were evaluated by monitoring the degradation of MB, as shown in Fig. 7. The “Dark environment” shows that MB almost cannot be degraded using catalysts without the visible-light irradiation. The ‘Blank’ shows that MB almost cannot be degraded under the visible-light irradiation without catalysts, indicating that the photolysis can be ignored. The Si- and Fe-doped samples present the better photocatalytic activity compared with the pure TiO$_2$. This is because Si doping can reduce the band gap of TiO$_2$, while the impurity states of Fe 3d is also easy to appear in the forbidden gap of TiO$_2$. For Si and Fe-codoped TiO$_2$ sample (see Fig. 7), it has the best photocatalytic activity compared with the pure, Si-, Fe-doped TiO$_2$ samples, which is due to the enhanced optical absorption of visible and UV-light through Si and Fe codoping. Therefore, the Si and Fe-codoped TiO$_2$ sample exhibits best photocatalytic activity than the pure, Si-, Fe-doped TiO$_2$ samples.

4. Conclusion

In conclusion, we have investigated the electronic and optical performances of pure, Si-doped, Fe-doped, Si and Fe-codoped anatase and rutile TiO$_2$ based on DFT calculations. Our calculated results show that Si doping TiO$_2$ will induce an obvious band gap narrowing by mixing O 2p with Si 3p states, and there are a series of impurity energy states (Fe 3d) appearing in edge of the VB and the CB through Fe doping. The synergistic effects of Si and Fe codoping may further reduce the electrons excited energy from the VB to the CB under the visible-light irradiation, which enhances the photocatalytic activity and the redshift of absorption edge. The photocatalytic and optical absorption properties obtained by experiments reveal that Si and Fe-codoped TiO$_2$ sample exhibits better optical absorption performance and higher photocatalytic activities for the degradation of methylene blue than pure and monodoped TiO$_2$, which verifies the reliability of our calculated results.
Acknowledgements

Yanming Lin would like to thank Dr. Kesong Yang and Dr. Run Long for helpful discussions. This work was supported by the National Natural Science Foundation of China under Grants (Nos. 10647008, 50971095, and 21176199), the Research Fund for the Doctoral Program of Higher Education (Nos. 20096101110017 and 20096101110013), Key Project of National Science Foundation of Shaanxi Province of China (Nos. 2010JZ002 and 2011J10001), and Graduate’s Innovation Fund of Northwest University of China (No. YZZ12082).

References