Electronic Structures of Cu/S Co-doped/Anatase TiO₂ by First-principles

Wei Su ¹, Rui Zhao ²
Shukai Zheng ²

¹ College of Art, Hebei University, Baoding 071002, P.R. China
² Research Center for Computational Materials & Device Simulations, College of Electronic & Information Engineering, Hebei University, Baoding 071002, P.R. China
e-mail: zhshk@126.com

ABSTRACT
The structural parameters, band structures and density of states of anatase TiO₂ co-doped with Cu and S were calculated by first-principles based on the density functional theory. The results indicate that the volumes of the co-doped TiO₂ increase due to the lattice distortion. The calculated X-ray diffraction pattern shows that the crystal phase of TiO₂ is still kept as anatase after Cu and S co-doping. The band gap of TiO₂ broadened when S substitutes for Ti or O along with Cu substitutes for Ti. The calculated partial density of states shows that the impurity energy levels mainly come from the Cu 3d and S 3p orbital. The calculated results may provide some theoretical foundations for the photocatalytic activity enhancement of TiO₂ co-doped with Cu and S.

Keywords: Anatase TiO₂; Cu/S co-doping; first-principles.

1. INTRODUCTION
TiO₂ has been widely used in the photocatalytic field due to its non-toxicity, anti-oxidation, long-term stability and strong redox ability. When TiO₂ particles are irradiated by photons with energy greater than the band gap of TiO₂, the electrons in the valence band will transit to the conduction band and leave holes in the valence band. The electron-hole pairs can participate into all kinds of chemical reactions on the surface of TiO₂ and eventually degrade the pollutants in the solution. Due to the quick recombination of electrons and holes, the photocatalytic activity of TiO₂ is decreased greatly. In order to obtain a higher photocatalytic activity, doping metal and/or non-metal ions into the crystal lattice of TiO₂ is one of the mostly used methods. Sahoo and Gupta [1] synthesized Ag and Fe ions doped microcrystalline TiO₂ following a liquid impregnation technology. It was found that the Ag doped TiO₂ could degrade as high as 99% of the pollutants under UV light. Under visible light, Fe doped TiO₂ could degrade more than 96% and 90% for methylene blue and methyl blue, respectively. Vu et al. [2] synthesized highly active photocatalytic TiO₂ nanotubes by hydrothermal treatment in base medium using commercial TiO₂ powder as Ti-source. Then non-metal doped TiO₂ samples were made by post-synthesis using urea, thiourea, ammonium fluoride and ethylene glycol as N, S, F and C source. The degradation of Rhodamine B indicated that non-metal doped TiO₂ samples exhibited much higher photocatalytic activity under visible light irradiation as compared to that of non-doped TiO₂ sample. Khan et al. [3] synthesized Ag/N co-doped TiO₂ photocatalyst by hydrothermal method. The photocatalytic response is evaluated by the photodegradation of methylene blue under visible light irradiations. The results indicated that the co-doped TiO₂ showed a higher photocatalytic activity compared to pristine TiO₂.

To understand the reasons for the photocatalytic activity enhancement of TiO₂ from an atomic level, theoretical calculations of the electronic structures of doped TiO₂ systems are always carried out using the first-principles based on the density functional theory. Zheng et al. [4] calculated the electronic structures of P doped anatase TiO₂. It was found that the interstitial P doping maybe play an important role in the photocatalytic activity improvement of TiO₂. The calculated electronic structures of Bi doped TiO₂ [5] indicated that Bi doping introduced impurity energy levels into the forbidden band of TiO₂ and resulted in a broadened band gap. The impurity energy levels were more important to the doped TiO₂ and could lead to a higher photocatalytic activity for TiO₂. Zhu and Liu [6] calculated the electronic structures of Mo, C and Mo/C doped TiO₂ using Vienna ab initio simulation package. The calculated results indicated that the optical
absorption edges of the Mo-C co-doped TiO$_2$ shifted towards the visible light region and the effective band gap was narrowed about 0.9 eV.

Recently, there are some papers reporting the photocatalytic activity of Cu/S co-doped TiO$_2$ (Cu/S-TiO$_2$). Yan et al. [7] synthesized Cu/S-TiO$_2$ by sol-gel method and the photocatalytic performance of the samples was evaluated by the degradation of neutral red under UV and visible light illumination. The results showed that Cu/S-TiO$_2$ calcined at 450°C had the highest photocatalytic activity among all the samples, and the photocatalytic degradation of neutral red solution could reach 98.4% under UV illumination. Yi et al. [8] prepared Cu/S-TiO$_2$ nanoparticles by sol-hydrothermal process. The photocatalytic activity of Cu/S-TiO$_2$ was investigated with Acid Orange 7 as the model compound under visible light illumination. The results showed that Cu/S-TiO$_2$ had the highest visible light photocatalytic activity and good reusability performance. Zhang et al. [9] and Li et al. [10] modified S-doped TiO$_2$ with Cu using electroless plating, wet impregnation and chemical reduction, respectively. It was found that Cu/S-TiO$_2$ prepared by electroless plating method showed excellent visible light absorption ability, and the catalyst exhibited the highest photocatalytic activity for hydrogen generation in methanol solution under simulated sunlight. Wang et al. [11] fabricated S-TiO$_2$ via calcination of TiO$_2$ precursor and thiourea, then Cu species were plated on the surface of S-TiO$_2$ by electroless plating method. The results showed that Cu/S-TiO$_2$ had an excellent visible light absorption and photocatalytic reduction of CO$_2$ could be achieved under UV and visible light irradiation. Hussain et al. [12] prepared S-doped TiO$_2$ nano-photocatalyst with different Cu loadings by hydrothermal method. The photocatalytic activity of S-TiO$_2$ and copper loaded S-TiO$_2$ nanocatalyst were determined for degradation of phenol into hydrocarbons (methane, ethene, and propene) and photo reduction of CO$_2$ into ethanol. The activity results revealed that degradation of phenol and photoreduction of CO$_2$ increased with increasing copper loadings. Hamadanian et al. [13] synthesized Cu/S-TiO$_2$ by sol-gel method using titanium(IV) isopropoxide, CuCl$_2$·2H$_2$O and thiourea as precursors. The photocatalytic activity of samples was tested for degradation of methyl orange solutions. The results indicated that the Cu/S-TiO$_2$ had higher activity than undoped and Cu or S doped TiO$_2$ catalysts.

As mentioned above, although Cu/S-TiO$_2$ photocatalysts were reported in previous works [7-13], the authors only measured the physical and chemical properties using modern technologies without theoretical calculation analysis. Therefore, we calculated the related electronic properties of Cu/S-TiO$_2$ in this paper and the results were discussed, aiming at providing some basic insight of the photocatalytic activity enhancement for the experimental researches. Because there have been a lot of works focused on the calculations of pristine, single Cu or S doped anatase TiO$_2$ [4,14,15], so we will not discuss the single element Cu or S doped TiO$_2$ in this paper. We just concentrate on the electronic structures of Cu and S co-doped TiO$_2$.

2. MATERIALS AND METHODS

Previous works [7-13] reported that Cu/S-TiO$_2$ was in the form of anatase phase. Therefore, a 108 anatase TiO$_2$ supercell was built to perform the calculations. As the experimental results indicated that Cu was in the form of cationic ion [6-13], and S was in the form of anionic [12,13] or cationic [8,9,13] ion, so we built two models: Cu cation and S anion co-doped TiO$_2$ (Cu-S/TiO$_2$), Cu cation and S cation co-doped TiO$_2$ (Cu$^+$S/TiO$_2$). As shown in Fig.1, the central Ti atom was substituted by one Cu atom, and Cu-S/TiO$_2$ and Cu$^+$S/TiO$_2$ models were obtained when one O atom (marked as S1) or one Ti atom (marked as S2) was substituted by one S atom.
Figure 1: Structural model of Cu/S co-doped TiO$_2$

All calculations were performed using CASTEP [16] software. The exchange-correlation function is Perdew-Burke-Ernzerhof. The interaction between valence electrons and the ionic core is described by ultrasoft pseudopotential. The valence electrons configurations are Ti: 3s$^2$3p$^3$3d$^2$4s$^2$, O: 2s$^2$2p$^4$ and S: 3s$^2$3p$^4$. The cut-off energy of plane wave basis is set as 300eV. The convergence threshold for the maximum energy change, maximum force, maximum stress and displacement tolerances are set as $2.0 \times 10^{-5}$ eV/atom, 0.05 eV/Å, 0.1 GPa and 0.002 Å, respectively. The special points sampling integration over the Brillouin zone is carried out using the Monkhorst-Pack method with a $2 \times 2 \times 2$ special-point mesh.

3. RESULTS AND DISCUSSION

The calculated structural parameters are listed in Table 1. Compared with the pristine TiO$_2$, the volumes of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ increased about 1.3% and 1.1%, respectively. This result means that S anion can induce more lattice distortion than S cation. Usually, lattice distortion always results in inner electronic field which can facilitate the separation of electron-hole pairs in the crystal, and thereby enhance the photocatalytic activity of TiO$_2$. The calculated results of the lattice distortion are in consistent with the photocatalytic activity improvement of Cu and S co-doped TiO$_2$ obtained from the experimental researches [7-13].

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.8073</td>
<td>3.8073</td>
<td>9.8232</td>
<td>1281.55</td>
</tr>
<tr>
<td>Cu+S/TiO$_2$</td>
<td>3.8579</td>
<td>3.7717</td>
<td>9.8967</td>
<td>1295.93</td>
</tr>
</tbody>
</table>

Although Cu and S co-doping induces lattice distortion of TiO$_2$, the crystal phase of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ keep unchanged, as shown in Fig.2. The calculated X-ray diffraction (XRD) pattern of pristine TiO$_2$ is in the form of anatase. The XRD peaks of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ are similar to those of pristine TiO$_2$, which indicates the crystal phases of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ are anatase. Because of the lattice distortion caused by the Cu and S co-doping, some XRD peak positions of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ shift a little when compared with those of TiO$_2$. Some peaks of the Cu-S/TiO$_2$ and Cu+S/TiO$_2$ show splitting in the graph, which also can be caused by the lattice distortion. This is in consistent with the calculated structural parameters. The lattice constants a, b and c of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ are different to those of pristine TiO$_2$. 

S1 Cu S2
The calculated energy band structures of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ are shown in Fig. 3. When the calculations were performed, the highest energy level occupied by electrons was set as the energy zero point. The band gaps of Cu-S/TiO$_2$ and Cu+S/TiO$_2$ are 2.43 eV and 2.30 eV, respectively. This means the Cu and S co-doping increase the band gap of TiO$_2$, as the calculated band gap of pristine TiO$_2$ is 2.20 eV [4]. As the experimental band gap of anatase is 3.2 eV [17], the smaller value calculated by DFT can be assigned to the GGA band gap underestimation. For a qualitative discuss, this underestimation will not affect the final conclusion. Four impurity energy levels (marked as 0, 1, 2, 3 in the figure) appear in the forbidden band of Cu-S/TiO$_2$ and Cu+S/TiO$_2$. The electrons in the valence band can be excited to the impurity energy levels and then transit to the conduction band, thereby reducing the photon energy needed for exciting the electrons. The impurity energy levels also can be the trap center for electrons and prolong the lifetime of electron-hole pairs, inhibiting the recombination of electrons and holes, and then the photocatalytic activity can be enhanced in the doped TiO$_2$ systems.
Density functional theory can be used to calculate the related electronic structures of many metal oxide semiconductors [18,19]. In order to know the component of the impurity energy levels in the forbidden band of Cu-S/TiO$_2$ and Cu+S/TiO$_2$, the partial density of states (PDOS) were calculated using the first-principles calculations based on the density functional theory, as shown in Fig. 4. For Cu-S/TiO$_2$, it is very clear that the impurity energy level at 0 eV is mainly composed of Cu 3d, S 3p and O 2p orbital. The impurity energy levels marked as “1” and “2” in Fig.3 (a) are the hybridization of Ti 3d, O 2p and S 3p orbital. The impurity energy level marked as “3” is mainly originated from Cu 3d orbital. The valence band of Cu-S/TiO$_2$ is the contribution of Ti 3d, O 2p, Cu 3d and S 3p orbital. Cu 3d and S 3p orbital almost have no effect on the conduction band. The conduction band is still composed of Ti 3d orbital, just like the pristine TiO$_2$ [4]. For Cu+S/TiO$_2$, the impurity energy level at 0 eV is only composed of Cu 3d orbital, which is different to the Cu-S/TiO$_2$. The impurity energy levels marked as “1” and “2” is the contribution of Cu 3d and O 2p orbital. The impurity energy level marked as “3” is originated from Cu 3d, Ti 3d and O 2p orbital. In Fig.4 (b), the S 3p orbital almost has no contribution to the valence band. Comparing Fig.4 (a) with Fig. 4 (b), it is obvious that S cation and S anion have very different effects to the impurity energy levels and valence band. S anion provides significant contributions to the impurity energy levels in the forbidden band and the valence band. But S cation has almost no contribution to the range of -7~2eV.

Figure 3: Band structures of (a) Cu-S/TiO$_2$, (b) Cu+S/TiO$_2$

![Graph showing band structures of Cu-S/TiO$_2$ and Cu+S/TiO$_2$.]
Above all, the photocatalytic activity enhancement of TiO$_2$ by Cu and S co-doping reported in the experimental researches can be explained as follow: the electrons in the impurity energy band can transit to the conduction band and leave holes staying in the impurity energy levels. Then the electrons in the valence band can transit to the impurity energy level and continue to transit to the conduction band under suitable photon’s irradiation. This process is an additional transition way for the electrons except those electrons transiting directly from the valence band to the conduction band. So the photocatalytic activity of TiO$_2$ co-doped with Cu and S is improved. At the same time, Cu and S Co-doping also provide a synergistic effect on the photocatalytic activity of TiO$_2$. From Fig. 3 it also can be seen that the Cu 3d orbital plays an important role to the doped TiO$_2$ during the photocatalytic process, because Cu 3d orbital provides contribution to the impurity energy levels in both Cu-S/TiO$_2$ and Cu+S/TiO$_2$.

4. CONCLUSIONS

The electronic structures of Cu and S co-doped anatase TiO$_2$ were calculated by the first-principles based on density function theory. Cu and S co-doping can result in the lattice distortion of TiO$_2$ with increased volume. The XRD patterns indicate that after co-doping, the crystal structure of co-doped TiO$_2$ remains similar to anatase. There are four impurity energy levels in the forbidden band of Cu and S co-doped TiO$_2$. The Cu 3d orbital may play an important role in the photocatalytic process. S cation and S anion have different contributions to the valence band and the impurity energy levels.

5. ACKNOWLEDGMENTS

The authors would like to express highly appreciation to Professor Baoting Liu at Hebei University for providing the CASTEP software and discussing the calculated results. This work is supported by the China Scholarship Council ([2014]-3012).

6. BIBLIOGRAPHY


