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Electronic Structures of Cu/S Co-doped/ Anatase TiO_2 by First-principles

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ABSTRACT

The structural parameters, band structures and density of states of anatase TiO_2 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 TiO_2 increase due to the lattice distortion. The calculated X-ray diffraction pattern shows that the crystal phase of TiO_2 is still kept as anatase after Cu and S co-doping. The band gap of TiO_2 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 TiO_2 co-doped with Cu and S.

Keywords: Anatase TiO_2; Cu/S co-doping; first-principles.

1. INTRODUCTION

TiO_2 has been widely used in the photocatalytic field due to its non-toxicity, anti-oxidation, long-term stability and strong redox ability. When TiO_2 particles are irradiated by photons with energy greater than the band gap of TiO_2, 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 TiO_2 and eventually degrade the pollutants in the solution. Due to the quick recombination of electrons and holes, the photocatalytic activity of TiO_2 is decreased greatly. In order to obtain a higher photocatalytic activity, doping metal and/or non-metal ions into the crystal lattice of TiO_2 is one of the mostly used methods. Sahoo and Gupta [1] synthesized Ag and Fe ions doped microcrystalline TiO_2 following a liquid impregnation technology. It was found that the Ag doped TiO_2 could degrade as high as 99% of the pollutants under UV light. Under visible light, Fe doped TiO_2 could degrade more than 96% and 90% for methylene blue and methyl blue, respectively. Vu *et al.* [2] synthesized highly active photocatalytic TiO_2 nanotubes by hydrothermal treatment in base medium using commercial TiO_2 powder as Ti-source. Then non-metal doped TiO_2 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 TiO_2 samples exhibited much higher photocatalytic activity under visible light irradiation as compared to that of non-doped TiO_2 sample. Khan *et al.* [3] synthesized Ag/N co-doped TiO_2 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 TiO_2 showed a higher photocatalytic activity compared to pristine TiO_2.

To understand the reasons for the photocatalytic activity enhancement of TiO_2 from an atomic level, theoretical calculations of the electronic structures of doped TiO_2 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 TiO_2. It was found that the interstitial P doping maybe play an important role in the photocatalytic activity improvement of TiO_2. The calculated electronic structures of Bi doped TiO_2 [5] indicated that Bi doping introduced impurity energy levels into the forbidden band of TiO_2 and resulted in a broadened band gap. The impurity energy levels were more important to the doped TiO_2 and could lead to a higher photocatalytic activity for TiO_2. Zhu and Liu [6] calculated the electronic structures of Mo, C and Mo/C doped TiO_2 using Vienna ab initio simulation package. The calculated results indicated that the optical

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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, $CuCl_2 \cdot 2H_2O$ 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 un-doped 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.

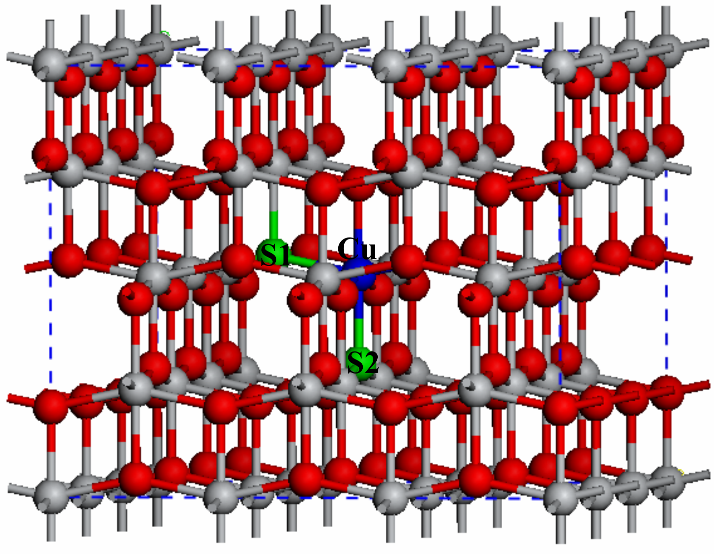


Figure 1: Structural model of Cu/S co-doped TiO_2

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: $3s^2 3p^6 3d^2 4s^2$, 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 2.0×10^{-5}eV/atom, 0.05eV/Å, 0.1GPa and 0.002Å, respectively. The special points sampling integration over the Brillouin zone is carried out using the Monkhorst-Pack method with a 2×2×2 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 1: Structural parameters for different TiO_2 systems

	a (Å)	b (Å)	c (Å)	Volume (Å^3)
TiO_2[4]	3.8073	3.8073	9.8232	1281.55
Cu-S/TiO_2	3.7996	3.8396	9.8870	1298.12
Cu+S/TiO_2	3.8579	3.7717	9.8967	1295.93

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.

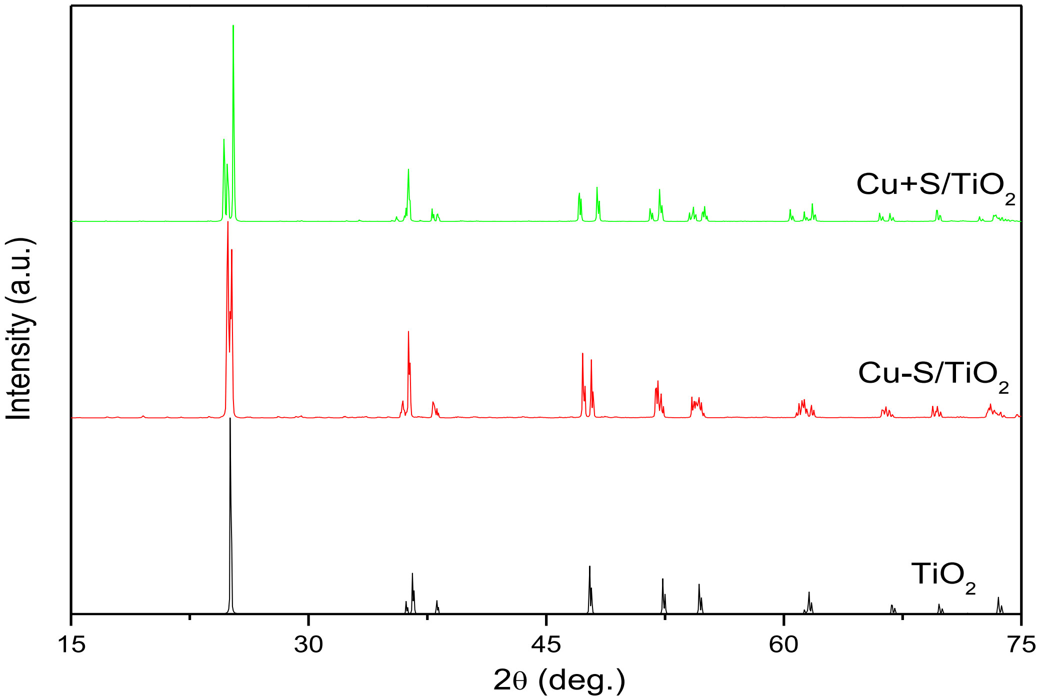
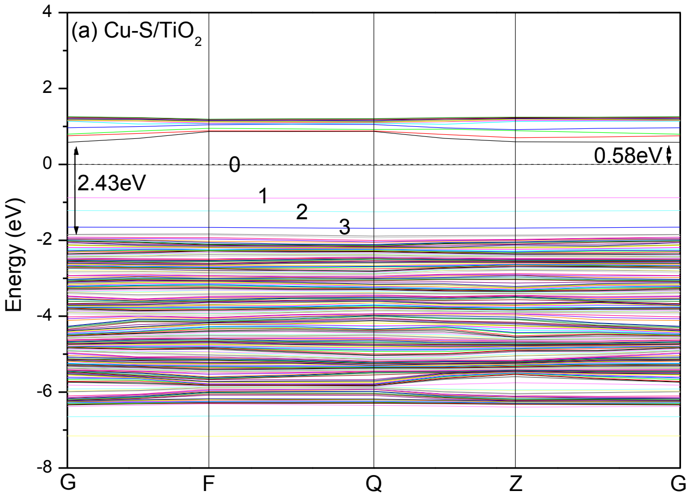


Figure 2: XRD patterns of different TiO_2 systems

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 2.43eV and 2.30eV, 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 2.20eV [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.



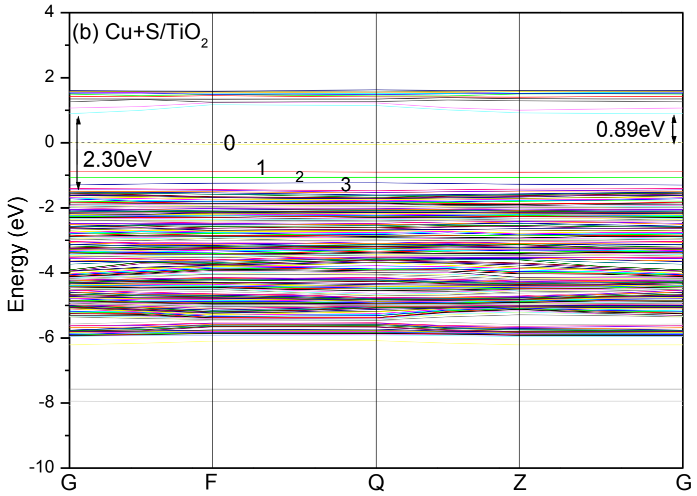
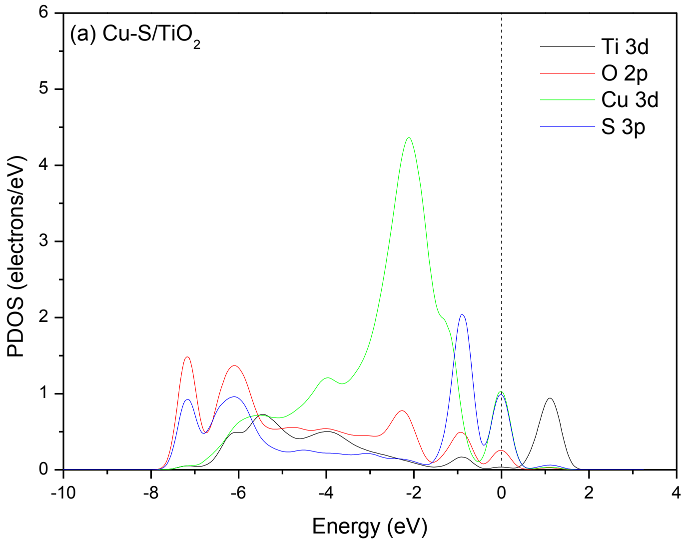


Figure 3: Band structures of (a) Cu-S/TiO$_2$, (b) Cu+S/TiO$_2$

Density function theory can be used to calculated 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.



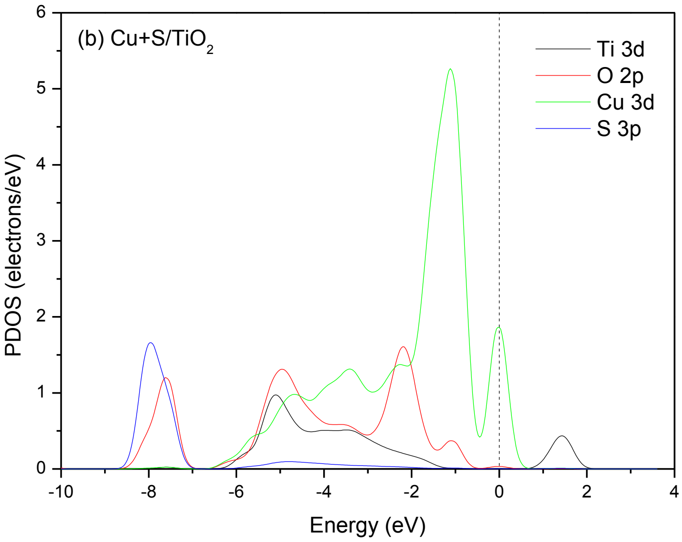


Figure 4: PDOS of (a) Cu-S/TiO$_2$, (b) Cu+S/TiO$_2$

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.

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