

Synergistic effect of Cu and Fe co-doping anatase TiO₂ on the electronic and optical properties

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The crystal structures optimizing, electronic and optical properties of pure, Cu or/and Fe doped anatase TiO₂ are studied by the method of the density functional theory (DFT) plane-wave ultrasoft pseudopotential in Materials Studio 5.5. The results suggested that the synergistic effect of Cu and Fe codoped anatase can facilitate the charge carrier mobility and reduce the undesired recombination, leading to enhanced photocatalytic activity.

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1. Introduction

TiO₂ is a metal oxide with a wide range of applications, such as hydrogen production [1], photoelectroncatalytic reduction of carbon dioxide [2], dye-sensitized solar cell [3] and conversion of carbohydrate into hydrogen fuel [4], because of the low cost to produce TiO₂ with photochemical stability and non-toxicity [5-7]. Also, TiO₂ has a wide band gap and the efficiency of photocatalytic reactions is limited by the high recombination rate of photoinduced electron-hole pairs formed in photocatalytic processes, these two intrinsic drawbacks limit the application of visible light and industrialized popularization application. Therefore, the photocatalytic efficiency improvement and the effective utilization under visible light are two of the most important points for TiO₂ as a photocatalyst. Many experimental [8-9] and theoretical studies [10-12] have been done on transition metal and nonmetal doping [13-14], semiconductor compounding [15] and organic dye sensitizing [6, 15] have been devoted to these points. Particularly, Yamashita et al. [8] had widely studied Fe, Mn, V ion doped TiO₂. They discovered that these metal ion-implanted TiO₂ can absorb visible light and work as a photocatalyst efficiently under visible light irradiation. Zheng et al. [9] studied Fe ion implanted TiO₂ films using Metal Vapor Vacuum Arc ion source technique. Their findings demonstrated that the absorption edge of the Fe:TiO₂ thin film has a red shift and the film also has a stronger absorption than the pure TiO₂ thin film in the visible region. Zhao et al. [10] reported 3d orbital of the transition metal doped in TiO₂, and found that Cr, Mn, Fe, Ni, Co and Cu did cause the absorption wave length to red

shift. The contradiction with the doping of Cu [11] and Fe [12-17] ion into TiO₂ lattice that it does result into reduction of photocatalytic activity.

The latest findings show that the double element co-doped TiO₂, such as N and Fe [18-20], N and Cu [21-22], Fe and Ce [23], Fe and Al [24], Fe and Ni [25], display higher photocatalytic activity compared to single doped. Some of the elements have synergistic effects in the photocatalytic experiments [18, 23]. It has not been reported that the cooperative effect of Cu/Fe codoped anatase (Cu:TiO₂:Fe) in theoretical calculation results. In present study, we calculate the electronic and optical properties of pure, Cu, Fe single and codoped anatase TiO₂ to better understand the microscopic mechanisms of the cooperative effect. This contribution will attract experimentalists to design novel catalysts based on our predictions.

2. Computational details

All calculations were carried out by the Cambridge Serial Total Energy Package (CASTEP) code within Material Studio 5.5, which uses a plane-wave ultra soft pseudo potential method [26]. The exchange-correlation energy was treated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [27]. The wave functions were expanded with the kinetic energy cut-off of 400 eV, and Monkhorst-Pack grid parameter fork-point sampling was 3×3×2. All convergence parameters were set as follows: 2.0×10⁻⁵ eV/atom for total energy tolerance, 0.05 GPa for

maximum stress component, and 0.002 Å for maximum displacement tolerance. The interaction between valence electrons and the ionic core is described by ultrasoft pseudopotential [28], which is used with 2s²2p⁴, 3d²4s², 3d⁶4s² and 3d¹⁰4s¹ as the valence electrons configuration for the O, Ti, Fe and Cu atoms, respectively.

Anatase TiO₂ has a tetragonal structure belonging to the spatial group I41/AMD. After structure optimization of the pure anatase TiO₂ super cell, the lattice parameters were obtained as follows: a=b=3.776 Å, c=9.486 Å. These datum are in good agreement with the measured results [23, 29], which implies the calculation methods are reasonable and the calculated results are considered to be reliable. For the similar ionic radius of Fe³⁺ (0.79 Å) [23], Cu²⁺ (0.72 Å) [30] and Ti⁴⁺ (0.75 Å), the doping anatase TiO₂ super cells were constructed by the Fe or/and Cu ion replaces the Ti⁴⁺ in the Ti lattice position forming the Fe:TiO₂, Cu:TiO₂, and Cu:TiO₂:Fe structure, respectively. After geometry optimization, the band structure, DOS, PDOS, optical properties and deformation charge density will be calculated.

3. Results and discussion

3.1 Band structures and density of states

The electronic band structures of pure anatase, Fe:TiO₂, Cu:TiO₂, and Cu:TiO₂:Fe (the conduction and upper valence bands) obtained along the Z-G-X-P-N-G path, Z-A-M-G-Z-R-X-Z path and G-Z-T-Y-S-U-X-R path in the first Brillouin zone, which are shown in Fig. 1 a), b), c), d), and their band gaps are about 3.16, 1.45, 0.36 and 0.14 eV, respectively. It is worth mentioning that the band gap of experimentally measured and theoretical calculation for pure and Fe doped anatase was 3.20 eV [31-32] and 1.85 eV [12, 20], which was slightly higher than our calculation results. This underestimation of the band gap is mainly due to the discontinuity in the exchange correlation potential [20, 32-33]. In the case of pure anatase (Fig. 1 a), the top of VB approximately locates near the X-point and the bottom of CB locates at the G-point, which means that anatase TiO₂ is an indirect-gap material, these is little probability that electrons from the CB transfer to the VB by emitting light. As shown in Fig. 1 b), c) and d), several impurity bands are located above the VB maximum. The presence of the intermediate levels separates the band-gap of TiO₂ into two parts: a wider lower gap and a significantly narrower upper gap [34]. These intermediate electronic states were generated by a substantial degree of hybridization between O 2p and Fe 3d (Fig. 2b 2d) and Cu 3d (Fig. 2c 2d). 3d states of Cu and Fe are introduced as an impurity state, which play an important role in changing the band gap and enhance the optical properties of TiO₂. The electrons in the VB can be excited to the impurity energy levels, and then subsequently be excited to the CB via absorption of visible light due to the formation of impurity energy levels [21] (see Fig. 4). Furthermore, it is

clearly noticed that the band gap of Cu:TiO₂:Fe is 0.14 eV which is much less than that of pure anatase, Cu:TiO₂ and Fe:TiO₂. This result further demonstrates that the cooperative effect during codoping of two metal ions in anatase.

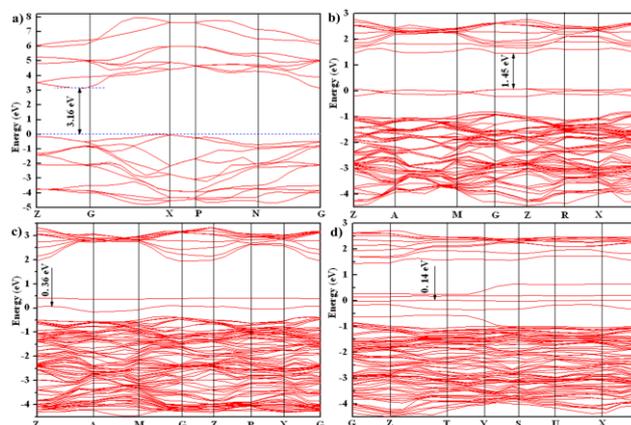


Fig. 1. Band structures of pure (a), Fe:TiO₂ (b), Cu:TiO₂ (c), Cu/Fe codoped anatase TiO₂ (d).

To better understand the constitution of the band structures and identify the possible mechanism of Cu:TiO₂, Fe:TiO₂ and Cu:TiO₂:Fe for narrowing the band gap of TiO₂ to cause significant red-shift, the density of states (DOS) and the PDOS of every atoms, were calculated (see Fig. 2). As shown in Fig. 2a, the VB of pure anatase TiO₂ mainly consists of O 2p and Ti 3p, 3d. In the highest level of VB, the O 2p and Ti 3d states are predominantly found between -5 and 0 eV. The CB can be described within two sub-bands lying very close to each other. The lower sub-band is formed mainly by the Ti 3d orbitals with small admixture of the O 2s, 2p states and the upper is due to the Ti 3d states. Distribution of the Ti 3d states has two clearly distinguished maxima at about 3.6 and 6.6 eV, their appearance is due to the existence of two sets of orbits (t_{2g} and e_g) arising from the 3d states after they are split by an octahedral crystal field at the Ti position. Meanwhile, the hybridization between the Ti 3d and O 2p levels at the VB can be observed, which is in good agreement with the previous calculated results [35]. Compared with the pure TiO₂, it is observed that the partially occupied 3d states of Cu or Fe mainly appear between the VB and CB in Fig. 2b, 2c, 2d, these states do not qualitatively change the distribution of O 2p and Ti 3d states, in consistent with the results of Wang et al. [36]. Several isolated energy states appear in the band structures of Cu or/and Fe doped anatase TiO₂ (see Fig. 1b, 1c, 1d) are due to the hybridization among Ti 3d with half-full 3d orbital of Fe or/and Cu, which can improve electron trapping in shallow trapping sites, thereby separating the arrival times between the electron-hole pairs at the surface. These gap states are able to act as electron traps and enhance photocatalytic activities [34]. As to anatase codoped with Cu and Fe, the

VB maximum is mainly composed of O 2p states with little Cu 3d states, whereas the CB minimum mainly consists of Ti 3d, Fe 3d and Cu 3d states. Cu 3d states and Fe 3d states are introduced as impurity states, which also play an important role in changing the band gap. The Cu 3d states may contribute to the rising of the energy levels of the O 2p gap states. By comparing different figures in Fig. 1(a), (c) and (d), the VB maximum of Cu/Fe codoped anatase (0.05 eV) is higher than that of pure anatase (0 eV), the O 2p level is pushed up by 0.05 eV, the existence of Cu 3d states will push up O 2p level, i.e. closer to the valence band as low acceptor level.

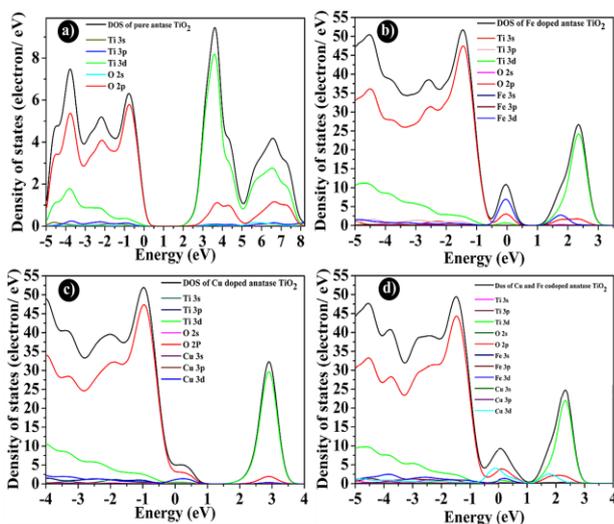


Fig. 2. DOS and PDOS of pure (a), Fe:TiO₂(b), Cu:TiO₂ (c), Cu/Fe codoped anatase TiO₂ (d).

3.2 Optical properties

The complex dielectric function: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, it is crucial to investigate the optical properties of a material, where $\varepsilon(\omega)$, $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ and ω are dielectric function, real part and the imaginary part and the angular frequency ($E = \hbar\omega$), respectively. The real and imaginary part of the dielectric function for doped anatase is presented in Fig. 3. There are two major peaks: first situated at 3.80, 3.68 and 3.53 eV, these values smaller than 4.93 eV for the pure TiO₂ [37] coming from the electron transition between O 2p in the highest valence band and Ti 3d in the lowest conduction band; second at 35.68, 35.65 and 35.64 eV. Based on the obtained dielectric function, the optical absorption spectrum of the pure and doped anatase TiO₂ were calculated by the

following equation: $I(\omega) = 2\omega \left(\frac{[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)] - \varepsilon_1(\omega)}{2} \right)^{1/2}$,

where $I(\omega)$ is the absorption coefficient, as shown in Fig. 4. It is obviously observed that the doped anatase induce a more obvious red-shift of the fundamental absorption edges towards the visible-light region. The intensity of adsorption spectrum increases in the following order: Cu:TiO₂:Fe > Fe:TiO₂ > Cu:TiO₂ > pure anatase, in ultraviolet region. While in the visible region, the order is Cu:TiO₂:Fe > Cu:TiO₂ > Fe:TiO₂ > pure anatase. This phenomenon is more obvious in Cu/Fe codoped anatase TiO₂ than Cu:TiO₂, Fe:TiO₂ and pure anatase TiO₂, which further indicates the synergistic effects of Cu/Fe codoped anatase. The codoped anatase TiO₂ is expected to be a more active photocatalyst. If the preparation methods can be controlled appropriately, the Cu/Fe codoped anatase TiO₂ can enhance the visible light response.

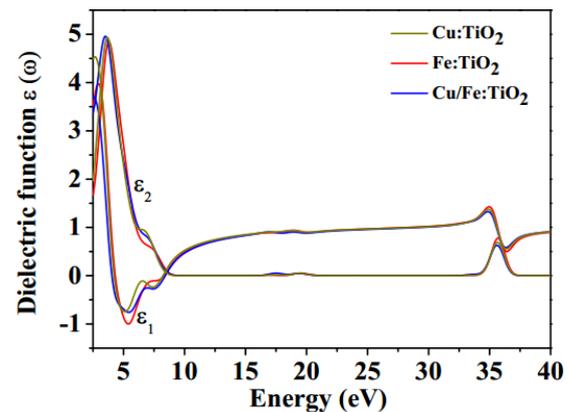


Fig. 3. Dielectric function of doped anatase.

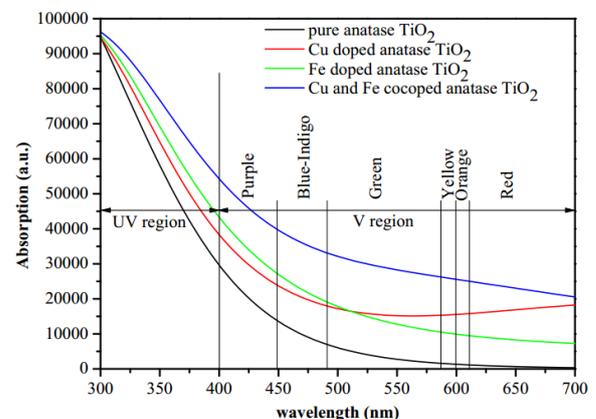


Fig. 4. Optical absorption spectrum calculated for the pure and doped anatase TiO₂.

Fig. 5 shows the def-ormation charge density of pure anatase (Fig. 5a, 5b), Fe:TiO₂ (Fig. 5c, 5d) and Cu:TiO₂ (Fig. 5e, 5f) for further investigating charge transfers. Different colors denote different charge density distribution. The color of red and blue indicates beneficitation and missing of electrons, respectively. For pure anatase, it is worth mentioning that the electrons between the Ti atoms and O atoms display the same local characteristics looking like a dumb bell structure, they indicate that the bonds between Ti atoms and O atoms exhibit anisotropy, i.e. different atomic configuration of different crystal orientation and lattice planes exhibits different performance, such as Gang Liu and his coworker [38] reported true photoreactivity order of {001}, {010}, and {101} facets of anatase TiO₂ crystals. For Fe:TiO₂ (Fig. 5c, 5d) and Cu:TiO₂ (Fig. 5e, 5f), the structures of electron clouds near the doped atoms are almost spherical. It can be clearly found that there are less electron clouds gathered between the bonding axis of the O atoms and Cu atom than that of Fe:TiO₂, as shown in Fig. 5e, 5f. This phenomenon can be expected to create much deeper electron traps and longer life time of photoinduced carriers compared with Fe:TiO₂. It's then obviously helpful for increasing the absorption coefficient of Cu:TiO₂ under visible light (see Fig. 4).

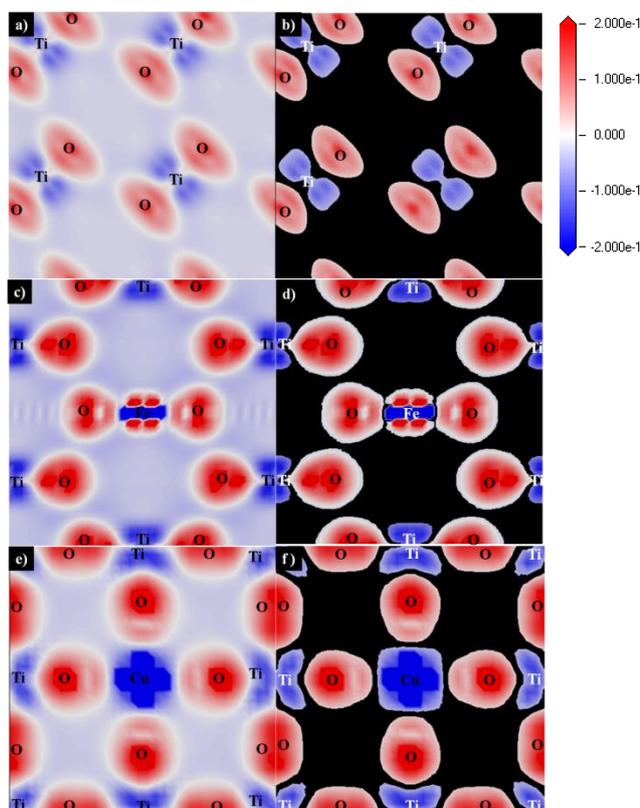


Fig. 5. Def-ormation charge density of the pure and doped anatase TiO₂.

4. Conclusions

The electronic and optical properties of Cu and Fe codoped anatase were calculated through the first principles method, with the corresponding properties of pure, single Cu or Fe doped anatase as a reference. Combining with the above mentioned electronic and optical results, we can conclude that the co-doping anatase of Cu and Fe changes the optical property and enhances the visible light photocatalytic activity with exhibiting synergistic effects. The intensity of adsorption spectrum increases in the following order: Cu:TiO₂:Fe > Cu:TiO₂ > Fe:TiO₂ > pure anatase, in visible light region. All the electronic and optical properties suggest that Cu and Fe ions, the common dopants of TiO₂, which will be useful for gaining deeper insights into the roles of dopants in photocatalysis.

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References

- [1] A. Fujishima, K. Honda, *Nature* **238**, 37 (1972).
- [2] T. Inoue, A. Fujishima, S. Konishi, et al. *Nature* **277**, 637 (1979).
- [3] B. O'Regan, M. Grätzel, *Nature* **353**, 737 (1991).
- [4] T. Kawai, T. Sakata, *Nature* **286**, 474 (1980).
- [5] A. Fujishima, Tata N. Rao, Donald A. Tryk, *J. Photochem. Photobiol. C* **1**, 1 (2000).
- [6] Z. G. Zou, J. H. Ye, K. Sayama, et al., *Nature* **1**, 625 (2001).
- [7] R. Asahi, T. Morikawa, T. Ohwaki, et al., *Science* **293**, 269 (2001).
- [8] Hiromi Yamashita, Masaru Harada, Junko Misaka, et al., *J. Photochem. Photobiol. A* **148**, 257 (2002).
- [9] S. K. Zheng, T. M. Wang, C. Wang, et al., *Nucl. Instr. Meth. B* **187**, 479 (2002).
- [10] Z. Y. Zhao, Q. J. Liu, J. Zhang, et al. *Acta Physica Sinica* **11**, 6592 (2011).
- [11] Y. Wang, D. J. Doren, *Solid State Commun* **136**, 186 (2005).
- [12] Q. H. Yu, J. Lei, C. G. Zhou, *Solar Energy Materials & Solar Cells* **95**, 2322 (2011).
- [13] M. Anpo, M. Takeuchi, *J. Catal.* **216**, 505 (2003).
- [14] M. Crisan, A. Brăileanu, M. Răileanu, et al., *J. Non-Cryst. Solids* **354**, 705 (2008).
- [15] H. Fujii, K. Inata, M. Ohtaki, et al., *J. Mater.Sci.* **36**,

- 527 (2001).
- [16] Hideo Otaka, Michie Kira, Kentaro Yano, et al., *J. Photochem. Photobiol. A Chem.* **164**, 67 (2004).
- [17] L. Z. Qin, H. Liang, B. Liao, et al., *Nuclear Instruments and Methods in Physics Research B* **307**, 385 (2013).
- [18] D. Dolat, S. Mozia, B. Ohtani, et al., *Chemical Engineering Journal* **225**, 358 (2013).
- [19] Tae-Ho Kim, Vicent Rodríguez-González, Gobinda Gyawali, et al., *Catalysis Today* **212**, 75 (2013).
- [20] ChungChih Yen, DaYung Wang, LiShin Chang, et al. *J. Solid State Chem.***184**, 2053 (2011).
- [21] R. H. Zhang, Q. Wang, J. Liang, et al., *Physica B* **407**, 2709 (2012).
- [22] Y. M. Liu, W. Liang, W. G. Zhang, et al. *Solid State Communications* **164**, 27 (2013).
- [23] X. J. Li, D. J. Si, J. Fang, et al., *Chin. J. Chem. Phys.*, **19**, 539 (2006).
- [24] R. F. Yuan, B. H. Zhou, D. Hua, et al. *Journal of Hazardous Materials* **262**, 527 (2013).
- [25] T. Sun, J. Fan, E. Z. Liu, et al., *Powder Technology* **228**, 210 (2012).
- [26] John P. Perdew, Kieron Burke, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [27] M. C. Payne, M. P. Teter, D. C. Allan, et al., *Rev. Mod.Phys.* **64**, 1045 (1992).
- [28] David Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [29] C. J. Howard, T. M. Sabine, F. Dickson, *Acta Crystall ogr. B: Struct. Sci.* **47**, 462 (1991).
- [30] F. X. Ye, T. Tsumura, K. Nakata, A. Ohmoric, *Mater. Sci. Eng. B* **148**, 154 (2008).
- [31] M. G. Brik, I. Sildos, V. Kiisk, *Physica B* **405**, 2450 (2010).
- [32] M. L. Guo, J. L. Dun, *Physica B* **407**, 1003 (2012).
- [33] S. M. Baizae, N. Mousavi, *Physica B* **404**, 2111 (2009).
- [34] YeldaYalçın, Murat Kılıç, *Applied Catalysis B: Environmental* **99**, 469 (2010).
- [35] Sutassana Na-Phattalung, M. F. Smith, Kwiseon Kim, et al., *Phys. Rev. B* **73**,125205 (2006).
- [36] Y. Q. Wang, R. R. Zhang, J. B. Li, *Nanoscale Research Letters* **9**, 46 (2014).
- [37] R. S. Zhang, Y. Liu, Q. Gao, et al., *Journal of Alloys and Compounds* **509**, 9178 (2011).
- [38] J. Pan, G. Liu, G. Q. (Max) Lu et al., *Angew. Chem. Int. Ed.* **50**, 2133 (2011).

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