Surface Photocatalytic Research of Fe-doped TiO2 (001) Based On the First-principles

JIA Xiaowei, WANG Min
College of Environment and Energy Engineering, Beijing University of Civil Engineering Beijing 100032, China
E-mail: 690567175@qq.com

Abstract. In this paper, the first-principles based on density functional theory was used to study the Fe/TiO2(001) band gap width and adsorption energy of C6H6 molecules at different positions on the surface of the molecule with different doping methods and different Fe content. Calculation of the band structure and density of states of Fe-doped TiO2 nanoparticles shows that, the surface gap doping is more favorable than the substitution doping to reduce the band gap of TiO2, and when the doping concentration is 6.122%, the maximum reduction of the band gap width is 59.3% higher than that of pure TiO2. According to the comparison of adsorption energy, it works out that the benzene molecule is mainly about horizontal adsorption on the surface of TiO2(001). Within the scope of the study, with the increase of Fe doping concentration, the adsorption energy does not decrease as the band gap, when the Fe atoms doping concentration is 4.167%, the maximum increase of adsorption energy is 63.2%.

1. Introduction:
Due to the extensive use of home decoration materials and automotive decoration materials, VOCs, which harms to the blood and nerve system of human body, is widespread in human settlements. Therefore, the preparation of environmentally friendly VOCs purifying materials and their research on degradation applications are attracting more and more attention. In numerous materials, nanometer TiO2 is often used in light catalytic degradation of low concentration VOCs because of its strong light catalytic properties, stable chemical performance, non-toxic feature and simple preparation[2][3]. In the process of TiO2 light catalytic degradation of VOCs, the VOC molecules are first adsorbed on the surface of the light catalyst and then reduced in the light exposure [4]. Therefore, the degradation rate of VOC is related to its adsorption performance on TiO2 surface. TiO2 Surface structure is an important factor which influences on the performance of the VOC molecular adsorption. There are three forms of TiO2 crystal are known in nature, namely, rutile, anatase type titanium ore and plate type, of which the light catalytic activity of TiO2 anatase phase is higher than that of rutile phase. A large number of experiments prove that part of the gas molecules can be adsorbed on the surface of TiO2 anatase phase and has degradation reaction. Weng jingzheng and wang[5] studied the adsorption energy of phenol on the surface of TiO2 (110) by the first principle and got the results that the adsorption capacity is maximum when the phenol molecule was placed in horizontal level. Yang et al.[6] studied the adsorption of TiO2 surface and NH3 molecules, and found that NH3 was easy to adsorb on the surface of oxygen-containing vacancy. Zhu hongqiang et al. [7][8] studied the adsorption of NH3 and H2S molecules on the surface of TiO2 (100), and found that the gas NH3 and H2S molecules were easy to adsorb on the surface with defects, and the higher the surface oxygen vacancy concentration, the better the adsorption effect. However, due to the large gap width of TiO2 material, the utiliza-
tion of visible light is low. Experiments show that doping some atoms can improve the visible light utilization and light catalytic activity of nano TiO$_2$ [9]. Theoretical calculation [10] shows that the TiO$_2$ crystals doped with some internal atoms will change the TiO$_2$ surface charge, which is conducive to the adsorption and at the same time the forbidden band width is reduced while the utilization ratio of visible light is improved with the adsorption spectrum redshift. Both theoretical calculation and experimental studies [11][12] have shown that the TiO$_2$ (001) surface has higher light catalytic activity than other surfaces. Zhang Peng [13] found that Si$^{4+}$ doping increased the surface hydroxyl species of the catalyst and enhances the surface adsorption and oxidation reduction ability when studying on the structure of Si doped TiO$_2$ visible light catalytic activity. Xu Ling et al. [14] studied V doping TiO$_2$ with the first principle, and found that with the increase of V concentration, the band width of TiO$_2$ gradually decreased and the visible response was increased. Zhang and Gao Pan [15] studied by first principles the electronic structure and optical properties of nitrogen iron doped TiO$_2$ anatase phase, it is concluded that the N, Fe were mixed at the same time at the top of the bottom of the conduction band and valence band formed the impurity level, narrowing the width of band gap of TiO$_2$, light absorption band edge red shift to the visible area. He [16] by using the first principle, studied the adsorption properties of Hydrogen halide gas on the surface of the titanium dioxide. And the calculation results show that the surface containing oxygen vacancy is more easily adsorb Hydrogen halide gas adsorption with the method of chemical adsorption, and the adsorption stability degree sequence is HF > HBr > HCl. Our preliminary experimental research work shows that [17], under different doping amount and different preparation conditions of titanium dioxide nanotube arrays (TNAs) is significantly different to the effect of light catalytic degradation of benzene content, TiO$_2$ doped Fe$_2$O$_3$ and Cu$_2$O nanotubes array is advantageous to the light catalytic degradation rate of benzene series, but lack of the theoretical calculation of the benzene content in mixed TNAs adsorption. In order to carry on the theoretical explanation, carrying out the adsorption theory calculation of benzene molecule on the surface of the TiO$_2$ doped nanotubes array, provides certain theoretical basis for the preparation of TNAs with strong adsorption performance and strong photocatalytic performance for benzene molecules were obtained.

2. Doping position and doping amount.

2.1Experimental method
In this paper, we calculate the VASP software package based on plane wave density functional theory. Exchange correlation can be calculated by PBE functional in the generalized gradient approximation (GGA) method. In the vector space, plane truncation can be set to 400 ev, take 3 * 3 * 1 K point, build (2 * 2 * 1) the supercell structure, to avoid occur mirror effect between the plates in the optimization, the vacuum layer thickness is set to 10 Å. In the process of crystal optimization, other atoms are locked except for the top and the adsorbed gas molecules.

For the adsorption of gas molecules, the following formula is adopted for the calculation of adsorption energy (Eads)

$$E_{\text{ads}} = (E_{\text{substrate}} + E_{\text{adsorbate}}) - E_{\text{adsorbate/substrate}}$$

among them, $E_{\text{adsorbate/substrate}}$ is the total energy of the substrate / adsorbate, $E_{\text{substrate}}$ is the energy to optimize the surface of doped TiO$_2$ (001), $E_{\text{adsorbate}}$ is the energy of the adsorbate. Obviously, the lowest energy state calculated by the above equation is the most stable state after gas molecules are adsorbed.

2.2Experimental Design
There are three elements on the surface of TiO$_2$ doped with Fe (001): Ti (Ti), O (oxygen) and Fe
(iron). Three kinds of Fe atoms doping position is designed, that is Fe substitution Ti doping, Fe substitution O doping doping and Fe atom surface gap doping respectively, as shown in Figure 1. By using the VASP software to calculate and study its energy band structure, the band width of TiO2 and the surface adsorption energy of benzene molecules in different forms on the surface of Fe/TiO2 were calculated under the three doping modes.

![Figure 1. Three different doping models](image)

3. Results and Discussion

3.1 The influence of doping position and doping concentration on band gap

In this paper, the supercell model of pure TiO2 and the supercell model of TiO2 doped Fe (Fe) were optimized by convergent calculation. The superconducting band gap of Fe / TiO2 (001) and pure anatase TiO2 is shown in Table 1.

Analysis of band gap results found that the band gap of pure anatase phase is 2.19 eV, which is different from the experimental value of 3.2 eV [18]. The difference is because of the inherent shortcomings of GGA method itself. But the relative results of the calculation method is very accurate and it doesn’t affect the result of qualitative research, which has been confirmed in relative studies [19][20]. As can be seen from Table 1, the gap doping with gap is narrower than the band gap, which indicates that the gap introduced to Fe atom makes the lattice distortion the largest. Because of the high degree of formation energy required by the Fe displacement O, the possibility of obtaining the TNAs with the Fe substituted O doped in the experiment is relatively low. Therefore, this paper does not consider the simulation calculation of the adsorption energy of TiO2 doped Fe substitution O on benzene. Visible light wavelength is about 400~760nm[21]. From the above table, the doping concentration is between 2.083% and 4.167%. The response of TiO2 to visible light is enhanced. When the photon collision energy is greater than the band gap, the valence band electrons excite the conduction band and at the same time generate positively charged holes on the valence band, electron-hole pairs. The potential of the photogenerated holes is 1.82-2.31eV, which is higher than that of KMnO4, Cl2, or even O3. It has a strong oxidizing property.

![Table 1. The superconducting band gap of Fe / TiO2 (001) and pure anatase TiO2 in different doping methods](table)

| Supercell structure | Doping methods | Doping concentration | Calculate the bandgap(Eg) | Correct the bandgap(Eg)/Corresponding wavelengths(λ) | Band gap reduction percentage (%) |
|---------------------|----------------|----------------------|---------------------------|--------------------------------------------------------|----------------------------------|
| 2*2*1               | none           | 0%                   | 2.16                      | 3.2/388.43                                             | ----                             |
2\*2\*1 Surface gap doping 2.041% 1.56 2.31/538.09 27.8

2\*2\*1 Fe substitution Ti doping 2.083% 1.62 2.4/517.91 25.0

2\*2\*1 Fe substitution O doping 2.083% 1.67 2.47/503.24 22.7

2\*2\*1 Fe substitution O and Ti doping 4.167% 1.23 1.82/682.97 43.1

2\*2\*1 Fe substitution of Ti atom and void doping 4.082% 0.95 1.48/881.56 56.0

2\*2\*1 Fe substitution of Ti atom and void doping 6.122% 0.88 1.31/948.85 59.3

* : Correct the bandgap = Correction factor\* calculated value: (Correction factor=3.2eV/2.16eV)

Figure 2. Density of states and band structure of Fe substitution Ti atoms and gap doping, concentration 6.122%

3.2 The influence of doping position and doping concentration on adsorption energy
Fe atom doped TiO$_2$ surface model is shown in Figure 1 (a), place the benzene ring in a different position relative to the surface of TiO$_2$(001) vertically as Figure 3 (a), horizontally Figure as 3 (b) in 45° as Figure 3 (c) The adsorption structure of the geometrically optimized benzene ring adsorbed on the TiO$_2$ (001) surface is shown in Fig. 3

Figure 3. Optimization structure of the adsorption of C$_6$H$_6$ molecule on the surface model of Fe atom doped TiO$_2$

As can be seen in Figure 3:
(1) When the benzene ring is placed vertically, the adsorption energy is 0.05eV. The change of the molecular morphology of benzene ring is the result of the intermolecular repulsion between H and Ti
on the benzene ring, and the distance between them is 0.1506 nm and 0.2171 nm.

(2) When the benzene ring is placed horizontally, the center of the benzene is above the doped Fe atoms and the adsorption energy is 1.49 eV by calculation. In addition, there is a huge change in the benzene ring form, C atoms bond with Fe atoms, and the new bond length is 2.05 Å.

(3) When the benzene ring is placed on the surface of TiO$_2$(001) in a 45° angle, it is calculated that the adsorption can be 0.51 eV, and the shape of benzene ring also has obvious deformation. O atom is close to the Fe atom and produces new chemical bonds.

When the Fe atom is doped with the TiO$_2$ phase gap, as shown in fig. 1 (c), the placement forms of the above three benzene molecules were also designed, and the adsorption configuration of benzene molecules adsorption TiO$_2$(001) surface after geometric optimization was shown in fig 4:

![Figure 4. Optimization structure of C$_6$H$_6$ molecule adsorption on surface model of Fe - doped TiO$_2$.](image)

As can be seen in fig 4:

1. When the benzene ring is placed horizontally, its center is above the doped Fe atoms and the adsorption energy calculated is 1.766 eV. A significant change in the molecular morphology of benzene ring takes place and the C=C double bond of benzene ring fractures. Fe atom, C atom and O atom all formed new bonds and the bond length of Fe-C is 1.977 Å and 2.026 Å and that of Fe-O is 2.05 Å.

2. When the benzene ring is placed vertically, it is calculated that the adsorption energy is 1.005 eV. The form of the benzene ring has changed and the C=C bond of benzene ring fractures. The new bond between C and Ti atoms is 2.164 Å, and the Fe-O bond is 2.054 Å.

3. When the benzene ring is inclined on the surface of TiO$_2$(001), it is calculated that the adsorption energy is 1.706 eV and the significant change in the molecular morphology of benzene ring also takes place. O atoms is close to the Fe atom and produces new chemical bonds with O bond length of 1.973 Å.

In conclusion, the adsorption energy of Fe doped nano-tio$_2$ on C$_6$H$_6$ molecules is related to the angle between the benzene ring plane and the surface of TiO$_2$, and the most stable adsorption structure is formed when the C$_6$H$_6$ plane is parallel to the surface of TiO$_2$.

### 3.3 The influence of doping concentration on adsorption energy

Figure 5 (a) is the model of two Fe atoms substituting the adjacent Ti atoms on the surface, figure 5 (b) is the model of a Fe atoms replacing a Ti with another Fe doped in the internal clearance gap of crystal phase. The doping concentration is 4.167% with the benzene ring placed horizontally. The adsorption structure after optimization is shown as fig 5.
As can be seen from the figure above, the morphological distortion of benzene ring occurs, and multiple C=C bonds break into C-C. C atoms bond with Ti and Fe atoms. When the number of Fe atom doping increases, the adsorption energy between benzene molecule and Fe/TiO₂ is significantly increased, A is 2.706eV and B is 2.882eV.

Figure 6 is the optimal structure of the surface model with a Fe atom replacing two adjacent Ti atoms and a doped Fe inside the crystal phase adsorbing a benzene molecule. The doping concentration is 6.122%. The adsorption of benzene molecule Fe/TiO₂ can be calculated as 1.911eV.

As shown in figure 6, when the doping concentration is 6.122%, although the benzene molecule forms a new chemical bond with Fe/TiO₂(001), the adsorption energy of benzene is only 1.21eV. It can be seen from table 2 that, when the doping concentration is 4.082%(4.167%), the increase of adsorption energy is 53.2% (63.2%) compared with the doping concentration of 2.041%. When the doping concentration was 6.122%, the adsorption energy increased by 28.3% compared with the doping concentration of 2.041%. It can be seen that the optimal Fe doping concentration can maximize the adsorption between Fe/TiO₂ surface and benzene molecules. When the doping concentration is 4.082%(4.167%), the stability of the crystal cell double atomic doping is the best, and the adsorption energy of benzene molecules is the largest.

| Doping Methods | Doping Concentration | Adsorption Energy (Eads/eV) | Bond length(d/Å) |
|----------------|----------------------|-----------------------------|-----------------|
|                |                      | C₆H₆ Vertically placement    | C₆H₆ Tilted     | C₆H₆ Horizontal placement |
|                |                      |                             | placement       | placement                 |
|                |                      |                             |                 |                            |
In order to further study the physical mechanism of C₆H₆ molecules on doping surface adsorption[22][23][24].Figure 3(b) was selected in the optimization structure of the adsorption of the above gas molecules, namely, the surface model of TiO₂(001) was further studied with the benzene ring level in Fe displacement doping. The electron state density and differential charge density were calculated. The distribution of differential charge density after adsorption is shown in FIG.7(a), it can be seen that the color between Fe and C atoms is red. It shows that the charge density is very high, there is a certain bonding between the Fe and C atoms, which should be chemical adsorption. The electron density after adsorption is shown in fig.7 (b), Fe-3d and C-2p have a state density resonance near the Fermi level, and form an obvious peak. It shows that the Fe and C atoms have a certain bonding, which is consistent with the analysis results of the previous adsorption energy.

![Figure 7](image)

**Figure 7.** Electron density difference and density of states of anatase Fe/TiO₂(001) surface after adsorption C₆H₆

### 4. Conclusions
This article uses the first principles method based on density functional theory studies the influence on the forbidden band width of three different positions doping Fe atoms in TiO₂ (001) crystal cell, and the influence of different doping methods on adsorption, the conclusion can be drawn as follow:

1. TiO₂ crystal distorts after doping, the concentration was 2.04%. Clearance doping is more beneficial to reduce the forbidden band width of TiO₂. Compared with the forbidden band width of pure TiO₂, the decrease amplitude is of 27.8% and 25% respectively (22.7%). With the increase of doping concentration, the band gap of TiO₂ will be significantly reduced, and the band width will decrease by up to 59.3% when the doping concentration is 6.122%.

2. In a certain range, the adsorption of benzene molecules on the surface of Fe/TiO₂ (001) on the surface of the iron oxide is mainly adsorbed to the surface by C₆H₆ molecular level, and the adsorption energy is the smallest when placed vertically. In the adsorption process, some C atoms in benzene molecules bond with the Fe and Ti atoms in TiO₂.

3. The surface of Fe/TiO₂ (001) has a higher adsorption capacity for benzene molecules when interstitial doping and displacement doping coexist. And within the scope of the study with the increase of Fe atoms doping concentration, TiO₂ forbidden band width is reduced, but in the benzene
molecule Fe/TiO$_2$ (001) surface adsorption cannot show an increasing trend, but in doping concentration was 4.082%, double doped atom adsorption is the largest.

References

[1] Wang X, Yang X H, Li X H et al 2015 J. Journal of Sun Yatsen University, (04):87-92.
[2] Tang P S, Zuo L 2014 J. Technology and Engineering, Vol.14, No. 8.
[3] F. Ning, D. Wang, L. M. Tang, Y. Zhang J 2014 J. Appl. Phys. 116, 094308.
[4] Wang P, Grtze M 2003 J. Nature Materials, 21:402 – 427.
[5] Weng J D, Chen L H, Qiu R H 2014 J. Material Review, (S2):182-184+191.
[6] Yang H G, Qiao S Z, Zou J, et al 2008 J. Nature, (453):638-641.
[7] Zhu H Q, Feng Q, Yue Y X, Zhou Q 2014 China Laser, (12):154-161.
[8] Zhu H, Feng Q 2014 J. Journal of Optics, (10):229-236.
[9] Sato S. 1985 J. Chemical Physics Letters, 123(1-2): 126—128.
[10] Wang X, Yang X H, Li X G, Xue X S 2015 J. Journal of Sun Yatsen University, (04):87-92.
[11] Gong X Q, Selloni A 2005 J. Phys Chem B, 109(42): 1560—1956.
[12] Han X G, Kuang Q, Jin M S, et al 2009. J Am Chem Soc, 131(9): 3152—3153
[13] Zhang P, Yu Y L, Zhai Y L, Yao J H, Cao Y 2013 J. Imaging Science and Photochemistry, 31(04):295-304.
[14] Xu L, Tang C Q, Qian J 2010 J. Chinese Journal of Physics, 59(04):2721-2727.
[15] Zhang X J, Gao P, Liu Q J 2010 J. Acta Physica Sinica, 59(07):4930-4938.
[16] He Z Q, Cai Q L, Hong F Y 2012 J. Ind Eng Chem Res, 51(16): 5662—5668.
[17] Zhang Y X 2016 D. Beijing University of Civil Construction and Architecture.
[18] Teobaldi 2017 J. Chemical Physics Letters. Vol.437(No.1-3): 73-78.
[19] Shi W M, Chen Q F, Xu Y, Wu D 2011 J. Journal of Atomic and Molecular Physics, 28(02):359-366
[20] Feng Q. 2009. Journal of Chongqing Normal University, 26(04):106-109.
[21] Tian W Q, Zhou K, Liu P 2017 J. Science Bulletin, 62(16):1729-1737.
[22] Zhao Y F, Li C, Lu S, et al 2016 J. Chemical Physics Letters, 647:36-41.
[23] Tang L P, Tang L M, Geng H, et al 2018 J. Applied Physics Letters, 112(1):012101.
[24] Wang X, Song Y, Tao L L, et al 2014 J. Applied Physics Letters, 105(26):1660.