Journal of Computational Science & Engineering 4 (2013) 170-177

Journal of Computational Science & Engineering

Available at http://www.asocse.org ISSN 1710-4068

Theoretical study on S-, N-doped anatase TiO_2: the visible-light-driven photocatalysts

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Article Information

Article history:
Received 16 January 2013
Revised 18 January 2013
Accepted 25 January 2013
Available online 30 January 2013

Keywords:
Anionic doped anatase TiO_2
$TiO_{2-x}N_x$
$TiO_{2-x}S_x$
Density functional theory
Visible-light-driven photocatalyst

Abstract

Density functional theory (DFT) calculations are used to characterize the doping effect of S, N elements substituting for oxygen in anatase TiO_2. Three cases, including pure, S-doped and N-doped TiO_2, were treated. For the two doping cases, DFT calculations show that the doping elements could lower the band gap of TiO_2 effectively. Excitations from the extended valence band to the conduction band may be responsible for the red shift of absorption edge observed in S, N-doped TiO_2. Band gap obtained in $TiO_{2-x}S_x$ was narrower than that in $TiO_{2-x}N_x$. Both Mulliken population and geometry structure analysis indicated that the carriers should have larger mobility in $TiO_{2-x}S_x$. It is expected that $TiO_{2-x}S_x$ might be a good photocatalyst comparable to $TiO_{2-x}N_x$.

1 Introduction

Titanium dioxide (TiO_2) has received a lot of attention as a promising semiconductor photocatalyst since it was found to be efficient for water splitting [1]. However, this material is only active upon UV (about 3% of the solar spectrum) excitation because of its large energy band gap (3.2 eV for anatase). Thus, effective utilization of visible light (about 45% of the solar spectrum) by band gap engineering becomes the aim of

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increasing researchers.

Doping is one of the most simple and effective methods to extend the photoresponse of semiconductor photocatalyst to low energy region. Recently, intense research [2-16] has concentrated on doping TiO_2 with nonmetal atoms after the report of N-doped TiO_2 with the visible light activity from Asahi et al. [2]. It is found that nitrogen atoms substituted the lattice oxygen sites and narrowed the band gap by mixing the N2p and O2p states. Because of the good performance of initial disclosed $TiO_{2-x}N_x$, the efforts to establish visible-light-driven photocatalyst with other nonmetal elements have prevailed quite a long period of time. According to literatures, S-doped TiO_2 seems to be a good one. But the understanding to the doping effect is far from details. It was synthesized successfully first by Umebayashi et al. [5-6] with S substituting on lattice O sites. They suggested that sulfur was doped as an anion and replaced the lattice oxygen in TiO_2. Ohno et al. [7] reported synthesis of new S-doped TiO_2 powders. In contrast to that reported by Umebayashi et al. [5-6], S atoms are incorporated as cations on Ti sites. Furthermore, it is reported that cationic S-doped TiO_2 absorbs visible light more strongly than the anionic N- and S-doped TiO_2 powders with higher photocatalytic activity. Whereas, a subsequent report [8] point out that the materials, synthesized using the same approach of Ohno et al. [7], do not contain sulfur but instead nitrogen as the doping component inducing visible light photocatalysis. Which is the fact? It is still in question. Thus it is in urgent need to do more work in this field for both theoretical and experimental researchers.

In this letter, we will perform density functional theory calculations on the two anionic doped visible light photocatalysts, $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$, reported in literatures, to get insight into the details of the doping element effect, so that to provide useful information for experimentalists. This option is somewhat based on the similarity between them. As for the cationic doping case, we have considered it in another work [11]. Our calculation confirmed that S, N doping can induce band gap lowering for anatase TiO_2, and it can be deduced to be the origin of the red shift of the absorption edge of doped TiO_2. And, the doping S is more efficient in the absorption edge shift. We also find that $TiO_{2-x}S_x$ can provide a better environment for the carriers transfer than $TiO_{2-x}N_x$.

As we know, it always needs to go through three steps for a semiconductor to realize photocatalyze: the first is the electron-hole pair generation; the second is the carriers can be transfer effectively to the surface of the photocatalyst; and the third is the effective surface reaction. There are so many factors that affect the performance of a photocatlyst, such as lifetime of charge carriers, surface structure, stability, etc. Among them, effective light absorption is the first basic factor. In our thought, all these factors can be divided into two parts, the bulk part and the surface part. The bulk part is related to the first two steps, and the surface part is involved in the third step. In this work, we focused our attention on the former part. We will try to give a rough comparison on $TiO_{2-x}N_x$ and $TiO_{2-x}S_x$. It is not so simple, but it is interesting.

2. Computational details

The plane-wave-based density function theory (DFT) calculation was performed using the CASTEP program [17] with the core orbitals replaced by ultrasoft pseudopotentials, and a kinetic energy cutoff of 300 eV. Three cases, including pure, S-doped and N-doped TiO_2, were treated. All the work was performed in a model consisting of two unit cells of anatase TiO_2 (Figure 1). The doping effects were modeled by replacing one oxygen atom with one doping atom. And, pure TiO_2 was calculated as comparison. All the electronic band structure and the optical absorption

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spectra were calculated on the corresponding optimized crystal geometries. The generalized gradient approximation (GGA) with the PBE exchange correlation functional was adopted.

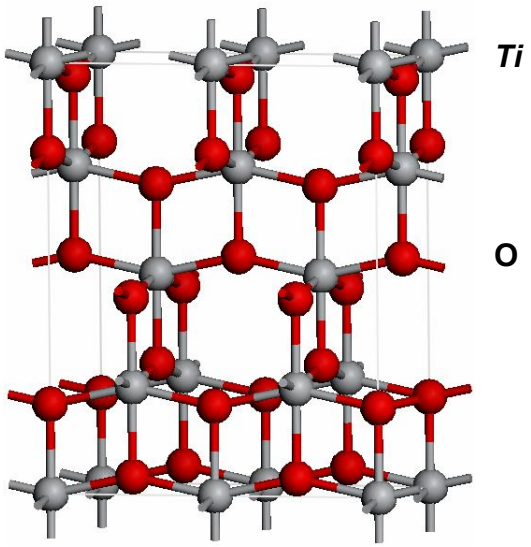

Fig. 1. The model of TiO_2

The underestimation of band gap is a well-known shortcoming of single particle Kohn–Sham approach. Therefore, a scissors operator of 1.16 eV was introduced to shift the conduction levels to agree with the measured value of the band gap. However, trends in band gaps and the qualitative features of band states are generally well predicted by this method. In any case, in this work our main interest is in qualitative trends, not in absolute values.

The absorption curves can be obtained easily from the imaginary part of the dielectric constant obtained in CASTEP calculation. The imaginary part of the dielectric constant ε_2 can be described as:

$$\varepsilon_2(\hbar\omega)=\frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{c,v}\sum_{k}\left|\left\langle\Psi_k^c\left|\hat{u}\cdot r\right|\Psi_k^v\right\rangle\right|^2\delta\left[E_k^c-E_k^v-\hbar\omega\right]$$

Where Ω is the volume of the elementary cell, k represents the k point, ω is the frequency of the incident light, c and v represent the conduction and valence bands, respectively. Ψ_k^c and Ψ_k^v are the eigenstates, r is the momentum operator and $\hat{u}$ is the external field vector.

3. Results and discussions

3.1 Comparison of electron structures

Figure 2 shows the calculated total and partial density of states after geometry relaxation. The left panel tells the difference of the band gap before and after doping and states distribution ways by displaying the total density of states of the three samples, pure TiO_2, $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$. The right panel displays the states related to the valence band corresponding to the left one, which can indicate the origin of the band gap change after doping. For the pure TiO_2, the valence band (VB) is consisted mainly of O2p states. A band gap of 2.04 eV was gained. The width of valence band of TiO_2 is about 4.17 eV. The covalent character of Ti-O bonds can be reflected somewhat by the contribution of O2p to the conduction band.

As for the doped materials, it can be found directly from Figure 2 that the band gaps of both of the two photocatalysts, $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$, are reduced to a smaller value with respect to the pure one. This confirmed that the doping element of S and N could engineer the band gap of TiO_2 effectively towards lower energy directions, as that reported from literatures [2, 5-6]. So we can deduced that density of states calculation confirmed the mixing of the S3*p* and N2*p* states with VB, which increases the width of the VB itself and results in a decrease of 0.45~0.66 eV in the band gap energy. This is consistent with the conclusion of Asahi et al. [2] and Umebayashi et al. [5]. Another interesting thing displayed here is the relative size of the band gap lowering by S or N doping. As we can see from the left panel, comparing to N doping, a narrower band gap was gained when the material was doped with S. The different behavior of $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ can be rationalized by checking the differences in the electronegativity and electronic properties of the two doping elements. One existing rule says that

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[18-19]: for a semiconductor, the smaller of the difference of electronegativities between anions and cations is, the narrower of the band gap. We check the initial results using this rule first before conducting further analysis. As we know, the electron negativity of S, N is smaller than that of O, so a lowered electronegativity difference can be obtained when S, N substitute for O, along with a narrowed band gap. Furthermore, the electronegativity of S is smaller than that of N, which makes S more effective for the band gap narrowing.

On the electronic properties point of view, the valence electron of S element is far from the core and has larger mobility than that of N or O element. Valence electron locating on the S3p level has higher energy than that on the O2p and N2p level. When S or N interacts with O, S3p will pull the mixing band to a higher level of energy than N2p. It can somewhat be reflected from the width of the valence band. From the band structure diagram, we can find that the width of valence band of $TiO_{2-x}N_x$ is about 4.65 eV or so, while the width of $TiO_{2-x}S_x$ is about 4.85 eV, 0.20 eV wider than that of $TiO_{2-x}N_x$. So we can speculate that S element can perform better in extending the absorption edge to visible light region for TiO_2. Besides, the wider valence band is a beneficial factor for the carrier transfer.

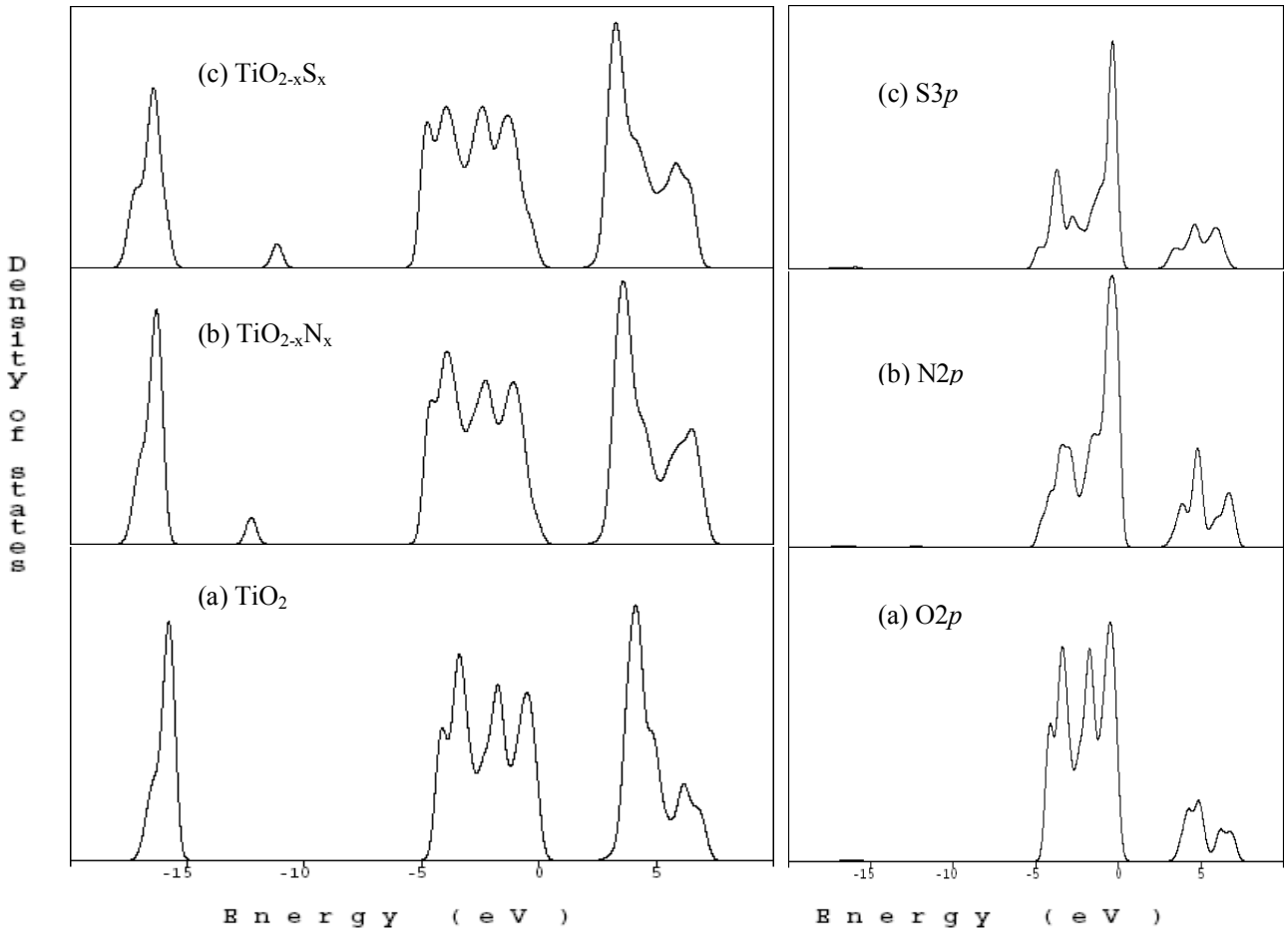

Fig. 2. Total density of states and the corresponding partial density of states of the level related to valence band for (a) pure TiO_2, (b) N-doped TiO_2 and (c) S-doped TiO_2 (In the right panel, the ordinate of (a) is about decuple of the other two.)

One point should be mentioned here is the difference between S and N from the traditional

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doping idea. The substituting of N for O is an electron reduction process, namely it can be seen as that a hole is introduced into the sample when one N replaces one O atom. It is always seen as an important condition for good performance of the electrical conductivity of the materials. While as an element with equal valence electron to O element, it is the larger ionic radius and the corresponding properties of S itself help it affect the electron structure of TiO_2 and then alter its absorption properties and subsequent photocatalytic activity when S substitutes for O. It may not be a good sign for the S-doped TiO_2 in the carriers transfer process.

3.2 Absorption spectra of pure and doped anatase TiO_2

Figure 3 shows a comparison of the calculated absorption spectra for pure and S, N-doped anatase TiO2. We can read from the figure that both the absorption edges of $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ are extended to the longer wavelength region, the visible light region. Comparing to $TiO_{2-x}N_x$, the absorption edge of $TiO_{2-x}S_x$ extends a little larger. It is consistent with the prediction to the band gap relationships by electron structure calculations and the subsequent analysis that the band gaps of $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ are lowered with respect to the pure TiO_2. And the band gap is narrower in $TiO_{2-x}S_x$ than in $TiO_{2-x}N_x$. Then we can come to a conclusion that the visible light activity of $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ is derived from the lowering of the corresponding band gap. This result is consistent very well with the present mainstream viewpoint in this field.

Besides, a broad band across the visible light region is found in the absorption spectra of $TiO_{2-x}N_x$. Based on detailed electron structure analysis, we considered it can be attributed to the absorption corresponding to the transition of the electron from O2p to N2p, because the N2p level is a half-occupied state with higher energy than O2p in the upper edge of the valence band.

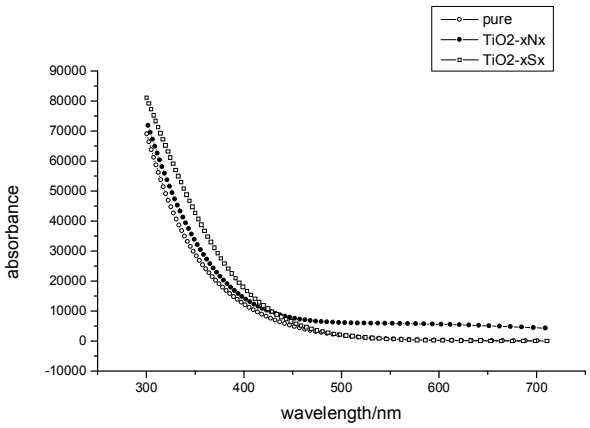

Fig. 3. The absorption spectra of $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ and pure TiO_2

3.3 Mulliken population analysis

Mulliken population analysis reveals that in $TiO_{2-x}N_x$, the hole is quite localized on the doping N with a charge of –0.41 comparable with that on the original O atoms (-0.44) in the pure TiO_2. And the charges (0.88, 0.88 and 0.92) on the three Ti atoms bonded to the doping atom are nearly the same as that (0.88) in the pure TiO_2. Which indicates that the doping N is acting as a deep electron trap site as disclosed in a very recent report [20]. Our calculation is qualitatively consistent with the report, although the absolute values of charge are different due to the different calculation basis. There is a kind of estimation [21] that the localized nature of the N-induced states has the consequence that the hole generated by visible irradiation is less mobile than that generated by UV irradiation.

As for the $TiO_{2-x}S_x$, we get a charge of –0.15 on the doping S atom, lowered largely than that on the original O atoms (-0.44). And the charges on the three Ti atoms bonded to the doping S are 0.76, 0.76 and 0.81. These positive charges are substantially smaller than those seen for Ti atoms bonded to six O neighbors in the pure TiO_2. An averaged trend can be found in the charge distribution in the S-doped TiO_2, which impresses us that the doping S and the neighboring region around it can be a shallow trap region for carriers. So a better carrier transfer rate can be expected.

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3.4 Geometry structure analysis

Figure 4 shows the structural change of $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ after relaxation. The Ti-N-Ti angle is 161.4° and Ti-S-Ti angle is 166.6°, the difference between them is about 5°. Table 1 shows the M－O－M/O-M-O bond angle along the zigzag chains in y-z planes in the optimum $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ structures. The four layers of Ti, O atoms are indicated as layer1 to layer4 along the direction of z-axis reducing. As we can see there is a two-layer of Ti, O atoms with M-O-M of about 160° in the lower side of z-axis in the $TiO_{2-x}S_x$. The larger ionic radius of S has ever been considered to be an adverse factor for the synthesis of $TiO_{2-x}S_x$ due to the larger formation energy [2]. We found, nevertheless, it may be the origin of many beneficial factors. The larger ionic radius is consistent with the higher energy and the high mobility of valence electron. The larger radius helps S change the M-O-M angle larger than that of N. And we found from geometry analysis that there may be a significantly large region flat for the carriers transfer in $TiO_{2-x}S_x$. It is said that the closer the M－O－M bond angle is to 180°, the more easily photogenerated electron-hole pairs can migrate, which is important for photocatalyst to hold high photocatalytic activity. The two-layer of Ti, O atoms with M-O-M of 160° consist a peculiar region in the lower side of z-axis of $TiO_{2-x}S_x$. This region we speculated will be a flat region for the carriers transfer.

Ought to say, the generation of a two-layer with angles closer to 180° is companied by the deviation of angles in another two-layer from 180°. While we then expected that, the larger deviation of angles from 180° of the two upper layers should make it more difficult for the carriers to migrate through in them, so the carriers may be forced to go along the flat region consisting of two layers of Ti, O atoms with M-O-M of 160° in the lower side of z-axis.

Then we can get a conclusion that, although from the traditional thought, S doping may not have advantages in the carrier generation and transfer, its performances in Mulliken population and geometry structure analysis make it not so serious. The carriers might have larger mobility in S-doped TiO_2.

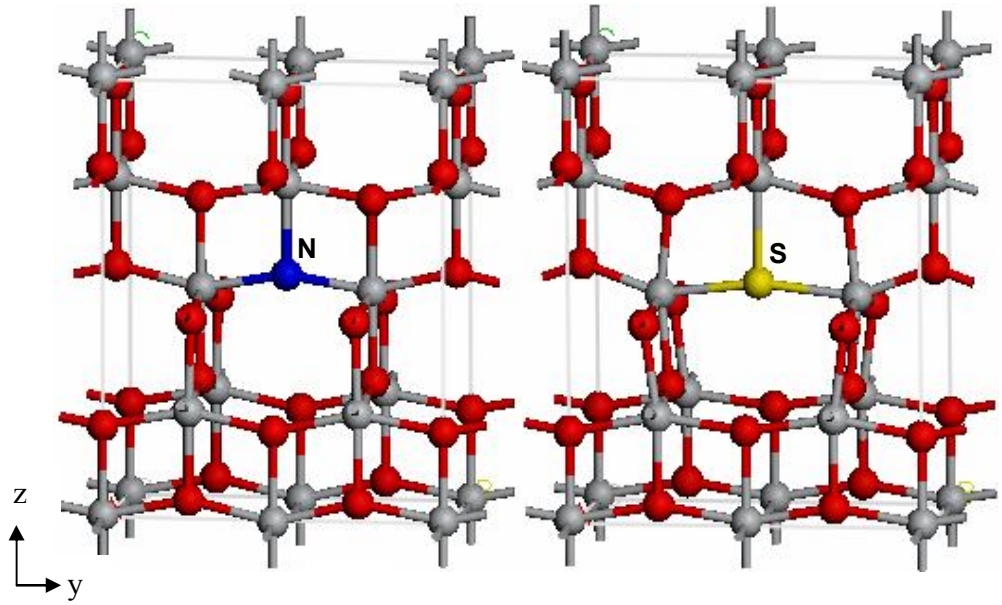

Fig. 4. The structural change of $TiO_{2-x}S_x$ and $TiO_{2-x}N_x$ after relaxation

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Table 1 The M – O – M/O-M-O bond angle along the zigzag chains in y-z planes of $TiO_{2-x}S_x$ and TiO_{2-}

M-O-M	Layer 1			Layer 2			Layer 3			Layer 4		
$TiO_{2-x}N_x$	158.3	160.6	158.3	157.6	**161.4**	157.6	157.1	155.4	157.1	156.3	153.9	156.3
$TiO_{2-x}S_x$	150.1	150.9	150.1	153.3	**166.6**	153.3	**161.3**	**163.2**	**161.3**	**160.9**	**160.7**	**160.9**
TiO_2	155.7											

4. Conclusions

From the discussions above, we can see that there are several factors beneficial for the $TiO_{2-x}S_x$ photocatalyst. A smaller band gap was obtained in $TiO_{2-x}S_x$. And a bigger red shift induced by doping S was confirmed in the absorption spectra. Both Mulliken population and geometry structure analysis indicated that the carriers might have larger mobility in S-doped TiO_2. So we speculated that $TiO_{2-x}S_x$ should be a good photocatalyst comparable to $TiO_{2-x}N_x$. Although it can't be the last, we hope our efforts will attract more scientists to explore further in this field.

Acknowledgments

This work was supported by National Natural Science projects of China (No. 20703027), Shandong excellent young scientist research award fund (No. BS2011NJ004), Foundation of Shandong Educational Committee (No. J09LB06), and Qingdao University Research Fund (No. 063-06300538).

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