



Impact of sulfur-, tantalum-, or co-doping on the electronic structure of anatase titanium dioxide: A systematic density functional theory investigation



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ABSTRACT

In order to achieve the purpose of further improving the photocatalytic performance of sulfur (S)-doped anatase titanium dioxide (TiO₂) and providing an example to design an efficient photocatalyst, the electronic and optical properties of pure, S-doped, tantalum (Ta)-doped and S+Ta-codoped anatase TiO₂ were systematically investigated by using the density functional theory within a GGA+U method. The results indicate that Ta codoping could improve the S incorporated into TiO₂ lattice under reducing conditions. And the incorporation of Ta into S-doped TiO₂ further increases the photocatalytic activity under visible-light irradiation compared with that of the S-doped TiO₂: the distance from S-related impurity energy levels to the top of valence band is obviously decreased in S+Ta-codoped TiO₂; and the calculated band gap of S+Ta-codoped TiO₂ is smaller than that of S-doped TiO₂; furthermore, through the synergistic effects between S and Ta, S+Ta-codoped TiO₂ not only has the similar high absorption rate to S-doped TiO₂ in the UV-light region, but also has higher absorption rate than S/Ta-doped TiO₂ in the visible-light region.

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1. Introduction

Titanium dioxide (TiO₂)-based compound semiconductors have received considerable attention over the recent years due to their potential application in the challenging photocatalytic water splitting reaction for hydrogen production using sunlight. However, it is only activated by UV-light irradiation, whose energy only accounts for about 5% of the whole solar energy, owing to its wide band gap (3.2 eV for anatase, 3.0 eV for rutile) [1,2]. Therefore, the controlled

narrowing of the band gap of TiO₂ is of great importance for improving the optical and photocatalytic properties of this material in the visible-light region. To obtain a more efficient utilization of solar energy, researchers adopted various modification methods, including the following: ions doping [3], noble metal loading [4,5], dye-sensitizing [6,7], semiconductor mixing [8,9], and so on, to improve the photocatalytic performance of TiO₂ under visible-light irradiation.

Among these modification methods, the ion doping has attracted extensive concerns, due to its simple and effective features. On one hand, the ion doping could form impurity level in the forbidden band, which not only can make the electrons excited by visible-light, but also can be the capture center of photo-generated electrons or holes, reducing the combination probability of photo-generated electron-hole

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pairs and prolonging the lifetime of the photo-generated carrier [10]. On the other hand, the ion doping could change the local crystal structure to produce local crystal distortion and the electrons distribution, which can produce the local internal electric field, and thus could further promote the separation of photo-generated electron–hole pairs [11]. However, ion doping is not always completely effective, for example, some metal ions doped causes TiO₂ thermal instability in certain chemical environment. Although ion doping would make TiO₂ respond to the visible-light, the oxidation of photo-generated holes excited by visible-light was weaker than that produced by UV-light, which can lead to the lower decomposition and mineralization rates in the cases of organic pollutants decomposition. What is more, if the impurity energy levels are located at the center of forbidden band, the probability of transition of electrons and holes to the impurity energy levels is almost equal to each other, resulting in enhancing the recombination of photo-generated electron–hole pairs. Therefore, for the ions doping modification of TiO₂ photocatalyst, the crucial challenge is how to maintain its strong photocatalytic oxidation and/or reduction activities under the visible-light irradiation.

Because single ion mono-doping is very difficult to meet the above requirements, researchers begin to try multiple ions codoping to overcome some shortcomings of single ion mono-doping [12,13]. The previous studies indicate that the recombination of photo-generated electron–hole pairs could be further suppressed, if choosing optimal multiple ions codoping [14–17]. Moreover, there are important synergistic effects between different ions. For instance, Li et al. prepared N+Fe codoped TiO₂ by the hydrothermal method, which narrowed the band gap and enhanced the photocatalytic activity of TiO₂ under the visible-light irradiation [17]. Their experimental results are well in agreement with theoretical study on the electronic and optical properties of N+Fe-codoped anatase TiO₂ photocatalyst [16]. These research works suggested that the synergistic effects between different ions could improve the photocatalytic activity of single ion doped TiO₂.

In our previous work, we found that the impurity energy levels of sulfur (S)-doped anatase TiO₂ (in which S atom occupies the lattice site of oxygen) are located at the top of valence band, resulting in broadening the solar light absorption range of TiO₂ [18]. However, there are still certain distances from the top of valence band to the impurity energy levels, which lead to a certain probability for the recombination of photo-generated electron–hole pair. In other words, there is still room to further improve the photocatalytic performance of S-doped TiO₂. Because there is a compensation effect between metal ions and anions, we hope to improve the S doping effects by codoping with metal ions. By comparing the initial pre-calculations, we found that tantalum (Ta) and S codoping can achieve this purpose. Furthermore, there are a few literatures to report that Ta mono-doping or Ta+N codoping can improve the photocatalytic performance of TiO₂ [14,19,20]. Although Ta doping can promote photocatalytic activity of TiO₂, it also suffers from the existence of carrier recombination center that is formed by the strong localized d states in the band gap of TiO₂. So, we expect to overcome their individual shortcoming of S or Ta mono-doping by the synergistic effects of S+Ta codoping.

Herein, we report theoretical investigation for S+Ta-codoped anatase TiO₂ and evaluate their photocatalytic performance, using the density functional theory (DFT) calculations.

2. Computational methods

DFT calculations were performed in the framework of density functional theory within the generalized gradient approximation (GGA) using the PBE exchange correlation potential, and utilizing the ultrasoft pseudopotential method as implemented in CASTEP code [21–23], which was embedded in the software package of Materials Studio 6.0. The ion–electron interaction is modeled by ultrasoft pseudopotential in the Vanderbilt form [24], which could yield satisfactory results in recent studies [25]. The valence atomic configurations are 3s²3p⁶3d²4s² for Ti, 2s²2p⁴ for O, 3s²3p⁴ for S and 5d³6s² for Ta. The energy cutoff for plane wave basis set was 380 eV. In order to obtain accurate electronic structure, the method of GGA+U was adopted to overcome the well-known shortcoming of GGA (underestimate the band gap about 20–50%) [26]. The Hubbard model is one of the most successful models to describe the correlated electrons in solids. To construct an appropriate functional theory, the GGA+U approach subdivides charge density into two subsystems: delocalized and localized. The former remains described by its charge density, while for the latter a site diagonal charge density matrix is introduced. In the present work, the *U* value of 4.2 eV was applied to the Ti-d states and the O-p states, and other *U* value of 4.0 eV was applied to the S-p states and the Ta-d states. Using these values, the accurate band gaps could be obtained, as well as the main electronic structure features with standard DFT calculations could be identified. The Monkhorst–Pack scheme K-points grid sampling was set as 2 × 2 × 2 for the irreducible Brillouin zone in the constructed supercell. A 120 × 120 × 120 mesh was used for fast Fourier transformation. The minimization algorithm was chosen from the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme. Its convergence criteria were set as follows: the force on the atoms was less than 0.01 eV/Å, the stress on the atoms was less than 0.02 GPa, the atomic displacement was less than 5 × 10^{−4} Å, and the energy change per atom was less than 5 × 10^{−6} eV. Based on the optimized crystal structure, the electronic structure and the optical properties were then calculated.

In the present work, a 3 × 3 × 1 supercell for anatase TiO₂ was used in constructing the doped models, in which three conventional cells are stacked along the *a*- and *b*-axis. Thus, every lattice parameter of the supercell model is larger than 9.5 Å, which could avoid the self-interaction of S or Ta impurity. For S doping, one O atom of TiO₂ is replaced by one S atom, and for Ta doping, one Ti atom of TiO₂ is replaced by one Ta atom. In the supercell, the total number of atoms is reached to 108, and the corresponding S or Ta concentration is about 0.926% (total atomic ratio), which is consistent with that of previous experiments and theoretical works. In the following context, the S-doped TiO₂ model, in which S atom replaces the oxygen atom in anatase TiO₂, is denoted by the label of TiO_{2−x}S_x, and other models were denoted by the same way. The symmetry of pure anatase TiO₂ is *I*₄₁/amd. The symmetry of all supercells is set as *P1*, as first. After geometry optimization, the symmetry is found to

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