



The structure, electronic, and optical properties of (Sm,N)-codoped anatase TiO₂ photocatalyst: A density functional study



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ABSTRACT

The geometrical, electronic, and optical properties of Sm-doped, N-doped, and (Sm,N)-codoped anatase TiO₂ were successfully calculated and simulated using the spin-polarized density functional theory. The researches of geometrical structures show that (Sm,N) codoping leads to lattice distortion, which reduces the recombination of the photogenerated electron–hole pairs. Moreover, the calculated results indicate that the synergistic effects of (Sm,N) codoping can lead to an obvious band gap narrowing and a N 2p state appearing in the forbidden gap, which leads to a significant redshift of the optical absorption edge and enhances the photocatalytic activity of the (Sm,N)-codoped anatase TiO₂.

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1. Introduction

Titanium dioxide (TiO₂) has been extensively studied in the past few years for being extremely useful in many technological applications. It is one of the most promising photocatalysts for environmental clean up, photogeneration of hydrogen from water, and solar energy utilization [1,2]. However, its wide band gap (3.2 eV for the anatase structure [3]) leads to a low photon utilization efficiency of sunlight because only the ultraviolet-light ($\lambda < 400$ nm) can afford the energy for the electron transition from the valence band (VB) to the conduction band (CB) [4,5]. Furthermore, the quantum yield is low due to rapid recombination between excited electrons and holes [6]. Therefore, to enhance the photocatalytic activity of TiO₂, extending optical absorption range of TiO₂ into visible-light region and reducing the recombination of excited electron–hole (e⁺–h⁻) pairs are two main subjects for the increased utility of TiO₂.

An effective approach to extend the TiO₂ optical absorption edge into visible-light region and reduce the photogenerated electron–hole pairs recombination rate is doping the TiO₂ with transition-metal (TM) or non-metal elements. The TM element doping can effectively lower the electron–hole pairs recombination rate, which promotes the photocatalytic efficiency and extends optical

response from ultraviolet to visible region. For example, Dholam et al. reported hydrogen production by photocatalytic water-splitting using Cr- or Fe-doped TiO₂ composite thin films photocatalyst [7]. Li et al. studied photocatalytic activity of nanoglued Sn-doped TiO₂, the results suggested that an appropriate amount of Sn dopant could greatly increase the amount of hydroxyl radicals generated by TiO₂ nanoparticles, which were responsible for the obvious increase in photocatalytic activity [8]. Lin et al. investigated visible-light photocatalytic activity of Ni-doped TiO₂ from *ab initio* calculations, the calculated results indicated that substitutionally Ni to O-doped anatase and rutile TiO₂ had a series of impurity energy levels appearing in the forbidden gap, which may be responsible for the redshift of optical absorption edge and visible-light photocatalytic activity in Ni-doped TiO₂ [9]. Chiou et al. examined photocatalytic degradation of phenol in aqueous solutions by Pr-doped TiO₂ nanoparticles [10]. The Pr-doped TiO₂ exhibited high activity for photocatalytic degradation of phenol in the experiment, which was due to the presence of Pr ions in the TiO₂ nanoparticles causing a significant absorption shift toward the visible-light region. For non-metal elements doping, the doping of N [11–14], C [15–18], Si [19,20], S [21,22], B [23], and P [24] in TiO₂ can reduce its band gap and shift its optical absorption edge into visible-light region because the related impurity states are near the valence band edge, which can minimize their possibility as recombination centers compared to transition-metal doping. Moreover, some scientists attempt to improve the photocatalytic

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of TiO₂ by TM and non-metal elements codoped approach. Tan et al. investigated visible-light absorption and photocatalytic activity of Mo- and N-codoped TiO₂, and found the codoped sample exhibits better absorption performance than monodoped sample in visible-light region [25]. Jia et al. found the mixing of O 2p, N 2p, S 3p, and Ti 3d states in the forbidden gap of (N,S)-codoped TiO₂, which can result in the higher visible-light photocatalytic activities than those monodoped TiO₂ [26]. Lin et al. reported synergistic effects of Eu/Si codoping can effectively extend the optical absorption edge [27]. These results indicate that codoping with TM and non-metal elements is one of the most effective approaches to extend the absorption edge to the visible-light range in anatase TiO₂. In addition, We recognize that the DFT + *U* methodology has successfully been applied to TiO₂ system including the setting of the *U*-parameter and the calculation of optical adsorption for defective systems [28–34]. For example, Morgan et al. used the DFT + *U* to study the formations of intrinsic n-type defects and calculated optical absorption spectra for all defects in TiO₂ material [28]. Jia et al. investigated the electronic and optical properties of (N,Fe)-codoped anatase TiO₂ photocatalyst by the DFT + *U* method [30]. Zhang et al. studied the effect of substitutional N, Ce, and Ce + N doping on the electronic structure and optical properties of anatase TiO₂ with the DFT + *U* approach [33].

Recently, visible-light induced (Sm,N)-codoped TiO₂ photocatalysts have been successfully synthesized by Ma et al. [35]. They show that N doping can extend the optical absorption edge to visible-light region, and the doping of Sm into TiO₂ can efficiently inhibit the recombination of electrons-holes pairs. The (Sm,N)-codoped TiO₂ sample presents much higher photocatalytic activity than N-doped TiO₂ and pure TiO₂ under visible-light irradiation. However, to the best of our knowledge, there has been no report on the geometrical, electronic, and optical properties of (Sm,N)-codoped anatase TiO₂. Therefore, the physical and chemical origin of the enhanced photocatalytic activity and the longer wavelength optical absorption remains unexplained.

In the present work, the electronic and optical properties of (Sm,N)-codoped anatase TiO₂ have been investigated using the density functional theory (DFT) to reveal the microscopic mechanism for band gap narrowing and the origin of the enhanced photocatalytic activity. For comparison, the corresponding calculation and theoretic analysis are also conducted for pure, Sm- and N-doped anatase TiO₂. Our theoretical analysis provides a probable explanation for the experimental work of Ma et al. We also discuss the thermodynamic properties of Sm-, N-, and (Sm,N)-codoped TiO₂ by analysis of the calculated formation energies.

2. Computational details

All of the spin-polarized calculations were performed using the projector augmented wave (PAW) pseudopotentials as implemented in the VASP code [36,37]. The exchange correlation potential was treated by the generalized gradient approximation (GGA) with the Perdew–Wang parameterization (known as GGA-PW91) [38]. The Brillouin-zone integrations were approximated by using the special *k*-point sampling of the Monkhorst–Pack scheme [39]. A cutoff energy of 500 eV and a mesh size of 5 × 5 × 5 were used for geometry optimization and electronic structure calculations. Using the block Davidson scheme, both the atomic positions and cell parameters were optimized until the residual forces were below 0.01 eV/Å. It was well-known that the traditional DFT method usually underestimated the band gap for semiconductors. However, the DFT + *U* approach introduced an on-site correction in order to describe systems with localized d and f electrons, which can produce better band gaps in comparison with experimental results. Therefore, our all calculations of the electronic and optical proper-

ties were conducted using the GGA + *U* method [40–43] for both Ti 3d and Sm 4f electrons. It was found that the band gap of pure anatase TiO₂ was 2.9 eV with *U* = 10.0 eV and *J* = 1.0 eV for Ti 3d electrons, and was only weakly dependent on *J* value. This accords well with the experimental value of 3.2 eV [44].

The valence electron configurations which included Ti (3d²4s²), O (2s²2p⁴), Sm (4f⁶5s²) and N (2s²2p³) were considered in this study. All the doped systems were constructed from a relaxed (2 × 2 × 1) 48-atom anatase TiO₂ supercell (see Fig. 1). A variety of possible doping model were considered, such as substitutional Sm at the Ti site (Sm@Ti), substitutional Sm at the O site (Sm@O), substitutional N at the Ti site (N@Ti), and substitutional N at the O site (N@O) for the bulk doped systems. For codoped systems, Sm locates either at Ti or at O and N locates either at O or at Ti, such as Sm@Ti&N@Ti, Sm@O&N@O, Sm@Ti&N@O, and Sm@O&N@Ti.

3. Results and discussion

3.1. Geometry analysis

Anatase has a tetragonal crystal structure with space group *I*₄₁/*a*md(141). The unit cell contains four TiO₂ formula units. We performed structure optimization for pure anatase TiO₂ supercell. The calculated lattice parameters of pure TiO₂ model are *a* = *b* = 3.816 Å and *c* = 9.618 Å at ambient conditions, which are in good agreement with the experiment value of *a* = *b* = 3.782 Å and *c* = 9.502 Å within 1.2%, respectively [44]. These results indicate that our calculation methods are reasonable, and the calculated results are authentic.

The average bond lengths of the doping TiO₂ after geometry optimization are summarized in Table 1. For pure anatase TiO₂, the average Ti–O bond length is 1.977 Å, there is no significant change compared with that of the Sm- and N-doped one. However, the average Ti–O bond lengths of the (Sm,N)-codoped TiO₂ in the supercell is shorter than Sm- and N-doped TiO₂. The average Ti–Sm bond length in Sm-doped and (Sm,N)-codoped systems are longer than the Ti–O bond length as the radius of Sm atom is larger than that of O atom. Due to the larger radius of N, the average Ti–N bond length of N-doped and (Sm,N)-codoped TiO₂ is also longer than that of the Ti–O bond. In the case of codoped TiO₂, the length of all these bonds is increased. The results show that (Sm,N)-codoping leads to a significant lattice distortion and a high defect formation energy, which in turn changes the dipole moments, makes the separation of photogenerated electrons and holes easier.

3.2. Defect formation energies

To study the relative stability of Sm-doped, N-doped, and (Sm,N)-codoped anatase TiO₂ systems, we have calculated the defect formation energy (*E*_{*f*}), which is defined by the expression,

$$E_{f(X@Y)} = E_{(X@Y)} - E_{(\text{pure})} - (\mu_X - \mu_Y) \quad (1)$$

$$E_{f(\text{Sm@Y}\&\text{N@Y})} = E_{(\text{Sm@Y}\&\text{N@Y})} - E_{(\text{pure})} - (\mu_{\text{Sm}} + \mu_{\text{N}} - \mu_Y - \mu_Y) \quad (2)$$

(*X* = Sm, N; *Y* = Ti, O)

where *E*_(pure) is the total energy of the pure anatase TiO₂ supercell, *E*_(*X*@*Y*) and *E*_(Sm@Y&N@Y) are the total energy of the monodoped and codoped systems, respectively. Under equilibrium conditions, the concentration of a point defect is controlled by its formation energy, which depends on the chemical potentials of the host and impurity atoms. For TiO₂, the chemical potentials of O and Ti satisfy the relationship $\mu_{\text{Ti}} + 2\mu_{\text{O}} = \mu_{\text{TiO}_2}$, $\mu_{\text{O}} \leq \mu_{\text{O}_2/2}$, and $\mu_{\text{Ti}} \leq \mu_{\text{Ti}}^{\text{metal}}$. The chemical potential μ_{O} is determined by the energy of an O₂ molecule in the O-rich growth condition (corresponding to a high value of μ_{O}). By referencing μ_{O} to the energy of an O atom in the O₂ molecule, μ_{Ti} in the Ti-rich condition (corresponding to a high value of μ_{Ti})

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