

Synergy Effect of Ce/N Co-doping on Anatase TiO₂ Photocatalysts from First Principles Calculation

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Abstract: Recent experiments have indicated that TiO₂ co-doped with cerium (Ce) and nitrogen (N) may show enhanced photocatalytic activity in the visible region with respect to TiO₂ doped only with Ce. Prompted by these findings, we have investigated Ce-N co-doped TiO₂ through a theoretical study. Density functional theory (DFT) calculations have been carried out with the generalized gradient approximation (GGA) to describe the electronic structure and photocatalytic activity of Ce-, N- and N/Ce-doped anatase TiO₂; substitutional locations of Ce and N in the TiO₂ lattice were considered: an O (Ti) atom is replaced by an N (Ce) atom. It was found that the Ce-N co-doped case narrows the band gap more significantly than the corresponding mono-doped anatase TiO₂. These findings give the theoretical understanding for recent experimental results.

Introduction

Titania (TiO₂)-based photocatalysts have received intense attention as promising photocatalytic materials for years [1-3]. However, as a wide band gap (BG) semiconductor ($E_g = 3.2$ eV), anatase titania allows only absorption of ultraviolet irradiation, which amounts to ~5% of solar energy ($\lambda < 387$ nm). Furthermore, its photo-excited electron-hole pairs recombine relatively easily. To enhance the optical absorption in the visible range, great efforts have been made to modify the band gap of TiO₂ by various methods.

Attempts have been made to enhance the efficiency of solar energy capture by metal doping [2]. It was demonstrated that metal-doped TiO₂ could induce a new d-band formation as a consequence of the interactions between metal ions and the host material. However, the photo-generated charge carrier is trapped during its migration from the inside to the surface of the lattice easily. Recently, lanthanide (Ln)-doped TiO₂ attracted increasing attention due to their special electron configuration. Bian et al investigated the effect on the band gap (BG) of 17 kinds of rare earths metal (RE) doped rutile TiO₂. The result showed that the band gap widths of most RE doped TiO₂ were less than pure TiO₂. However, Ln-doped photocatalyst suffer from an increase in recombination centers, which limit its photocatalytic activity [4].

Another attempt was incorporation of non-metal elements, such as C, N and S, into the TiO₂ crystal structure [5-7]. Among these reports, N-doped TiO₂ was proved to be a more promising method [7]. However, the photocatalytic efficiency of N-doped TiO₂ was limited due to the strongly localized N 2p states at the top of valence band [8].

Recently, co-doped TiO₂ with two different elements, especially nitrogen and other metal elements co-doping has become a rapidly growing field of interest for computational studies. Gai et al. [9] proposed using passivated co-doping of metal and nonmetal elements. Long et al have worked on N/W co-doped and N/Ta co-doped anatase TiO₂, which suggested that a continuum band is formed at the top of the valence band, therefore reducing the BG, afterwards enhancing the photocatalytic activity of TiO₂ [10, 11]. Ma et al [12] calculated the N/V co-doped anatase TiO₂, indicating the same feature, as well as confirming that the incorporation of V promoted N doping. Recent experiments have indicated that TiO₂ co-doped with Ce and N show enhanced photocatalytic activity in the visible region with respect to TiO₂ doped only with Ce. [13] Prompted by these findings, we have investigated Ce/N co-doped TiO₂ through a theoretical study.

Calculation model and methods

Anatase TiO₂ is a body-centered tetragonal crystal system, space group I41/amd. Each unit cell contains four TiO₂ units, in other words, four Ti and eight O atoms. The Ti center is six-coordinated by six O atoms via two long apical and four short equatorial bonds of lengths 1.979 Å and 1.932 Å at 15 K^[14] respectively, and at the same time, O atom is surrounded by four Ti atoms via one long bond and two short bonds^[15]. The anatase crystal is formed by chains of distorted TiO₆ octahedron, and its tetragonal structure can be described in terms of three parameters: two cell edges: a, c, one internal parameter d which indicates the length of apical bond.

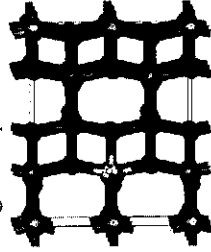


Fig.1 Supercell(2×2×1) model for defective anatase TiO₂ showing the location of the dopants. The ion doping sites are marked with N and Ce, respectively.

The doped systems were constructed from a 2×2×1 (48-atom) anatase supercell. The N atom was substituted for O atom and the Ce atom was substituted for Ti atom. N/Ce-doped TiO₂ was modeled by single substitution of N for one O atom, and its adjacent Ti atom was replaced by one Ce atom per supercell. The supercell system is shown in Fig. 1.

All the DFT calculations were performed using projector augmented wave (PAW) pseudopotentials as implemented in the Vienna ab initio Simulation Package (VASP) code.^[16, 17, 18] The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional was adopted for the exchange-correlation potential.^[19, 20] The cutoff energy was 400 eV and a Monkhorst-Pack k-point mesh^[21] of 4×4×4 was used. Both atomic positions and cell parameters were optimized until all the residual forces were smaller than 0.01 eV/Å, by performing GGA method and GGA + U^[22] method with U=6.6eV for Ti 3d and U=5.0eV for Ce 4f electrons. The DFT + U approach introduces an intra-atomic electron-electron interaction as an on-site correction in order to describe systems with localized d and f electrons, which can produce better band gaps relative to GGA. From the next section we can see that the calculated band gap of pure anatase TiO₂ with GGA + U method is 3.11eV, which agrees well with the experimental value of 3.20 eV.

Results and discussion

The minimum-energy configurations of pure anatase TiO₂ obtained by GGA and GGA+U methods in our study were compared with experimental data^[14] as shown in Table 1. It showed that the agreement between GGA method results and experiment data is better for the structural parameters than ones of GGA+U method. Therefore, we first optimized the atomic positions and cell parameters using the GGA method and then perform GGA+U calculations of electronic properties based on the structural parameters optimized by GGA. Dai et al. and Long et al have performed this method in their calculations of N/Ta co-doped and C-doped TiO₂ and also received good results.^[10, 23]

To compare the modifications in the band structure with different doping configurations, we have calculated the total density of states (TDOS) and partial density of states (PDOS) plotted in Fig. 2. For pure TiO₂, the valence-band maximum (VBM) is mainly composed of O 2p states, while the conduction-band minimum (CBM) is mainly composed of Ti 3d states, as shown in Fig. 2a.

For Ce-doped TiO₂, Fig. 2b shows that the VBM consists mainly of O 2p and Ce 4f states, whereas the CBM has Ti 3d and Ce 4f states, the impurity states change the construction of band, and thus led to a band gap reduction by about 0.29 eV, which would be expected to lead to but a little enhancement in photocatalytic efficiency.

Table 1 Comparison of two cell edges a and c and one internal parameter d between the experimental data and our computational obtained data

	experimental data ^[14]	GGA+U data	GGA data
a [Å]	3.782	3.869	3.786
c [Å]	9.502	9.586	9.506
c/a	2.512	2.478	2.511
d [Å]	1.979	2.008	1.988

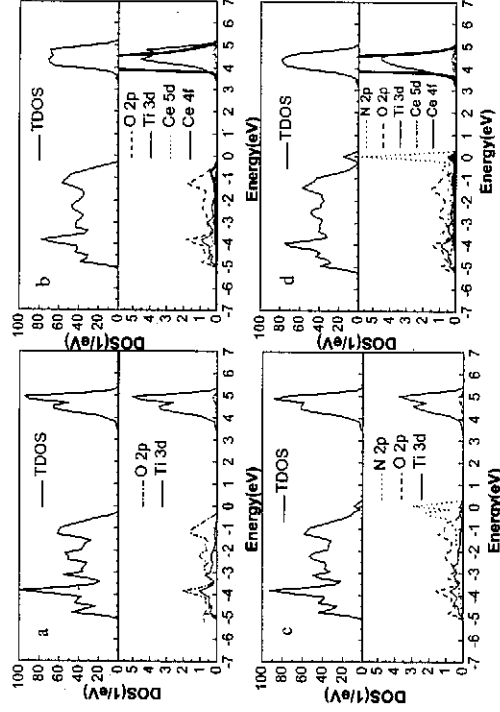


Fig. 2 The corresponding TDOS and PDOS of: a) pure TiO_2 , b) Ce-doped TiO_2 , c) N-doped TiO_2 , and d) Ce/N co-doped TiO_2

For N-doped TiO_2 , it is clear in Fig. 2c that: N 2p are hybridized with O 2p states at the VBM, in which some N 2p localized in the band gap, the electron in the valence band can be excited into gap states and then subsequently to the conduction band by visible-light absorption, suggesting that gap-to-conduction band transitions are responsible for red shifts in the absorption edge. However, because N is less electronegative than O, the emptied N 2p states which localized in the band gap can act as traps for excited electrons, subsequently promoting electron-hole recombination rates. Therefore, the photocatalytic activity of N-doped TiO_2 is more limited in the visible-light region.

For Ce/N co-doped TiO_2 which is shown in Fig. 2d, the VBM consists mainly of N 2p states and Ce 4f states, whereas the CBM consists of Ti 3d and Ce 4f states, the Ce 4f states localize on the frontier orbitals, there are still some impurity states locating in the band gap. However, the impurity states also change the band gap, the CBM are pushed to lower energy regions, the band gap is reduced to 2.26 eV, which can contribute to enhance visible-light absorption upon addition of N to Ce-doped TiO_2 . Yu et al.^[13] synthesized Ce/N co-doped anatase TiO_2 NPs (nanoparticles) using a one-step technique, suggested that the co-doping of Ce and N into TiO_2 NPs narrowed the band gap from 2.40 eV (Ce-doped) to 2.21 eV (Ce/N co-doped), which was one of the main reasons for the enhancement of photocatalytic activity within the visible light region. Our calculation results reach good agreement with this experimental observation.

Conclusions

Recent experiments have indicated that TiO_2 co-doped with Ce and N show enhanced photocatalytic activity in the visible region with respect to TiO_2 doped only with Ce. In this paper, we studied the electronic structure of pure, Ce-doped, N-doped and N/Ce co-doped anatase TiO_2

based on first principle calculations. The results showed that N/Ce co-doped TiO₂ narrowed the band gap of anatase TiO₂ more than Ce-doped TiO₂, rationalizing the experimental observation of the synergy effect of Ce/N co-doping.

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