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Visible-light responsive boron and nitrogen codoped anatase TiO_2 with exposed {0 0 1} facet: Calculation and experiment

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ABSTRACT

To fully understand the synergistic effect of B/N codoping on the visible-light photocatalytic activity of anatase TiO_2 with exposed {0 0 1} facet, a combination of Density Functional Theory (DFT) calculation by GGA + *U* method and experiment has been performed. Bader charge and Electronic Location Function (ELF) analysis reveal that there is free electron-gas like behavior around N and neighbor B for B/N-codoped anatase TiO_2 with exposed {0 0 1} facet, and its visible-light absorbance increases, which may promote Ti^{4+} reduction to Ti^{3+}. The results of calculation and experiment demonstrate that B/N codoping leads to the shift of the absorption edge of the TiO_2 to lower energy region, and thus makes its photocatalysis active within the wavelength of 600 nm.

1. Introduction

The internal and surface structure, the surface area and the specifically exposed crystal faces are key features that influence the photocatalytic activity of the photocatalytic materials [1–4]. TiO_2 is famous for its unique physical and chemical properties of excellent chemical stability, safety, non-toxicity and low cost and has been extensively used in coating, photoelectric conversion, environmental treatment, sensors, battery materials and so on[5–9]. The photocatalytic activity of anatase TiO_2 is higher than that of rutile TiO_2 despite the fact that anatase TiO_2 is a metastable phase. However, the sunlight absorption and utilization of anatase TiO_2 is significantly limited by its wide energy band gap of about 3.2 eV. So far, various methods have been adopted to modulate the band gap and improve the visible-light adsorption of TiO_2, such as metal and non-metal mono-doping, metal and non-metal cooping [10–19]. Our previous work has revealed that the band gap and photocatalytic activity of anatase TiO_2 can be well modulated by appropriate S doping [9].

B-doped and N-doped anatase TiO_2 has been attested to have narrower band gap both theoretically and experimentally [15]. Xiang et al. showed that N/S-codoped anatase TiO_2 with exposed {0 0 1} facet has enhanced the visible-light absorbance over three times than that of pure TiO_2 nanosheets [20]. Zhou et al. investigated the properties of N/S codoped anatase TiO_2 and found that the energy band of N/S codoped anatase TiO_2 shifts toward the lower energy area and thus enhances the oxidizability of photogenerated hole [21]. Recently, Hu et al. demonstrated that the synergistic effects of different ordered TiO_2 nanoarrays and different exposed active surfaces can effectively enhance the photocatalytic activity of TiO_2 [22].

Anatase TiO_2 with exposed {0 0 1} has higher photocatalytic activity than that with {1 0 1} facet, which is thermodynamically stable. The reason is due to the presence of abundant uncoordinated Ti atoms [23,24]. However, the rapid recombination of photogenerated electron-hole pairs leads to the low quantum efficiency for anatase TiO_2 with exposed {0 0 1} facet. Therefore, it is necessary to explore how to restrain the recombination of photogenerated electron-hole pairs for feasible charge separation and transfer, and expand the absorption edge to the visible-light region for the anatase TiO_2 with exposed {0 0 1} facet [25–27].

Liu et al. considered that the photocatalytic activity of anatase TiO_2 can be improved by B- or N-doping and B/N codoping. Additionally, the photocatalytic activity of B/N codoping anatase TiO_2 can be directly modulated by B-doping concentration, its different valence state and doping process [28]. However, the published paper just explained that the formation of B-N structure in TiO_2 surface can enhance the visible-light photocatalytic activity [28]. The plausible sites of B and N atoms doped into anatase TiO_2 and the synergistic effect between B/N codoping need further exploration. In addition, the enhanced mechanism that the special exposed {0 0 1} facet works on boron and nitrogen codoped TiO_2, the influence of valence states on this codoped

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photocatalyst and the synergistic effect of boron and nitrogen codoping in this semiconductor are key issues deserved to be investigated in detail. Thus, a systematic investigation of synergistic effect and mechanical properties for B/N-codoped anatase TiO_2 with {0 0 1} facet is carried out in this work.

An accurate band gap allows the quantitative prediction of defect energies and impurity levels, and helps to evaluate the influence of doping on optical absorption [29]. In general, the energy band gap of transition metal oxides is underestimated with standard DFT functional, which includes general gradient approximation (GGA) and local density approximation (LDA), for the absence of the electron self-interaction of strong-correlation systems. Therefore, GGA + U approaches are essential for the calculations of strong-correlation TiO_2 systems. Herein, we have investigated B/N-codoped anatase TiO_2 with exposed {0 0 1} facet with quantum theoretical method by employing the GGA + U schemes, in which the on-site two-electron integrals are expressed in terms of two parameters, Hubbard parameter U and exchange parameter J [30]. As implemented in Vienna Ab-initio Simulation Package (VASP), the GGA + U is realized by the rotationally invariant approach, and the parameters U and J do not enter separately but the difference ($U - J$) is meaningful [31]. Additionally, the geometries, electronic structures, and photocatalytic performance of pure anatase, pure anatase TiO_2 with exposed {0 0 1} facet (noted as TiO_2s), B-doped anatase TiO_2 with exposed {0 0 1} facet (B-TiO_2s), N-doped anatase TiO_2 with exposed {0 0 1} facet (N-TiO_2s), and B/N-codoped anatase TiO_2 with exposed {0 0 1} facet (B/N-TiO_2s) were explored based on the theoretical calculations, which were compared with experimental and theoretical results in previous studies [15,32].

2. Calculation model and experimental methods

2.1. Calculation model and method

The geometries, electronic structure and optical property for the materials with different dopant on surface structures were performed using the frozen-core projector augmented wave (PAW) method within the Perdew-Burke-Ernzerhof of generalized gradient approximation (GGA-PBE) for exchange-correlation energy as implemented in VASP [9]. The electronic states were expanded by plane wave basis set, and kinetic energy cutoff of 500 eV was taken for all calculations to ensure the accurate results. The pseudo-atomic calculations were performed for the material model with $2s^22p^4$(O), $2s^22p^1$(B), $2s^22p3$(N) and $3s^23p^63d^34s^1$(Ti) in all calculations.

In anatase TiO_2, the conduction bands below 8 eV mainly consist of Ti 3d states, which are highly localized and produce the localized defect states observed in experiment. GGA + U functional is widely used to address this strong, localized valence orbit issue [33,34]. The parameter U is usually an empirical parameter, and a variety U value from 2.5 to 10 eV for GGA + U calculation of titanium oxide has been recommended by previous work. The values of U suitable for the band gap of TiO_2, the energy of the states in the band gap of partially reduced TiO_2, and so on, have been determined based on most of previous calculations [35]. Through the comparison of the calculated results of pure anatase TiO_2 and dopant TiO_2s systems with the corresponding experimental results, the values of Hubbard U was set to be 7.8 eV for 3d electrons of Ti, and J was generally set to be zero for all calculations, which is in agreement with the literature [36].

A 7 × 7 × 7 Monkhorst-Pack set for Brillouin zone integration was used to calculate the anatase TiO_2 bulk geometry and an improved k-point mesh of 11 × 11 × 11 was used for the electronic properties calculations. Besides, the k-point meshes and the energy cutoff used in our calculations had been tested to have enough computational accuracy. The structures of our models were optimized by minimizing the total energy and atomic forces simultaneously. The optimized lattice parameters for unit cell anatase TiO_2 were a = b = 3.8054 Å and c = 9.7367 (comparable to experimental lattice parameters of a = b = 3.7821 Å and c = 9.5022 Å[9]), and optimal internal coordinate $u = d_{ap}/c = 0.206$, where d_{ap} is the apical Ti—O bond length. The calculated values here were in accordance with previous theoretical and experimental results [9,37]. A p (2 × 2) supercell anatase TiO_2 {0 0 1} facet slab was built based on the optimized geometry, and a 15 Å thick vacuum slap was added for eliminating slab-slab interactions. A central TiO plane with a bridging oxygen atom symmetrically placed above or below the central plane was consisted of a trilayer, which is similar to the model constructed by Scott et al.[38].

Zhao et al. found that it is energetically favored for O substituted by B in anatase TiO_2 [39]. Gopal et al. concluded that N and B appears as proximal neighbors in the anatase lattice, and it is a divacancy consisting of two nearest neighbor oxygen vacancies, in which one is substituted by a Nitrogen atom and the other is substituted by a Boron atom [40]. To simulate the different doping effects of B and N atoms in TiO_2s, we considered B and N atoms substituting lattice O atom in the supercells, which has the doping concentration of about 2.08 at.%.

In all of our calculations, the atoms in the bottom two trilayers were constrained at the bulk position [38], while the atoms in the upper two trilayers were relaxed with a maximal force criterion of 0.01 eV/Å and an energy tolerance of 1.0×10^{-5} eV/atom. For all surface calculations, k-space was sampled using a 5 × 5 × 1 Monkhorst-Pack grid. By GGA + U (with a Dudarev + U correction of $U = 7.8$ eV) calculation, the band gap of undoped anatase supercell was 3.230 eV, which is consistent with the experimental value [41]. On the basis of optimized crystallographic structures of TiO_2s, the spin-polarized band structure, density of state (DOS), Bader charge distribution and ELF analysis were calculated for exploring the correlation between photocatalytic activity and electronic structure of catalyst anatase TiO_2. Besides, the optical absorption spectra were calculated for different dopant anatase TiO_2. The absorption coefficient $\alpha(\omega)$ and the dielectric complex function ε were calculated using the following expressions:

$$\alpha(\omega) = \sqrt{2}\,\omega * \left((\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^{\frac{1}{2}} - \varepsilon_1(\omega) \right)^{\frac{1}{2}}$$

where$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, and ε_2 is calculated using appropriate matrix elements [9]:

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

where Ψ_k^C and Ψ_k^V are the eigenstates at k point of conduction band and valence band respectively, Ω is the volume of elementary cell, ω is the frequency of incident light, and $\hat{u}$ is the external field vector.

2.2. Experiment

2.2.1. Material synthesis

Synthesis of TiO_2s, B-TiO_2s, and N-TiO_2s. In a typical TiO_2s synthesis, 1.0 mL $Ti(C_4H_9O)_4$ was added to a 30 mL of 2 M $NaBF_4$ and hydrochloric acid aqueous solution. The mixture had been stirred for 30 min and then was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and put into a preheated oven to perform hydrothermal decomposition treatment at 140 °C for 24 h. After hydrothermal process, the gray fluffy powders were collected and washed with copious amounts of distilled water and absolute alcohol for three times, and then dried in air at 80 °C overnight. The powders were further heated in a tube furnace at 450 °C for 3 h in air. As-prepared sample was denoted as TiO_2s. For the synthesis of B-TiO_2s and N-TiO_2s, the whole process was similar to that for TiO_2s except that the precursor was different. At the beginning, 500 mg TiB_2 and TiN was added to the 30 mL of 2 M $NaBF_4$ and hydrochloric acid aqueous solution for the preparation of B-TiO_2s and N-TiO_2s respectively. The following procedure was the same as that for TiO_2s. The final obtained sample was denoted as B-TiO_2s and N-TiO_2s respectively.

Synthesis of B/N-TiO_2s. In a typical synthesis, 500 mg of B-TiO_2s powder was annealed under NH_3 flow at 550 °C for 3 h as a reference