A first-principles calculation on electronic structure and optical performance of chromium and nitrogen codoped anatase titanium dioxide

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A B S T R A C T

In this article, the supercells of pure anatase titanium dioxide, nitrogen and/or chromium doping anatase titanium dioxide were computed using first-principles with the plane-wave ultrasoft pseudopotentials method, and the electronic structure and optical properties of different ions doping models were also studied. The results indicated that the band gap and charge carriers recombination rate of nitrogen and chromium codoped system are all decreased effectively, and the separation of electron–hole pairs becomes more favorable due to impurity energy levels formation in the band gap of anatase titanium dioxide, which could play an important role in enhancing the catalytic activity and visible light absorption of anatase titanium dioxide. Furthermore, the optical absorption curves of nitrogen and chromium codoped anatase titanium dioxide indicate the highest photoresponse for visible-light, which is consistent with the previous experimental results. The above results would be quite helpful for research guiding and further developing of titanium dioxide photocatalyst.

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1. Introduction

Along with the rapid development of modern society, energy exhaustion and environmental pollution have become two of the most serious issues, which requires handling emergently. The photocatalysis technology based on the semiconductor photocatalysts has many advantages on solving the above problem, compared with the traditional methods. At present, scientists have obtained many photocatalysts materials with application potential since Fujishima and Honda reported the photocatalytic hydrogen production using splitting of water on titanium oxide electrodes in 1972, such as TiO_2, ZnO, ZnS, WO_3, Fe_2O_3, CdS and PbS. Among the different oxide and nonoxide semiconductor photocatalysts, titanium dioxide as one of the most efficient and economical photocatalysts has been studied extensively in the fields of energy and environmental related applications due to its strong catalytic activity, a long lifetime of photon-generated carrier, chemical inertness, low cost and nontoxicity [1–5]. Generally, titanium dioxide has

three basic crystalline phases containing brookite, anatase and rutile. Especially, anatase titanium dioxide has attracted much attention because of its higher catalytic activity. Generally, sunlight includes almost 4% of ultraviolet light and 43% of visible light. Nevertheless, anatase titanium dioxide has a disadvantage of its intrinsic wide band gap (E_g = 3.23 eV), which indicates that titanium dioxide can be activated only under the ultraviolet radiation from sunlight with only a small portion of the solar energy, leading to its quite low solar energy usage. Consequently, the high efficient usage of visible light has become one of the most main purposes for the photocatalytic materials, and a large number of related theoretical and experimental researches have been performed to adjust the band gap of titanium dioxide.

Nowadays, efforts on enhancing the photocatalytic performance of titanium dioxide often focus on the following methods: transition metal doping, nonmetal doping, noble metal loading, organic dye sensitizing, semiconductor compounding, etc. [6–11]. Among these methods, ion doping has been regarded as one of the most effective ways. The previous studies mostly have focused on the single ion doping for titanium dioxide [12,13], but relatively few latest experimental work shows that various ions codoping into titanium dioxide can enhance the optical absorption scope and

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photocatalytic activity. However, the above experimental work on ions codoping into titanium dioxide has disadvantages of changeable experimental conditions and sample preparation methods, leading to the difficulty in studying the modification mechanism and limitation of application research [14–17]. Instead, the computer simulation could break through the experimental drawback and be applied to analyzing the ion doping effects and modification mechanism deeply.

In the present work, the plane-wave ultrasoft pesudopotentials method within the first-principles framework has been applied to investigating the crystal structure, electronic structure, and optical properties of different ions doping models, including pure anatase titanium dioxide, nitrogen and/or chromium doping anatase titanium dioxide. Based on the above mentioned work, the effect of these ions on the photocatalytic activity of anatase titanium dioxide has also been demonstrated.

2. Computational details

We have constructed a $2 \times 2 \times 1$ supercell, which is composed of forty-eight atoms in the calculations. As shown in Fig. 1, in nitrogen and chromium doped titanium dioxide model, a titanium atom was substituted by a chromium and an oxygen atom was substituted by a nitrogen atom. Consequently, one supercell consisted of fifteen titanium atoms, thirty-one oxygen atoms, one chromium atom and one nitrogen atom. The atomic concentration of impurity was about 2.08% (atomic fraction) in total, which could be compared with the experimental results [18,19]. The other models are set up by means of the similar method.

First-principles calculations based on the density functional theory were performed with the CASTEP code in Materials Studio 5.5 developed by Accelrys Software Inc. [20]. The ultrasoft pseudopotential was applied to describing the interaction between electrons and ionic core. The electronic exchange–correlation energy was treated within the framework of the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) function [21,22]. The energy cutoff for the plane wave basis was set to be 340 eV and Brillouin zone integrations were done by using a Monklorst–Pack grid of $3 \times 3 \times 3$ k-points. In order to obtain stable atomic configuration and accurate results that can be compared with experimental results, pure and doped models were geometrically optimized using the Broyden–Fletcher–Golafarb–Shanno (BFGS). The convergence threshold for self-consistent tolerance was set to 1×10^{-5} eV per atom and atomic relaxations were conducted until the residual forces were below 0.03 eV/Å. The above parameters were good enough to obtain well-converged total energy and geometry optimization calculations. After the geometry optimization, the band structure, density of states and optical properties of the optimized supercells were calculated. For optical properties calculations, polycrystalline models and "scissors operators" were utilized.
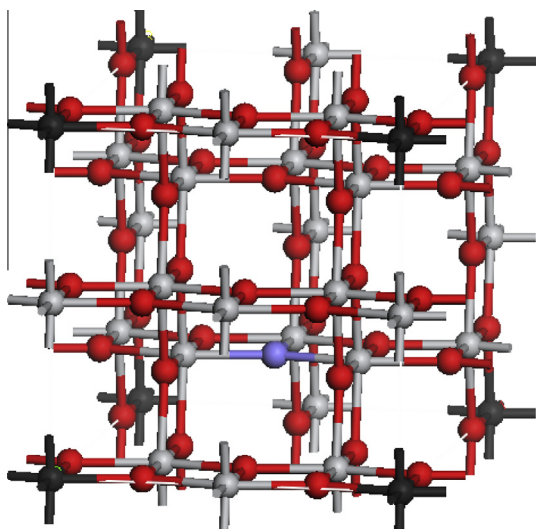

Fig. 1. Supercell model for N + Cr codoped anatase titanium dioxide in the present work (black ball represents the Cr atom; red ball represents the O atom; blue ball represents the N atom; white ball represents Ti the atom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussions

By means of optimizing the pure anatase titanium dioxide supercell, we have obtained the lattice parameters as follows: a = 7.593913 Å, b = 7.593913 Å, c = 9.817123 Å. The above values are in good agreement with the experimental results [23], which indicates that our calculation methods are reasonable. For all models, the same k-points mesh is set to sample the first Brillouim zone, in order to conveniently compare the electronic structures of different ions doping models. The computed band gap of pure anatase titanium dioxide is 2.20 eV at G (gamma point) shown as Fig. 2, which is similar to the reported results [24]. However, the above value is much lower than 3.23 eV as the experimental value, because the discontinuity in the exchange–correlation potential is not taken into account within the framework of density functional theory, and the calculated band gap value is often lower than the experimental value [25,26]. The calculated band structures of N-doped, Cr-doped and N + Cr-codoped are shown in Fig. 2, respectively.

From Fig. 2, it can be concluded that the energy levels are decreased and split due to the decrease of their degree of crystal symmetry and destruction of periodic potential field after doping. As a result, the valence band top and conduction band bottom of anatase titanium dioxide are both removed toward low energy. Moreover, the decrease grade of valence band top is larger than that of conduction band bottom, thus the band gap of anatase titanium dioxide itself has become a little wider after doping. At the same time, the new energy levels between valence band and conduction band are formed by means of electrons in impurity orbit atoms, leading to the band gap decrease of the doped system. Specifically, the band gap decrease of N-doped, Cr-doped and N + Cr-codoped anatase titanium dioxide doped system are 0.51, 0.62 and 1.35 eV, respectively. For N-doped anatase titanium dioxide, the impurity energy levels are mainly formed above the valence band as acceptor states, thus leading to the decrease of band gap and photoelectron transition energy. For Cr-doped anatase titanium dioxide, isolated impurity energy levels are mainly situated just below the conduction band bottom of anatase titanium dioxide. The above impurity energy levels overlap with valence band maximum or conduction band minimum of anatase titanium dioxide fully. For N + Cr-codoped anatase titanium dioxide, the energy levels splitting becomes more obvious due to the further decrease of crystal symmetry degree, and more impurity energy levels are formed in the band gap of anatase titanium dioxide. Compared with the single N- or Cr-doped anatase titanium dioxide, the overlapping between impurity energy levels and valence band maximum or conduction band minimum is more obvious. In a word, nitrogen and chromium codoping can adjust the band structure of anatase titanium dioxide, and impurity energy levels are formed in the band gap of anatase titanium dioxide. Therefore, the band gap of doped system is decreased effectively, and the separation of electron–hole pairs becomes more favorable, which could play an important role in enhancing the catalytic activity and visible light absorption of anatase titanium dioxide.

In order to study the origin of the band gap change and analyze the variation of electronic structures caused by doping, the total density of states and partial density of states of doped models are calculated and shown in Fig. 3. Among them, Fig. 3a indicates the total density of states of all the models, and the vertical dot line at 0 eV is Fermi level; Fig. 3b–e show the calculated partial density of states of different doped models.

From Fig. 3, it can be seen that valence band and conduction band are composed of O 2p states and Ti 3d states in the pure anatase titanium dioxide. For the pure anatase titanium dioxide mentioned above, the conduction band is primarily provided by