

Structural stability and electronic structure of N- or C-monodoped TiO₂ from first-principles calculations

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Abstract. Plane-wave ultrasoft pseudopotential calculations are performed to study the structural stability and the electronic structure of N- or C-monodoped TiO₂. Firstly, various models of nonmetal doped TiO₂ are optimized to calculate the defect formation energy of different dopants. It is found that the Ti-rich condition facilitates N- or C-doping. The nonmetallic oxide of C and N in high valence facilitates doping under the Ti-rich condition. The element and the oxide of C and N in low valence facilitate doping under the O-rich condition. Secondly, the energy band structure of doped TiO₂ is analyzed. The results show that N-doping generates a semi-filled shallow impurity energy level near the top of the valence band. C-doping generates three deep impurity energy levels within the band gap which easily become the recombination centers of electrons and holes. Finally, the bonds between atoms are analyzed using the electron density map and the bond population. It is found that the electronegativity of impurities determines the position of the impurity energy level. These results help to understand the effects of nonmetal doping on the photocatalytic properties of TiO₂.

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Key words: photocatalysis, stability, first-principles, TiO₂

1 Introduction

TiO₂ is a promising semiconductor material with wide band gap which presents excellent photoelectric and photocatalytic properties. It has received intense attention in the photocatalytic technology [1,2] and dye sensitized solar cells [3,4]. However, the wide band gap (3.23 eV) and high photo-generated electron-hole recombining rate limit its application in the photocatalytic field. So it is necessary to perform modification. A common modifying method is transition metal doping, such as V-, Cr-, Mn-, Fe-, Co- and Nb-doping [5,6].

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The photocatalytic activity of transition metal cation doped TiO_2 is decreased except for few cases, since these doping methods generate deep local level of dopant which easily becomes recombination center of electrons and holes [5–7]. However, nonmetal doped TiO_2 is the photocatalytic material with excellent performance. For example, sputtering has been used to prepare $\text{TiO}_{2-x}\text{N}_x$ coating by Asahi *et al.* [8]. It is found that the electronic states of N $2p$ orbital narrow the band gap by mixing those of O $2p$ orbits. Also, the spectral response clearly moved to the visible region. The experimental results show that N-, C- and other nonmetal doping help to improve the photocatalytic performance [9]. It is also found that the impurity energy levels of nonmetal doped TiO_2 are likely to form the recombination centers of electrons and holes, which reduce the photocatalytic efficiency [10,11].

The preparation methods and conditions of these photocatalyst materials are different, which leads to the difference of the geometry structure and the material composition. It is very difficult to analyze the modification mechanism of nonmetal doped TiO_2 using experiment. Thus, it is necessary to study the stability of geometry structure and energy band structure using first-principle method [12]. Valentin *et al.* [13] have used ultrasoft pseudopotential method to study the electronic structure and the defect formation energies of C-doped TiO_2 . But they have not considered the charged defect formation energies. Recently, the C- or N-doped TiO_2 have been studied by Yang *et al.* [14] and Tao *et al.* [15] and have been found to have ferromagnetism. However, the type and stability of the doped structure have not been studied. Many studies have shown that nonmetal doped TiO_2 can effectively enhance the range of spectral response [16–19]. High concentrations of nonmetal doping are difficult to achieve, which restricts its application in the photocatalytic fields. Thus, first-principles calculations are performed to study nonmetal doped TiO_2 . Then the defect formation energies are calculated. After that, the effects of doping species on the impurity concentration are discussed. Finally, the electronic structure and the electrical charge population are analyzed.

2 Computational methods

Plane-wave ultrasoft pseudopotential method based on the density functional theory is used in the calculations. The configurations of valence electrons are selected as C: $2s^2 2p^2$, N: $2s^2 2p^3$, O: $2s^2 2p^4$ and Ti: $3s^2 3p^6 3d^2 4s^2$ when describing the ion solid interaction with the valence electrons. The other orbital electrons are calculated as core electrons. The PW91 generalized gradient approximation formulism for the exchange and correlation function is chosen [20] in the calculations of anatase TiO_2 . According to the reference [21], geometry parameters of TiO_2 calculated by PBE [22] formulism and RPBE [23] formulism are closer to the experimental values [24]. The Pulay density mixing method is used in the computations of self-consistent field. The self-consistent accuracy is set to the degree that every atomic energy converges to 2.0×10^{-6} eV and the force on every atom is smaller than 0.1 eV/nm. The BFGS algorithm is used in the structural optimization of the