Effects of B site doping on electronic structures of InNbO$_4$ based on hybrid density functional calculations

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Abstract. In order to improve the photocatalytic activity under visible-light irradiation, we adopted first principle calculations based on density functional theory (DFT) to calculate the electronic structures of B site transition metal element doped InNbO$_4$. The results indicated that the complete hybridization of Nb 4d states and some Ti 3d states contributed to the new conduction band of Ti doped InNbO$_4$, barely changing the position of band edge. For Cr doping, some localized Cr 3d states were introduced into the band gap. Nonetheless, the potential of localized levels was too positive to cause visible-light reaction. When it came to Cu doping, the band gap was almost same with that of InNbO$_4$ as well as some localized Cu 3d states appeared above the top of VB. The introduction of localized energy levels benefitted electrons to migrate from valence band (VB) to conduction band (CB) by absorbing lower energy photons, realizing visible-light response.

1. Introduction

Since the energy shortage is becoming a big headache of threatening the human’s sustainable development, semiconductor photocatalysis has brought about widespread attention on account of its potential applications for new energy resources like CO$_2$ reduction, hydrogen generation and pollutants decomposition [1~10]. Recently, indium niobate (InNbO$_4$) has been studied for its numerous advantages of wide absorption range, stable thermodynamic property and simple catalytic system [11-14]. Unfortunately, InNbO$_4$ was inert in visible-light region owing to its relatively wide band gap (~3.83 eV) [15]. Therefore, it is an emergency of founding an appropriate way to modify the band structures of InNbO$_4$ to realize visible-light response. Lee et al [16] utilized solid phase reaction method to produce InTaO$_4$ samples as well as InNbO$_4$ synthesized with NiO and Co$_3$O$_4$ cocatalysts, aiming at characterizing the activity for photo-reduction of carbon dioxide. Zhou et al [17] have studied the electronic structures of N doped InNbO$_4$ with first principle and pointed out that the occurrence of localized N 2p states was beneficial to realizing photocatalytic reactions under visible light.

Actually, B site transition metal elements can be introduced into the crystal lattices of semiconductor photocatalytic materials, bringing localized energy levels into energy gap. Through these levels, electrons in VB can transit to CB by absorbing lower energy photons, consequently expanding spectral response range. Herein, the electronic structures and photocatalytic activities of the first series of transition metals (Ti, Cr, Cu) doped InNbO$_4$ have been investigated by DFT first principles.

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2. Calculations and models
In this work, InNbO$_4$ with supercell structure (2×1×2) was adopted as a calculation model (figure 1) and calculated by Cambridge Sequential Total Energy Package (CASTEP). As for (Ti, Cr, Cu) doped InNbO$_4$, one transition metal atom took the place of Nb atom. The GGA-PBE was served to describe the exchange correlation potential. The electronic wave function was expanded with a kinetic energy cut-off (370 eV) and the k point mesh of the Brillouin zone integration was set to 5×4×5. Geometry optimization was implemented to pick the doping structure with the minimum total energy as the model. The maximum stress was smaller than 0.1 GPa, the maximum displacement was 2×10$^{-4}$ nm, and the convergence criteria parameter of the maximum force on atoms was not greater than 0.05 eV Å, respectively.

![Figure 1. The crystal structure diagrams of InNbO$_4$ and (Ti, Cr, Cu) doped InNbO$_4$.](image)

3. Results and discussions

3.1. Geometry optimization
Table 1 lists the optimized lattice parameters of InNbO$_4$ and (Ti, Cr, Cu) doped InNbO$_4$. The calculated crystal parameters of InNbO$_4$ were a=10.450 Å, b=11.846 Å, c=4.946 Å, in accordance with the experimental values of a=10.288 Å, b=11.542 Å, c=4.834 Å. This indicated that the present computing method were reasonable and credible. Additionally, the atom sites and lattice parameters have not significantly changed after introducing the impurity atoms.
Table 1. The optimized lattice parameters of InNbO$_4$ and (Ti, Cr, Cu) doped InNbO$_4$.

|          | a (Å) | b (Å) | c (Å) | α (Å) | β (Å) | γ (Å) |
|----------|-------|-------|-------|-------|-------|-------|
| InNbO$_4$ | 10.450| 11.846| 4.946 | 89.999| 91.332| 90.000|
| Ti-InNbO$_4$ | 10.457| 11.861| 4.945 | 90.003| 91.215| 90.026|
| Cr-InNbO$_4$ | 10.477| 11.892| 4.967 | 90.014| 91.303| 90.059|
| Cu-InNbO$_4$ | 10.473| 11.867| 4.955 | 90.007| 91.302| 90.041|

3.2. Electronic structures

The band structures of B site (Ti, Cr, Cu) doped InNbO$_4$ (figure 2) were discussed combined with their band gaps. As shown in figure 2(a), the calculated band gap of InNbO$_4$ (3.38 eV) was much lower than the experimental value (3.83 eV). The calculated band gap energy is generally underestimated simply because of the inherent error of the DFT algorithm [18]. However, it is still considered to be persuasive to investigate the change trends of energy band structures of materials. It could also be inferred that InNbO$_4$ was a sort of indirect band gap semiconductors because the positions of its conduction band minimum (CBM) and valence band maximum (VBM) were not located in the same G point.

It could be observed from figure 2(b-d) that the localized energy levels were introduced after B site doping. After Ti doping, the impurity levels composed of Ti 3d states and Nb 4d states resulted in the formation of a new CB. It also turned out that there was little change of the bang gap of Ti doped InNbO$_4$ (3.28 eV), which was just 0.10 eV smaller than that of InNbO$_4$ (3.38 eV). As for Cr doping, the band gap (3.33 eV) kept almost unchanged compared with that of InNbO$_4$ as well as the localized levels lay near the bottom of CB. In contrast with InNbO$_4$, the band gap of Cu doped InNbO$_4$ (3.07 eV) diminished 0.31 eV along with the appearance of localized Cu 3d states above the top of VB. The introduction of localized energy levels changed the electrons transition method in the band gap so that InNbO$_4$ could absorb photons of longer wavelength to realize visible-light reaction, improving the utilization efficiency of solar energy and photocatalytic activity.

Figure 2. The band structures of InNbO$_4$ and (Ti, Cr, Cu) doped InNbO$_4$. 
Figure 3 exhibits the density of states (DOS) of InNbO$_4$ and (Ti, Cr, Cu) doped InNbO$_4$. Figure 3(a) implied that CB of InNbO$_4$ mainly consisted of Nb 4d states while VB was composed of O 2p states. There was partial overlap of Nb 4d and O 2p states in both CB and VB because of the existence of Nb-O covalent bonds. In the Ti doping case (figure 3(b)), the complete overlap of Ti 3d and Nb 4d peaks barely changed the position of CB and thereby had little influence on the photocatalytic activity of InNbO$_4$, which confirmed the former analysis in figure 2(b). It was perceived from figure 3(c, d) that the Cr 3d peak was formed in the band gap of Cr doping while the impurity peak constituted of Cu 3d states turned up beside the VB edge of Cu doping. This fact was also consistent with the calculated results of the above band structures.

![Image of Figure 3](image-url)

**Figure 3.** The density of states (DOS) of InNbO$_4$ and (Ti, Cr, Cu) doped InNbO$_4$.

### 3.3. Schematic band structures

Redox potential and the position of band edge played a leading role in the photocatalytic activity of semiconductor photocatalysts. The band edge positions of semiconductor materials before and after doping were determined by the calculated band gap, and the schematic band structures were shown in figure 4. The calculation formula of the energy band position is as follows: $E_{VB} = \chi + 0.5E_g - E_e$, where $E_{VB}$, $E_g$, $E_e$ are valence band maximum, band gap energy, and the free electron energy on the surface of the hydrogen atoms (4.5 eV), respectively; $\chi = \sqrt[n]{\chi_1 \chi_2 \chi_3 \ldots \chi_n}$ represents the geometric mean of the Mulliken electronegativity of the constituent atoms [19, 20].

As we know, the redox ability of water is measured by the normal hydrogen electrode (NHE). From the schematic diagram, we learnt that the top of VB was fairly higher than the electric potential...
of O$_2$/H$_2$O. B site transition metal element doping barely changed the band gap values while the positions of their CB and VB were a bit different from each other. Thereinto, for Ti doping, the mixture of Ti 3d and Nb 4d states slightly narrowed the band gap. As for Cr doping, the positions of CB and VB obviously shifted up and the localized energy levels were introduced to the band gap. Unfortunately, the potential of localized Cr 3d states was below the standard electrode potential of hydrogen. Although the band gap of Cu doped InNbO$_4$ was almost same with that of InNbO$_4$, the electrons in VB could transfer to CB through the localized energy levels to realize visible-light response.

![Figure 4. The schematic band structures of InNbO$_4$ and (Ti, Cr, Cu) doped InNbO$_4$.](image)

4. Conclusions
In this paper, we mainly investigated the electronic structures of B site (Ti, Cr, Cu) doped InNbO$_4$ on the basis of DFT.

For Ti doped InNbO$_4$, the Ti 3d states mixed with Nb 4d states changed the position of conduction band edge so little that there was almost no effect on the photocatalytic activity of InNbO$_4$.

For Cr doping, the localized energy levels consisting of Cr 3d states helped to expand the spectral response range. Whereas, the potential of localized Cr 3d states could not achieve the standard electrode potential of hydrogen, which indicated that Cr doped InNbO$_4$ was not an appropriate candidate for photocatalytic reaction.

As for Cu doping, the appearance of localized energy levels changed the electron transition way, making for the red shift of absorption spectrum and the realization of visible-light reaction. Above all, the Cu doped InNbO$_4$ was the most promising photocatalyst for InNb$_{1-x}$M$_x$O$_4$ (M= Ti, Cr, Cu).

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