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Band gap narrowing in nitrogen-doped La$_2$Ti$_2$O$_7$ predicated by density-functional theory calculation

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In order to reveal the origin of enhanced photocatalytic activity of N-doped La$_2$Ti$_2$O$_7$ in both the visible light and the ultraviolet light regions, its electronic structure has been studied using the spin-polarized density functional theory (DFT) and the Heyd-Scuseria-Ernzerhof (HSE06) hybrid approach in this work. The results show that the deep localized states are formed in the forbidden band when nitrogen solely substitutes for oxygen. Introducing the interstitial Ti atom into the N-doped La$_2$Ti$_2$O$_7$ photocatalyst still causes the presence of localized energy band. Two nitrogen substitutes co-exist stably with one oxygen vacancy, creating a continuum energy band just above the valence band maximum. The formation of a continuum band instead of mid-gap states can extend the light absorption to the visible light region without increasing the charge recombination, explaining the enhanced visible light performance without deteriorating the ultraviolet light photocatalytic activity.

1. Introduction

Since discovery of photocatalysis by Fujishima and Honda$^1$, semiconductor-based materials have been found wide applications in removing organic pollutants from water and air, splitting water into hydrogen and oxygen, as well as reducing CO$_2$$^{2-4}$. Of the numerous photocatalysts, layer-structured semiconductors have received extensive attention because the reduction and oxidation reactions, e.g. H$_2$ and O$_2$ evolution sites, are separated out$^{5,7}$. Perovskite-type photocatalysts consist of the network of corner-sharing octahedra that benefit to the mobility of charge carriers, leading to high photocatalytic activity$^{6,9-10}$. Perovskite-type La$_2$Ti$_2$O$_7$ with a layered structure possesses the merits of both perovskite and layered structures, which exhibits high photocatalytic activity toward organic decomposition, water splitting and CO$_2$ reduction. For example, layered perovskite La$_2$Ti$_2$O$_7$ (110) loaded with nickels showed a quantum yield as high as 12% in water splitting under ultraviolet (UV) irradiation, which exhibited much better photocatalytic activity than Pt-loaded TiO$_2$. In the absence of a co-catalyst, La$_2$Ti$_2$O$_7$ nanosheets demonstrated similar activity to Degussa P25 in photocatalytic hydrogen evolution from the water-ethanol solution$^{11}$. It has also been reported that 98% Cr(VI) ions in water was removed by La$_2$Ti$_2$O$_7$ after 3 hours of UV irradiation$^{12}$.

La$_2$Ti$_2$O$_7$ has a wide band gap ($\sim 4.0$ eV), which depends on the synthesis method and the resulting morphology$^{9,11,13,14}$. Hence it shows photocatalytic activity only under UV light irradiation. Rh-doped La$_2$Ti$_2$O$_7$ was active for H$_2$ evolution from an aqueous methanol solution under visible light irradiation owing to the photo-excitation of localized energy levels resulting from the Rh$^+$ doping$^{14}$. Similarly, Cr and/or Fe doping in La$_2$Ti$_2$O$_7$ induced intensive light absorption in the visible light region and photocatalytic hydrogen production from the water–methanol solution due to the formation of a partially filled 3d band in the band gap$^{17,20}$. The recent experimental results demonstrated that the nitrogen-doped La$_2$Ti$_2$O$_7$ nanosheets not only showed significant visible light photocatalytic activity but also exhibited enhanced ultraviolet light photocatalytic activity$^{13,21}$. Nitrogen doping in La$_2$Ti$_2$O$_7$ narrowed the band gap rather than creating the localized mid-gap states, which was different from N-doped anatase TiO$_2$. These results could not be explained by the first-principles calculations, which showed that nitrogen substituting for oxygen caused the formation of the localized energy band in the band gap of La$_2$Ti$_2$O$_7$$^{22,23}$. Since the energy band gap is a critical factor governing the photocatalytic activity, and doping is the most common method for altering the energy band gap$^2$, it is essential to understand the effect of doping on the electronic band structure of a semiconductor.

Herein, we investigate the influence of N-doping on the crystal and the electronic structures of La$_2$Ti$_2$O$_7$ using first-principles calculations. We assume that nitrogen substitutes for oxygen when it is doped in La$_2$Ti$_2$O$_7$ based on the experimental evidence$^{13}$. We check whether the deep states will be formed in the forbidden band when nitrogen solely replaces oxygen. We also examine whether a localized energy band will still exist when the nitrogen substitutes co-exist with an interstitial Ti atom. Furthermore, we explore how the oxygen vacancies are used to stabilize the dopants, leading to an enhancement of visible light absorption without reducing the charge carrier lifetime. In particular, we investigate what is the case if one oxygen vacancy ($V_O$) stably exists with two nitrogen substitutes ($N_2$).

2. Calculation methods

The calculations have been performed using the Vienna ab-initio simulation program (VASP)$^{24}$. Adopting Perdew-Burke-Ernzerhof
(PBE) prescription, the generalized gradient approximation (GGA) was used to represent the electronic exchange-correlation energy during the geometry relaxation. Hybrid-functional Heyd-Scuseria-Ernzerhof (HSE06) method was also employed to calculate the electronic structure. The projector-augmented-wave (PAW) potentials were used to describe the electron-ion interaction. The valence configurations including valence and semicore electrons were \(^{2}s^{2}2p^{4}\) for oxygen, \(^{2}s^{2}2p^{3}\) for nitrogen, \(^{3}p^{3}3d^{3}4s\) for titanium and \(^{5}s^{2}5p^{6}6s\) for lanthanum. The cut-off energy was 450 eV and the Monkhorst-Pack k-point mesh was \(6 \times 8 \times 4\) for a 44-atom supercell. Structural relaxations were performed until the self-consistent total energy difference reached \(10^{-5}\) eV and the residual forces on atoms fallen below 0.02 eV/Å.

### 3. Results and Discussion

The monoclinic \(\text{La}_2\text{Ti}_2\text{O}_7\) has a layered perovskite structure with \(P2_1\) space group. The calculated lattice parameters using GGA are respectively \(a = 7.795\ \text{Å}, b = 5.604\ \text{Å} and c = 13.264\ \text{Å}\) (Fig.1(a)), agreeing well with the experimental values of \(a = 7.812\ \text{Å}, b = 5.544\ \text{Å}, and c = 13.010\ \text{Å}\). For the supercell containing 44 atoms, there were 14 lattice sites of oxygen atom for nitrogen to enter, giving rise to a doping concentration of 3.6 at% similar to the experimental value. We calculated the total energies for all the 14 configurations, and the relaxed geometry with the minimum total energy is shown in Fig.1(b). It can be seen that doping N into \(\text{La}_2\text{Ti}_2\text{O}_7\) had little influence on the crystal structure.

Fig.1 Supercells showing the optimized crystal structure of pristine (a), N-doped \(\text{La}_2\text{Ti}_2\text{O}_7\) (b), \(\text{La}_2\text{Ti}_2\text{O}_7\) with complex \(N^{+}\text{Ti}\) (c) and \(\text{La}_2\text{Ti}_2\text{O}_7\) with complex defects (2\(N^{+}\text{Ti}\) (d). The grey, red, light-blue and blue spheres denote the Ti, O, La, and N atoms, respectively.

Fig.2 shows the density of states (DOS) of pristine \(\text{La}_2\text{Ti}_2\text{O}_7\) resulting from the calculations of DFT and HSE06 hybrid function. It can be seen that the components of the DOS curves obtained with the two methods were very similar. The valence band maximum was composed of \(\text{O}\ 2p\) in majority and of \(\text{Ti}\ 3p, \text{Ti}\ 3d\) and \(\text{La}
^{5}s^{2}\text{La}\ 5d\) in minority. The conduction band minimum was mainly constructed by \(\text{Ti}\ 3d\) with minor \(\text{O}\ 2p\) and few \(\text{La}
^{5}s\text{La}\ 5d\) states. Since all the elements contribute to the valence band maximum (VBM) and the conduction band minimum (CBM), the subtle stoichiometric change, e.g. by doping other elements, forming the vacancies or interstitial atoms, will definitely affect the electronic structure of the system.

The indirect band gap of pristine \(\text{La}_2\text{Ti}_2\text{O}_7\) calculated with DFT was 2.9 eV (Fig.3 (a)), underestimating the experimental value due to well-known limitations in DFT. When HSE06 hybrid method was used, the calculated band gap was 4.4 eV (Fig.3(b)), which was slightly larger than the typical experimental value obtained with the solid-state reaction (3.8 eV) and the molten salt synthesis method (3.9 eV).
Fig.3 Band structure of pristine La$_2$Ti$_3$O$_7$ calculated with DFT (a) and HSE06 method (b). The dash line annotates the Fermi level.

Fig.4 and Fig.S1 reveal the DOS and band structure of N-doped La$_2$Ti$_3$O$_7$. The zero energy point was set to the Fermi level of pristine La$_2$Ti$_3$O$_7$. The systems with defects were corrected by aligning the average electrostatic potential ($V_{av}$) of La, Ti and O atoms located far from the defects and the $V_{av}$ for the same elements in the pristine La$_2$Ti$_3$O$_7$. When N substituted for O to form the $N_5$ defect, the localized deep energy states appeared in the middle of the forbidden band, which came from the mixture of N 2p, O 2p, Ti 3d and La 5d orbitals. Furthermore, Fig.4(c) shows that the Ti d orbitals were which came from the mixture of N 2p, O 2p, Ti 3d and La 5d orbitals. The formation energy of the system containing point-defects, $E_{form}$, was the total energy of the system containing point-defects, $E_{tot}$ is the total energy of the system at interstitial site ($Ti_i$), giving rise to defect-impurity band thermally connected with the host VBM and eliminating the localized $N_S$-related states. The suggested model mechanism gives a reasonable explanation for the photocatalytic oxidation reactions as well as the red-shift of the light absorption edge observed in N-doped TiO$_2$. In this La$_2$Ti$_3$O$_7$ system, we also investigated the electronic structure when $N_5$ and $Ti_i$ were bound together to form a complex defect. One Ti atom is inserted into the largest interstitial site in the 44-atom supercell so as to bring minimum lattice distortion to the system, as shown in Fig.1(c). The point-defect formation energy was calculated using the formula:

$$E_{form} = E_2 - E_1 + \sum a_i n_i \mu_i$$ (1)

where $E_{form}$ is the point-defect formation energy, $E_2$ is the total energy of the system containing point-defects, $E_1$ is the total energy of the pristine system, $a_i = -1$ or 1 if an i atom is added or removed, $n_i$ is the number of the i atom, and $\mu_i$ is the chemical potential of the i atom calculated using the method as shown in the supporting information.

The formation energy of $N_5$ + $Ti_i$ is plotted in Fig.S2. It can be seen that under the O-poor and Ti-rich condition, the formation energy is negative, which indicates that the N dopant and the interstitial Ti atoms are prone to co-exist. The formation energy comparison in Fig.S3 also indicates that forming interstitial Ti atom is energetically favourable when one oxygen atom is substituted by nitrogen atom in the O-poor condition.

When $N_i$ and $Ti_i$ co-existed, the electronic structures calculated using HSE06 hybrid method were very similar to the model where N solely doped La$_2$Ti$_3$O$_7$, i.e., localized mid-gap states formed as
shown in Fig.5 and Fig.S4. According to the hybrid results, the two localized energy bands, composed of mainly Ti 3d and least O 2p states, covered a large range below the CBM, unlike the system with only the $N_i$ defect where one deep energy band lies in the middle of the band gap. Furthermore, the mixed N 2p and O 2p energy band (denoted by $L_2$) was located 0.4 eV above the VBM, rather than being close to the VBM as in the N mono-doped system. The hybridization among the N p and Ti d orbitals can be clearly observed using the partial electron densities in Figs. 5(c) and 5(d). The localized energy bands were occupied, thus the Fermi level was substantially upraised to just below the CBM. Again, the deep localized energy band 0.3 eV above the VBM (Fig.S4). The DOS and the band structure obtained with DFT also indicated the formation of localized energy band 0.3 eV above the VBM (Fig.S4).

Fig.5 DOS (a), band structure (b), the partial electron densities of the VBM (c) and of the localized energy level (L1) at point D (d) at a 0.01 eV/Å$^3$ isosurface level of La$_2$Ti$_2$O$_7$ with the $N_i$ and the Ti$^{3+}$ defects in a supercell calculated using HSE06 method. The dash line annotates the Fermi level.

Both DFT-calculations and experiments have showed that nitrogen doping leads to formation of oxygen vacancies in bulk TiO$_2$. The complex defects ($N_i + V_o$) alter the band gap, also cause the formation of a localized energy band mid-gap. The 3d states of Ti$^{3+}$ below the conduction band, which are associated with oxygen vacancies, have been found to act as the electron-hole recombination sites, leading to the reduction of photocatalytic activity. Herein we also found that the formation energy was substantially reduced after $V_o$ was introduced into the N-doped La$_2$Ti$_2$O$_7$ lattice (Fig. s3), which indicated that oxygen vacancies were easily formed during the introduction of N into the lattice. But the complex defects influence on the electronic structures was greatly different for La$_2$Ti$_2$O$_7$ and TiO$_2$. In order to achieve the electrical neutrality, the model was built to contain two $N_i$ and one $V_o$ (Fig.1 (d)). As shown in Fig.6 and Fig.S5, the localized energy band completely disappeared when two $N_i$ co-existed with one $V_o$. The mixed N 2p, O 2p and Ti 3d formed a continual energy band on the top of the valence band (obtained by HSE06 method) or thermally connect with VBM (obtained by DFT), which accounted for the parallel red shift of the whole optical absorption edge of the added band edge as seen experimentally with N doping in La$_2$Ti$_2$O$_7$, wherein the absorption can be described by a superimposed direct and indirect gap.
Fig.6 DOS (a), band structure (b) and partial electron densities of the VBM at a 0.01 eV/Å isosurface level (c) of La$_2$Ti$_3$O$_7$ with two $N_s$ and one $V_o$ defects in a supercell calculated using HSE06 method. The dash line annotates the Fermi level.

In TiO$_2$, the N dopant concentration has an effect on the electronic structure of N-doped TiO$_2$\cite{2}. If high concentration of N (e.g. 6.25 at\%) was employed in the calculation, the N 2p state was mixed with O 2p, leading to band gap narrowing rather than localized deep energy state formation\cite{2}. If low concentration of N (e.g. 1.56 at\%) was used in the calculation, a deep localized energy band formed in the forbidden band\cite{31,34,35}. In order to study the influence of the nitrogen concentration on the electronic structure, we also investigated the DOS and band structure of La$_2$Ti$_3$O$_7$ with 7.1 at\% of N concentration, corresponding to the system containing two $N_s$ and one $V_o$ in a supercell in Fig.1 (d). By comparing Fig.4 and Fig.7, it can be confirmed that solely doping N into La$_2$Ti$_3$O$_7$ led to the formation of a localized deep energy state in the forbidden gap, independent of the concentration change. For the two systems containing either two $N_s$ (Fig.7 and Fig.S6) or two $N_s$ plus one $V_o$ (Fig.6 and Fig.S5), the electronic structures were very similar, except that the localized deep energy band disappeared completely in the latter case. This has further confirmed that the localized energy state can be removed and the band gap can be narrowed simultaneously only when $N_s$ and $V_o$ co-exist in La$_2$Ti$_3$O$_7$.

In comparison with the systems containing $N_s$ and $N_s+V_o$, the Ti 4d orbits contributed more to the VMB in La$_2$Ti$_3$O$_7$ containing both $N_s$ and $V_o$, clearly demonstrated by the inserted DOS in Fig.6 (a). This indicated that orbits hybridization between non-metal and metal was enhanced in the case when $N_s$ and $V_o$ existed simultaneously, which can also be verified by the partial electron density of the VBM of La$_2$Ti$_3$O$_7$ containing different defects. In comparison with other configurations, strong orbits hybridization between N and Ti occurred in La$_2$Ti$_3$O$_7$ containing both $N_s$ and $V_o$, as shown in Fig.6(c). The extended nature of the valence band edge caused by the hybridized N 2p and Ti 3d states is beneficial to the migration of photo-induced holes, which increases the oxidation power of the photocatalysts\cite{11,41}. As a result, the N doped La$_2$Ti$_3$O$_7$ nanosheets perform well in photocatalytic decomposition of methyl orange\cite{13}. N doping is an effective method to realize the visible light photocatalytic activity. In short, if N doping in La$_2$Ti$_3$O$_7$ occurs in a reducing atmosphere, the presence of $V_o$ will reduce the band gap and eliminate the localized energy band, leading to enhancement in the photocatalytic activity in both the ultraviolet and the visible light regions.

![DOS and band structure of La$_2$Ti$_3$O$_7$](image)

Fig. 7 DOS (a) and band structure (b) of La$_2$Ti$_3$O$_7$ with two $N_s$ defects in a supercell calculated using HSE06 method. The dash line annotates the Fermi level.

### 4. Conclusions

The DFT and HSE06 hybrid methods were employed to investigate the influence of the N substitute doping co-existing with the oxygen vacancy and the interstitial Ti atom on the electronic structures. Solely doping N into La$_2$Ti$_3$O$_7$ caused the formation of the deep localized energy state, independent on the doping concentration. When interstitial Ti co-existed with $N_s$, the localized energy band was still present. However, when $N_s$ co-existed with $V_o$, the localized energy state was completely removed and the band gap can be substantially narrowed. Further, the added DOS altered the VBM, which facilitated the migration of photo-induced holes and the oxidation power of the photocatalyst, introduced the direct transition at lower energy to increase light absorption. As a result, the $N_s$ plus $V_o$ model in La$_2$Ti$_3$O$_7$ can accurately interpret the fact that N doping into La$_2$Ti$_3$O$_7$ can not only lead to strong visible light photocatalytic activity but also enhance the performance under UV irradiation. This work reveals that tuning the non-neutral
point defects with the oxygen vacancy is an effective strategy for alleviating the problem associated with doping to increase light absorption, which have implication in engineering band gap of semiconductor photocatalysts.

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Notes and references