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Bandgap engineering of Magnéli phase Ti_nO_{2n-1}: Electron-hole self-compensation

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An electron-hole self-compensation effect is revealed and confirmed in nitrogen doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) by using hybrid density functional theory calculations. We found that the self-compensation effect between the free electrons in Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) and the holes induced by p-type nitrogen doping could not only prevent the recombination of photo-generated electron-hole pairs, but also lead to an effective bandgap reduction. This novel electron-hole self-compensation effect may provide a new approach for bandgap engineering of Magnéli phase metal suboxides. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4928062]

I. INTRODUCTION

Developing new semiconducting materials for solar-driven photocatalysis has been a very active field in recent years.[1–4] The ideal material requires the appropriate bandgap around 2.0 eV for visible-light absorption and the intrinsic semiconducting character to prevent the recombination of photo-generated electron-hole pairs.[5–10] In addition, for photo-electrochemical (PEC) water splitting, the desirable materials should have correct band-edge positions that straddle the water redox potentials. Among these semiconducting materials, TiO_2 is one of the most promising photocatalysts. More recently, it is reported that the reduced TiO_2 nanocrystals, such as hydrogenated TiO_2 and colored TiO_{2-x}, exhibit extremely high photocatalytic activities for water splitting and dye degradation.[11–14] The enhanced photocatalytic performance of such reduced TiO_2 nanocrystals can be attributed to the generation of disordered nanophase and the bandgap narrowing after the reduction of TiO_2.[13,15] In general, the reduction of metal-oxides induces oxygen vacancies in their lattices, leading to new crystalline phases, which are known as Magnéli phases.[16] Magnéli phases have been observed in a homologous series of oxides such as TiO_2, WO_3, and VO_2.[17–19] The TiO_2 system is particularly rich in such non-stoichiometric Magnéli phase.

Magnéli phases can be regarded as oxygen-deficient TiO_2, where the oxygen vacancies can be organized in a shear-plane structure. The formation of these extended defects is exemplified by the operation $(121)\frac{1}{2}[0\bar{1}1]$ in the rutile structure, where the first three indices refer to a plane in the rutile structure and the last three for the displacement vector in the same structure. The structures contain rutile-like chains of edge-sharing TiO6 octahedra interrupted every nth octahedron at a shear plane {121}, where the octahedra share faces in addition to edges and corners.[20,21] Because Magnéli phase titanium sub-oxides Ti_nO_{2n-1} ($4 \le n \le 9$) is a highly disordered phase, it may posses higher photocatalytic performance than the ordered stoichiometric TiO_2 phase does. However, the reduction of TiO_2 can also result in the free electrons in the Magnéli phase Ti_nO_{2n-1}, which could serve as charge recombination centers and thus lead to the decrease of photocatalytic activity. So far, no satisfactory theory has been proposed to solve these challenges.

In this work, we report an electron-hole self-compensation effect in the nitrogen doped Magnéli phase titanium sub-oxides Ti_nO_{2n-1} ($4 \le n \le 9$). We find that the self-compensation effect between the free electrons in Magnéli phase Ti_nO_{2n-1} and the holes induced by nitrogen doping could remove the recombination centers of free electrons in Magnéli phase Ti_nO_{2n-1}, which could dramatically lengthen the lifetime of photoexcited electron-hole pairs and therefore enhance the photocatalytic efficiency. More importantly, the nitrogen impurity states are mixed with the valence band of Ti_nO_{2n-1}, which lead to a significant bandgap reduction. The nitrogen doped Magnéli phase titanium sub-oxide of $Ti_9O_{15}N_2$, with a bandgap of 2.089 eV, could be a promising candidate for visible-light photocatalytic applications (see Fig. 1). Our results suggest that the electron-hole self-compensation effect could be an effective approach for bandgap engineering of Magnéli phase metal suboxides.

II. COMPUTATIONAL DETAILS

The density functional theory (DFT) calculations were performed using the frozen-core projector-augmented-wave (PAW)[22,23] method within the Perdew-Burke-Ernzerhof (PBE)[24] parameterization of generalized gradient approximation (GGA) as implemented in the Vienna *ab initio* simulation package (VASP) code.[25,26] The wave function is expanded in plane waves with a cutoff energy of 500 eV. The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme[27] with a grid mesh of 0.04/Å k-point separation. Extensive tests were carried out to ensure the convergences

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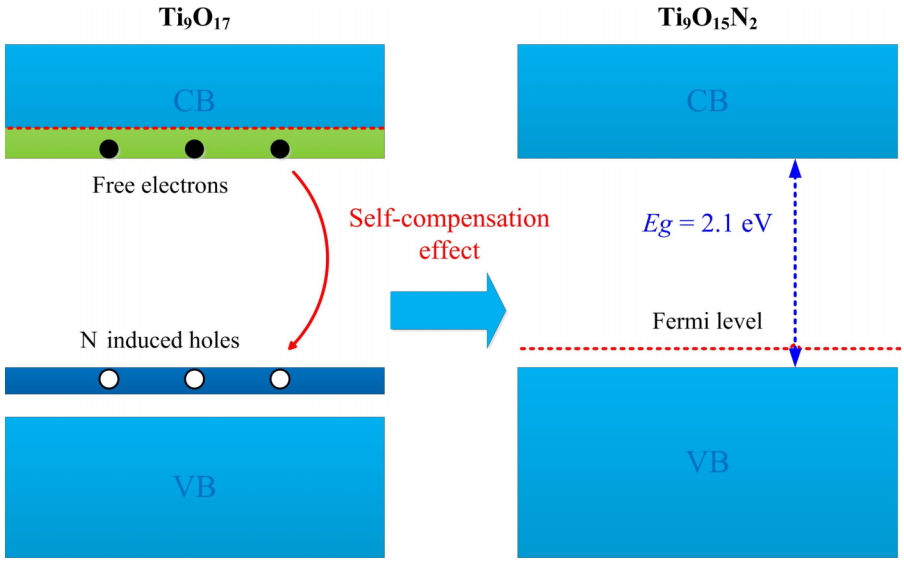

FIG. 1. Schematic diagram of the self-compensation mechanism in nitrogen mono-doped Magnéli phase Ti_9O_{17} ($Ti_9O_{17}N_2$).

with respect to the cutoff energy and k-point meshes. The geometry optimizations were performed until the forces on each ion were reduced below 0.01 eV/Å, and the resulting structures were then used to calculate the electronic structures.

The calculation models of Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$) were constructed by using the lattice parameters and the Wykoff positions in previous studies.[20,21] The primitive cell of Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$) was used for theoretical calculations except for Ti_5O_9 (using a $2 \times 1 \times 1$ supercell). The optimized lattice parameters of Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$) are listed in the Table S1 [see supplementary material],[28] which are in good agreement with previous studies.[20]

To obtain the correct electronic structures, we used the Heyd-Scuseria-Ernzerhof (HSE06)[29,30] hybrid density functional for these calculations. In HSE06 hybrid functional, the exchange contribution is divided into short- and long-ranged parts and the short-ranged part of PBE exchange is weighted by 25% Hartree-Fock[31] exchange. The expression for the exchange-correlation in HSE06 is given by

$$E_{XC}^{HSE} = \frac{1}{4}E_X^{HF,SR}(\mu) + \frac{3}{4}E_X^{PBE,SR}(\mu) + E_X^{PBE,LR}(\mu) + E_C^{PBE}, \quad (1)$$

where SR and LR refer to the short- and long-ranged parts of the exchange interaction, $\mu = 0.2$ Å^{-1} is the parameter for the range-separation of Coulomb kernel.

III. RESULTS AND DISCUSSION

After TiO_2 loses oxygen, it can form new crystalline of non-stoichiometric TiO_2 structures known as Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$).[16] To make use of these materials as photocatalysts, we first need to known the electronic structures of Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$). The simulation models of Ti_nO_{2n-1} were constructed based on the corresponding experimental data and the electronic structures of anatase TiO_2 were also investigated for comparison. As can be seen from the total density of states (TDOSs) plot for anatase TiO_2 in Fig. 2, the Fermi level of anatase TiO_2 locates just above its valence band maximum (VBM), showing a typical semiconductor character. The HSE06 calculated bandgap of anatase TiO_2 is 3.15 eV, which is in excellent agreement with the experimental value of 3.2 eV. Generally, the energies of the VBM and conduction band minimum (CBM) measured on an absolute energy scale determine the difficulty of doping. The lower the VBM energy, the more difficult it is to obtain p-type doping. Similarly, the higher the CBM energy, the higher probability that the material is difficult to be n-type doped. For example, anatase TiO_2 has a low VBM energy. Therefore, it will be difficult to dope p-type TiO_2.[5,32]

For Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$), the Fermi level moves into its conduction band (CB), indicating that there are free electrons filled in the bottom of CB (see in Fig. 2). It is found that the Magnéli phase Ti_4O_7 has a metallic character, which is consistent with previous DFT calculations.[33] As a result, the Magnéli phase Ti_nO_{2n-1} has excellent electrical conductivity.[34] The energy shifts of VB and CB for Magnéli phase Ti_nO_{2n-1} compared with pure anatase TiO_2 were illustrated in Fig. 2, in which the VB and CB energy levels of pure anatase TiO_2 are considered as the reference. It is found that the band edge positions of Magnéli phase Ti_nO_{2n-1} match well with the redox potentials of water. The energy positions of the VBM and CBM for Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$) with respect to the water redox potentials are summarized in Table S2 in the supplementary material.[28] It is found that the CBM locates about 1.0 eV above the hydrogen production potential, indicating that Magnéli phase Ti_nO_{2n-1} have stronger reduction power than that of pure anatase TiO_2. Because the VBM of Magnéli phase Ti_nO_{2n-1} locates below the water oxidation potential, Magnéli phase Ti_nO_{2n-1} keeps the oxidation power of pure anatase TiO_2. In addition, the bandgap energy of Magnéli phase Ti_nO_{2n-1} is about 0.5 eV smaller than that of anatase TiO_2, indicating that Magnéli phase Ti_nO_{2n-1} has potential applications in photocatalysis. However, the free electrons in Magnéli phase Ti_nO_{2n-1} can act as recombination sites and thus reduce the photoexcited electron-hole pairs.[35] To overcome this problem, we proposed to passivate the free electrons in Magnéli phase Ti_nO_{2n-1} through p-type nitrogen doping. Such electron-hole self-compensation effect in nitrogen mono-doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) is similar to

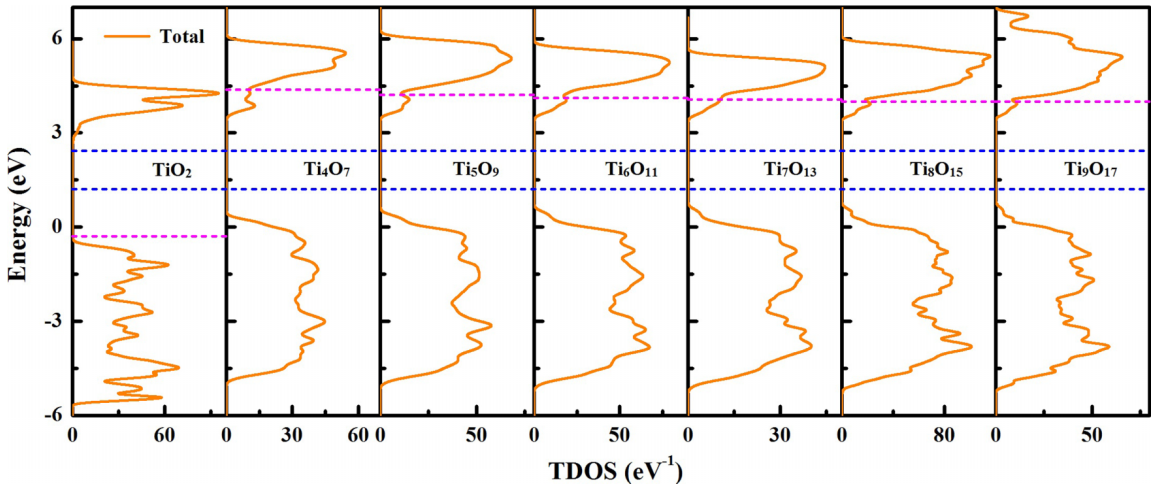

FIG. 2. The HSE06 calculated TDOS of pure anatase TiO_2 and Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$). The highest occupied state is chosen as the Fermi level and is displayed with a red dashed line. The two horizontal blue dashed lines indicate the energy positions of the hydrogen production level (up) and the water oxidation level (down), respectively.

the compensation effect in donor-acceptor codoped TiO_2.[5] On the one hand, since the Magnéli phase Ti_nO_{2n-1} has a higher VBM energy than that of anatase TiO_2, the p-type nitrogen doping would be easier for Magnéli phase Ti_nO_{2n-1}. On the other hand, because the neutral 2p-orbital energy of nitrogen is higher than that of oxygen, the p-type nitrogen doping would further narrow the bandgap of Magnéli phase Ti_nO_{2n-1}.

By scanning the TDOSs of the Magnéli phase Ti_nO_{2n-1} ($4 \le n \le 9$), we choose Ti_7O_{13}, Ti_8O_{15}, and Ti_9O_{17} as the candidates for nitrogen doping because these samples have the narrowest bandgap (about 2.6 eV) among these systems. The N-doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) models were constructed by randomly replacing the O atoms in the Magnéli phase lattice with N atoms. Fig. 3(a) shows the TDOSs and partial density of states (PDOSs) of N doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9), labeled as $Ti_7O_{12}N$, $Ti_8O_{14}N$, and $Ti_9O_{16}N$, respectively. As expected, the incorporation of N on oxygen lattice sites induces the acceptor states (N-2p) above the VBM of Ti_nO_{2n-1} (n = 7, 8, and 9). The position of the acceptor level with respect to VBM, which is dominated by O-2p character, is largely determined by the anions' 2p orbital energies. Because the neutral 2p orbital energy of nitrogen is 2.0 eV higher than O-2p orbital energy, the N acceptor level is relatively shallow. In fact, as nitrogen has one less valence electron than oxygen, the substitution of N on O site in anatase TiO_2 acts as a single acceptor and induces partially occupied N-2p impurity states.[36,37] However, it is found that the N-2p states are fully occupied in $Ti_7O_{12}N$, $Ti_8O_{14}N$, and $Ti_9O_{16}N$ [see in Fig. 3(a)] indicating that these accepter states have been passivated by a part of the free electrons in Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9). Because the Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) have free electrons, the donor doping for them is not needed anymore. The Fermi level of $Ti_7O_{12}N$, $Ti_8O_{14}N$, and $Ti_9O_{16}N$ locates a few tenths of eV above their CBMs, indicating that there are free electrons still remaining in these systems.

In fact, the Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) should have two electrons in their CB states arising from the missing oxygen. Therefore, two holes (induced by N acceptor) are needed to compensate the free electrons. As a result, two N dopants are needed to model compensation adequately for Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9). Fig. 3(b) shows the TDOSs and PDOSs of $Ti_7O_{11}N_2$, $Ti_8O_{13}N_2$, and $Ti_9O_{15}N_2$, with the nitrogen doping molar ratio of 15.4%, 13.3%, and 11.8%, respectively. It is found that the Fermi level of these three systems locates just above their VBMs, indicating that the $Ti_7O_{11}N_2$, $Ti_8O_{13}N_2$, and $Ti_9O_{15}N_2$ systems still keep semiconductor character. In these cases, the free electrons in Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) were passivated by the same amount of holes induced by the nitrogen doping. It is also found that the N-2p states of $Ti_7O_{11}N_2$, $Ti_8O_{13}N_2$, and $Ti_9O_{15}N_2$ are fully hybridized with the O-2p and Ti-3d states in VBMs (see in Fig. 3), indicating that the photoexcited holes can transfer in the lattice and are not localized around N-2p states. As expected, the hybridization of N-2p states leads to a significant bandgap reduction: the HSE06 calculated bandgaps of $Ti_7O_{11}N_2$, $Ti_8O_{13}N_2$, and $Ti_9O_{15}N_2$, are 2.150, 2.138, and 2.089 eV, respectively. Furthermore, it is noticed that the nitrogen mono-doping in Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) is quite different from the nitrogen mono-doped TiO_2, in which the nitrogen impurities induce partially occupied N-2p states above the VBM of TiO_2 and thus act as recombination centers.[35,37] For $Ti_7O_{11}N_2$, $Ti_8O_{13}N_2$, and $Ti_9O_{15}N_2$, since the recombination of electron-hole pairs can be prevented by the self-compensation effect, their photocatalytic performances can be greatly improved. We suggest that the nitrogen doped Magnéli phase Ti_9O_{17} ($Ti_9O_{17}N_2$) could be a promising candidate for visible-light photocatalysis due to the narrowest bandgap and lowest nitrogen doping ratio among $Ti_7O_{11}N_2$, $Ti_8O_{13}N_2$, and $Ti_9O_{15}N_2$.

The schematic explanation of the self-compensation effect in nitrogen doped Magnéli phase Ti_9O_{17} ($Ti_9O_{15}N_2$) is shown in Fig. 1. In the beginning, the Magnéli phase Ti_9O_{17} provides free electrons in the bottom of its CB. Then, these electrons are compensated by the same amount of holes induced by nitrogen doping. After the self-compensation between the electrons and the holes, the nitrogen mono-doped Magnéli phase Ti_9O_{17} ($Ti_9O_{15}N_2$) become a semiconductor material and thus

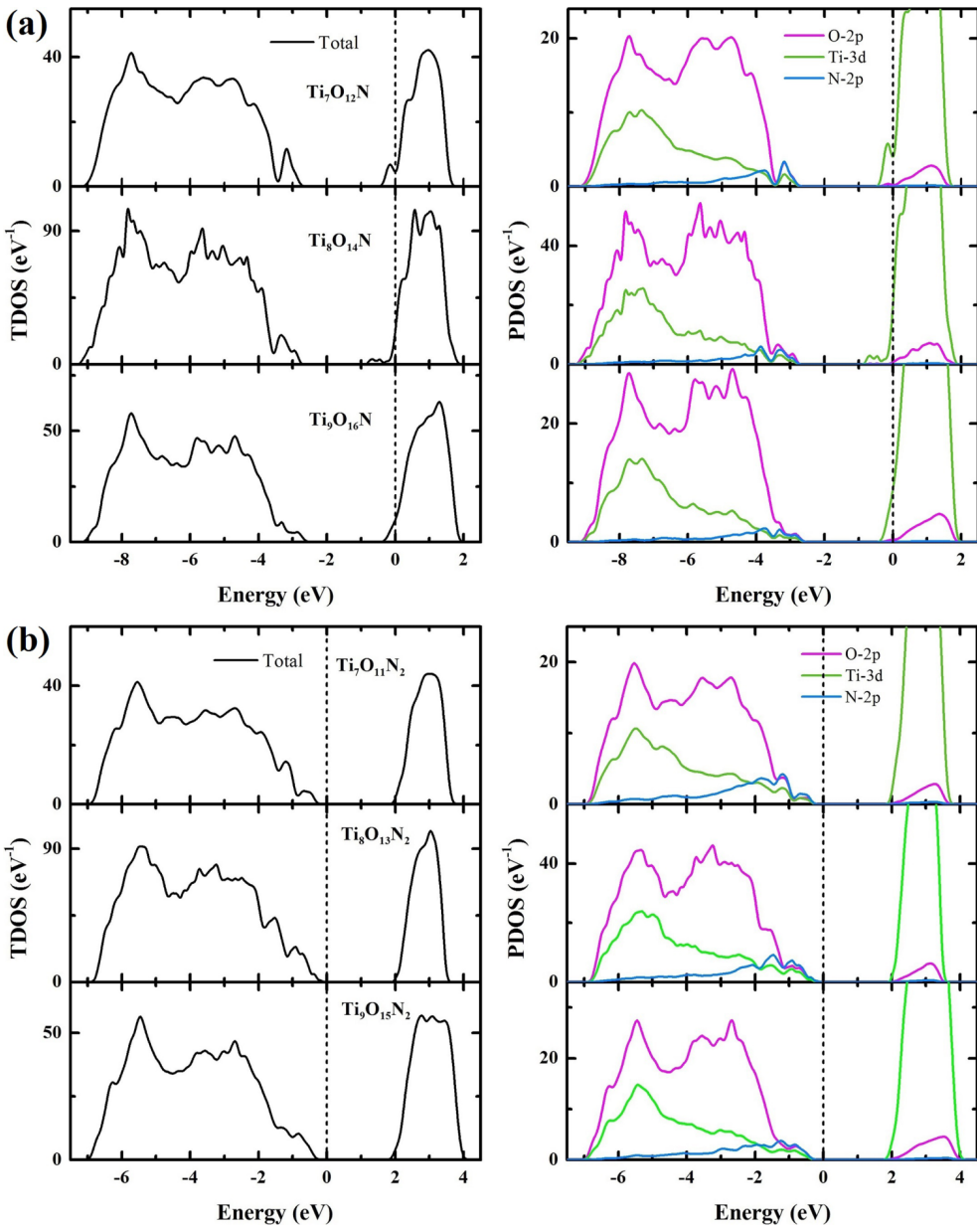

FIG. 3. (a) The HSE06 calculated TDOSs (left side) and the corresponding PDOSs of $Ti_7O_{12}N$, $Ti_8O_{14}N$, and $Ti_9O_{16}N$. (b) The HSE06 calculated TDOSs (left side) and the corresponding PDOSs of $Ti_7O_{11}N_2$, $Ti_8O_{13}N_2$, and $Ti_9O_{15}N_2$. The Fermi level of these systems is displayed with a black dashed line.

could prevent the recombination of photo-generated electron-hole pairs. Furthermore, because N generates higher 2p orbital states than that of O, the self-compensation effect would lead to a significant bandgap reduction.

Because the DFT calculation results are strongly associated with the simulation models, we choose Magnéli phase $Ti_9O_{15}N_2$ system as an example to test how the relative positions of N dopants affect the calculation results. Here, we have constructed three $Ti_9O_{15}N_2$ models with different relative positions of N dopants [labeled as config-1, config-2, and config-3, see Fig. S1 in the supplementary material].[28] The calculated DOSs of these three $Ti_9O_{15}N_2$ models (see Fig. S2 in the supplementary material)[28] indicate that the evenly dispersed N dopants in $Ti_9O_{15}N_2$ lead to the delocalized N-2p impurity states in the valence band, whereas the aggregation of N dopants results in the localized N-2p impurity states in the top of valence band. Therefore, Magnéli phase $Ti_9O_{15}N_2$ with the evenly dispersed N dopants is favorable for charge transfer due to the delocalized N-2p impurity states in the system.

To confirm the improved visible-light absorption of the nitrogen doped Magnéli phase Ti_9O_{17} ($Ti_9O_{15}N_2$) against that of pure anatase TiO_2, we calculated the corresponding optical absorption spectra and the results were displayed in Fig. 4. It is found that pure anatase TiO_2 can only respond to the ultraviolet light (photon energy large than 3.0 eV), indicating that there is no absorption activity in the visible-light region. In contrast, the optical absorption edge of nitrogen doped Magnéli phase Ti_9O_{17} ($Ti_9O_{15}N_2$) shows a significant redshift in comparison with that of anatase TiO_2, due to the bandgap reduction in Magnéli phase $Ti_9O_{15}N_2$ by the self-compensation effect. It is expected that the nitrogen doped Magnéli phase Ti_9O_{17} ($Ti_9O_{15}N_2$) can respond to the visible light, with a wavelength less than 600 nm.

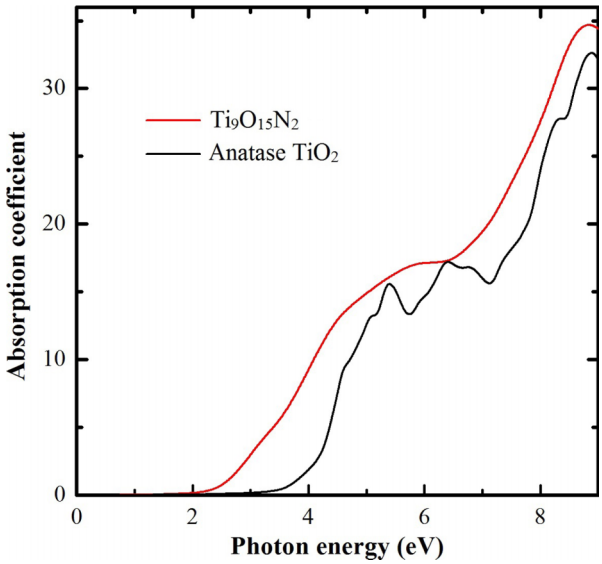

FIG. 4. The HSE06 calculated optical absorption spectra of anatase TiO_2 and nitrogen mono-doped Magnéli phase Ti_9O_{17} ($Ti_9O_{15}N_2$).

In order to evaluate the relative difficulty of the incorporation of nitrogen dopants into the Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9), the formation energies of N doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) were calculated by

$$E_{form} = E(doped) - E(pure) - \frac{1}{2}\mu(N_2) + \frac{1}{2}\mu(O_2), \quad (2)$$

where $E(doped)$ and $E(pure)$ are the total energies of Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) with and without dopants, respectively. $\mu(N_2)$ and $\mu(O_2)$ represent the calculated ground state energies of free molecule N_2 and O_2, respectively. The formation energy of N doped anatase TiO_2 was also calculated for comparison. The larger the formation energy, the more difficult nitrogen doping is. The calculated formation energy of N doped anatase TiO_2 is 5.237 eV, which is in good agreement with the previous theoretical value of 5.69 eV.[38] The large formation energy of N doped anatase TiO_2 attributes to the low VBM energy of anatase TiO_2, which indicates that the harsh experimental condition is needed in order to synthesize it (difficulty of p-type doping). The formation energies of N doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) are listed in Table I. It is found that the formation energies of N doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) are about 3.0 eV for both one and two N atom doping cases, which is 2.0 eV smaller than that of N doped anatase TiO_2. These small formation energies are mainly due to the high VBM energies of Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9), as well as the self-compensation effect between the free electrons in Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) and the holes induced by nitrogen doping. Our calculation results indicate that the p-type nitrogen doping is relatively easy for Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9).

TABLE I. The formation energies of N doped Magnéli phase Ti_nO_{2n-1} ($7 \le n \le 9$). Both one and two N atoms doping in the Magnéli phase cells were considered.

	Formation energy		
Doping case	Ti_7O_{13}	Ti_8O_{15}	Ti_9O_{17}
One N atom doping	2.812	3.098	2.837
Two N atoms doping	2.962	3.137	3.014

IV. CONCLUSIONS

In summary, we have proposed an electron-hole self-compensation effect, which was confirmed in nitrogen doped Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) by using first-principles calculations with HSE06 hybrid functional. The electron-hole self-compensation effect can effectively prevent the photoexcited electron-hole pairs from recombination and also further narrow the bandgap of Magnéli phase Ti_nO_{2n-1} (n = 7, 8, and 9) significantly. The recombination prevention and the bandgap narrowing have great advantages for the improvement of photocatalytic performance. Our calculation results indicate that the nitrogen doped Magnéli phase Ti_nO_{2n-1} of $Ti_9O_{15}N_2$ could be a promising candidate for visible-light photocatalysis due to the ideal bandgap (2.089 eV). We also suggest that the electron-hole self-compensation effect could be a new approach for the development of Magnéli phase metal sub-oxide materials for solar-driven photocatalysis. It is expected that this work can motivate experimental scientists to synthesize the designed materials.

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