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Bandgap engineering of Magnéli phase Ti_{n}O_{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_{n}O_{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_{n}O_{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 photoelectrochemical (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 (112) \[\frac{1}{2}[01\bar{1}]\] 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 TiO_{6} octahedra interrupted every nth octahedron at a shear plane \[\{1\bar{1}\}\], where the octahedra share faces in addition to edges and corners.20,21 Because Magnéli phase titanium sub-

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 scheme27 with a grid mesh of 0.04\AA\ \textit{k}-point separation. Extensive tests were carried out to ensure the convergences...
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 $\text{Ti}_{n}\text{O}_{2n-1}$ ($4 \leq n \leq 9$) were constructed by using the lattice parameters and the Wyckoff positions in previous studies.\textsuperscript{20,21} The primitive cell of Magnéli phase $\text{Ti}_{n}\text{O}_{2n-1}$ ($4 \leq n \leq 9$) was used for theoretical calculations except for $\text{Ti}_{9}\text{O}_{8}$ (using a $2 \times 1 \times 1$ supercell). The optimized lattice parameters of Magnéli phase $\text{Ti}_{n}\text{O}_{2n-1}$ ($4 \leq n \leq 9$) are listed in the Table S1 [see supplementary material],\textsuperscript{28} which are in good agreement with previous studies.\textsuperscript{20}

To obtain the correct electronic structures, we used the Heyd-Scuseria-Ernzerhof (HSE06)\textsuperscript{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.\textsuperscript{31} The energy shifts of VB and CB for Magnéli phase $\text{Ti}_{n}\text{O}_{2n-1}$ ($4 \leq n \leq 9$) were illus-

drated in Fig. S2 in the supplementary material.\textsuperscript{28} It is found that the CBM locates just above its valence band maximum (VBM), showing a typical semiconductor character.

The HSE06 calculated bandgap of anatase $\text{TiO}_{2}$ 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 $\text{TiO}_{2}$ has a low VBM energy. Therefore, it will be difficult to dope p-type $\text{TiO}_{2}$.

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

III. RESULTS AND DISCUSSION

After $\text{TiO}_{2}$ loses oxygen, it can form new crystalline of non-stoichiometric $\text{TiO}_{2}$ structures known as Magnéli phase $\text{Ti}_{n}\text{O}_{2n-1}$ ($4 \leq n \leq 9$).\textsuperscript{16} To make use of these materials as photocatalysts, we first need to known the electronic structures of Magnéli phase $\text{Ti}_{n}\text{O}_{2n-1}$ ($4 \leq n \leq 9$). The simulation models of $\text{Ti}_{n}\text{O}_{2n-1}$ were constructed based on the corresponding experimental data and the electronic structures of anatase $\text{TiO}_{2}$ were also investigated for comparison. As can be seen from the total density of states (TDOSs) plot for anatase $\text{TiO}_{2}$ in Fig. 2, the Fermi level of anatase $\text{TiO}_{2}$ locates just above its valence band maximum (VBM), showing a typical semiconductor character.

![Diagram](image-url) FIG. 1. Schematic diagram of the self-compensation mechanism in nitrogen mono-doped Magnéli phase $\text{Ti}_{n}\text{O}_{17}$ ($\text{Ti}_{n}\text{O}_{17}\text{N}_{2}$).
the compensation effect in donor-acceptor codoped TiO$_2$. On the one hand, since the Magnéli phase Ti$_{n}$O$_{2n-1}$ has a higher VBM energy than that of anatase TiO$_2$, the p-type nitrogen doping would be easier for Magnéli phase Ti$_{n}$O$_{2n-1}$. 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$_{n}$O$_{2n-1}$.

By scanning the TDOSs of the Magnéli phase Ti$_{n}$O$_{2n-1}$ (4 ≤ $n$ ≤ 9), we choose Ti$_7$O$_{11}$, Ti$_8$O$_{13}$, and Ti$_9$O$_{15}$ 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$_n$O$_{2n-1}$ (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 phases Ti$_n$O$_{2n-1}$ (n = 7, 8, and 9), labeled as Ti$_7$O$_{11}$N, Ti$_8$O$_{13}$N, and Ti$_9$O$_{15}$N, respectively. As expected, the incorporation of N on oxygen lattice sites induces the acceptor states (N-2p) above the VBM of Ti$_n$O$_{2n-1}$ (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 states above the VBM of TiO$_2$, respectively. However, it is found that the N-2p states are fully occupied in Ti$_7$O$_{11}$N, Ti$_8$O$_{13}$N, and Ti$_9$O$_{15}$N [see in Fig. 3(a)] indicating that these acceptor states have been passivated by a part of the free electrons in Magnéli phase Ti$_n$O$_{2n-1}$ (n = 7, 8, and 9). Because the Magnéli phase Ti$_n$O$_{2n-1}$ (n = 7, 8, and 9) have free electrons, the donor doping for them is not needed anymore. The Fermi level of Ti$_7$O$_{11}$N, Ti$_8$O$_{13}$N, and Ti$_9$O$_{15}$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$_n$O$_{2n-1}$ (n = 7, 8, and 9) should have two holes 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$_n$O$_{2n-1}$ (n = 7, 8, and 9). Fig. 3(b) shows the TDOSs and PDOSs of Ti$_7$O$_{11}$N$_2$, Ti$_8$O$_{13}$N$_2$, and Ti$_9$O$_{15}$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 VBM, indicating that the Ti$_7$O$_{11}$N$_2$, Ti$_8$O$_{13}$N$_2$, and Ti$_9$O$_{15}$N$_2$ systems still keep semiconductor character. In these cases, the free electrons in Magnéli phase Ti$_n$O$_{2n-1}$ (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$_7$O$_{11}$N$_2$, Ti$_8$O$_{13}$N$_2$, and Ti$_9$O$_{15}$N$_2$ are fully hybridized with the O-2p and Ti-3d states in VBM (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$_7$O$_{11}$N$_2$, Ti$_8$O$_{13}$N$_2$, and Ti$_9$O$_{15}$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$_n$O$_{2n-1}$ (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. For Ti$_7$O$_{11}$N$_2$, Ti$_8$O$_{13}$N$_2$, and Ti$_9$O$_{15}$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$_8$O$_{17}$ (Ti$_8$O$_{17}$N$_2$) could be a promising candidate for visible-light photocatalysis due to the narrowest bandgap and lowest nitrogen doping ratio among Ti$_{11}$O$_{17}$N$_2$, Ti$_8$O$_{13}$N$_2$, and Ti$_9$O$_{15}$N$_2$.

The schematic explanation of the self-compensation effect in nitrogen doped Magnéli phase Ti$_8$O$_{17}$ (Ti$_8$O$_{17}$N$_2$) is shown in Fig. 1. In the beginning, the Magnéli phase Ti$_8$O$_{17}$ 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$_9$O$_{17}$ (Ti$_9$O$_{17}$N$_2$) become a semiconductor material and thus...
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$_9$O$_{15}$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$_9$O$_{15}$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]. The calculated DOSs of these three Ti$_9$O$_{15}$N$_2$ models (see Fig. S2 in the supplementary material) indicate that the evenly dispersed N dopants in Ti$_9$O$_{15}$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$_9$O$_{15}$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$_9$O$_{17}$ (Ti$_9$O$_{15}$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$_9$O$_{17}$ (Ti$_9$O$_{15}$N$_2$) shows a significant redshift in comparison with that of anatase TiO$_2$, due to the bandgap reduction in Magnéli phase Ti$_9$O$_{15}$N$_2$ by the self-compensation effect. It is expected that the nitrogen doped Magnéli phase Ti$_9$O$_{17}$ (Ti$_9$O$_{15}$N$_2$) can respond to the visible light, with a wavelength less than 600 nm.
The HSE06 calculated optical absorption spectra of anatase TiO$_2$ and nitrogen mono-doped Magnéli phase Ti$_6$O$_{2n-1}$(Ti$_6$O$_{17}$N$_2$).

In order to evaluate the relative difficulty of the incorporation of nitrogen dopants into the Magnéli phase Ti$_6$O$_{2n-1}$(n = 7, 8, and 9), the formation energies of N doped Magnéli phase Ti$_6$O$_{2n-1}$(n = 7, 8, and 9) were calculated by

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

where $E(\text{doped})$ and $E(\text{pure})$ are the total energies of Magnéli phase Ti$_6$O$_{2n-1}$(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$_6$O$_{2n-1}$(n = 7, 8, and 9) are listed in Table I. It is found that the formation energies of N doped Magnéli phase Ti$_6$O$_{2n-1}$(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$_6$O$_{2n-1}$(n = 7, 8, and 9), as well as the self-compensation effect between the free electrons in Magnéli phase Ti$_6$O$_{2n-1}$(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$_6$O$_{2n-1}$(n = 7, 8, and 9).

### IV. CONCLUSIONS

In summary, we have proposed an electron-hole self-compensation effect, which was confirmed in nitrogen doped Magnéli phase Ti$_6$O$_{2n-1}$(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$_6$O$_{2n-1}$(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$_6$O$_{2n-1}$ of Ti$_6$O$_{17}$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.

### ACKNOWLEDGMENTS

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![Absorption coefficient vs. photon energy](image)

**FIG. 4.** The HSE06 calculated optical absorption spectra of anatase TiO$_2$ and nitrogen mono-doped Magnéli phase Ti$_6$O$_{17}$ (Ti$_6$O$_{17}$N$_2$).

### TABLE I.

The formation energies of N doped Magnéli phase Ti$_6$O$_{2n-1}$(7 ≤ n ≤ 9). Both one and two N atoms doping in the Magnéli phase cells were considered.

<table>
<thead>
<tr>
<th>Doping case</th>
<th>Ti$<em>6$O$</em>{13}$</th>
<th>Ti$<em>6$O$</em>{15}$</th>
<th>Ti$<em>6$O$</em>{17}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>One N atom doping</td>
<td>2.812</td>
<td>3.098</td>
<td>2.837</td>
</tr>
<tr>
<td>Two N atoms doping</td>
<td>2.962</td>
<td>3.137</td>
<td>3.014</td>
</tr>
</tbody>
</table>

See supplementary material at http://dx.doi.org/10.1063/1.4928062 for the optimized lattice parameters of Magnéli phase $\text{Ti}_{n}\text{O}_{2n-1}$ and the DOSs of $\text{Ti}_{9}\text{O}_{15}\text{N}_{2}$ with different N doping configurations.