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Effects of oxygen impurity and nitrogen vacancy on surface properties of the Ta₃N₅ photocatalyst: a DFT study

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Abstract: Surface defects and impurities play important roles in the photocatalytic performance of semiconductors. In this study, the DFT calculations are performed to investigate effects of oxygen impurity and nitrogen vacancy on surface stabilities and electronic structures of Ta₃N₅ (100), (010) and (001) low-index surfaces. The results show that, for each surface, the oxygen impurity and nitrogen vacancy are beneficial and harmful, respectively, to surface stabilities of Ta₃N₅. The oxygen impurity and nitrogen vacancy mainly have two effects on the surface electronic structures of Ta₃N₅. One is saturating surface states on the clean surface; the other is inducing the downshift of conduction band minimum. In addition, the Ta₃N₅ (100) surface with oxygen impurity is expected to have the strongest reduction ability in practice, providing useful guidance for further investigations of Ta₃N₅ in the photocatalytic hydrogen evolution.
1. Introduction

Semiconductor-based photocatalytic or photoelectrochemical (PEC) water splitting is a promising strategy for solving energy shortage and environmental crisis, because it supplies an environmentally approach to split water into H₂ and O₂ under irradiation of solar light. Since the pioneer work by Fujishima and Honda, metal oxides such as BiVO₄, Fe₂O₃ and WO₃ have been extensively studied. However, due to the large band gaps or insufficient redox potentials, the photocatalytic activities of most metal oxides are not high. Recently, the tantalum nitride (Ta₃N₅) emerges as one promising candidate for photocatalytic or PEC water splitting. Due to the smaller band gap (about 2.1 eV), Ta₃N₅ is able to absorb more visible portion of the solar light. Moreover, the valence band maximum (VBM) and conduction band minimum (CBM) of Ta₃N₅ straddle the water oxidization (H₂O/O₂) and reduction (H⁺/H₂) potentials, suggesting that Ta₃N₅ theoretically has sufficient redox potentials to split water into H₂ and O₂.

Although Ta₃N₅ is theoretically an ideal photocatalyst, its practical photocatalytic and PEC performances are unsatisfactory. In recent years, great efforts such as loading of cocatalysts, morphology control and elements doping have been made to improve the photocatalytic and PEC activities of Ta₃N₅. Unfortunately, the current solar-to-hydrogen (STH) efficiency of Ta₃N₅ is merely 1.5%, which is much smaller than its maximum theoretical STH efficiency of 15.9% (under AM 1.5 G irradiation).

One proper cause of the lower practical photocatalytic activities of Ta₃N₅ comes from the inner defects or impurities. In Ta₃N₅, the nitrogen vacancy (VN) is the major intrinsic defect because anion vacancies such as nitrogen vacancy and oxygen vacancy
are usually the most common defects in metal nitrides and oxides, respectively. Besides the VN, the practical Ta3N5 naturally consists of abundant oxygen impurities which exist in the form of substitution for nitrogen (ON).23, 24 One proper source of the ON impurities is the residual O of Ta2O5 precursor after the nitridation treatment. Furthermore, the ON impurities are very difficult to be totally eliminated under different growth conditions.24 Our theoretical calculations reveal that the ON impurities help maintain the mechanical stability and strengthen the atomic cohesion within Ta3N5,25 validating that the natural existence of ON impurity is theoretically favorable in Ta3N5.

Generally, defects and impurities affect photocatalytic performance of semiconductors by regulating some important properties such as band gaps, band edge positions and surface properties. To our knowledge, effects of ON and VN on band gap and band edge positions of Ta3N5 have been extensively studied from experiments23, 24 and theoretical calculations,26-28 while that on surface properties of Ta3N5 are still less known. Based on the density functional theory (DFT) calculations, the surface energies and electronic structures of Ta3N5 (100) surface with ON and VN have been studied by our previous work.29 However, besides the (100) surface, other typical low-index surfaces such as the (010) and (001) surfaces are also important for Ta3N5, thus the effects of ON and VN on these low-index surfaces should be studied either. Although Watanabe et al.30 compared the (100), (010) and (001) surfaces of Ta3N5 by DFT calculations, effects of ON and VN on (010) and (001) surfaces were still not investigated in their work.

The motivation of this study is to make an in-depth understanding of surface
properties of Ta$_3$N$_5$ with O$_N$ and V$_N$. Experimental study of semiconductor surfaces is
sometimes a challenging task, while theoretical investigations, for example the DFT
calculations, are easily able to provide microscopic descriptions of surface properties.
To our knowledge, the most stable surface of Ta$_3$N$_5$ has not been experimentally
investigated. Considering that the Ta$_3$N$_5$ semiconductor is orthorhombic lattice, we
choose the typical (100), (010) and (001) low-index surfaces to perform surface
property investigations for Ta$_3$N$_5$. Based on the DFT calculations, effects of O$_N$ and V$_N$
on surface stabilities and electronic structures of Ta$_3$N$_5$ (100), (010) and (001) surfaces
will be investigated in this study. Our calculations will not only elucidate experimental
observations associated with Ta$_3$N$_5$, but also provide useful guidance for improving
photocatalytic activities of Ta$_3$N$_5$.

2. Computational details

2.1 Computational method

The DFT calculations in this study are performed by the VASP$^{31, 32}$ with the
projected-augmented-wave (PAW$^{33}$) method. All the DFT calculations are performed in
the unrestricted formalism. For the exchange-correlation functional, the generalized
gradient approximation (GGA$^{34}$) in the scheme of Perdew-Bueke-Ernzerhof (PBE$^{35}$) is
used. For N, O and Ta, the 2s$^2$2p$^3$, 2s$^2$2p$^4$ and 5p$^6$5d$^4$6s$^1$ orbital, respectively, are treated
as valence states. The cutoff energy for basis functional is 500 eV. Geometry
relaxations are performed until the residual forces on each ion converged to be smaller
than 0.02 eV Å$^{-1}$. 
It is worthy of mentioning that, due to underestimation of band gap, the PBE functional is sometimes not accurate enough to calculate electronic structures of semiconductors. Using the hybrid functional, for example the Heyd-Scuseria-Ernzerhof (HSE\textsuperscript{36}) functional, is able to get more accurate results, but the computational cost of HSE is much more than that of PBE. In our previous work, the PBE and HSE functional were both adopted to calculate electronic structures of the bulk Ta\textsubscript{3}N\textsubscript{5} with O\textsubscript{N} and V\textsubscript{N}\textsuperscript{25}. The results showed that the in-gap defect states and band edge shift calculated by PBE were in good agreement with that by HSE, suggesting that the PBE functional was sufficient to make reasonable qualitative analysis for Ta\textsubscript{3}N\textsubscript{5}.

2.2 Surface energy calculation method

Surface energies of Ta\textsubscript{3}N\textsubscript{5} surfaces with and without defects are calculated using the following equation\textsuperscript{37}:

\[
E_{\text{surf}} = [E_{\text{slab}} - \sum_i n_i (\Delta \mu_i + E_i)]/(2A) \tag{1}
\]

where \(E_{\text{slab}}\) is the total energy of the slab model, \(n_i\) and \(\Delta \mu_i\) \((i=\text{N, O, Ta})\) are the number and chemical potential of constituent \(i\), respectively, and \(E_i\) \((i=\text{N, O, Ta})\) is the energy per atom in the source element. The chemical potential calculation details can be found in SI-1 of the electronic support information (ESI). \(A\) is the surface area of the slab model. If the factor ‘2’ is not divided in Eqn. (1), the calculated surface energies are the sum of top and bottom ends of the slab model. Since the top and bottom ends of the constructed slab model are identical, the factor ‘2’ should be divided. More surface energy calculation details can be found in SI-2 of the ESI.
2.3 Surface models

To simulate different Ta$_3$N$_5$ surfaces, we firstly perform geometry relaxation of the conventional bulk Ta$_3$N$_5$, whose atomic structure is shown in Fig. 1a. The relaxed lattice constants of the conventional bulk Ta$_3$N$_5$ are a=3.91, b=10.32 and c=10.35 Å, which agree within the estimated experimental uncertainty (a=3.89, b=10.21 and c=10.26 Å). Then, the (100), (010) and (001) surfaces are constructed by cutting through corresponding planes of the conventional bulk Ta$_3$N$_5$.

Fig. 1b to d show the slab models of Ta$_3$N$_5$ (100), (010) and (001) surfaces, respectively. It is seen that: (i) The Ta$_3$N$_5$ (100) surface is very simple because it has only one termination. (ii) The Ta$_3$N$_5$ (010) surface is a little complex because it may be exposed by different terminations. Since it is difficult to enumerate all terminations of the (010) surface, we consider three possible terminations which are named as T1, T2, and T3, respectively. During the geometry relaxation, however, the two outmost N atoms on the T1 termination leave away from the surface, and the T1 termination finally becomes the T2 termination. Therefore, only T2 and T3 terminations are finally considered for the (010) surface. (iii) Similar with the (010) surface, the (001) surface is also complex and three terminations T1, T2 and T3 are considered for the (001) surface. In this study, the top and bottom ends of each constructed slab model are identical, thus the dipole correction is not needed. More discussion of different surface terminations can be found in SI-3 of the ESI.

As can be seen in Fig. 1a, the Ta atom is coordinated with six neighboring N atoms,
while N atoms are coordinated with three (N3) or four (N4) Ta atoms. Then, the N3 and N4 sites should be both considered to construct oxygen impurity and nitrogen vacancy. For clarity purpose, all considered terminations in this study are denoted by the combination of surface name, termination name and defect name. For example, the T2 termination of (001) surface with and without the $V_{N3}$ are denoted by (001)$_{T2}+V_{N3}$ and (001)$_{T2}$, respectively. Since only one termination is considered for the (100) surface, the termination name is not needed for describing the (100) surface. For example, the (100) surface with and without the $O_{N3}$ can be easily denoted by (100)+$O_{N3}$ and (100), respectively. What should be noted is that, when the (010) surface is terminated with the T2 and T3 terminations, the N atoms are mainly exposed by the N3 and N4 atoms, respectively. Therefore, the N3 atom is adopted to construct $O_N$ and $V_N$ for (010)$_{T2}$, while the N4 atom is adopted to construct $O_N$ and $V_N$ for (010)$_{T3}$.

To ensure the reliability of calculated surface properties, all slab models should be constructed by sufficient number of atomic layers. The convergence of atomic layers for different surfaces has been carefully tested by calculating surface energies. More details of the convergence test, as well as other important computational parameters, can be found in SI-4 of the ESI.

3. Results and discussion

3.1 The properties of bulk Ta$_3$N$_5$

Although the properties of bulk Ta$_3$N$_5$ have been extensively studied in other theoretical work,\textsuperscript{40,41} it is still necessary to make a discussion of the bulk Ta$_3$N$_5$ before discussing
the surface properties. Fig. 2a and b show band structures calculated by the primitive cell and conventional cell, respectively, of the pure bulk Ta$_3$N$_5$. Due to the band gap underestimation of the PBE functional, the calculated band gap of Ta$_3$N$_5$ is smaller than the experimental band gap (about 2.1 eV). Fig. 2a reveals that Ta$_3$N$_5$ is an indirect semiconductor, with VBM and CBM locating at the $\Gamma$ and Y points, respectively. The indirect ($\Gamma$-Y) and direct ($\Gamma$-$\Gamma$) band gaps are 1.27 and 1.50 eV, respectively, which agree well with other theoretical work. The band gap in Fig. 2b calculated by the conventional cell is still 1.27 eV. However, due to the Brillouin zone (BZ) folding effects, the VBM and CBM in Fig. 2b are both locating at the $\Gamma$ point, resulting in the direct gap character of Ta$_3$N$_5$.

In this study, to investigate the surface electronic structures, the projected band structures of clean Ta$_3$N$_5$ surfaces will be calculated in below Section 3.3. We originally used the conventional cell of bulk Ta$_3$N$_5$ to calculate the projected band structures, because the conventional cell of Ta$_3$N$_5$ was orthorhombic lattice, which was very convenient for constructing the (100), (010) and (001) surfaces. Unfortunately, due to the BZ folding effects, the conventional cell was not suitable for calculating the projected band structures. Therefore, in below Section 3.3, the projected band structures are calculated by using the primitive cell of bulk Ta$_3$N$_5$. More details of the projected band structure calculation can be found in SI-5 of the ESI.

Effects of O$_N$ and V$_N$ on electronic structures of the bulk Ta$_3$N$_5$ have been studied elsewhere. Fig. 3 shows the schematic band structures (data derive from Ref. 42) of the bulk Ta$_3$N$_5$ with O$_N$ (Ta$_3$N$_5$+O$_N$) and V$_N$ (Ta$_3$N$_5$+V$_N$). In Ta$_3$N$_5$, the O$_N$ and V$_N$ are
both electron donors. Due to the extremely low defect transition energy for reducing Ta
atoms in $\text{Ta}_3\text{N}_5$, the donated electrons from $\text{O}_N$ and $\text{V}_N$ are easily able to reduce the Ta
atoms, which further induce the downshift of CBM of the bulk $\text{Ta}_3\text{N}_5$. For the $\text{V}_N$ which
donates more electrons than $\text{O}_N$, besides the electrons that reduce the Ta atoms, the rest
of electrons induce an in-gap defect state whose charge densities are mainly localized
near the $\text{V}_N$ site. Although the $\text{O}_N$ and $\text{V}_N$ are both electron donors, their effects on the
structural stability of $\text{Ta}_3\text{N}_5$ are totally different. The $\text{O}_N$ impurity strengthens the
atomic cohesion within the $\text{Ta}_3\text{N}_5$ thus improving the structural stability, while the $\text{V}_N$
defect is harmful to the structural stability of $\text{Ta}_3\text{N}_5$.

3.2 Surface stabilities

In this section, we begin to discuss surface stabilities of $\text{Ta}_3\text{N}_5$. Surface stabilities can be
thermodynamically evaluated by surface energies. Generally, the smaller the surface
energy is, the more stable the surface will be. Fig. 4a to f show surface energies of (100),
(010)$_2$, (010)$_3$, (001)$_1$, (001)$_2$ and (001)$_3$, respectively, with and without $\text{O}_N$ and $\text{V}_N$
as a function of the chemical potential of $\text{N}$ ($\Delta \mu_\text{N}$). The negative and zero $\Delta \mu_\text{N}$
correspond to the N-poor and N-rich growth conditions, respectively. The $\text{Ta}_3\text{N}_5$
semiconductor is usually prepared by the nitridation treatment of the $\text{Ta}_2\text{O}_5$ precursor,
thus more attentions should be paid to the N-rich growth condition.

The surface energies of (100), (010) and (001) surfaces have two common grounds.
First, regardless of the growth conditions, the surface energies of (100), (010) and (001)
surfaces with $\text{O}_N$ and $\text{V}_N$ are smaller than that with $\text{O}_N$ and $\text{V}_N$, respectively. This is
consistent with the experimental observation that the O atom mainly substitutes the N3 atom but not the N4 atom.\textsuperscript{24} Then, calculation and discussion hereinafter only consider O\textsubscript{N3} and V\textsubscript{N3}. Second, under the N-rich growth condition, the surface energies of (100), (010) and (001) surfaces with V\textsubscript{N} are always the largest, suggesting that the V\textsubscript{N} defect is harmful to surface stability of Ta\textsubscript{3}N\textsubscript{5}. This is consistent with previous theoretical work that the V\textsubscript{N} defect is harmful to structural stability of the bulk Ta\textsubscript{3}N\textsubscript{5}.\textsuperscript{25}

As mentioned above, the O\textsubscript{N} impurity naturally exists in Ta\textsubscript{3}N\textsubscript{5}. Previous theoretical work provides two proper explanations to this phenomenon. One is that the O\textsubscript{N} impurity is beneficial to structural stability of Ta\textsubscript{3}N\textsubscript{5} by improving the mechanical stability,\textsuperscript{25} the other is that the O\textsubscript{N} impurity helps stabilize the Ta\textsubscript{3}N\textsubscript{5} (100) surface by decreasing surface energy of the clean (100) surface.\textsuperscript{29} In this study, besides the (100) surface (Fig. 4a), we find that surface energies of (010)\textsubscript{T2}+O\textsubscript{N3} (Fig. 4b) and (001)\textsubscript{T2}+O\textsubscript{N3} (Fig. 4e) are also smaller than that of clean (010)\textsubscript{T2} and (001)\textsubscript{T2} surfaces, respectively. This result further confirms that the O\textsubscript{N} impurity is beneficial to surface stability of Ta\textsubscript{3}N\textsubscript{5}, providing stronger explanations to the natural existence of O\textsubscript{N} impurity in Ta\textsubscript{3}N\textsubscript{5}.

Note that, when the (010) surface is terminated with the T3 termination (Fig. 4e), the surface energy of clean (010)\textsubscript{T3} is smaller than that of (010)\textsubscript{T3}+O\textsubscript{N4} under the N-rich growth condition, suggesting that the O\textsubscript{N} impurity does not always play a positive role in stabilizing Ta\textsubscript{3}N\textsubscript{5} surfaces. However, for the (010) surface, regardless of whether the surface is clean or not, the surface energies of T3 termination are much bigger than that of T2 termination (Fig. 4b). Although it is inappropriate to determine the exact
termination of a surface merely by comparing surface energies, termination with smaller surface energy is generally more stable and has more possibilities to be exposed.\textsuperscript{43} Therefore, due to the smaller surface energies, the T2 termination is expected to occupy the major part of the (010) surface. Similar conclusions can also be arrived at the (001) surface, whose major termination should be the T2 termination either. Then, for the simplicity purpose, only the T2 termination is considered for both the (010) and (001) surfaces in the following electronic structure calculations.

3.3 Surface electronic structures

Fig. 5a-c, d-f and g-i show density of states (DOS) of the (100), (010)$_{T2}$ and (001)$_{T2}$ surfaces, respectively, with and without O$_{N3}$ and V$_{N3}$. The DOS in Fig. 5a-c (the same for d-f and g-i) correspond to (100), (100)+O$_{N3}$ and (100)+V$_{N3}$ surfaces, respectively. It is seen that:

(i) In Fig. 5a, the band gap of (100) surface is about 0.8 eV, which is much smaller than that of the bulk Ta$_3$N$_5$ (1.27 eV). Such a smaller band gap of (100) is properly coming from the surface states on the clean (100) surface, because the 0.8 eV band gap may be ascribed to the energy separation between surface states and CBM. However, no obvious evidences can be seen for the presence of surface states in Fig. 5a. What should be mentioned is that, in our previous DFT investigation on the clean Ta$_3$N$_5$ (100) surface,\textsuperscript{29} one surface state is clearly observed on the top of VBM because the surface state lies alone in the band gap. In this study, when a denser $k$-point mesh ($12\times12\times12$) is used, we find that the surface state is not alone in the band gap but mixed with the VBM,
leading to the difficulty in recognizing surface states in Fig. 5a (more details of the
effects of $k$-points on the DOS of $\text{TaN}_5$ (100) surface can be found in SI-6 of the ESI).

To reveal the truth of surface states on $\text{TaN}_5$ (100) surface, the band structure of the


clean (100) surface, together with its projected band structure (shaded area), are shown

in Fig. 6a. It is seen that, two surface states B1 and B2 lie on the top of VBM,
suggesting that the 0.8 eV band gap of the clean (100) surface in DOS results is indeed
coming from the energy separation between surface states and CBM. Partial charge
densities of B1 and B2 states are mainly distributed on the N atoms of top atomic layers,
further confirming that the B1 and B2 states are both surface states on $\text{TaN}_5$ (100)
surface.

In Fig. 5b and c, in which the $\text{O}_3\text{N}$ and $\text{V}_3\text{N}$, respectively, are introduced onto the

clean (100) surface, the CBM of (100)+$\text{O}_3\text{N}$ and (100)+$\text{V}_3\text{N}$ shift left compared with that

of the clean (100) surface. Furthermore, the energy separations between VBM and CBM

of (100)+$\text{O}_3\text{N}$ and (100)+$\text{V}_3\text{N}$ gradually increase compared with that of the clean (100)
surface. We also calculate surface band structures of (100)+$\text{O}_3\text{N}$ and (100)+$\text{V}_3\text{N}$, which

are shown in Fig. 6b and c, respectively. Partial charge densities of the downshift B3

and B5 states are both uniformly distributed on all Ta atoms. This is consistent with the
discussion in Fig. 3 that the $\text{O}$ and $\text{V}$ are both able to reduce Ta atoms, which further
induces the downshift of CBM of the bulk $\text{TaN}_5$. Besides the downshift of CBM,
another important effect induced by $\text{O}$ and $\text{V}$ is the saturation of surface states.

Compared with the clean (100) surface, the (100)+$\text{O}_3\text{N}$ has only one B4 surface state on

the top of VBM. In (100)+$\text{V}_3\text{N}$, the surface states completely disappear.
(ii) Fig. 5d-f show DOS of (010)$_{T2}$, (010)$_{T2}$+O$_{N3}$ and (010)$_{T2}$+V$_{N3}$, respectively. Similar with the clean (100) surface, the clean (010)$_{T2}$ surface also has a smaller band gap. The surface and projected band structures of the clean (010)$_{T2}$ surface in Fig. 7a show that two surface states B1 and B2 locate on the top of VBM, leading to the smaller band gap of the clean (010)$_{T2}$ surface. The effects of O$_N$ and V$_N$ on electronic structures of clean (010)$_{T2}$ surface are also similar with that of the clean (100) surface. First, the O$_N$ and V$_N$ are both able to saturate surface states on the clean (010)$_{T2}$ surface. Second, the O$_N$ and V$_N$ are both able to reduce the Ta atoms (see B3 and B5 states), which further induce the downshift of CBM.

What the major difference between the (010)$_{T2}$ and (100) surfaces is that, the O$_N$ and V$_N$ are both able to induce in-gap defect states (B4 in Fig. 7b and B6 in Fig. 7c), which are not seen in (100)+O$_{N3}$ and (100)+V$_{N3}$. Partial charge densities reveal that the electrons of B4 and B6 states are mainly localized in the spaces next to O$_{N3}$ and V$_{N3}$, respectively. The B6 state in the band gap of (010)$_{T2}$+V$_{N3}$ is theoretically reasonable because similar defect state is also presented in the band gap of bulk Ta$_3$N$_5$+V$_N$ (as shown in Fig. 3). What is beyond expectation is that the O$_N$ also induces an in-gap defect state B4. The above surface energies provide proper explanations to the in-gap state of (010)$_{T2}$+O$_{N3}$. As can be seen in Fig. 4b, under the N-rich growth condition, the surface energy of (010)$_{T2}$+O$_{N3}$ is not obviously smaller but very close to that of the clean (010)$_{T2}$ surface. This means that, unlike the clean (100) and (001)$_{T2}$ surfaces, the clean (010)$_{T2}$ surface does not extremely need the O$_N$ to improve its surface stability. In other words, the donated electrons from O$_N$ are not extremely needed for (010)$_{T2}$,
leading to the in-gap state B4 and its localized charge distribution.

(iii) For \((001)_{T2}\), \((001)_{T2}+O_{N3}\) and \((001)_{T2}+V_{N3}\), their DOS results and corresponding surface band structures are shown in Fig. 5g-i and 8a-c, respectively.

Cutting the bulk \(Ta_3N_5\) through the \((001)_{T2}\) surface also introduces a surface state (B1 in Fig. 8a), which is consistent with the situations in clean (100) and (010)\(_{T2}\). However, unlike the clean (100) and (010)\(_{T2}\) surfaces whose surface states are below the Fermi level, the B1 state of clean \((001)_{T2}\) surface locates above the Fermi level, suggesting that the B1 state is not occupied with electrons but with holes. Since the \(O_N\) is an electron donor, the charge compensation is expected to considerably facilitate doping of \(O_N\) onto the \((001)\(_{T2}\) surface. This may be the reason why the surface energy of \((001)_{T2}+O_{N3}\) largely drops compared with that of the clean \((001)_{T2}\) surface (as shown in Fig. 4e).

In Fig. 8b, based on the charge compensation mechanism, the surface states disappear in the band gap of \((001)_{T2}+O_{N3}\). Furthermore, since the electrons donated from \(O_{N3}\) have compensated with the B1 state, no more electrons can reduce the Ta atoms, thus the CBM of \((010)_{T2}+O_{N3}\) does not shift down. In Fig. 8c, when the \(V_{N3}\) is introduced onto the clean \((001)_{T2}\) surface, the surface state B1 also disappears because of the charge compensation between B1 state and \(V_{N3}\). In addition, since \(V_{N3}\) donates more electrons than \(O_{N3}\), the rest of electrons donated from \(V_{N3}\) induce the B2 state, whose charge densities are mainly localized in the space next to the \(V_{N3}\) site. What should be noted is that, the B2 state is obviously below the CBM in Fig. 8c, while the corresponding states of B2 state in the DOS results (Fig. 5i) almost interact with the CBM. Actually, the surface band structures of Fig. 8a-c are calculated along the Y-\(\Gamma\) and
Γ-S surface BZ paths. For the visualization purpose, only band structure along the Γ-S path is shown in Fig. 8a-c, leading to the disagreement between surface band structures and DOS results. If the Y-Γ and Γ-S paths are both adopted for presentation, the surface band structures will be in good agreement with the DOS results. More details of the surface band structures of Fig. 8c can be found in SI-7 of the ESI. In addition, due to the delocalized character of the GGA functional, the HSE calculations with single Γ point are also performed to verify the GGA results, which can be found in SI-8 of the ESI.

3.4 Discussion

As mentioned above, surfaces with smaller surface energies are thermodynamically more stable and have more possibilities to be exposed. Therefore, due to the smaller surface energies, the (100)+O_{N3}, (010)_{T2}+O_{N3} and (001)_{T2}+O_{N3} have more possibilities to be exposed for the (100), (010) and (001) surfaces, respectively. Electronic structures reveal that, except the (001)_{T2}+O_{N3}, the CBM of (100)+O_{N3} and (010)_{T2}+O_{N3} are both occupied with electrons which are uniformly distributed on the Ta atoms. Since the electrons on reduced Ta atoms are very easy to transfer, the reduction abilities of (100)+O_{N3} and (010)_{T2}+O_{N3} are expected to be stronger than that of (001)_{T2}+O_{N3}.

To confirm the above discussion, we use the Cl atom as a probe to compare the reduction abilities of (100)+O_{N3}, (010)_{T2}+O_{N3} and (001)_{T2}+O_{N3}. Due to the strong electronegativity of Cl element, the reduction abilities of Ta_3N_5 surfaces can be evaluated by the charge integrated on Cl atoms, which is calculated by the Bader population analysis. The charge integrated on Cl, as well as the adsorption energy of Cl
on (100)+O$_{N3}$, (010)$_{T2}$+O$_{N3}$ and (001)$_{T2}$+O$_{N3}$ surfaces are listed in Table 1 (More details of the adsorption calculation can be found in SI-9 of the ESI). Since the more electrons integrated on Cl indicate the stronger reduction ability of the surface, the (010)$_{T2}$+O$_{N3}$ surface shows the strongest reduction ability, while the (001)$_{T2}$+O$_{N3}$ shows the lowest reduction ability. This is in good agreement with the above electronic structure analysis. Moreover, the order of charge integrated on Cl is also in good agreement with that of adsorption energies. Therefore, the charge integrated on Cl and the adsorption energies provide reasonable evaluation for the reduction abilities of different Ta$_3$N$_5$ surfaces.

Although the (010)$_{T2}$+O$_{N3}$ theoretically shows the strongest reduction ability, its practical reduction ability may be weakened by the surface terminations. As discussed in Fig. 4b, under the N-rich growth condition which is usually the practical growth condition of Ta$_3$N$_5$, the surface energy of (010)$_{T2}$+O$_{N3}$ is very close to that of the (010)$_{T2}$ surface, suggesting that the (010)$_{T2}$ and (010)$_{T2}$+O$_{N3}$ have the same possibilities to be exposed. Since the CBM of (010)$_{T2}$ is not occupied with electrons, the reduction ability of (010)$_{T2}$ is lower than that of (010)$_{T2}$+O$_{N3}$. When the (010)$_{T2}$ is partly exposed on the (010) surface, the reduction ability of (010) surface will be weakened. Therefore, the practical reduction ability of the (010) surface may be not as high as expectation. In other words, the (100) surface is expected to have stronger reduction ability in practice.

Our calculation results are consistent with Lu et al.’ experiments.$^{45}$ To our knowledge, Lu et al. used to synthesize a needle-like Ta$_3$N$_5$, which was controlled to grow along the [100] direction. Then, only two ends of the needle-like Ta$_3$N$_5$ were (100) plane. Lu et al. found that, when the sacrificial AgNO$_3$ was used in the experiment, the
pure Ag metals were only observed to deposit on the (100) surface but not on other surfaces. Since electrons are needed for the transition from Ag$^+$ ion to Ag metal, this experiment suggests that the Ta$_3$N$_5$ (100) surface is more reductive than other surfaces in practice, agreeing with our calculation results. In addition, their experiments revealed that the photocatalytic H$_2$ evolution abilities of the needle-like Ta$_3$N$_5$ were much weaker than that of the common bulk Ta$_3$N$_5$, which was also explained by the fewer reductive (100) surfaces of the needle-like Ta$_3$N$_5$. Therefore, in further experimental studies on Ta$_3$N$_5$, more attentions should be paid to the (100) surface because this surface plays the vital role in the photocatalytic performance of Ta$_3$N$_5$.

4. Conclusions

In summary, based on the DFT calculations, the effects of O$_N$ and V$_N$ on surface properties of Ta$_3$N$_5$ (100), (010) and (001) surfaces are detailed investigated in this study. For each surface, we find that the O$_N$ impurity is beneficial to surface stability, providing strong explanations to the natural existence of O$_N$ impurity in Ta$_3$N$_5$. By calculating surface and projected band structures, we find that there are surface states on the clean (100), (010) and (001) surfaces. When the O$_N$ and V$_N$ are introduced onto the clean surface, the surface states on clean surface are saturated, along with the downshift of CBM or appearance of in-gap defect states. Furthermore, using the single Cl atom as a probe, we compare the reduction abilities of (100), (010) and (001) surfaces. It is found that the (100) surface shows the strongest reduction ability in practice, which is expected to be helpful for further investigations of the Ta$_3$N$_5$ photocatalyst.
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References

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Table 1: The charge integrated on Cl and the adsorption energies ($E_{\text{ads}}$) of Cl on (100)+O$_{N3}$, (010)$_{T2}$+O$_{N3}$ and (001)$_{T2}$+O$_{N3}$ surfaces. The charge integrated on Cl is relative to the number of valence electrons of Cl (7).

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Charge on Cl (electrons)</th>
<th>$E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)+O$_{N3}$</td>
<td>0.58</td>
<td>3.96</td>
</tr>
<tr>
<td>(010)$<em>{T2}$+O$</em>{N3}$</td>
<td>0.63</td>
<td>4.45</td>
</tr>
<tr>
<td>(001)$<em>{T2}$+O$</em>{N3}$</td>
<td>0.44</td>
<td>1.55</td>
</tr>
</tbody>
</table>
Fig. 1 Atomic structures of (a) the conventional cell of bulk $\text{Ta}_3\text{N}_5$, (b) (100), (c) (010) and (d) (001) surfaces of $\text{Ta}_3\text{N}_5$. In (b) to (c), possible terminations for each surface are labeled. For the visualization purpose, only one side of each slab is depicted, and the slab in (d) is extended by two times.
Fig. 2 Band structures calculated by the (a) primitive cell and (b) conventional cell of pure bulk Ta$_3$N$_5$. 
Fig. 3 Schematic diagram of the band structures of bulk Ta₃N₅, Ta₃N₅+O₅ and Ta₃N₅+V₅ (data derived from Ref. 42). The blue shaded area denotes the electron occupied states. The partial charge densities (in yellow) of the CBM and in-gap states for Ta₃N₅+O₅ and Ta₃N₅+V₅ are shown near the band structures.
Fig. 4 Surface energies of Ta₃N₅ (a) (100), (b) (010)₂, (c) (010)₃, (d) (001)₁, (e) (001)₂, and (f) (001)₃ surfaces with and without defects as a function of the chemical potential of N ($\Delta \mu_N$). The negative and zero values of $\Delta \mu_N$ correspond to N-poor and N-rich growth conditions, respectively.
Fig. 5 DOS of Ta₃N₅ (a-c) (100), (d-f) (010)₂ and (g-i) (001)₃ surfaces with and without O₃N and V₃N. The DOS in (a-c) [the same for (d-f) and (g-i)] correspond to (100), (100)+O₃N and (100)+V₃N, respectively. The vertical red dash line in each case is the Fermi level. In (a-c) [the same for (d-f) and (g-i)], the horizontal axes of (b) and (c) are aligned with that of (a) by the electrostatic potentials.
**Fig. 6** Surface band structures of Ta$_3$N$_5$ (a) (100), (b) (100)+O$_{N3}$ and (c) (100)+V$_{N3}$. The horizontal red dash line is the Fermi level. In (a), the shaded area is the projected band structure corresponded to the clean (100) surface. In each case, the partial charge densities (in yellow) of some labeled states are shown near the band structures (isosurface level = 0.001 electron per Å$^3$).
Fig. 7 The same as Fig. 6 but for Ta$_3$N$_5$ (a) (010)$_{T2}$, (b) (010)$_{T2}$+O$_{N3}$ and (c) (010)$_{T2}$+V$_{N3}$.
Fig. 8 The same as Fig. 6 but for Ta₃N₅ (a) (001)₁₂, (b) (001)₁₂+O₃ and (c) (001)₁₂+V₃. The green and yellow charge densities correspond to the holes and electrons occupied states, respectively.