

Compensation of band-edge positions in titanium-doped Ta₃N₅ photoanode for enhanced water splitting performance: A first-principles insight

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Ta₃N₅ is a promising photoanode for solar water splitting. However, it often suffers from high onset potential for water oxidation, which may be partially ascribed to the oxygen impurities in Ta₃N₅. Oxygen impurities, which are always introduced into Ta₃N₅ during the preparation process, are difficult to remove due to the low formation energy of O-doped Ta₃N₅. The valence- and conduction-band-edge positions shift almost in parallel towards more positive potentials with addition of oxygen impurities, which may increase the onset potential for water oxidation. In this study, the hybrid-DFT (density functional theory) calculations of Ti-doped Ta₃N₅ show that as Ti doping concentration increases, both the valence- and conduction-band-edge positions of Ta₃N₅ move towards more negative potentials, which is opposite to the role of oxygen impurities. In the case of Ti-O codoped Ta₃N₅, Ti doping can compensate the effect of oxygen impurities and may reduce the onset potential for water oxidation. Defect formation energies reveal that Ti-O codoped Ta₃N₅ is thermodynamically stable. Therefore we propose that by controlling the amount of O and Ti, the band-edge positions can be modified to a proper level so that better photoelectrochemical performances for solar water splitting can be achieved.

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I. INTRODUCTION

The aggravated global energy crisis and environmental pollution lead to an urgent and high demand of renewable nonpolluting energy. Photoelectrochemical (PEC) water splitting is a promising candidate to solve such problems. For commercial application, a solar-to-hydrogen efficiency (STH) of at least 10% appears to be necessary for PEC cells [1]. However, many factors, for example, the poor transport property, may limit the energy conversion efficiency and the commercial application of semiconductor photocatalysis [2].

Early studies have been focused on TiO₂ since the Honda-Fujishima effect was discovered [3,4]. Because of the large band gap (about 3.2 eV), TiO₂ can only absorb ultraviolet light while visible light constitutes 43% solar energy, which limits the STH efficiency of TiO₂ even with dopant elements [5–7]. Recently, many efforts have been made to develop (oxy)nitrides, such as Ta₃N₅ [8–10], BaTaO₂N [11], and SrTaO₂N [12], on accounts of their proper band-edge positions and comparative narrow band gaps. Incorporation of nitrogen will greatly modify their electronic structure. On the one hand, the N-2*p* orbital potentials referenced to a normal hydrogen electrode (NHE) are more negative than those of O-2*p* orbitals, resulting in the negative shifts of the valence-band maximum (VBM) of (oxy)nitrides. On the other hand, the orbitals of metals consist of the conduction-band minimum (CBM) of metal oxides and (oxy)nitrides. Hence (oxy)nitrides have similar potential levels of CBM with metal oxides. Therefore the band gaps of (oxy)nitrides are much narrower than the corresponding oxides [13,14].

Due to the proper band structure, the Ta₃N₅ semiconductor is visible light responsive and has a high theoretical STH

efficiency [15]. The flat potential of Ta₃N₅ is more negative than the water reduction potential [16], suggesting its low onset potential for water oxidation. However, the actual photocurrent onset potential of Ta₃N₅, where the photocurrent can be observed, is often about 0.9 V more positive than the flat potential [8–10], which will limit the STH efficiency and the photocatalytic properties. Considerable efforts have been made to reduce the onset potential of Ta₃N₅ photoanodes [16–19]. Wang *et al.* have reported that the band-edge positions of Ta₃N₅ will move towards more positive positions when exposed to liquid water [16], indicating that the so-called self-limiting surface oxidation suppresses the photoelectrochemical activities and increases the onset potential of Ta₃N₅. Zhang *et al.* have shown that the TiO₂ overlayers fabricated by ALD method can passivate the surface states of Ta₃N₅, resulting in a lower overpotential for the water oxidation reaction and a negative shift of the onset potential [17]. Mg-Zr cosubstituted Ta₃N₅ photoelectrode provides negative changes in the band-edge positions and a negative shift of the onset potential towards 0.55 V versus RHE under AM 1.5G-simulated sunlight [9,18].

Previous experiments and DFT calculations demonstrate that defects like oxygen impurities are abundant in bulk Ta₃N₅ [19,20]. The oxygen impurities will shift the CBM positively, which may increase the onset potential for water oxidation. We propose that doping Ti into Ta₃N₅ can compensate the effect of oxygen impurities and reduce the onset potential for water oxidation. In addition, ionic radii and valence state of Ti⁴⁺ (60.5 pm) are comparable with those of Ta⁵⁺ (64 pm), indicating that Ti⁴⁺ is suitable for dopant elements. Therefore we have calculated Ti-doped Ta₃N₅ and combined a series of possible defects, including nitrogen vacancies and oxygen impurities. Various properties of Ti-doped Ta₃N₅, including defect formation energies, electronic structure, and band-edge positions have been theoretically studied by hybrid-DFT calculations.

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II. COMPUTATIONAL DETAILS

A. Computational methods

The DFT calculations are performed by using the Vienna *ab initio* simulation package (VASP) code [21]. The exchange correlation potential is calculated with the projected-augmented-wave (PAW) method [22]. For the computational screening of the possible defects, the exchange correlation potential is calculated with the generalized gradient approximation (GGA) [23] in the form of Perdew-Bueke-Ernzerhof (PBE) functional [24]. For further precise and fine calculations, hybrid-DFT calculations are used [25–28] in the scheme of Heyd-Scuseria-Ernzerhof (HSE) functional [28]. The HSE06 functional is adopted, demonstrating that the two critical parameters of hybrid-DFT calculations, mixing parameter α and screening parameter ω , are 25% and $0.2 \text{ \AA}^{-1}$, respectively [28]. The cutoff energies for all calculations are 500 eV and have been tested enough for the computational accuracy. In general, GGA-DFT plus Hubbard- U framework (GGA+ U) [29] are often applied on the models containing Ti. In this work, we ignored this effect because the energy differences of band gap and band edges between GGA and GGA+ U methods are less than 0.03 eV. The relaxed lattice constant parameters of Ta_3N_5 ($a = 3.91 \text{ \AA}$, $b = 10.32 \text{ \AA}$, and $c = 10.35 \text{ \AA}$) are in a good agreement with experimental values [30] ($a = 3.88 \text{ \AA}$, $b = 10.21 \text{ \AA}$, and $c = 10.26 \text{ \AA}$), suggesting that the calculations are reliable. For the calculations of the defect formation energies, density of states (DOS), and band-edge positions, the $3 \times 1 \times 1$ conventional bulk Ta_3N_5 supercells are chosen (space group: $Cmcm$) to use $2 \times 2 \times 2$ K meshes.

B. Defect formation energies

We have calculated the thermodynamic properties, including defect formation energies, in the neutral states and charge states q . The defect formation energies in the neutral states are defined as

$$E_{\text{defect}}^f = E_{\text{defect}}^t - E_{\text{bulk}}^t + \sum n_i \Delta\mu_i, \quad (1)$$

where E_{defect}^f are the defect formation energies. E_{defect}^t and E_{bulk}^t are the total energies of Ta_3N_5 supercell with defects and for the pure bulk Ta_3N_5 supercell, respectively. n_i represents the number of constitute i ($i = \text{Ta}, \text{N}, \text{O}$ and Ti), while $\Delta\mu_i$ is the chemical potential of different constitutes i . $\Delta\mu_{\text{N}}$ and $\Delta\mu_{\text{Ta}}$ should obey the following equation:

$$5\Delta\mu_{\text{N}} + 3\Delta\mu_{\text{Ta}} = E_{\text{Ta}_3\text{N}_5}^f. \quad (2)$$

The formation energy of Ta_3N_5 is the sum of the chemical potentials of N and Ta. In the N-rich region, $\Delta\mu_{\text{N}}$ is zero. Similarly, $\Delta\mu_{\text{Ta}} = 0$ for the Ta-rich region. By introducing external elements, various secondary phases should be avoided. The secondary phases include Ta_2TiO_6 , TaON , Ti_2O_3 , Ti_2O , TiO_2 , TiO , Ti_3O_2 , Ti_3O_4 , TiN , Ta_2O_5 , and TaO_2 . To avoid the secondary phases, taking TaON as an example, the following equation should be satisfied:

$$\Delta\mu_{\text{Ta}} + \Delta\mu_{\text{O}} + \Delta\mu_{\text{N}} < E_{\text{TaON}}^f, \quad (3)$$

where E_{TaON}^f is the formation energy of TaON . The chemical potentials of Ta, N, O, and Ti are calculated based on their

most stable solids. The detailed calculation procedure can be found in our group's previous work [31]. It is worthwhile to note that all chemical potentials $\Delta\mu_i$ should be less than or equal to zero. Because defects can be presented in different valence states, it is necessary to consider the formation energies of intrinsic defects or impurities in charge state q , the formation energies are defined as [32,33]

$$E_{\text{defect}}^f[X_q] = E_{\text{defect}}^t[X_q] - E_{\text{bulk}}^t + \sum n_i \Delta\mu_i + q[E_F + E_v + \Delta V]. \quad (4)$$

$E_{\text{defect}}^t[X_q]$ is the total energy derived from a calculation of a Ta_3N_5 supercell with defect X , and E_{bulk}^t is the total energy for a pure bulk Ta_3N_5 supercell in neutral state. E_F is the Fermi level, which is referenced to the VBM (E_v) in the pure model. However, the defects may strongly affect the band structure. To align the reference potential in a Ta_3N_5 supercell with a defect X in charge state q with that of pure Ta_3N_5 [33], a correction term ΔV derived from the electrostatic potentials between the pure model and the model with defects should be added.

C. Band-edge positions

The band-edge positions have been calculated by using the following equation [34]:

$$\Delta E_v[A/B] = \Delta E_{v,C'}[B] - \Delta E_{v,C}[A] + \Delta E_{C,C'}[A/B]. \quad (5)$$

Here, $\Delta E_{v,C'}[B]$ is the energy difference between the valence-band maximum and core level ($\Delta E_{v,C'}[B] = \Delta E_v[B] - \Delta E_{C'}[B]$) and the same is for $\Delta E_{v,C}[A]$. $\Delta E_{C,C'}[A/B]$ is the core level difference between A and B heterostructure. In this paper, A is the pure Ta_3N_5 supercell, while B is the Ta_3N_5 supercell with defects.

III. RESULTS AND DISCUSSION

A. Thermodynamic properties of Ti-doped Ta_3N_5

Oxygen impurities and nitrogen vacancies are the most common defects in Ta_3N_5 and are difficult to eliminate, therefore it is necessary to take these defects into account when calculating Ti-doped Ta_3N_5 . Here, we have calculated the formation energies of the following defects: O_N impurities (one O atom replaces one N atom), Ti and O codoped Ta_3N_5 (denoted as $\text{Ti}_{\text{Ta}} + n\text{O}_\text{N}$, n is number of O_N impurities), Ti-doped Ta_3N_5 (denoted as Ti_{Ta}), the interstitial Ti atom (denoted as Ti_{int}), N atom vacancy (V_N), Ta atom vacancy (V_{Ta}), and $\text{Ti}_{\text{Ta}} + \text{V}_\text{N}$. Figure 1 shows the pure bulk Ta_3N_5 supercell and Ta_3N_5 supercells with defects. These four Ta_3N_5 supercells with defects are the most thermodynamically stable. For each defect, different configurations have been taken into account. For instance, N atoms may coordinate with three Ta atoms (three-coordinated N) or four Ta atoms (four-coordinated N). In this case, O impurities will replace either three-coordinated N atoms or four-coordinated N atoms. The defect formation energies reveal that O impurities prefer replacing three-coordinated N atoms. Therefore further studies of O_N impurities sites will focus on three-coordinated N sites. Analogously, the most stable configurations of Ta_3N_5 supercells with defects are chosen and displayed in Fig. 1.

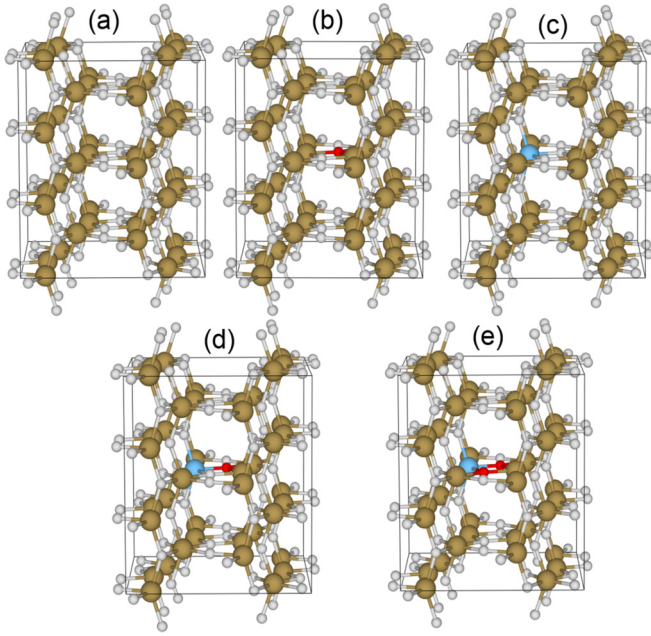


FIG. 1. Atomic structure of the $3 \times 1 \times 1$ (a) pure bulk Ta_3N_5 supercell, (b) Ta_3N_5 supercell with O_N impurity, (c) Ta_3N_5 supercell with Ti_{Ta} impurity, (d) Ta_3N_5 supercell with $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$ impurity, and (e) Ta_3N_5 supercell with $\text{Ti}_{\text{Ta}} + 2\text{O}_\text{N}$ impurity. The clay brown, light grey, blue, and red balls represent Ta, N, Ti, and O atoms, respectively.

As mentioned above, all bulk calculations are performed using $3 \times 1 \times 1$ conventional bulk Ta_3N_5 supercells. Figure 2(a) shows different defect formation energies calculated using the GGA (PBE) functional. The formation energies of $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$, O_N , $\text{Ti}_{\text{Ta}} + 2\text{O}_\text{N}$, and Ti_{Ta} in N-rich region are much lower than other defect formation energies (V_{Ta} , V_N , $\text{Ti}_{\text{Ta}} + \text{V}_\text{N}$, Ti_{int} and $\text{Ti}_{\text{Ta}} + 3\text{O}_\text{N}$). The formation energy of an O_N impurity is comparatively low, demonstrating that doping with oxygen impurities is easy, which agrees with the previous results [19,31]. The lowest formation energy of $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$ in the N-rich

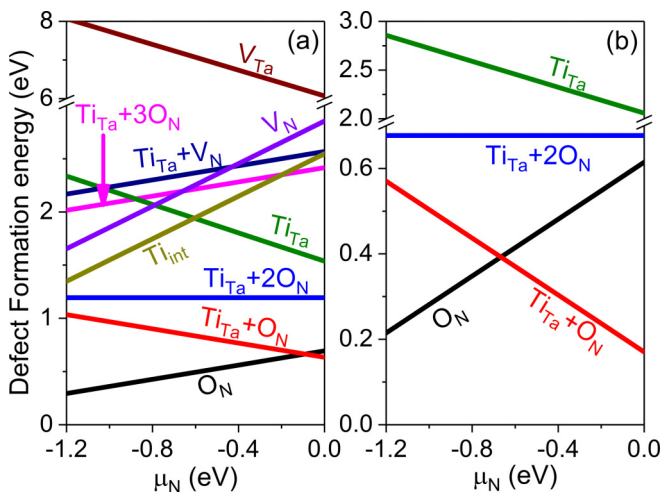


FIG. 2. (a) Calculations of defect formation energies of Ta_3N_5 supercells using DFT-GGA in the PBE scheme. (b) Four defects with the lowest formation energies have been further calculated using hybrid-DFT (HSE06) methods.

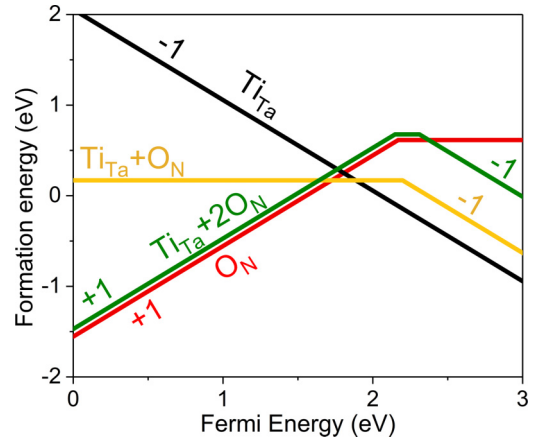


FIG. 3. Defect formation energy calculations of Ta_3N_5 supercells with various defects in different charge states using the hybrid-DFT (HSE06) method as a function of the Fermi level in the N-rich region. The horizontal line shows the formation energy in the neutral charge state.

region indicates that the charge balanced $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$ impurity is easy to generate and thermodynamically stable. The formation energies of $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$, $\text{Ti}_{\text{Ta}} + 2\text{O}_\text{N}$, and $\text{Ti}_{\text{Ta}} + 3\text{O}_\text{N}$ increase with the addition of oxygen concentrations, which is contrary to Ba-doped Ta_3N_5 [31]. In Ba-doped Ta_3N_5 system, the addition of O_N impurities help to dope Ba_{Ta} into Ta_3N_5 , which is attributed to the charge compensation between one Ba atom and three O atoms. However, $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$ is charge balanced, suggesting that $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$ is thermodynamically stable. Thereby as the oxygen concentrations further increase, the formation energies increase. V_N and V_{Ta} are intrinsic defects in bulk Ta_3N_5 . The defect formation energies of V_N and V_{Ta} are comparatively high. Ti doping has a limited effect on the formation energy of V_N .

To verify the accuracy of the formation energies, hybrid-DFT (HSE06) calculations are performed in the following sections. Comparing Figs. 2(a) and 2(b), the agreement of the defect formation energies among different calculations shows the reliability of DFT calculations. Both Figs. 2(a) and 2(b) illustrate that charge-balanced Ti-O codoped Ta_3N_5 is thermodynamically stable in the N-rich region, suggesting Ti atoms can trap oxygen impurities. Defects with positive or negative charge states influence the electronic structure and may introduce levels in or near the band gaps of semiconductors. For instance, Ti_{Ta} acts as an electron acceptor while O_N is an electron donor. Herein, it is essential to calculate the defect formation energies of Ta_3N_5 supercells as a function of the Fermi energy level to analyze the defect characterization. Figure 3 shows the defect formation energies of Ta_3N_5 supercells as a function of the Fermi level in the N-rich region, which are calculated according to Eq. (4). At the same time, Fig. 3 shows the thermodynamic transition level $\epsilon_\alpha(q/q')$ of different defects. The thermodynamic transition level $\epsilon_\alpha(q/q')$ defines the Fermi energy level where the defect formation energies in the charge state q and q' share the same value. $\epsilon_{\text{O}_\text{N}}(+1/0)$, $\epsilon_{\text{Ti}_{\text{Ta}} + \text{O}_\text{N}}(0/-1)$, and $\epsilon_{\text{Ti}_{\text{Ta}} + 2\text{O}_\text{N}}(+1/0)$ are 2.17, 2.20, and 2.15 eV above the VBM, respectively. Figure 3 proves that Ti_{Ta} behaves as an electron acceptor, while

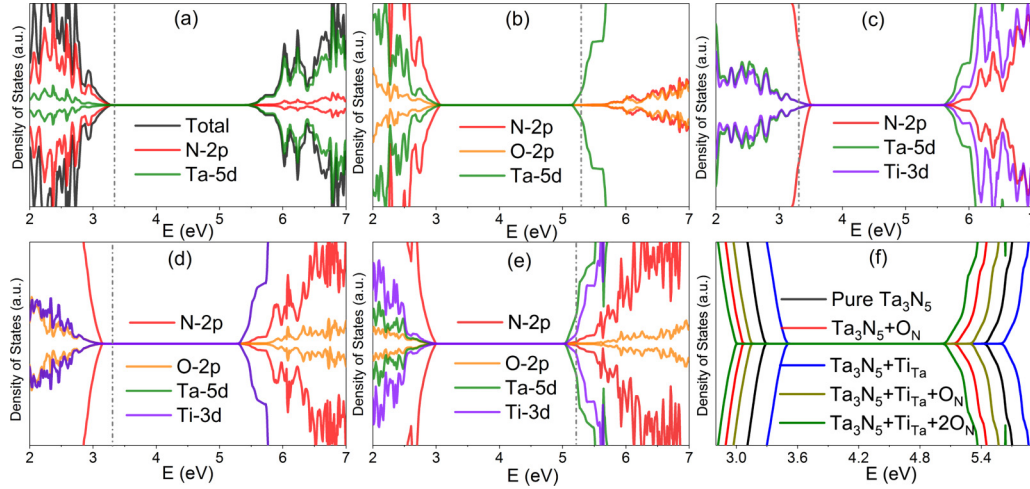


FIG. 4. Calculated DOS or PDOS of (a) pure Ta_3N_5 , (b) $\text{Ta}_3\text{N}_5 + \text{O}_\text{N}$, (c) $\text{Ta}_3\text{N}_5 + \text{Ti}_{\text{Ta}}$, (d) $\text{Ta}_3\text{N}_5 + \text{Ti}_{\text{Ta}} + \text{O}_\text{N}$, and (e) $\text{Ta}_3\text{N}_5 + \text{Ti}_{\text{Ta}} + 2\text{O}_\text{N}$. (f) The total DOS of pure Ta_3N_5 and Ta_3N_5 with various defects. The hybrid-DFT (HSE06) method has been adopted for all calculations. The vertical grey dashed line is the Fermi level. (a) The DOS of pure Ta_3N_5 . (b)–(e) show the PDOS of doping Ti, O and neighboring N, Ta atoms (the cutoff distance is 3 Å).

O_N prefers acting as an electron donor when the Fermi level is lower than 2.17 eV above VBM. The neutral $\text{Ti}_{\text{Ta}} + \text{O}_\text{N}$ is thermodynamically stable and is in agreement with the defect formation energies illustrated in Fig. 2. When O impurities further increase, the property of $\text{Ti}_{\text{Ta}} + 2\text{O}_\text{N}$ is similar to O_N .

The formation energies reveal that Ti-O codoped Ta_3N_5 is thermodynamically stable, suggesting that in Ti-doped Ta_3N_5 , O impurities play an indispensable role. Ti as well as O should be considered when calculating the properties of Ta_3N_5 .

B. Electronic structure of Ti-doped Ta_3N_5

The density of states (DOS) and partial density of states (PDOS) describe the occupied number of states per energy levels, revealing the details of the electronic structure of the pure bulk Ta_3N_5 and Ta_3N_5 with impurities. Figure 4 shows the DOS and PDOS of the pure Ta_3N_5 and Ta_3N_5 with various defects. For bulk Ta_3N_5 , N-2p orbitals mainly contribute to the valence band and Ta-5d orbitals contribute to the conduction band, which consists with the previous report on metal oxides [35,36]. O-2p orbitals behave similarly as N-2p orbitals, mainly contributing to the valence band. In the meantime, Ti-3d orbitals mainly contribute to the conduction band, analogous to Ta-5d orbitals. The PDOS of foreign Ti and O atoms with adjacent N and Ta atoms are illustrated in Figs. 4(b)–4(e). From Figs. 4(b)–4(e), it is notable that the 3d orbitals of the Ti atoms show strong hybridization with the adjacent N-2p and Ta-5d orbitals in the CBM. O-2p orbitals mainly hybridize with orbitals of adjacent atoms in VBM. However, the PDOS of O-2p orbitals in VBM is negligible, compared with adjacent N-2p orbitals, implying that the O impurity has limited effects on the DOS in the VBM. Figure 4(f) reveals the total DOS of pure Ta_3N_5 and Ta_3N_5 with defects. Except $\text{Ta}_3\text{N}_5 + \text{Ti}_{\text{Ta}}$, all the other VBM and CBM of Ta_3N_5 with defects shift left, indicating that the CBM is closer to the H^+/H_2 potential, which is harmful to the H^+ reduction reaction and beneficial to the oxygen evolution reaction. Simultaneously, the addition of Ti will enhance the

H^+ reduction reaction and reduce the onset potential. To confirm the shifts of the VBM and the CBM, the band-edge positions have been calculated by taking the deformation potential of the core states into consideration in the following section [31].

The vertical grey dashed line in Fig. 4 is the Fermi level. As is shown in Figs. 4(a) and 4(b), the Fermi level moves from VBM to CBM by introducing O impurities. On the contrary, Fig. 4(c) indicates that the Fermi level of Ti-doped Ta_3N_5 moves to the left, showing that Ti-doped Ta_3N_5 is *p*-type doped. The Fermi level of the charge balanced $\text{Ta}_3\text{N}_5 + \text{Ti}_{\text{Ta}} + \text{O}_\text{N}$ is similar to pure Ta_3N_5 while with further increase of O impurities, as shown in Fig. 4(e), the Fermi level moves to CBM. Combining the shifts of band-edge positions and the Fermi level, the introduction of foreign element Ti can counteract the effects of O impurities on the band-edge positions, enhance the H^+ reduction reaction, and reduce the onset potential.

C. Band-edge position modifications with various O and Ti concentrations

The band-edge positions of a photoelectrode material play a key role in water splitting reaction, therefore it is meaningful to calculate the band-edge positions with various O and Ti concentrations. All calculations have been performed using $3 \times 1 \times 1$ conventional bulk Ta_3N_5 supercells. Various Ti and O configurations at different concentrations have been considered. Ti_{Ta} and O_N are the most stable configurations and have been applied in the following calculations. To drive water splitting reaction, the valence-band-edge position must be more positive than the $\text{O}_2/\text{H}_2\text{O}$ potential (1.23 V versus NHE) and the conduction-band-edge position must be more negative than the H^+/H_2 potential. The band-edge positions of Ta_3N_5 satisfy the above conditions, indicating that Ta_3N_5 alone may drive water splitting reaction without any bias theoretically. Here, we use precious hybrid-DFT (HSE06) calculations to study the effect of O and Ti concentrations on the band-edge

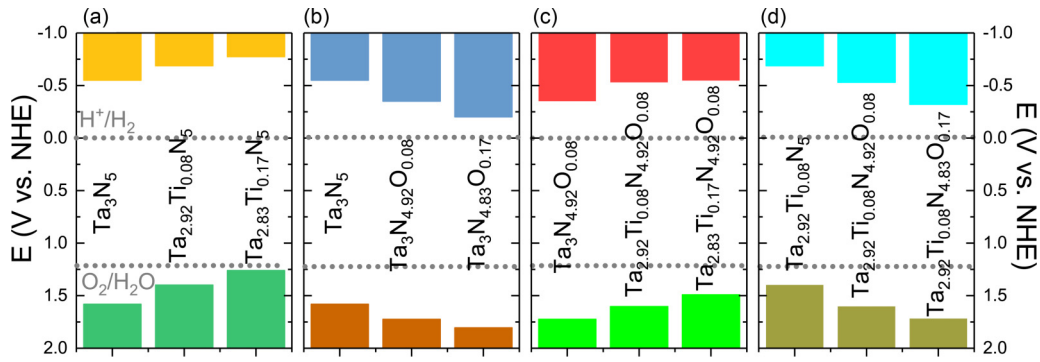


FIG. 5. Calculated valence and conduction-band-edge positions of Ta_3N_5 with (a) various Ti/Ta ratios, (b) various O/N ratios, (c) various Ti/Ta ratios and a constant O/N ratio, and (d) various O/N ratios and a constant Ti/Ta ratio using the hybrid-DFT (HSE06) method and $3 \times 1 \times 1$ supercells. The grey dashed lines represent $\text{O}_2/\text{H}_2\text{O}$ (1.23 V vs NHE) and H^+/H_2 (0 V vs NHE) potentials, respectively.

positions. The calculated VBM are obtained from Eq. (5). The shifts of either VBM or CBM will greatly influence the kinetic overpotentials for HER and OER. For Ta_3N_5 , previous work [36] has focused on the effects of O/N ratios on the band-edge positions. In this study, we have explained the synergistic effects of doping metal element Ti and oxygen impurities on the band-edge positions of Ta_3N_5 . Figures 5(a) and 5(b) display the variation trends of valence- and conduction-band-edge positions with different Ti/Ta ratios and O/N ratios. Figure 5(a) reveals both valence- and conduction-band-edge positions increasing towards more negative potentials with the increase of Ti/Ta ratios. The negative shift of CBM is beneficial for water reduction reaction because of the better kinetic condition. Meanwhile, the negative shift of VBM will restrain water oxidation reaction. Contrary to Ti doping, with the increase of O/N ratios, both valence and conduction-band-edge positions shift towards more positive potentials. This suggests that O impurities are harmful to water reduction reaction and enhance oxygen evolution reaction. For a very low O/N ratio ($\text{O/N}=1/30$, $\text{Ta}_3\text{N}_{4.83}\text{O}_{0.17}$), the valence-band edge moves towards a more positive potential by 0.22 eV compared with the pure Ta_3N_5 . This indicates that partially oxidized Ta_3N_5 can greatly affect the band-edge positions and photocatalytic properties of Ta_3N_5 .

The charge balanced $\text{Ta}_3\text{N}_5 + \text{Ti}_{\text{Ta}} + \text{O}_{\text{N}}$ is thermodynamically stable, demonstrating that O impurity can stabilize the Ti-doped Ta_3N_5 . At the same time, O and Ti have a contrary influence on the band-edge positions of Ta_3N_5 . Hence the cooperative effect of O and Ti on Ta_3N_5 should be emphasized. The O and Ti codoped Ta_3N_5 supercells with different O/N and Ti/Ta ratios are calculated and illustrated in Figs. 5(c) and 5(d). Figure 5(c) reveals that with the addition of Ti atoms and a constant concentration of O impurities, both the valence- and conduction-band-edge positions move towards more negative potentials, showing the same tendency with Ti-doped Ta_3N_5 . On the contrary, Fig. 5(d) reveals that with the addition of O impurities and a constant concentration of Ti, both the valence and conduction-band-edge positions move towards more positive potentials. To conclude, both the valence- and conduction-band-edge positions move towards more positive potentials with addition of O impurities, while with increasing Ti concentration, both the valence- and conduction-band-edge positions move towards more negative potentials. O impurities in Ta_3N_5 are difficult to remove because of their low formation

energy. Meanwhile O impurities may greatly influence the band-edge positions. As mentioned above, the positive shift of the conduction-band edge ascribed to O impurities is harmful to water reduction reaction. At the same time, the shift of the conduction-band edge will affect the onset potential of the photoanode [37,38]. The onset potential is an important parameter of the photoanode and the cathodic shift of the onset potential will enhance the STH efficiency. Previous analysis indicates that oxygen impurities are detrimental to the performance of the onset potential. By introducing a foreign metal element Ti, the conduction-band-edge position moves towards a more negative potential, which can compensate the effect of oxygen impurities and may improve the onset potential performance.

Here, we suggest that by controlling the amount of Ti and O concentrations, the band-edge positions can be adjusted to a proper potential level. Introducing Ti atoms can eliminate the effect of O impurities on the band-edge positions and may shift the onset potential of Ta_3N_5 negatively, thereby improving the photoelectrochemical property of photoanode Ta_3N_5 .

IV. CONCLUSIONS

In summary, we have calculated Ti-doped Ta_3N_5 based on the hybrid-DFT method. First, we calculate the thermodynamic properties and the results demonstrate that Ti and O codoped Ta_3N_5 is thermodynamically stable. Then according to the DOS and PDOS calculations, O-2p orbitals and N-2p orbitals mainly contribute to the valence band while Ti-3d orbitals and Ta-5d orbitals mainly contribute to the conduction band. The 3d orbitals of the Ti atoms show strong hybridization with the adjacent N-2p and Ta-5d orbitals in the CBM. O-2p orbitals mainly hybridize with orbitals of adjacent atoms in VBM. Finally, the band-edge positions with various O and Ti concentrations have been investigated. The addition of O impurities shifts both the valence- and conduction-band-edge positions in parallel towards more positive potentials, while with increasing Ti concentration, band-edge positions show the opposite tendency. This reveals that controlling the amount of O impurities and foreign Ti atoms can modify the band-edge position to a proper level for photocatalysis. Ti doping can compensate the positive shifts of band-edge positions arising from O impurities and enhance the onset potential performance of Ta_3N_5 for water oxidation.

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