Support Information

For

Effects of oxygen impurity and nitrogen vacancy on surface properties of the Ta_3N_5 photocatalyst: a DFT study

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by

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SI-1 Chemical potentials of N, O and Ta in Ta₃N₅

Under the thermal equilibrium growth conditions, the bulk Ta₃N₅ should satisfy:

$$3\Delta\mu_{Ta} + 5\Delta\mu_{N} = E_{Ta_{3}N_{5}}^{f} = -8.47eV$$
(S1)

where $E_{Ta_3N_5}^f$ is the formation energy of pure bulk Ta₃N₅. Then, we can get $\Delta\mu_N$ and $\Delta\mu_{Ta}$ under different growth conditions: under the N-poor (Ta-rich) growth condition, $\Delta\mu_N = -$ 1.69 and $\Delta\mu_{Ta} = 0$ eV; under the N-rich (Ta-poor) growth condition, $\Delta\mu_N = 0$ and $\Delta\mu_{Ta} = -$ 2.82 eV. To calculate the $\Delta\mu_O$, precipitation of secondary phases such as TaON and Ta₂O₅ should be avoided:

$$\Delta \mu_N + \Delta \mu_O + \Delta \mu_{Ta} < E_{TaON}^f = -5.79 eV$$
(S2)

$$5\Delta\mu_{O} + 2\Delta\mu_{Ta} < E_{Ta_{2}O_{5}}^{f} = -20.20eV$$
(S3)

where $E_{Ta_2O_5}^f$ and E_{TaON}^f are formation energies of Ta₂O₅ and TaON, respectively. Then, $\Delta\mu_o$ can be calculated from the lower bound for each growth condition: -4.10 and -2.97 eV under N-poor and N-rich growth conditions, respectively.

It is necessary to discuss the origin of $\Delta \mu$. Using the Ta₃N₅ semiconductor as an example, the chemical potentials of N and Ta satisfy the following relation:

$$3\mu_{Ta} + 5\mu_N = \mu_{Ta_3N_5}$$
(S4)

where μ_{Ta} , μ_N and $\mu_{Ta_3N_5}$ are chemical potentials of N, Ta and bulk Ta₃N₅, respectively. Under the thermal equilibrium growth conditions, the chemical potential of bulk Ta₃N₅ is equal to the total energy of bulk Ta₃N₅:¹

$$\mu_{Ta_3N_5} = E_{Ta_3N_5} \tag{S5}$$

The total energy $E_{Ta_3N_5}$ can be expressed as follows:

$$E_{Ta_{3}N_{5}} = 3E_{Ta} + 5E_{N} + E_{Ta_{3}N_{5}}^{f}$$
(S6)

where E_{Ta} and E_N are energy per atom in the bulk metal Ta and N₂ gas, respectively, and $E_{Ta_3N_5}^{f}$ is the formation energy of bulk Ta₃N₅. Then, based on the Eqn. (S4) to (S6), we can

get

$$3(\mu_{Ta} - E_{Ta}) + 5(\mu_N - E_N) = E_{Ta_3N_5}^f$$
(S7)

If we define

$$\Delta \mu_i = \mu_i - E_i (i = N, Ta) \tag{S8}$$

then Eqn. (S7) becomes:

$$3\Delta\mu_{Ta} + 5\Delta\mu_N = E^J_{Ta_2N_5} \tag{S9}$$

The Eqn. (S9) is the same as the Eqn. (S1), which is the general form in many literatures. In some literatures, the ' Δ ' symbol is omitted. Note that, the $\Delta\mu_i$ must satisfy $\Delta\mu_i < 0$, because the precipitation of source elements such as pure bulk Ta and N₂ gas must be avoided.² This is exactly the reason why the upper bound of $\Delta\mu_i$ is always zero. Then, based on the Eqn. (S9), we can get the accessible ranges of $\Delta\mu_N$ and $\Delta\mu_{Ta}$: under the Tarich growth condition, $\mu_N = E_{Ta_3N_5}^f / 5$ and $\mu_{Ta} = 0$; under the N-rich growth condition, $\mu_N = E_{Ta_3N_5}^f / 3$.

SI-2 Surface energy calculation details

The surface energy can be calculated by the following equation:³

$$E_{surface} = \frac{1}{2A} (E_{slab} - nE_{bulk})$$
(S10)

where E_{slab} is the total energy of the slab model, E_{bulk} is the total energy per unit cell of the bulk, *n* is the number of unit cells that the slab model contains, and *A* is the surface area of the slab model. The Eqn. (S10) is applicable to many situations, especially to the pure metal surfaces. However, the Eqn. (S10) has its limitations. We use the typical semiconductor SrTiO₃ as an example to discuss the limitation of Eqn. (S10). As can be seen in below **Fig. S1**, the SrTiO₃ (100) surface is the stack of TiO₂ and SrO atomic layers. Therefore, the SrTiO₃ (100) surface can be exposed by the TiO₂-termination or SrO-termination. Generally, when we calculate surface energy of the SrTiO₃ (100) surface with TiO₂-termination, the top and bottom ends of the constructed slab model will be both exposed by the TiO₂ atomic layer. Then, the number of TiO₂ atomic layer will be more than that of the SrO atomic layer. When the number of TiO₂ atomic layer is more than that of the SrO atomic layer, the Eqn. (S10) is not suitable to calculate surface energy. Using the below **Fig. S1** as an example, the TiO₂-terminated SrTiO₃ (100) surface contains 3 TiO₂ atomic layers and 2 SrO atomic layers. Since one TiO₂ atomic layer plus one SrO atomic layer equals to one unit cell of bulk SrTiO₃, the slab model in **Fig. S1** contains 2 unit cells of bulk SrTiO₃ and one TiO₂ atomic layer. Then, we cannot give the factor '*n*' in Eqn. (S10) and thus the Eqn. (S10) cannot be used to calculate surface energy.



Fig. S1 Schematic diagram of the symmetrical TiO₂-terminaed SrTiO₃ (100) surface.

To calculate the surface energy of the slab model in **Fig. S1**, we can use the following equation:¹

$$E_{\text{surf}} = \frac{1}{2A} \left(E_{slab} - \sum_{i} n_{i} \mu_{i} \right) \tag{S11}$$

where the n_i and μ_i (*i*=N, O, Ta) are the number and chemical potential of constituent *i*, respectively. Compared with the Eqn. (S10) which requires the number of unit cells in the slab model, the Eqn. (S11) only needs the number of each constituent in the slab model. Therefore, the Eqn. (S11) has larger application range than the Eqn. (S10). Based on the Eqn. (S11), the surface energy of the TiO₂-terminated SrTiO₃ (100) surface in **Fig. S1** can be written as:

$$E_{\rm surf} = \frac{1}{2A} (E_{\rm slab} - n_{\rm O}\mu_{\rm O} - n_{\rm Ti}\mu_{\rm Ti} - n_{\rm Sr}\mu_{\rm Sr})$$
(S12)

where $n_{\rm O}$, $n_{\rm Ti}$ and $n_{\rm Sr}$ are 8, 3 and 2, respectively.

It is necessary to discuss the relationship between Eqn. (S10) and (S11). We still use the semiconductor $SrTiO_3$ to carry out the discussion. Under the thermal equilibrium growth

conditions, the chemical potential of SrTiO₃ is equal to the total energy of bulk SrTiO₃:¹

$$\mu_{SrTiO_3} = E_{SrTiO_3} \tag{S13}$$

Since μ_{SrTiO_3} can be expressed as:

$$\mu_{SrTiO_3} = 3\mu_0 + \mu_{Ti} + \mu_{Sr} \tag{S14}$$

then, based on Eqn. (S13) and (S14), we can get:

$$3\mu_{\rm O} + \mu_{Ti} + \mu_{Sr} = E_{SrTiO_3} \tag{S15}$$

If we replace Eqn. (S12) with Eqn. (S15) and eliminate the μ_{Ti} term, we can get the surface energy:

$$E_{\text{surf}} = \frac{1}{2A} [E_{\text{slab}} - n_{\text{Ti}} E_{\text{SrTiO}_3} + (3n_{\text{Ti}} - n_{\text{O}})\mu_O + (n_{\text{Ti}} - n_{\text{Sr}})\mu_{\text{Sr}}]$$
(S16)



Fig. S2 Schematic diagram of the asymmetrical SrTiO₃ (100) surface.

It is seen from the Eqn. (S16) that, when the number of unit cells in the slab is the integer multiple of the bulk, (*i.e.*, the ratio of $n_{Ti} : n_{Sr} : n_O = 1 : 1 : 3$, for example the **Fig. S2**), the Eqn. (S16) becomes

$$E_{\text{surf}} = \frac{1}{2A} \left[E_{\text{slab}} - n_{\text{Ti}} E_{\text{SrTiO}_3} \right]$$
(S17)

which is exactly equal to the Eqn. (S10). Therefore, the Eqn. (S11) is essentially the general form of the Eqn. (S10). What should be noted is that, the surface energy of the slab in **Fig. S2** calculated by Eqn. (S17) does not belong to the TiO_2 -termiantion, but the average of the sum of TiO_2 -termiantion and SrO-termiantion. This is exactly the reason why the top and bottom ends would better to be the same when we construct the slab model.

Since the Eqn. (S11) is the general form for surface energy calculation, it can also be used to calculate surface energy of system with vacancy/impurity. The following **Fig. S3a**

and **b** are TiO_2 -terminaed $SrTiO_3$ (100) surface with O vacancy and N impurity, respectively. The surface energies of **Fig. S3a and b** can be written as:

$$E_{\rm surf} = \frac{1}{2A} (E_{\rm slab} - 6\mu_o - 3\mu_{\rm Ti} - 2\mu_{\rm Sr})$$
(S18)

and

$$E_{\rm surf} = \frac{1}{2A} (E_{\rm slab} - 6\mu_{\rm O} - 3\mu_{\rm Ti} - 2\mu_{\rm Sr} - 2\mu_{\rm N})$$
(S19)

respectively. Note that, in Eqn. (S19), the chemical potential μ_N should be carefully calculated to avoid precipitation of secondary phases. More details of the surface energy calculation please refer to Ref. 1.

(a)	(b)	
TiO ₁	TiO ₁ N ₁	
SrO		SrO
TiO2		TiO ₂
SrO		SrO
TiO ₁		TiO ₁ N ₁

Fig. S3 Schematic diagram of the TiO_2 -terminaed $SrTiO_3$ (100) surface with (a) one O vacancy and (b) one N_O impurity at each side of the slab model.

SI-3 Discussion of different surface terminations

Among the Ta_3N_5 (100), (010) and (001) surfaces, the (100) surface is the simplest because it has only one termination. The atomic structures of (100) surface are also relatively simple since the N/Ta ratio of this surface is 5/3, which is equal to that of the bulk Ta_3N_5 . Compared with the (100) surface, the (010) and (001) surfaces are more complex, thus more attentions should be paid to these two surfaces. In the main manuscript, two (T2 and T3) and three (T1, T2 and T3) terminations are selected for the (010) and (001) surfaces, respectively. Here, we will make a short discussion about why these terminations are selected.

Fig. S4 shows the front view and side view of the (010) surface. It is seen that the (010) surface can be regarded as the N4-Ta tetrahedron (blue shared area) connected by two N3 atoms. Since the N3 atom is easier removed than the N4 atom^{4,5}, we then initially consider

the T1, T2 and T3 terminations which all cut through the N3 atoms. However, during the geometry relaxations of T1, T2 and T3 terminations, 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.

Fig. S5 shows the front view and side view of the (001) surface. Theoretically, the atomic structures of (001) surface are also very simple, because it can be regarded as the stack of Ta-N octahedrons (shown in red). However, when the (001) surface is exposed with the T1 termination, the N-Ta-N atoms are in the same plane. When the (001) surface is exposed with the T2 or T3 termination, the N-Ta-N atoms are not in the same plane. Therefore, we choose the T1, T2 and T3 terminations for the (001) surface.



Fig. S4 Atomic structures of the Ta_3N_5 (010) surface.



Fig. S5 Atomic structures of the Ta_3N_5 (001) surface.

SI-4 Convergence test and other computational parameters

Table S1 lists convergence test of the number of atomic layers for Ta₃N₅ (100), (010) and (001) surfaces by calculating surface energies (E_{surf}). The definitions of atomic layers for (100), (010) and (001) surfaces can be found in **Fig. S6a-c**, respectively. After the convergence test, the 7, 6, 6, 19, 23 and 27 atomic layers are found to be sufficient to simulate the (100), (010)_{T2}, (010)_{T3}, (001)_{T1}, (001)_{T2} and (001)_{T3}, respectively. For each termination, a vacuum space of 15 Å is added at each side of the slab model, which is sufficient to avoid interactions between the neighboring images. Furthermore, for (100), (010)_{T2}, (010)_{T1}, (001)_{T2} and (001)_{T3}, the Γ-centered *k*-point meshes of 12×12×1, 2×6×1, 2×6×1, 5×5×1, 5×5×1 and 5×5×1, respectively, are adopted for the Brillouin zone integration.

Surfaces	Termination s	E_{surf} (down) as a function of the number of atomic layers (up)		
(100)	(100)	5	7	9
		1.26	1.23	1.22
(010)	(010) _{T2}	2	4	6
		1.42	1.43	1.43
	(010) _{T3}	2	4	6
		3.43	3.45	3.45
(001)	(001) _{T1}	7	13	19
		1.79	1.73	1.73
	(001) _{T2}	11	17	23
		2.28	2.28	2.29
	(001) _{T3}	15	21	27
		1.62	1.63	1.63

Table S1 Surface energies (E_{surf} J/m²) as a function of the number of atomic layers for Ta₃N₅ (100), (010) and (001) surfaces. The definitions of atomic layers for (100), (010) and (001) surfaces can be found in Fig. S6a-c, respectively.



Fig. S6 Definitions of atomic layers for Ta_3N_5 (a) (100), (b) (010) and (c) (001) surfaces.

SI-5 Projected band structure calculation details

In this study, the projected band structures were originally calculated by using the conventional cell of Ta₃N₅. However, testing calculations revealed that the conventional cell was not suitable for calculating the projected band structures. **Fig. S7a and b** show the projected band structures of clean Ta₃N₅ (100) surface calculated by conventional cell and primitive cell of the bulk Ta₃N₅, respectively. **Fig. S7c** shows the surface band structure of clean Ta₃N₅ (100) surface. It is seen that, due to the Brillouin zone folding effects, the band gap at the Γ point in Fig. S7a is 1.27 eV. If the projected band structure in Fig. S7a is adopted to compare with the surface band structure in Fig. S7c, the surface states cannot be correctly presented. Compared with the conventional cell, the primitive cell can be used to analyze surface states, because the band gap at the Γ point in Fig. S7b is equal to that in Fig. S7c.

To calculate the projected band structures, we must find out the relationship between the path in the surface Brillouin zone and the equivalent path in the bulk Brillouin zone. As mentioned in the main manuscript, the conventional cell of Ta_3N_5 would have been very convenient to calculate the projected band structures, because the normal directions of the (100), (010) and (001) planes are equal to the three axes of the conventional cell of Ta_3N_5 . When we use the primitive cell of Ta_3N_5 to calculate the projected band structures, we firstly need to find out the normal directions of the (100), (010) and (001) planes in the primitive cell of Ta_3N_5 . As can be seen in **Fig. S8**, when a 3×3 super primitive cell is depicted, the relationship between primitive cell and conventional cell can be clearly seen. Then, it is easy to get the normal directions of the (100), (010) and (001) planes in the primitive cell of Ta_3N_5 (the axes shown in Fig. S8).

Based on the normal directions of the (100), (010) and (001) planes in the primitive cell of Ta_3N_5 , we can obtain the relationship between the path in the surface Brillouin zone and the equivalent path in the bulk Brillouin zone of primitive cell. **Fig. S9a** shows the Brillouin zone of the primitive cell of Ta_3N_5 . **Fig. S9b to d** show the equivalent paths for (100), (010) and (001) surfaces, respectively, in the Brillouin zone of primitive cell of Ta_3N_5 .

For the simplicity purpose, we use the Ta₃N₅ (001) surface as an example to discuss the projected band structure calculation. In **Fig. S9d**, the equivalent paths in the Brillouin zone of primitive cell for the (001) plane are along the Y- Γ -S path. Then, along the direction of dash arrows, an increasing constant k_{\perp} can be added to the Y- Γ -S path until the Y- Γ -S path reaches the Brillouin zone boundary. For each k_{\perp} , we can calculate the band structure along the Y- Γ -S path. When the band structures for all k_{\perp} values are depicted together into one picture, the projected band structures can be easily obtained. **Fig. S10** shows the projected band structure of the clean Ta₃N₅ (001) surface.

Note that, for visualization purpose, only the band structures along the Γ -Z, Z- Γ and Γ -S paths are shown for (100), (010) and (001) surface, respectively, in the main manuscript. For more information about the projected band structure calculation, please refer to Charpter #1 of the book "Principles of Surface Physics" (Friedhelm Bechstedt, Springer-Verlag, 2003).



Fig. S7 Projected band structures of clean Ta_3N_5 (100) surface calculated by (a) conventional cell and (b) primitive cell of bulk Ta_3N_5 , respectively. (c) is the surface band structure of the clean Ta_3N_5 (100) surface.



Fig. S8 Schematic diagram of the relationship between primitive and conventional cells of the bulk Ta_3N_5 .



Fig. S9 (a) The Brillouin zone of the primitive cell of bulk Ta_3N_5 . (b) to (d) show the equivalent paths for (100), (010) and (001) planes, respectively, in the Brillouin zone of primitive cell.



Fig. S10 Projected band structures of the clean Ta_3N_5 (001) surface.

SI-6 Effects of k-points on the DOS of Ta₃N₅ (100) surface

In our previous theoretical work⁵, we used the *k*-point mesh of $3 \times 3 \times 1$ to calculate the DOS of Ta₃N₅ (100) surface (**Fig. S11a**). It is seen that, a surface state lies alone on the top of VBM. In the present study, when the denser *k*-point meshes of $4 \times 4 \times 1$ (**Fig. S11b**), $6 \times 6 \times 1$ (**Fig. S11c**) and $12 \times 12 \times 1$ (**Fig. S11d**) are attempted to be used, we find that the surface state is not alone in the band gap but gradually mixed with the VBM, Therefore, a denser *k*-point mesh is needed to represent the true DOS of the Ta₃N₅ (100) surface. In other words, the $3 \times 3 \times 1$ *k*-point mesh in our previous work is not sufficient. However, regardless of the dense of *k*-point meshes, the energy states above the VBM can be undoubtedly confirmed to be the surface state, and its corresponding partial charge densities are proved to be distributed on the top atomic layer of the (100) surface. This means that the less *k*-points in our previous work merely affects the shape of DOS curves around the VBM, but not affects the qualitative analysis of the DOS results. Note that, we only pay attention to the relative variations between DOS with different *k*-point meshes. Therefore, for simplicity purpose, the DOS in Fig. S11 are only calculated by the non-spin-polarized DFT calculation.



Fig. S11 DOS of the clean Ta_3N_5 (100) surface calculated by *k*-point meshes of (a) $3 \times 3 \times 1$, (b) $4 \times 4 \times 1$, (c) $6 \times 6 \times 1$ and (d) $12 \times 12 \times 1$. The vertical red dash line in each case is the Fermi level.

SI-7 Surface band structures of (001)_{T2}+V_{N3}

For the visualization purpose, the band structures of $(001)_{T2}+V_{N3}$ in the main manuscript are shown along the Γ -S path, leading to the disagreement between band structure and DOS results. As can be seen in the below **Fig. S12a**, the in-gap state along the Γ -S path is obviously below the CBM, while the corresponding state in the DOS results (**Fig. S12b**) almost interacts with the CBM. If the Y- Γ and Γ -F paths are both adopted for presentation, the surface state in the band gap also interacts with the CBM, agreeing with the DOS results.



Fig. S12 (a) Band structure and (b) DOS of the $(001)_{T2}+V_{N3}$ surface. The horizontal red dash line is the Fermi level.

SI-8 The HSE calculation

To verify the GGA results, it is necessary to perform some HSE calculations. Since some Ta_3N_5 surface models contain more than 100 atoms, the HSE calculation needs large amount of computational resources, especially when more than one *k*-point is used for HSE calculations. Due to the large computational cost, only the single Gamma *k*-point is adopted for the HSE calculations.

The accuracy of the HSE method is mainly determined by two important parameters α and ω , where α represents the fraction of the semilocal PBE exchange interaction replaced by a screened nonlocal functional and ω is the inverse screening length. The parameters α and ω are set as 25% and 0.2 Å⁻¹, respectively, which refers to the HSE06 functional. The band gap of the pure bulk Ta₃N₅ calculated by the HSE06 functional is 2.2 eV, which is very close to the experimental results (about 2.1 eV), suggesting that the HSE method is very accurate indeed.

Fig. S13a to c show the DOS of (100), (100)+ O_{N3} and (100)+ V_{N3} , respectively, calculated by the PBE functional. The DOS results of (100), (100)+ O_{N3} and (100)+ V_{N3}

calculated by the HSE functional are shown in **Fig. S13d to f**, respectively. It is seen that, due to the insufficient *k*-points, the DOS curves calculated by the HSE method are discontinuous. For example, the energy regions A (about -2.3 to -2.0 eV) and B (near the 0 eV) in **Fig. S13a** should have DOS curves. Similar situations can also be found in **Fig. S13b** (C, D, E regions) and **c** (F, G regions). However, the discontinuous DOS curves of the HSE results do not affect any qualitative analysis. The comparisons between HSE and PBE results reveal that: (i) the charge densities of VBM in (100) surface calculated by PBE (**Fig. S13g**) and HSE (**Fig. S13k**) are both localized on the top atomic layers; (ii) the charge densities of VBM in (100)+O_{N3} surface calculated by PBE (**Fig. S13h**) and HSE (**Fig. S13i**) are both uniformly distributed on all Ta atoms; (iv) the charge densities of CBM in (100)+V_{N3} surface calculated by PBE (**Fig. S13j**) and HSE (**Fig. S13n**) are both uniformly distributed on all Ta atoms.

Fig. S14a to c show the DOS of (010), (010)+ O_{N3} and (010)+ V_{N3} , respectively, calculated by the PBE functional. The DOS results of (010), (010)+ O_{N3} and (010)+ V_{N3} calculated by the HSE functional are shown in Fig. S14d to f, respectively. Similar with the situations in Fig. S13, the DOS curves calculated by HSE in Fig. S14 are also discontinuous, which is ascribed to the insufficient k-points either. However, the charge densities of some labeled states in the PBE results are in good agreement with that in the HSE results. What should be mentioned is the in-gap states in $(010)_{T2}+O_{N3}$ and $(010)_{T2}+V_{N3}$ surfaces. For the simplicity purpose, we use the $(010)_{T2}+O_{N3}$ surface as an example to perform the discussion. Fig. S14h shows the charge densities of the in-gap state in $(010)_{T2}$ +O_{N3} surface calculated by the PBE functional. It is seen that, the charge densities are mainly distributed next to the O_{N3} site. However, due to the delocalized character of the GGA functional, the charge densities are found on more atoms. Based on the HSE functional, the charge densities of the in-gap state in (010)_{T2}+O_{N3} are shown in Fig. S14k. Compared with PBE result in Fig. S14h, the HSE results clearly show that the charge densities of the in-gap state in $(010)_{T2}+O_{N3}$ are localized next to the O_{N3} sites, confirming the PBE results. Similar conclusions can also be arrived in the charge densities in the $(010)_{T2}$ +V_{N3} surface (Fig. S14i and I).

Fig. S15a to c show the DOS of (001), (001)+ O_{N3} and (001)+ V_{N3} , respectively,

calculated by the PBE functional. The DOS results of (001), (001)+ O_{N3} and (001)+ V_{N3} calculated by the HSE functional are shown in **Fig. S15d to f**, respectively. We can see that the charge distributions calculated by the PBE functional (**Fig. S15g and h**) are still in good agreement with that by the HSE functional (**Fig. S15i and j**).

The above comparisons between the PBE and HSE results reveal that, although the PBE functional has its limitations, our calculated electronic structures by the PBE functional are theoretically reliable.



Fig. S13 Calculated DOS of Ta_3N_5 (a) (100), (b) (100)+ O_{N3} and (c) (100)+ V_{N3} surfaces at the PBE level. Calculated DOS of Ta_3N_5 (d) (100), (e) (100)+ O_{N3} and (f) (100)+ V_{N3} surfaces at the HSE level. The vertical dashed line in each case is the Fermi level. The horizontal axes of (100)+ O_{N3} and (100)+ V_{N3} are aligned with that of pure (100) by the electrostatic potential calculations. In each case, the partial charge densities of some labeled states (g to n) are also shown.



Fig. S14 Calculated DOS of Ta_3N_5 (a) $(010)_{T2}$, (b) $(010)_{T2}+O_{N3}$ and (c) $(010)+V_{N3}$ surfaces at the PBE level. Calculated DOS of Ta_3N_5 (d) $(010)_{T2}$, (e) $(010)_{T2}+O_{N3}$ and (f) $(010)_{T2}+V_{N3}$ surfaces at the HSE level. The vertical dashed line in each case is the Fermi level. The horizontal axes of $(010)_{T2}+O_{N3}$ and $(010)_{T2}+V_{N3}$ are aligned with that of pure $(010)_{T2}$ by the electrostatic potential calculations. In each case, the partial charge densities of some labeled states (g to l) are also shown.



Fig. S15 Calculated DOS of Ta₃N₅ (a) $(001)_{T2}$, (b) $(001)_{T2}+O_{N3}$ and (c) $(001)+V_{N3}$ surfaces at the PBE level. Calculated DOS of Ta₃N₅ (d) $(001)_{T2}$, (e) $(001)_{T2}+O_{N3}$ and (f) $(001)_{T2}+V_{N3}$ surfaces at the HSE level. The vertical dashed line in each case is the Fermi level. The horizontal axes of $(001)_{T2}+O_{N3}$ and $(001)_{T2}+V_{N3}$ are aligned with that of pure $(001)_{T2}$ by the electrostatic potential calculations. In each case, the partial charge densities of some labeled states (g to j) are also shown. The green and yellow charge densities correspond to the holes and electrons occupied states, respectively. For the visualization purpose, the slab in (g) to (j) is extended by two times.

SI-9 Adsorption energy calculation details

The adsorption energy is defined as:

$$E_{ads} = E_{slab} + E_{Cl} - E_{Cl/slab}$$
(S20)

where $E_{Cl/slab}$ and E_{slab} are total energies of the slab with and without Cl adsorption, respectively, and E_{Cl} is the total energy of one Cl atom. Note that, to ensure the reliability of calculated adsorption energies, the cell sizes for calculating $E_{Cl/slab}$, E_{slab} and E_{Cl} should be identical. **Fig. S16** shows the initial atomic structures of Cl adsorption on (100)+O_{N3}, (010)_{T2}+O_{N3} and (001)_{T2}+O_{N3}.



Fig. S16 The initial atomic structures of Cl adsorption on $(100)+O_{N3}$, $(010)_{T2}+O_{N3}$ and $(001)_{T2}+O_{N3}$. For the visualization purpose, the atomic structures of Cl adsorption on $(001)_{T2}+O_{N3}$ are extended by two times.

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