Supporting Information

For

Effects of Ba-O codoping on the photocatalytic activities of Ta_3N_5 photocatalyst: a DFT study

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SI-1 Chemical potentials of N, O, Ba and Ta

The chemical potentials of N, O, Ba and Ta are calculated by two steps: First, we calculate the chemical potentials of N ($\Delta\mu_N$) and Ta ($\Delta\mu_{Ta}$). Under thermal equilibrium growth conditions, Ta_3N_5 should satisfy:

$$3\Delta\mu_{Ta} + 5\Delta\mu_N = E^f_{Ta_3N_5} = -8.47eV \quad \text{(S1)}$$

where $E^f_{Ta_3N_5}$ is the calculated formation energy of the undoped Ta_3N_5. Then, $\Delta\mu_N$ and $\Delta\mu_{Ta}$ under different growth conditions can be determined: under Ta-rich (N-poor) growth condition, $\Delta\mu_N$ = -1.69 and $\Delta\mu_{Ta}$ =0 eV; under N-rich (Ta-poor) growth condition, $\Delta\mu_N = 0$ and $\Delta\mu_{Ta}$ =-2.82 eV.

Second, we calculate chemical potentials of the two doped elements, Ba ($\Delta\mu_{\mathrm{Ba}}$) and O ($\Delta\mu_O$). In the doped materials, precipitation of secondary phases should be avoided.[1] For the Ba-O codoped Ta_3N_5, precipitation of secondary phases such as Ta_2O_5, TaON, BaO, BaN_6, BaN_2O_6, Ba_2TaN_3, N_2 gas, O_2 gas, bulk Ba and bulk Ta must be avoided:

$$5\Delta\mu_O + 2\Delta\mu_{Ta} < E^f_{Ta2O5} = -20.20eV \quad \text{(S2)}$$

$$\Delta\mu_N + \Delta\mu_O + \Delta\mu_{Ta} < E^f_{TaON} = -5.79eV \quad \text{(S3)}$$

$$\Delta\mu_{\mathrm{Ba}} + \Delta\mu_O < E^f_{BaO} = -4.97eV \quad \text{(S4)}$$

$$\Delta\mu_{Ba} + 6\Delta\mu_N < E^f_{BaN6} = -1.39eV \quad \text{(S5)}$$

$$\Delta\mu_{Ba} + 2\Delta\mu_N + 6\Delta\mu_O < E^f_{BaN2O6} = -10.25eV \quad \text{(S6)}$$

$$2\Delta\mu_{Ba} + \Delta\mu_{Ta} + 3\Delta\mu_N < E^f_{Ba2TaN3} = -6.50eV \quad \text{(S7)}$$

$$\Delta\mu_{\mathrm{N}} < 0, \Delta\mu_O < 0, \Delta\mu_{\mathrm{Ba}} < 0, \Delta\mu_{Ta} < 0 \quad \text{(S8)}$$

where $E^f_{Ta_2O_5}$, E^f_{TaON}, E^f_{BaO}, E^f_{BaN6}, E^f_{BaN2O6} and $E^f_{Ba2TaN3}$ are formation energies of Ta_2O_5, TaON, BaO, BaN_6, BaN_2O_6 and Ba_2TaN_3, respectively. Based on the above inequations (S2)-

(S8), we can calculate the chemical potentials of Ba and O under Ta-rich and N-rich growth conditions, which are shown in Fig. S1(a) and S1(b), respectively. It can be seen that, to simultaneously avoid precipitation of all secondary phases, the values of $\Delta\mu_{\mathrm{Ba}}$ and $\Delta\mu_O$ can only be selected in the accessible regions [shaded in Fig. S1(a) and S1(b)]. In the accessible regions, the values of $\Delta\mu_{\mathrm{Ba}}$ and $\Delta\mu_O$ under Ti-rich and N-rich growth conditions are selected at the blue points in Fig. S1(a) and S1(b), respectively, because formation energies of Ba_{Ta}+$3O_N$ at the blue points are relatively smaller. This means that the codoped concentrations of Ba and O at the blue points are larger. Under the Ti-rich condition, $\Delta\mu_{\mathrm{Ba}}$ = -0.87 and $\Delta\mu_O$ = -4.10 eV; under the N-rich condition; $\Delta\mu_{\mathrm{Ba}}$ = -2.00 and $\Delta\mu_O$ = -2.97 eV.

SI-2 The S_{bottom} term

In geometry relaxation of the undoped, O_N-doped, Ba_{Ta}-doped, Ba_{Ta}+O_N codoped, Ba_{Ta}+$2O_N$ codoped and Ba_{Ta}+$3O_N$ codoped Ta_3N_5 (100) surfaces, the two bottom atomic layers are fixed while other layers are allowed relaxation. This slab model is the non-symmetrical structure. After geometry relaxation, the atomic structure of the bottom surface is different from that of the top surface, and thus surface energy of the bottom surface is also different from that of the top surface. Therefore, to obtain the surface energy of the top surface, which is exactly what we really concern, the surface energy of the fixed bottom surface, i.e., the S_{bottom}, must be subtracted. The S_{bottom} is defined as:[2,3]

$$S_{\mathrm{bottom}} = (E_{slab} - n_N\Delta\mu_N - n_{Ta}\Delta\mu_{Ta})/(2A) \quad \text{(S9)}$$

where n_i and $\Delta\mu_i$ (i=N, Ta) are the number and chemical potential of constituent *i*, respectively, and A (106.81 Å^2) is the surface area of the slab model. The E_{slab} term in

equation (S9) is calculated by using of the undoped Ta_3N_5 (100) surface model WITHOUT any geometry relaxations. Since the two sides of the non-relaxed Ta_3N_5 (100) surface model are completely identical, the term "2" should be divided.

To assure the reliability of our calculated surface energies, we also calculate surface energies of the undoped and O_N-doped Ta_3N_5 (100) surfaces using the symmetrical slab model. The symmetrical slab model is constructed by eleven Ta_6N_{10} atomic layers. In the process of geometry relaxations, the central Ta_6N_{10} atomic layer is fixed while the rest five Ta_6N_{10} atomic layers on each side of the slab model are allowed to relax. The calculated surface energies using the symmetrical and non-symmetrical slab models are listed in Table S1. It can be seen that, the surface energies calculated by the symmetrical slab model are in good agreement with that by the non-symmetrical model. This means that the seven non-symmetrical slab model is sufficient in this study, and the method of subtraction the S_{bottom} term in surface energy calculation is reasonable.

SI-3 Atomic structures of the $Ba_{Ta}+O_N$, $Ba_{Ta}+2O_N$ and $Ba_{Ta}+3O_N$ models

The Fig. S2 shows the atomic structure of the Ta_3N_5 surpercell. It can be seen that, the Ta atom is coordinated with six N atoms. Among the six N atoms in the Ta-N octahedron, four N atoms are the 4-coordinated N atoms while the other two N atoms are the 3-coorindated N atoms. Note that, the position of the N_a is EQUIVALENT to that of the N_b. Although many N atoms in this supercell can be substituted by the O atom, only N atoms in the Ta-N octahedron are substituted in this study for simplicity purpose. Since both theoretical calculations[3] and experiments[4] have proved that the 3-corridnated N atom is easily substituted

by the O atom, the O_N impurities in Ba_{Ta}+O_N and Ba_{Ta}+$2O_N$ are simulated by substitution of O atoms for the 3-coordinated N atoms.

We use the Fig. S3 to illustrate configurations of all possible Ba_{Ta}+$3O_N$ codoped bulk Ta_3N_5 structures. For clarity purpose, four N atoms are denoted as the 'plane' atoms, while the left two N atoms are denoted as the 'point' atoms. As shown in the Fig. S2, positions of the two 'point' N atoms are equivalent to each other. Then, substitutions of three O atoms for three N atoms can be divided into three conditions:

First, zero 'point' N atoms are substituted by O atoms, while three 'plane' N atoms are substituted by three O atoms, which can be simply denoted as '0point+3plane'. There are four possible configurations of '0point+3plane'. The second and third conditions are '1point+2plane' and '2point+1plane', which include six and four possible atomic configurations, respectively. Moreover, the total energies (relative to the total energy of the undoped Ta_3N_5) of all 14 configurations are listed in the following Table S2, which is helpful for readers to make a direct and in-depth understanding. It can be seen that, the total energy of the atomic configuration (h) is relatively smaller among all considered configurations. Therefore, the configuration (h) is adopted to simulate the Ba_{Ta}+$3O_N$ codoped bulk Ta_3N_5 in our study.

SI-4 Atomic structures of the (100)+O_N, (100)+Ba_{Ta}+O_N, (100)+Ba_{Ta}+$2O_N$ and (100)+Ba_{Ta}+$3O_N$ surface models

As can be seen in Fig. S4, on the Ta_3N_5 (100) surface, one 'point' N atom is removed and thus the Ta atom is now coordinated with five N atoms. Then, all possible configurations of the Ba_{Ta}+$3O_N$ codoped Ta_3N_5 (100) surface are shown in Fig. S5. It can be seen that, the substitutions of three O atoms for three N atoms on Ta_3N_5 (100) surface can be divided into '0point+3plane' and '1point+2plane', which include four and six atomic configurations, respectively. Furthermore, the total energies (relative to the total energy of the undoped Ta_3N_5 (100) surface) of all 10 configurations are listed in the following Table S3. It can be seen that, the total energy of the atomic configuration (c) is relatively smaller among all considered configurations. Therefore, the configuration (c) is adopted to simulate the Ba_{Ta}+$3O_N$ codoped Ta_3N_5 (100) surface in our work.

References

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2. L. Liu, W. Fan, X. Zhao, H. Sun, P. Li and L. Sun, *Langmuir*, 2012, 28, 10415-10424.
3. J. Wang, W. Luo, J. Feng, L. Zhang, Z. Li and Z. Zou, *Phys. Chem. Chem. Phys.*, 2013, 15, 16054-16064.
4. S. J. Henderson and A. L. Hector, *J. Solid State Chem.*, 2006, 179, 3518-3524.

Table S1. Surface energies of the undoped and O_N-doped Ta_3N_5 (100) surface calculated using the non-symmetry and symmetry slab surface models. Surface energies under two growth conditions, Ta-rich and N-rich, are shown.

Slab model	Growth condition	Surface energies (J/m^2)	
		(100)	(100)+O_N
non-symmetry	Ta-rich	1.22	1.10
	N-rich	1.22	1.19
symmetry	Ta-rich	1.23	1.13
	N-rich	1.23	1.22

Table S2 total energies (relative to the total energy of the undoped Ta_3N_5) of all 14 configurations in Fig. S3.

Configurations	Total energy (eV)	Configurations	Total energy (eV)
(a)	3.66	**(h)**	**3.10**
(b)	3.60	(i)	3.59
(c)	3.43	(j)	3.42
(d)	3.27	(k)	3.41
(e)	3.33	(l)	3.53
(f)	3.63	(m)	3.65
(g)	3.42	(n)	3.38

Table S3 total energies (relative to the total energy of the undoped Ta_3N_5 (100) surface) of all 10 configurations in Fig. S5.

Configurations	Total energy (eV)	Configurations	Total energy (eV)
(a)	3.02	(f)	3.75
(b)	2.97	(g)	3.43
(c)	**2.41**	(h)	3.23
(d)	2.70	(i)	3.54
(e)	3.59	(j)	3.80

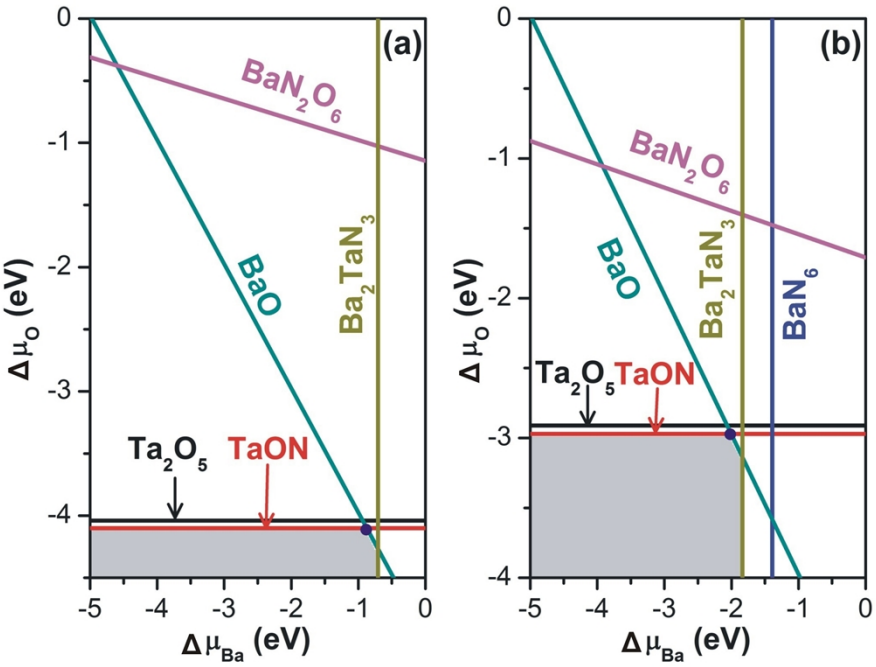

Fig. S1 (Color online) Chemical potentials of $\Delta\mu_{\mathrm{Ba}}$ and $\Delta\mu_O$ at the (a) Ta-rich and (b) N-rich growth conditions. The shaded areas in (a) and (b) are the accessible range of chemical potentials of Ba and O for equilibrium growth of the Ba-O codoped Ta_3N_5. In (a), the values at the blue point are selected for $\Delta\mu_{\mathrm{Ba}}$ and $\Delta\mu_O$ under the Ti-rich condition. In (b), the values at the blue point are selected for $\Delta\mu_{\mathrm{Ba}}$ and $\Delta\mu_O$ under the N-rich condition.

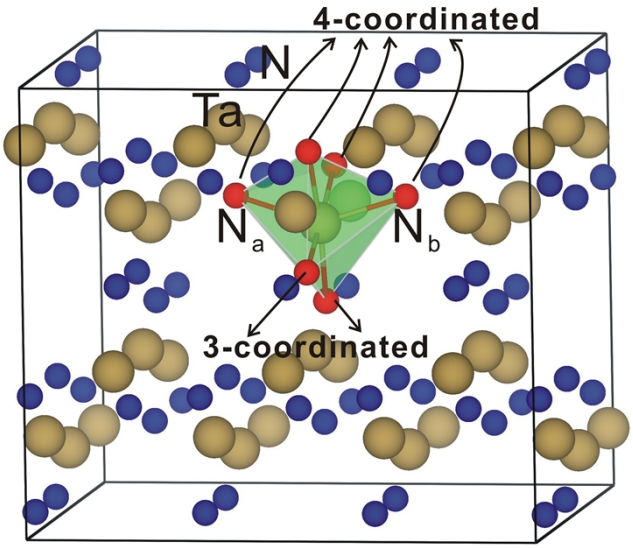

Fig. S2 (Color online) Atomic structure of the 3×3×1 Ta_3N_5 surpercell. In this supercell, the Ta atom is coordinated with six N atoms. Among the six N atoms in the Ta-N octahedron, four N atoms are the 4-coordinated N atoms while other two N atoms are the 3-coorindated N atoms. The position of the N_a is equivalent to that of the N_b.

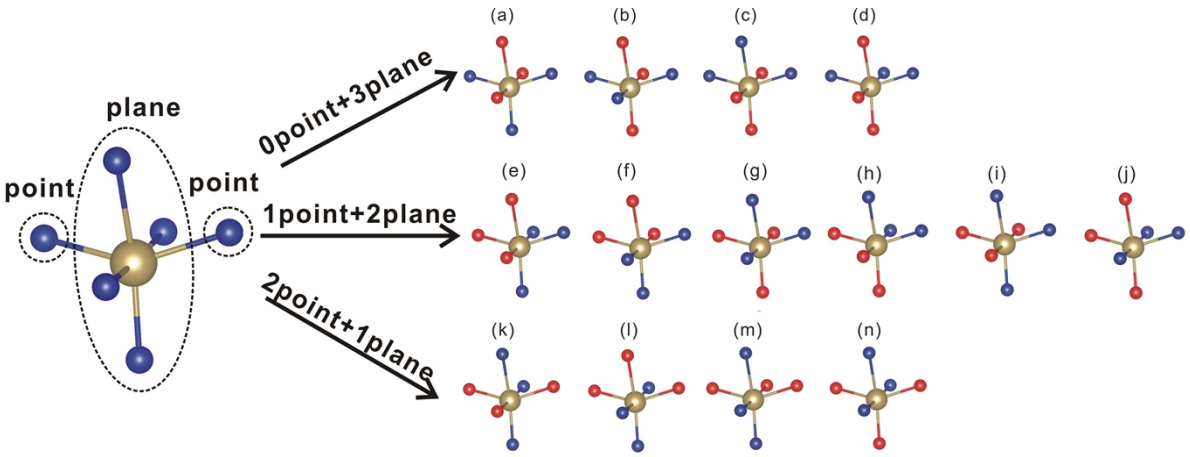

Fig. S3 (Color online) Schematic diagram of the configurations of the $3O_N$-doped bulk Ta_3N_5 structures. The yellow, blue and red balls are Ta, N and O atoms, respectively.

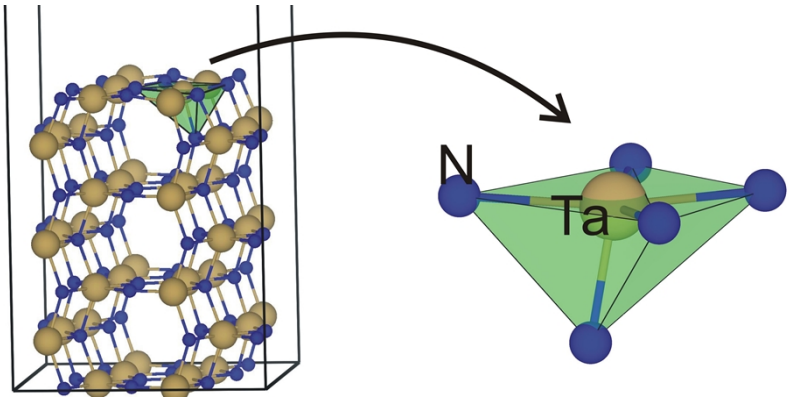

Fig. S4 (Color online) Atomic structure of the Ta_3N_5 (100) surface. On the top surface, the Ta atom is coordinated with five N atoms.

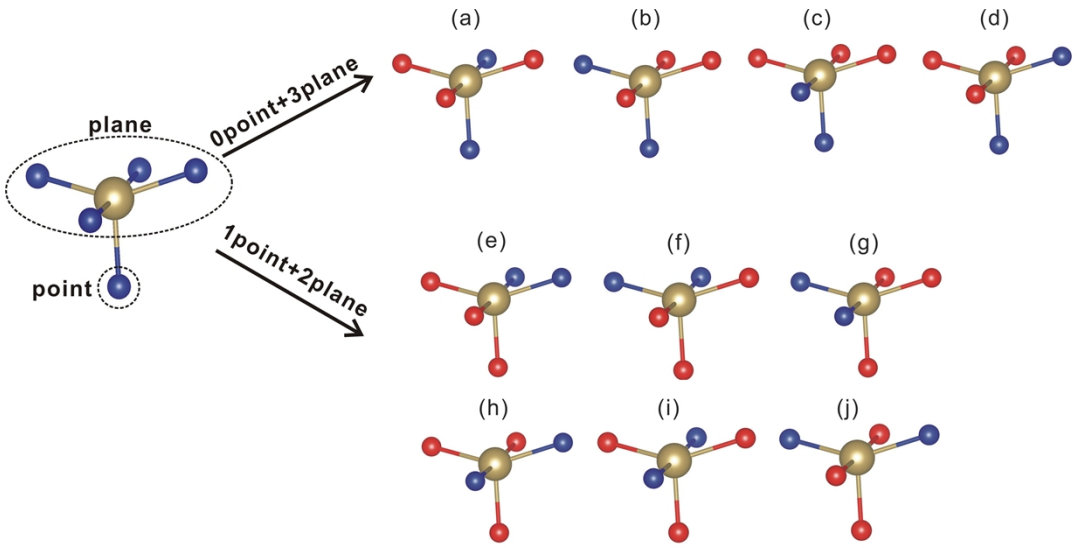

Fig. S5 (Color online) Schematic diagram of the configurations of the $3O_N$-doped Ta_3N_5 (100) surface. The yellow, blue and red balls are Ta, N and O atoms, respectively.