SUPPORTING INFORMATION

Electronic Structures of Anatase $(TiO_2)_{1-x}(TaON)_x$ Solid Solutions: First-Principles Study

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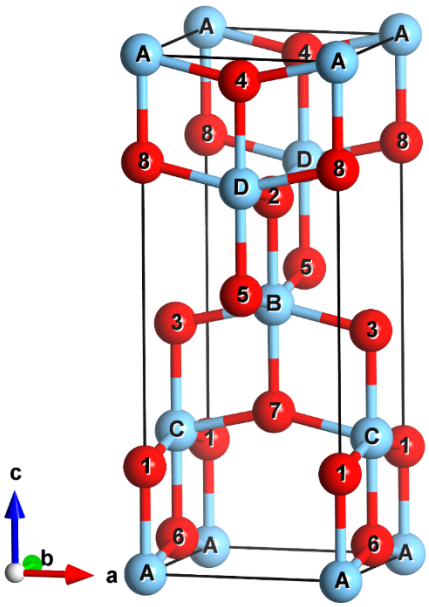

Fig. S1. The positions of ions. The positions of cations are labeled as A, B, C and D. The positions of anions are labeled from1 to 8.

The atomic configuration distinctly affects the thermodynamic stability, as well as the band gap. For all of the possible configurations of solid solutions (x=0.25, 0.5, 0.75) except the situations in which the N and Ta are separated, the band gap and total energy were calculated as presented in table S1. In table S1, the positions of cations are labeled as A, B, C and D, while the positions of anions are labeled from1 to 8 as shown in Fig. S1. We can see that the most stable configurations have the lowest total energy and the largest band gap (colored in green for easier read). The structures, which possess exceptionally narrow band gap, have the highest energy in most cases.

Table S1 (a). Band gap and total energy of $(TiO_2)_{0.75}(TaON)_{0.25}$ solid solutions with different atomic configuration. The total energy of the most stable model is set to zero for reference.

Position of Ta	Position of N	Total energy (eV)	Band gap(eV)	Notes
B	5	0	1.423975	Fig. 1 (b)
	2	0.09029	1.370039	
	8	0.17693	1.243925	
	4	0.09126	1.228378	

Table S1 (b). Band gap and total energy of $(TiO_2)_{0.5}(TaON)_{0.5}$ solid solutions with different atomic configuration. The total energy of the most stable model is set to zero for reference.

Position of Ta	Position of N	Total energy (eV)	Band gap(eV)	Notes
B, D	5, 7	0.20468	1.183163	
	3, 5	0.22014	1.147106	
	2, 5	0.22465	0.396382	Fig. 7 (a)
	3, 7	0.55961	0.231648	
	2, 7	0.5134	0.874240	
	4, 7	0.26864	1.503967	
	7, 8	0.2782	1.544749	
	2, 3	0.21284	1.398299	
	3, 8	0.38411	1.489194	
C, D	3, 4	0.44686	1.521448	
	7, 8	0	1.628186	Fig. 1 (c)
	2, 7	0.52215	0.829508	
	3, 8	0.27969	1.433617	
	1, 7	0.04254	1.350099	
	3, 5	0.55188	1.097990	
	4, 5	0.86962	0.777211	
	4, 8	0.52686	0.122396	
	2, 4	0.32356	1.169937	
	5, 7	0.37496	1.230466	

Table S1 (c). Band gap and total energy of $(TiO_2)_{0.25}(TaON)_{0.75}$ solid solutions with different atomic configuration. The total energy of the most stable model is set to zero for reference.

Position of Ti	Position of N	Total energy (eV)	Band gap(eV)	Notes
A	2,5,7	0.46235	0.241885	
	2,5,6	0.21415	0.713636	
	1,5,8	0.64549	1.149371	
	4,2,7	0.39487	1.166088	
	2,3,5	0.2677	0.377061	
	1,2,5	0.11652	0.679925	
	3,5,8	0.20477	0.894403	
	5,7,8	0	1.570878	Fig. 1 (d)
	5,6,8	0.32884	1.372789	
	1,2,4	0.16805	1.357091	
	2,3,4	0.10852	1.334264	
	2,4,6	0.2559	1.191956	
	2,3,8	0.03628	1.079608	
	2,7,8	0.19981	1.184573	
	1,2,8	0.43653	1.130659	
	2,6,8	0.21157	1.052686	
	3,4,5	0.56542	0.992160	
	4,5,7	0.4792	1.067938	
	1,4,5	0.70082	1.121656	
	4,5,6	0.68986	1.083891	
	3,4,8	0.46585	0.370351	
	4,7,8	0.30013	0.389891	
	1,4,8	1.14529	0	
	4,6,8	0.75996	0.105370	
	2,4,8	0.38568	0.323204	
	4,5,8	0.87453	0.130361	
	2,4,5	0.7536	0.167372	
	2,5,8	0.24734	0.544718	

Table S1 (d). Band gap and total energy of TaON with different atomic configuration. The total energy of the most stable model is set to zero for reference.

Position of N	Total energy (eV)	Band gap(eV)	Notes
1,2,5,6	0.19197	0.895461	
2,3,5,7	1.02647	0	
3,4,5,6	0.74614	0.969210	
2,4,6,7	0.51426	0.721709	
2,3,4,6	0.44281	1.024072	
1,2,3,4	0	1.545430	Fig. 1 (e)

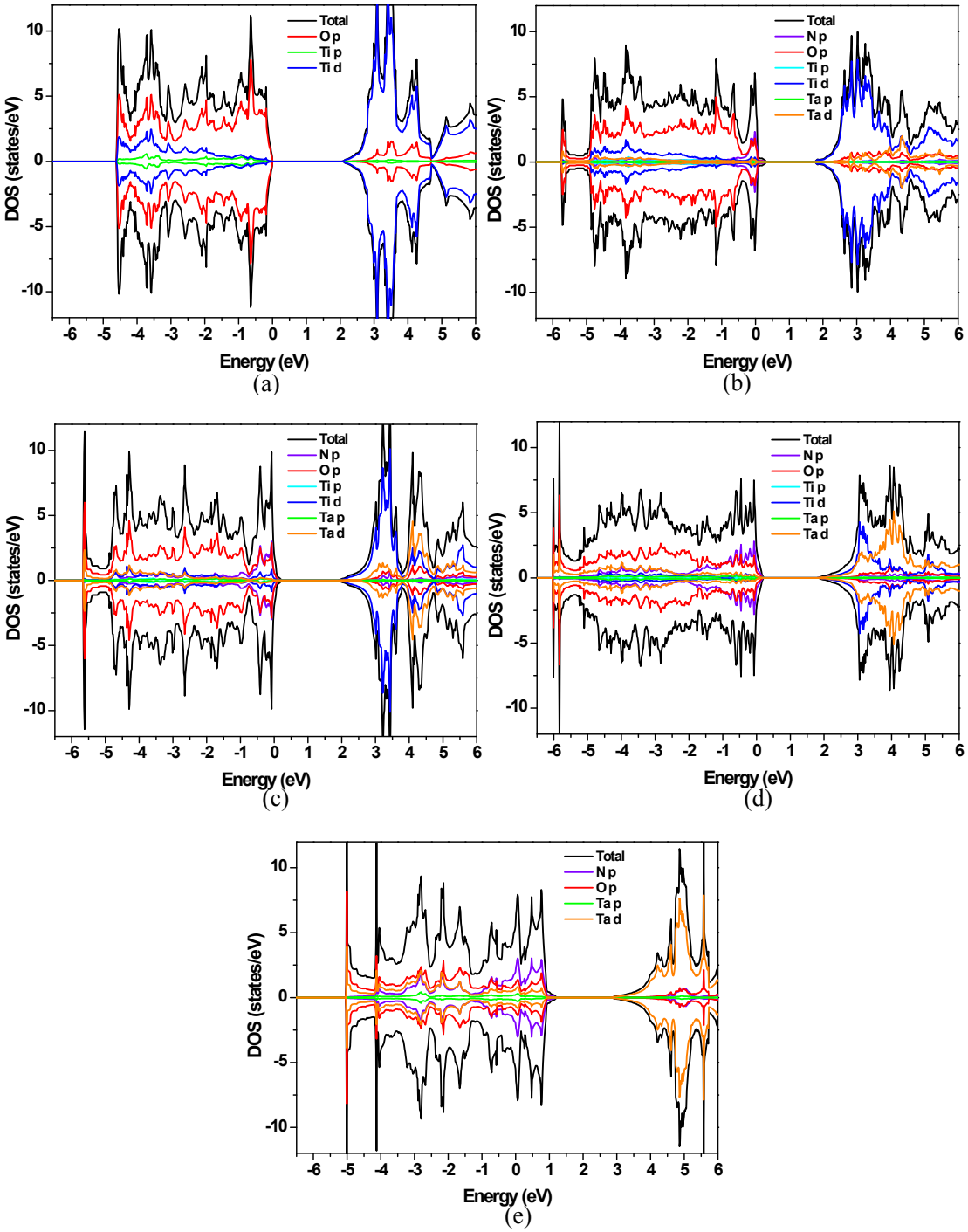

Fig. S2. Total density of states (TDOS) and partial density of states (PDOS) of (TiO2)1-x(TaON)x when x=0(a), 0.25(b) , 0.5(c), 0.75(d) and 1.0(e). The zero energy is at the valence band maximum of pristine TiO_2.

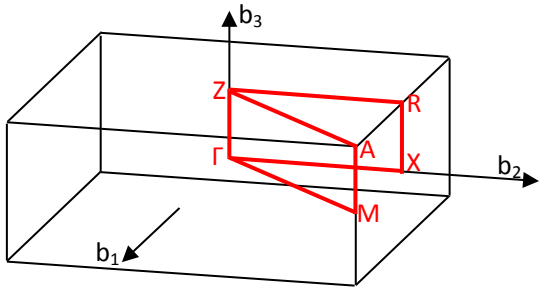

Fig. S3. High symmetry lines of Brillouin zone.

In order to explain the difference of photocatalytic performance between TiO_2 and solid solutions, the effective mass of electrons along selected directions in the Brillouin zone (see Fig. S3) was calculated by fitting parabolic functions around the CBM or the VBM according to the following equations:

$$m^* = \hbar^2\left(\frac{d^2E_k}{dk^2}\right)^{-1}$$

where m* is the effective mass of the charge carrier, k is the wave vector, and E_k is the energy corresponding to the wave vector k. The obtained results are summarized in Table S2.

Table S2. Effective mass of CBM electrons and VBM holes obtained from parabolic fitting to the CBM and VBM along selected directions in the Brillouin zone. The unit is the mass of a bare electron. The VBM of TiO_2 slightly deviates from M to M' (Figure 5a).

x		$m^*_{\Gamma\to X}$	$m^*_{\Gamma\to Z}$	$m^*_{\Gamma\to M}$	$m^*_{M'\to M}$	$m^*_{M'\to\Gamma}$	$m^*_{Z\to R}$
0	CBM	0.420	3.975	0.401			
	VBM				2.789	1.418	
0.25	CBM	0.384	5.968	0.410			
	VBM						0.259
0.5	CBM	0.413	3.075	0.300			
	VBM	0.897	4.156	0.434			
0.75	CBM	0.309	2.619	0.266			
	VBM	0.381	4.455	0.459			
1	CBM	0.268	2.188	0.256			
	VBM	0.525	1.116	0.405			

In order to compare the absorption coefficient of the materials, we calculated the absorption coefficient spectra. Optical properties are determined by the frequency dependent complex dielectric function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$. The corresponding absorption coefficient was estimated using the following equation:

$$\alpha = \frac{\varepsilon_2(\omega)\omega}{n(\omega)c},$$

where $n = \sqrt{\frac{\varepsilon_1(\omega) + \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2}}$ is the real part of the refractive index, c represents the speed of light in vacuum.

The plane wave cut-off energy was 500 eV and a 15×15×7 grid of Monkhorst-pack points were employed for optical calculation. In order to get the reasonable results, we tripled the number of band states (148 empty conduction band states, 192 band states in total), since the method requires an appreciable number of empty conduction band states.

Fig. S4 shows the calculated optical absorption coefficient spectra. These curves indicate that the absorption edges of the solid solutions red shift with respect to that of the pristine TiO_2. In addition, the absorption coefficients of the solid solutions are larger in the range near the absorption edges, which indicates that the solid solutions exhibit distinct merit against their end-members.

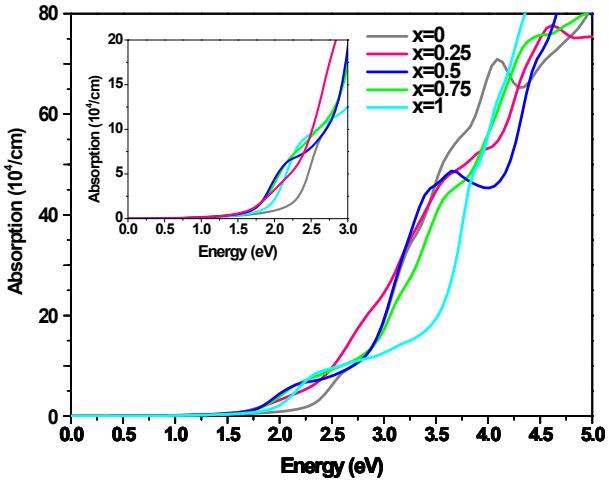

Fig. S4. Absorption coefficient spectra obtained from the average over the *x*, *y* and z components of the real and imaginary parts of the dielectric functions.