Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Suppression of Charge Carrier Recombination in Ta_3N_5 Photoanode via Defect Regulation

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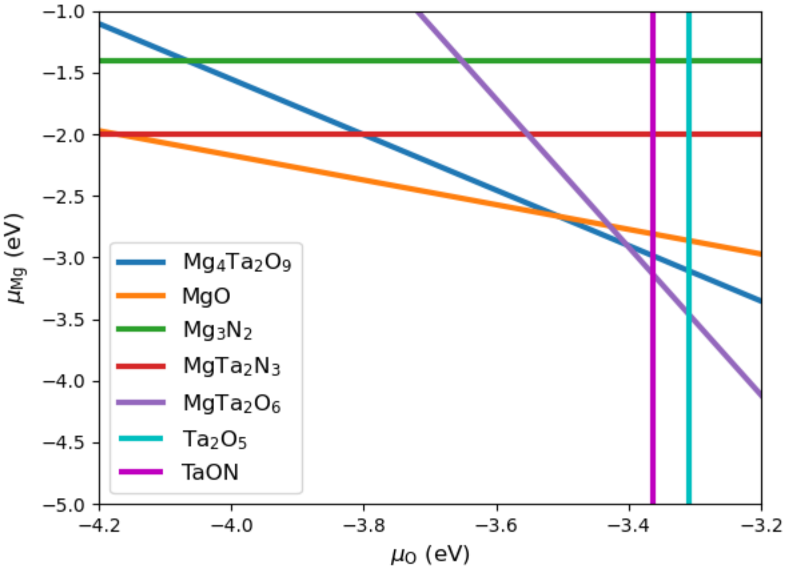

Figure S1: Chemical potentials of Mg and O co-doped Ta_3N_5 system under N-rich region.

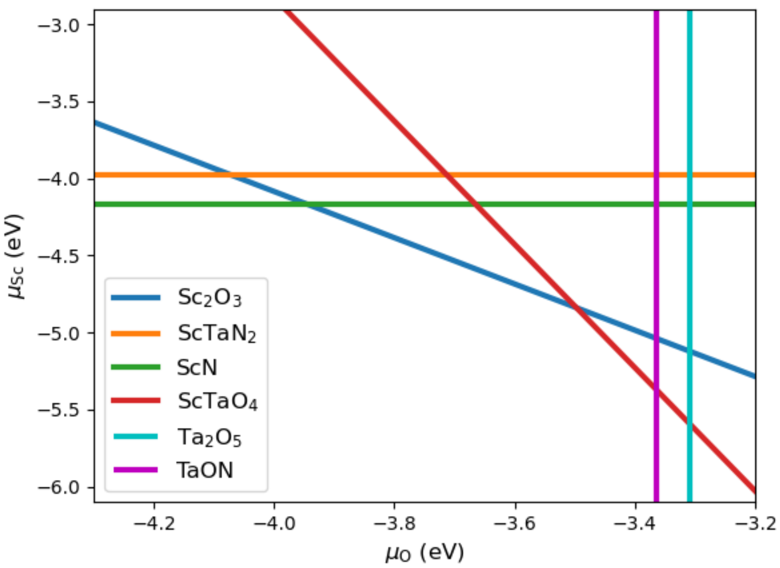

Figure S2: Chemical potentials of Sc and O co-doped Ta_3N_5 system under N-rich region.

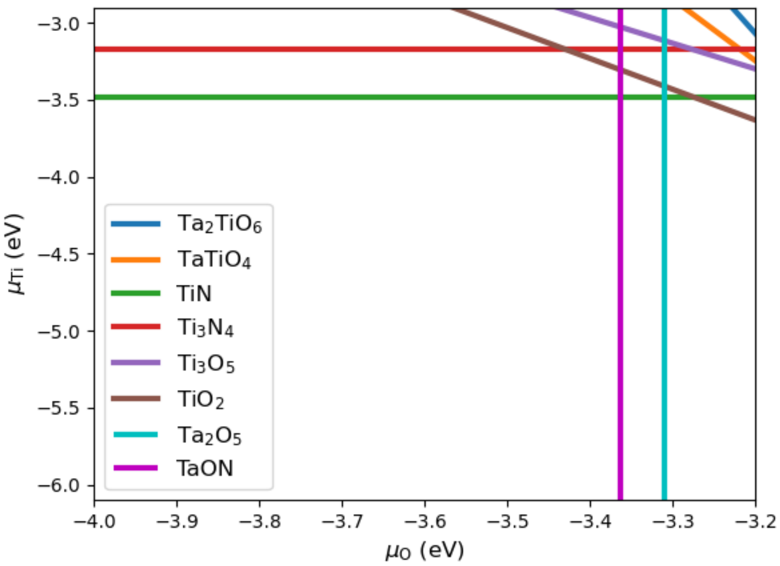

Figure S3: Chemical potentials of Ti and O co-doped Ta_3N_5 system under N-rich region.

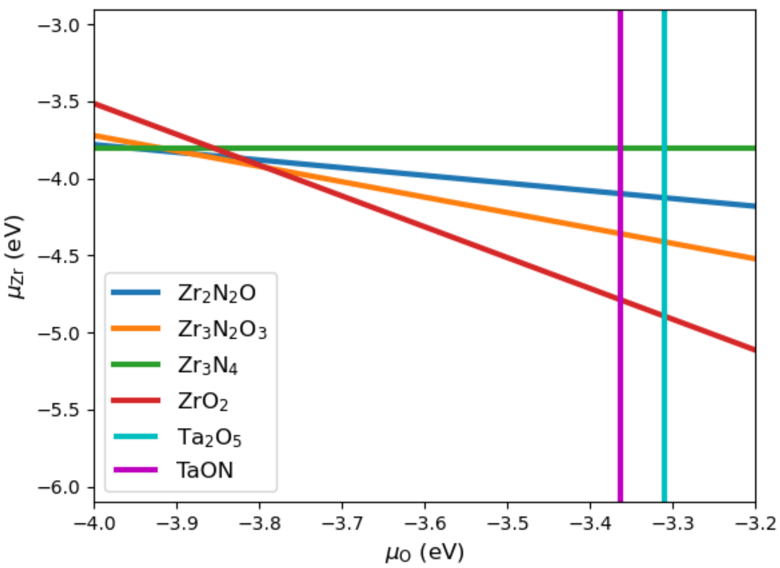

Figure S4: Chemical potentials of Zr and O co-doped Ta_3N_5 system under N-rich region.

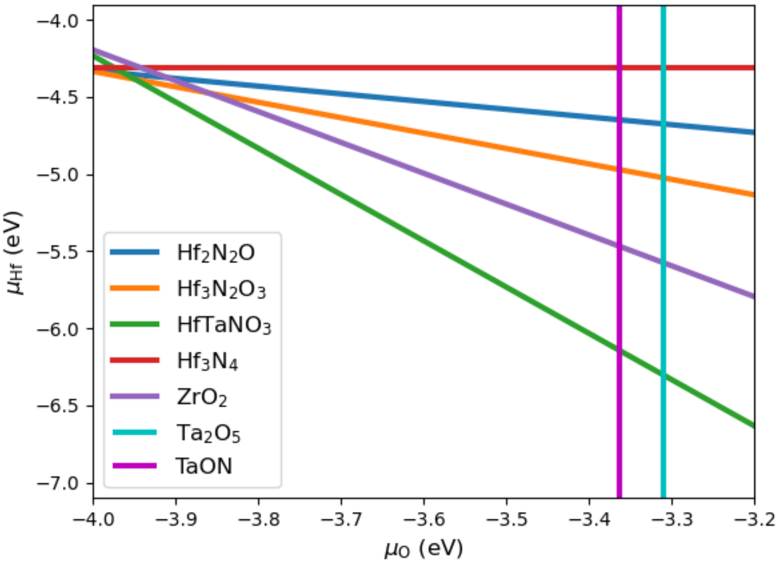

Figure S5: Chemical potentials of Hf and O co-doped Ta_3N_5 system under N-rich region.

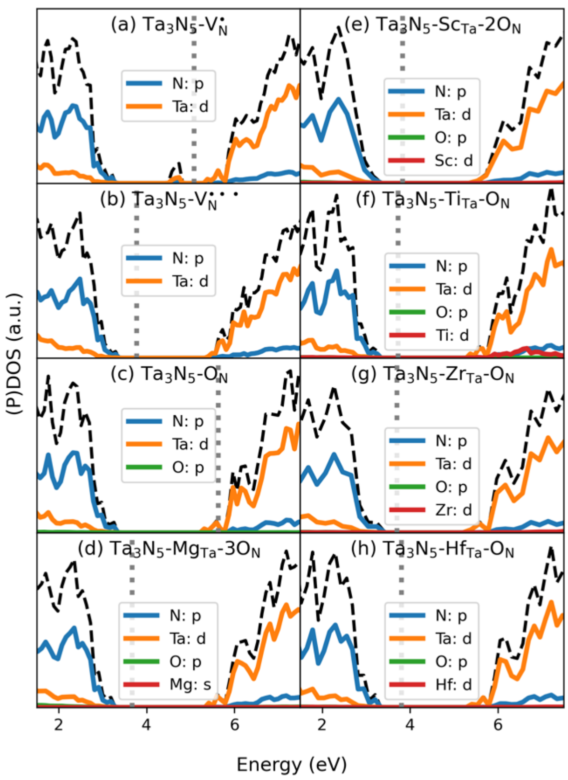

Figure S6: (P)DOS of (a) Ta_3N_5-$V_N^{\bullet}$, (b) Ta_3N_5-$V_N^{\bullet\bullet\bullet}$, (c) Ta_3N_5-O_N, (d) Ta_3N_5-Mg_{Ta}-$3O_N$, (e) Ta_3N_5-Sc_{Ta}-$2O_N$, (f) Ta_3N_5-Ti_{Ta}-O_N, (g) Ta_3N_5-Zr_{Ta}-O_N, and (h) Ta_3N_5-Hf_{Ta}-O_N. The vertical gray line is the Fermi energy (eV) and the dashed black line is the total DOS.

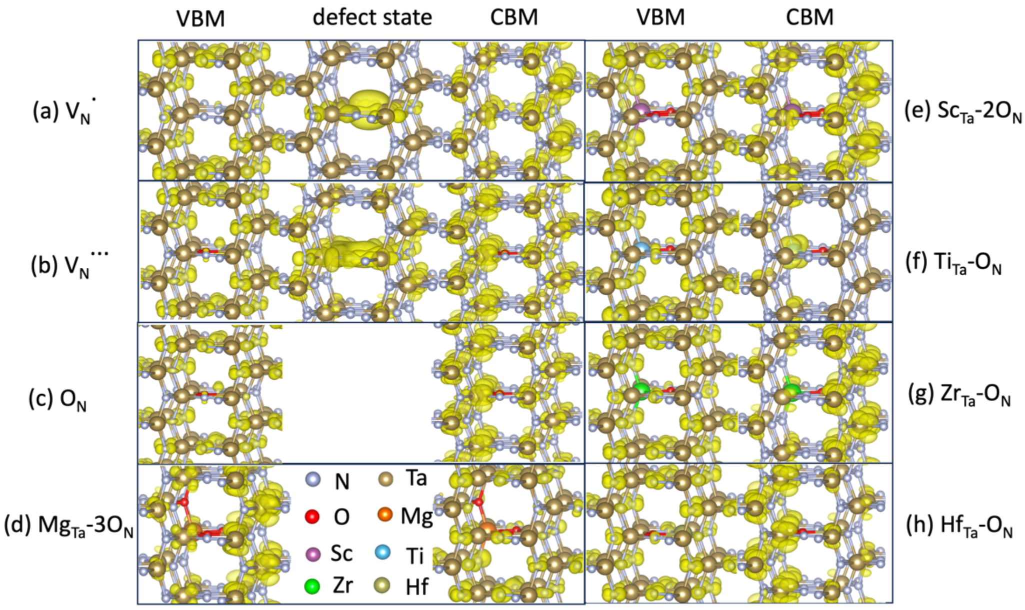

Figure S7: Partial electron densities of (a) Ta_3N_5-$V_N^{\cdot}$, (b) Ta_3N_5-$V_N^{\cdot\cdot\cdot}$, (c) Ta_3N_5-O_N, (d) Ta_3N_5-Mg_{Ta}-$3O_N$, (e) Ta_3N_5-Sc_{Ta}-$2O_N$, (f) Ta_3N_5-Ti_{Ta}-O_N, (g) Ta_3N_5-Zr_{Ta}-O_N, and (h) Ta_3N_5-Hf_{Ta}-O_N.

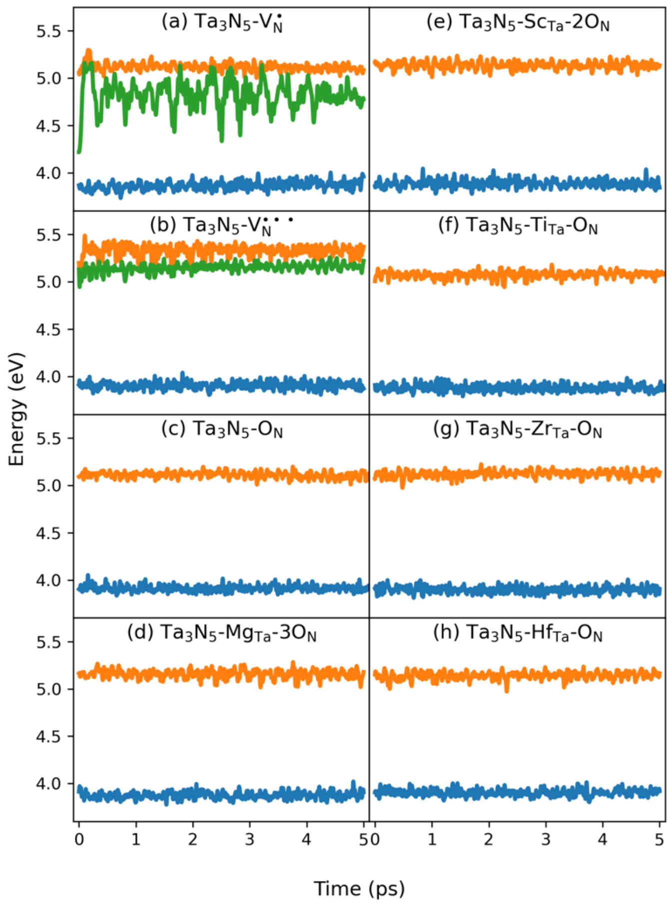

Figure S8: Time evolution of the VBM, CBM and the defect state of (a) Ta_3N_5-$V_N^{\cdot}$, (b) Ta_3N_5-$V_N^{\cdot\cdot\cdot}$, (c) Ta_3N_5-O_N, (d) Ta_3N_5-Mg_{Ta}-$3O_N$, (e) Ta_3N_5-Sc_{Ta}-$2O_N$, and (f) Ta_3N_5-Ti_{Ta}-O_N, (g) Ta_3N_5-Zr_{Ta}-O_N, and (h) Ta_3N_5-Hf_{Ta}-O_N. The green lines are the energies of the defect level.

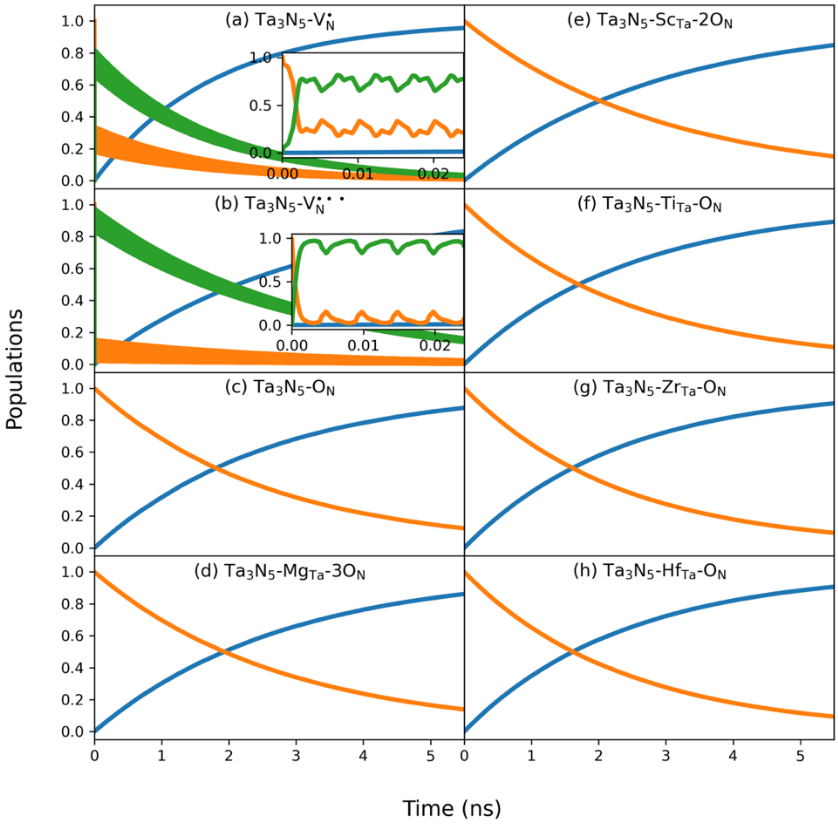

Figure S9: Time-dependent state population evolutions of (a) Ta_3N_5-$V_N^{\cdot}$, (b) Ta_3N_5-$V_N^{\cdot\cdot\cdot}$, (c) Ta_3N_5-O_N, (d) Ta_3N_5-Mg_{Ta}-$3O_N$, (e) Ta_3N_5-Sc_{Ta}-$2O_N$, (f) Ta_3N_5-Ti_{Ta}-O_N, (g) Ta_3N_5-Zr_{Ta}-O_N, and (h) Ta_3N_5-Hf_{Ta}-O_N. The blue lines are VBM populations, while the orange lines and green lines are those of CBM and defect state, respectively.

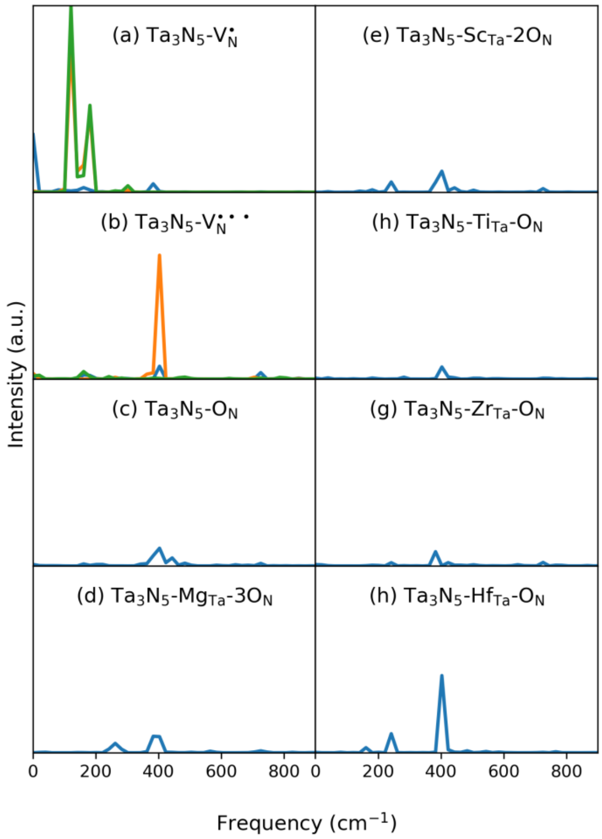

Figure S10: FT spectra of autocorrelation functions of the time evolution at 300K of (a) Ta_3N_5-$V_N^{\bullet}$, (b) Ta_3N_5-$V_N^{\bullet\bullet\bullet}$, (c) Ta_3N_5-O_N, (d) Ta_3N_5-Mg_{Ta}-$3O_N$, (e) Ta_3N_5-Sc_{Ta}-$2O_N$, (f) Ta_3N_5-Ti_{Ta}-O_N, (g) Ta_3N_5-Zr_{Ta}-O_N, and (h) Ta_3N_5-Hf_{Ta}-O_N.

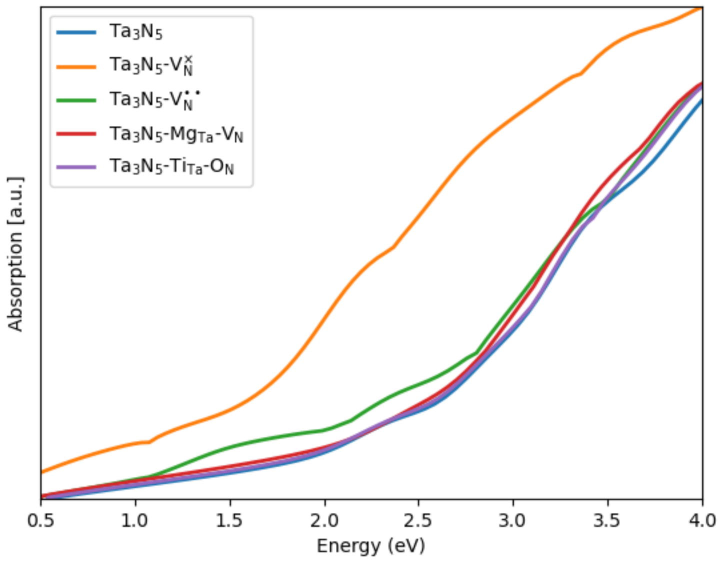

Figure S11: Light absorption coefficients of Ta_3N_5, Ta_3N_5-$V_N^{\times}$, Ta_3N_5-$V_N^{\cdot\cdot}$, Ta_3N_5-Mg_{Ta}-$V_N^{\times}$, and Ta_3N_5-Ti_{Ta}-O_N systems.

Table S1: e−h recombination time, NACs, dephasing time, and Bader charges of Ta atoms in Figure 1(c) of Ta_3N_5 with doping metal and oxygen atoms. The transition state is CBM to VBM.

	e−h recombination time (ns)	NACs (meV)	Dephasing time (fs)	Bader charge of Ta^1	Bader charge of Ta^2	Bader charge of Ta^3
Ta_3N_5-$V_N^{\cdot}$	1.75	1.22	11.33	2.14	2.10	2.34
Ta_3N_5-$V_N^{\cdot\cdot\cdot}$	3.07	0.84	10.5	2.42	2.37	2.40
Ta_3N_5-O_N	2.62	1.34	17.35	2.46	2.46	2.48
Ta_3N_5-Mg_{Ta}-$3O_N$	2.78	1.35	12.51	2.46	2.47	2.49
Ta_3N_5-Sc_{Ta}-$2O_N$	2.41	1.33	13.09	2.47	2.48	2.49
Ta_3N_5-Ti_{Ta}-O_N	2.46	1.35	16.78	2.47	2.47	2.48
Ta_3N_5-Zr_{Ta}-O_N	2.33	1.39	15.96	2.46	2.47	2.49
Ta_3N_5-Hf_{Ta}-O_N	2.33	1.36	14.02	2.46	2.47	2.49

Table S2: Bader charges of N atoms in Figure 1(c) and NACs of Ta_3N_5 systems with doping metal and N vacancies (different charge states). The first transition state with superscript 1 is between VBM and the defect state, and superscript 2 is between the defect state and CBM. The superscripts of N are consistent with the labels in Figure 1.

	Bader charge of N^1	Bader charge of N^2	Bader charge of N^3	Bader charge of N^4
Ta_3N_5	1.40	1.40	1.53	1.55
Ta_3N_5-$V_N^{\times}$	1.45	1.45	1.59	1.55
Ta_3N_5-$V_N^{\cdot\cdot}$	1.46	1.44	1.59	1.56
Ta_3N_5-Mg_{Ta}-$V_N^{\times}$	1.48	1.48	1.56	1.55