Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Plasma-enhanced chemical vapor deposition Ta_3N_5 synthesis leading to high current density during PEC oxygen evolution

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Table S1. EDS elemental analysis of Ta, N, and O on Ta_3N_5 in the Hitachi SU8020 /Horiba EDS apparatus before and after nitridation at 900 °C for 1 h in 500 cm^3 min^{-1} NH_3. The values of weight % contain substantial errors due to low N and O sensitivities.

Element	**Concentration, Wt%**	
	As-prepared	Nitrided
Ta	91.4	92.2
N	7.4	6.8
O	1.2	1.0
Total	**100.0**	**100.0**

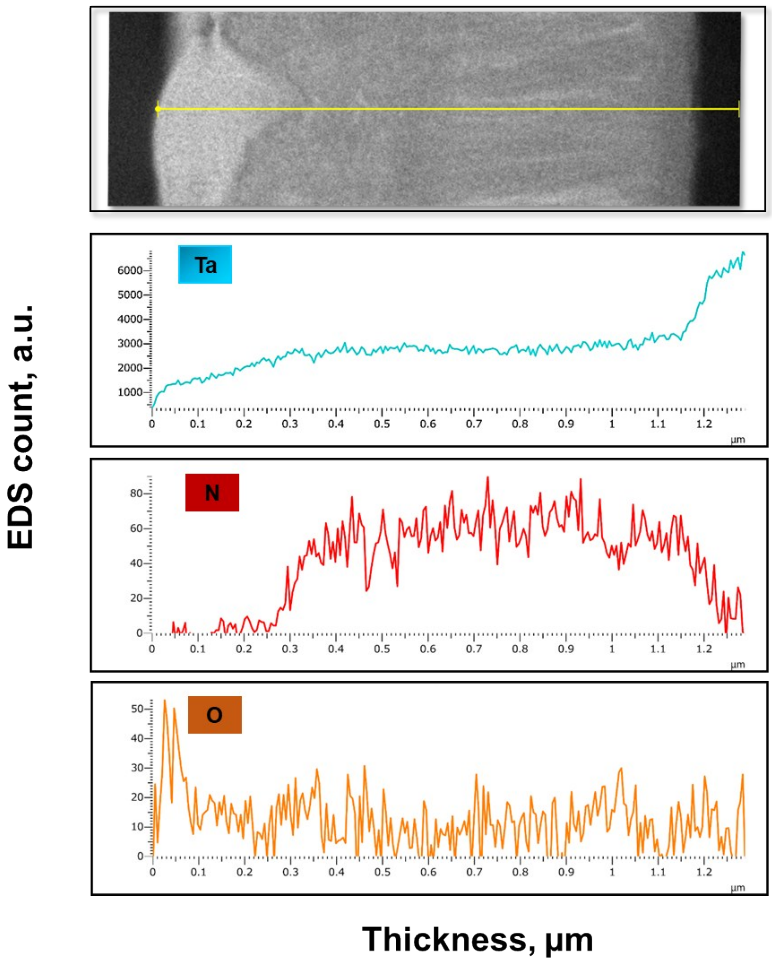


Figure S1. EDS line scan of the Ta_3N_5/Ta after nitridation. The abscissa of each viewgraph corresponds to the position on the yellow line in the STEM image.

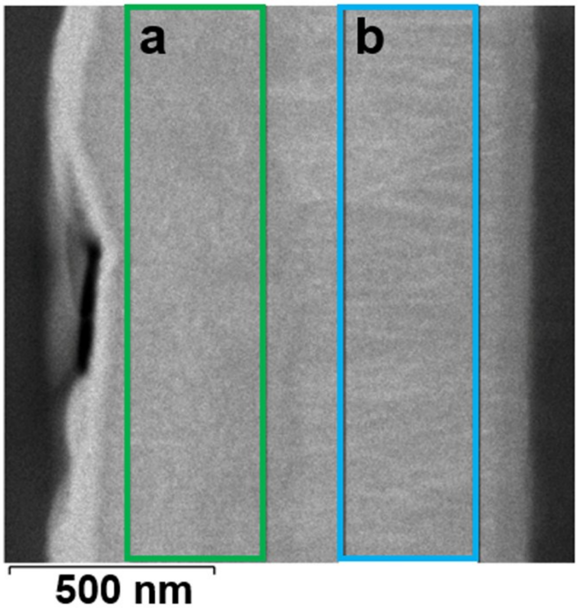
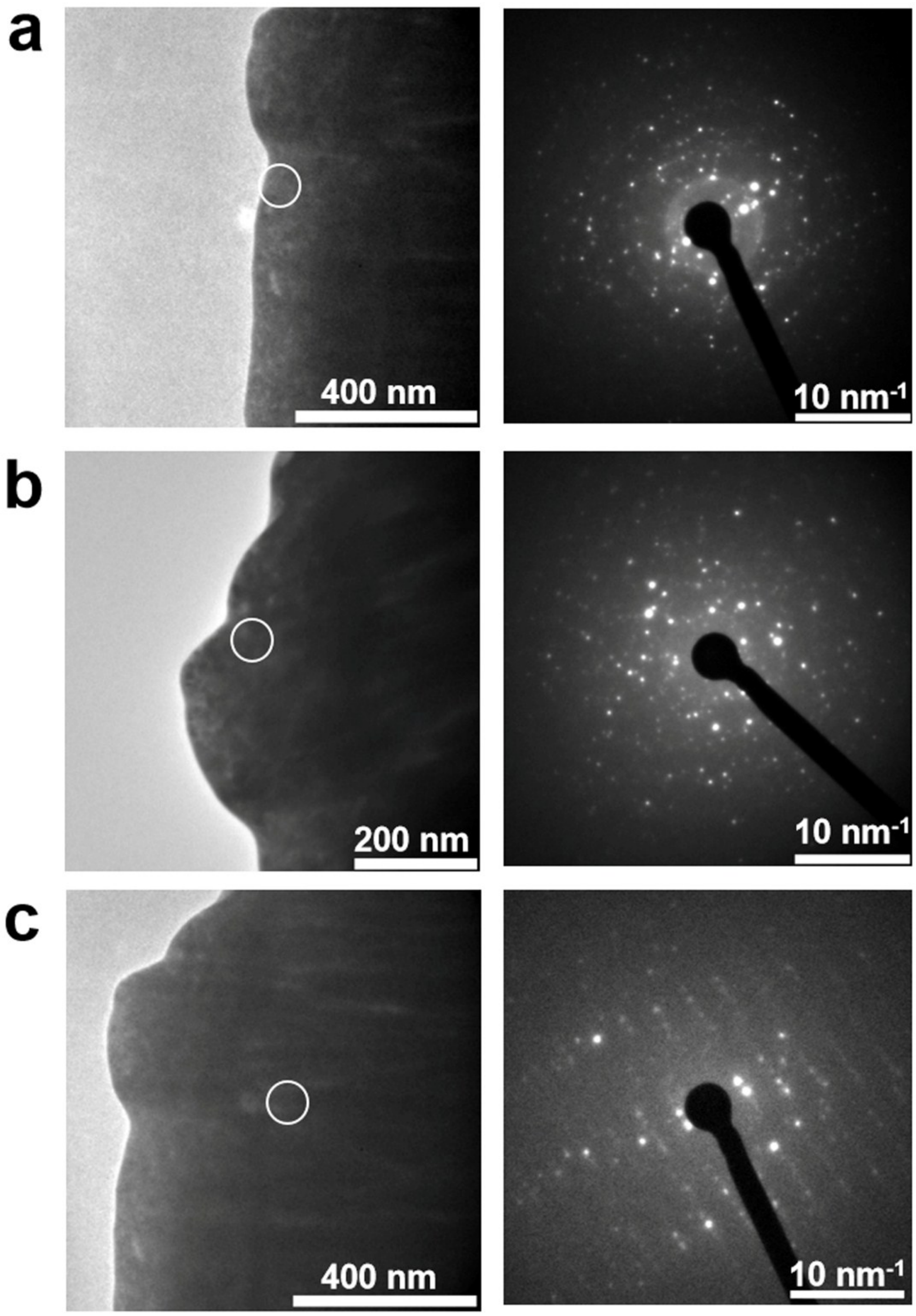


Figure S2. Cross-sectional STEM image of NH3-nitrided Ta_3N_5 thin film on Ta plate, and signal integration areas of EDS. Area a represents layer 2 (the top layer), and b layer 3 (the embedded layer). The apparatus used was a JEM-2800 STEM (JEOL) attached with an X-MAX 100TLE SDD detector (Oxford Instruments).

Table S2. The results of EDS signal areal integration for the sampling areas a (layer 2, the top layer) and b (layer 3, the embedded layer) in Fig. S2. indicated in atomic %. Due to the low EDS sensitivities for N and O, the absolute atomic % values contain substantial errors. Anyway in comparison between a and b, the mutual amount relationships for N and O contents are correct.

Element	**Concentration, atomic %**	
	a: top layer	b: embedded layer
Ta	91.7	92.33
N	7.14	6.51
O	1.12	1.16
Total	**100.0**	**100.0**

Figure S3.



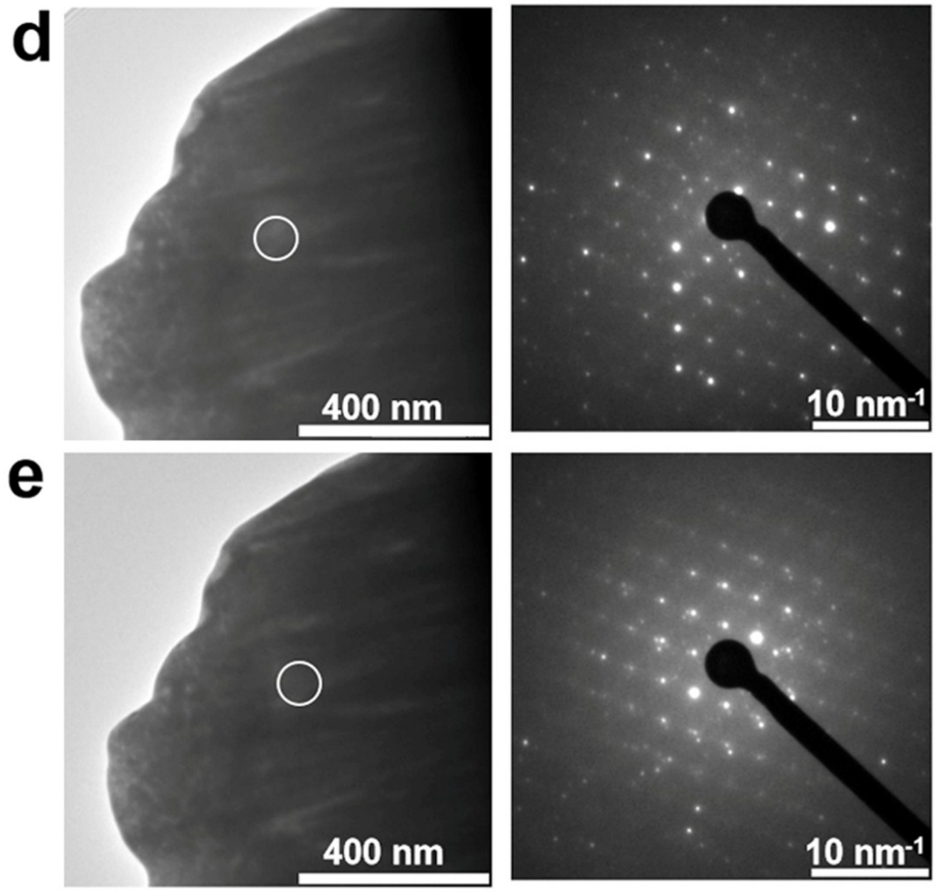


Figure S3. Cross-sectional TEM images and SAED patterns of nitrided-Ta_3N_5/Ta. The circle in each pair of photographs indicates the beam position where the diffraction pattern was recorded. a., b.: within the top layer, c., d., e.: within the embedded layer.

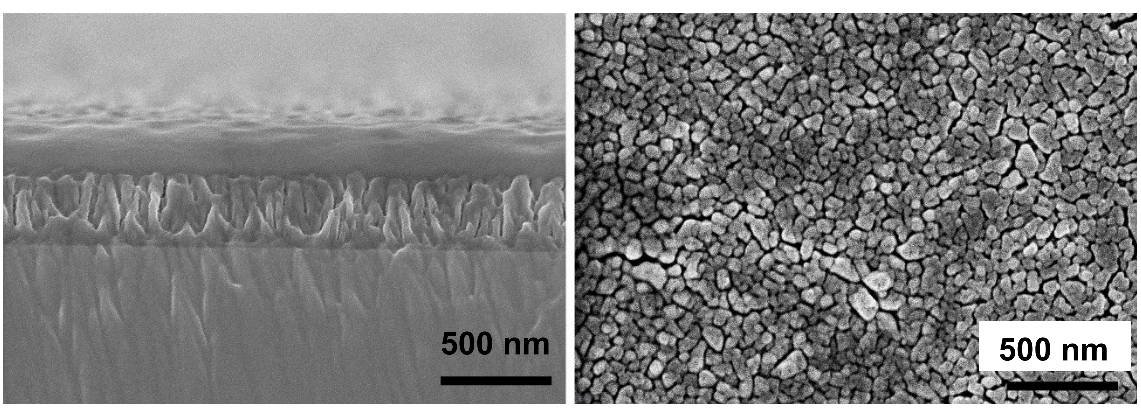


Figure S4. SEM images of the as-deposited-Ta_3N_5/Ta. Right: top view, Left : cross sectional view after Ar ion milling. The top layer in the left image is a debris layer deposited during ion milling, which does not exist in the right image.

Figures S5 and S6. DFT simulation of the electronics and optical spectroscopy of Ta_3N_5 and Ta_2N

DFT calculations were performed with CASTEP (Version 18.1.0, Dassault-Biovia) package.[1,2] The Perdew-Burke-Ernzerhof (PBE) functional[3,4] and the norm-conserving potentials were applied.[5] The basis set cutoff energy was adjusted at 10 eV. The atomic electron configurations were N: $2s^2$ $2p^3$ and Ta: $4f^{14}$ $5d^3$ $6s^2$. The lattice parameters and atomic positions were taken after the experimental values from previous reports for Ta_3N_5[6] and β-Ta_2N.[7] The electronic band diagram and the partial density of states for the orbitals of Ta and N were calculated accordingly. The partial densities of states (PDOS) for Ta and N were plotted with an energy smearing width of 0.2 eV. On the basis of these data, the optical reflection and absorption spectra were simulated in the "polycrystalline" mode. The spectral smearing width was set to 0.5 eV.

Figure S5 shows the calculated partial densities of states for Ta_3N_5. Fig. S5 also involves the simulated reflection and absorption spectra for polycrystalline layers. The density of state distribution of Ta_3N_5 involves a band gap smaller than 1 eV above BE (binding energy) = 0 eV. This semi-conductive property also appears as a cut-off photon energy of 0.6 eV in the simulated absorption spectrum. In accordance with the two peaks of the density-of-state curve right below BE = 0 eV, the absorption spectrum involves two weak shoulders, which seem corresponding with two shoulders that frequently appear in experimental spectra.[8],

Similarly, the PDOS's and optical spectra for Ta_2N are shown in Figure S5. Ta_2N PDOS does not involve a band gap, suggesting a metallic nature of Ta_2N. The simulated absorption coefficient is all non-zero up to the visible-ultraviolet range.

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3. Perdew, P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
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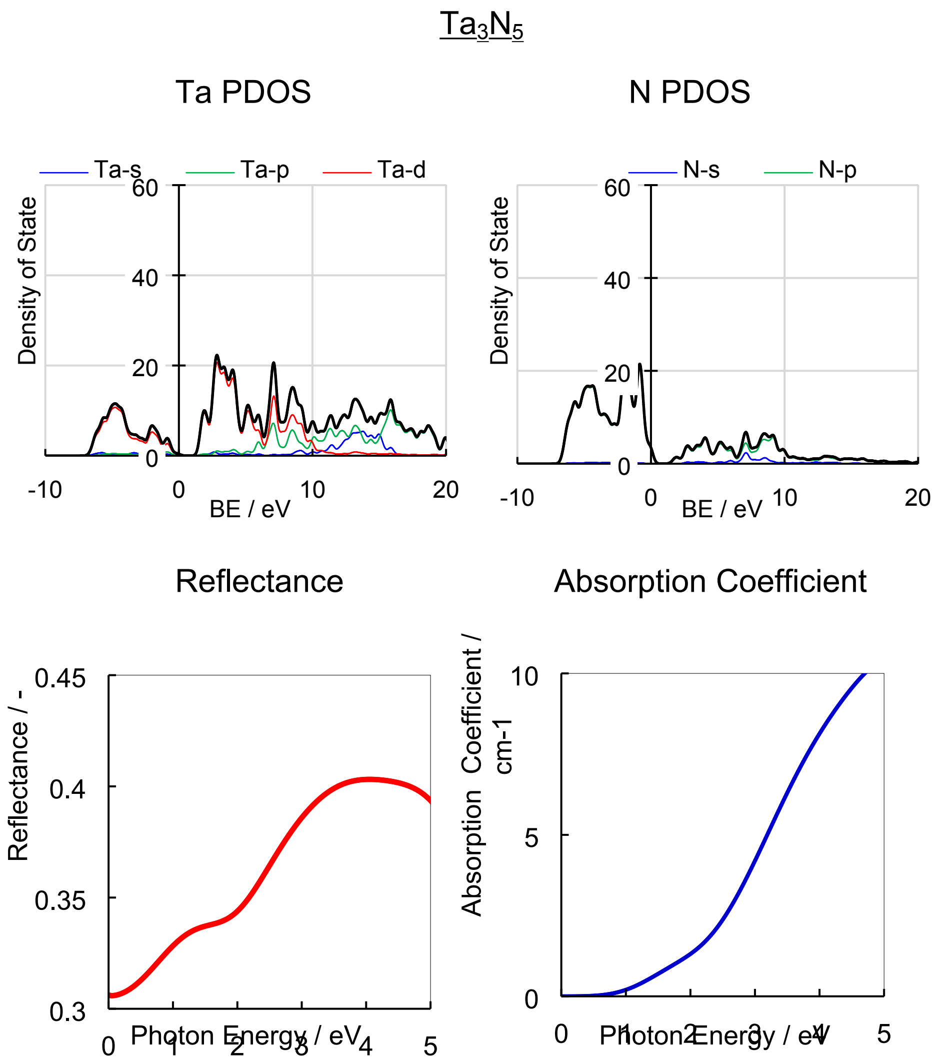

Figure S5. Ta_3N_5 calculated partial densities of states for Ta and N for each of the orbitals, and spectra for reflectance and absorption coefficient.

$\underline{Ta_2N}$

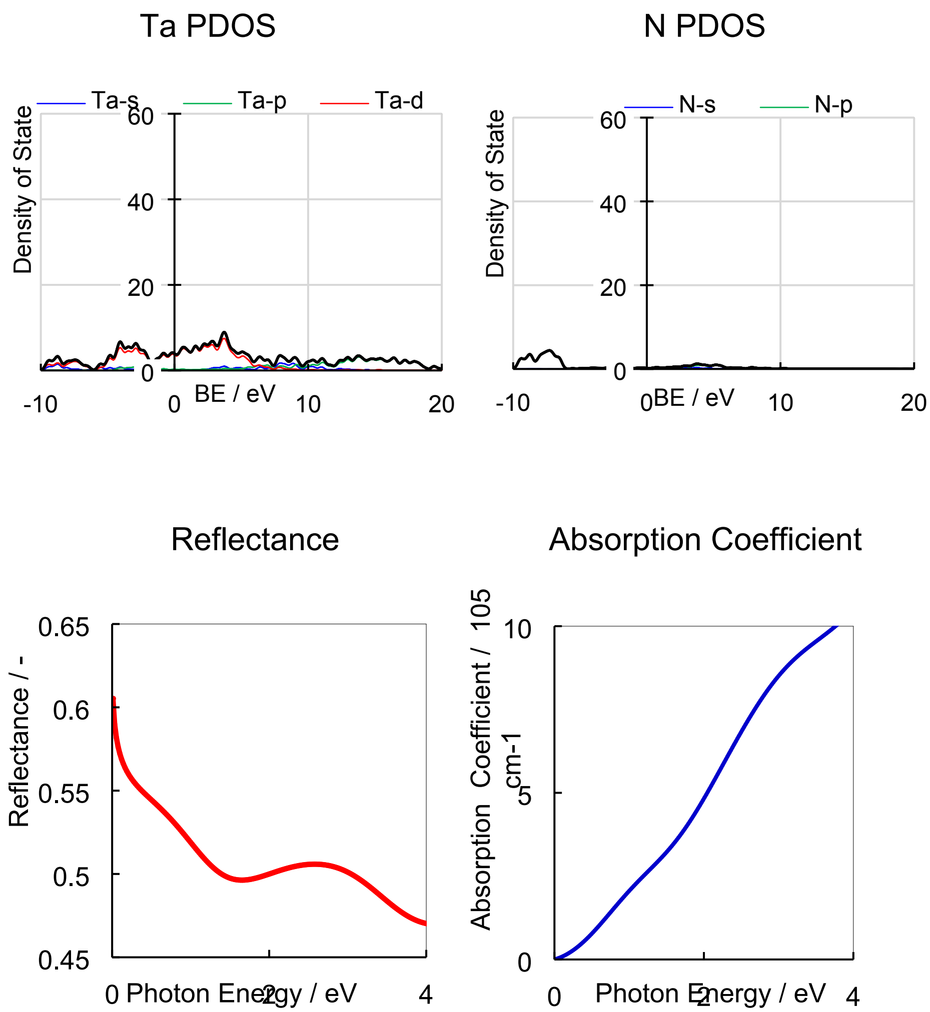

Figure S6: Ta_2N calculated partial densities of states for Ta and N for each of the orbitals, and spectra for reflectance and absorption coefficient.

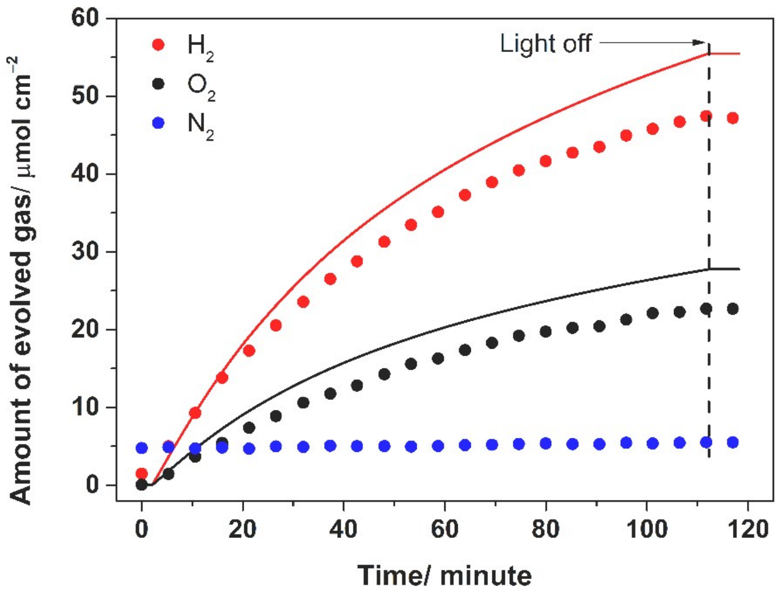

Figure S7. The plots for the amounts of the evolved gases (H_2, O_2, and N_2) for CoPi/Ta_3N_5/Ta_2N+Ta_3N_5/Tia recorded at 1.23 V RHE under simulated AM 1.5G light irradiation. A 0.5 M K_2HPO_4 solution adjusted to pH 13 by adding KOH was used as an electrolyte. The O_2 amount was corrected by subtracting the initial O_2 amount that remained during setting of the reactor chamber. The red and black lines indicate the expected gas amounts of H_2 and O_2, respectively, calculated from the total charge by integrating the simultaneously recorded photocurrent ($2e^-$ for H_2, $4e^-$ for O_2).

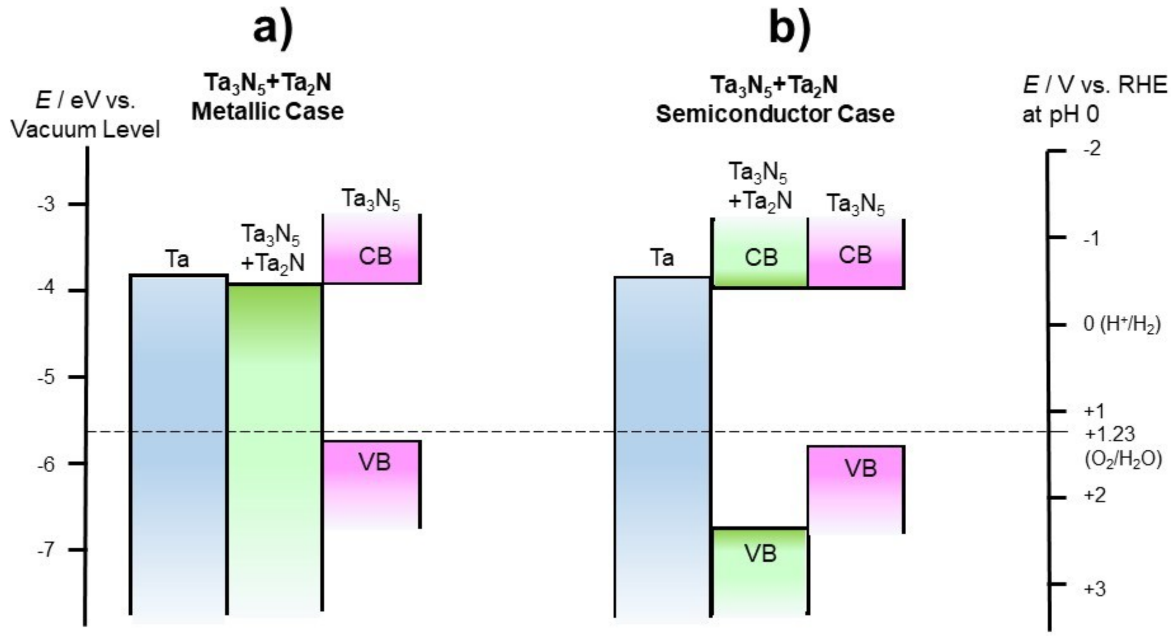

Figure S8. Energy band diagram of Ta_3N_5/Ta_3N_5+Ta_2N/Ta system for a) assuming that Ta_3N_5+Ta_2N layer behaves as metallic species b) Ta_3N_5+Ta_2N layer behaves as semiconductive species.

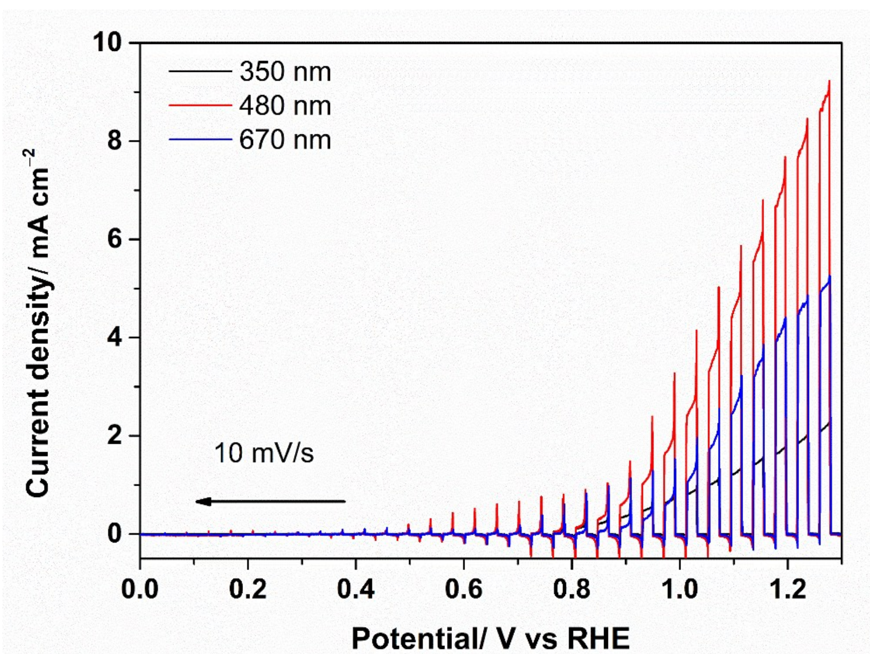

Figure S9. LSV of Ta_3N_5/Ta with different Ta_3N_5 thickness.

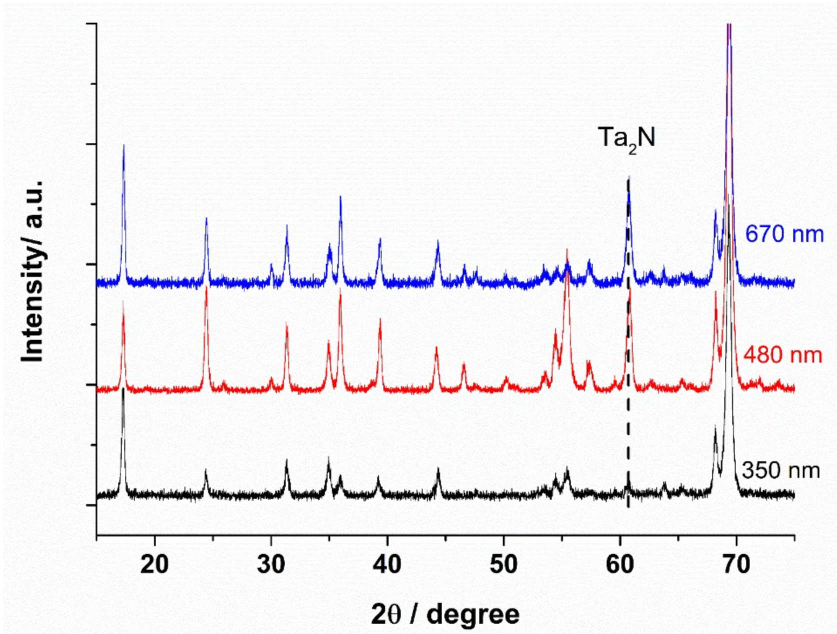

Figure S10. XRD pattern Ta_3N_5/Ta with different Ta_3N_5 thickness.

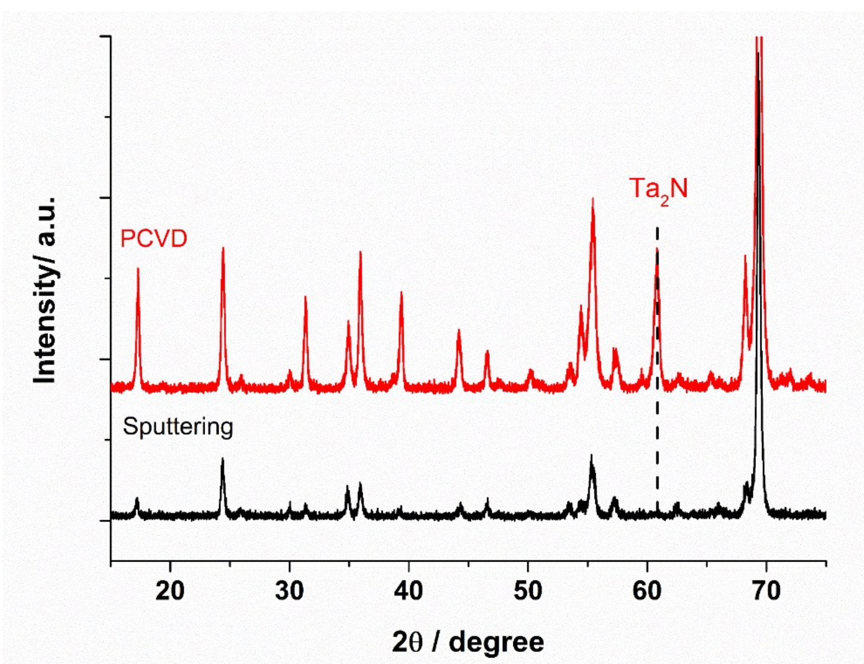

Figure S11. Comparison of XRD pattern of Ta_3N_5/Ta synthesized by sputtering and PCVD method.

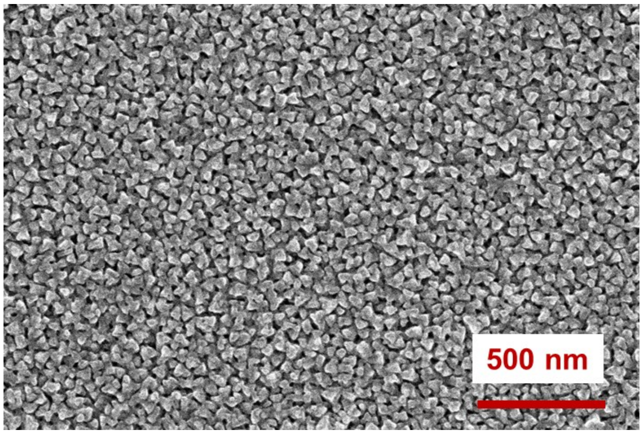

Figure S12. SEM image of Ta_3N_5/Ta synthesized by sputtering method followed by nitridation.

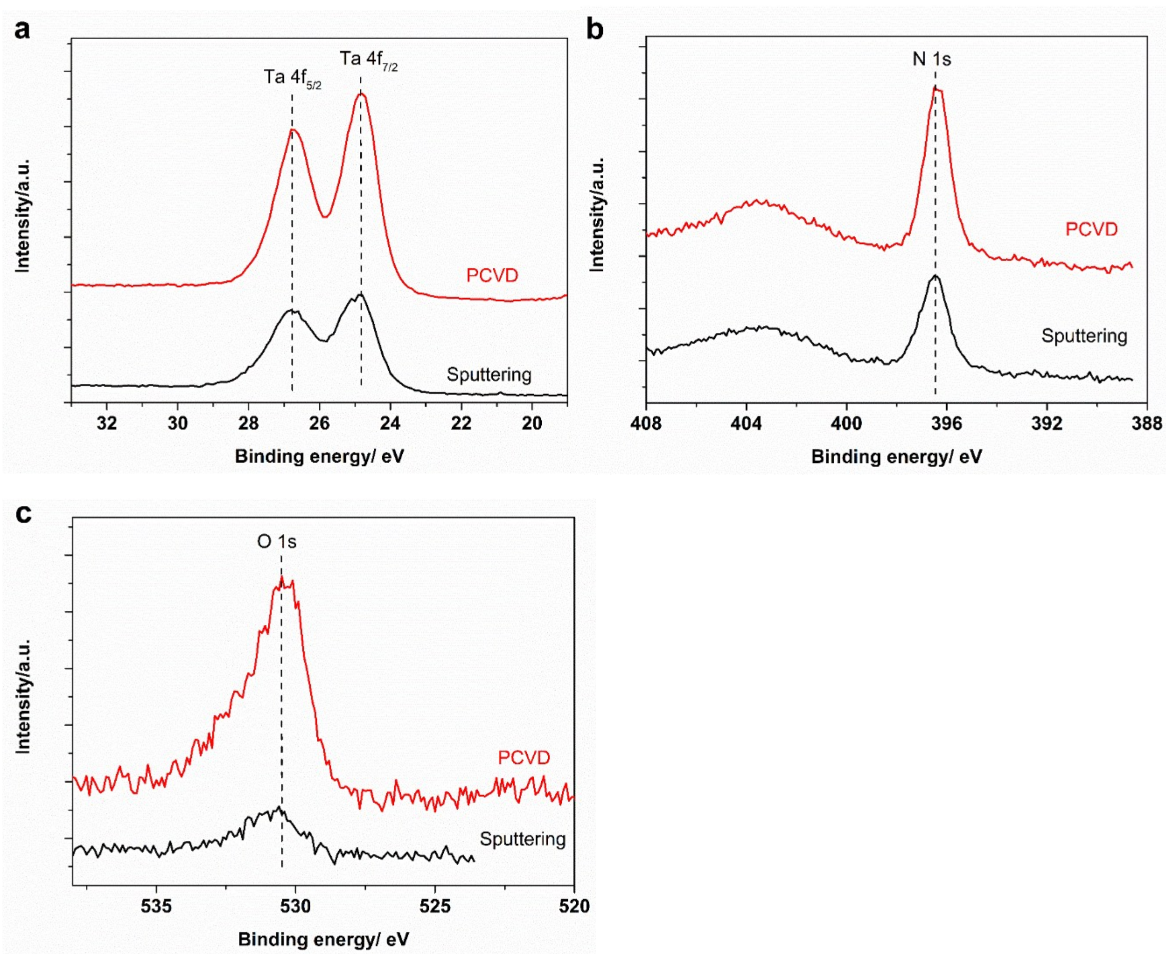

Figure S13. Comparison of XPS elemental peaks of Ta_3N_5/Ta synthesized by sputtering and PCVD method. a) Ta 4f peaks, b) N 1s peak, and c) O 1s peak.

Table S3. Elemental analysis of XPS signal for PCVD and sputtered-Ta_3N_5

Synthesis method	Experimental value (mol/mol)			Theoretical value (mol/mol)	
	O/Ta	N/Ta	O/N	O/Ta	N/Ta
Sputtering	2.9	1.3	0.1	0	1.67
PCVD	3.2	1.2	0.1	0	1.67

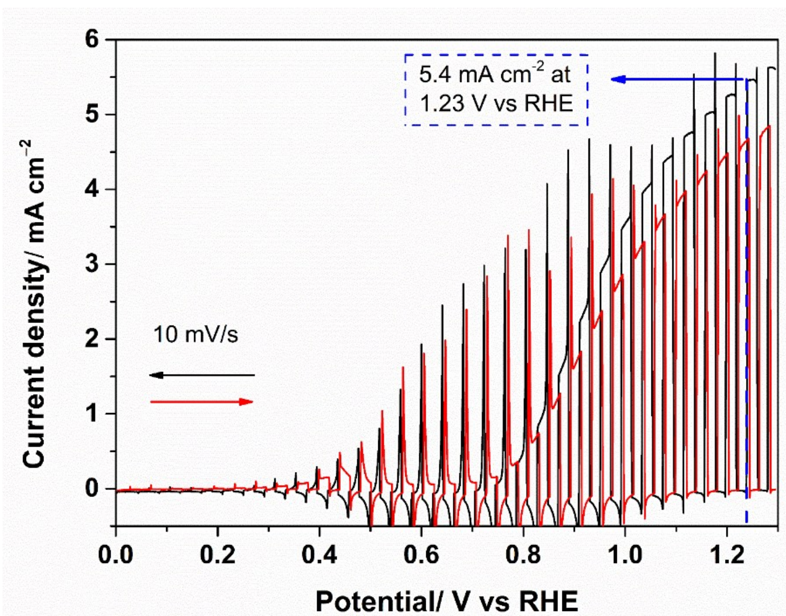

Figure S14. LSV of Ta_3N_5/Ta film synthesized by sputtering method followed by nitridation.