Supplementary Information

Effects of interfacial layers on the photoelectrochemical properties of tantalum nitride photoanodes for solar water splitting

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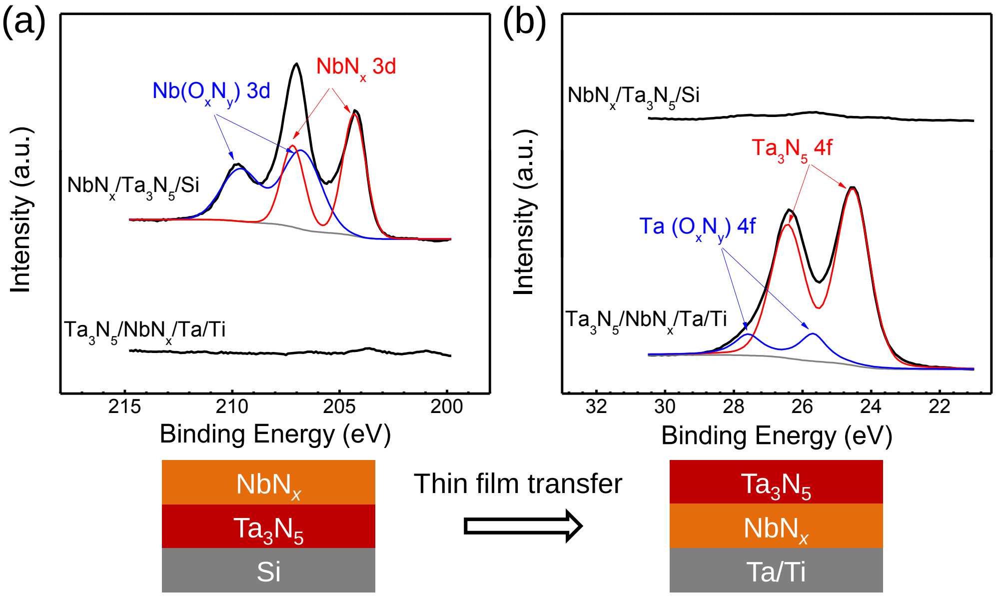

Fig. S1. (a) Nb 3d and (b) Ta 4f XPS spectra for NbN_x/Ta_3N_5/Si and transferred Ta_3N_5/NbN_x/Ta/Ti samples.

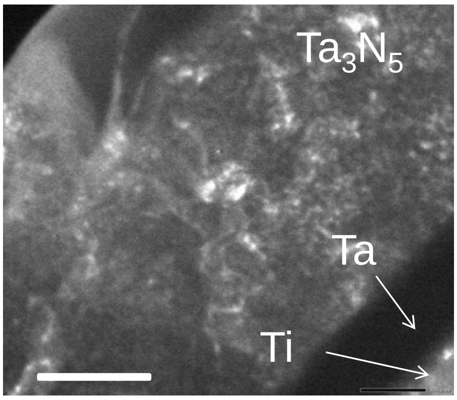

Fig. S2. Zone-axis TEM image of the cross-section of a Ta_3N_5/Ta/Ti sample without a NbN_x interlayer. The scale bar is 200 nm.

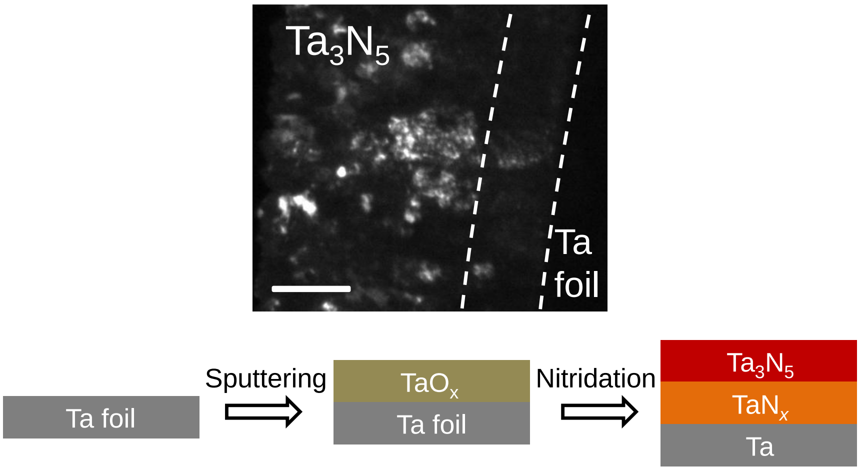

Fig. S3. Zone-axis TEM image of the cross-section of a Ta_3N_5 film on a Ta foil substrate. The scale bar is 200 nm. To investigate the growth of the Ta_3N_5 film on the metallic Ta foil substrate, an amorphous TaO_x film was sputtered onto a highly-polished Ta foil substrate (1×1 cm^2 in size) at a working pressure of 3.0×10^{-2} Torr. Ar gas in a flow rate of 10 sccm was fed into the sputtering chamber along with the unintentional introduction of trace amount of molecular O_2. The TaO_x/Ta sample was subsequently nitrided in a flow of NH_3 gas (100 sccm) at 900 ℃ for 2 h with a temperature ramp rate of 20 ℃ min^{-1}.

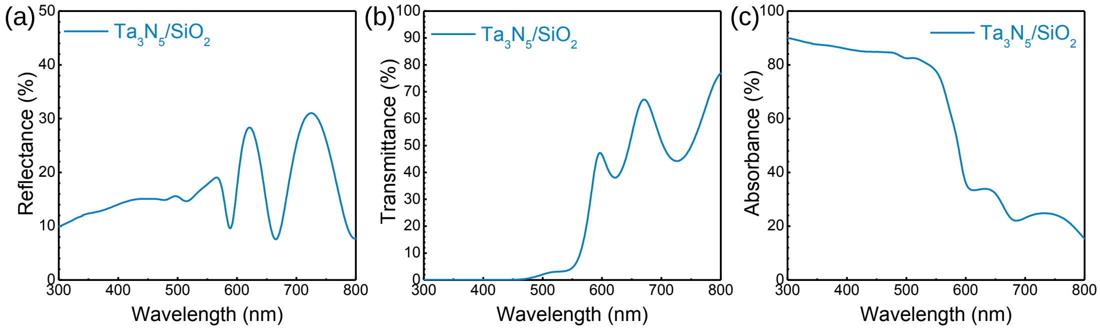

Fig. S4 (a) Light reflectance, (b) transmittance and (c) absorbance of a Ta_3N_5 thin film (approximately 600 nm thick) on fused silica substrate.

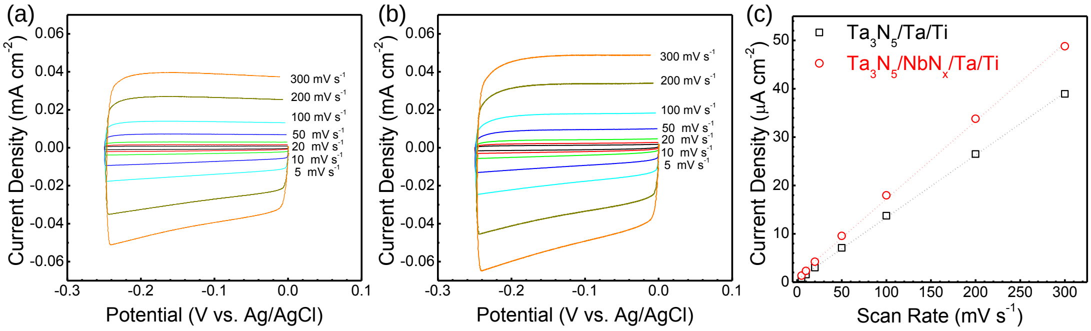

Fig. S5. Cyclic voltammograms for (a) Ta_3N_5/Ta/Ti, and (b) Ta_3N_5/NbN_x/Ta/Ti as measured with scan rates varying from 5 to 300 mV s^{-1}, and (c) the relationship between the capacitive current density in cyclic voltammograms (a) and (b) at −0.1 V vs. Ag/AgCl and the scan rate. The ratio for the ECSA of Ta_3N_5/Ta/Ti (S_1) to Ta_3N_5/NbN_x/Ta/Ti (S_2) was estimated to be 0.8 on the basis of the slopes of the linear plots.

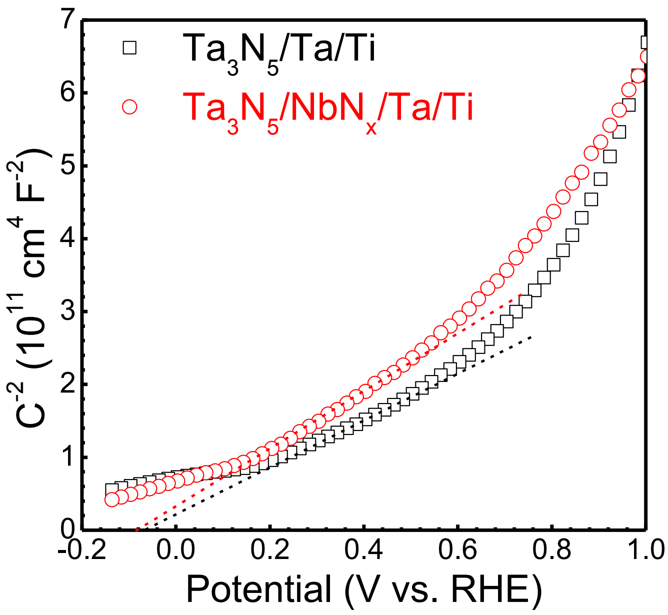

Fig. S6. Mott−Schottky (M−S) plots for the Ta_3N_5/Ta/Ti and Ta_3N_5/NbN_x/Ta/Ti photoelectrodes. The flat band potentials of the Ta_3N_5/Ta/Ti and Ta_3N_5/NbN_x/Ta/Ti photoelectrodes, derived from the intersection points with the potential axis, and were estimated to be −0.06 and −0.08 V vs. RHE, respectively. The carrier density can be estimated using the equation $N_D = 2(\varepsilon\varepsilon_0 erk_{MS})^{-1}$, where k_{MS} is the slope of the fitted line from the M−S plot, and r is the roughness factor for Ta_3N_5 photoelectrodes, obtained from the ECSA data in Fig. S5. The ratio for the carrier density of Ta_3N_5/Ta/Ti (N_{D1}) to Ta_3N_5/NbN_x/Ta/Ti (N_{D2}) was estimated to be 1.1.

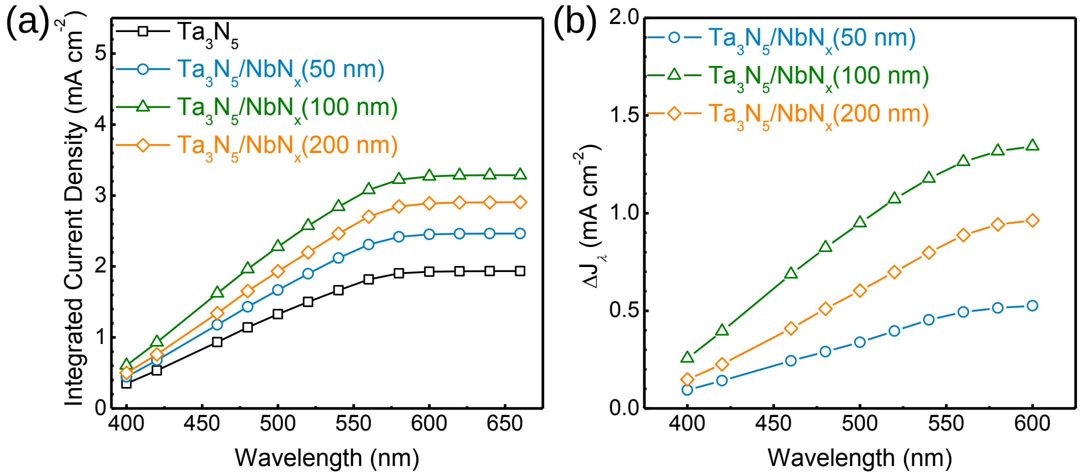

Fig. S7. (a) Integrated photocurrent densities (J_λ) at 1.23 V vs. RHE calculated on the basis of the standard AM 1.5G (ASTM G173-03) spectrum and the IPCE spectra shown in Fig. 7 in the main text. (b) Increment of the integrated photocurrent densities by the presence of the NbN_x interlayers calculated from panel (a).

Table S1. Series resistances R_s and charge transfer resistances R_{CT} of the fitted Nyquist plots from Fig. 8 in the main text.

NbN_x thickness (nm)	R_s (Ω)	R_{CT} (Ω)
0	11	7215
50	12	5098
100	12	4416
200	19	4860