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Supporting Information

Reducing the surface defects of Ta_3N_5 photoanode towards enhanced photoelectrochemical water oxidation

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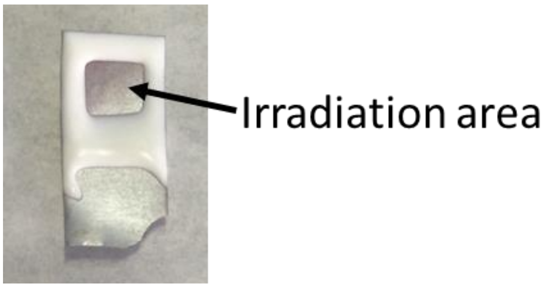

Fig. S1 The photograph of $Co(OH)_x/Ta_3N_5$-15-15 photoanodes.

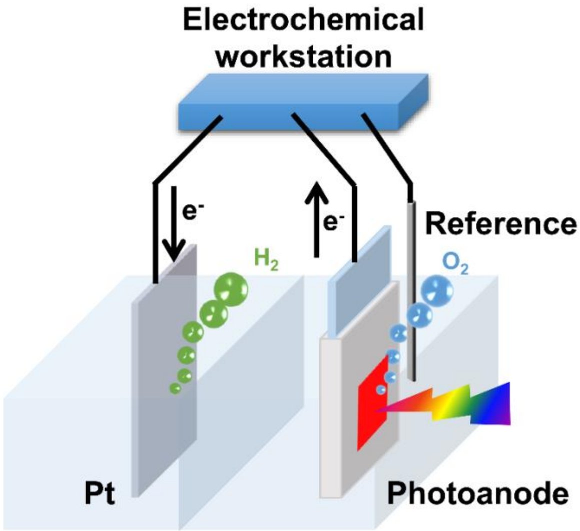

Fig. S2 Schematic diagrams of PEC measurement system.

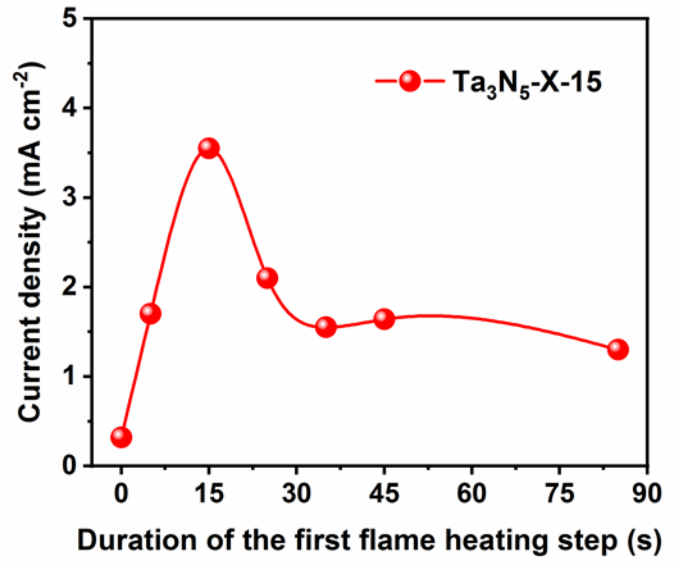

Fig. S3 Dependence of the photocurrent density of Ta_3N_5-X-15 measured at 1.23 V vs. RHE on the duration of the first flame heating step.

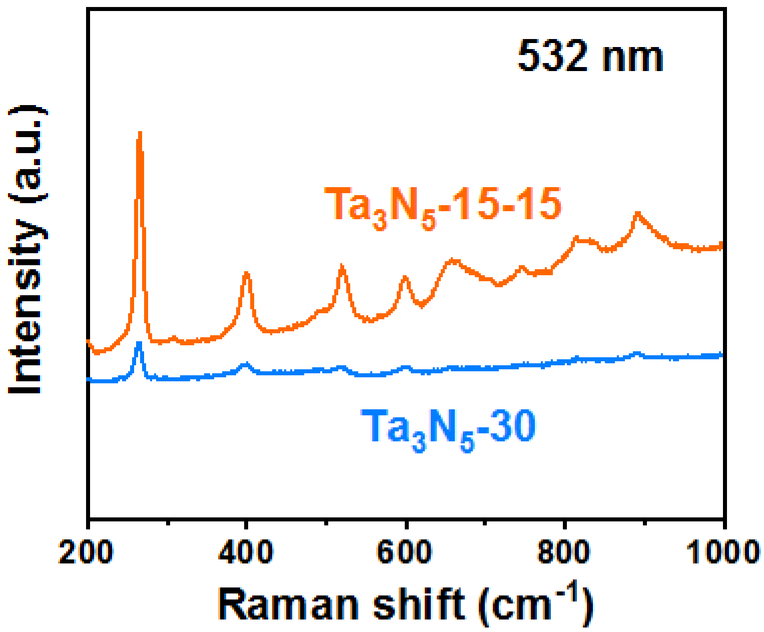

Fig. S4 The visible Raman spectra of Ta_3N_5-30 and Ta_3N_5-15-15; exciting source: 532 nm laser.

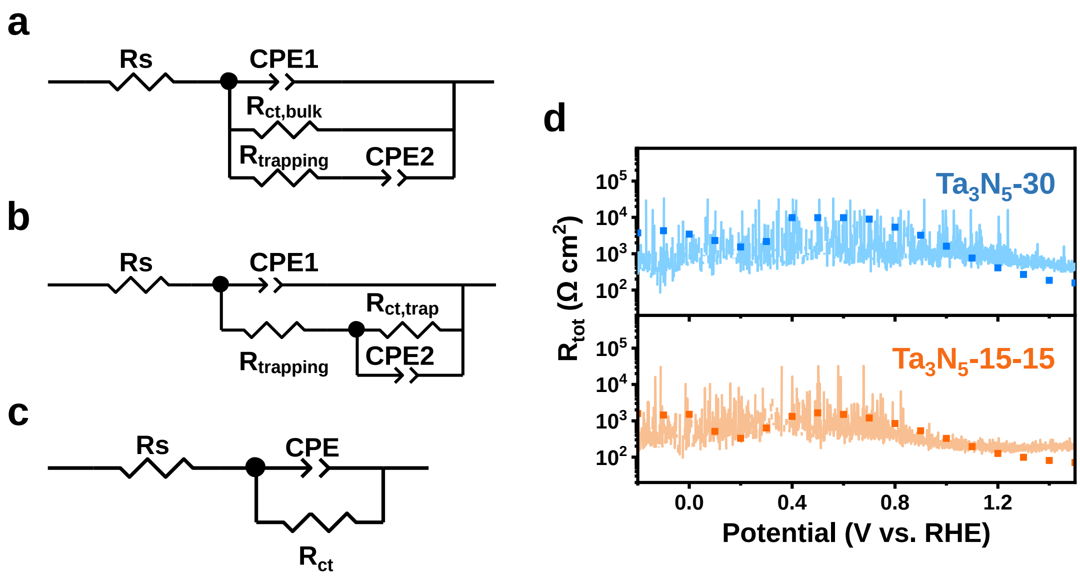

Fig. S5 The equivalent AC circuits for the simulation of PEIS data showing two time constants: circuit in a) approximates the situation that photogenerated holes injected into the electrolyte are mainly transferred though the valence band of Ta_3N_5; circuit in b) approximates the situation that photogenerated holes injected into the electrolyte are mainly transferred though the surface states. c) Randles circuit. The assignation was made as follows. R_s was the series resistance attributed to the resistances of electrolyte and the substrate; $R_{trapping}$ was the trapping resistance related with the charge recombination at surface states; R_{ct} was the charge transfer resistance at the semiconductor/electrolyte interface. $R_{ct,bulk}$ was the charge transfer resistance at the semiconductor/electrolyte interface when photogenerated holes injected into the electrolyte are mainly transferred though the valence band of Ta_3N_5; $R_{ct,trap}$ was the charge transfer resistance at the semiconductor/electrolyte interface when photogenerated holes injected into the electrolyte are mainly transferred though surface states; the capacitance of the bulk for Ta_3N_5 photoanode (C_{bulk}) was incorporated into the EC by a constant phase element (CPE1), which considers the space charge region; the capacitance of the surface states (Css) was calculated through a constant phase element (CPE2). d) Comparison of total resistance values (R_{tot}) obtained by PEIS simulations (squares) and those by calculating dV/dJ from the J(V) curves in Fig. S7 (lines). The colors correspond to different samples: Ta_3N_5-30 (blue) and Ta_3N_5-15-15 (orange).

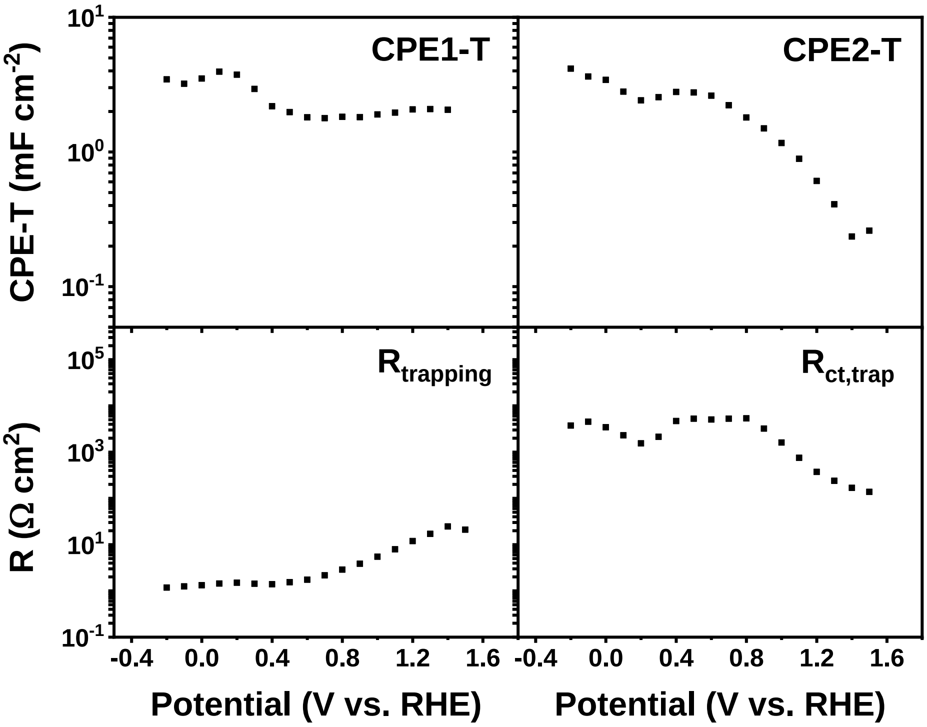

Fig. S6 CPE-T and resistance values obtained on Ta_3N_5-30 when the PEIS data in Fig. 5a,b are modeled using the equivalent circuit shown in Fig. S5b. The results are almost identical with that (Fig. 6) obtained on Ta_3N_5-30 using the equivalent circuit shown in Fig. S5a.

Both equivalent circuits shown in Fig. S5a,b were employed to fit the EIS data of Ta_3N_5-30 in Fig. 5a,b. The results obtained with both circuits exhibit similar values for CPE1-T, CPE2-T, and $R_{trapping}$. However, it is more convincing that $R_{ct,bulk}$ which is physically related with CPE-1 (represent the capacitance of the bulk) shows a valley corresponding to the peak observed in CPE-1, rather than $R_{ct,trap}$ which is not directly physically related to CPE-1. Therefore, the equivalent circuit shown in Fig. S5a is more preferable than that in Fig. S5b. In other words, in Ta_3N_5 photoanodes, the photogenerated holes injected into the electrolyte are mainly transferred from the valance band and the surface states function as charge recombination centers. Hence, the equivalent circuit shown in Fig. S5a was used to derive the data which is discussed within this paper.

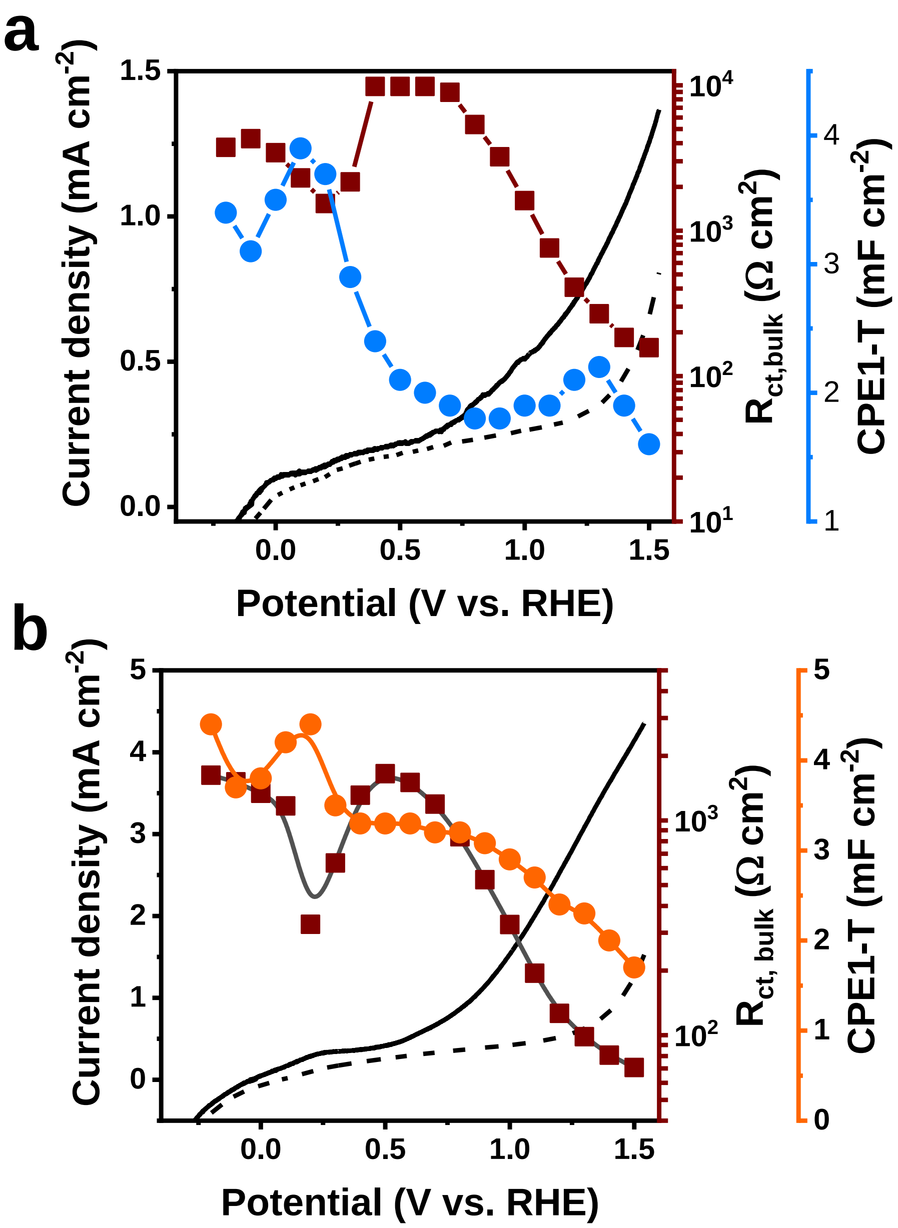

Fig. S7 LSV curves acquired under illumination (black solid line) and in the dark (black dashed line), $R_{ct,bulk}$ (squires), and CPE1-T (circles) obtained on a) Ta_3N_5-30 and b) Ta_3N_5-15-15 in 1.0 M NaOH (pH 13.6). Illumination: AM 1.5G.

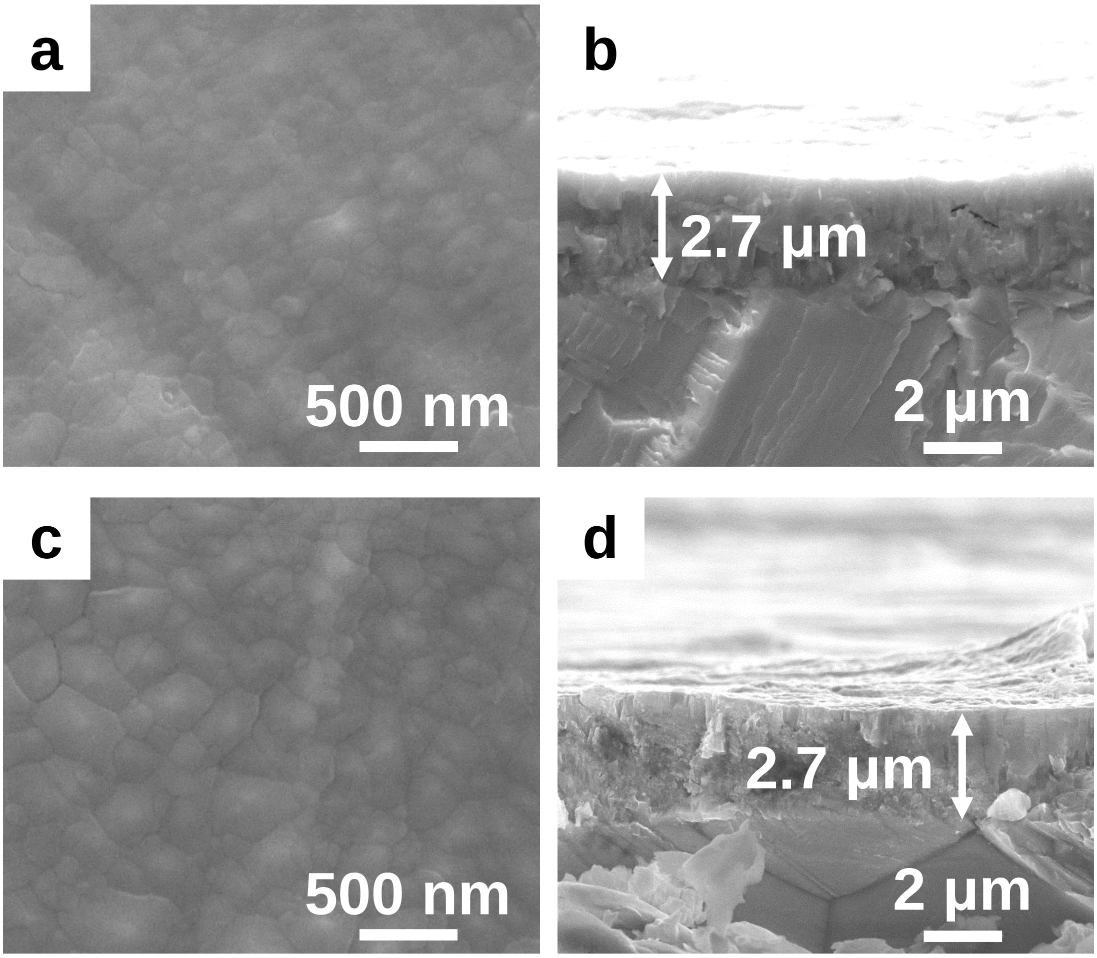

Fig. S8 Top and cross-sectional SEM images of a,b) Ta_2O_5-15-15 and c,d) Ta_2O_5-30.