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

Supporting Information

Carrier Engineering of Zr-mediated Ta_3N_5 Film as Efficient Photoanode for Solar Water Splitting

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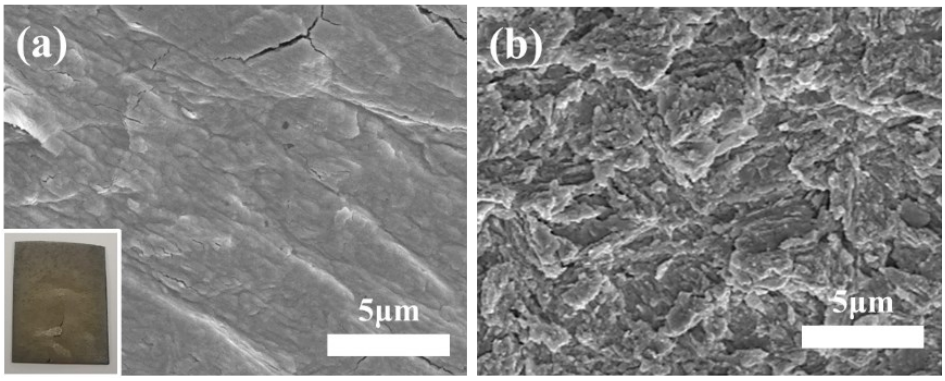

Figure S1. Top-view SEM image of (a) Ta_2O_5 film before surface exfoliation, (b) Ta_2O_5 film after surface exfoliation. The inserted picture shows the corresponding photograph of Ta_2O_5 film before surface exfoliation.

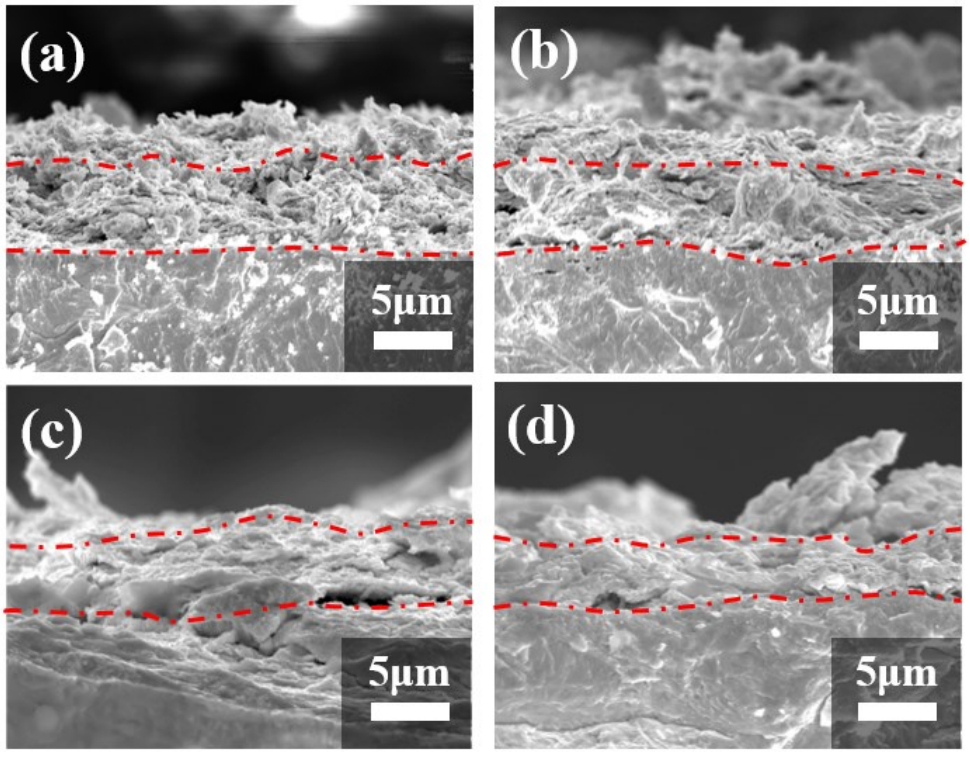

Figure S2. SEM cross section view of (a) Ta_3N_5, (b) ZTN-0.1, (c) ZTN-0.3 and (d) ZTN-0.5. The red dash line highlighted the thickness of the nitride layer.

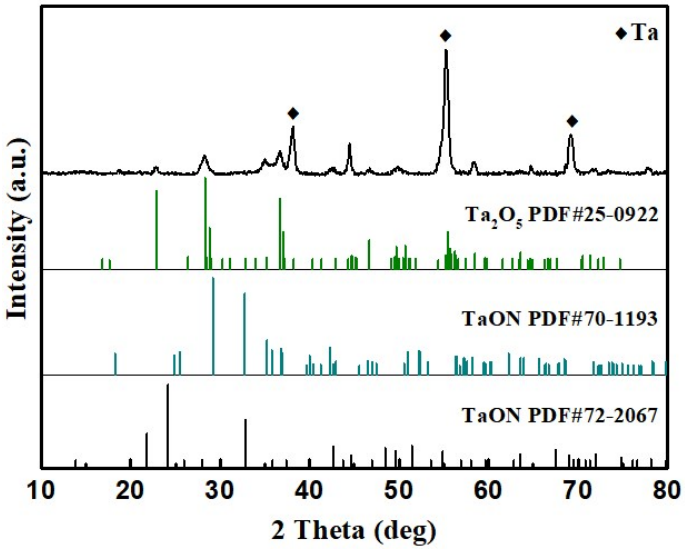

Figure S3. XRD patterns of Ta_2O_5 film.

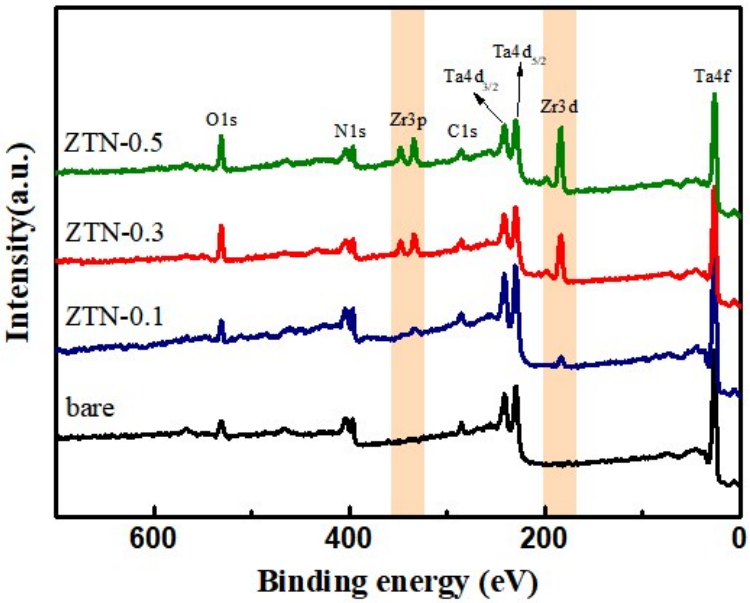

Figure S4. XPS spectra of bare Ta_3N_5 and ZTN-x samples with binding energy from 0 to 700eV. The orange regions show the peak positions of Zr 3p and Zr 3d corresponding to different samples.

Table S1. Data analysis of XPS spectra of O, the ratio is calculated based on the peak areas of OH^- and O^{2-} in the fitted spectra.

Sample ID	The Area of OH^-	The Area of O^{2-}	The Ratio of OH^-/ O^{2-}
Ta_3N_5	1683.7	1278.1	1.32
ZTN-0.1	2175.2	1729.7	1.26
ZTN-0.3	3120.1	3991.2	0.78
ZTN-0.5	2607.8	4518.0	0.57

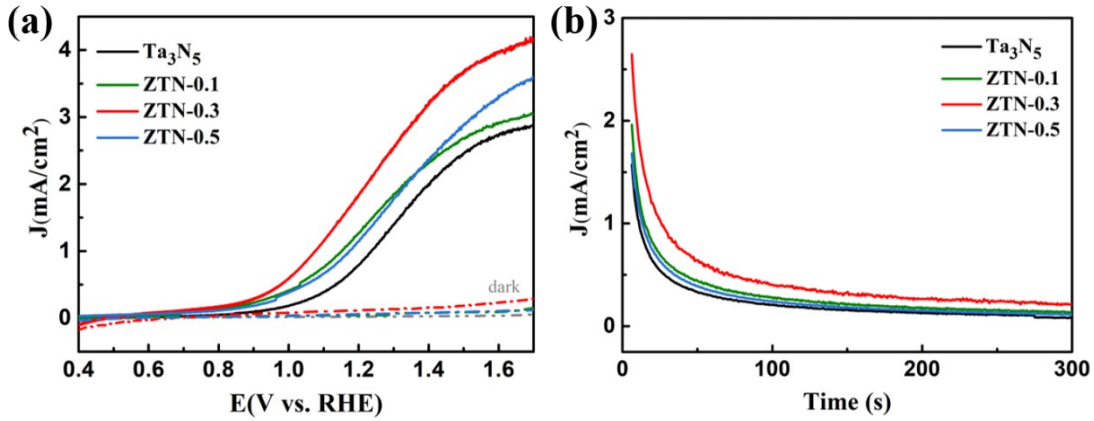

Figure S5. (a) Current-potential curves in dark and under AM 1.5G-simulated sunlight (b) Steady-state photocurrent held at 1.23 V_{RHE} under AM 1.5G-simulated sunlight of pristine Ta_3N_5 and ZTN-x photoanodes without $Co(OH)_x$. Note that all the current–potential curves were performed in 1 M KOH (pH = 13.6).

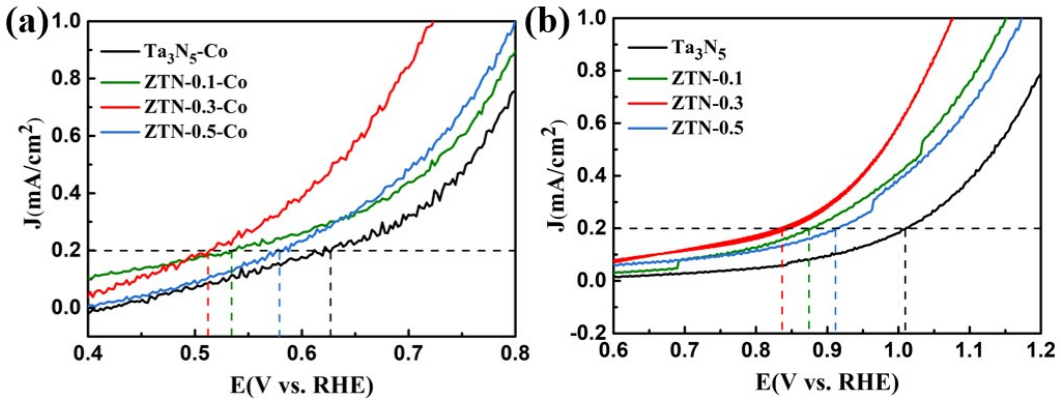

Figure S6. Enlarged Current-potential curves in dark and under AM 1.5G-simulated sunlight of Ta_3N_5 and ZTN-x photoanodes (a)without $Co(OH)_x$ and (b) with $Co(OH)_x$. The onset potentials are defined as the potentials corresponding to the current of 0.2 $mA \cdot cm^{-2}$, different samples are marked with different color dotted lines.[1]

Table S2. The water oxidation performance of Ta_3N_5 and ZTN-x samples

	Ta_3N_5	**ZTN-0.1**	**ZTN-0.3**	**ZTN-0.5**
J at 1.23 V_{RHE} ($mA \cdot cm^{-2}$)	1.0	1.5	2.0	1.4
Onset-Potential(V_{RHE})	1.02	0.87	0.84	0.91

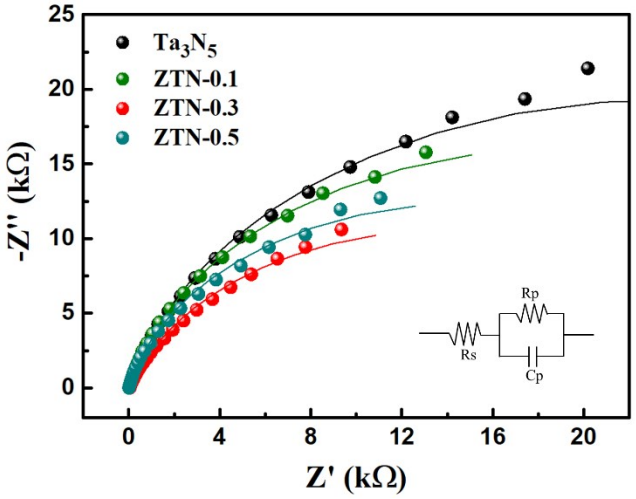

Figure S7. Nyquist plot at 1.23 V_{RHE} under dark conditions with frequency range from 100 kHz to 0.1 Hz at 10 mV of pristine Ta_3N_5 and ZTN-x photoanodes. Illustration is a fitted circuit diagram.

Table S3. The parameters of circuit components by fitting the Nyquist plots

	Rs (Ω)	Error (%)	Rp (kΩ)	Error (%)	Cp			
					Yo (μMho)	Error (%)	N	Error (%)
Ta_3N_5	35.6	1.2	**47.2**	4.3	3.0	1.8	0.87	0.44
ZTN-0.1	43.8	0.7	**38.4**	3.6	5.1	1.1	0.89	0.32
ZTN-0.3	39.5	1.1	**28.1**	4.7	5.8	1.8	0.82	0.49
ZTN-0.5	11.7	1.1	**29.8**	4.8	6.1	1.6	0.88	0.37

Due to the defects on Ta_3N_5 surface, these defects are the main traps for capturing charge carriers. The accumulation of photogenerated carriers at the interface is obtained by measuring the OCP of Ta_3N_5 under light conditions. When the light is switched off, the photogenerated carriers recombine rapidly in the bulk, and the photogenerated electrons get trapped at the surface, so the OCP of Ta_3N_5 rises to a stable level. It is well known that the recombination rate in bulk is always on the order of ns-μs.[2] The OCP transient decay of Ta_3N_5 is on the order of seconds. Therefore, the OCP transient decay curve reflects the process of capturing photogenerated electrons by the surface state, the recombination rate is reflected by the rate at which the OCP of Ta_3N_5 rises to a stable level after the lights are turned off.

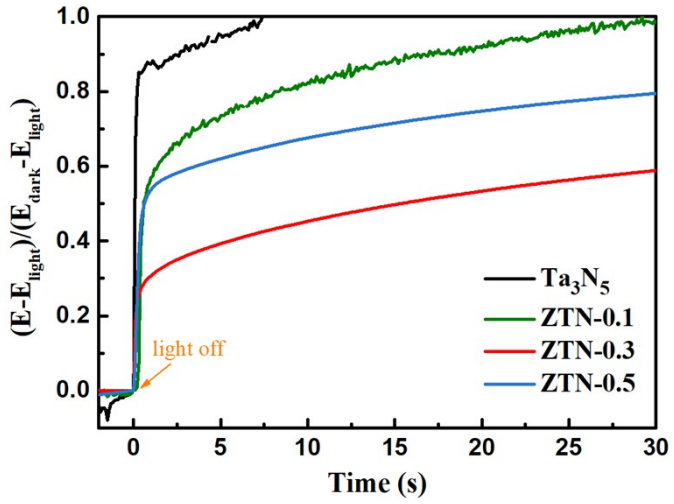

Figure S8. The normalized transient OCP decay profiles of Ta_3N_5 and ZTN-x samples.

Table S4. The flat band potential and carrier density of Ta_3N_5 and ZTN-x samples

Samples	**Ta_3N_5**	**ZTN-0.1**	**ZTN-0.3**	**ZTN-0.5**
V_{FB} (V vs.RHE)	-0.09	-0.17	-0.19	-0.23

[1] L. Pei, B. H. Lv, S. B. Wang, Z. T. Yu, S. C. Yan, R. Abe and Z. G. Zou, *Acs Appl Energ Mater* 2018, 1, 4150-4157.
[2] X. Y. Song, W. Q. Li, D. He, H. Y. Wu, Z. J. Ke, C. Z. Jiang, G. M. Wang and X. H. Xiao, *Adv Energy Mater* 2018, 8.