Electronic Supplementary Material (ESI) for Nanoscale.

Bridging the Transport Pathway of Charge Carriers in a Ta_3N_5 Nanotube Array Photoanode for Solar Water Splitting

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Materials: Ta foil (99.5%) with the thickness of 0.25 mm was purchased from Beijing Sunstone Tungsten Molybdenum Co., Ltd. H_2SO_4 (98%, chemical grade), ammonium hydroxide (25%) and $Co(CH_3COO)_2\cdot 4H_2O$ (99%, chemical grade) were purchased from Tianjin Jiangtian Chemistry Technological Co., Ltd. HF (40%, chemical grade) and NaOH (96%, chemical grade) were purchased from Tianjin Windship Chemistry Technological Co., Ltd. All chemicals were used as received without any further purification

Synthesis of Ta_3N_5 NTAs: The as received Ta foil was cut into 1×2 cm^2 small foils which were cleaned ultrasonically in acetone, ethanol and water baths for 30 min in each step. Then the foils were rinsed with deionized water and further dried with flowing nitrogen. Anodization was conducted to synthesize Ta_2O_5 NTAs in a standard two-electrode electrochemical cell configuration with the Ta foil as the anode and platinum foil (2×2 cm^2) as the cathode. The distance between the electrodes was kept at 1 cm in all experiments. The electrolyte consisted of 2.7 ml H_2SO_4, 0.3 ml HF and 27 ml deionized water. Anodization bias was varied from 5 V to 35 V by a potentiostat (DH1718-5, Beijing Dahua Electronic Group). After anodization, Ta_2O_5 NTAs were carefully rinsed with deionized water to remove the excess HF and H_2SO_4.

In the two-step anodization, the first anodization step was conducted with the electrolyte consisted of 2.5 ml H_2SO_4, 0.5 ml HF and 27 ml deionized water for 15 min at a bias of 30 V. Then the Ta_2O_5 NTAs were removed by sonication in a deionized water bath and dried with flowing nitrogen. The second anodization process was then conducted according to the description above.

The obtained Ta_2O_5 NTAs were then annealed under a NH_3 flow (500 ml min^{-1}) in a tube furnace at 900 °C for 8 hours to get Ta_3N_5 NTAs.

Loading of Co_3O_4 co-catalyst: Co_3O_4 co-catalyst was loaded on the Ta_3N_5 NTAs through a previously reported hydrothermal method.[1] Specifically, 0.40 mL of 25% ammonium hydroxide was added into 25.0 ml of 5 mM $Co(CH_3COO)_2 \cdot 4H_2O$ ethanol solution under vigorous stirring. Then the obtained brown solution, after stirring for 10 min, was transferred into an autoclave with Ta_3N_5 NTA anode placed inside. The hydrothermal reaction was conducted at 120 ^oC for 1 h by putting the autoclave into an oven. The obtained Co_3O_4-Ta_3N_5 NTA anode was then washed with deionized water thoroughly and dried in air.

Characterizations: The morphology and microstructure of the samples were characterized by field-emission scanning electron microscopy (S-4800, Hitachi). The crystal structure of the sample was investigated using an X-ray diffractometer (D/MAX-2500) with Cu K_α radiation (λ = 1.5416 Å) at 40 kV and 140 mA. Optical transmittance measurements were performed using a Shimadzu UV-2550 spectrophotometer.

Electrochemical measurements: Electrochemical measurements of Ta_3N_5 NTAs electrodes were performed using a three-electrode configuration with the Ta_3N_5 NTAs as the working electrode; saturated Ag/AgCl as the reference electrode; and platinum foil (2×2 cm^2) as the counter electrode. A 1.0 M NaOH aqueous solution (pH 13.6) was used as the electrolyte which was purged with N_2 for 20 min to remove the oxygen. Potentials *vs.* Ag/AgCl were converted into potentials *vs.* RHE according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.196$). An electrochemical workstation (CompactStat.e20250, IVIUM) was used to measure the I-V curve, EIS, Mott-Schottky plot and IPCE.

The I-V curves were measured with a scan rate of 50 mV/s under the irradiation of a 300 W xenon lamp (Beijing Perfectlight Technology Co. Lt, LS-SXE300CUV) equipped with an AM1.5 filter.

The intensity of the light was adjusted to 100 mW cm^{-2}. Before the test, the electrode was encapsulated by epoxy and covered with a mask to expose 0.28 cm^2 surface area to the irradiation. The I-t curves were collected at the bias of 1.23 V *vs.* RHE. EIS data were gathered at a bias of 1.6 V *vs.* RHE using a 50 mV amplitude perturbation of between 10,000 and 0.1 Hz. Data were fitted using Zview software (Scribner Associates). The Mott-Schottky plot was obtained at a frequency of 100 Hz and amplitude of 15 mV. The ABPE was calculated according to the equation:

$$\mathrm{ABPE} = \frac{|I_{light}| \times (1.23 - V)}{\mathrm{P}} \times 100\%$$

where I_{light} is the photocurrent density under irradiation, V is the applied bias (vs. RHE) and P is the incident light power density. The IPCE was measured under monochromatic irradiation from a 150 W Xe lamp (Zolix LSH-X150) equipped with monochromator (Omni-λ 300) at 1.2 V *vs.* RHE according to the equation:

$$\mathrm{IPCE} = \frac{\left[\left(\frac{1240}{\lambda}\right) \times \left(I_{light} - I_{dark}\right)\right]}{\mathrm{P}} \times 100\%$$

where λ is the wavelength and I_{dark} is the photocurrent density under dark condition.

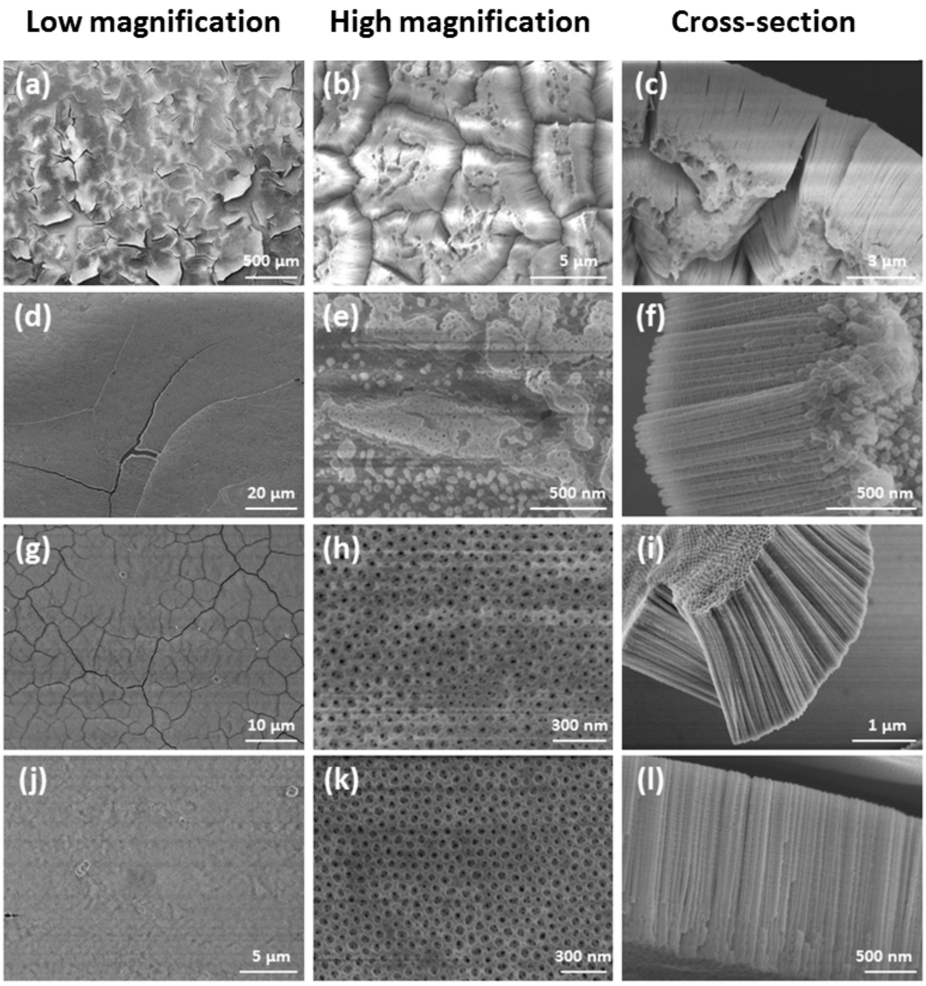

Figure S1. Low magnification top-view (the first column), high magnification top-view (the second column) and cross-section (the third column) SEM images of Ta_2O_5 NTAs synthesized in different conditions: (a, b and c) one-step anodization in a H_2SO_4 solution consisted of 1.7% (v/v) HF at room temperature; (d, e and f) one-step anodization in a H_2SO_4 solution consisted of 1.0% (v/v) HF at room temperature; (g, h and i) two-step anodization in a H_2SO_4 solution consisted of 1.0% (v/v) HF at room temperature; (j, k and l) two-step anodization in a H_2SO_4 solution consisted of 1.0% (v/v) HF at 0 °C. The anodization reactions were conducted with a bias of 15 V for 10 min.

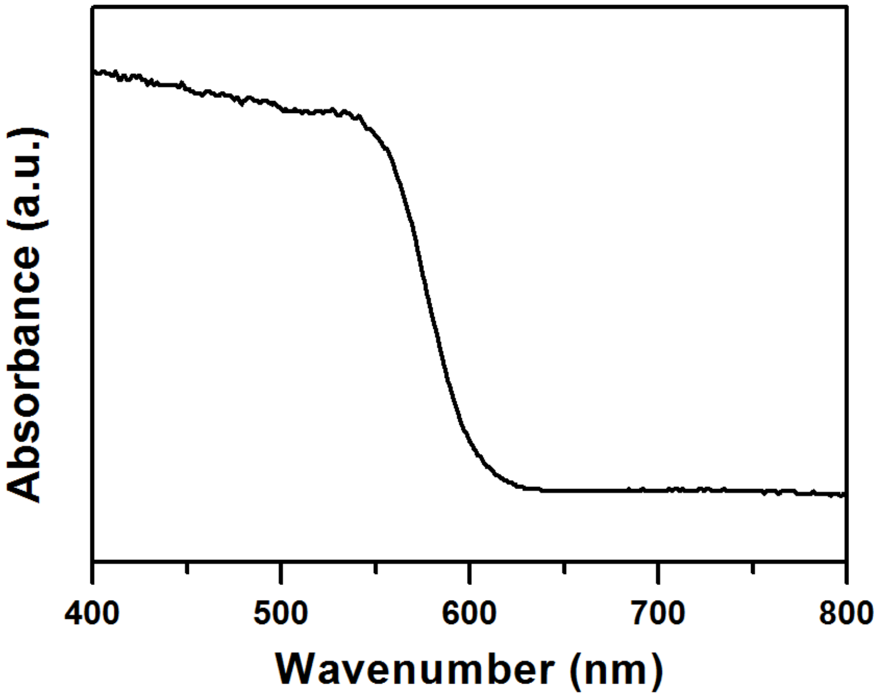

Figure S2. UV-Vis absorption spectrum of the Ta_3N_5 NTAs.

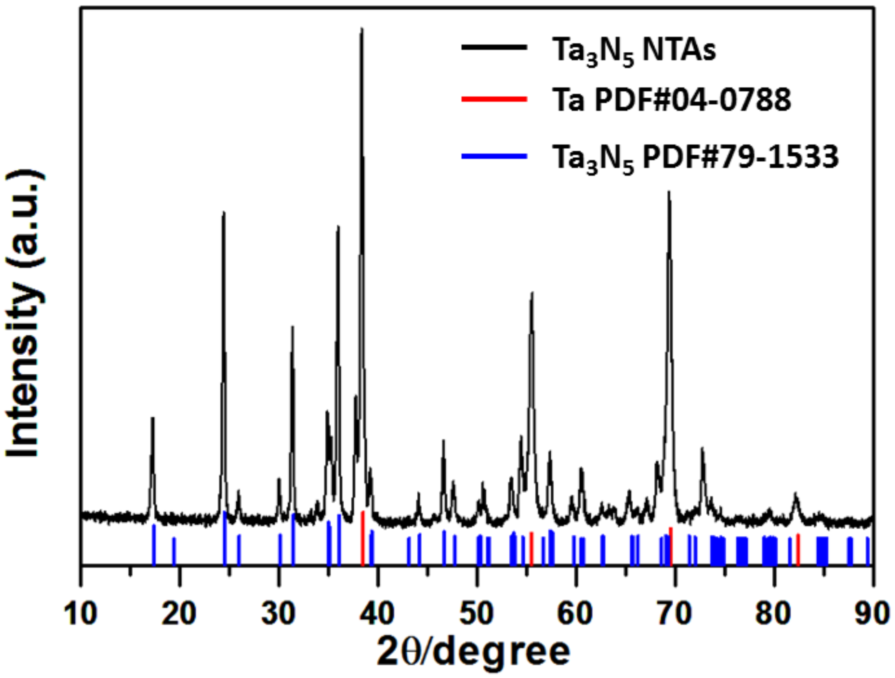

Figure S3. XRD pattern of the Ta_3N_5 NTAs.

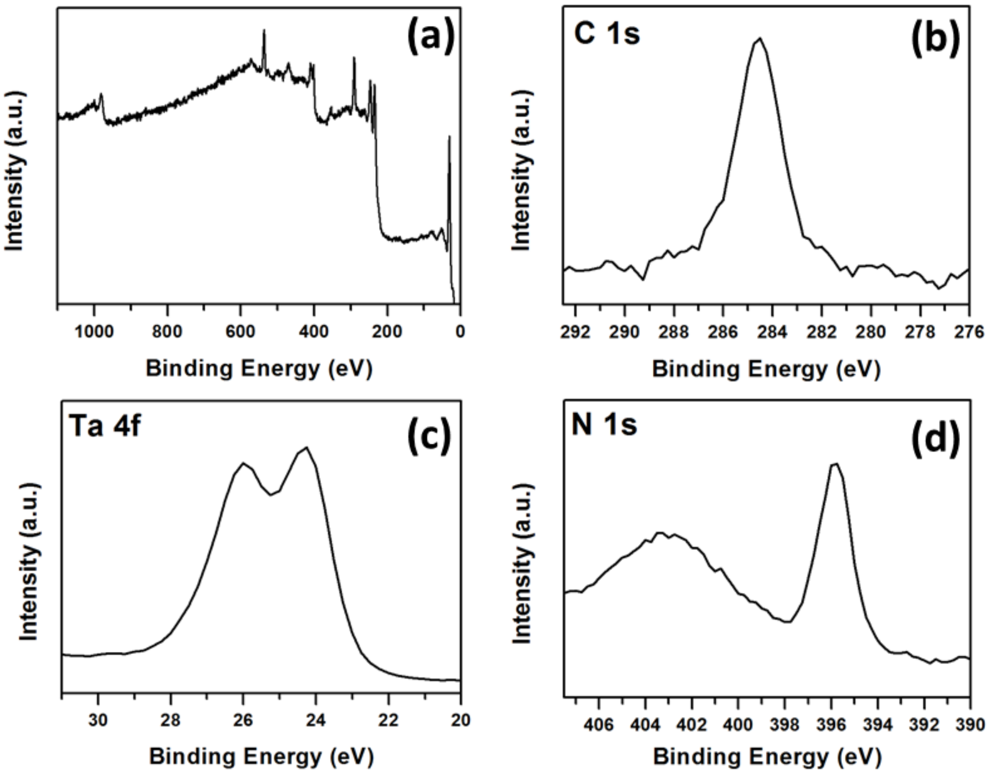

Figure S4. XPS spectra of (a) survey scan; (b) C 1s; (c) Ta 4f and (d) N 1s recorded from Ta_3N_5 NTAs.

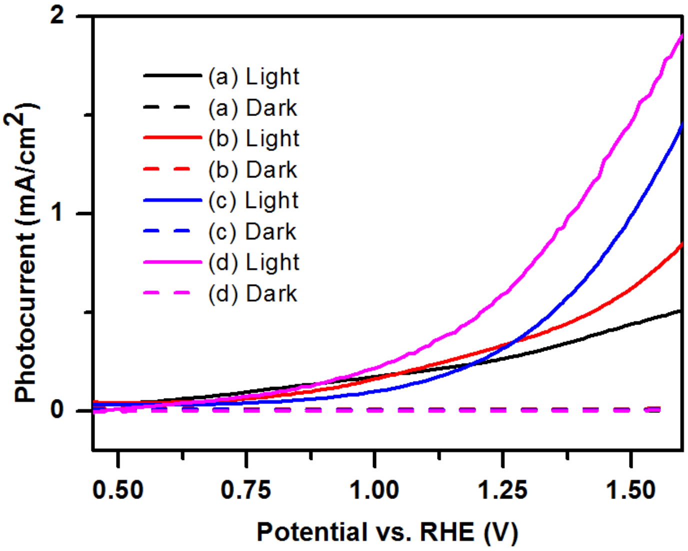

Figure S5. I-V curves of Ta_3N_5 NTAs after nitridation of Ta_2O_5 NTAs synthesized in different conditions: (a) one-step anodization in a H_2SO_4 solution consisted of 1.7% (v/v) HF; (b) one-step anodization in a H_2SO_4 solution consisted of 1.0% (v/v) HF at room temperature; (c) two-step anodization in a H_2SO_4 solution consisted of 1.0% (v/v) HF at room temperature; (d) two-step anodization in a H_2SO_4 solution consisted of 1.0% (v/v) HF at 0 °C. The anodization reactions were conducted with a bias of 15 V for 10 min.

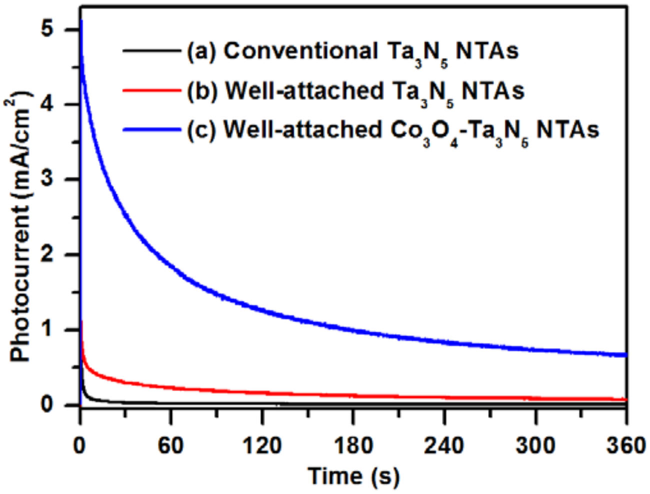

Figure S6. I-t curves of Ta_3N_5 NTAs at 1.23 V *vs.* RHE: (a) Ta_3N_5 NTAs synthesized by the conventional one-step anodization mehtod; (b) Well-attached Ta_3N_5 NTAs syntheized by the improved two-step anodization method (5 min, 25 V) and (c) Co_3O_4 co-catalyst loaded Ta_3N_5 NTAs in (b).

Table S1. Fitting results of the EIS of the Ta_3N_5 NTAs synthesized with different anodization durations. The anodization bias is 15 V for all samples.

Anodization duration/min	R_s/Ω	R_{ct}/Ω	R_b/Ω	C/μF	CPE/μF	Chi-squared
2.5	12.36	18349	46.51	2.50	7.50	0.00111
5	12.65	12717	34.24	7.04	17.17	0.00037
7.5	11.55	98825	77.54	1.69	8.02	0.00207
10	24.09	26381	16019	1.63	8.92	0.00056

Table S2. Fitting results of the EIS of the Ta_3N_5 NTAs synthesized with different anodization biases. The anodization duration is 5 min for all samples.

Anodization bias/V	R_s/Ω	R_{ct}/Ω	R_b/Ω	C/μF	CPE/μF	Chi-squared
5	13.57	23280	118.80	0.73	2.59	0.00111
15	12.65	12717	34.24	7.04	17.17	0.00037
25	2.94	8090	4.96	35.44	187.45	0.00007
35	11.97	11660	53.96	5.21	15.24	0.00149

[1] G. Liu, J. Shi, F. Zhang, Z. Chen, J. Han, C. Ding, S. Chen, Z. Wang, H. Han, C. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 7295.