Electronic Supplementary Information

Template-free synthesis of Ta_3N_5 nanorod arrays for efficient photoelectrochemical water splitting

Fabrication of Ta_3N_5 nanorod arrays: Ta foil with a thickness of 0.25 mm (Alfa Aesar) was successively washed in ethanol, acetone, isopropanol and deionized water each for 30 minutes before used. The clean Ta foil was suspended above a 0.1 M HF aqueous solution in a Teflon-lined autoclave, which was then heated at 180 ^{o}C for 24 h to grow Ta_2O_5 nanorod arrays on the Ta foil. Heating the resultant Ta_2O_5 nanorod arrays on the Ta foil under a gaseous atmosphere of NH_3 with a flow of 50 mL/min at 1000 ^{o}C for 6 h led to the formation of Ta_3N_5 nanorod arrays.

Deposition of $Co(OH)_x$ nanoparticles on Ta_3N_5 nanorod arrays: A successive ionic layer adsorption and reaction method was used to deposit $Co(OH)_x$ nanoparticles on the photoelectrodes. The Ta_3N_5 nanorod array photoelectrodes were successively immersed in an aqueous solution of $Co(CH_3COO)_2$ (0.05 M), deionized water, an aqueous solution of NaOH (0.1 M) and deionized water each for one minute to finish one cycle deposition of $Co(OH)_x$ nanoparticles. By repeating the above deposition cycle, the desired amount of $Co(OH)_x$ nanoparticles can be loaded on the photoelectrodes.

Characterization: X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using Cu Kα irradiation. SEM and TEM images were obtained on a Nova NanoSEM 430 and JEOL 2010, respectively. Diffuse reflectance absorption spectra were recorded using a UV-visible spectrophotometer (JASCO-550). The chemical states were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al Kα X-ray source). Binding energy was referenced to the C 1s peak (284.6 eV) arising from adventitious carbon.

Photoelectrochemical measurements: The photoelectrochemical water splitting was carried out in a three-electrode system, where the prepared nanorod array films, Ag@AgCl electrode and Pt foil act as working electrode, reference electrode and

counter electrode, respectively, in the electrolyte of aqueous 1 M NaOH solution under AM 1.5G illumination with a density of 100 $mWcm^{-2}$ (Newport). According to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.196$), the measured potentials vs the RHE scale can be obtained from the potentials vs Ag/AgCl. The wavelength dependent incident photon-to-current conversion efficiency was calculated according to the following equation:

IPCE (%) = [1240 × photocurrent density ($mAcm^{-2}$)] / [wavelength (nm) × photon flux ($mW\ cm^{-2}$)] × 100%

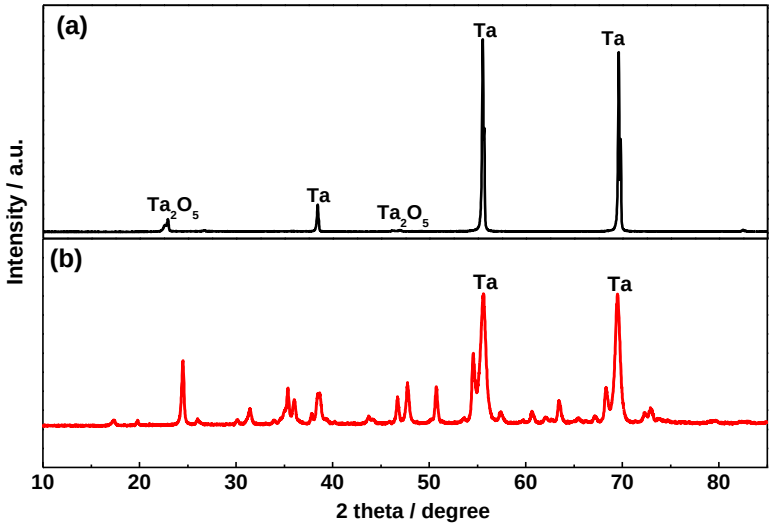

Figure S1 XRD patterns of (a) F-Ta_2O_5 nanorod arrays and (b) Ta_3N_5 nanorod arrays on the Ta substrates.

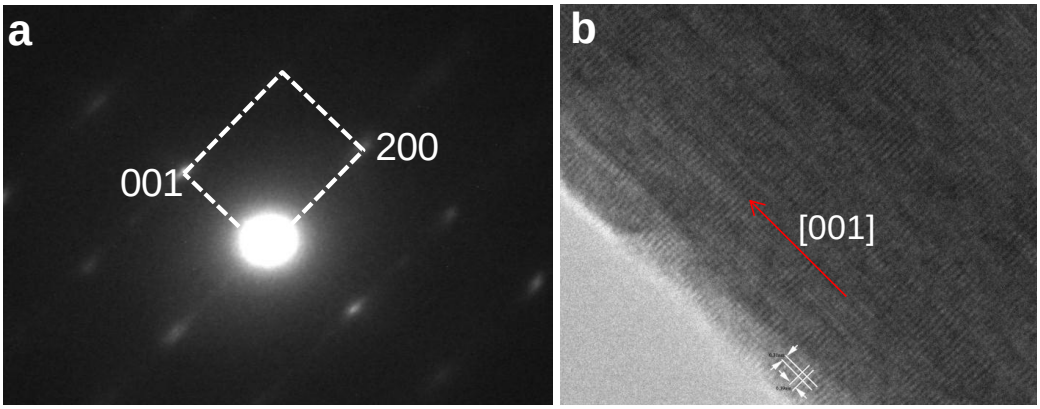

Figure S2 Selected electron area diffraction pattern and high resolution TEM image recorded from a single Ta_2O_5 nanorod.

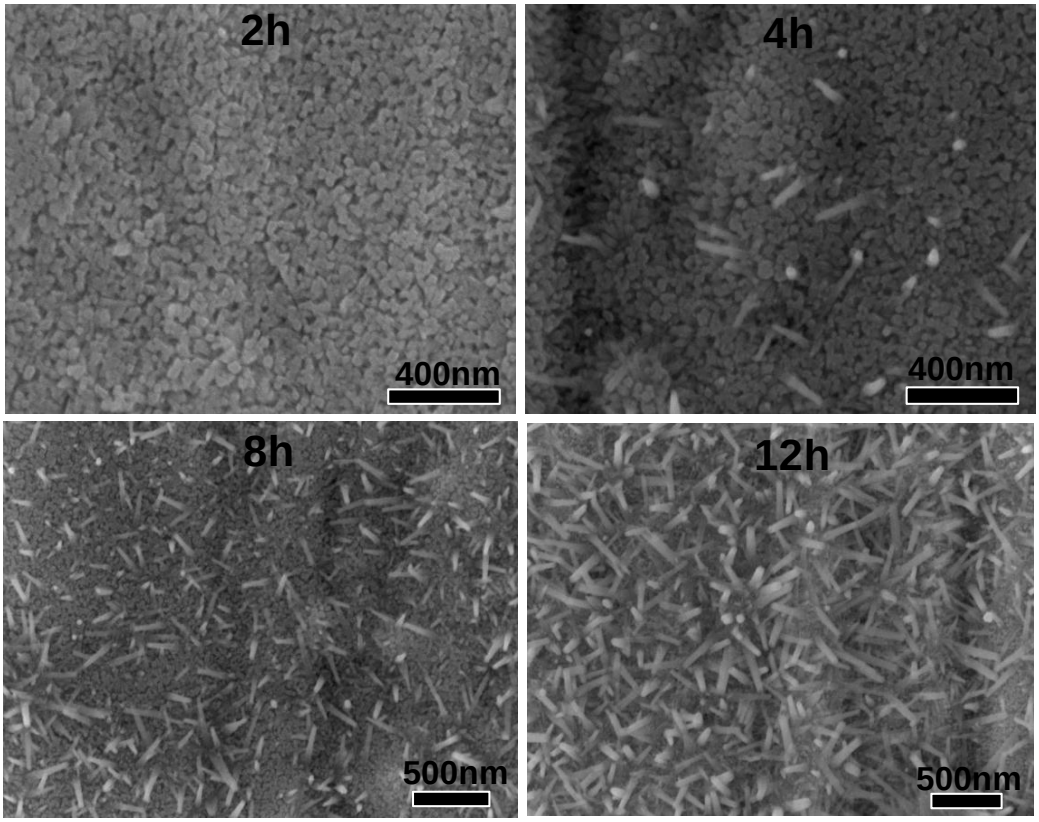

Figure S3 Time dependent growth processes (2 h, 4 h, 8 h and 12 h) of F-Ta_2O_5 nanorods on Ta substrates during the VPH process.

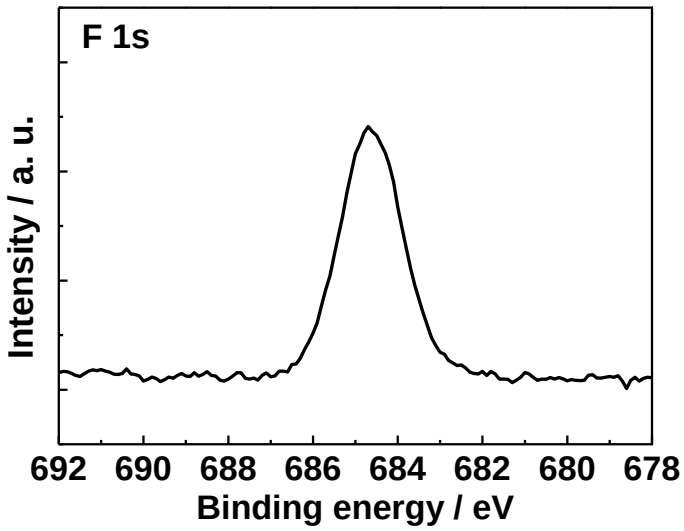

Figure S4 High resolution XPS spectrum of F 1s recorded from the F-Ta_2O_5 nanorod array film.

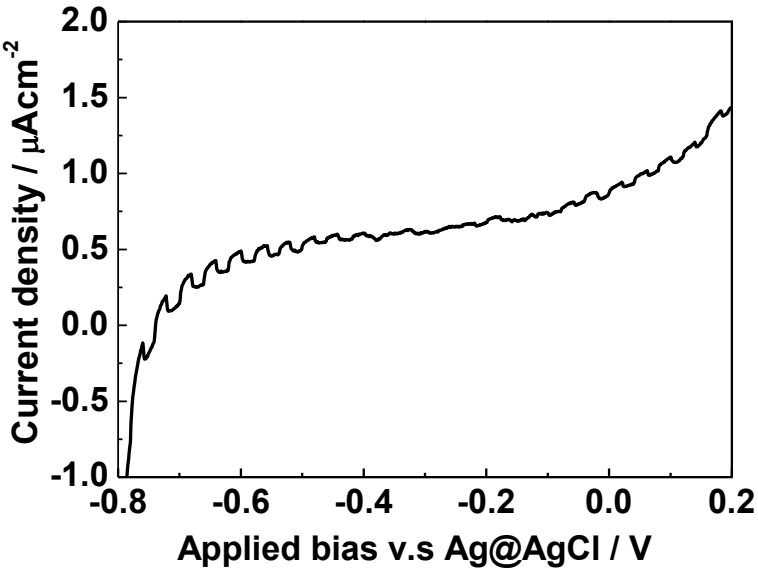

Figure S5 Applied potential bias-dependent photocurrent density of F-Ta_2O_5 nanorod arrays. The curves were measured in 0.2 M Na_2SO_4 aqueous solution (pH=6.8) under AM 1.5G simulated sunlight at 100 $mWcm^{-2}$.

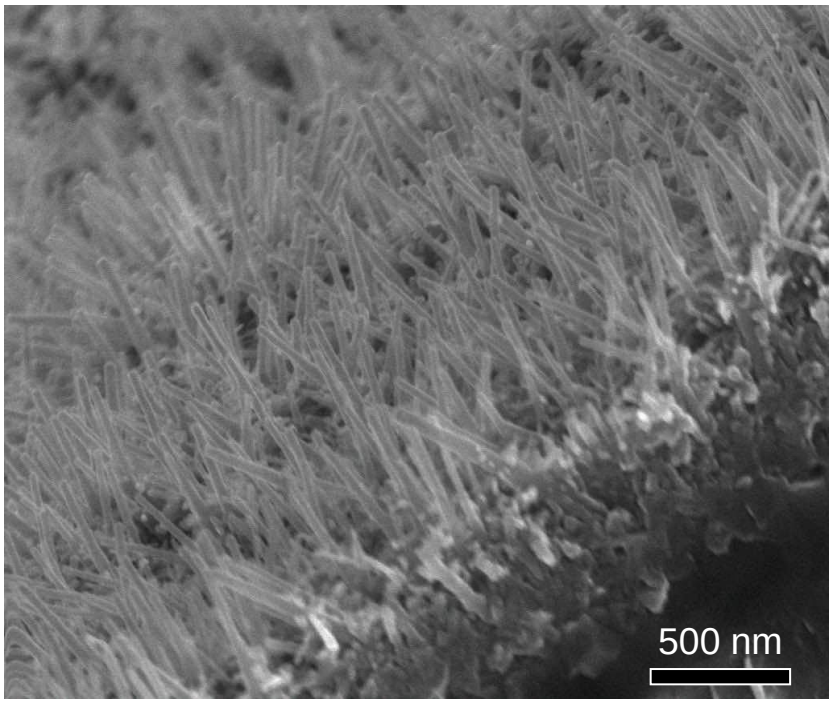

Figure S6 The cross-section SEM image of the Ta_3N_5 nanorod arrays on the Ta substrate.

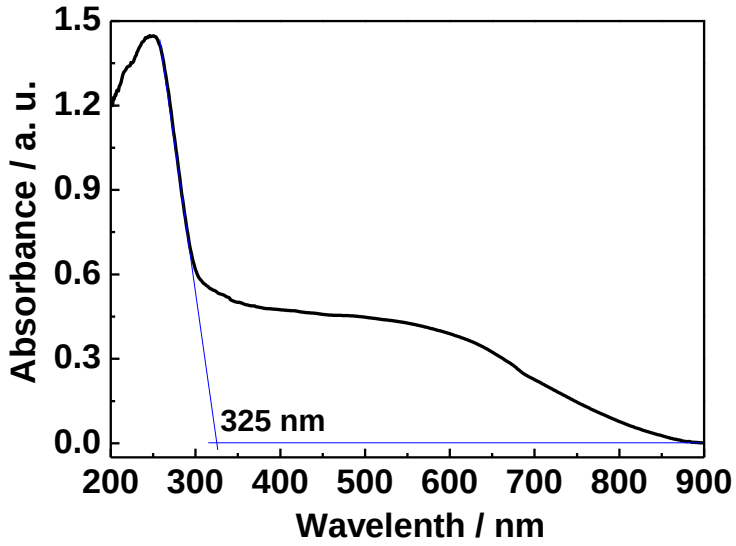

Figure S7 UV-visible absorption spectrum of F-Ta_2O_5 nanorod arrays.

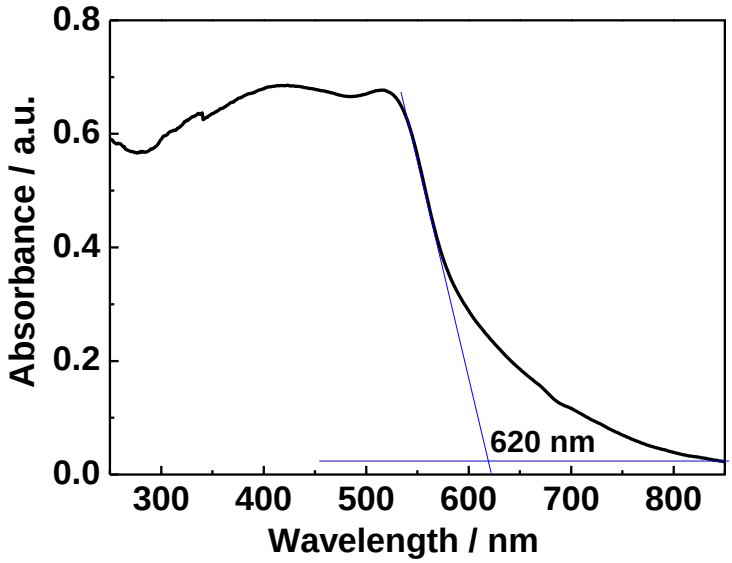

Figure S8 UV-visible absorption spectrum of Ta_3N_5 nanorod arrays.

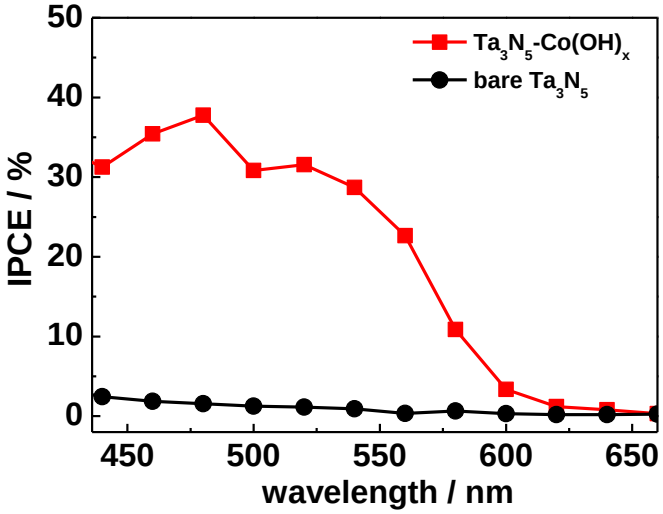

Figure S9 Wavelength dependent IPCE curves of bare Ta_3N_5 and $Co(OH)_x$-modified Ta_3N_5 nanorod arrays, measured in 1 M NaOH aqueous solution at $1.23V_{RHE}$.