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One-step synthesis of single-crystal wedge-shaped Ta_3N_5 nanoflake with ultrathin top end

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Method

Ta foil (0.2*0.7*1.6 mm^3, 99.5% purity) was washed ultrasonically with ethanol and acetone in succession for 1 h. All the alkali metal salts (purchased from Aladdin Co., China) were 99.9% purity and used without further purification. For the mixed CsI-Cs_2CO_3 flux, the CsI was 1 g and the Cs_2CO_3 varied from 2 mg to 50 mg. For other mixed fluxes, the amount alkali halide salt (including KI, RbI, RbCl, and CsCl) was fixed at 1 g, and the corresponding alkali carbonate (K_2CO_3, Rb_2CO_3 and Cs_2CO_3) was fixed at 10 mg. For all kinds of fluxes, the Ta foil and the flux were put into an Al_2O_3 crucible and annealed in a tube furnace under 400 ml min^{-1} NH_3 flow. The temperature was ramped to 850 °C at a rate of 10 °C min^{-1} and kept for 300 min. Then the crucible was allowed to cool down naturally. In the time-course experiment, the holding time was varied from 0 min to 60 min. When using 1 g pure CsI as flux, a pre-oxidation step was added that annealing the Ta foil in air at 550 °C for 20 min, 30 min, 45 min, and 60 min respectively.

Crystal structure of the film was determined by X-ray diffraction (XRD, Rigaku, Ultima III, Cu Kα irradiation). A scanning electron microscope (SEM, FEI Nova Nanosem 230) was used to obtain the morphology and cross-sectional images of the samples. The high resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) images were taken by a transmission electron microscope (TEM, FEI TF-20). An atomic force microscope (AFM, Asylum Research, MFP-3D-SA) was utilized to give the thickness of nanoflakes. The photocurrent was measured with an electrochemical analyzer (Shanghai Chenhua, CHI 660e) in a three-electrode system of Pt counter electrode and Ag/AgCl reference electrode. The electrolyte was 1 M NaOH solution, and the light source was AM 1.5G simulated sunlight (100 mW cm^{-2}, oriel 92251A-1000).

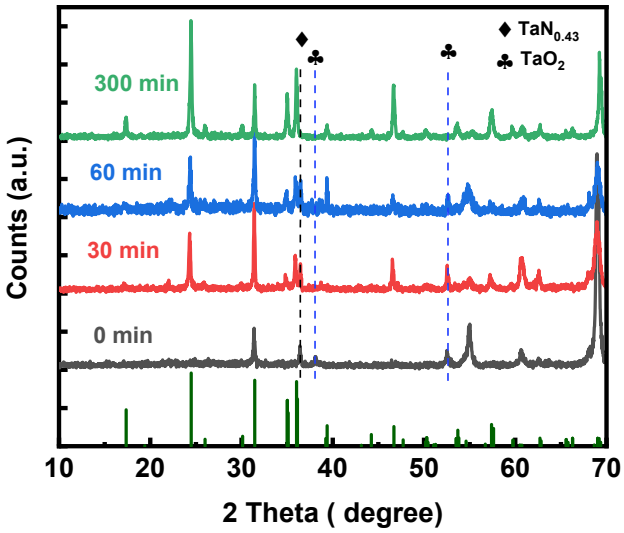

Fig. S1 XRD patterns of Ta_3N_5-10 films obtained at varied growth durations.

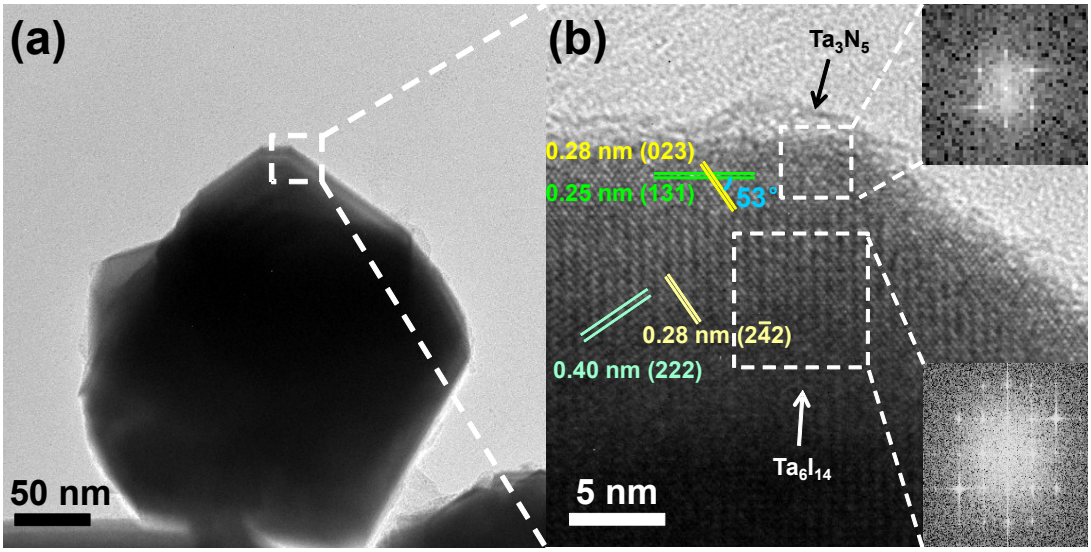

Fig. S2 TEM images of the polyhedron scratched from 0-min Ta_3N_5-10 sample.

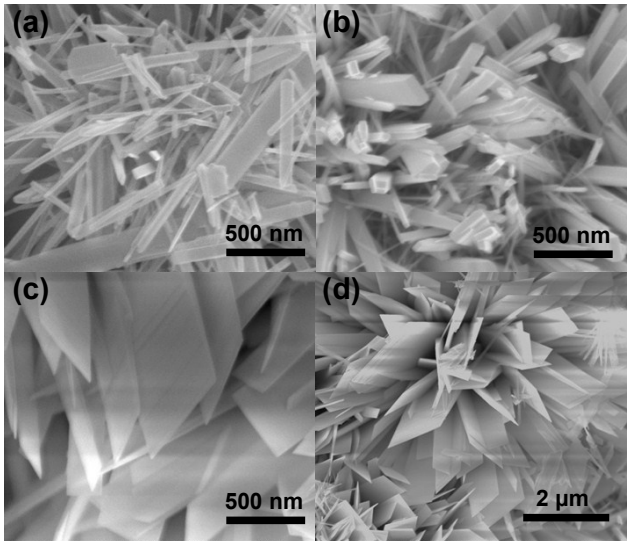

Fig. S3 SEM image of Ta_3N_5 films obtained using a) KI-K_2CO_3 flux; b) RbI-Rb_2CO_3 flux; c) and d) CsCl-Cs_2CO_3 flux.

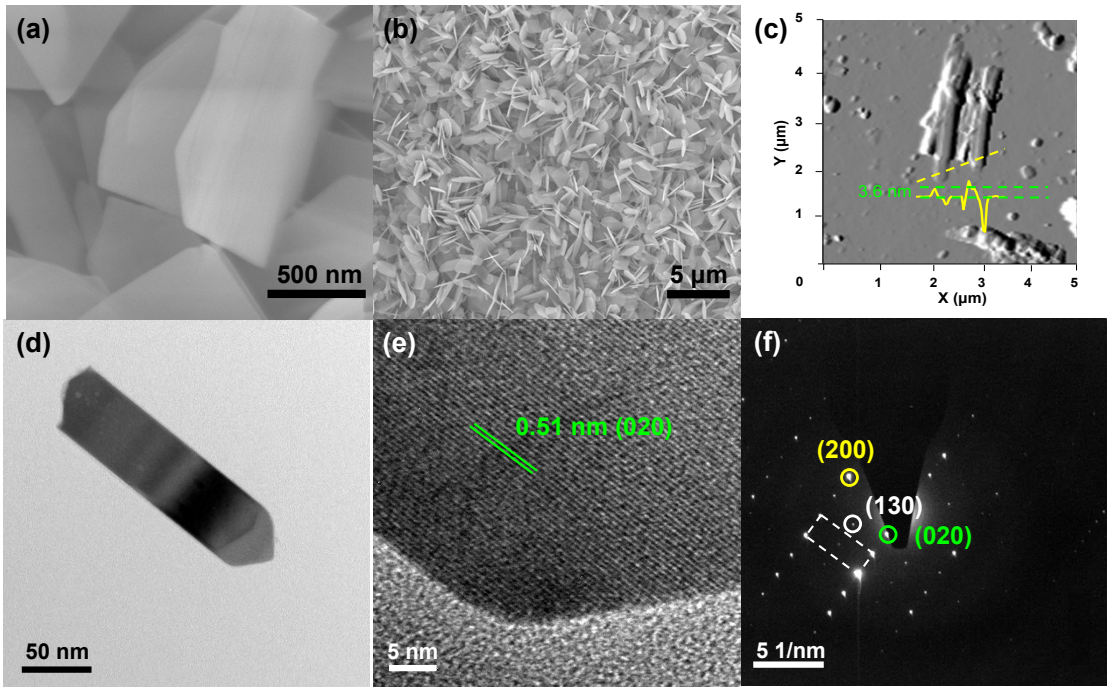

Fig. S4 a) and b) SEM iamges of the Ta_3N_5 using RbCl-Rb_2CO_3 flux. c) AFM of the as-synthesized nanoflake. d) Low resolution image, e) high resolution image, and f) SAED pattern of the nanoflake measured in TEM.

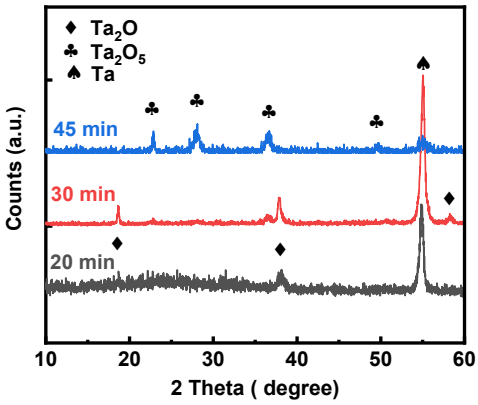

Fig. S5 XRD patterns of the pre-oxidized Ta foil.

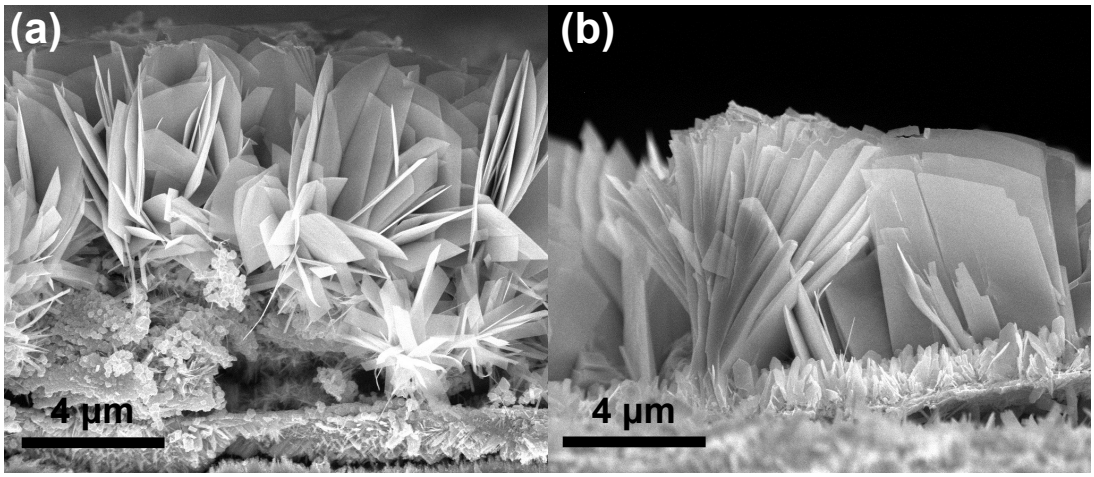

Fig. S6 Cross section images of Ta_3N_5-10 of a) 60 min; b) 300 min holding time.

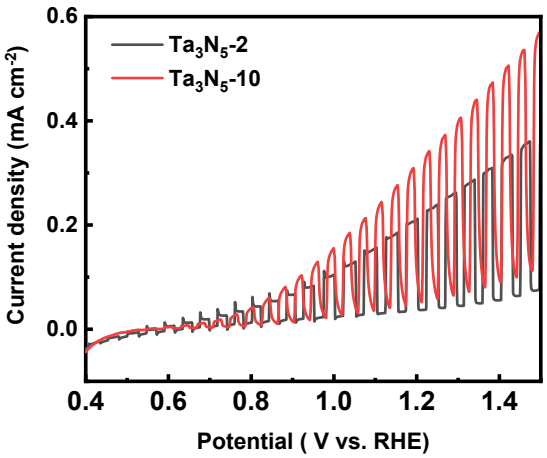

Fig. S7 Photocurrents of the Ta_3N_5-2 and Ta_3N_5-10 loading $Ni_{0.9}Fe_{0.1}OOH$ co-catalyst.