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Supporting Information

Facile and economical synthesis of nitrogen-rich tantalum nitrides via an ammonia looping process under confined space

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Synthesis of the Ta_3N_5 and Ta_4N_5. In a typical synthesis, 2 mmol of tantalum pentachloride ($TaCl_5$, 99.9%, J&K Scientific Ltd.) was homogeneously mixed with 30 mmol cyanamide (H_2NCN, 95%, J&K Scientific Ltd.) under magnetic stirring under nitrogen atmosphere. After complete reaction, the obtained product was ground, washed with ethanol, and filtered. The obtained faint yellow Ta-containing precursor was then dried at 80 °C and ground into powder. Then the Ta-containing precursor was added into a clean quartz tube. After the quartz tube was evacuated and sealed, the confined space was formed. Ta_3N_5 was prepared by pyrolysis of the Ta-containing precursor in the evacuated quartz tube at different temperatures at a heating rate of 10 °C min^{-1} for one hour. Ta_3N_5-900, Ta_3N_5-950, and Ta_3N_5-1000 denoted the corresponding sample synthesized at 900 °C, 950 °C, and 1000 °C, respectively. The Ta_4N_5 was synthesized via pyrolysis of the same precursor under argon atmosphere at 900 °C at a heating rate of 10 °C min^{-1} for one hour. Both Ta_3N_5 and Ta_4N_5 samples were directly obtained after cooling without further treatment.

Characterization. The morphology of the samples was characterized by field-emission scanning electron microscope (FESEM, JEOL 7800F) and transmission electron microscope (TEM, JEOL 2100F). Phase analysis was performed by X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer with Cu-Kα (1.5406 Å) irradiation. X-ray photoelectron spectroscopy (XPS) was obtained using an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV). Raman spectra were collected with a LabRAM HR Evolution spectrometer

(Horiba Scientific) with an excitation wavelength of 633 nm. The UV-visible spectra were recorded in the range of 300 to 800 nm using a U-4100 spectrometer. Fourier-transform infrared spectroscopy (FTIR) measurements were carried out in a Spotlight 400. Thermogravimetry coupled with Fourier transform infrared analysis (TG-FTIR) analysis was carried out in the temperature range of 25 to 900 °C with a heating rate of 20 °C min^{-1} under nitrogen atmosphere.

Photocatalytic degradation of methylene blue over Ta_3N_5. Methylene blue solution (50 ml, 1 mg L^{-1}) was mixed with 10 mg of the as-prepared Ta_3N_5. After being stirred in the dark for 60 min at room temperature to achieve absorption-desorption equilibrium, the solution was placed in a quartz vessel and irradiated by a Xenon lamp at 300 W. Then the solution was collected, centrifuged at 8000 rpm for 3 min to remove the catalysts, and analyzed using a UV–vis spectrophotometer at given time intervals.

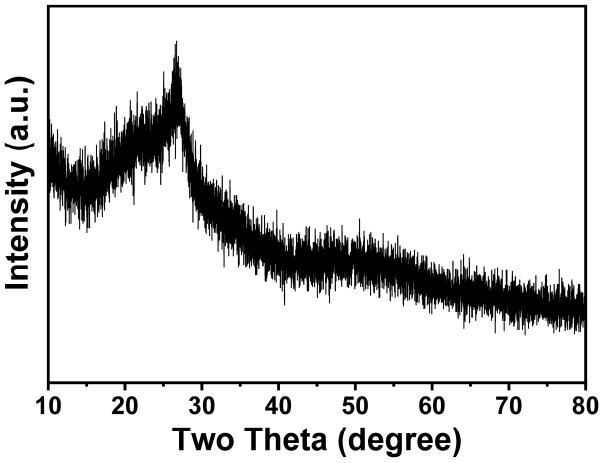

Figure S1. The XRD pattern of the Ta-$(NCNH_2)_x$ precursor.

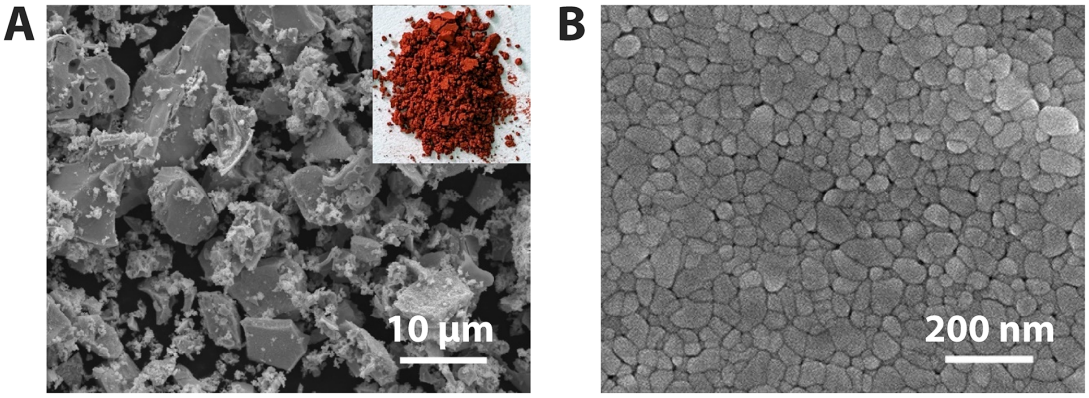

Figure S2. (A, B) FESEM images of the product synthesized by pyrolyzing the precursor at 900 °C under NH_3 atmosphere (inset is the picture showing the color of the product).

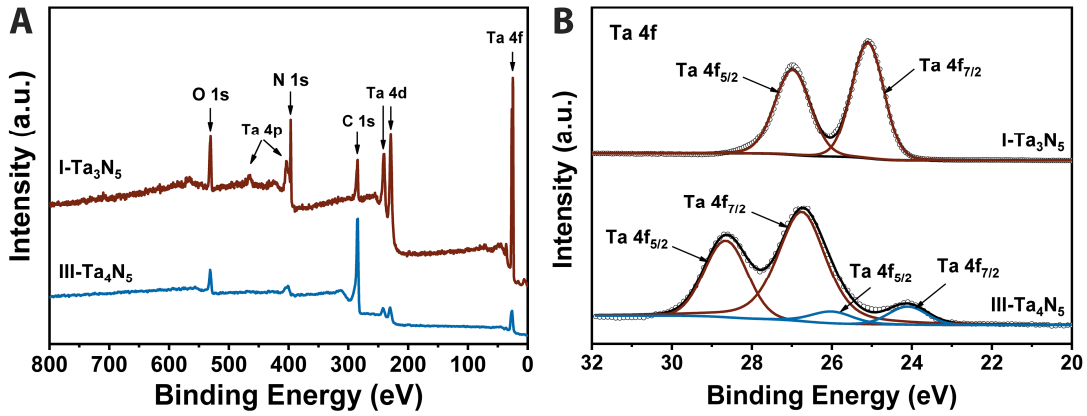

Figure S3. (A) XPS survey spectra, and (B) high-resolution Ta 4f XPS spectra of I-Ta_3N_5 and III-Ta_4N_5.

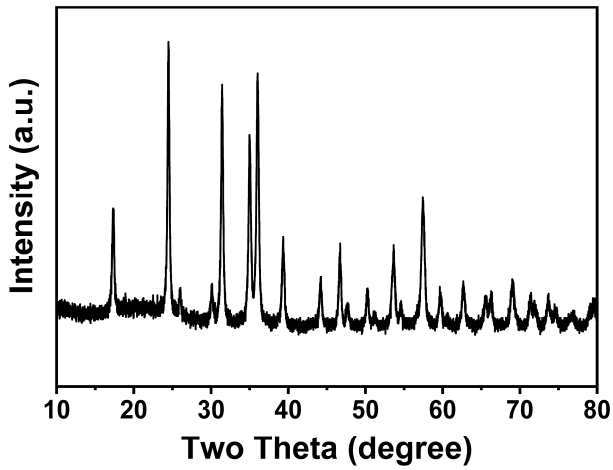

Figure S4. The XRD pattern of the Ta_4N_5 after being nitridized by NH_3.

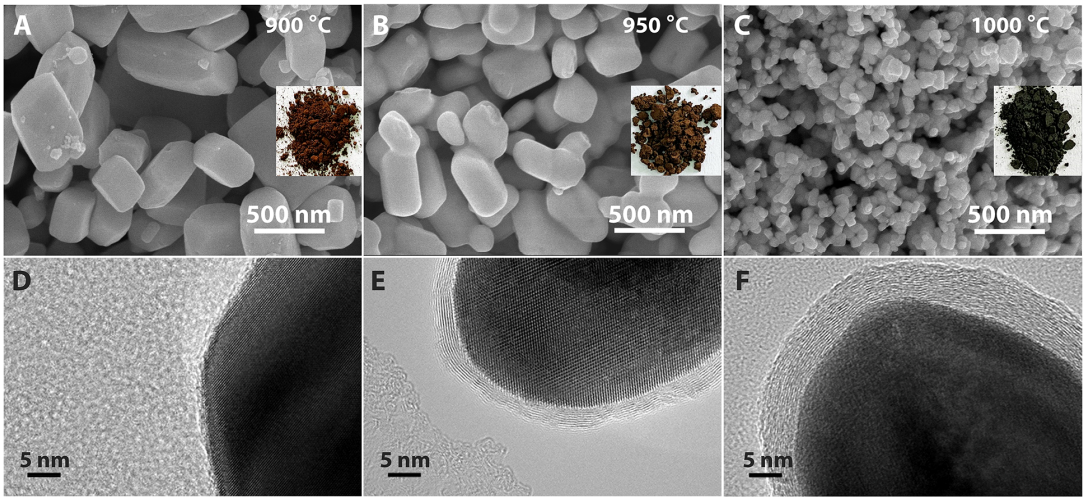

Figure S5. (A, B, C) FESEM images (insets are pictures showing the color of the corresponding products) and (D, E, F) TEM images of the product generated under vacuum at different temperatures.

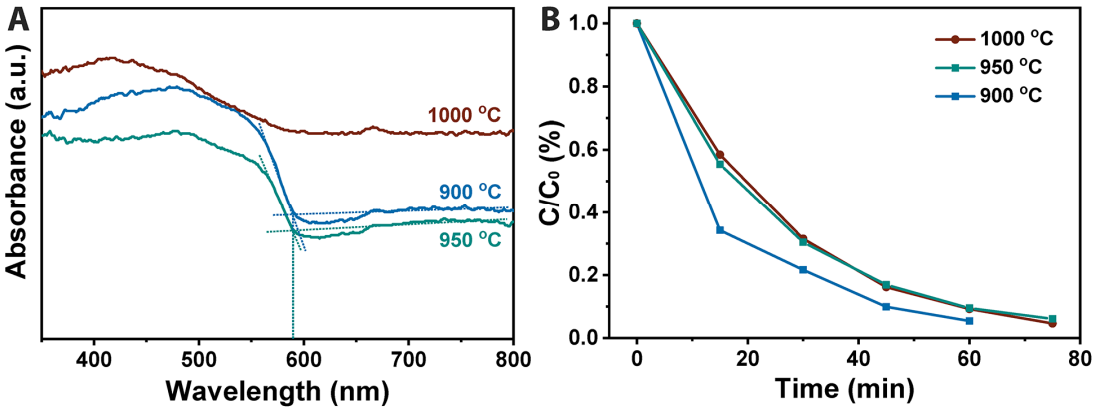

Figure S6. (A) UV-vis spectra and (B) the performance of photocatalytic degradation of methylene blue of the Ta_3N_5 particles generated under vacuum at different temperatures.

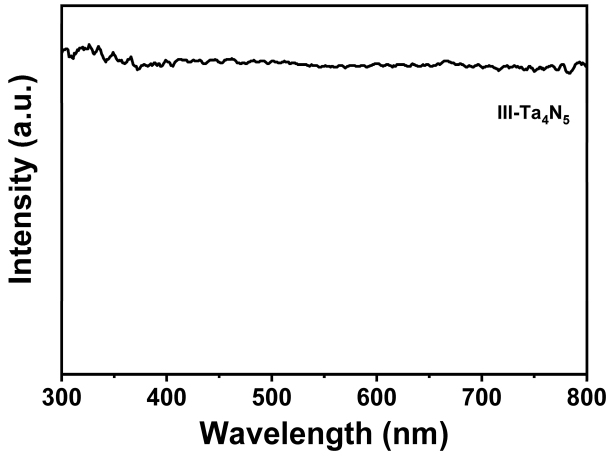

Figure S7. The UV-vis spectrum of III-Ta_4N_5.