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Supplementary Information

Promoted Nitrogen Photofixation over Periodic WS_2@TiO_2 Nanoporous Film

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Experimental Section

The anodic growth of the periodic TiO_2 nanoporous film. The periodic TiO_2 nanoporous film was prepared *via* anodization of Ti foil in an electrolyte solution of 3 M HF/H_3PO_4 (98%, Alfa Aesar, US) at 80 ^oC with the potential of 10 V for 4 hours. After that, the obtained sample was washed with ethanol and water several times and then dried in air. The oxygen vacancies rich sample was obtained by further heating at 450 ^oC for 1 hour in Ar. In comparison, the oxygen vacancies deficient sample was obtained by heating at 450 ^oC for 1 hour in the air.

W deposition and sulfurization. The deposition of W on the periodic TiO_2 nanoporous film was performed on an e-Beam evaporator (AJA International, Inc., ATC 2200-V), and the deposition thickness was set at 10 nm, 20 nm, and 30 nm, respectively. After deposition, the W/TiO_2 composite was further sulfurized by a CVD method. Briefly, a 0.5 M Na_2S containing 1 M sulfur was put at the upstream side of a tube furnace, and the temperature was set at 150 ^oC with a heating speed of 2 ^oC min^{-1}. A piece of W/TiO_2 sample was placed in the center of a tube furnace, and the temperature was set at 400 ^oC with a heating speed of 5 ^oC min^{-1}. The sulfurization was performed for 30 min under vacuum.

Materials characterizations. The morphology of the samples was observed by field-emission scanning electron microscope (FE-SEM, ZEISS ultra 55) and transmission electron microscope (TEM, FEI Tecnai F30). The composite and chemical states of the samples were investigated by X-ray photoelectron spectroscopy (XPS) measurement. The X-ray diffraction (XRD) patterns were obtained from an X'pert Powder machine (PANalytical, equipped with a Panalytical X'celerator detector using Cu Kα radiation). Raman spectra were recorded on a Renishaw InVia Microscope equipped with an excitation laser of 532 nm. The optical properties of the samples were tested by a Cary Win UV-visible spectrometer. The decay time measurement was performed on a fluorescence lifetime spectrometer (Quantaurus-Tau, C11367, HAMAMATSU) and the excitation source is a LED lamp at the wavelength of 365 nm.

Photocatalytic N_2 fixation. The photocatalytic N_2 reduction was performed in a single-compartment electrochemical cell, which contained a 30 ml solution with 0.01 M Na_2SO_3 as a sacrificial electron donor. The films with a size of 2×2 cm^2 were measured. Simulated sunlight (AM1.5) was used as the light source. A constant high-purity N_2 flow was bubbled through the solution for one hour to remove the oxygen before light irradiation and then was continuously bubbled during the reaction. 1.0 ml of the reaction solution was taken out every 3 hours. The concentration of ammonia produced in the solution was analyzed by the indophenol blue method, namely, 1.0 ml of the remained solution was added with 2 ml of a 1M NaOH solution (5 wt% salicylic acid and 5 wt% sodium citrate), 1mL of 0.05 M NaClO solution and 0.2 mL of sodium nitroferricyanide solution (1 wt%). After the complete color development for 2 h, the absorption spectra of the mixture solution were determined with a UV-vis spectrophotometer. In order to quantify the NH_3 in the reaction solution, the calibration curves were obtained by using standard NH_4Cl solutions.

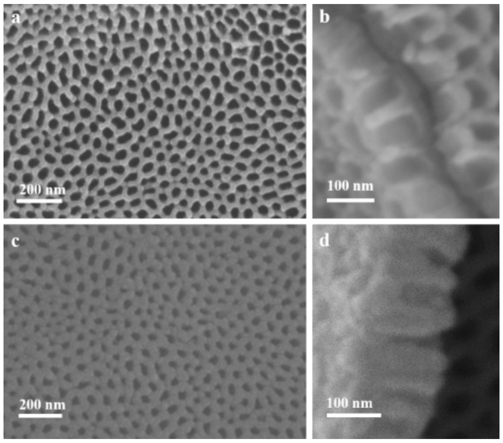

Figure S1. SEM images of (a, b) 10nm W@TiO_2 composite and (c, d) 30nm W@TiO_2 composite.

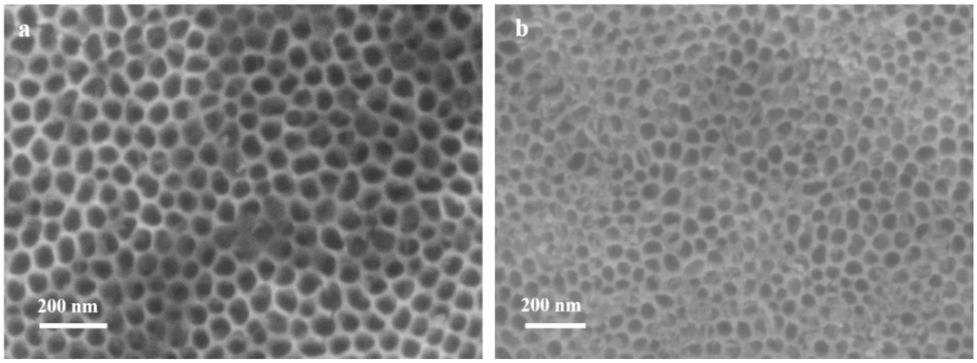

Figure S2. SEM images of (a) 10WS_2@TiO_2 and (b) 30WS_2@TiO_2.

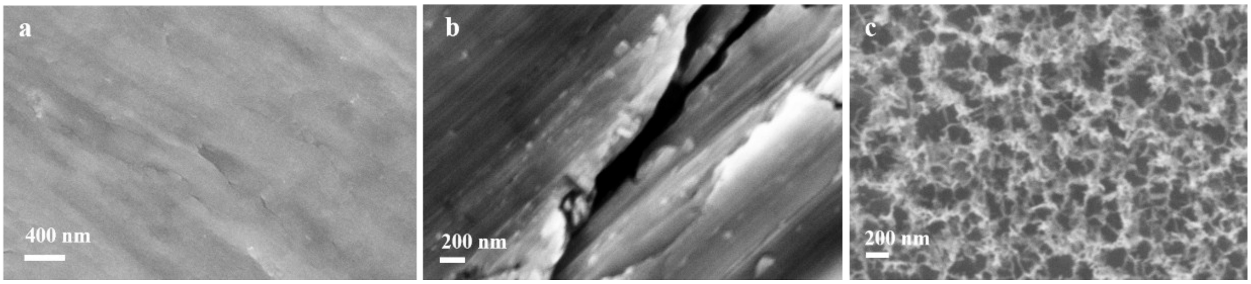

Figure S3. SEM images of (a, b) flat TiO_2 film, (c) 20WS_2/flat TiO_2. The 20WS_2/flat TiO_2 was prepared using the same method as 20WS_2@TiO_2, except that flat TiO_2 film was used as a substrate instead of a TiO_2 nanoporous film.

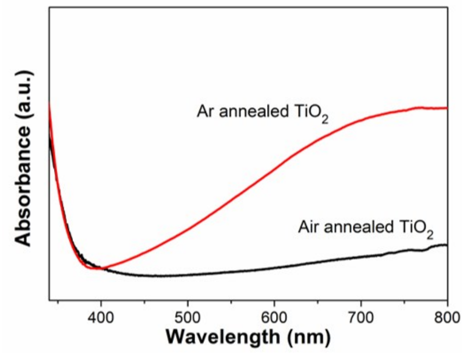

Figure S4. UV-vis spectra of the Ar-annealed TiO_2 film and air-annealed TiO_2 film.

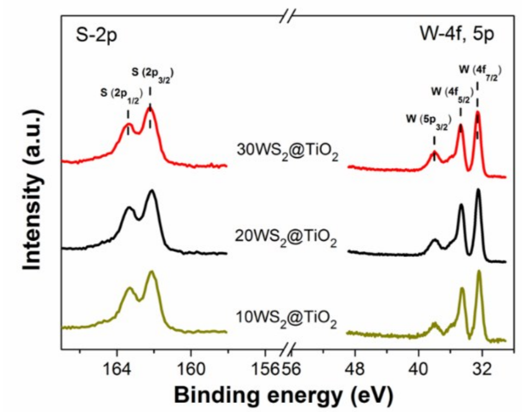

Figure S5. XPS peaks of W and S for different samples.

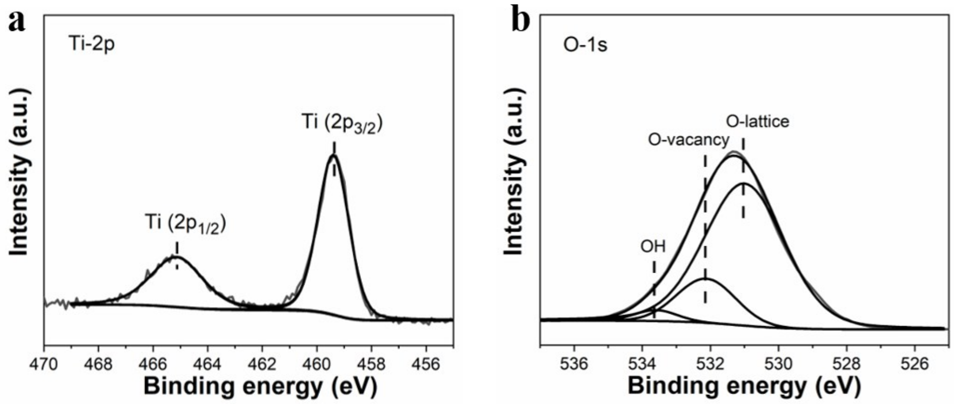

Figure S6. XPS peaks of Ti and O for Air annealed TiO_2 NFs.

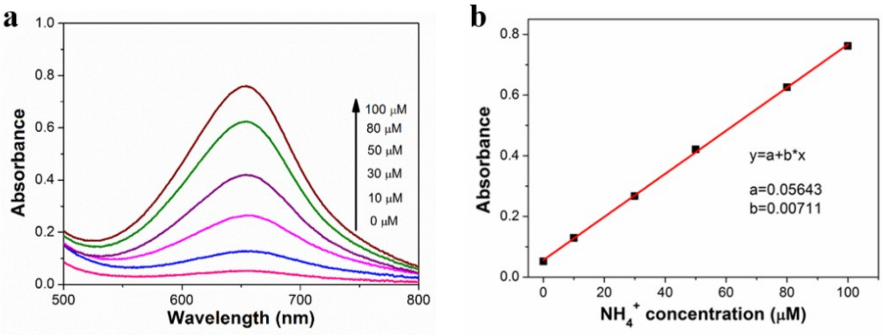

Figure S7. The UV-Vis absorption spectra and corresponding calibration curves for the colorimetric detection of ammonia.

Table S1. Comparison of the photocatalytic N_2 fixation performances with different catalysts.

Catalysts	NH_3 production rate	Light source	Reaction solution	References
20WS$_2$@TiO$_2$ film	**0.13 μmol/h (1.39 mmol g^{-1} h^{-1})**	**AM 1.5G**	**Water/Na$_2$SO$_3$**	**This work**
TiO$_2$/Au/a-TiO$_2$ film	0.0134 μmol/h	AM 1.5G	Water	[1]
GNP/bSi/Cr film	0.08 μmol/h	300 W Xe lamp	Water/Na$_2$SO$_3$	[2]
Au-NPs/Nb-SrTiO$_3$/Zr/ZrO$_x$ film	0.007 μmol/h/cm^2	xenon light 550 nm<λ<800 nm	Water/ethanol	[3]
FeMoS-Chalcogels	0.09 μmol/h (0.45 μmol g^{-1} h^{-1})	150 W xenon lamp	Water/pyridinium hydrochloride /sodium ascorbate	[4]

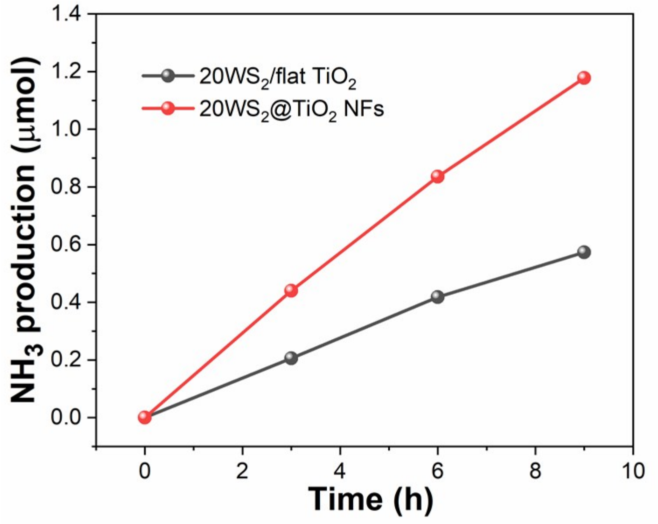

Figure S8. Photocatalytic NH_3 evolution over 20WS$_2$/flat TiO$_2$ and 20WS$_2$@TiO$_2$ NFs respectively.

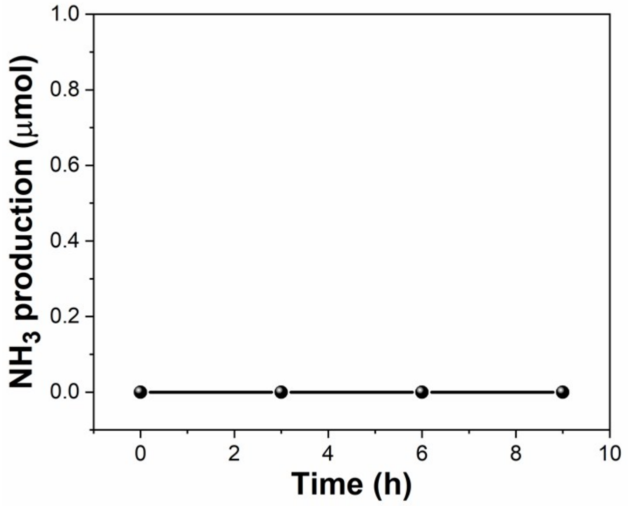

Figure S9. Photocatalytic NH_3 evolution over 20WS$_2$@TiO$_2$ NFs under visible light.

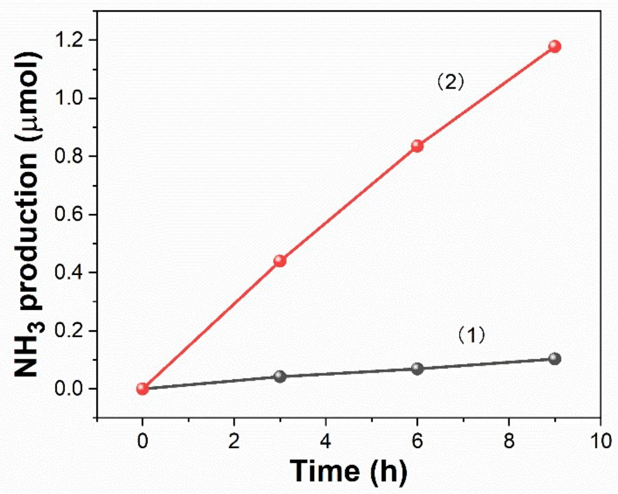

Figure S10. Photocatalytic NH_3 evolution over $20WS_2@TiO_2$ NFs in (1) pure water and (2) H_2O/Na_2SO_3 solution.

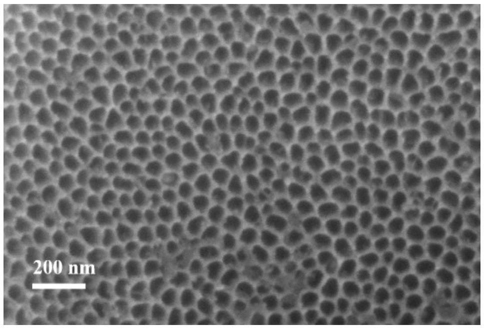

Figure S11. SEM image of $20WS_2@TiO_2$ after four successive cycles test.

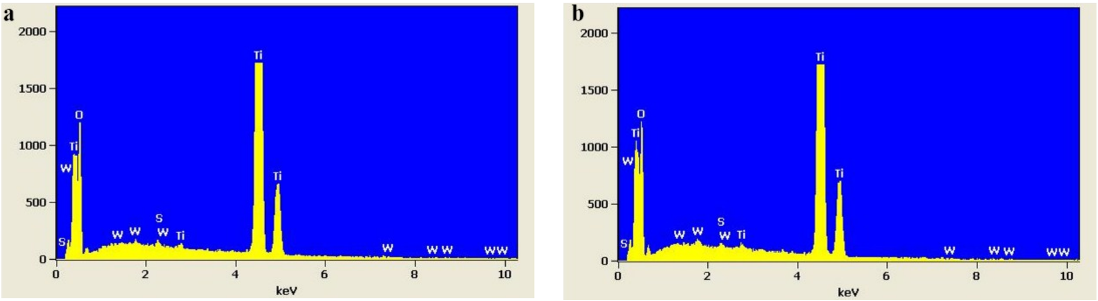

Figure S12. EDS of $20WS_2@TiO_2$ (a) before and (b) after four successive cycles test.

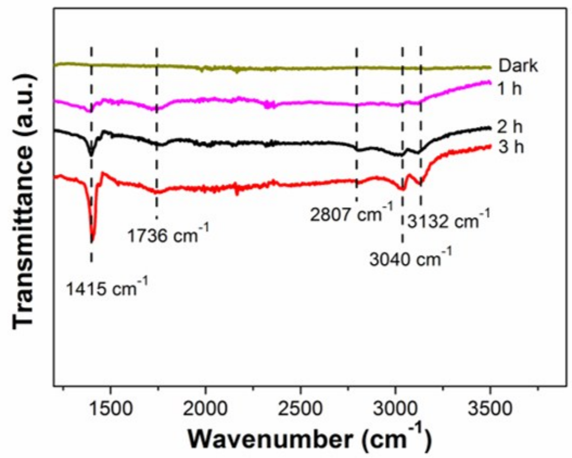

Figure S13. In situ DRFTIRS recorded from $20WS_2@TiO_2$ during the photocatalytic N_2 fixation.

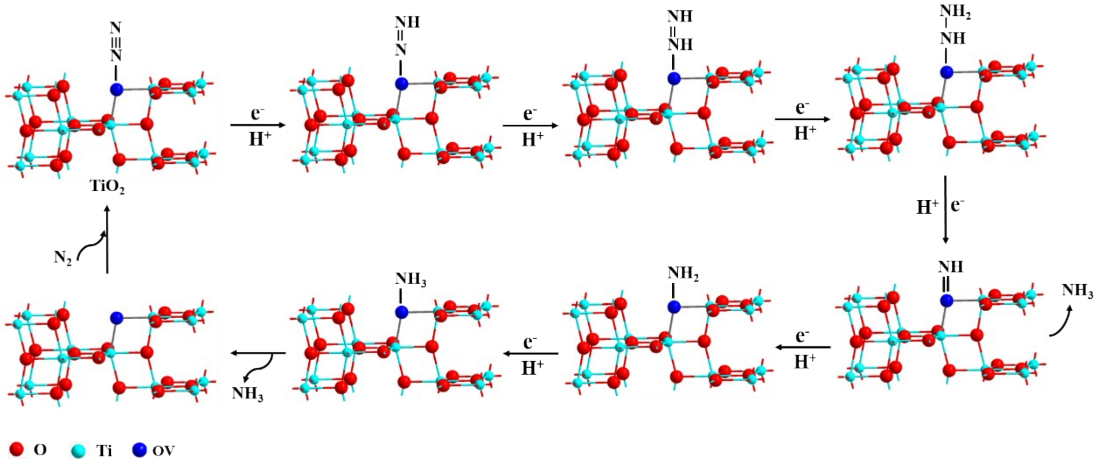

Figure S14. Proposed mechanism for photocatalytic activation and fixation of N_2 over the oxygen vacancies of TiO_2. OV refers to oxygen vacancies.

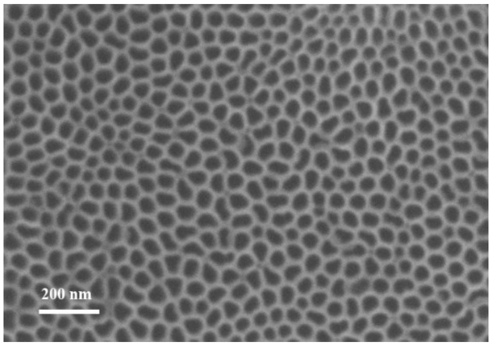

Figure S15. SEM image of the air-annealed TiO_2 film.

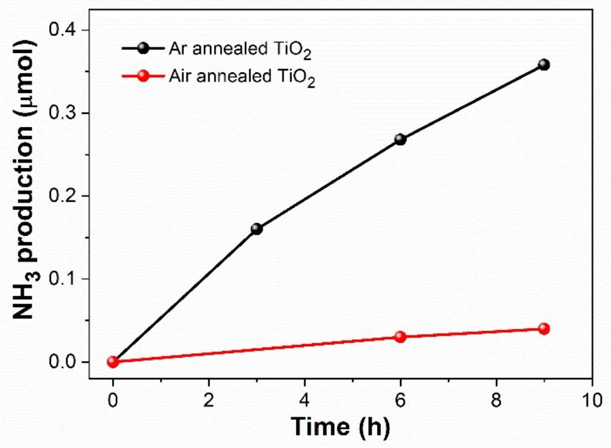

Figure S16. Photocatalytic NH_3 evolution over Ar and Air annealed TiO_2 respectively.

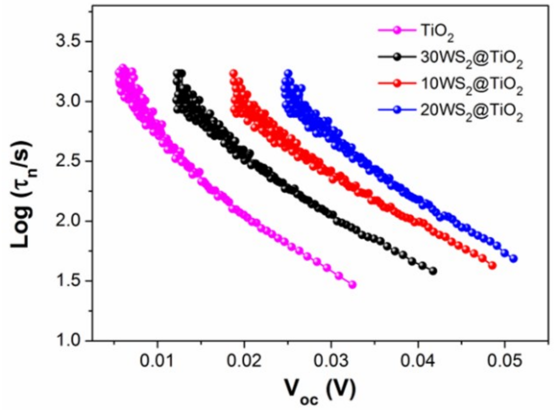

Figure S17. Electron lifetime (τ_n) vs. photovoltage under open-circuit conditions (Voc).

References

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