

Supporting information

Type II heterojunction promotes photoinduced effects of TiO₂ for enhancing photocatalytic performance.

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Experimental Section

Preparation of the photocatalyst

Preparation of UiO-66-NH₂

The synthesis of UiO-66-NH₂ was prepared via the classical solvothermal method with a simple modification. In detail, 27 ml DMF and 2 ml ethanol mixed solution of 1.5 mmol ZrCl₄ (0.3498 g) and 1.5 mmol H₂ATA (0.2718 g) were mixed in a 100ml Teflon-lined autoclave. Then, 9ml formic acid was added and stirred for 10 min. The autoclave was sealed and allowed to react at 150 °C for 24 h statically. After natural cooling, the precipitate was obtained by centrifugation and washed with DMF and methanol for several times. Finally, UiO-66-NH₂ was dried overnight at 60 °C under vacuum.

Preparation of TiO₂/UiO-66-NH₂

100 mg UiO-66-NH₂ was dispersed in 4 ml TBOT and sonicated for 2 h, then standing for 24 h. Secondly, the suspension was transferred into a glass bottle (200 ml) with 100 ml ethanol and adding hydrolysis solution (2 ml ethanol, 2 ml acetylacetone, and 3ml deionized water). After stirring for 6 h, the suspension was transferred into a 200 ml Teflon-lined autoclave and heated at 150 °C for 24 h. After that, the product was cooled to room temperature, and the precipitate was collected by centrifugation and then purified with ethanol once. The yellow powders were dried in a blast oven at 60 °C and denoted as TiO₂/UiO-66-NH₂ (TUN).

Preparation of pure TiO₂

The pure TiO₂ was prepared using the same method as that for the preparation of TiO₂/UiO-66-NH₂. The difference is the no introduction of UiO-66-NH₂ in the first step.

Characterizations

UV-vis spectra of the samples were collected by using Shimadzu UV-2600. Quasi *in situ* UV-vis diffuse reflectance spectra of sample before and after irradiation were conducted: The sample powders were sealed in Powder Sample Holder Support with vacuum grease under Ar. The sample spectra were collected before and after 6 h of

irradiation by a PCX50C Discover, 5W, 365 nm lamp.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a K-Alpha+ photoelectron spectrometer (Thermo Fisher Scientific Co. Ltd.) instrument with Al K α as the excitation source ($h\nu = 1486.6$ eV). *In situ* X-ray photoelectron spectroscopy (XPS) measurements of the sample before and after light irradiation was carried out by a 300 W Xe lamp, which provides light directly on the sample through the test window of X-ray photoelectron spectroscopy (XPS) measurements.

PL spectra were acquired by a fluorescence spectrophotometer (FL4500, Shimadzu). Quasi *in situ* PL spectra were collected by dispersing sample powders in water in an enclosed cuvette of 1×10 mm fulfilled with Argon gas. PL spectra of samples before and after irradiation were collected before and after 6h of irradiation by a PCX50C Discover, 5 W, 365 nm lamp.

Electron paramagnetic resonance (EPR) spectra were recorded on Bruker E500 (X-band). Quasi *in situ* EPR measurements of the sample were carried out by sending the sample to an enclosed EPR tube with Argon gas as the protective gas. EPR spectra of samples before and after irradiation were collected before and after irradiation by a PCX50C Discover, 5 W, 365 nm lamp.

The crystalline structures of the prepared samples were characterized by powder X-ray diffraction (XRD, TTRIII-18KW, Japan) patterns with Cu-K α radiation ($\lambda = 0.1541$ nm) operating at 40 kV and 40 mA. The Brunauer–Emmett–Teller (BET) specific surface area of the powders was analyzed by 3H-2000PS2 sorption analyzer, and the porosity of the samples was evaluated on the basis of nitrogen adsorption isotherms, measured at 77 K. Transmission electron microscopy (TEM) images were acquired on a JEOL JEM-2100 Ltd. Scanning electron microscopy (SEM) images were acquired on Nova Nano SEM 450.

The characterization conditions for photoactivation process were summarized in Table S1.

Table S1. Experiment conditions for photoactivation in different characterization.

	Light source	Atmosphere
UV-Vis	365 nm lamp	Ar gas
XPS	Xe lamp	Vacuum
PL	365 nm lamp	Ar gas
EPR	365 nm lamp	Ar gas
Photocatalysis	Xe lamp	Vacuum
Photoelectrochemical	Xe lamp	Ar gas

Photocatalytic H₂ measurements

Photoinduced activation

The photoinduced activation experiments are carried out using the multi-channel photochemical reaction system (PCX50C Discover, 5 W, 365 nm, Perfectlight, Beijing, China) and the 50 ml reaction bottle with optical grade quartz bottle bottom. Firstly, 10 mg photocatalyst dispersed in the reaction bottles with 30 ml deionized water, and the reactor was placed on the multi-channel reaction system at 20 °C for 6 h.

Photocatalytic H₂ evolution

The photocatalytic hydrogen production experiments were performed in Labsolar-6A (Beijing Perfectlight Technology Co., LTD, China) at 20 °C. After photoinduced activation, the suspension of the 50 ml reaction bottle was transferred into an optical reaction vessel. Then add 60 ml deionized water and 30 ml methanol by stirring for 20 min under vacuuming to maintain an inert environment inside the optical reaction vessel. A 300W Xe lamp (Microsolar 300) was used as simulated sunlight source. The amount of hydrogen evolution under irradiation was determined by TCD (GC-9790 II) by using argon (Ar) as carrier gas.

Photoelectrochemical measurements

Mott-Schottky plot measurements were carried out with (CHI760E, CH Instruments, Inc.) electrochemical workstation. The 2 mg catalysts were added into 0.5 mL ethanol and 20 μ L Nafion mixed solution. The indium-tin oxide (ITO) glass coated 4 cm² mixed solution was used as working electrodes. The measurements were performed in a three-electrode system with Pt plate as the counter electrode and an Ag/AgCl as a reference electrode. A 300 W Xe lamp was used as the light source. The low vacuum argon environment provided by photoelectric test system PEC2000 and Labsolar-6A. A 0.2 M Na₂SO₄ solution was used as the electrolyte. The frequencies of Mott-Schottky plot measurements are 1000 Hz.

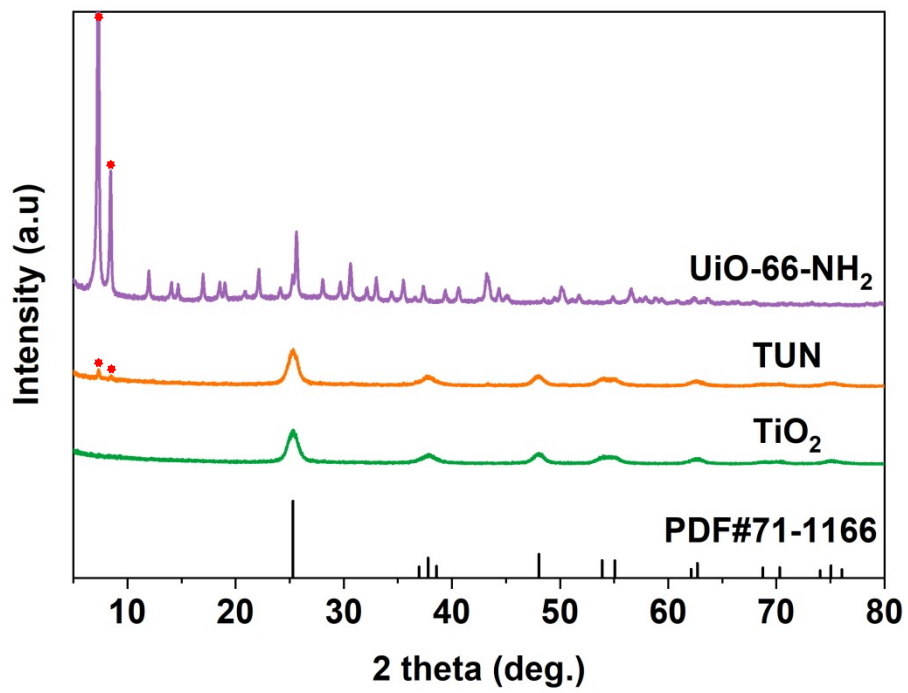


Fig. S1 XRD patterns of UiO-66-NH₂, TUN and TiO₂.

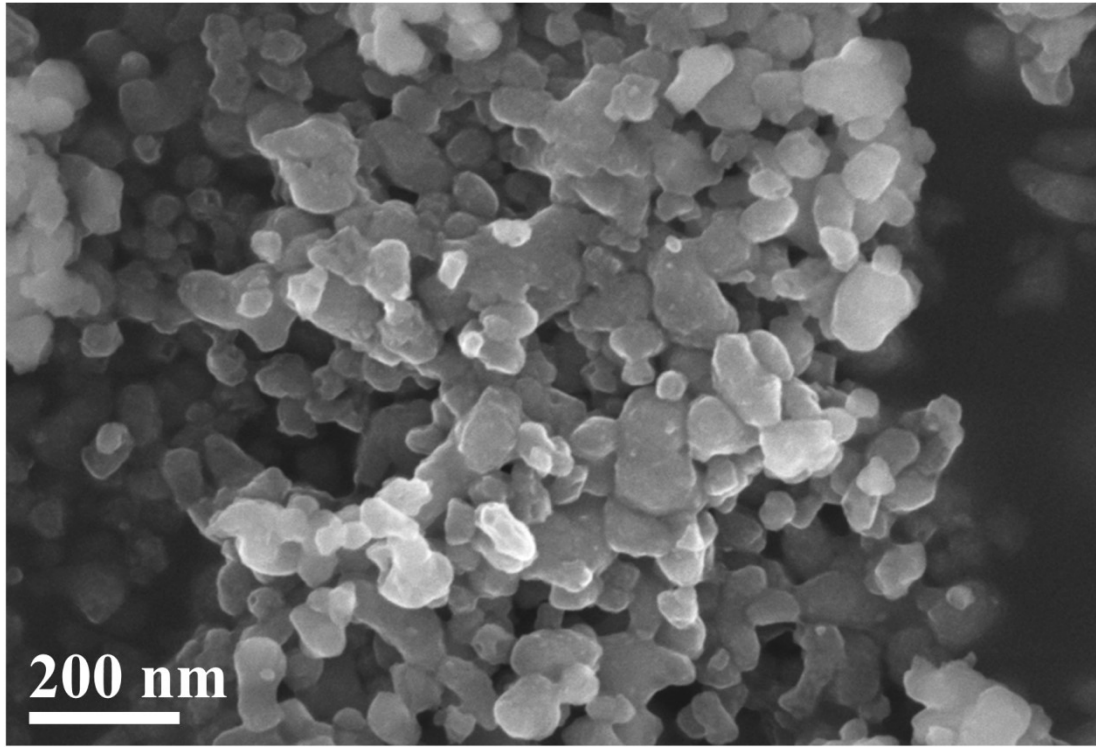


Fig. S2 SEM images of pure UiO-66-NH₂.

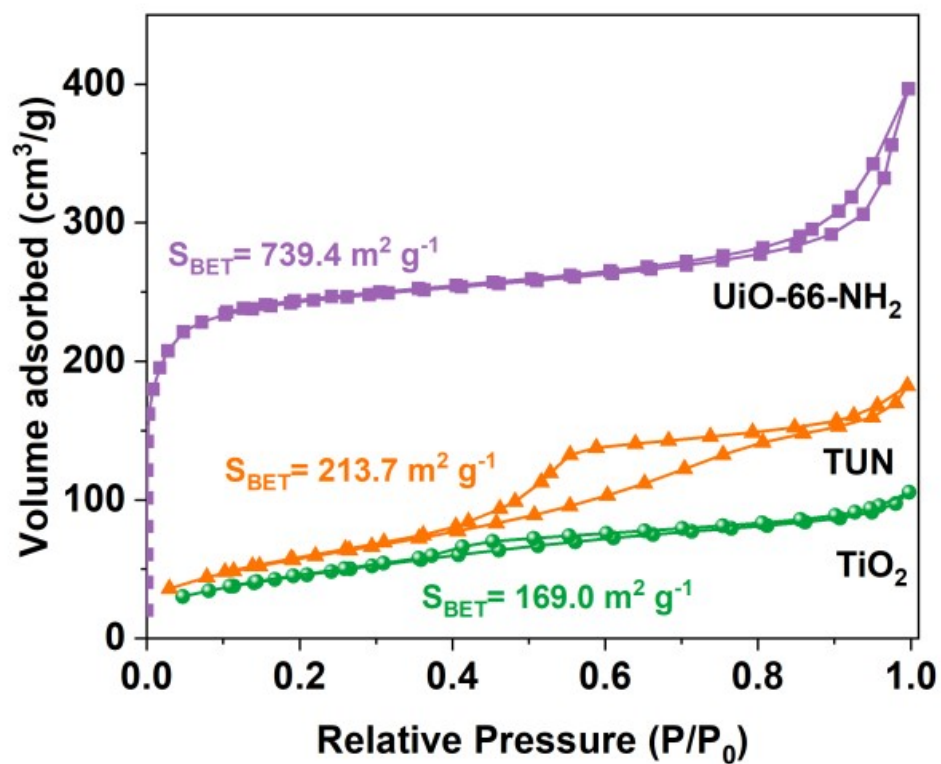


Fig. S3 N₂ sorption isotherms of UiO-66-NH₂, TUN and TiO₂.

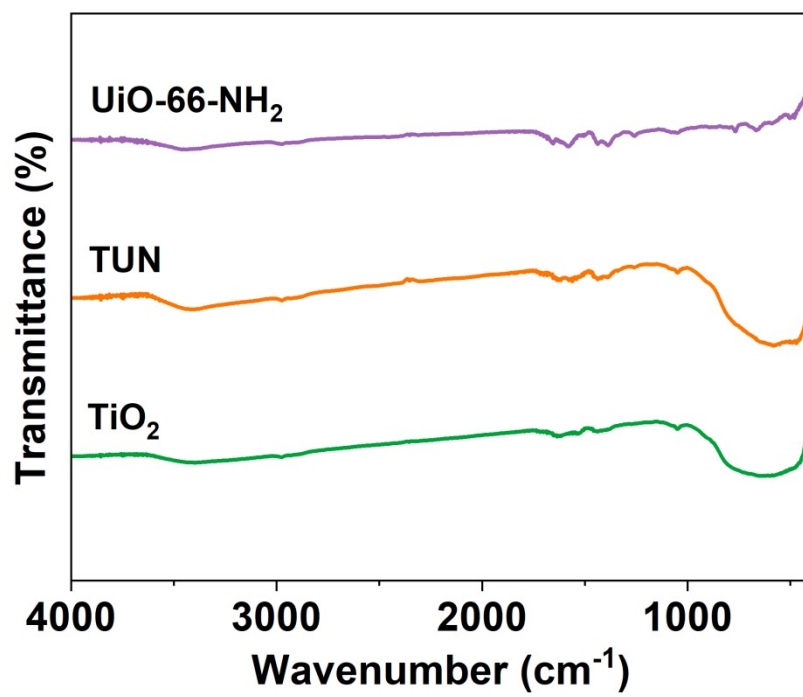


Fig. S4 FT-IR spectra of UiO-66-NH₂, TUN and TiO₂.

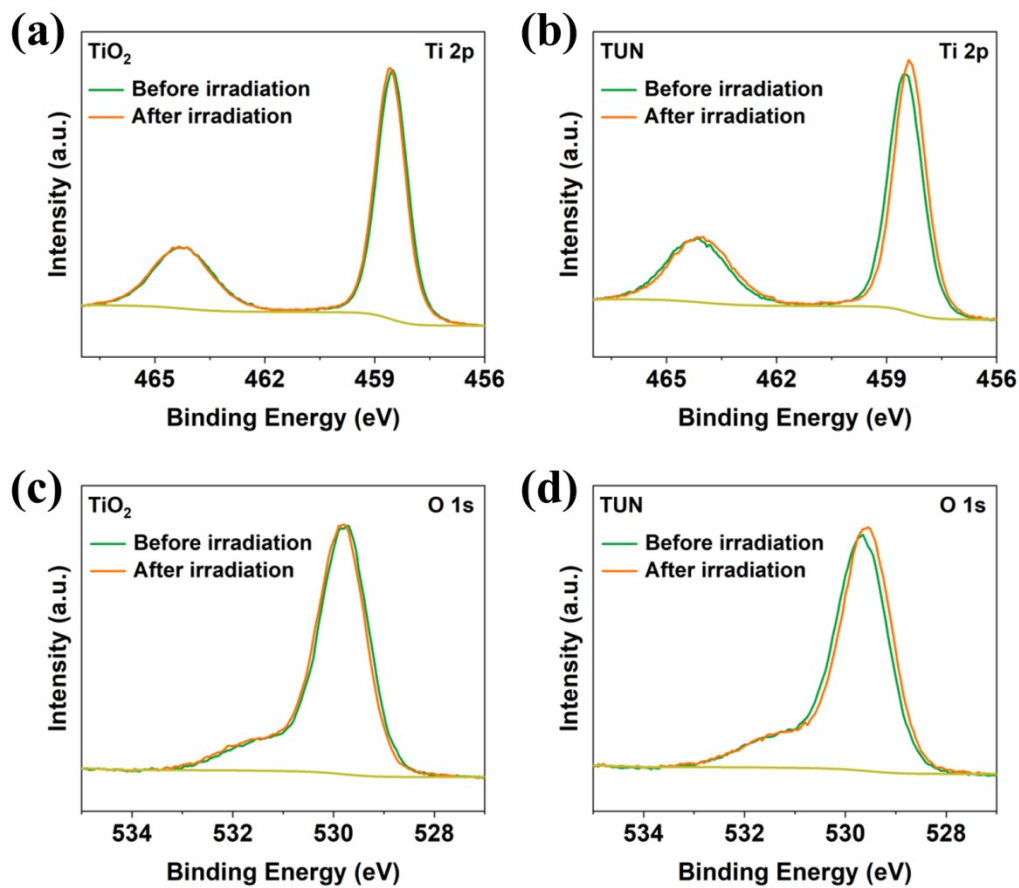


Fig. S5 In situ high-resolution XPS of Ti 2p (a, b) and O 1s (c, d).

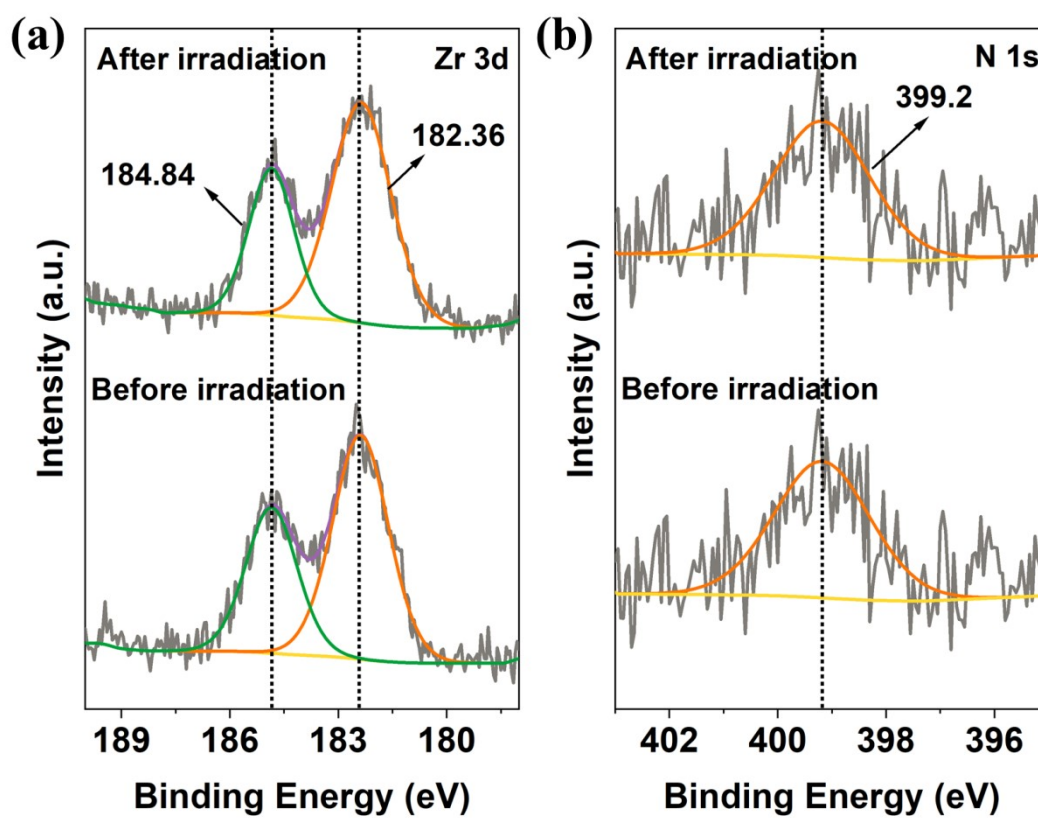


Fig S6 *In situ* high-resolution XPS of Zr 3d (a) and N 1s (b) in TUN, before and after irradiation conditions.

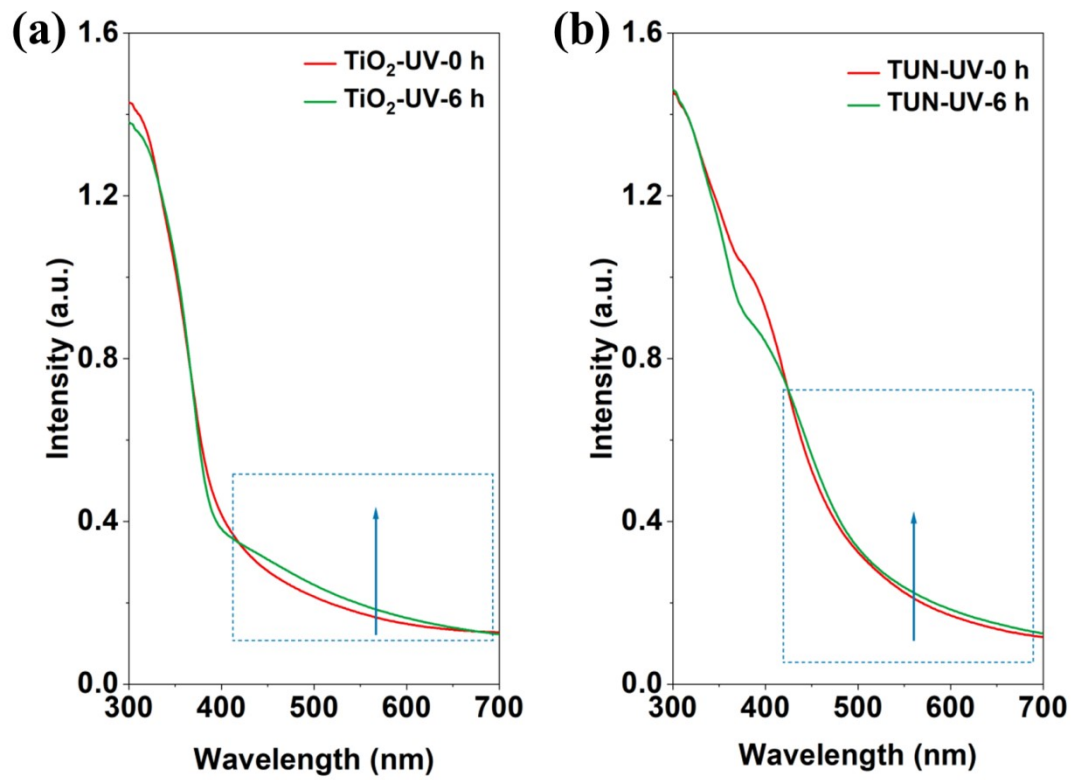


Figure S7. Quasi in situ UV-visible absorption spectra of TiO₂ (a) and TUN (b).

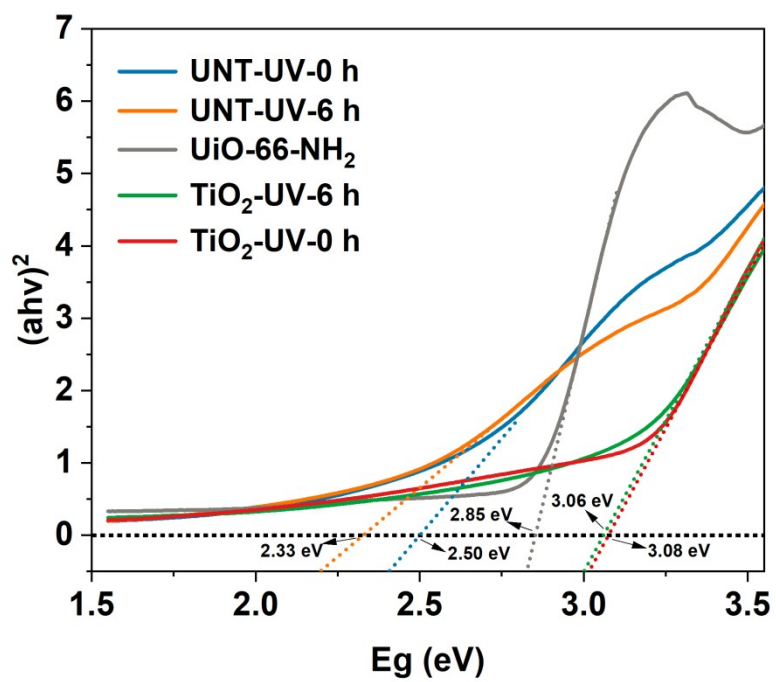


Figure S8. Tauc plots of different sample.

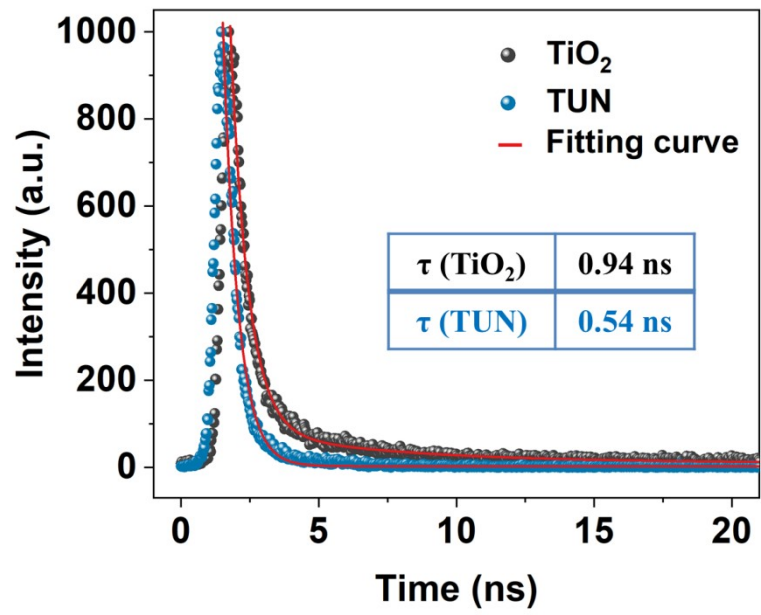


Fig. S9 Time-resolved transient PL decay of TiO₂ and TUN.

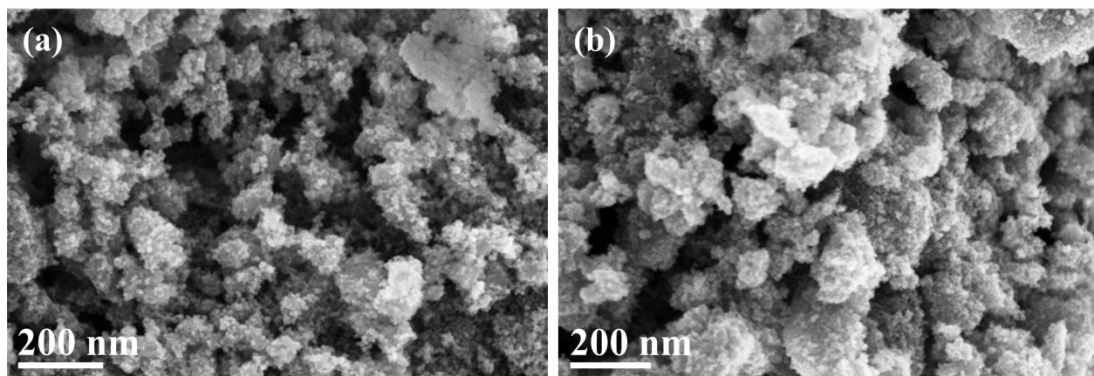


Fig. S10 SEM images of TUN before reaction (a) and after four times reaction (b).

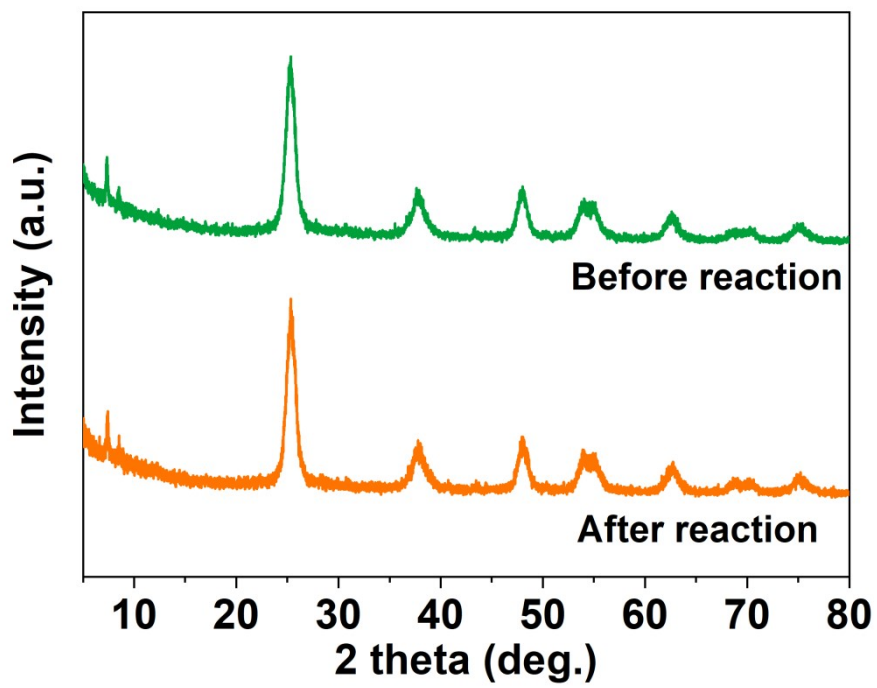


Fig. S11 XRD patterns of TUN before reaction and after four times reaction.

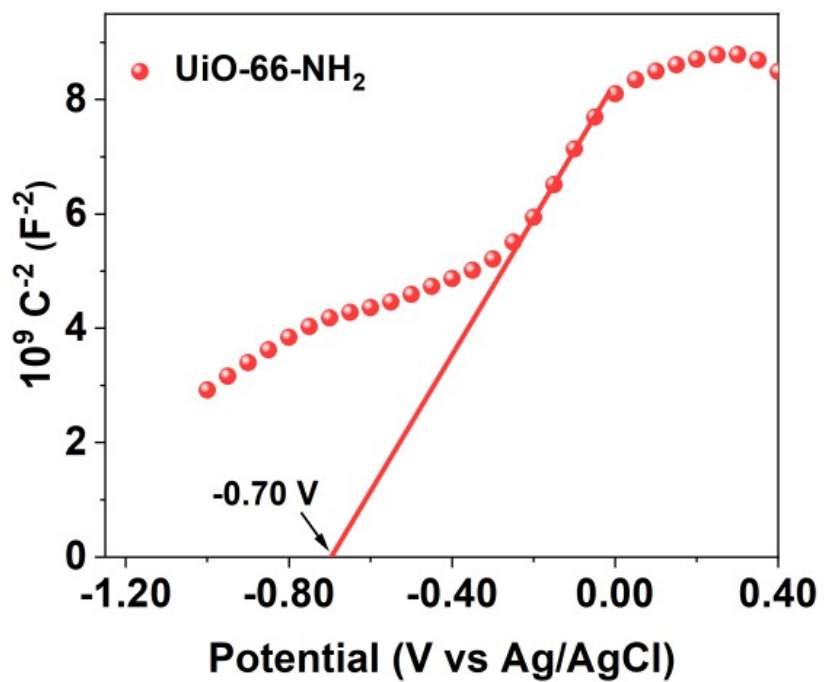


Fig S12 Mott-Schottky plots of UiO-66-NH₂.

Table S2 Surface composition ratio from XPS

Ratio (at.%)	TiO ₂		TUN	
	Before irradiation	After irradiation	Before irradiation	After irradiation
Ti ³⁺ /Ti	/	6.7	/	12.8
O _v /O	6.2	8.5	6.1	9.8