

Supporting Information for

Construction of nanorod-shaped TiO₂/Cu₃N p-n heterojunction for efficient visible-light hydrogen evolution

Zhengwang Cheng^a, Neng Gan^a, Gang Yuan^b, Aobo Wang^a, Jiyan Liu^c, Hui Lv^a, Changcun Han^a,
Mei Wang^a, Mengdai Luoshan^a, Xinguo Ma^a, Wei Zou^{a,*}

^a *School of Science, Hubei University of Technology, Wuhan 430068, China*

^b *School of Materials Science and Engineering, Central South University, Changsha 410083,
China*

^c *Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education,
Jiangnan University, Wuhan 430056, China*

*Corresponding author. E-mail: weizou@hbut.edu.cn (W. Zou)

1. Experimental details

1.1 Synthesis of rutile TiO₂ nanorods (NRs)

Rutile TiO₂ nanorods were synthesized on fluorine-doped tin oxide (FTO) glass substrates through a hydrothermal method.¹⁻³ Initially, 10 mL of concentrated hydrochloric acid (37 wt%) was diluted with 20 mL of deionized water. Subsequently, 0.3 mL of tetrabutyl orthotitanate (TBOT) was added to the aforementioned hydrochloric acid dilution and stirred magnetically for 30 minutes. Next, the solution was divided into six parts and transferred into six 25 mL Teflon-lined stainless-steel autoclaves. Each autoclave contained a piece of FTO substrate with the conductive surface facing downward. Subsequently, the system was placed in a drying oven at 180°C for 21 hours. Following natural cooling, the obtained films were sequentially rinsed with anhydrous ethanol and deionized water, and then dried in air at 60°C for 30 minutes. At last, the films were annealed in a muffle furnace under air at 500 °C for 1 hour, with a temperature increase rate of 2 °C/min.

1.2 Deposition of Cu₃N film

The Cu₃N films were deposited onto bare FTO through the reactive direct-current (DC) magnetron sputtering (MS) method,⁴ with the pure copper target (99.9%

purity, diameter Φ 60 mm \times thickness t 4 mm; purchased from Prmat (Shanghai) Technology Co., Ltd.) used as the sputtering source. The substrates were mounted onto a sample holder, which was capable of being heated to < 500 °C through thermal radiation and kept rotating during the deposition process. After sample insertion, the background vacuum of the MS system (PD-500, Wuhan PDVACUUM Technologies Co., Ltd) was evacuated to be better than 7.5×10^{-4} Pa.⁵ Then, the substrate underwent an additional degassing, and the target was pre-sputtered for 10 min to remove the surface contaminant. Finally, Cu₃N was deposited onto FTO at a substrate temperature of 80 °C and a gas flow ratio of Ar₂:N₂=5:1 for a duration time of 10 s.

1.3 Construction of TiO₂/Cu₃N heterojunction

After the synthesis of rutile TiO₂ NRs array on FTO substrate, the sample was transferred to the MS system through a vacuumed container. Then, the Cu₃N film was deposited onto the TiO₂-coated substrate following the above procedure, except for the difference of substrate.

1.4 Characterization

The crystal phase was investigated through grazing incidence X-ray diffraction (GIXRD), using a Phillips X'Pert Panalytical diffractometer, operated at 40 mA and 45 kV, employing monochromated Cu K α ₁ radiation (incident angle = 3°, λ = 1.54056 Å, scan rate = 10°/min). The interface structure and interplanar distance were characterized by transmission electron microscopy (TEM, FEI Talos F200s). The elemental composition and chemical valence state were analyzed using X-ray photoelectron spectroscopy (XPS, ThermoFisher ESCALAB Xi+) with monochromatized Al K α radiation (1486.8 eV). The surface/interface morphology and elemental distribution of the specimens were examined through scanning electron microscopy (SEM, JEOL JSM-7800F) and energy-dispersive spectroscopy (EDS).

UV-Vis diffuse reflectance spectroscopy (DRS) was performed on a double-beam spectrophotometer (UH4150, Hitachi). The photoluminescence spectra (PL) were recorded using a steady-state transient fluorescence spectrometer (OmniFluo900, Zolix), excited by 300 nm UV light. Time-resolved photoluminescence (TRPL)

spectra were measured on a fluorescence spectrophotometer (FLS1000, Edinburgh Instruments), with excitation and emission wavelength of 300 nm and 410 nm, respectively. Surface photovoltage (SPV) was measured using a surface photovoltage spectrometer (PL-SPS/IPCE1000), which was composited with a sample chamber, a monochromatic light source, and a phase-locked amplifier (SR830) with a chopper (SR540). The valence band maximum (VBM) of TiO₂ and Cu₃N was estimated by ultraviolet photoelectron spectroscopy (UPS, ThermoFischer, ESCALAB Xi+). All characterizations were carried out at room temperature.

1.5 Photoelectrochemical performance test

Electrochemical testing was performed using an electrochemical analyzer (CHI660E) with a standard three-electrode system. The working, counter and reference electrodes were sample, platinum sheet, and Ag/AgCl electrodes, respectively. The electrolyte was 0.1M Na₂SO₄ solution (pH=7) and the effective area of the sample was about 2.5 cm². The electrochemical impedance spectra (EIS) were gained using a 10 mV AC voltage amplitude. The Mott-Schottky (MS) curves were obtained at frequency of 1000 Hz, amplitude of 5 mV, and quiet time of 2 s. A 500 W xenon lamp and UV-420 filter were used with incident light output wavelength > 420 nm, and the incident light intensity was 100 mW/cm². A solar simulator provides illumination with AM 1.5G filter. A LabSolar II photocatalytic hydrogen evolution system (Labsolar-6A, Beijing Perfectlight) and a gas chromatograph were used to measure the evolution of hydrogen under illumination. The potential was converted to a reversible hydrogen electrode (RHE) based on the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.196$.

2. Supplemental figures

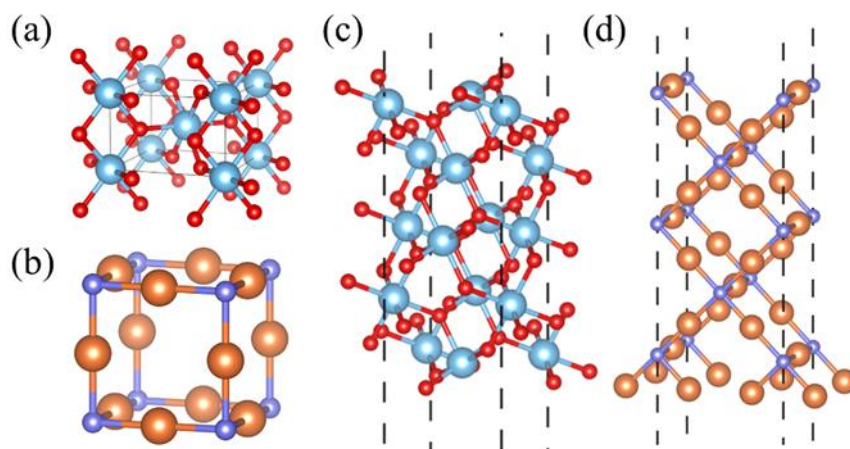


Fig. S1 The atomic structures of (a) TiO_2 , (b) Cu_3N , (c) TiO_2 (101) slab and (d) Cu_3N (110) slab.

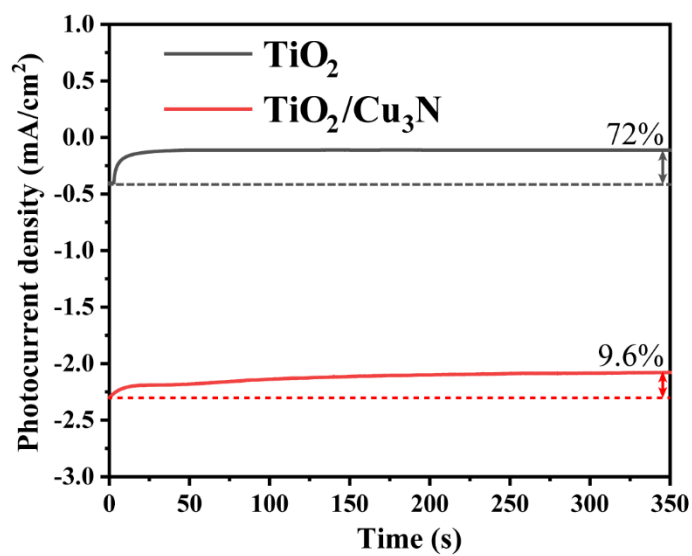


Fig. S2 The photocurrent response by time of TiO_2 and $\text{TiO}_2/\text{Cu}_3\text{N}$ heterojunction.

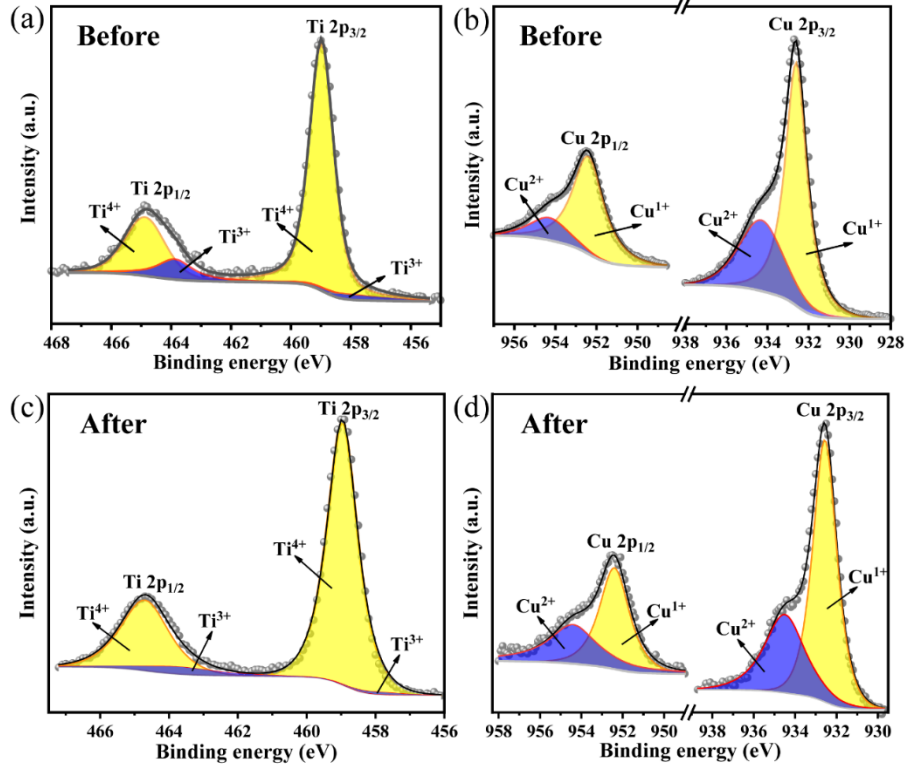


Fig. S3 XPS results of Ti 2p and Cu 2p before and after PEC hydrogen evolution of 8 cycles.

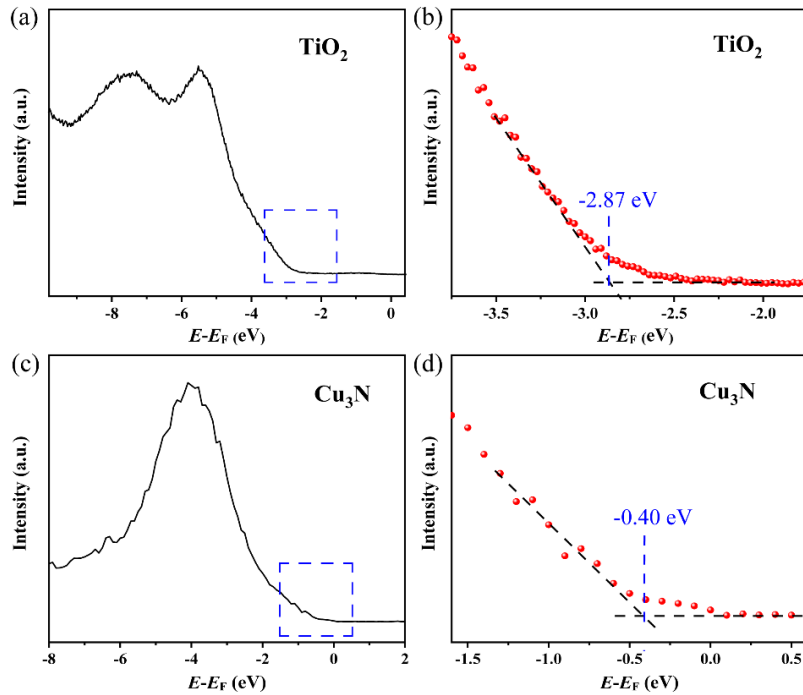


Fig. S4 UPS spectra measured by He I α ($h\nu = 21.218$ eV). (a, c) and (b, d) are the valence band and valence band maximum ($E_{VBM} = E_V - E_F$) of TiO₂ and Cu₃N with referring to the Fermi level (E_F), respectively.

Table S1. Fitted PL decay parameters of TiO₂ and TiO₂/Cu₃N.

	τ_1 , ns	τ_2 , ns	τ_3 , ns	A_1	A_2	A_3	τ_{ave} , ns
TiO ₂	0.727	3.319	30.000	3821.35	252.49	32.59	7.43
TiO ₂ /Cu ₃ N	0.545	3.356	43.384	3751.38	367.72	85.22	23.74

Table S2. The summarized percentage of +4/+3 states in Ti 2p and +2/+1 states in Cu 2p, which were obtained by fitting the XPS results of Ti 2p and Cu 2p before and after PEC hydrogen evolution in Fig. S3.

	Ti ⁴⁺	Ti ³⁺	Cu ²⁺	Cu ⁺
Before	89.61%	10.39%	29.24%	70.76%
After	92.73%	7.27%	37.76%	62.24%

Table S3. Band gap (E_g), positions of the conduction and valence bands of TiO₂ and Cu₃N refer to the Fermi level E_F , *i. e.* E_C-E_F and E_V-E_F .

	E_g (eV)	E_V-E_F (eV)	E_C-E_F (eV)
TiO ₂	3.09	-2.87	0.22
Cu ₃ N	1.69	-0.40	1.29

Supplemental references:

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<https://doi.org/10.1021/acs.jpcc.2c02798>.

- 3 Z. Hu, Z. Cheng, N. Gan, Z. Liu, C. Han, M. Wang, A. Wang, J. He, W. Zou, X. Ma, Enhancing the photoelectrochemical performance of TiO₂ through decorating a topological insulator Bi₂Te₃ film and non-noble plasmonic Cu nanoparticles, *J. Phys. Chem. C*, 2022, **126**, 19047-19055, <https://doi.org/10.1021/acs.jpcc.2c05394>.
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