

Supplementary Information

Metallic TiN Nanoparticles Loaded on g-C₃N₄ for Plasmon Enhanced Visible and NIR Photocatalytic H₂ Evolution from Water Splitting

Ikram Ullah,^a Cong Ling,^a Jing-Han Li,^a Xiao-Jie Lu,^a Zhengkun Yang,^b Gang Wang,^{a*} and An-Wu Xu^{a*}

^aDivision of Nanomaterials and Chemistry, Hefei National Research Center for Physical Sciences at the Microscale, The First Affiliated Hospital, University of Science and Technology of China, Hefei, 230026, P. R. China.

^bInstitutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Anhui University, Hefei, 230601, P. R. China.

*Corresponding authors:

E-mail: anwuxu@ustc.edu.cn (A.W.X.)

E-mail: wanggang829@126.com (G. Wang.)

1. Characterizations

X-ray diffraction (XRD) patterns of as-made samples were captured via a Rigaku X-ray diffractometer with Cu K radiation source ($\lambda = 1.5 \text{ \AA}$). Fourier transform infrared (FTIR) spectra of the samples with KBr pellets were characterized via Nicolet Nexus FTIR spectrometer. The actual content of CN and TiN in the composite CN/TiN photocatalysts were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, ICAP 7400, Thermo Scientific). The as-prepared photocatalysts were digested according to the following steps before the ICP-OES measurements. 5 mg sample was dissolved in 1 mL mixed solution ($\text{H}_2\text{O}_2 : \text{HNO}_3 = 2 : 8, \text{ v/v}$) and 9 mL deionized water, and then transferred into a 25 mL Teflon-lined autoclave. The autoclave was kept in an oven and heated at $150 \text{ }^\circ\text{C}$ for 3 h. The light absorption characteristics of the as-synthesized photocatalysts have been investigated by UV-vis diffuse reflectance spectra (DRS) (Shimadzu UV-2501 PC spectrometer). The electron paramagnetic resonance (EPR) spectrum of the samples were obtained by a Bruker model A300 spectrometer. Scanning electron microscopy (SEM, JEOL SM-6601F), transmission electron spectroscopy (TEM, HITACHI H-7650), and HAADF-STEM with corresponding EDS elemental mapping (HAADF-STEM JEOL-2010) were employed to evaluate the surface properties of the as-made samples. The X-ray photoelectron (XPS) spectra of the samples have been investigated via Perkin-Elmer RBD upgraded PHI-5000C ESCA technique. The photoluminescence (PL) spectra of the samples were recorded on a JY Fluorolog-3-Tau technique. The time-resolved photoluminescence (TRPL) spectra of the samples were collected on a 914-photomultiple detection system. Multiple point Brunauer-Emmett-Teller (BET) procedure was used to obtain specific areas of the samples.

2. Photoelectrochemical measurements

The photoelectrochemical tests, such as transient photocurrent response (TPR) and electrochemical impedance spectroscopy (EIS) were conducted in a typical three-electrode cell through a CHI 760 electrochemical analyzer (Chenhua Shanghai, China), using Ag^+/AgCl , Pt-wire, and ITO glass electrode as the reference, counter, and working electrode, respectively. The Na_2SO_4 (0.5 M) aqueous solution was used as the electrolyte with a xenon lamp (300 W) as a light-source. For preparation of working electrodes, 0.002 g of sample was spread in 1 mL ethanol and 15 μL Nafion solution via sonication. Then well-mixed solution (100 μL) was drop-casted onto a piece of ITO glass with a $\approx 1 \text{ cm}^2$ exposed area and followed by drying in the microwave oven at 60 °C for 3 h. The TPR of the samples were analyzed via on/off switch phenomena through a bias voltage of 0.5 V under visible light irradiation, while the EIS of the samples was measured through a bias potential of -0.2 V.

3. Photocatalytic Hydrogen evolution measurements

The photocatalytic H_2 was evolved under visible and NIR light illumination ($\lambda \geq 420$ and 700 nm). The reaction was taken place in a 500 mL quartz cell connected with a water splitting assembly (Labsolar 6A, Beijing Perfect Light Co. Ltd, China). For each test, 0.05 g of the catalyst was dissolved in a mixed solution of distilled water (90 mL) and TEOA (10 mL, sacrificial agent) with 1 wt% Pt ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution). The obtained solution was sonicated for 30 min before the photocatalytic H_2 evolution reaction. The solution was vacuumed with N_2 gas for 45 min to eradicate the internal air before being exposed to light. Afterward, Pt was successfully deposited on the catalyst surface via a photo deposition process under stirring. A xenon lamp (300 W) was used as a light-source with an optical filter ($\lambda \geq 420$ and 700 nm) throughout the experiments. The evolved H_2 was analyzed by connected gas chromatograph (GC 1120, HTCD, with N_2 carrier gas). The photocatalytic reaction time for each experiment was set as 4 h.

The AQE of CN/TiN-2 at different monochromatic light ($\lambda = 420, 450, 500, 550, \text{ and } 600 \text{ nm} \pm 5 \text{ nm}$) was calculated via the following equation:

$$AQE = \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{incident photons number}} \times 100\%$$

The solar-to-hydrogen (STH) conversion efficiency was calculated from equation as follows:

$$STH = \frac{R(H_2) \times \Delta Gr}{P \times S} \times 100\%$$

$R(H_2)$, ΔGr , P , and S indicates H_2 evolution rate, Gibbs free energy for the water splitting reaction, AM 1.5G solar illumination energy intensity (100 mW/cm^2), and the illuminated sample area (1 cm^2), respectively.

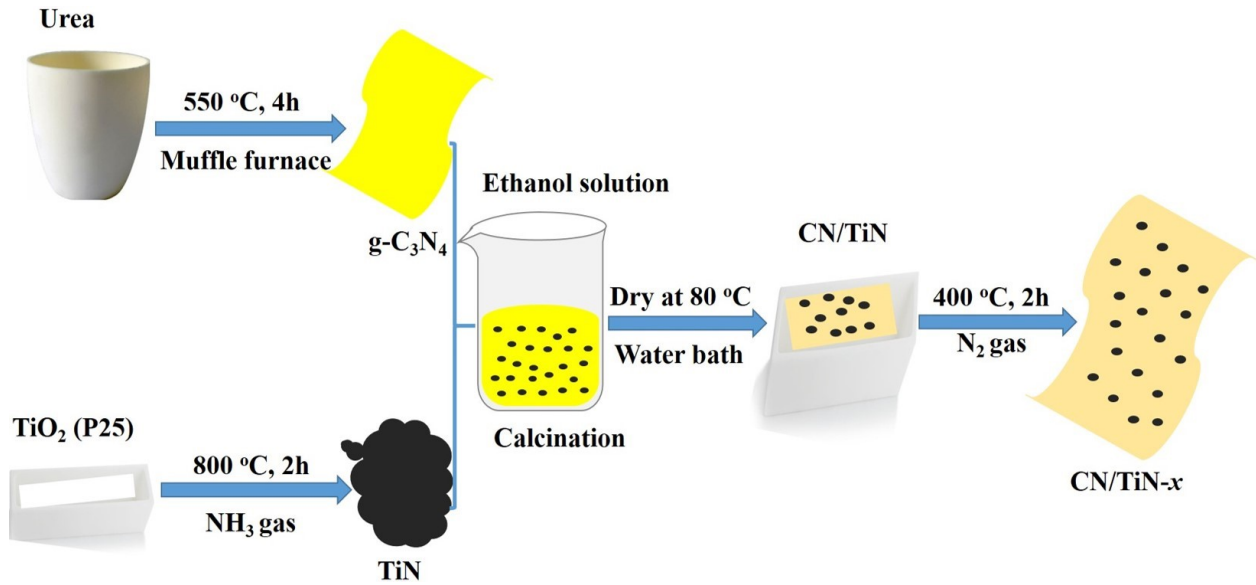


Figure S1. The schematic synthesis path of g-C₃N₄, Ni@C, and CN/Ni@C-x samples.

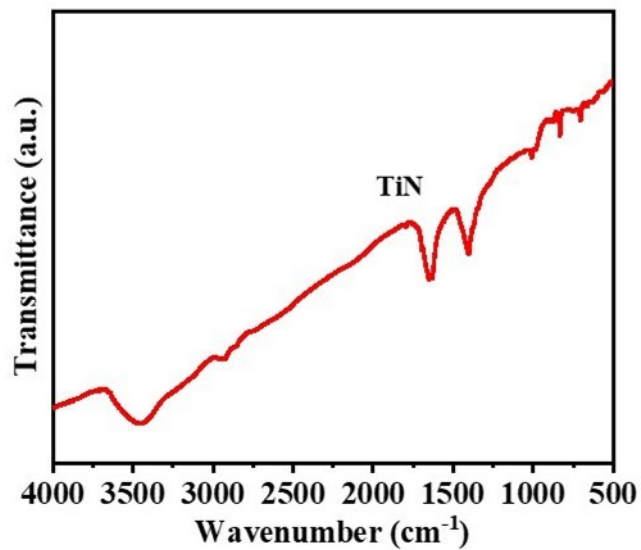


Fig. S2. Enlarged FTIR spectra of plasmonic metallic TiN nanoparticles.

Table S1 Elemental analysis and ICP-OES results of the CN/TiN-*x* samples.

Photocatalysts	g-C ₃ N ₄ wt. %	TiN wt. %
CN/TiN-1	99.188	0.812
CN/TiN-2	97.397	2.603
CN/TiN-3	96.626	3.374
CN/TiN-4	95.625	4.375

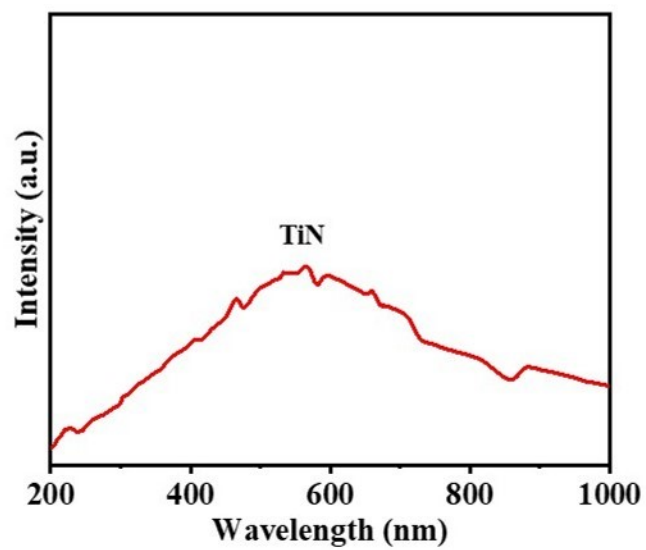


Fig. S3. UV-DRS spectra of plasmonic metallic TiN nanoparticles.

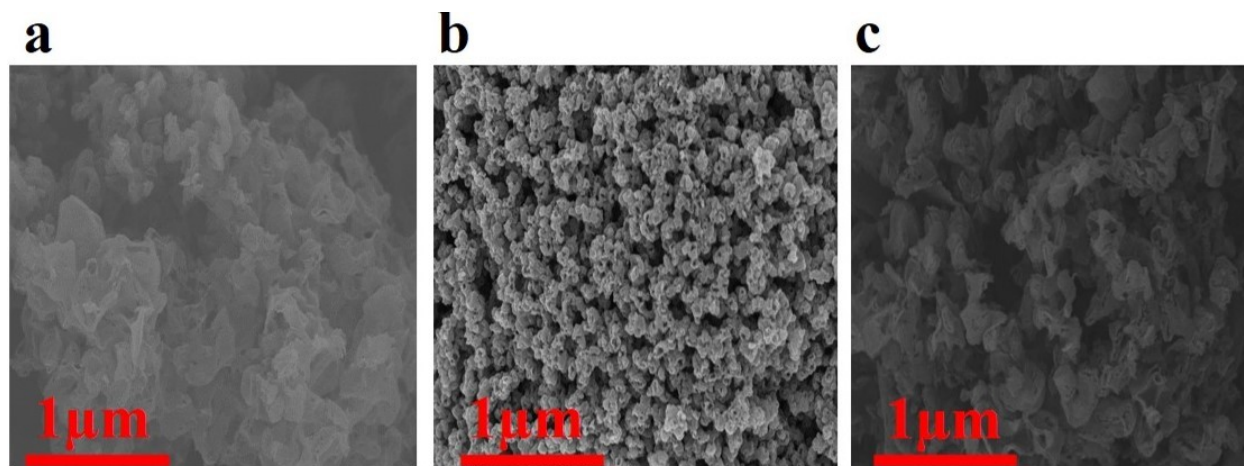


Fig. S4. SEM images of g-C₃N₄ nanosheets (a), TiN NPs (b), and CN/TiN-2 nanocomposite (c).

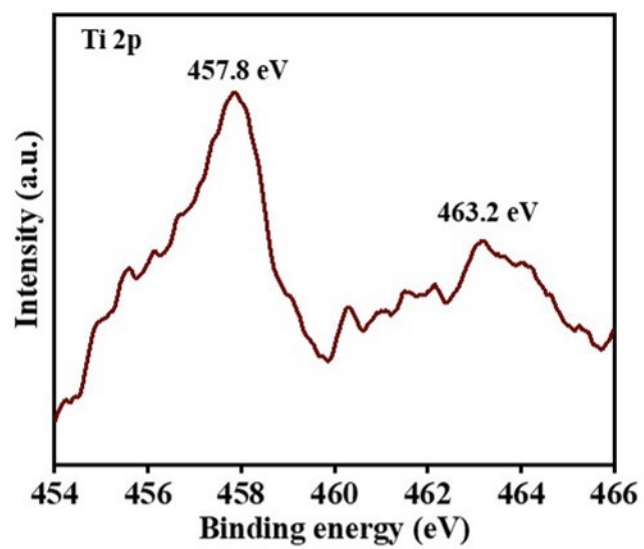


Fig. S5. High-resolution XPS spectra of Ti 2p of CN/TiN-4 sample.

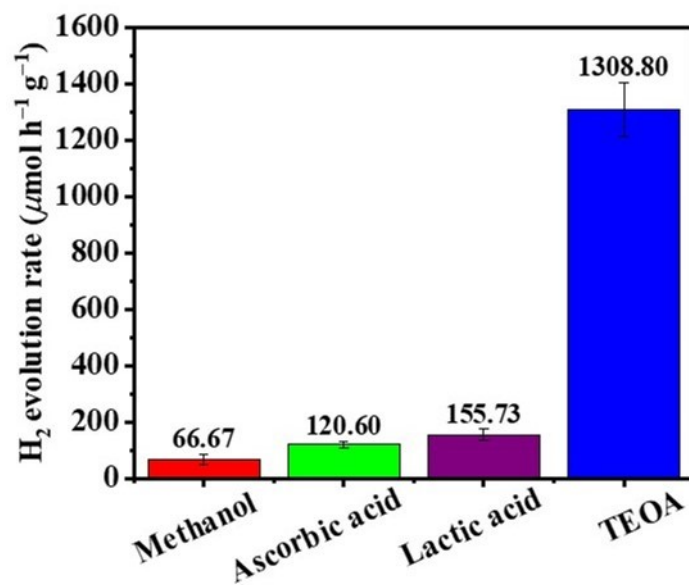


Fig. S6. Photocatalytic H₂ evolution rate under visible light over CN/TiN-2 nanocomposite using different sacrificial agents.

Table S2. Comparison of our study H₂ evolution rate over plasmonic CN/TiN-2 photocatalyst with previous reported metallic plasmon-based photocatalysts.

S.#	Photocatalysts	Reaction conditions	Light source	H ₂ evolution rate (μmol h ⁻¹ g ⁻¹)	Refs
1	CN/TiN-2	TEOA (10 vol. %), 1 wt% Pt	300 W Xe-lamp, λ ≥ 420 nm (visible-light)	1308.80	This work
2	CN/TiN-2	TEOA (10 vol. %), 1 wt% Pt	300 W Xe-lamp, λ ≥ 700 nm (NIR light)	169.20	This work
3	Pt/CNU	TEOA (10 vol. %), 3 wt% Pt	300 W Xe-lamp, λ > 420 nm (visible-light)	300.0	1
4	Au/g-C ₃ N ₄	TEOA (10 vol. %), 1 wt% Au	300 W Xe-lamp, λ > 400 nm (visible-light)	565.0	2
5	Au/PtO/g-C ₃ N ₄	methanol (25 vol. %), 0.6 wt% Au, 0.6 wt% Pt	350 W Xe-lamp, λ > 400 nm (visible-light)	338.0	3
6	CN-Au-Pt	methanol (50 vol. %), 0.3 wt% Au, 0.3 wt% Pt	300 W Xe-lamp, λ > 420 nm (visible-light)	139.0	4
7	0.5-Pt-Au-CN	TEOA (10 vol. %), 10 mg/L Au, 0.5 wt% Pt	300 W Xe-lamp, λ > 700 nm (NIR light)	51.60	5

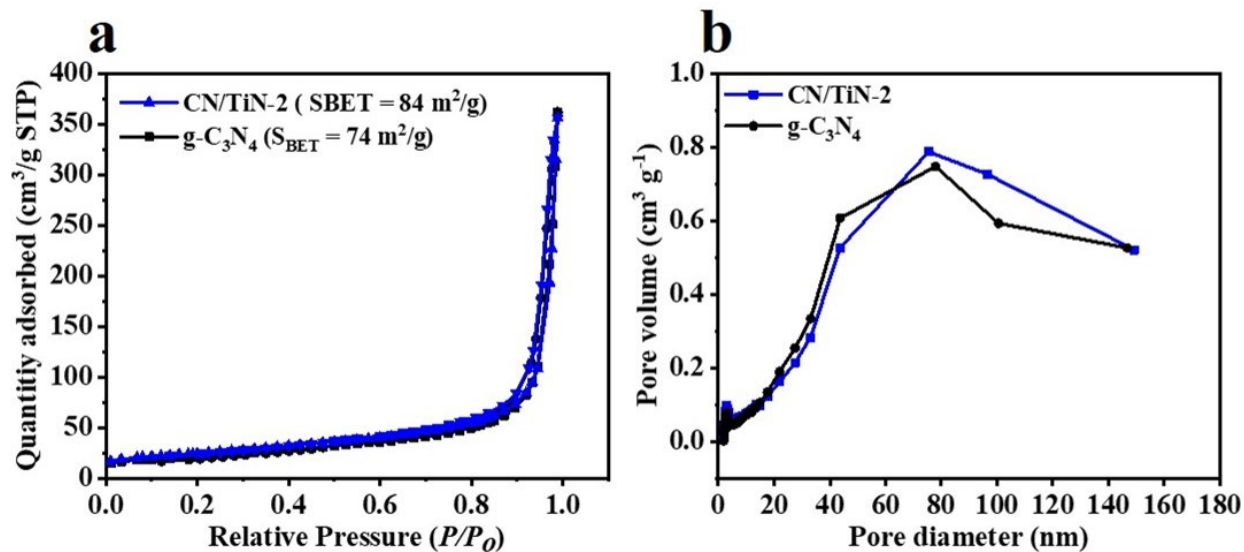


Fig. S7. N₂ adsorption-desorption isotherms of pristine g-C₃N₄ and CN/TiN-2 photocatalysts (a). Pore size distribution curves of g-C₃N₄ and CN/TiN-2 samples (b).

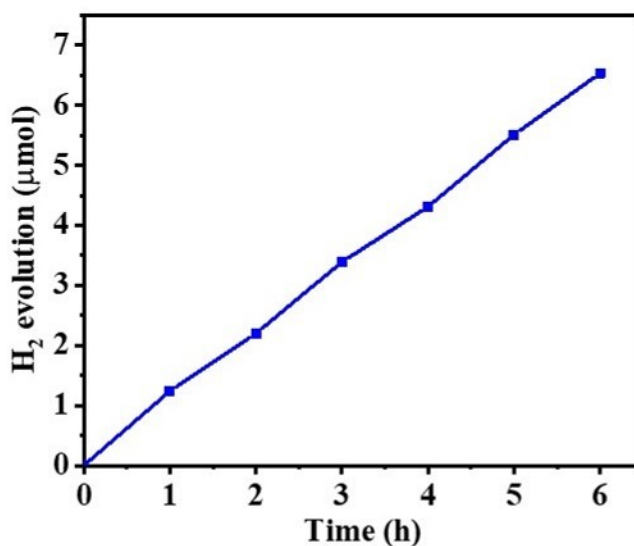


Fig. S8. Time course of H₂ evolution over CN/TiN at AM 1.5G simulated sunlight. Reaction parameters: 50 mg sample; distilled water (100 mL); Xe lamp (300 W) fitted with standard filter (AM 1.5G); 1 wt.% Pt as cocatalyst.

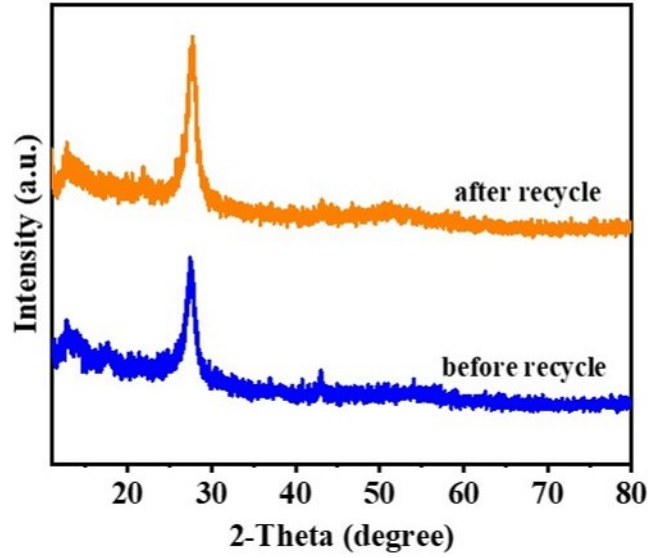


Fig. S9. XRD spectra of CN/TiN-2 nanocomposite photocatalyst before and after recycling experiment.

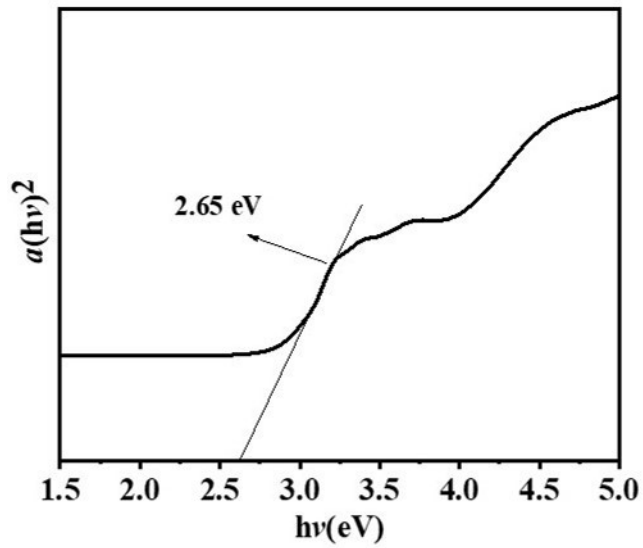


Fig. S10. The calculated Kubelka-Munk energy band gap plot of g-C₃N₄ nanosheets.

REFERENCES

1. G. Li, J. Shi, G. Zhang, Y. Fang, M. Anpo and X. Wang, The Facile Synthesis of Graphitic Carbon Nitride from Amino Acid and Urea for Photocatalytic H₂ Production. *Res. Chem. Intermed.* 2017, **43**, 5137-5152.
2. Z. Mo, H. Xu, Z. Chen, X. She, Y. Song, P. Yan, Y. Xu, Y. Lei, S. Yuan and H. Li, Gold/Monolayer Graphitic Carbon Nitride Plasmonic Photocatalyst for Ultrafast Electron Transfer in Solar-to-Hydrogen Energy Conversion. *Chinese J. Catal.* 2018, **39**, 760-770.
3. J. Jiang, J. Yu and S. Cao, Au/PtO Nanoparticle-Modified g-C₃N₄ for Plasmon-Enhanced Photocatalytic Hydrogen Evolution under Visible Light. *J. Colloid Interface Sci.* 2016, **461**, 56-63.
4. . Guo, L. Kong, J. Xu, J. Chen and L. Li, Au Nanoparticle-Controlled Formation of Metallic and Oxidized Pt Nanoparticles on Graphitic Carbon Nitride Nanosheets for H₂ Evolution. *Dalton Trans.* 2021, **50**, 9529-9539.
5. Y. Guo, Q. Zhou, X. Chen, Y. Fu, S. Lan, M. Zhu and Y. Du, Near-Infrared Response Pt-Tipped Au Nanorods/g-C₃N₄ Realizes Photolysis of Water to Produce Hydrogen. *J. Mater. Sci. Technol.* 2022, **119**, 53-60.