

Electronic Supplementary Information

A Novel Nickel-Thiourea-Triethylamine Complex Adsorbed on Graphitic C₃N₄ for Low-Cost Solar Hydrogen Production

Donghong Wang, Yuewei Zhang and Wei Chen*

*i-Lab, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences,
Suzhou, 215123, China. E-mail: wchen2006@sinano.ac.cn;*

Experimental Section

1. C₃N₄ Preparation. Graphitic carbon nitride (g-C₃N₄) was synthesized according our previous report.¹ Typically, the C₃N₄ is obtained by thermal treatment of urea (10g, AR, Sinopharm Chemical Reagent Co.,Ltd) in a crucible with a cover under ambient pressure in air. After dried at 80 °C, the urea was put in a Muffle Furnace (Isotemp Programmable Muffle Furnace 650–750 Series, Fisher Scientific) and heated to 550 °C for 3 hours to complete the reaction. The yellow-colored product was washed with nitric acid (0.1 mol L⁻¹) and distilled water to remove any residual alkaline species (e.g. ammonia) adsorbed on the sample surface, and then dried at 80 °C overnight.

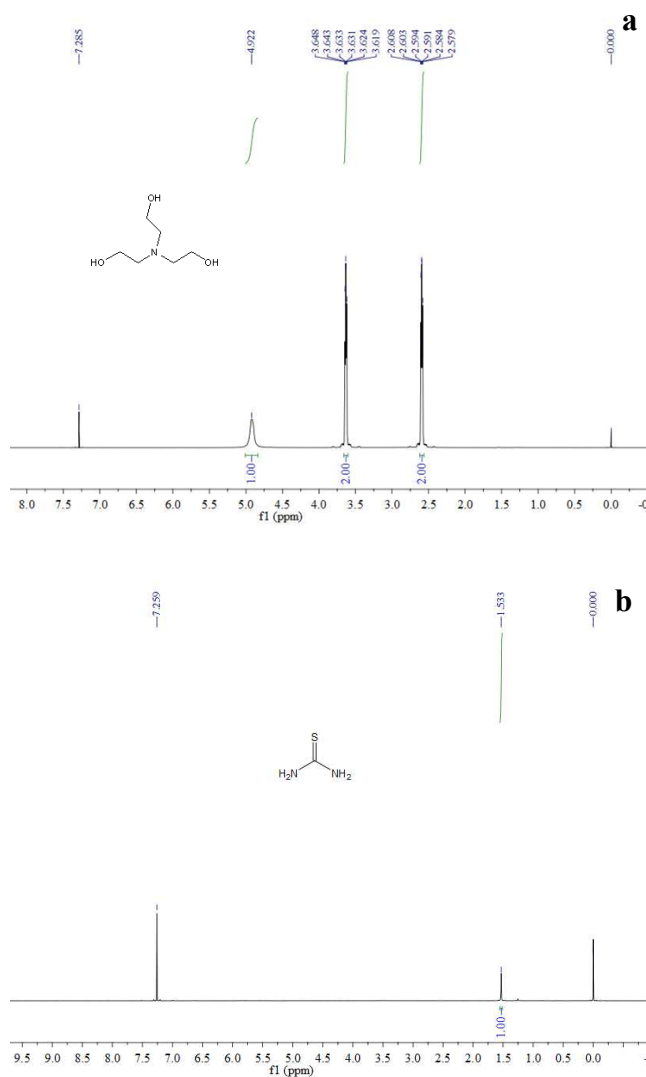
2. Preparation of Ni–Tu–TETN based molecular H₂ system and photocatalytic activity measurement

C₃N₄–Ni–Tu–TETN was obtained in situ during the photocatalysis. Photocatalytic water splitting reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. 100 mg g-C₃N₄ was dispersed in 20 mL DI water by sonication, and given amounts of Ni(NO₃)₂•6H₂O was added and stirred for several hours to reach the adsorption equilibrium of Ni²⁺ on C₃N₄. Then, excess amount of thiourea was added. The obtained reactant dispersion was put into the reaction vessel, added with 70 ml water and 10 ml TEOA and stirred. The reaction system was evacuated three times with half an hour each time to remove air completely prior to irradiation under a 300 W Xe lamp (PLS-SXE 300, trusttech) and a water filter. The wavelength of the incident light was controlled by using a solar simulator filter for solar light irradiation. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The

C_3N_4 -Ni-Tu-TETN appeared when the color of the suspension changed from yellow to black. The evolved gases were analyzed by gas chromatography (GC 7890II, Shanghai Techcomp Instrument Ltd.).

The C_3N_4 -Ni-Tu-TETN powders produced after irradiation for 8 h were collected by filtration and washed with water and ethanol for several times. Then Ni-Tu-TETN complex can be obtained by sonication C_3N_4 -Ni-Tu-TETN in ethanol and removing the solid C_3N_4 .

Characterization: TEM images and high resolution TEM images were obtained using FEI Tecnai G2 F20 S-Twin 200 KV. The UV-Vis absorption spectra were obtained on a ShimadzuUV-2550 UV-Vis spectrophotometer equipped with an integrating sphere. NMR spectra were recorded at room temperature on Varian 400 MHz spectrometer. Cyclic voltammetry experiments were performed on CHI 660D electrochemical station under a three-electrode cell system consisting of working electrode consisting of a glassy carbon working electrode, a Pt wire counter electrode and Ag/AgCl reference electrode, the mixture was purged with argon for 30 min before performing cyclic voltammetry.



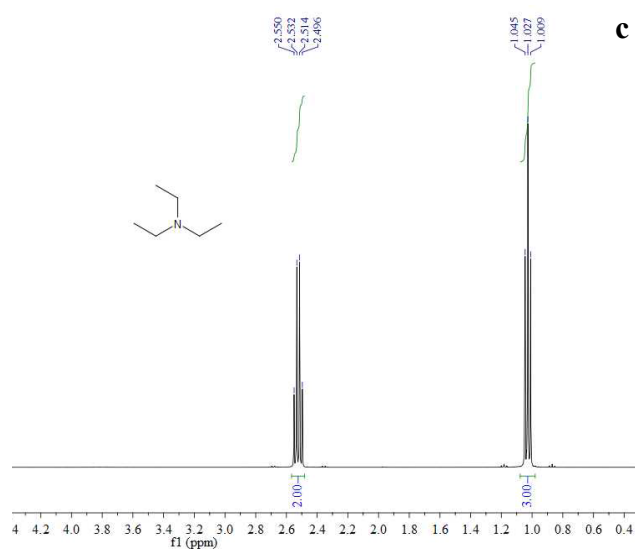


Fig. S1 ^1H NMR spectra of TEOA (a), Tu (b) and TETN (c). (solvent: CHCl_3)

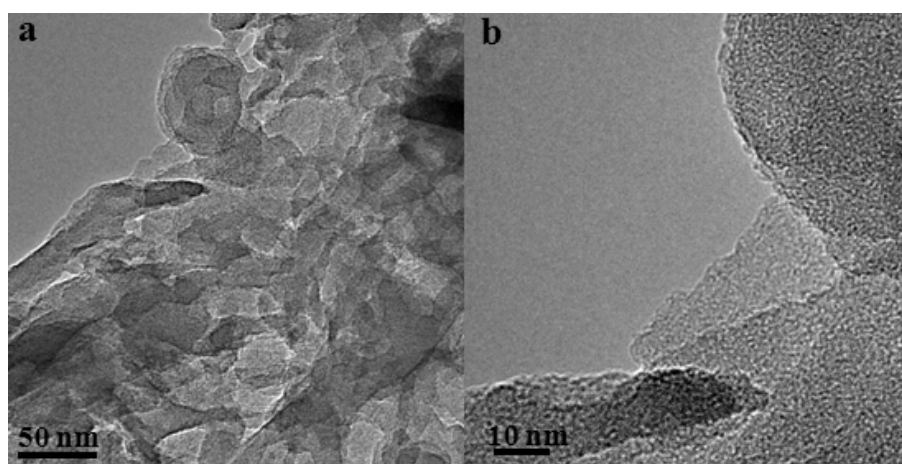


Fig. S2 a) TEM and b) magnified TEM images of $\text{C}_3\text{N}_4\text{-Ni}$ -complex

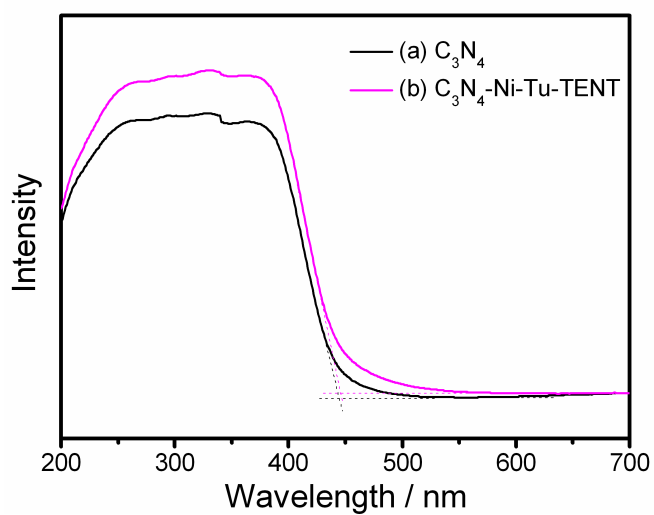


Fig. S3 UV-Vis absorption spectra of C_3N_4 (a), and C_3N_4 -Ni-Tu-TETN (b)

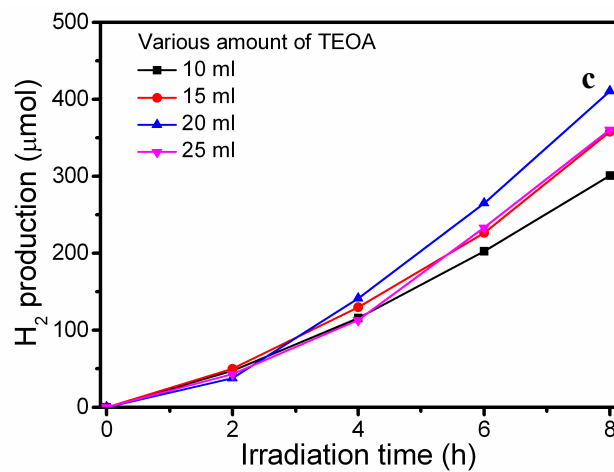
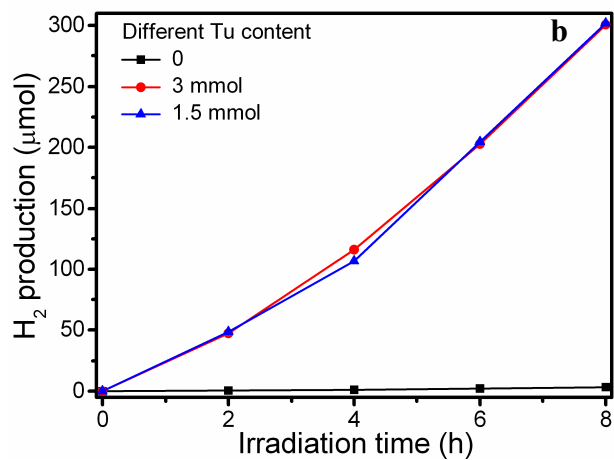
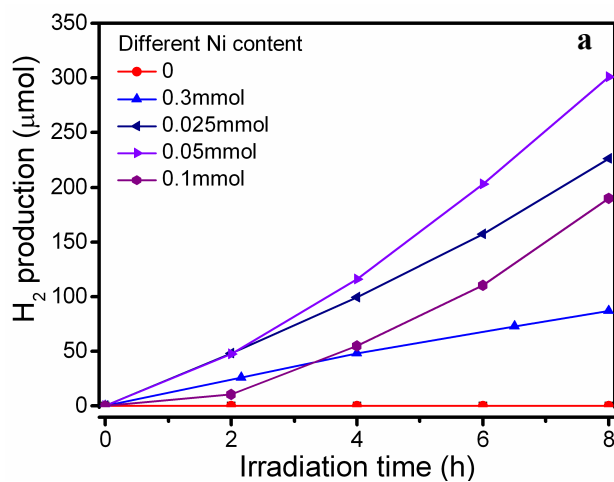


Fig. S4 The experimental parameters: the concentrations of Ni²⁺ ions (a), Tu content (b), and TEOA (c) content was optimized.

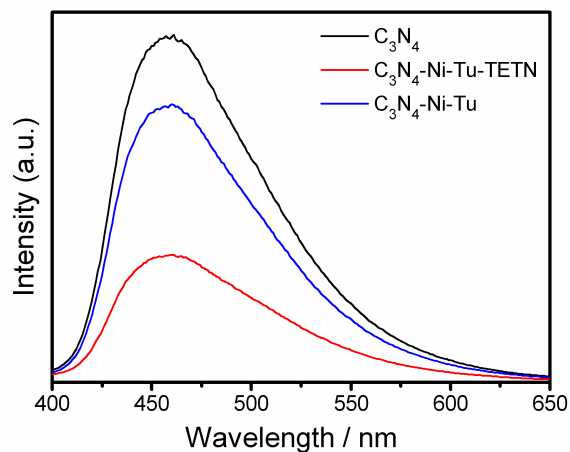
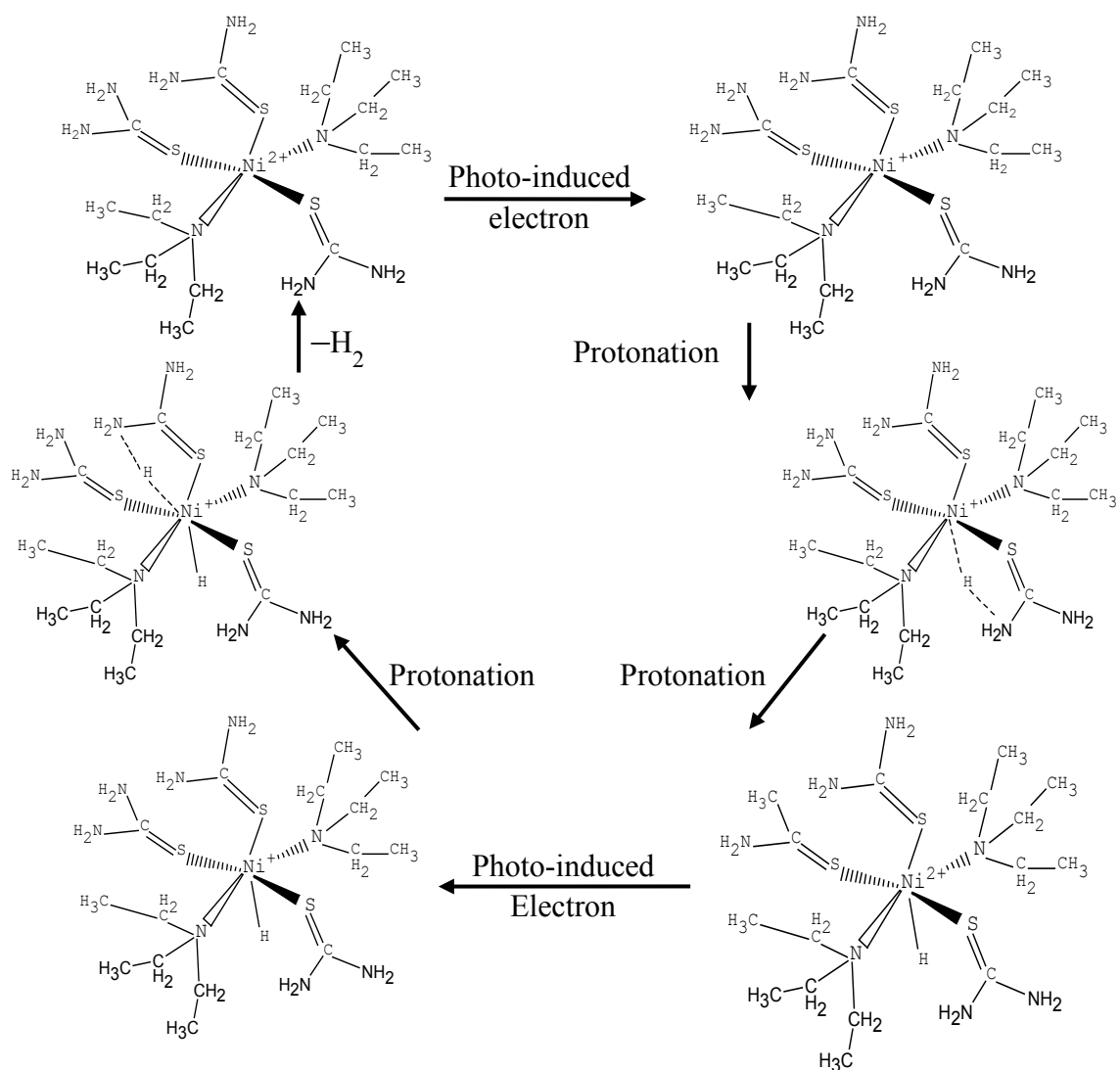


Fig. S5 Photo-luminescence (PL) spectra for C₃N₄, C₃N₄-Ni-Tu-TETN and C₃N₄-Ni-Tu dispersion (1 mg/ml, water was used as the solvent) under 365 nm excitation.



Scheme S1. H₂ formation process catalyzed by Ni–Tu–TETN complex

- 1 J. H. Liu, T. K. Zhang, Z. C. Wang, G. Dawson and W. Chen, *J. Mater. Chem.*, 2011, **21**, 14398.