Electronic Supplementary Information

A Novel Nickel-Thiourea-Triethylamine Complex Adsorbed on Graphitic C$_3$N$_4$ 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. C$_3$N$_4$ Preparation. Graphitic carbon nitride (g-C$_3$N$_4$) was synthesized according to our previous report. Typically, the C$_3$N$_4$ 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 H$_2$ system and photocatalytic activity measurement

C$_3$N$_4$–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-C$_3$N$_4$ was dispersed in 20 mL DI water by sonication, and given amounts of Ni(NO$_3$)$_2$•6H$_2$O was added and stirred for several hours to reach the adsorption equilibrium of Ni$^{2+}$ on C$_3$N$_4$. 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.
C₃N₄–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 C₃N₄–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 C₃N₄–Ni–Tu–TETN in ethanol and removing the solid C₃N₄.

**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 Shimatzu UV-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** $^1$H NMR spectra of TEOA (a), Tu (b) and TETN (c). (solvent: CHCl$_3$)

**Fig. S2** a) TEM and b) magnified TEM images of C$_3$N$_4$–Ni–complex
Fig. S3 UV-Vis absorption spectra of C$_3$N$_4$ (a), and C$_3$N$_4$–Ni–Tu–TETN (b)
Fig. S4 The experimental parameters: the concentrations of Ni$^{2+}$ ions (a), Tu content (b), and TEOA (c) content was optimized.

Fig. S5 Photo-luminescence (PL) spectra for C$_3$N$_4$, C$_3$N$_4$–Ni–Tu–TETN and C$_3$N$_4$–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