Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Amorphous Co_3S_4 nanoparticles modified tubular g-C_3N_4 formed Step-scheme hetrojunction for photocatalytic hydrogen production

Yuanpeng Wang[1,3,4], Xuqiang Hao[1,3,4], Lijun Zhang[1,3,4], Zhiliang Jin[1,2,3,4*], Tiansheng Zhao[2*]

1. School of Chemistry and Chemical Engineering, North Minzu University, Yinchuan 750021, P.R.China

2. State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Ningxia University, Yinchuan,750021, PR China

3. Ningxia Key Laboratory of Solar Chemical Conversion Technology, North Minzu University, Yinchuan 750021, P.R.China

4. Key Laboratory for Chemical Engineering and Technology, State Ethnic Affairs Commission, North Minzu University, Yinchuan 750021, P.R.China

Corresponding author: zl-jin@nun.edu.cn (Z. L. Jin); zhaots@nxu.edu.cn (T. S. Zhao)

Experimental Section

Preparation of Photocatalysts

All chemicals used in experiments were analytical grade and used without further purification.

Preparation of tubular g-C_3N_4

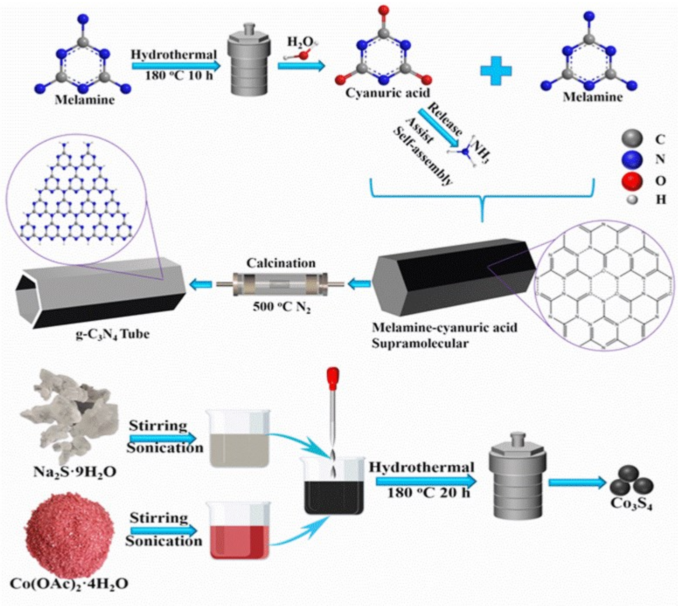
The tubular g-C_3N_4 was prepared using the reported method [1] with a little modification. In a typical synthesis process, 1.26 g (10 mmol) melamine was added into a beaker contained 100 mL deionized water and kept at 85 ^oC for 30 min under continuous stirring. The mixture was transferred into an autoclave with Teflon liner and kept for 10 h with a temperature of 180 ^oC. The product was collected by washing and centrifuging the precipitate for at least three times using deionized water and ethanol and dried in an oven at 60 ^oC. The tubular g-C_3N_4 was obtained by calcining the collected product at 500 ^oC for 4 h with a heating rate of 2.5 ^oC/min under the atmosphere of nitrogen. In addition, bulk g-C_3N_4 were prepared by calcining untreated melamine under conditions of air and N_2 with the same calcination temperature and heating rate.

Preparation of Co_3S_4

Co_3S_4 ultra-fine nanoparticles were prepared by using following process. 1 mmol $Co(OAc)_2$ $4H_2O$ was added into a beaker contained 30 mL deionized water and stirred for 30 min, and a certain amount of $Na_2S{\cdot}9H_2O$ was dissolved into a beaker and stirred for 30 min. Then the $Na_2S{\cdot}9H_2O$ aqueous solution was poured slowly into the $Co(OAc)_2$ $4H_2O$ aqueous solution and stirred for 30 min. The addition amount of $Na_2S{\cdot}9H_2O$ should make sure that the molar ratio of Co and S was maintained at 1:5. The mixed solution was transferred into an autoclave with Teflon liner and kept for 20 h with the reaction temperature of 120 ^oC. The amorphous Co_3S_4 was obtained by centrifuging and washing the precipitate for at least three times with deionized water and ethanol and dried at 60 ^oC overnight.

Preparation of g-C_3N_4/Co_3S_4

The composite catalysts were denoted as CC-x (x represents the amount of Co_9S_8 added into the system, x = 10, 15, 20, 25, 30, 35). Taking the CC-25 sample for example to illustrate the synthesis process of all composite catalysts. 0.1 g tubular g-C_3N_4 was poured into a beaker, and then determined amount of Co_3S_4 was added into the above system and 20 mL ethanol was used as the solvent. The mixture was treated using the ultrasound for 2 h to disperse the system uniformly. And the mixture was dried at 60 ^oC for one night.



Scheme. S1 Synthesis process of g-C_3N_4 tubes and Co_3S_4 ultra-fine nanoparticles.

Photocatalytic H_2-Production Measurements

A certain amount of catalyst and Eosin Y (denoted as EY) were put into the quartz reaction bottle and then 30 mL Triethanolamine solution (TEOA: 15 % (vol %)) was poured into the system as the sacrificial reagent. The mixture was treated for 5 min utilizing the ultrasound in order to disperse photocatalyst and EY into the sacrificial reagent uniformly. The reaction system should be a anaerobic environment so nitrogen was used to remove residual air in the reaction system. The quartz bottle was put in the multichannel reaction system (PCX50A Discover: Beijing Perfectlight Technology Co., LTD, China) to produce H_2. The constitutes of the produced gas and its yield were analyzed using the gas chromatography (Tianmei GC7900, TCD, 13X column, with N_2 as the carrier). The specific process can be described as follows: 0.5 mL of the produced gas was extracted from the reaction bottle using a sampling probe and then injected into the gas chromatography once an hour. Some parameters of the multichannel reaction system used in the photocatalytic hydrogen evolution activity experiments are as follows: the temperature of the reaction system was kept at about 25 ^{o}C, the light source was a xenon lamp with wattage of 5 W and the wavelength range of light source was >400 nm, the integrated intensity of the light was 100 mW/cm^2.

Table S1 Amount of catalysts used in hydrogen production experiments

Samples	g-C_3N_4	Co_3S_4	CC-10	CC-15	CC-20	CC-25	CC-30	CC-35
Amount of catalyst (g)	0.0121	0.0131	0.0133	0.0135	0.0134	0.0131	0.0128	0.0128
Amount of EY (g)	0.0212	0.0214	0.0211	0.0211	0.0225	0.0218	0.0213	0.0218

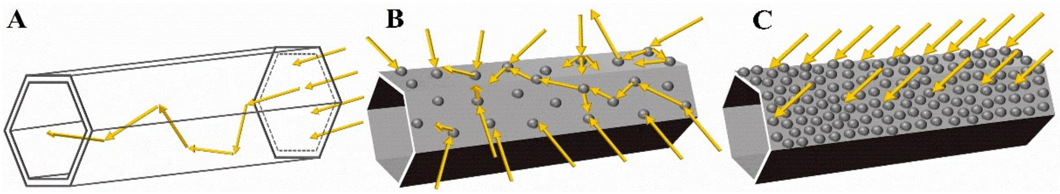
Photoelectrochemical Measurements

Some preparation work must be done before the test. In detail, fluorine-doped tin oxide (FTO) pieces were cut to be 1×1 cm^2, and sonicated for 5 min to clear dirt on the the surface of FTO slices. Five milligrams of catalyst were dissolved in a sample tube and dissolved with 100 μL ethanol (contained 10 μL of 5% Nafion solution). The mixture was sonicated for 1 h to disperse catalyst in the solution uniformly. Then the mixed solutions of g-C_3N_4, Co_3S_4 and CC-25 were smeared on the surface of FTO one by one, and these pieces of FTO with sample were placed in the dark at room temperature till they are all dried. The tests of Transient Photo-current (IT), Linear Scan Voltammetry (LSV), Electrochemical Impedance Spectra (EIS), and Mott−Schottky (MS) plots were conducted in a standard three-electrode cell utilizing the electrochemical workstation (VersaSTAT4-400 AMETEK). The FTO slices coated with photocatalysts were used as the work electrode, Pt electrode as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. A 300 W Xenon lamp with a 420 nm filter was used as the light source and Na_2SO_4 solution with the concentration of 0.2 $mol\cdot L^{-1}$ was applied as the electrolyte. The transient photo-current was measured at the applied potential of 0.4 V vs SCE under the illumination of light. The Linear Scan Voltammetry of g-C_3N_4, Co_3S_4 and CC-25 were conducted with a scan rate of 0.05 V/s, and the initial and final potential were - 0.6 and 1 V respectively. The Electrochemical Impedance Spectra of g-C_3N_4, Co_3S_4 and CC-25 were obtained with the scan rate of 0.005 V/s, the start and end frequency were 100000 and 0.1 Hz respectively. Mott−Schottky plots of g-C_3N_4 and Co_3S_4 were carried out at the frequency of 1000 Hz and an amplitude of 10 mV (RMS).

Characterization

X-ray diffraction (XRD) patterns of all samples were obtained using the Rigaku SmartLab diffractometer with nickel-filtered Cu Kα radiation (HORIBA Scientific). FTIR-650 spectrometer was used to acquire the Fourier transform infrared spectroscopy (FT-IR) spectra of g-C_3N_4

(synthesized using different methods, Co_3S_4 and CC-25. The microstructure and morphology were acquired using the emission scanning electron microscope (SEM: EVO-10, ZEISS) and the transmission electron microscope (TEM: JEM-2100F, JEOL). The chemical composition of all elements was conducted on Thermo Scientific ESCALAB-Xi^+ electron spectrometer with Al Kα X-ray source. $BaSO_4$ was used as the reference background to obtain the UV−vis diffuse reflectance spectra (DRS) on the PerkinElmer Lambda-750S. The N_2 adsorption−desorption isotherms were obtained by using the instrument Quanta Chrome Instrument (ASAP2020HD88) at a condition of 77 K. The photoluminescence (PL) and time-resolved photoluminescence (TRPL) were carried out on a FLUOROMAX-4 spectrophotometer.



Scheme. S2 The schematic diagram of the scattering / reflection effect for the incident light on the surface of CC-25.

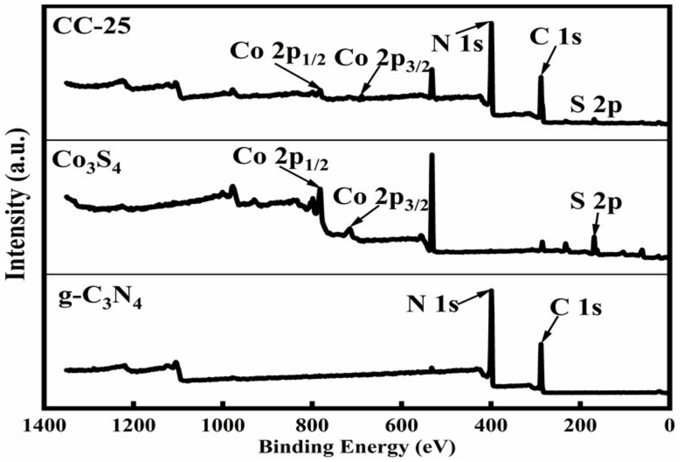


Fig. S1 XPS survey spectra of g-C_3N_4, Co_3S_4 and CC-25.

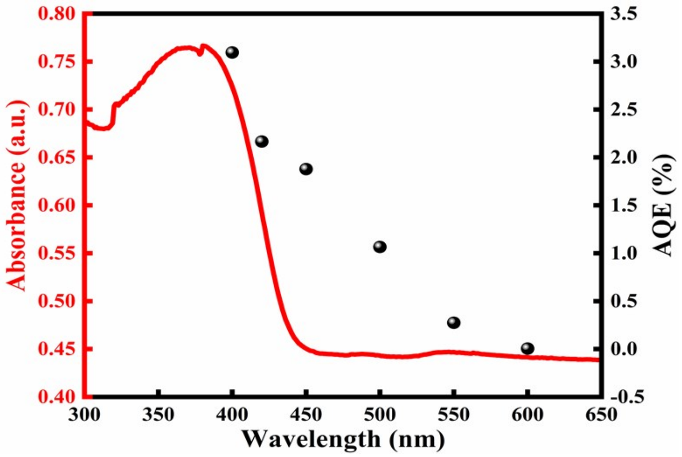


Fig. S2 Apparent quantum efficiency (AQE) of CC-25.

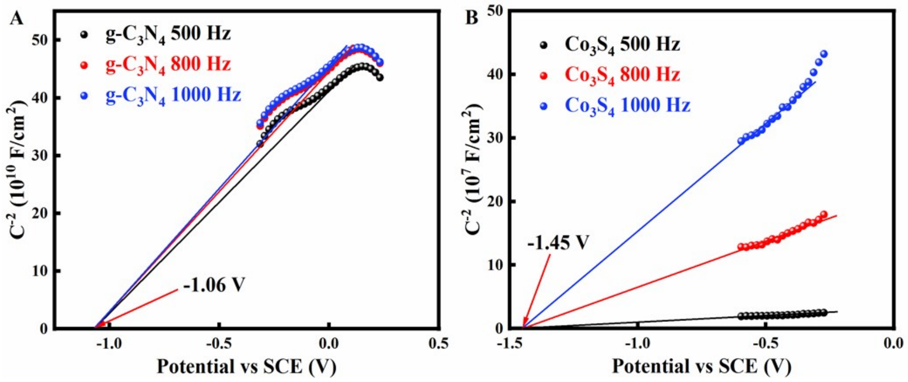


Fig. S3 Mott−Schottky curses of g-C_3N_4 and Co_3S_4 at different frequencies.

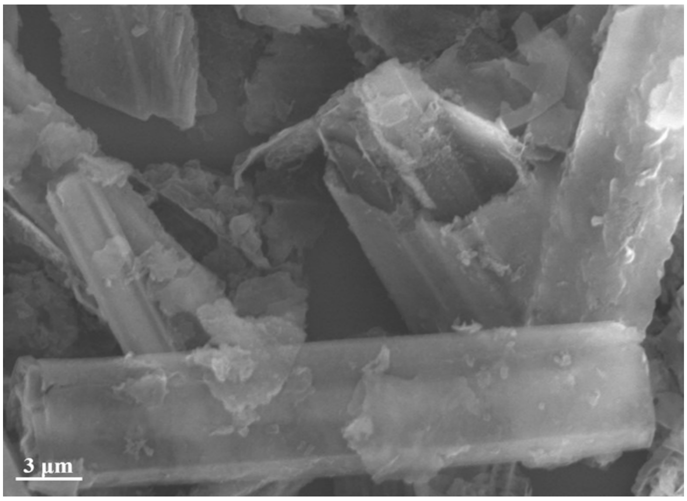


Fig. S4 SEM image of CC-25 after photocatalytic hydrogen evolution.

[1] S. Guo, Y. Tang, Y. Xie, C. Tian, Q. Feng, W. Zhou, B. Jiang, P-doped tubular g-C_3N_4 with surface carbon defects: Universal synthesis and enhanced visible-light photocatalytic hydrogen production, Applied Catalysis B: Environmental, 218, (2017), 664-671.