

Supporting Information for

High mobility organic semiconductor for constructing high efficiency carbon nitride heterojunction photocatalysts

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1. Experimental Section

1.1 Molecular structure and coordination environment of CuPc

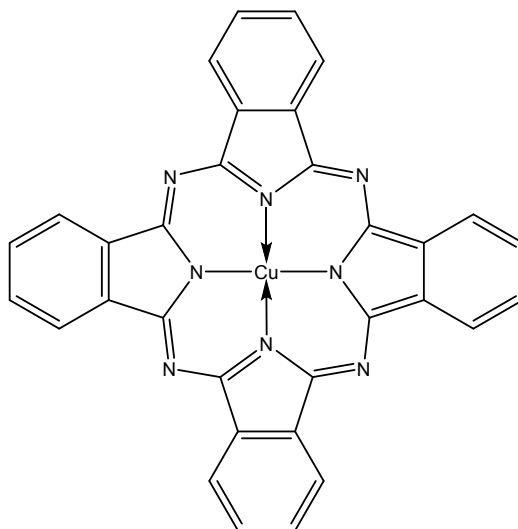


Fig. 1 Molecular structure of CuPc.

CuPc has a special two-dimensional conjugated π -electronic structure. In the molecular structure of CuPc, the Cu atom is surrounded by 4 N atoms. Copper is connected with two of the N atoms by ionic bonds, and with the other two N atoms by coordination bonds.

1.2 Synthesis of bulk CN

Bulk CN was synthesized by thermal condensation of urea. Typically, 25g urea was put in a sealed crucible and then heated to 550 °C at a speed of 3°/min in a muffle furnace. The temperature was maintained at 550 °C for 4 hours and then cooled down to room temperature.

1.3 Two-step method for fabrication of CN nanosheet

Step 1: Secondary calcination. Bulk CN was first grinded by a mortar. Then CN powders were put in an open crucible to allow the materials to be well exposed to air. Then it was heated to 520 °C at a speed of 5°C/min and maintained at 520 °C for 2 hours.

Step 2: High-power ultrasonic exfoliation. Typically, 50mg CN powders obtained after step 1 were dispersed in 10ml IPA. Then CN nanosheets were obtained by ultrasonic treatment of the suspension using a 500w ultrasonic apparatus.

1.4 Preparation of CN/CuPc heterojunction photocatalysts

A certain amount of CuPc (0 wt%, 3 wt%, 5 wt%, 7 wt%, 10 wt%) was added into the IPA suspension of CN nanosheet. The hybrid suspension was ultrasonic for 2 hours at low power of 50w. Then the well mixed suspension was centrifuged at 5000r/min for 10min. The supernatant was discarded and CN/CuPc heterojunction photocatalysts were obtained.

1.5 Electrochemical characterization

1.5.1 Photocurrent response of CN/CuPc

0.5M Na_2SO_4 solution was used as the electrolyte. 2mg/ml CN (or CN/CuPc) isopropanol suspension was dripped onto the ITO electrode and baked dry with an infrared lamp. A 300w Xenon lamp was used as the light source.

1.5.2 EIS of CN and CN/CuPc

5mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (1:1) solution containing 0.1 M KCl was used as the electrolyte. 2mg/ml CN (or CN/CuPc) isopropanol suspension was dripped onto the glassy carbon electrode and baked dry with an infrared lamp. EIS was tested using a three-electrode system (Reference electrode: saturated calomel electrode).

1.5.3 Mott-Schottky test of CN and CuPc

0.5M Na_2SO_4 solution was used as the electrolyte. 2mg/ml CN (or CuPc) isopropanol suspension was dripped onto the glassy carbon electrode and baked dry with an infrared lamp. The Mott-Schottky test was conducted using a three-electrode system (Reference electrode: saturated calomel electrode).

2. Characterization

2.1 Nitrogen adsorption–desorption isotherms

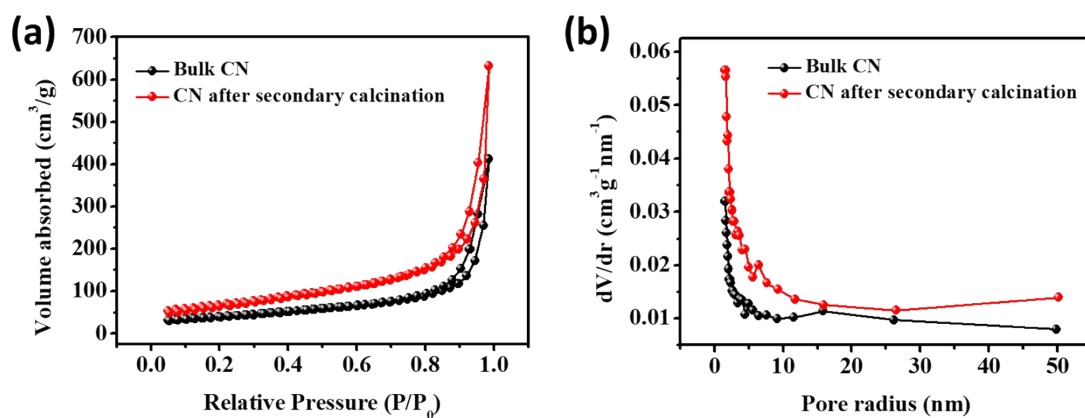


Fig. S2 The nitrogen adsorption–desorption isotherms of Bulk CN and CN after secondary calcination. (a) BET and (b) BJH.

2.2 XRD of CN before and after ultrasonic treatment

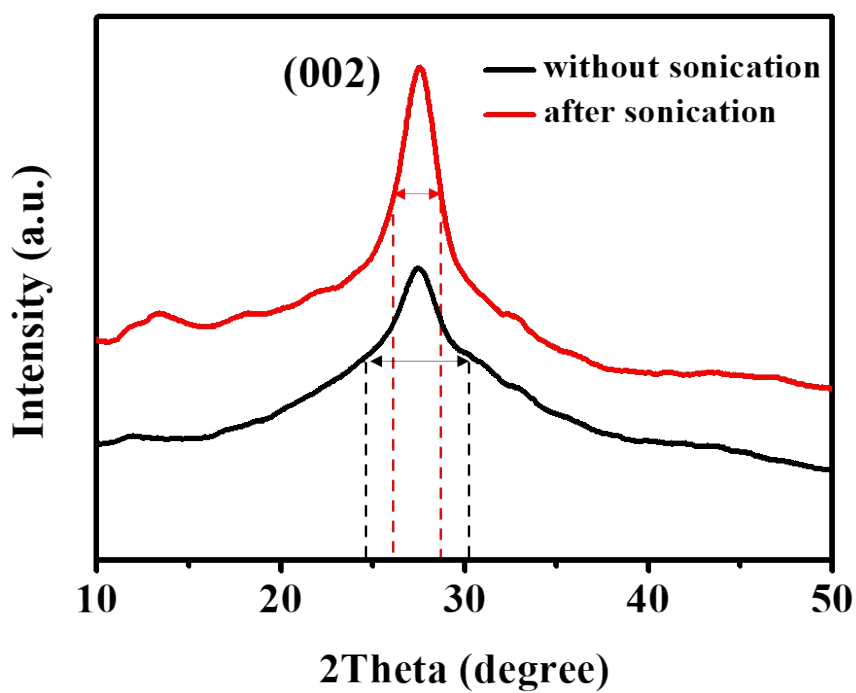


Fig. S3 XRD of CN before and after ultrasonic treatment.

2.3 AFM characterization of CN nanosheets

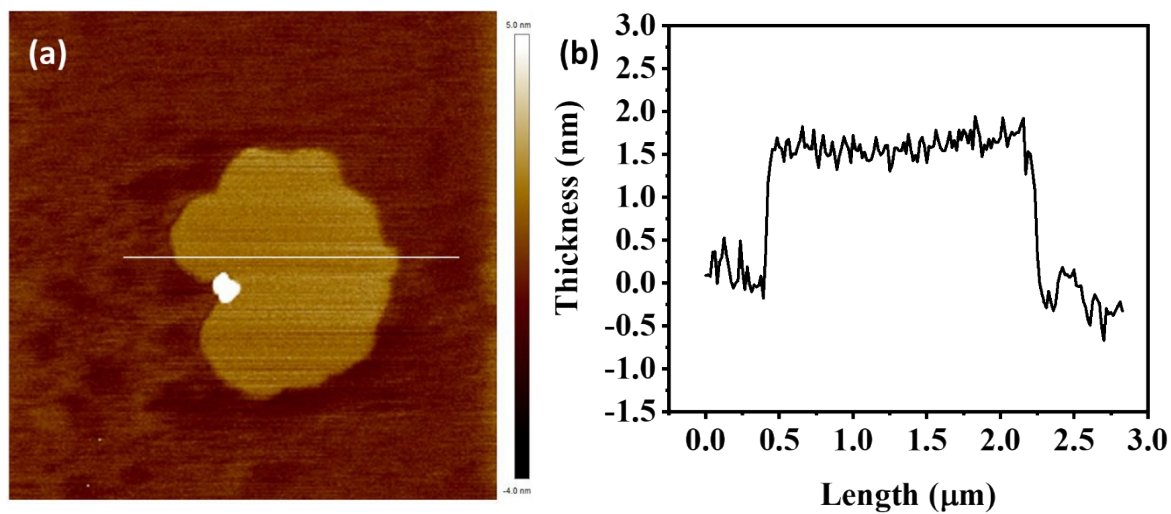


Fig. S4 (a) AFM height image of CN nanosheet and (b) corresponding height results.

2.4 TEM-assisted Energy Disperse Spectroscopy (EDS) of CN/CuPc heterojunction

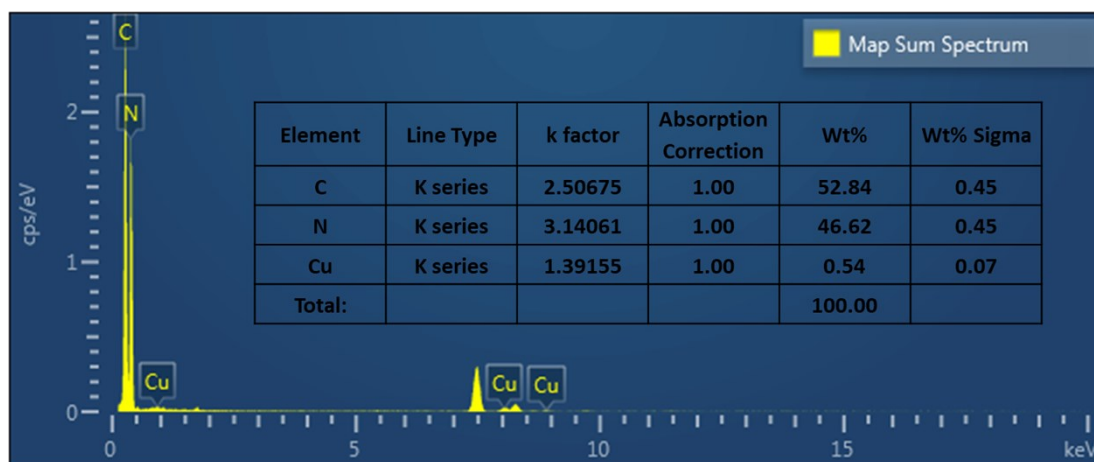


Fig. S5 Sum spectrum of TEM assisted EDS of CN/CuPc heterojunction (7 wt% CuPc).

2.5 N XPS of CN and CN/CuPc heterojunction

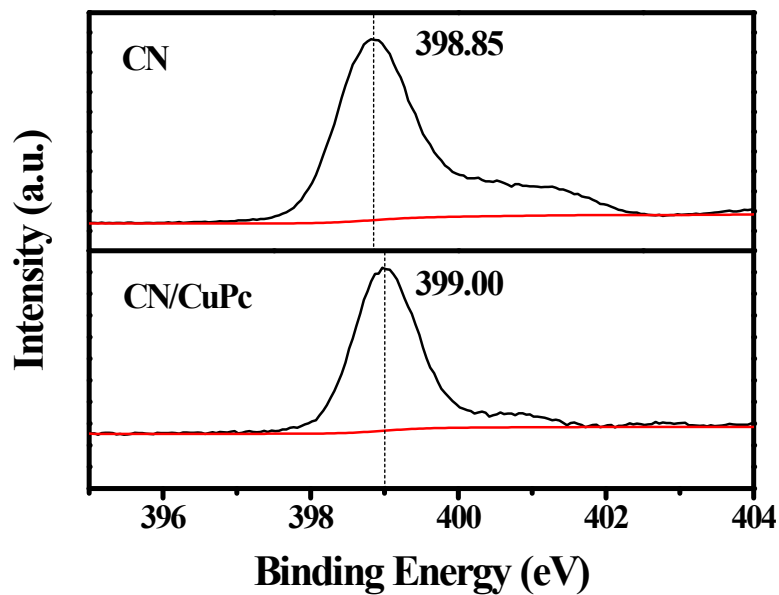


Fig. S6 N 1s XPS of CN and CN/CuPc.

2.6 PHE measurements of CN and CN/CuPc heterojunctions

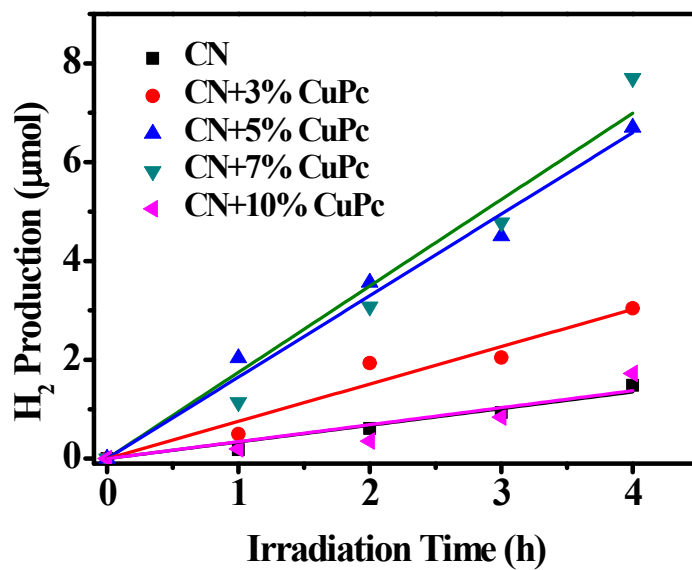


Fig. S7 PHE measurements of CN and CN/CuPc heterojunctions. TEOA was used as hole sacrificial agent and no cocatalyst was used. A 300w Xenon lamp was used as the light source.

Table S1 Summary of the PHE rates derived from Fig. S7

| Photocatalysts | Hydrogen Evolution Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) |
|----------------|--|
| CN | 15.2 |
| CN+3%CuPc | 29.9 |
| CN+5%CuPc | 64.9 |
| CN+7%CuPc | 71.2 |
| CN+10%CuPc | 16.9 |

2.7 XRD of CN/CuPc before and after PHE test

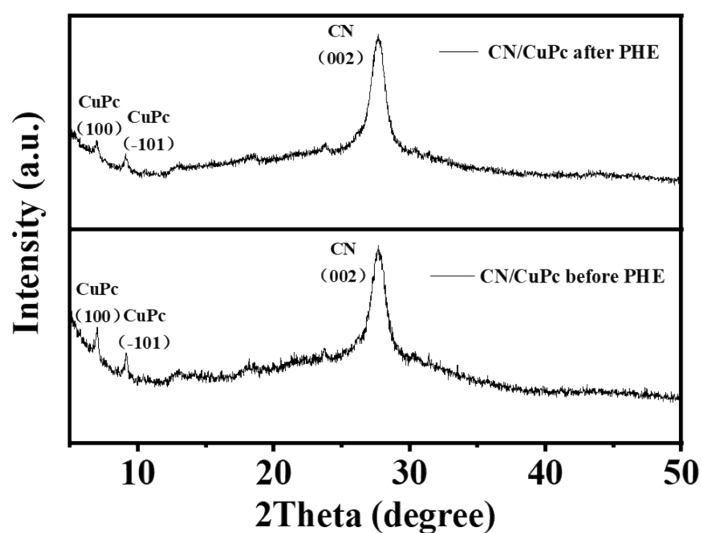


Fig. S8 XRD of CN/CuPc before and after the PHE test.

2.8 PHE testing irradiated at monochromatic light

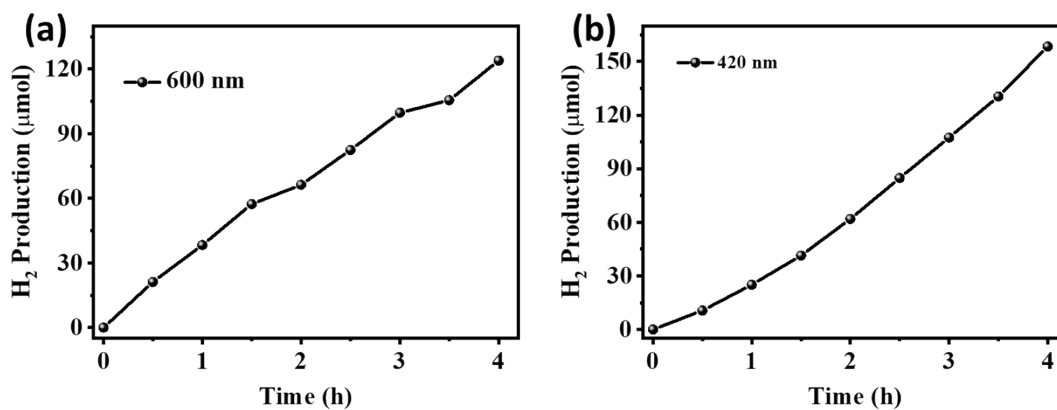


Fig. S9 PHE testing of CN/CuPc irradiated at (a) 600nm and (b) 420nm.

2.9 PHE testing of pure CuPc

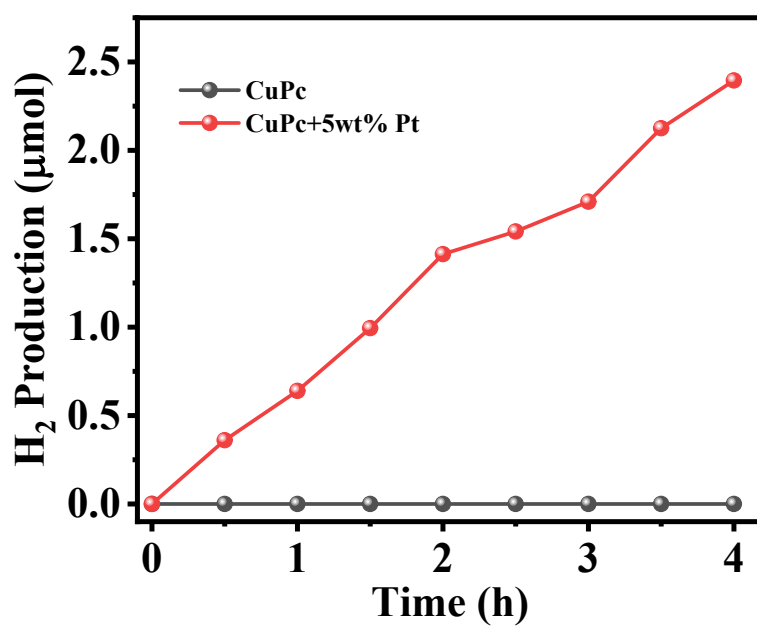


Fig. S10 PHE testing of pure CuPc with and without Pt.