Electronic Supplementary Information

Two Dimensional Conjugated Polymers with Enhanced Optical Absorption and Charge Separation for Photocatalytic Hydrogen Evolution

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Experimental section

Synthesis. The sample of CND, using dicyandiamide (3g) as precursor, was heated at 550 °C for 4 h with a ramping rate of 2.3 °C/min in air. The sample of CNU, using urea (10g) as precursor, was heated at 550 °C for 2 h with a ramping rate of 5.0 °C/min in air. The modified CNU samples were synthesized by mixing urea (10 g) with 10 mg of a variety of organic monomers in 10 mL water with stirring at room temperature for 12 h and then stirring at 80 °C to remove water. The mixture were ground into powder and calcined at 550 °C for 2 h with a ramping rate of 5.0 °C/min in air to obtain the final samples. The samples thus obtained were denoted as CNU-BA, CNU-ABN, CNU-ATCN and CNU-DAMN. All of the modified CNU samples are synthesized with very good reproducibility.

Characterization. XRD measurements were performed on a Bruker D8 Advance diffractometer with Cu Ka1 radiation. The UV/Vis spectra were recorded on a Varian Cary 500 Scan UV/Vis system. FTIR spectra were recorded on a BioRad FTS 6000 spectrometer. Nitrogen adsorption-desorption isotherms were performed at 77 K using Micromeritics ASAP 2010 equipment. TEM was performed on a FEI Tencai 20 microscope. X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI Quantum 2000 XPS system with a monochromatic Al Kα source and a charge neutralizer. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker model A300 spectrometer.

Photocatalytic Test. Photocatalytic H_2 production was carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. For each reaction, 50 mg well ground catalyst powder was dispersed in an aqueous solution (100 mL) containing triethanolamine (10 vol.%) as sacrificial agent. 3 wt.% Pt was photodeposited onto the catalysts using H_2PtCl_6 dissolved in the reaction solution. The reaction solution was evacuated several times to remove air completely prior to irradiation under a 300 W Xe lamp and a water cooling filter. The wavelength of the incident light was controlled by using an appropriate long pass cut-off filter. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector.

Electrochemical Analysis. They were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode, the active area is confined to 0.25 cm^2. The working electrode was prepared by dip-coating catalyst slurry (5 mg mL^{-1} in DMF) on indium–tin oxide (ITO) glasses. After air-drying, the working electrode was further dried at 393 K for 2 h to improve adhesion. A 0.2 mol L^{-1} Na_2SO_4 aqueous solution (pH = 6.8) was chosen as the supporting electrolyte and was purged with nitrogen to remove O_2 before any measurements. The visible light was generated by Spot light source LC8 (Hamamatsu Co.) with a 420 nm cut-off filter was used as a photoexcitation light source.

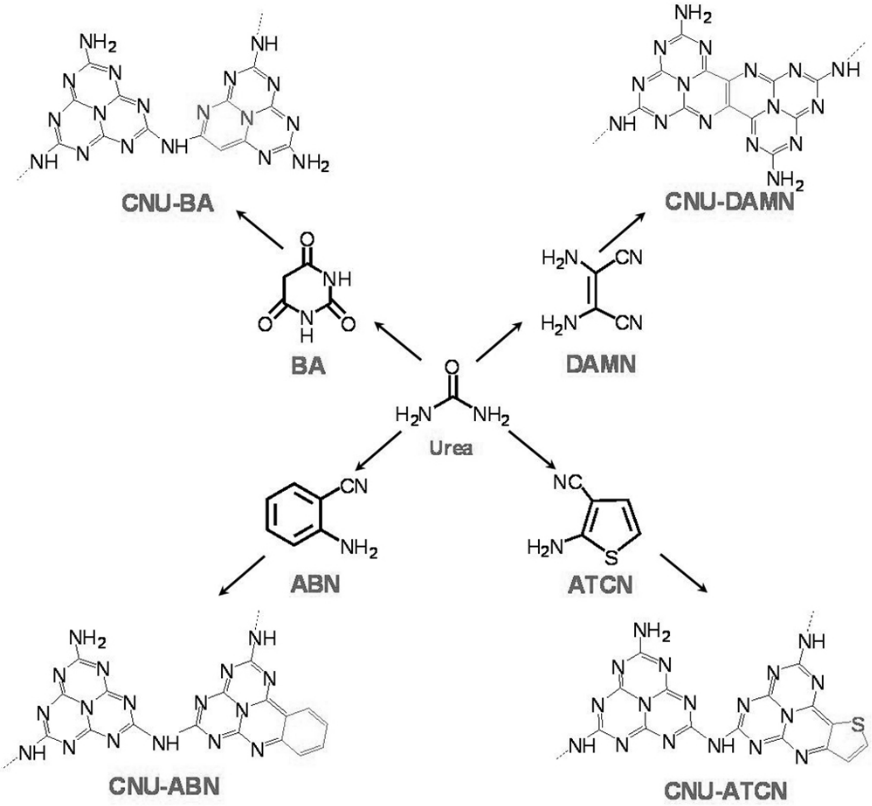


Fig. S1 Proposed structure of products through the copolymerization processes of urea with organic monomers at high temperature.

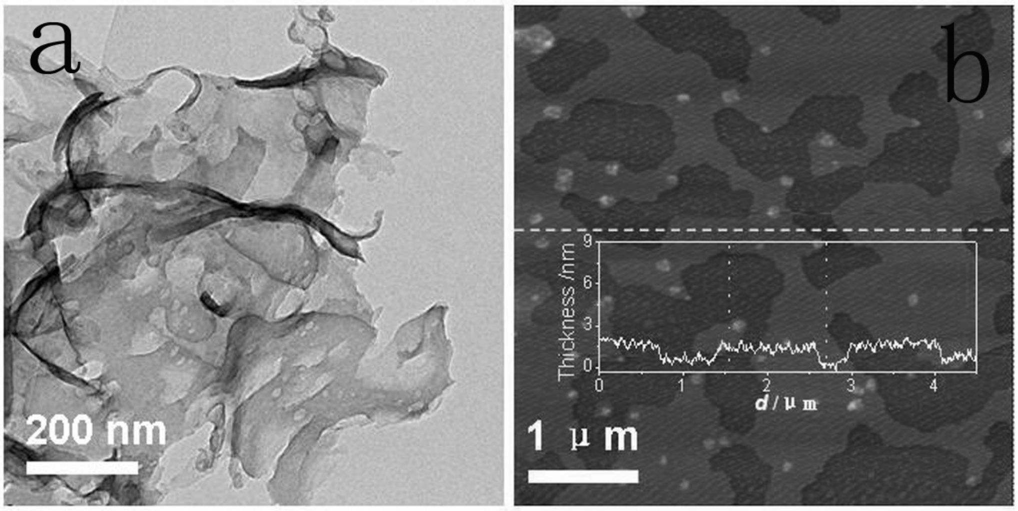


Fig. S2 Morphology characterization of TEM (a) and AFM (b) for CNU-ABN. The inset is the corresponding thickness curve determined along the line and reveals a uniform thickness about 2.2 nm.

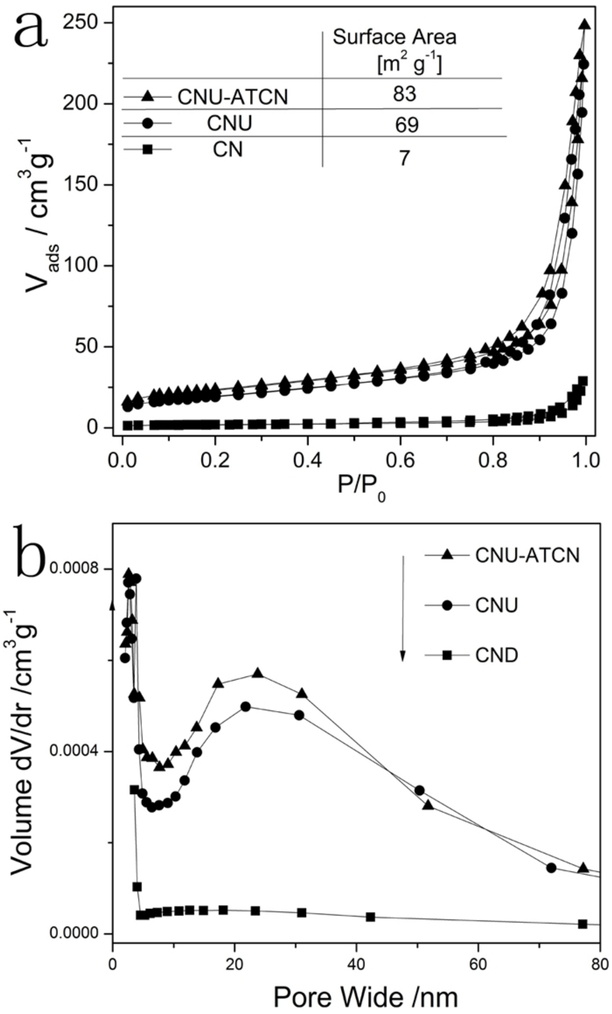


Fig. S3 (a) N_2-sorption isotherms and (b) corresponding BJH pore-size distribution of CND, CNU and CNU-ATCN. The inset in (a) shows the BET surface area of the samples.

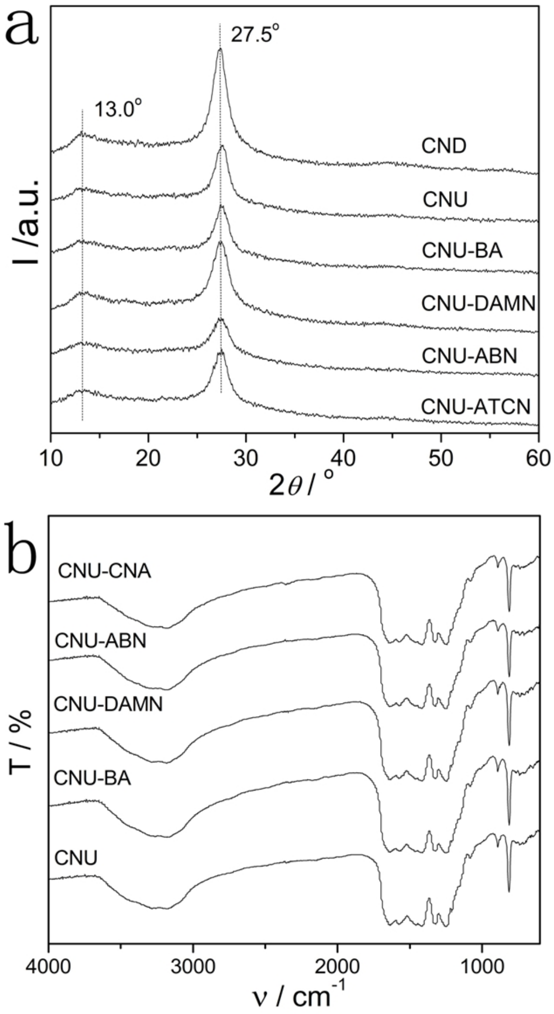


Fig. S4 (a) XRD patterns and (b) FT-IR spectra of CND and CNU-based samples. The XRD patterns exhibits the graphite-like interlayer (002) peak at 27.5°. Another peak with low-angle reflection at 13.0°, which corresponds to the lattice planes parallel to the c-axis, is weak and broadened. Compared for bulk g-CN (CND), the intensity of this (002) peak of CNU-based samples show significantly decreases. These features could result from the decreased planar size and the ragged edges of the layers. The FT-IR spectra show characteristic bands of aromatic CN heterocycles (1200~1600 cm^{-1}) and heptazine units (810 cm^{-1}). Being contributed by the N-H stretching, the broad peaks between 3000 and 3600 cm^{-1} prove the presence of NH and/or NH_2 groups, which are integral parts of melon.

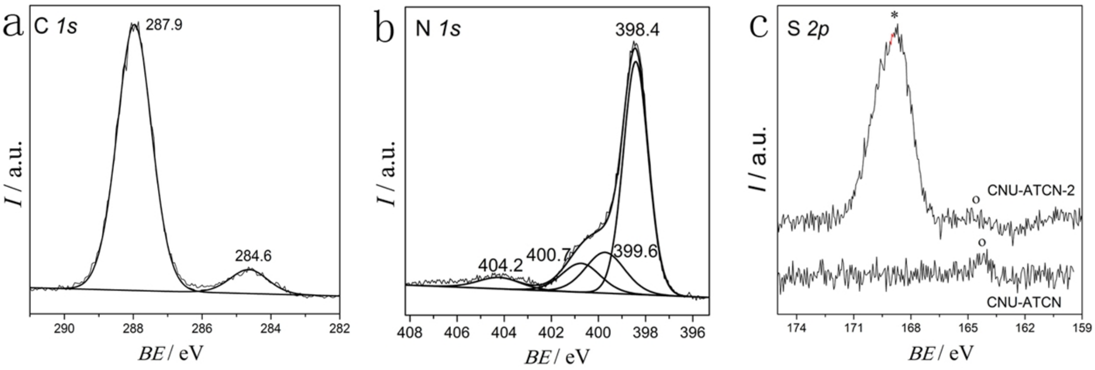


Fig. S5 XPS spectra. High-resolution C*1s* (a) and N*1s* (b) for CNU-ATCN. High-resolution S*2p* (c) for CNU-ATCN and CNU-ATCN-2 (CNU-ATCN and CNU-ATCN-2 was synthesized by mixing 10g urea with 10 mg and 20 mg ATCN, respectively). ∗ and o indicate the S_{2p} of sulfone and thiophene, respectively.

The two BEs at 287.9 and 284.6 eV in C*1s* signal are identified as the sp^2-bonded carbon (N-C=N) and the sp^2 C-C bonds. The contribution at 398.7, 400.3, 401.4 and 404.2 eV in N*1s* spectrum are ascribed as sp^2-bonded N in the triazine rings (C-N=C), the tertiary nitrogen $N-(C)_3$, the amino functions (C-N-H) and the charging effects or positive charge localization in the heterocycles, respectively. Thus, the molecular structure of CNU-ATCN is based on the NH-bridged melem ($C_6N_7(NH_2)_3$) monomers. The typical thiophene-S peaks were observed at around 164 eV which contains the contribution from the $S_{2p3/2}$ and $S_{2p1/2}$ multiplets. With the increased amount of the monomer used, the thiophene-S motifs partially were oxidized to SO_x groups, as indicated by the sulfonic peaks in XPS centered at ca. 169 eV. Such a thiophene-S to sulfone transformation changed the nature of chemical interaction between sulfur specie and g-CN, as thiophene is electron donation group while sulfone is electron attractive. Thus, the photocatalytic performance of g-CN was modulated by this simple chemical control: thiophene group is more beneficial for photocatalytic hydrogen evolution than sulfone group, as shown in Fig. S7.

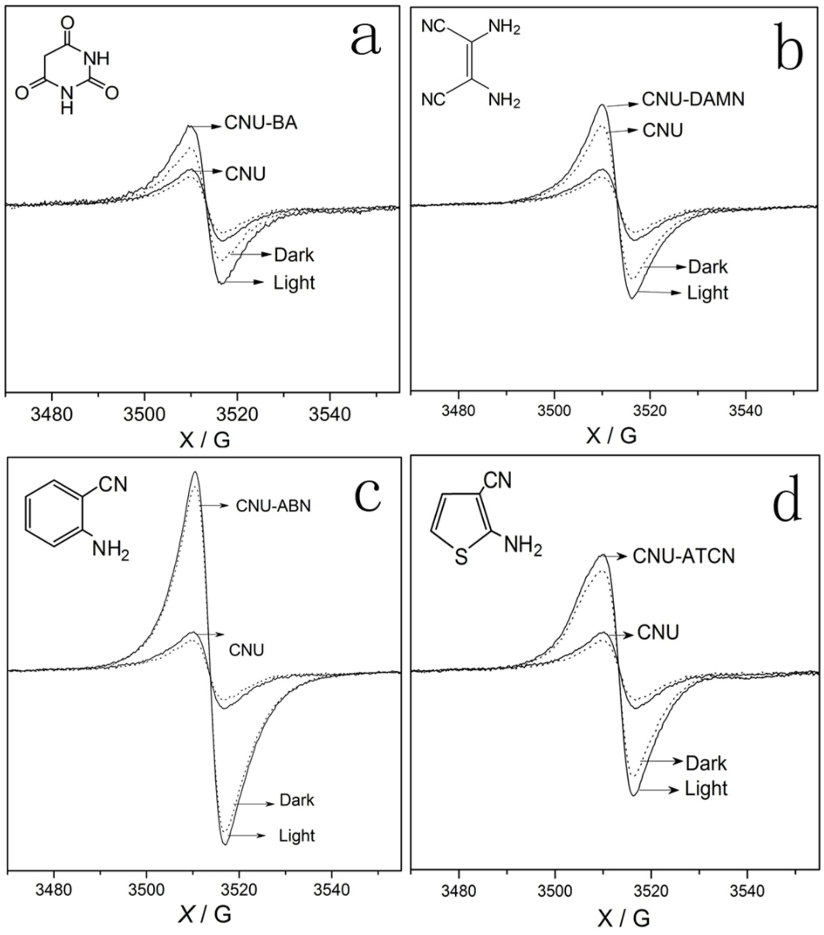


Fig. S6 Room temperature EPR spectra in dark (solid) and visible light irradiation (dashed) for CNU-BA (a), CNU-DAMN (b), CNU-ABN (c) and CNU-ATCN (d).

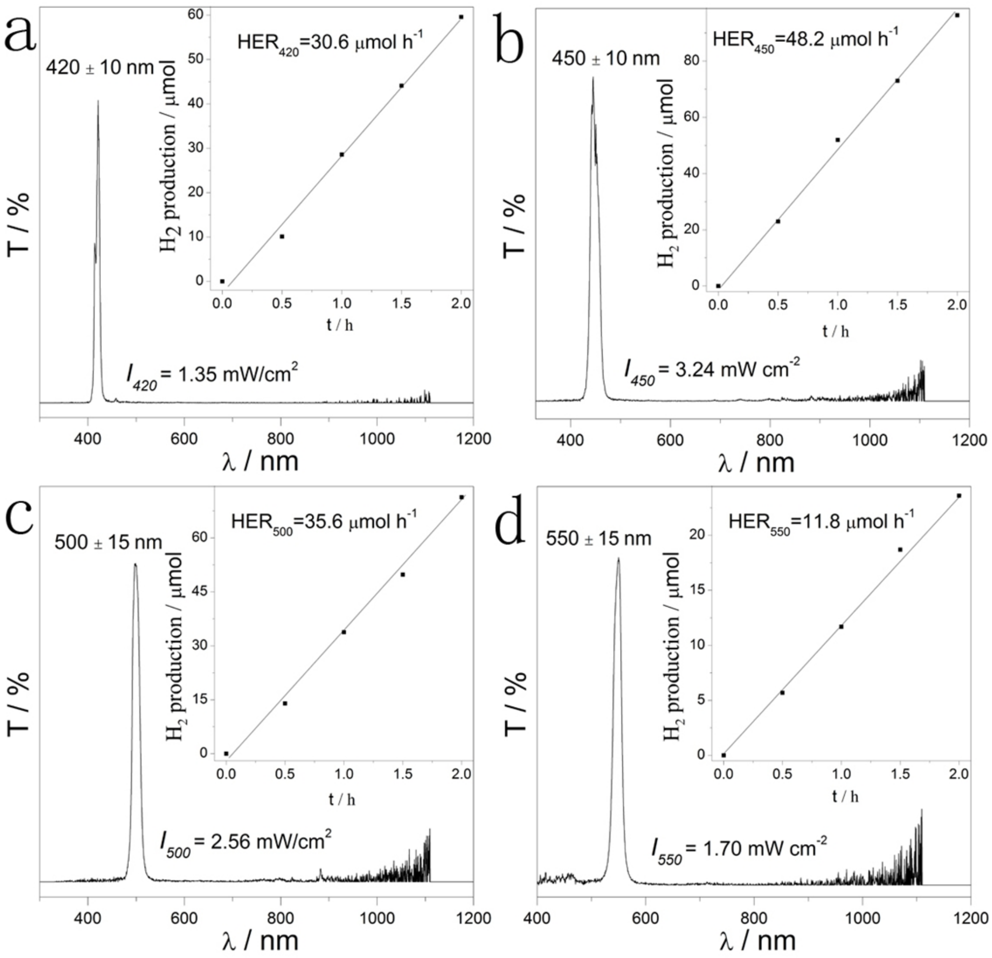
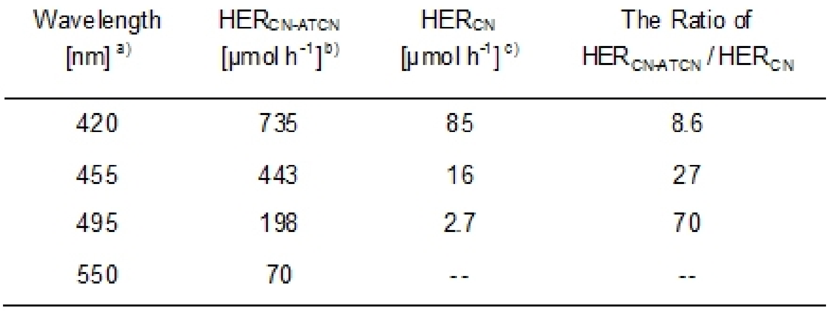


Fig. S7 Characterization of a variety of band-pass filter and the corresponding photocatalytic activity (inset) of CNU-ATCN for the AQY determination. The apparent quantum yield (AQY) for H_2 evolution was measured using the 420 nm (a), 450 nm (b), 500 nm (c) and 550 nm (d) band-pass filter. The average intensity of irradiation was measured by ILT 950 spectroradiometer and the irradiation area was controlled as 40.7 cm^2. The AQY was estimated as:

$$\text{AQY (\%)} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$

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

Table S1. Physicochemical properties and photocatalytic activity of CNU-ATCN for the hydrogen evolution reaction under visible light irradiation.



Wavelength [nm] [a)]	$HER_{CN\text{-}ATCN}$ [μmol h^{-1}] [b)]	HER_{CN} [μmol h^{-1}] [c)]	The Ratio of $HER_{CN\text{-}ATCN}$ / HER_{CN}
420	735	85	8.6
455	443	16	27
495	198	2.7	70
550	70	--	--

a) Controlled by using an appropriate long pass cut-off glass filter. b) H_2 evolution rate obtained on CNU-ATCN. c) H_2 evolution rate obtained on CNU.

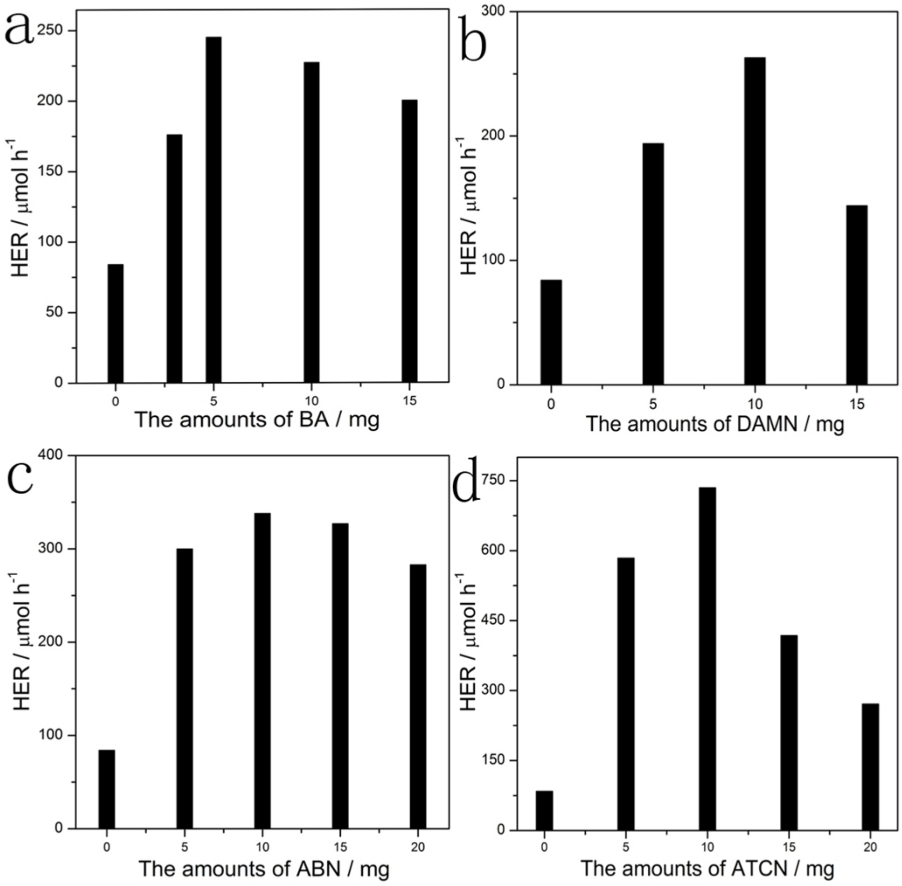


Fig. S8 The effect of the amount of organic monomers on the photocatalytic activity of the carbon nitride nanosheets.

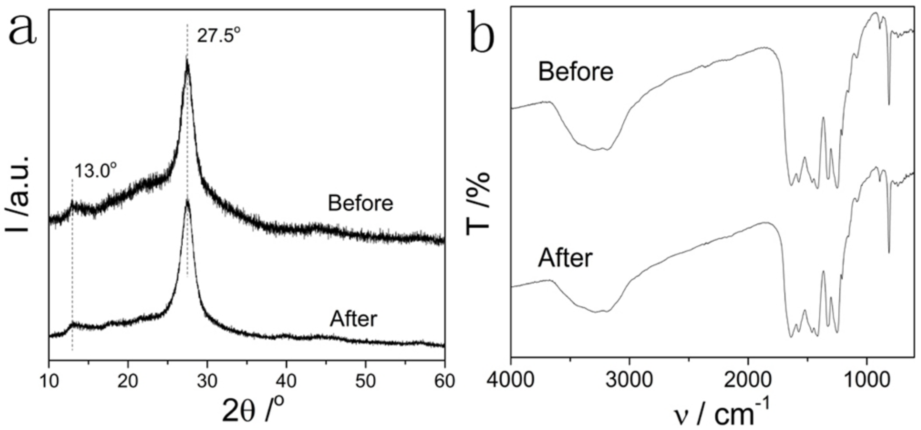


Fig. S9. (a) XRD patterns and (b) FT-IR spectra of CNU-ATCN samples before and after hydrogen evolution reaction.