Electronic Supplementary information for:

Thermal-annealing induced structure reorganization in polymeric photocatalyst for enhanced hydrogen evolution

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Experimental Section

Materials: All reagents were obtained from Alfa Aesar or Sigma-Aldrich and used as received.

Synthesis of CTP-1: 4 mmol of 1,4-dicyanobenzene was dissolved in the CF_3SO_3H (10 mL) under nitrogen at 0 °C. The obtained viscous solution was then stirred for 2 h before the heating treatment of 100 °C for 12 hours. The resultant products were carefully poured into 200 ml H₂O. The collected solid was grounded into powder with an agate mortar then washed with Milli Q water, ethanol and acetone followed by further purified with Soxlet extraction with CH_2Cl_2 and dried at 80 °C.

Synthesis of CTP_T: In a typical synthesis, 0.2 g of as-prepared CTP-1 was calcined at different temperature (250 - 400 °C) in air for 2 h at a heating rate of 2.5 °C min⁻¹. The obtained solid was grounded into powder with an agate mortar and noted as CTP_T (where T is the treatment temperature).

Characterization: Thermal gravimetric analysis (TGA) was performed on TG209 (NETZSCH Co.). X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with CuK α 1 radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) was operated by Tecnai20 FEG microscope and Titan G2 60-300 with image corrector. The fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 670 FT-IR spectrometer with KBr as the diluents. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al K α line source (200 W). UV-Vis diffuse reflectance spectra (UV-Vis DRS) were performed on Varian Cary 500 Scan UV-visible system. The electron paramagnetic resonance (EPR) measurements were carried out on a Bruker Model A300 spectrometer. Nitrogen adsorption-desorption isotherms were performed at 77 K using Micromeritics ASAP 3020 equipment. The solid-state ¹³C NMR experiments were performed on a Bruker Advance III 500 spectrometer. Photocurrent performance was 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 (3 M KCl) electrode as the reference electrode. The working electrode was prepared on indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 5

mg sample was dispersed in 1 mL of DMF by sonication to get a slurry. The slurry was spread onto pretreated ITO glass. After air-drying, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin.

Photocatalytic test: Photocatalytic hydrogen evolution arrays were performed in a Pyrex top-irradiation reaction vessel linked to a glass closed gas system. H₂ production was carried out by dispersing 50 mg of photocatalyst powder in an aqueous solution (100 mL) containing triethanolamine (10 vol.%) as sacrificial electron donor. 3.0 wt.% of Pt was loaded on the surface of photocatalyst by the in-situ photodeposition approach using H₂PtCl₆. The mixture was evacuated several times to remove air completely before 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 reaction solution was kept at 12 °C by a flow of cooling water. The generated gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) with Argon as the carrier gas.

The wavelength-dependent experiments were carried out similarly to previous experiments, only changing the cutoff filters to a different cutoff wavelength. The biomimetic experiment for hydrogen production was carried out by adding additional K_2HPO_4 ·3H₂O (2.28 g, 0.01 mol) to the reaction solution.

The apparent quantum yield (AQY) for the H_2 evolution was determined by replacing the Xe lamp with a 405 nm semiconductor laser. The irradiation area was 7.92 cm². The total intensity irradiation was measured by averaging 40 points in the irradiation area. For the 405 nm monochromatic light, the average intensity was 4.24 mW cm⁻² (ILT 950 spectroradiometer). The AQY was calculated as

$$AQY = \frac{N_{e}}{N_{p}} \times 100\% = \frac{2MN_{A}hc}{SPt\lambda} \times 100\%$$

where N_e is the amount of reaction electrons, N_p is the amount of incident photons, M is the amount of H₂ molecules, N_A is Avogadro's constant, h is the Planck constant, c is the speed of light, S is the irradiation area, P is the intensity of the irradiation, t is the photoreaction time, and λ is the wavelength of the monochromatic light.

Sample	S _{BET} ^a (m ² g ⁻¹)	HER ^b (μmol h ⁻¹ g ⁻¹)	HER _s ^c (µmol h ⁻¹ m ⁻²)
CTP-1	5.6	120	21
CTP ₂₅₀	3.3	280	85
CTP ₃₀₀	1.3	500	385
CTP ₃₅₀	1.1	320	291
CTP ₄₀₀	1.1	60	55

Table S1. Specific surface area and photocatalytic activity of CTPs

 $^{\rm a}$ BET surface area calculated from the $\rm N_2$ adsorption isotherm.

^b Reaction conditions: polymer (50 mg), TEOA/H₂O (1/10 in vol, 110 mL), 300 W Xe lamp with cut-off filter > 420 nm. ^c Hydrogen evolution rate normalized by their BET surface areas: HER_s=HER/S_{BET}.

Notes: The specific surface areas may influence the number of active sites. To consider this factor, we calculate the corresponding photocatalytic activity (HER_s) of CTPs normalized by their BET surface areas. According to the results, we can find that after excluding the effect of the number of active sites, all the CTP_T shows the better photocatalytic performance than pristine CTP-1 and the CTP_{300} still has the superior activity (over 17 times higher than CTP-1). Besides, it is worth to mention that the CTP_{400} has the lower HER value but higher HER_s valve than CTP-1, indicating that the low HER of CTP_{400} is highly limited by its decreased active sites.



Fig. S1 FT-IR spectra of CTPs.



Fig. S2 Solid-state ¹³C NMR spectra of CTPs.



Fig. S3 a) N 1s and b) C 1s XPS spectra of CTPs.



Fig. S4 Surface morphology characterization. SEM images of a) CTP-1, b) CTP₃₀₀, and c) CTP₄₀₀; d) TEM image of the

CTP₃₀₀.



Fig. S5 Powder X-ray diffraction (PXRD) patterns of the CTPs.



Fig. S6 UV-Raman spectra of the CTPs.



Fig. S7 EPR spectra of CTPs tested without light irradiation.

Notes: All samples show one single Lorentzian line centering at 3512 G with a *g* value of 2.0051 in dark, generally being originated from unpaired electrons in the π -conjugated aromatic rings of CTPs. The intensity of this line increased in the dark condition, illustrating the gradually increased amount of unpaired electrons in the π -conjugated aromatic rings of CTPs. It is worth to metion that the annealing process may also cause hemolysis of chemical bonds to produce organic radicals, which make the annealed materials EPR active.



Fig. S8 EPR spectra of CTP₃₀₀ tested with/without light irradiation.



Fig. S9 The effect of Pt loading on the H₂ evolution rate of CTP₃₀₀ (λ > 420 nm).



Fig. S10 Diffuse reflectance spectra of CTPs.



Fig. S11 Kubelka-Munk-transformed reflectance spectra of CTP-1 and CTP₃₀₀.



Fig. S12 XPS valance spectra of CTP-1 and CTP₃₀₀.



Fig. S13 Photoluminescence spectra of CTPs measured in the solid-state powder ($\lambda_{\text{excitation}}$ = 350 nm).



Fig. S14 Electrochemical impedance spectra of CTP-1 and CTP $_{300}$ tested at a -0.2 V bias potential vs. Ag/AgCl in a 0.2 M Na $_2$ SO $_4$ aqueous solution without light irradiation.



Fig. S15 Long-term H_2 evolution for CTP₃₀₀ under visible light irradiation ($\lambda \ge 420$ nm).



Fig. S16 Long-term H₂ evolution for CTP₃₀₀ tested with adding K₂HPO₄ ($\lambda \ge 420$ nm).



Fig. S17 a) FT-IR spectra, and b) DRS spectra of CTP₃₀₀ before and after photocatalytic measurements.



Fig. S18 Wavelength dependence of H_2 evolution rate for CTP_{300} .