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Shallow trap state-enhanced photocatalytic hydrogen evolution over thermal-decomposed polymeric carbon nitride

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Section 1. Experimental details

1.1. Material Preparation.

Preparation of reference p-CN (CN) and thermal-decomposed p-CN (TCN). CN and the TCN were synthesized by directly polymerizing thiourea at 550 and 660 °C in air, respectively.[1] In detail, thiourea (6g) was placed in a covered crucible and heated to 550 or 660 °C in a muffle furnace for 4 h using a heating rate of 2 °C min^{-1}. Then, the agglomerates were grounded into powder.

1.2. Characterization. The samples were characterized using X-ray diffraction (XRD, Rigaku, Smartlab; operated at 40 kV and 200 mA, Cu Kα source) and transmission electron microscopy (TEM, JEOL, JEM 3000F). The XPS measurements were carried out on a PHI X-tool 8ULVAC-PHI instrument. Fourier transformed infrared (FTIR) measurements were conducted by a PerkinElmer spectrometer. The steady-state diffuse reflection spectra were measured on a UV-vis-NIR spectrophotometer (JASCO, V-570) at room temperature.

1.3. Photocatalytic Hydrogen Evolution. Normally, 5 mg of the sample was dispersed in 5 mL of triethanolamine (TEOA) DI water solution (V_{TEOA}:V_{H_2O} = 1:4) and added into a 35 mL cylinder reactor. Then, 3 wt % (respect to Pt, acting as co-catalysts) $H_2PtCl_6 \cdot 6H_2O$ was deposited onto the photocatalyst by the photodeposition method. The reactor was sealed, and then bubbled with argon for 30 min to completely remove the dissolved oxygen and ensure that the reactor was in an anaerobic condition. Subsequently, the suspension with continuous stirring was irradiated under a Xe lamp (Asahi Spectra, HAL-320; 350 mW cm^{-2}) equipped with a 420/480 nm cut-off filter at room temperature. The volume of produced H_2 was measured by using a Shimadzu GC-8A gas chromatograph equipped with an MS-5A column and a thermal conductivity detector.

1.4. Femtosecond Time-Resolved Diffuse Reflectance Spectroscopy

The femtosecond time-resolved diffuse reflectance (TDR) spectra were measured by the pump and probe method using a regeneratively amplified titanium sapphire laser

(Spectra-Physics, Spitfire Pro F, 1 kHz) pumped by a Nd:YLF laser (Spectra-Physics, Empower 15). The seed pulse was generated by a titanium sapphire laser (Spectra-Physics, Mai Tai VFSJW; FWHM 80 fs). The output (420 nm, 1.9 μJ per pulse) of the optical parametric amplifier (Spectra-Physics, OPA-800CF-1) was used as the excitation pulse. A white light continuum pulse, which was generated by focusing the residual of the fundamental light on a sapphire crystal after the computer controlled optical delay, was divided into two parts and used as the probe and the reference lights, of which the latter was used to compensate for the laser fluctuation. Both probe and reference lights were directed to the sample powder coated on the glass substrate, and the reflected lights were detected by a linear InGaAs array detector equipped with the polychromator (Solar, MS3504). The pump pulse was chopped with a mechanical chopper synchronized to one-half of the laser repetition rate, resulting in a pair of spectra with and without the pump. The transient absorption (TA) signal of the TDR measurements is presented as percentage absorption, % Abs = $100(1 - R/R_0)$, where R and R_0 are the intensities of the diffuse reflected light with and without pump, respectively, because the % Abs is proportional to the concentration of transient species within the experimental error for % Abs values below 10% in the present measurement.[2] Therefore, in the manuscript TDR spectra are interchanged with the term TA spectra. All measurements were carried out at room temperature.

Section 2. Supplementary data

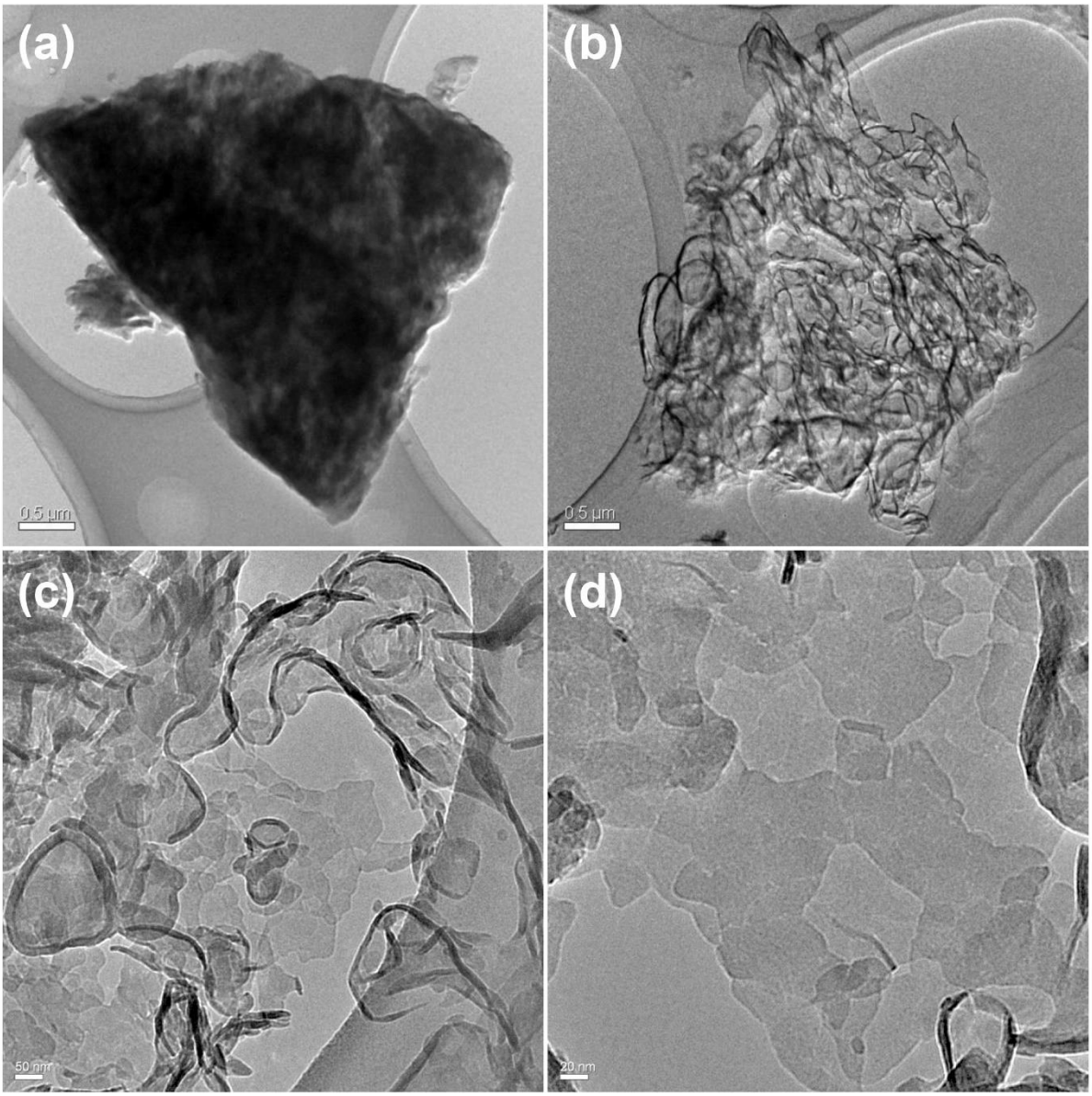
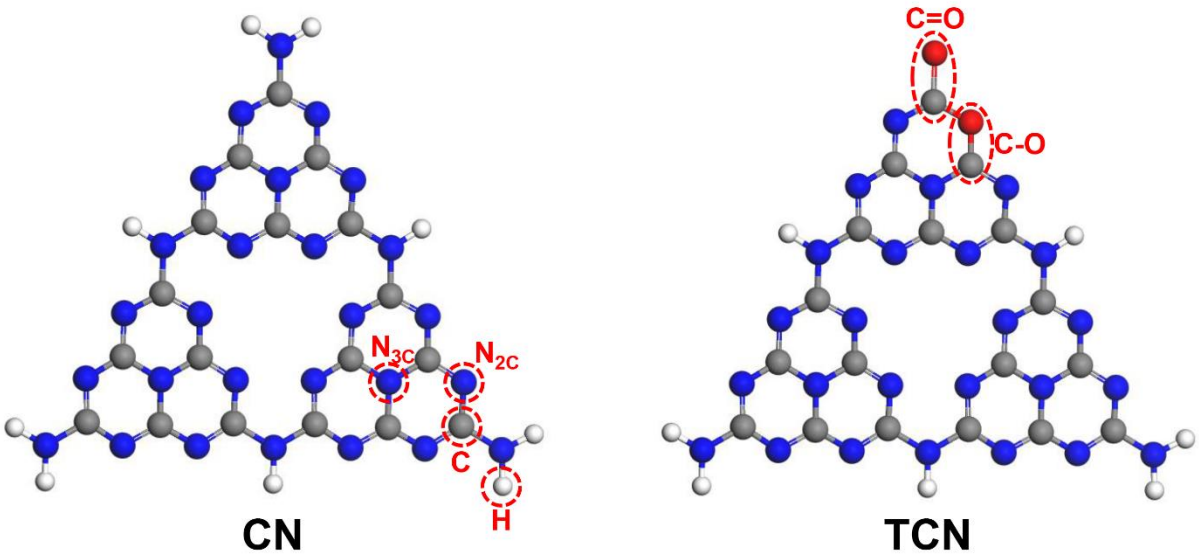


Figure S1. TEM images of (a) CN and (b-d) TCN.

Table S1. N/C atomic ratios of CN and TCN determined by the CNH elemental analysis.

Samples	N (wt. %)	C (wt. %)	H (wt. %)	N/C (at.)	H/C (at.)
CN	60.18	34.06	1.96	1.51	0.69
TCN	59.10	34.67	1.72	1.46	0.60



Scheme S1. Schematic illustration of the atomic structures of CN and TCN.

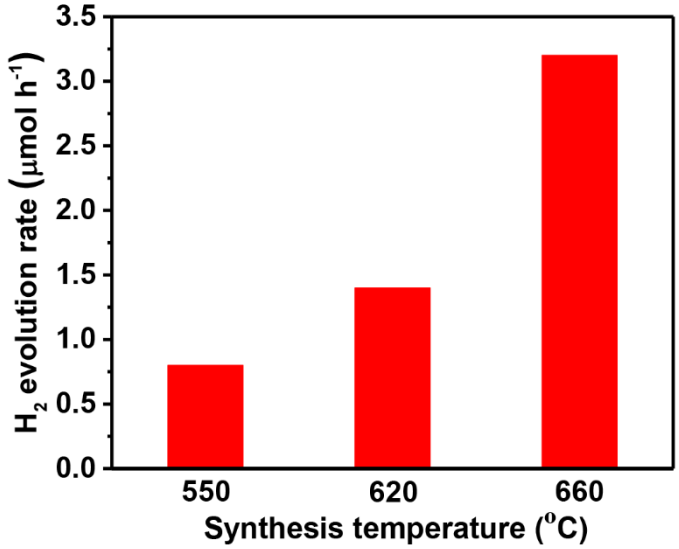


Figure S2. Photocatalytic H_2 evolution over p-CN synthesized at different temperatures.

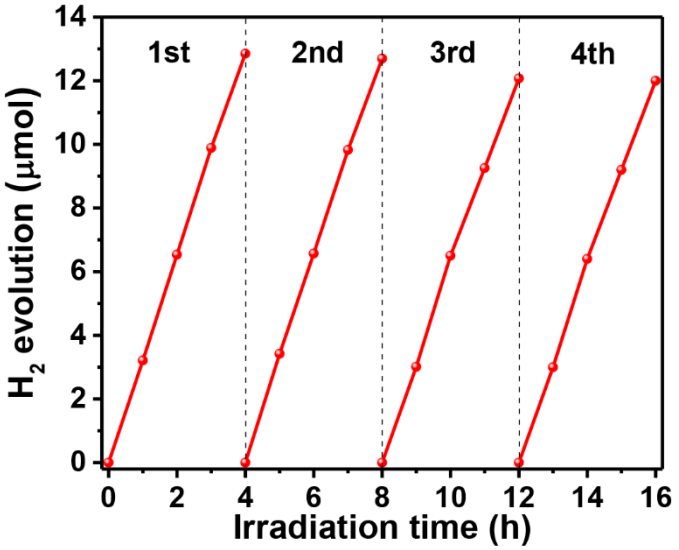


Figure S3. Stability test of TCN under light with $\lambda > 420$ nm irradiation.

References:

(1) G. Zhang, J. Zhang, M. Zhang and X. Wang, *J. Mater. Chem.*, 2012, **22**, 8083−8091.

(2) J. Xue, M. Fujitsuka and T. Majima, *ACS Appl. Mater. Interfaces*, 2020, **12**, 5920−5924.