# **Supporting information**

# Partially cross-linked carbon nitride with unimpeded charge transfer between different chains for boosting photocatalytic hydrogen production

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# Synthesis of 1D-CN

The 1D-CN sample was prepared by the thermal polycondensation of melamine: 5.0 g melamine was placed into a covered crucible, and then heated at 550 °C for 4h with a rate of 2.5 °C·min<sup>-1</sup> in a muffled furnace. After cooled to room temperature, the product was ground in a mortar and collected.

### Synthesis of PTI

PTI was prepared by a slight modification of the procedure reported in the previous literature [S1]: 2.0 g melamine and 20 g LiCl/KCl salts (45/55 wt %, m.p. = 352 °C) were thoroughly ground. The resulting mixture was transferred into a porcelain crucible and heated in a muffle furnace at 550 °C for 4 h. The heating rate was 2.5 °C·min<sup>-1</sup>. After cooling to room temperature, the obtained product was washed with boiling water and then ethanol several times, collected by filtration and dried at 60 °C.

#### Synthesis of PC-CN

The PC-CN sample was prepared by a solid chloride salts assisted polycondensation method: 2.0 g melamine and 20 g NaCl/KCl salts (71/29 wt %, m.p. = 652 °C) were thoroughly ground. The resulting mixture was transferred into a porcelain crucible and heated in a muffle furnace at 550 °C for 4 h. The heating rate was 2.5 °C·min<sup>-1</sup>. After cooling to room temperature, the obtained product was washed with boiling water and then ethanol several times, collected by filtration and dried at 60 °C.

# Acid dissolution experiments

The 1D-CN/H<sub>2</sub>SO<sub>4</sub> solution was obtained by a modification of the reported procedure [S2]: The mixture of 200 mg 1D-CN and 2.00 mL H<sub>2</sub>SO<sub>4</sub> was stirred at 100  $^{\circ}$ C for 1 h. Then the mixture gradually turned into a clear pale yellow solution. The PTI and PC-CN samples were treated with H<sub>2</sub>SO<sub>4</sub> under the same condition.

### **Photocatalytic experiments**

The photocatalytic hydrogen evolution reactions were carried out in a topirradiation reaction vessel connected to a glass closed system. Typically, 50 mg prepared photocatalyst was dispersed in the mixture of 90 mL deionized water and 10 mL triethanolamine (TEOA). Then, 3 wt%  $H_2PtCl_6$  (based on Pt) as the precursor of cocatalyst Pt was added. After degassed under vacuum to completely remove air, the reaction solution was irradiated by a 300 W Xe-lamp with a cut-off filter ( $\lambda > 420$  nm). During the irradiation, the reaction temperature was maintained at 15 °C by cycle water. The generated H<sub>2</sub> was analyzed by an on-line gas chromatography (GC-7900, thermal conductive detector, 5 Å molecular sieve column), using Ar as the carrier. For the photocatalytic stability test, additional 5 mL TEOA was added to the system after three cycling tests.

The apparent quantum efficiency (AQE) for  $H_2$  evolution was measured by replacing the cut-off filter with corresponding band-pass filter. The AQE is calculated from the following equation:

$$AQE = \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{the number of incident photos}} \times 100\%$$

### Characterization

X-ray diffraction (XRD) patterns were obtained from a PW3040/60 X'pert PRO X-ray diffractometer (PANalytical) using CuK $\alpha$ 1 radiation ( $\lambda$  = 1.5406 Å), ranging from 5 to 80° with a scanning speed of 4° min<sup>-1</sup>. Elemental analysis (EA) was performed on a vario MICRO cube element analyzer. Field emission scanning electron microscopy (FESEM) and energy-dispersive spectroscopy (EDS) mapping images were recorded on a ZEISS Sigma 500 microscope equipped with an Oxford Instruments X-Max<sup>N</sup> 50 energy-dispersive spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterization was performed on a JEM-2100 instrument at an acceleration voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were measured on a Thermo Nicolet iS10 spectrometer. UV-vis diffuse reflection spectra (DRS) were recorded on a Shimadzu UV-2600 spectrophotometer using BaSO<sub>4</sub> as the reference. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Fisher ESCALAB Xi+ spectrometer with monochromic Al K $\alpha$  X-ray. Steady-state and time-resolved photoluminescence (PL) spectra were measured on a FluoroMax+ spectrophotometer (HORIBA).

## Photoelectrochemical measurements

All the photoelectrochemical measurements (Mott-Schottky plots,

electrochemical impedance spectra (EIS) and photocurrent) were performed by CHI-760E workstation (CH Instruments) in a standard three-electrode system using the prepared samples as the working electrodes, Ag/AgCl electrode as a reference electrode, and a Pt sheet as the counter electrode. The electrolyte was 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The working electrodes were prepared as follows: ~5 mg sample was dispersed in 0.02 wt% Nafion solution to afford a suspension. The suspension was sonicated for 1 h and then spread on to a 1.0 cm × 1.0 cm exposed ITO glass, dried in the air. The photocurrent was measured under -0.3 V bias voltage and the light source was a 300 W Xe-lamp with a cut-off filter ( $\lambda > 420$  nm).



**Fig. S1**. Illustration of the synthetic procedures of 1D-CN (traditional graphitic CN), PTI, and PC-CN.



**Fig. S2**. Proposed formation mechanism of covalent bonds between different chains in PC-CN.

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Sample	C [wt %]	N [wt %]	H [wt %]	C/N molar ration
PTI	27.26	46.02	2.50	0.691
1D-CN	34.34	57.54	1.96	0.696
PC-CN	27.04	43.54	2.17	0.724

Table S1 Elemental compositions of PTI, 1D-CN, and PC-CN.

Sample	$A_1 / \%$	$ au_1$ / ns	$A_2$ / %	$ au_2$ / ns	$\tau_{avg.}$ / ns
PTI	10.0	28.6	90.0	1.55	1.71
1D-CN	57.5	11.1	42.5	1.74	3.37
PC-CN	42.5	12.2	57.5	1.96	3.06

**Table S2** The fitting parameters of the time-resolved transient PL decay curves for PTI,1D-CN, and PC-CN.

The emission decay curves of the samples were fitted by biexponential kinetics function (equation 1). The average PL lifetime  $(\tau_{avg})$  was deduced by the following equation 2:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$
(1)  
$$\tau_{avg} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$
(2)



Fig. S3. FESEM images of (a) PTI, (b) 1D-CN, and (c) PC-CN. (d) Elemental mappings, (e) TEM, and (f) HRTEM images of PC-CN.



**Fig. S4.** Proposed structures of (a) PTI, (b) 1D-CN, and (c) PC-CN. The amino and imide groups are marked green. It is obvious that due to the cross-linking, there are fewer amino/imide groups in PC-CN.



Fig. S5. XPS (a) K 2p and (b) Cl 2p spectra of PTI and PC-CN.

Sample	$S_{ ext{C-defects}}/S_{ ext{total}}$ (%)	$S_{ m N-Hx}/S_{ m total}$ (%)
PTI	7.26	28.6
1D-CN	_	21.8
PC-CN	16.1	9.03

**Table S3.** Peak area ratios of C-defects and amino/imide  $(N-H_x)$  groups in high resolution XPS spectra of the as-prepared PTI, 1D-CN and PC-CN.



**Fig. S6.** N<sub>2</sub> adsorption and desorption isotherm curves of the as-prepared PTI, 1D-CN and PC-CN.



Fig. S7. Proposed mechanism for the photocatalytic  $H_2$  production of 1D-CN and PC-CN. The 1D molecular structure of 1D-CN blocks the charge transport between different chains, while the cross-linking in PC-CN makes the charge transport between different chains possible.

molten salt	Method	AQE	Ref.
NaCl/KCl	post-calcination in molten salt	32 <sup><i>a</i></sup>	S3
LiCl/KCl	post-calcination in molten salt	26.7	S4
LiCl/KCl	post-calcination in molten salt	15 <sup>b</sup>	S5
KC1	one-step calcination in molten salt	11.4	S6
LiCl/KCl	post-calcination in molten salt &	8.57 <sup>c</sup>	S7
	sonication-centrifugation		
LiCl/KCl	post-calcination in molten salt	6.8 <sup>c</sup>	S8
NaCl/KCl	one-step calcination in molten salt	24.8	this work

Table S4 Comparison of AQE at 420 nm between this work and previous studies.

Note: The photocatalytic  $H_2$  evolution reactions were carried out in the presence of triethanolamine as the sacrificial agent and Pt as the co-catalyst.

<sup>a</sup> the super-high AQE of 60 % has been achieved in "sea water" (with additional 3 % NaCl).
<sup>b</sup> the AQE of 57 % has been achieved in "sea water" (with additional 3 % NaCl).
<sup>c</sup> Using MeOH as the sacrificial.

# References

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