## **Supporting Information (SI)**

# Atomically Thin Mesoporous Nanomesh of Graphitic C<sub>3</sub>N<sub>4</sub> for High-efficiency Hydrogen Evolution

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Experimental Section Supporting Figures and Table References

#### **PART I: EXPERIMENTAL SECTION**

Synthesis of the directly dried DCDA derived g-C<sub>3</sub>N<sub>4</sub> bulk. The DCDA solution was directly drying and designated as directly dried DCDA, then calcinations from room temperature to 600°C with a ramp rate of 2.3°C/min in Ar flow and stabilized for 2 h, the obtained sample was designated as directly dried DCDA derived g-C<sub>3</sub>N<sub>4</sub> bulk.

Synthesis of different nanostructured DCDA precursors derived g-C<sub>3</sub>N<sub>4</sub> bulk. 0.50g, 0.25g and 0.10g DCDA were added into 12.5 mL of water, respectively, and all were kept in liquid nitrogen, followed by freeze drying, the different nanostructured DCDA precursors were obtained. Then calcinations of these nanostructured **DCDA** from room temperature to 600°C with a ramp rate of 2.3°C/min in Ar flow and stabilized for 2 h, the obtained samples were designated as the 0.50g nanostructured DCDA-derived g-C<sub>3</sub>N<sub>4</sub> bulk, 0.25g nanostructured DCDA-derived g-C<sub>3</sub>N<sub>4</sub> bulk and 0.10g nanostructured DCDA-derived g-C<sub>3</sub>N<sub>4</sub>, respectively.

**Photochemical measurement.** Wavelength dependence of  $H_2$  evolution rate was measured by using appropriate band pass filters (400, 420, 450, 500 and 550 nm, respectively) to perform the water splitting experiment under the designated monochromic light. The intensity of the monochromic light was averaged at 13 representative points by PL-MW2000 Photoradiometer and the active area of the reactor was approximately 38.5 cm<sup>2</sup>.

The external quantum yield was then calculated by the following Equation (1):

$$\Phi = \frac{2 \times \text{amount of H}_2 \text{ molecules evolved}}{\text{number of incident photons}} \times 100$$
(1)

The turnover number (TON) was estimated by the following Equation (2):

$$TON = \frac{\text{moles of } H_2 \text{ molecules evoled}}{\text{moles of platinum on the photocatalyst}}$$
(2)

The transient photocurrent measurements were performed on the Keithley 6300 semiconductor parameter analyzer in a conventional three electrode cell where a sample-coated clean fluoride-tin oxide (FTO) glass, Pt wire and a Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively. The aqueous solution of 0.2 M Na<sub>2</sub>SO<sub>4</sub> purged with nitrogen gas was used as the electrolyte.

#### **PARPT II: SUPPORTED FIGURES**



Figure S1. Photograph of the nanostructured DCDA (a). SEM image of the nanostructured DCDA.

The formation of such a well-ordered architecture is generated by fast nucleation and the oriented growth of DCDA nanocrystals within ice crystals at undercooling temperature that is far below the freezing point of the solution.<sup>1, 2</sup> The nanocrystal DCDA was grown from water solution by cooling quickly along a line at 35° to c,<sup>3</sup> and the ice crystals sweep along with the DCDA nanocrystals face to form parallel ice fingers between adjacent DCDA nanocrystals. Subsequent freeze-drying gives rise to form the nanostructured DCDA.



Figure S2. SEM image of the pristine DCDA.



**Figure S3.** (a) XRD patterns of the pristine DCDA and nanostructured DCDA, (b) FT-IR spectra of the pristine DCDA and nanostructured DCDA and (c) TGA curves of the pristine DCDA and nanostructured DCDA.



**Figure S4.** (a) SEM and (b) TEM images of the mesoporous  $g-C_3N_4$  bulk.



**Figure S5.** The pore size distribution of the mesoporous  $g-C_3N_4$  bulk.



**Figure S6.** (a) SEM and (b) TEM images of the traditional  $g-C_3N_4$  bulk.



**Figure S7.** SEM image of the directly dried DCDA (a), the directly dried DCDA derived  $g-C_3N_4$  bulk (b). (c) TEM image of directly dried DCDA derived  $g-C_3N_4$  bulk. SEM images of the nanostructured DCDA with the DCDA mass of 0.50g (d), 0.25g (e) and 0.10g (f). TEM images (g-i) and the pore size distributions (j-l) of the 0.50g, 0.25g and 0.10g nanostructured DCDA-derived  $g-C_3N_4$  nanomeshes obtained from exfoliating their corresponding bulk counterparts for 24h. The hydrogen evolution

rates (m) and  $N_2$  adsorption isotherms (n) of 0.50g, 0.25g and 0.10g nanostructured DCDA-derived g-C<sub>3</sub>N<sub>4</sub> nanomeshes obtained from exfoliating their corresponding bulk counterparts for 24h.

The pores formation of g-C<sub>3</sub>N<sub>4</sub> bulk was analyzed by calcinating the precursors of different morphologies. As shown in Figure S7a, the directly dried DCDA has a smaller square crystal grain size than the original DCDA (Figure S2), and its derived g-C<sub>3</sub>N<sub>4</sub> bulk displays flake-like structure (Figure S7b, c) which seems thinner than that of the traditional bulk (Figure S6), indicating structure optimization occurred after recrystallization. However, there is no pore in the sheets of the directly dried DCDA derived g-C<sub>3</sub>N<sub>4</sub> bulk (Figure S7b, c), in sharp contrast to the nanostructured DCDA derived mesoporous g-C<sub>3</sub>N<sub>4</sub> bulk (Figure S4), suggesting the freeze-drying technology caused nanostructured precursor can lead to mesopores during thermal polymerization.

Furthermore, the size of nanocrystal strips in the obtained nanostructured DCDA monoliths actually decrease as we decrease the weight of DCDA in the same volume of water, meaning greater spacing between adjacent DCDA nanocrystals. Further calcinations of the various nanostructured precursors generated a series of the porous  $g-C_3N_4$  bulk as observed in Figure S7d-f. Clearly, the 0.50g nanostructured DCDA-derived  $g-C_3N_4$  nanomesh exhibits a silk-like nanostructure (Figure S7g) that changes to the typical layered morphology with mesoporous surface for the 0.25g nanostructured DCDA-derived  $g-C_3N_4$  nanomesh features (Figure S7h), and the size of pores for the 0.10g DCDA-derived  $g-C_3N_4$  nanomesh is slightly increased (Figure

S7i), which is further confirmed by the pore size distributions (Figure S7j-l). This illustrates the nanostructure of the precursors with different spacing between adjacent DCDA nanocrystals could affect morphology of final g-C<sub>3</sub>N<sub>4</sub> products, the smaller the dimensions of strips, the bigger gap between adjacent DCDA nanocrystals, which results in the formation of mesopores during the thermal polycondensation. BET surface areas of the 0.50g DCDA-derived g-C<sub>3</sub>N<sub>4</sub> nanomesh, the 0.25g DCDA-derived g-C<sub>3</sub>N<sub>4</sub> nanomesh and the 0.10g DCDA-derived g-C<sub>3</sub>N<sub>4</sub> nanomesh are *ca.* 146 cm<sup>2</sup> g<sup>-1</sup>, 331 cm<sup>2</sup> g<sup>-1</sup> and 207 cm<sup>2</sup> g<sup>-1</sup>, respectively, consistent with the TEM observation. The hydrogen evolution rate of the 0.25g DCDA-derived g-C<sub>3</sub>N<sub>4</sub> nanomesh is the highest versus other samples (Figure S7m), which can be ascribed to its bigger surface area and confirm that different nanostructured precursors cause the different photocatalytic activities.



**Figure S8.** Photographs of 30 mg mesoporous  $g-C_3N_4$  bulk dispersed solutions in 25 mL IPA (a), water (b) and mixed solution of IPA-water (c) after 1h under ambient conditions. The insets show the corresponding enlarged view of the rectangle areas in

(a), (b) and (c), respectively.

The mesoporous g-C<sub>3</sub>N<sub>4</sub> bulk can be homogenously dispersed in IPA-water at concentrations of 1.2 mg mL<sup>-1</sup> without precipitation after storage for 1h under ambient conditions (Figure S8c, its inset), which is in sharp contrast to the poor dispersity observed in bulk samples dispersed in IPA or water (Figure S8a, b and their insets).



Figure S9. Photographs of monolayer mesoporous  $g-C_3N_4$  nanomesh dispersed solutions in water with concentration of 0.1 mg ml<sup>-1</sup> after one month under ambient conditions.



Figure S10. (a) Low-, (b) high-magnification SEM images of the monolayer  $g-C_3N_4$  nanomesh.



**Figure S11.** TEM images of g-C<sub>3</sub>N<sub>4</sub> nanomesh obtained from exfoliating the bulk counterpart for 9h (a), 12h (b), 36h (c) and 48h (d). The increase of the transparence with reaction time indicates the increased degree of exfoliation.



**Figure S12.** AFM images of the obtained  $g-C_3N_4$  nanomesh from exfoliation of the bulk counterpart for 9h (a), 12h (c), 36h (e) and 48h (g). (b, d, f and h) The corresponding height profiles along the lines in (a, c, e and g). (i) The thickness of the obtained  $g-C_3N_4$  nanomesh as the function of solvothermal exfoliation time.



Figure S13. N<sub>2</sub> adsorption isotherm of the traditional g-C<sub>3</sub>N<sub>4</sub> bulk.



Figure S14. XRD patterns of  $g-C_3N_4$  nanomesh with the exfoliation of 9h, 12h, 36h and 48h from bottom to top.



Figure S15 Raman spectra (b) of the monolayer  $g-C_3N_4$  nanomesh and the bulk counterpart (633 nm excitation).



Figure S16. X-ray photoelectron spectroscopy (XPS) of the monolayer  $g-C_3N_4$  nanomesh and the bulk counterpart.



Figure S17. The corresponding high-resolution C1s XPS spectrum of the monolayer

 $g\text{-}C_3N_4 \text{ nanomesh.}$ 



Figure S18. Energy dispersive X-ray (EDX) spectrum of the monolayer  $g-C_3N_4$  nanomesh.



Figure S19. Hydrogen evolution of the monolayer  $g-C_3N_4$  nanomesh, the bulk counterpart and the traditional  $g-C_3N_4$  bulk in 6h irradiation under visible light ( $\lambda$ > 420 nm).



Figure S20. AFM images of the obtained  $g-C_3N_4$  nanomesh of the monolayer mesoporous  $g-C_3N_4$  nanomesh collected after 30 h photocatalytic hydrogen evolution reaction.



Figure S21. N<sub>2</sub> adsorption isotherms of the atomically thin  $g-C_3N_4$  nanomesh, 5 nm  $g-C_3N_4$  nanomesh, 25 nm  $g-C_3N_4$  nanomesh and the bulk counterpart.

Table S1. Summary of 2D  $g-C_3N_4$  nanostructures photocatalysts reported for HER rate, BET surface area and QE.

Samples <sup>[a]</sup>	HER rate μmol h <sup>-1</sup>	HER rate μmol h <sup>-1</sup> g <sup>-1</sup>	Surface area m <sup>2</sup> g <sup>-1</sup>	Ф%	ref
monolayer mesoporous	85.1	8510	331	5.1	This
$g-C_3N_4$ nanomesh	(10 mg)			(420 nm)	work
$5 \text{ nm g-}C_3N_4$	32.5	3250	244	N/A	This
nanomesh					work
25 nm g-C <sub>3</sub> N <sub>4</sub>	19.3	1930	86	N/A	This
nanomesh					work
bulk counterpart	3.5	350	10	N/A	This
					work
PCN	18.8	401	112.5	N/A	4
	(4.69 mg)				
$g-C_3N_4$ nanosheets <sup>1</sup>	93	1860	384	3.75	5
	(50 mg)			(420 nm)	
$g-C_3N_4$ nanosheets <sup>2</sup>	<i>ca</i> . 33	650	306	N/A	6
	(50 mg)				
HGCN	82.9	8290	196	N/A	7
	(10 mg)				
mpg-C <sub>3</sub> N <sub>4</sub>	149 (1000 mg)	149	68-373	N/A	8
PTI	3.5	1750	N/A	1.3	9
nanosheets	(2 mg)			(400 nm)	
IGCNSs	44.5	890	80.2	3.0%	10
	(50 mg)			(420 nm)	
UGCNPs	68.3	1365	97	3.6%	11
	50 mg			(420 nm)	
CNUB	278 (50 mg)	5560	144	N/A	12
ACN	(50mg)	157.9	N/A	N/A	13
CN-NS	<i>ca</i> . 310	ca. 6200	N/A	N/A	14

	(50mg)				
PCN-S	79.8	1596	122.6	3.56%	15
	(50mg)			(420 nm)	

<sup>[a]</sup> All photocatalysts listed were loaded with 3 wt% Pt co-catalyst; 10 vol% triethanolamine scavenger in an aqueous solution, excepting PCN which was loaded with 1 wt% Pt co-catalyst, 65 vol% triethanolamine scavenger in an aqueous solution, ACN was loaded with 6 wt% Pt co-catalyst and PCN-S which was loaded with 1 wt% Pt co-catalyst, 20 vol% triethanolamine scavenger in an aqueous solution. N/A= no applicable.

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