Supporting Information

Biopolymer-assisted synthesis of assembled g-C₃N₄ open frameworks with electron delocalization channels for prompted H₂ production

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Characterization

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on FEI Nova Nano SEM 430 and JEOL 2010, respectively. The mapping images were conducted on the TEM microscope equipped with an energy dispersive X-ray spectroscopy detector. XRD measurements of powder samples were performed with a Bruker D8 Advance diffractometer. Fourier transform infrared (FTIR) spectra were recorded on o Bruker Tensor 27. Optical diffuse reflectance spectra were collected at room temperature with a uv-vis diffuse reflectance spectrometry (DRS; V-560, Jasco). A white standard of BaSO₄ was used as a reference. The thermosanalysis (TG, PerkinElmer) was conducted up to 700 °C at a heating rate of 5 °C min⁻¹ in air. Electron spin resonance (ESR) experiments were conducted on an ER-200D spectrometer (Bruker, Germany) at a microwave frequency of 9.5 GHz under room temperature. Steady-state photoluminescence (PL) emission spectra (332 nm excitation) were collected on a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920) at room temperature. An X-ray photoelectron spectroscopy (XPS) spectrometer (K-Alpha 1063) was used to detect the surface elemental configuration composition and bonding of the as-prepared samples. Photoelectrochemical measurements were monitored by a CHI 660 electrochemical station with a standard three-electrode system. The working electrodes were prepared by using samples coated on FTO glass. Pt plate and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively, the electrolyte was Na₂SO₄ solution (0.2 M). All photoelectrochemical experiments were carried out under visible light irradiation (λ >420nm).

Calculation methods

All the density functional theory (DFT) calculations are performed by use of VASP code ¹. The interaction between valence electrons and core is described by projector-augmented wave (PAW) ²method. The generalized gradient approximation (GGA) ³ in the form of Perdew-Burke-Ernzerhof (PBE) ⁴ is employed to treat the exchange-correlation potential. The cutoff energy is set to 500 eV. The convergence criterion for energy and force are considered as 10⁻⁵ eV and 0.02 eV/Å, respectively. The Brillouin zone are sampled using a 7×7×1 Monkhorst-Pack k-point mesh. A vacuum space of 20 Å is used to avoid the interaction between neighboring images, and DFT-D3 ⁻⁵ correction is adopted to describe the van der Waals (vdW) interactions. The electronic structures are obtained by utilization of hybrid functional of Heyd-Scuseria-Ernzerhof (HSE06) ⁶.

Gibbs free energy for H₂ absorption

The Gibbs free energy of the absorption of intermediate hydrogen on CN and 3-CN samples can be given by:

 $\Delta G = \Delta E_{\rm H} + \Delta E_{\rm ZPE} \text{ - } T\Delta S_{\rm H}$

where ΔE_{ZPE} and ΔS_H are the differences in the zero point energy and entropy between atomic hydrogen adsorption and hydrogen gas, and ΔE_H is the hydrogen adsorption energy, given by:

$$\Delta E_{\rm H} = E_{\rm H} - E_{\rm C} - 0.5 E_{\rm H2}$$

where E_H and E_C are respectively the total energies of CN and 3-CN with and without

one adsorbed hydrogen atom, and $E_{\rm H2}\, is$ the total energy of hydrogen gas.



Figure S1 The schematic molecular structure of gelatin.



Figure S2 The SEM images of as-prepared $g-C_3N_4$ under the engineering various used gelatin: (a) 1 mg, (b) 2 mg, (c) 3 mg and (d) 8 mg.



Figure S3 The schematics of stable models of 2×2 supercell of (a) CN and (b) 3-CN



Figure S4 FT-IR spectra of control CN and x-CN as indicated.



Figure S5 Photocurrent measurement of (a) CN and (b) 3-CN



Figure S6 Summary of reported g-C₃N₄-based materials for H₂ evolution reaction.



Figure S7 XRD patterns of fresh and used samples, and TEM image of used sample.



Figure S8 Different calcination temperatures and rates of g- C_3N_4 for H_2 evolution reaction.



Figure S9 photocatalytic H_2 evolution activities of prepared g-C₃N₄ samples prepared by various amount of gelatin as indicated.

Table S1 The fitted emission peaks and relative intensity of δ^* – LP, π^* – LP and π^* – π transitions in CN and 3-CN samples

	δ^* – LP		π* - LP		$\pi^* - \pi$	
	Peak, nm	Intensity	Peak, nm	Intensity	Peak, nm	Intensity
CN	446.7	674.7	469.8	989.2	504.2	603.2
3-CN	449.6	190.2	478.5	286.6	526.7	191.7
Notes	Red-shift	decrease	Red-shift	decrease	Red-shift	decrease

 Table S2
 The AQE calculation

λ (nm)	$H_2(\mu mol)$	the optical power density	AQE(%)
		of the light source	
		(mw/cm ⁻²)	
450	5.85	15.5	7.43
475	4.13	24.2	3.18
500	2.51	20.1	2.21
550	0.97	21.9	0.72
650	0.61	29.7	0.28

Table S3 Summary of reported $g-C_3N_4$ -based materials for H_2 evolution reaction.

	H ₂ yield	EQE	Experimental	Reference	Year
Catalyst	(µmol/h)	(nm/%)	conditions		published
g-C ₃ N ₄	99.4	450/7.43	1 wt% Pt	This	
			10% TEOA	work	
Lettuce-like	38.4	425/8.53	3 wt% Pt	7	2020
$g-C_3N_4$			10% TEOA		

Caral lilea D ~	101	420/4 22	2t0/ Dt	8	2020
Coral-like P-g-	101	420/4.32	3 W1%0 P1	v	2020
C_3N_4 tubes			10% TEOA		
Holey g-C ₃ N ₄	180.6	450/4.2	3 wt% Pt	9	2020
			10% TEOA		
N-deficient g-	38.8	420/8.6	3 wt% Pt	10	2020
C_3N_4			10% TEOA		
m-CN-0.067	25	no	0.5 wt% Pt	11	2019
			15% TEOA		
C-doping C ₃ N ₄	50.2	no	3 wt% Pt	12	2019
			10% TEOA		
g-C ₃ N ₄ /Carbon	23	no	0.5 wt% Pt	13	2020
graphite			10% TEOA		
g-C ₃ N ₄	76.1	420/1.76	3 wt% Pt	14	2020
			10% TEOA		
Ring-like C ₃ N ₄	19	no	3 wt% Pt	15	2018
tubes			10% TEOA		
$3D g-C_3N_4$	29	no	3 wt% Pt	16	2015
monolith			10% TEOA		
Benzene-	139	420/6.21	1 wt% Pt	17	2020
grafted g-C ₃ N ₄			10% TEOA		
nomotubes					
g-C ₃ N ₄	33.3	no	3 wt% Pt	18	2020
			10% TEOA		

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