Supplementary Information

Nanorods g-C_3N_4 with N defect via molten salt method: An efficient photocatalysts for hydrogen production

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Experimental Section

Text 1. Materials

The raw material melamine ($C_3H_6N_6$, 99%) was obtained from Shanghai Titan Scientific Co., Ltd. The KCl was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The K_2SO_4 and Na_2SO_4 were both obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. The co-catalysts chloroplatinic acid hydrate ($H_2PtCl_6 \cdot 6H_2O$, 99.995%) and sacrificial agent triethanolamine ($C_6H_{15}NO_3$, TEOA, 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd and Shanghai Lingfeng Chemical Reagent Co., Ltd, respectively. Sodium sulfate (Na_2SO_4, 99%) was obtained from Shanghai Gaoxin Chemical Glass Instrument Co., Ltd. Above materials were participated in experiment without further treatment.

Text 2. Computational methods

The DFT calculations were performed by the CP2K software package and the C_3N_4 structure was founded in Materials Project (ID: 1193580). The defect structure is constructed by Gauss View 6 and set as a single layer. The calculation level of structural optimization is PBEsol-D3(BJ)/pob-DZVP-ref2 and adopted variable cell optimization, multiplicity was set to 3, OT was turned on and set to IRAC, inner SCF and outer SCF both set to 20 steps, preconditioner was changed to FULL_KINETIC. Then the optimization was performed again with multiplicity 1, K-point 2,2,6.

The calculation level of the band structure is HLE17/MOLOPT-TZV2P and the k point set to 3,3,9. The information of the highly symmetric points in the first Brillion zone is generated by the Seek-Path online website, calculate 20 additionally empty orbitals energy levels.

The density of states (DOS) calculation level is HLE17/pob-TZVP-ref2, the cell expanded to 2*2*2 and calculated 500 additional empty orbits. In addition, the calculated level of reaction energy was PBE0/MOLOPT-TZV2P, where PBE0 was accelerated by Auxiliary Density Matrix Methods (ADMM) and the cell expanded to 1*1*3 supercells.

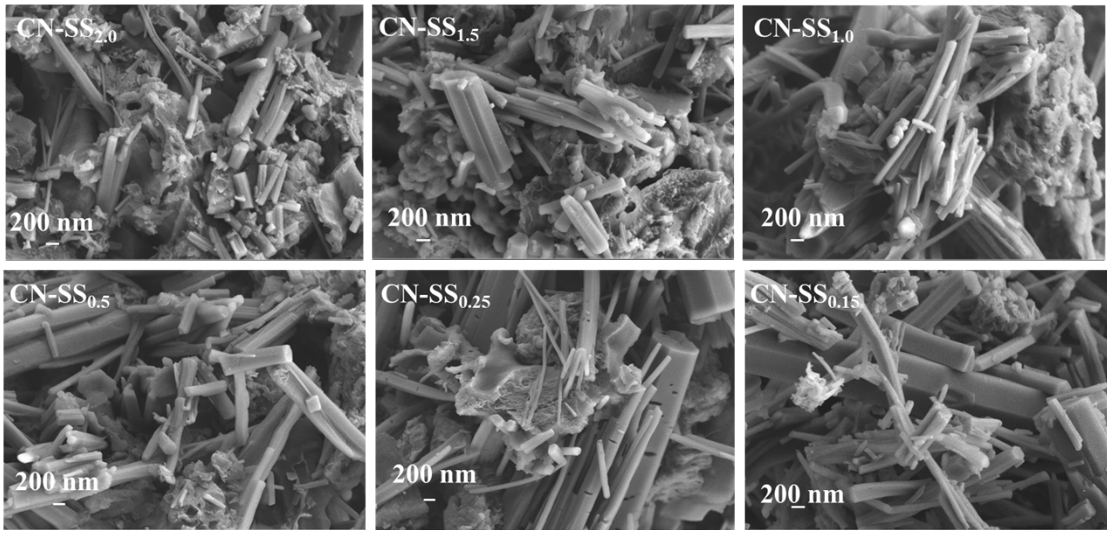

Fig. S1 SEM images of CN-SS with different Na_2SO_4 usage.

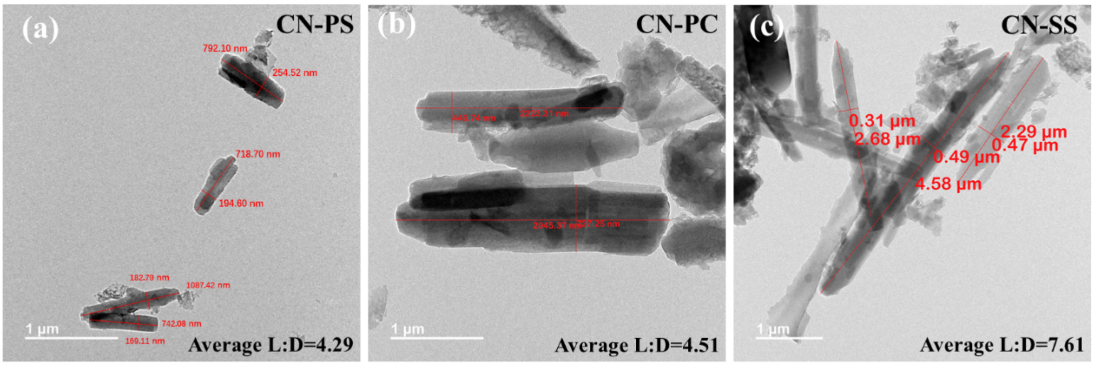

Fig. S2 TEM images of (a) CN-PS, (b) CN-PC and (c) CN-SS with average ratio of length (L) to diameter (D).

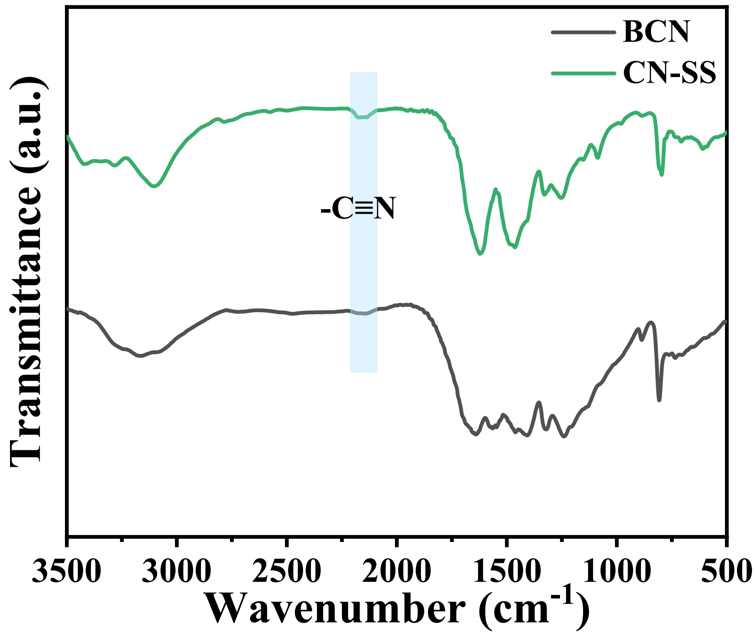

Fig. S3 FTIR spectra of BCN and CN-SS.

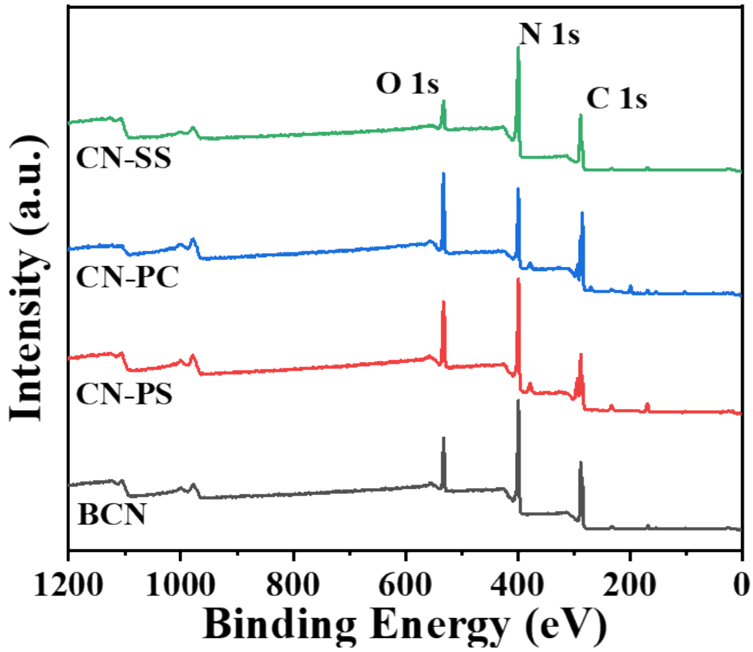

Fig. S4 XPS survey spectra of BCN and modified catalysts with alkalis metal salt.

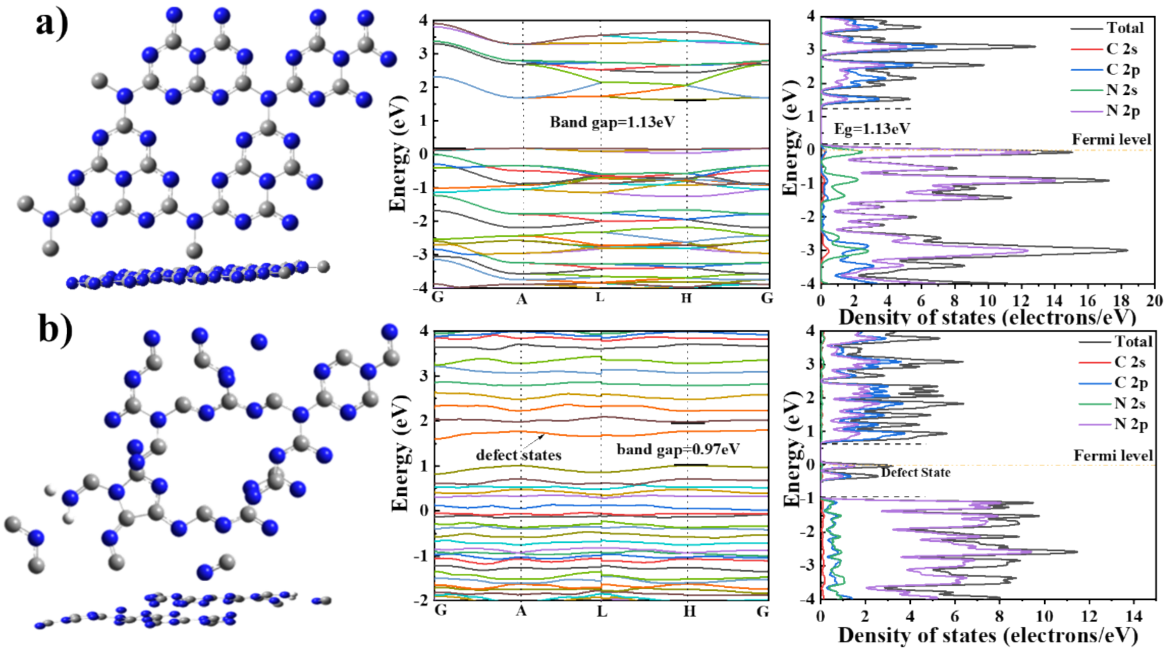

Fig. S5 (a) Structure model, calculated band structure and corresponding DOS of g-C_3N_4; (b) Structure model, calculated band structure and corresponding DOS of g-C_3N_4 with N1 vacancy and -C≡N.

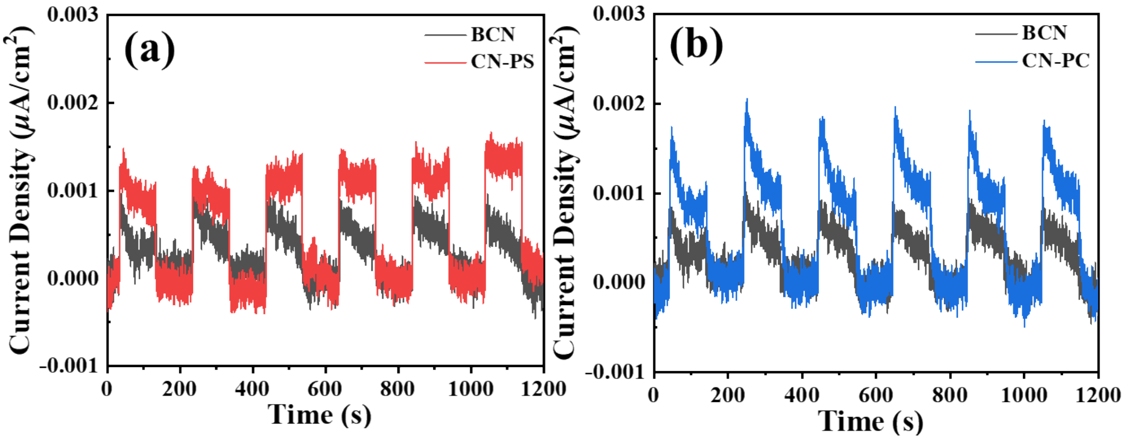

Fig. S6 (a) Transient photocurrent responses of BCN and CN-PS. (b) Transient photocurrent responses of BCN and CN-PC

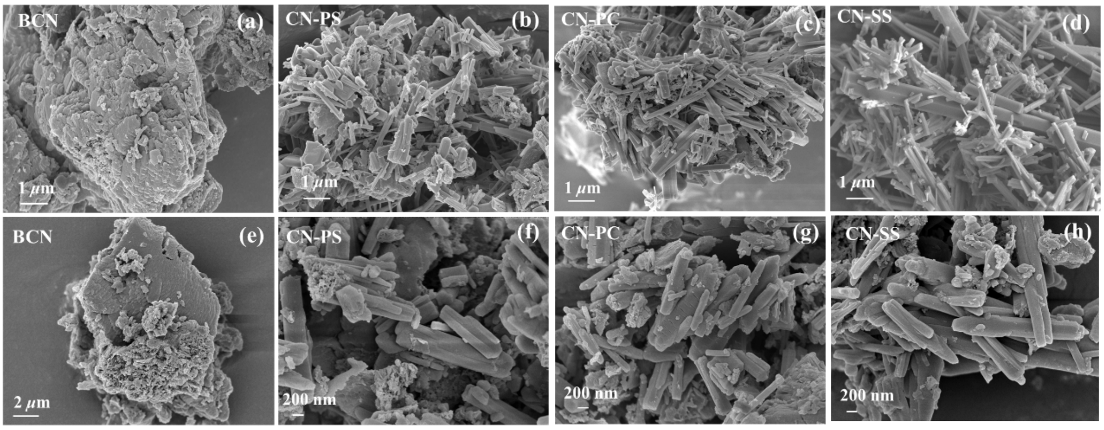

Fig. S7 SEM images of (a, e) BCN, (b, f) CN-PS, (c, g) CN-PC and (d,h) CN-SS before and after photocatalytic.

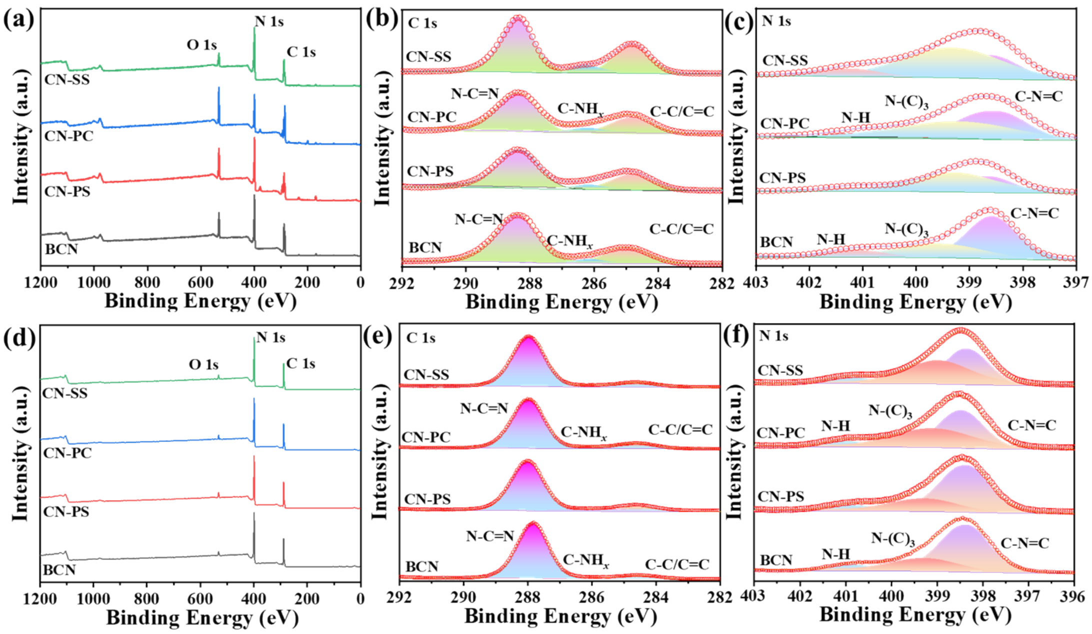

Fig. S8 XPS survey spectra (a, d), XPS C 1s spectra (b, e) and XPS N1 spectra (c, f) of BCN and modified catalysts with alkalis metal salt before and after photocatalytic.

Table S1 Organic element content of BCN and modified catalysts with alkalis salt

Photocatalysts	N%	C%	H%	N/C
BCN	61.47	32.98	1.780	1.86
CN-$PS_{2.5}$	23.19	12.68	0.974	1.82
CN-$PS_{2.0}$	35.59	19.13	1.941	1.86
CN-$PS_{1.5}$	50.46	27.36	2.504	1.84
CN-$PC_{2.5}$	49.49	26.66	2.916	1.86
CN-$PC_{2.0}$	36.99	19.96	1.948	1.85
CN-$PC_{1.5}$	53.66	29.00	2.593	1.85
CN-$SS_{2.0}$	40.80	22.18	2.201	1.84
CN-$SS_{1.5}$	53.19	28.90	3.036	1.84
CN-$SS_{1.0}$	53.89	28.88	3.442	1.86
CN-$SS_{0.5}$	55.28	29.45	3.497	1.87
CN-$SS_{0.25}$	58.17	31.53	3.004	1.84
CN-$SS_{0.15}$	56.75	30.71	3.367	1.84
CN-$SS_{0.1}$	56.54	30.32	3.424	1.86

Table S2 Comparisons of results from different catalysts towards PWS

Photocatalysts	Dosage, Light source, Cocatalyst	PWS (μmol·g^{-1}·h^{-1})	Ref.
CN-SS	**25 mg, 300 W Xe, λ>420nm, 2.0 wt.% Pt**	**738**	**This work**
CN	50 mg, 300 W Xe, λ≥420 nm, 1wt.% Pt	270.95	1
Zn-PCN	10 mg, 300 W Xe, λ≥420 nm, 1wt.% Pt	35.2	2
cPCNt	50 mg, 300 W Xe, λ>420 nm, 3wt.% Pt and Co	48.2	3
COCNT	20 mg, 300 W Xe, λ≥420 nm, 1wt.% Pt, 1wt.% Co	37.4	4
TCN	50 mg, 300 W Xe, λ>350 nm, 3wt.% Pt, 1wt.% Ru	110	5
CoP/TH-CN-x	50 mg, 300 W Xe, λ>420 nm, 1.5 wt.% Pt	204	6
g-C_3N_4-D_2/3%Co_3O_4	20 mg, 300 W Xe, λ≥420 nm, 1wt.%Pt	49.6	7
$SrTiO_3$-PCN	50 mg, 300 W Xe, λ>420nm, 3wt.% Pt	200	8
BP@C_3N_4	20 mg, 300 W Xe, λ≥420 nm	31.5	9

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Table S3 Comparisons of results from different catalysts towards PHE

Photocatalysts	Dosage, Light source, Cocatalyst	Sacrificial agent, dosage	PHE (μmol·g^{-1}·h^{-1})	Ref.
CN-SS	**25 mg, λ>420 nm, 2wt.% Pt**	**TEOA, 0.5 vol.%**	**3516**	**This work**
CN/CNQDs	20 mg, λ>420 nm, 2wt.% Pt	TEOA, 10 vol.%	1820.8	10
C_3N_4 sheets	30 mg, λ≥420 nm, Pt	TEOA, 10 vol.%	1254.8	11
MCP-CN	100 mg, λ>420 nm, 3wt.% Pt	TEOA, 10 vol.%	145.8	12
CN-*x*	100 mg, λ≥420 nm, 3wt.% Pt	TEOA, 10 vol.%	1690	13
D-CNNS$_{(0.3)}$	50 mg, λ>420 nm, 3wt.% Pt	TEOA, 12 vol.%	2497.1	14
3DOM CN	20 mg, λ≥420 nm, 3wt.% Pt	TEOA, 10 vol.%	2300	15
Ni_2P/CNN	10 mg, λ>420 nm	TEOA, 10 vol.%	2062	16
hCNNS	20 mg, λ≥420 nm, 3wt.% Pt	TEOA, 10vol.%	2380	17
CN-40	25 mg, λ≥420 nm, 3wt.% Pt	TEOA, 10 vol.%	1210.3	18

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