Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

In-situ growth of triazine-heptazine based carbon nitride film for efficient (photo)electrochemical performance

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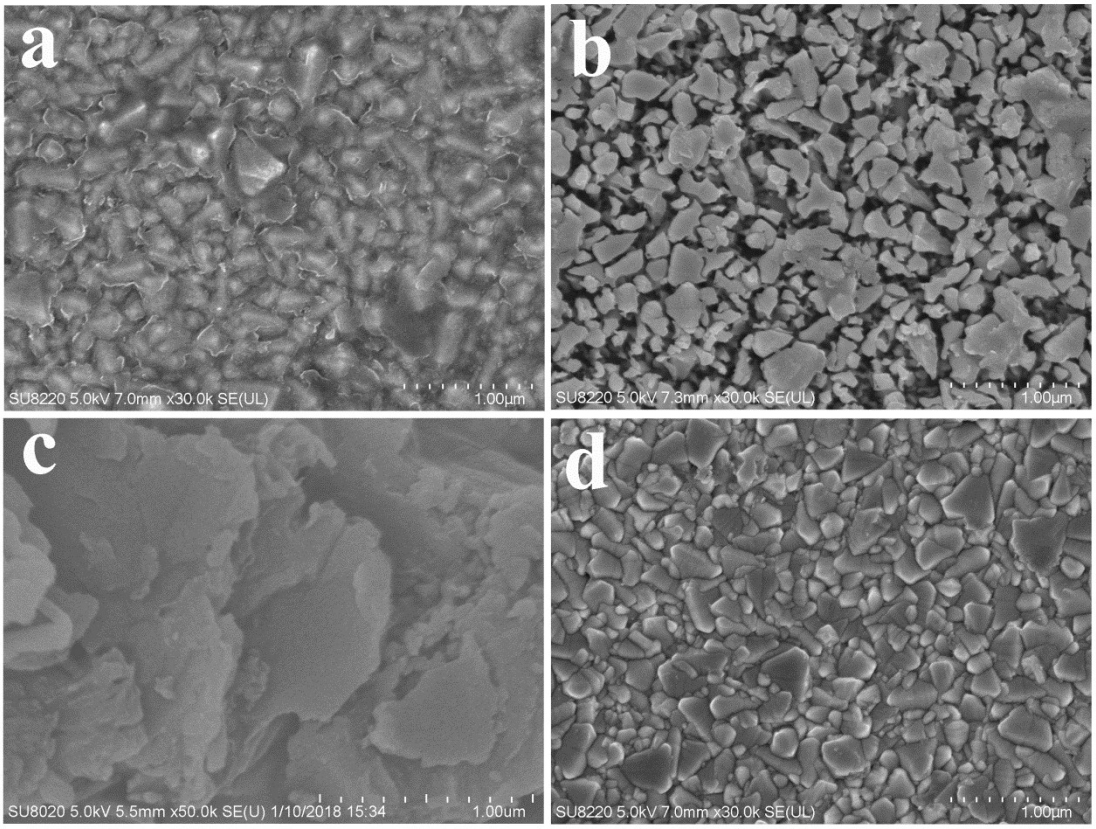

Figure S1 SEM images of CN-Me/FTO (a), CN-CC/FTO (b), g-C_3N_4/FTO (c), and FTO reference (d).

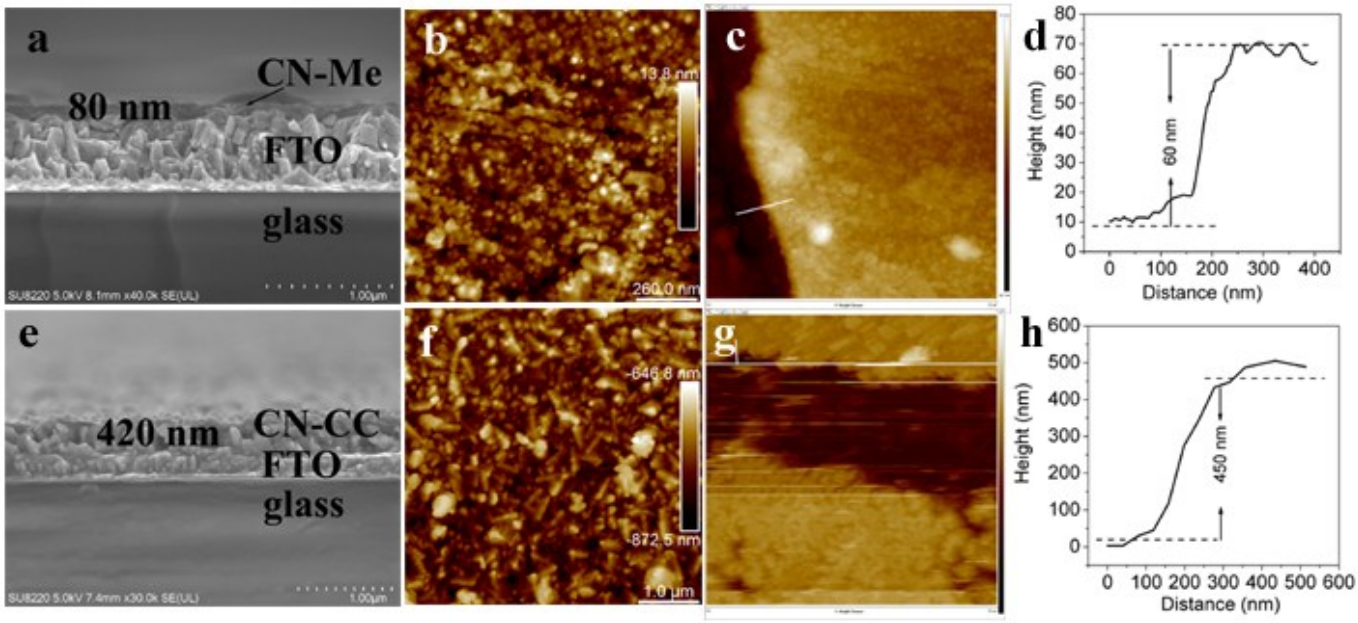

Figure S2 SEM images of cross-section of CN-Me/FTO (a) and CN-CC/FTO (e). AFM images of surface morphology and a typical thickness of CN-Me/FTO (b-d) and CN-CC/FTO (f-h).

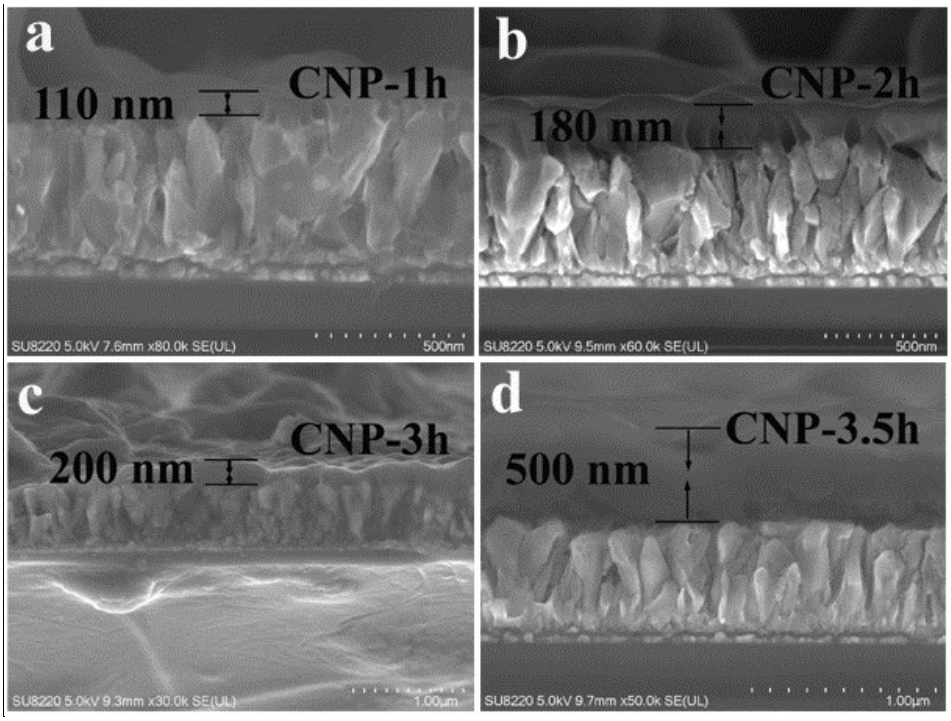

Figure S3 SEM images of cross-section of CNP/FTO films obtained from different growth time.

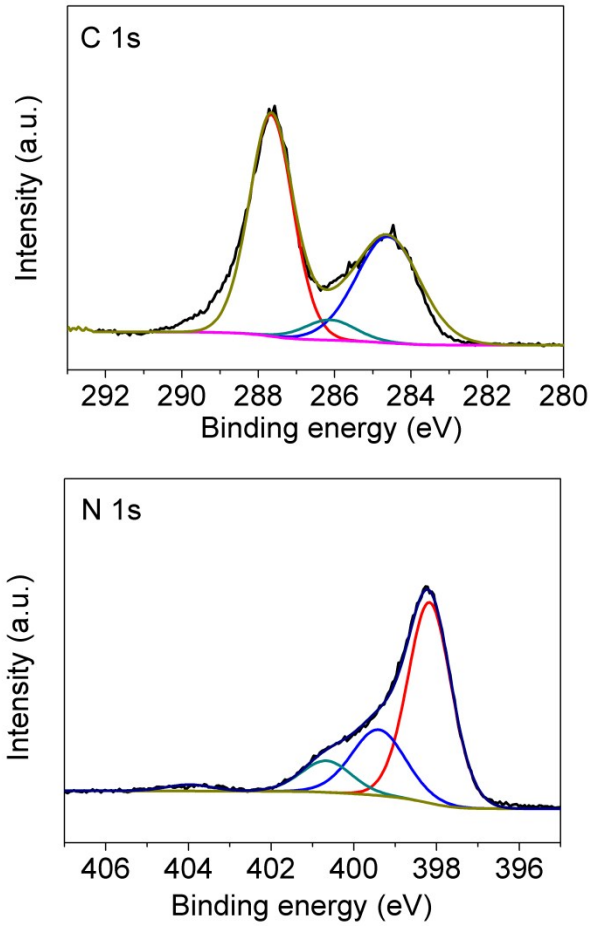

Figure S4 The high-resolution C 1s (a) and N 1s (b) XPS spectra of g-C_3N_4.

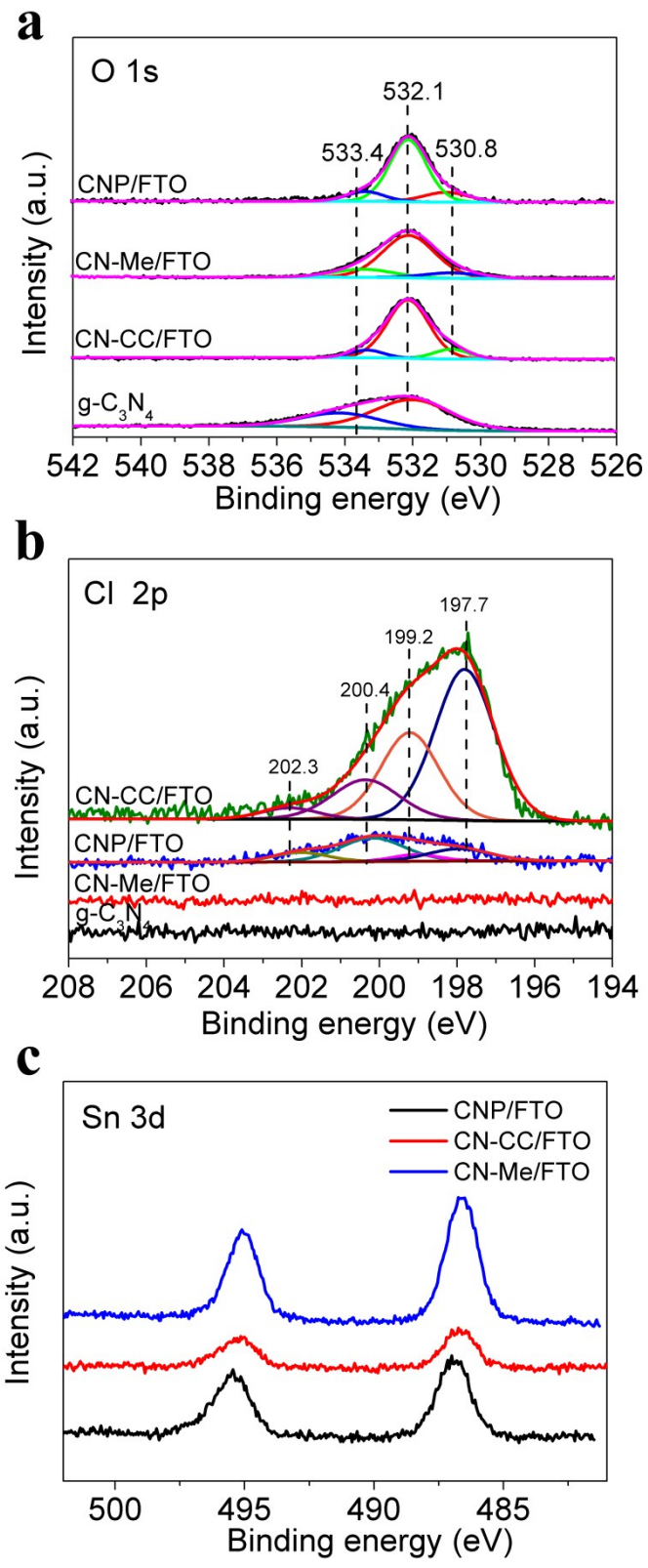

Figure S5 The high-resolution O 1s (a) and Cl 2p (b) XPS spectra of g-C_3N_4, CN-CC/FTO, CN-Me/FTO, and CNP/FTO; the high-resolution Sn 3d (c) XPS spectra of CN-CC/FTO, CN-Me/FTO, and CNP/FTO.

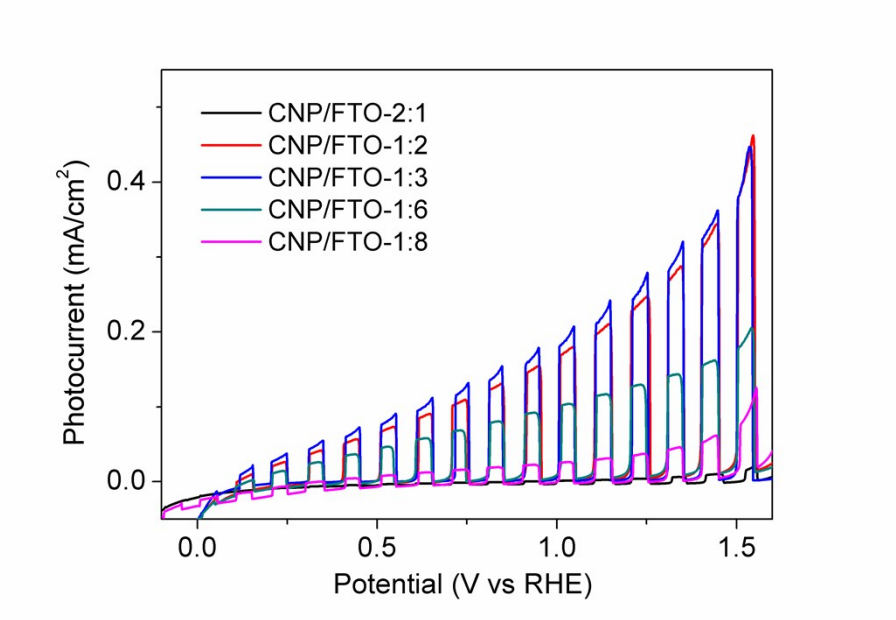

Figure S6 Linear sweep voltammetry (LSV) curves of CNP/FTO photoanodes obtained from different ratio of melamine and cyanuric chloride.

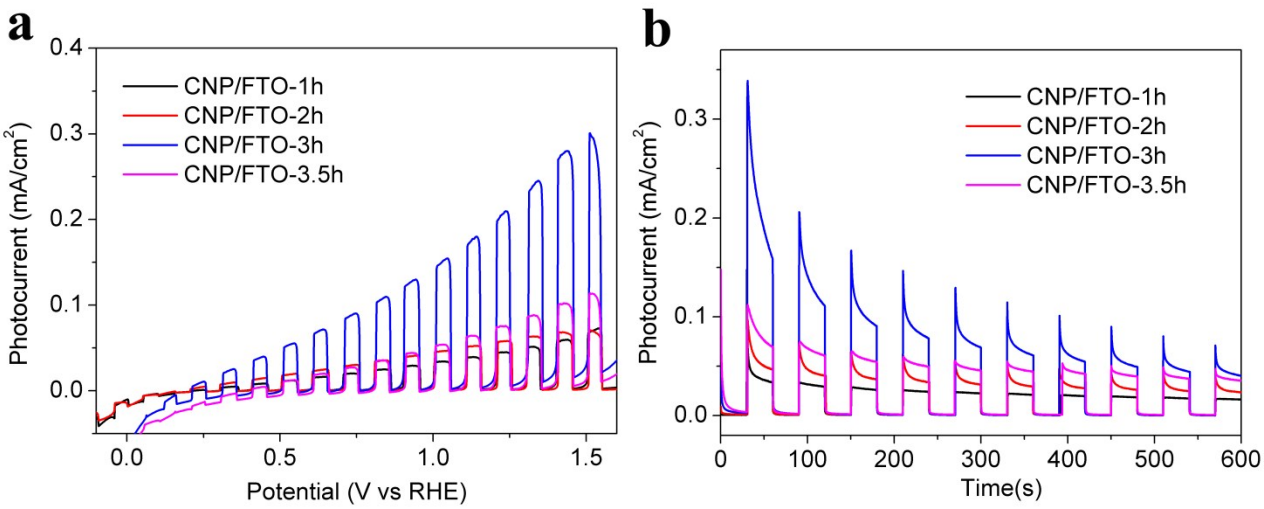

Figure S7 (a) Linear sweep voltammetry (LSV) curves of CNP/FTO photoanodes with different thickness of CNP film. (b) Long-time photocurrent response (i-t curve) of CNP/FTO photoanodes with different thickness of CNP film.

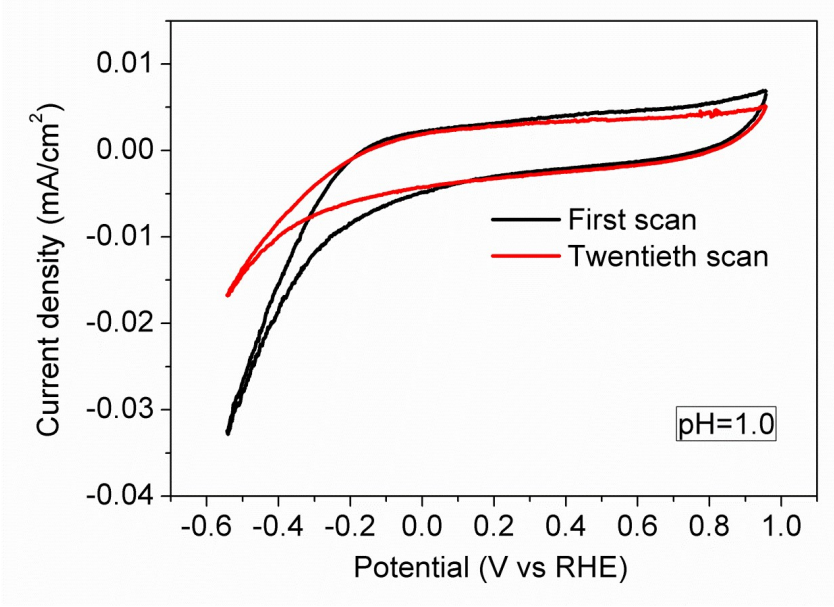

Figure S8 Cyclic voltammetry curves of CNP/FTO in 0.05 M H_2SO_4 solution (pH=1.0).

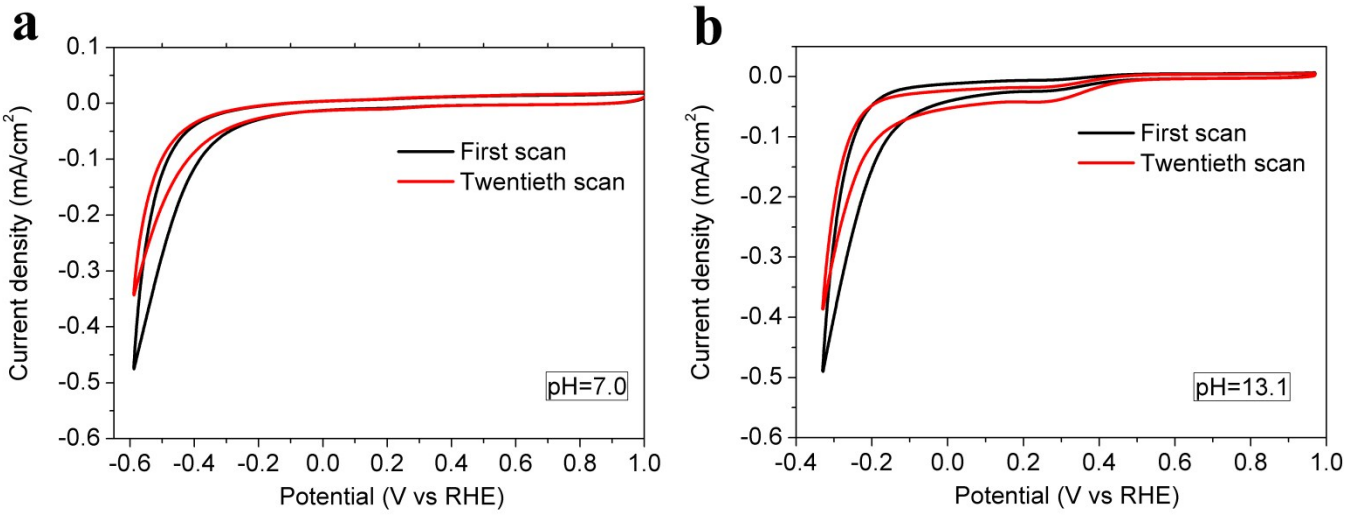

Figure S9 Cyclic voltammetry curves of CNP/FTO for the first and twentieth scans in (a) phosphate buffer solution (pH=7.0) and (b) 0.1m KOH solution (pH=13.1).

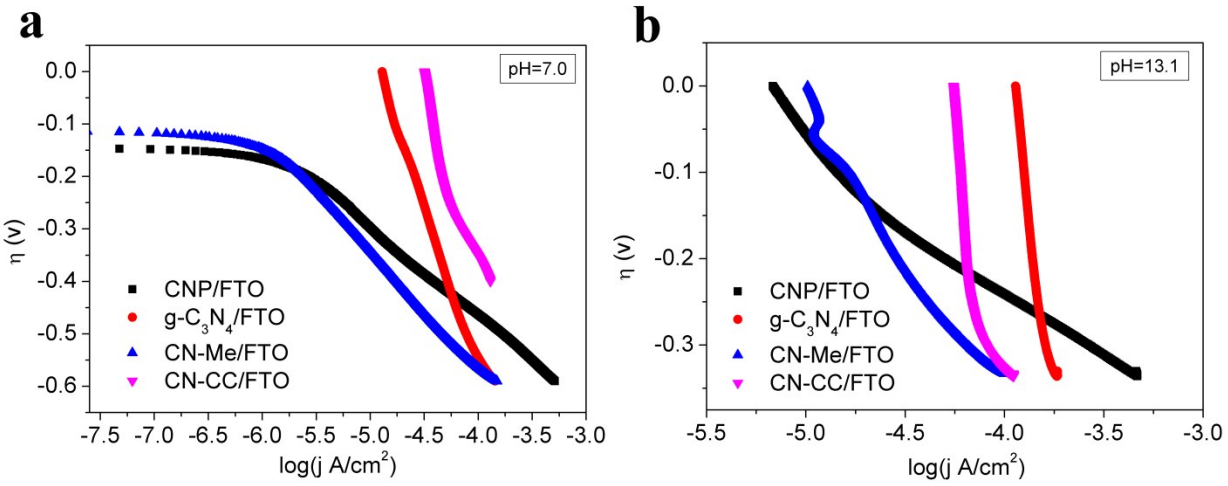

Figure S10 Tafel plots of g-C_3N_4/FTO, CN-CC/FTO, CN-Me/FTO, and CNP/FTO at pH=7.0 (phosphate buffer solution) and pH=13.1 (KOH 0,1M), respectively.

Table S1 Element contents of C, N, O, and Cl determined by elemental analysis.

samples	Elemental content (wt%)				N/C mole ratio
	N	C	H	Cl	
g-C_3N_4	58.56	35.33	2.72	-	1.53
CN-CC	36.79	22.01	2.98	6.9	1.45
CN-Me	61.78	35.19	1.88	-	1.51
CNP	18.84	13.93	1.95	3.5	1.16

Table S2 Assignments of the FTIR bands in ATR-FTIR spectra of the g-C_3N_4, CN-CC/FTO, CN-Me/FTO, and CNP/FTO films.

Wavenumber(cm^{-1})				Assignment	References
g-C_3N_4	CN-CC/FTO	CN-Me/FTO	CNP/FTO		
3259, 3156		3262, 3156	3260, 3156	The stretching vibrations of primary amines or hydrogen-bonding primary amines	[1-6, 9]
3081		3079	3080	The stretching vibrations of secondary amines	[1, 9, 10]
1640, 1564	1638	1638, 1560	1637, 1560	The stretching vibrations of the C=N in C-N heterocycles skeletal	[1, 4-9]
1460, 1406	1440	1455, 1403	1400	The stretching vibrations of C-N in C-N heterocycles skeletal	[1, 4, 6, 8, 9]
1324, 1236	1317, 1270	1320, 1236	1301, 1208, 1144	The stretching vibrations the C-NH-C unit	[10-14]
807	809	807	806	The breathing vibrations of triazine or heptazine units	[1, 3-10, 12]

Table S3 XPS peak positions of C1s, N1s, O 1s, Cl $2p_{3/2}$ and Sn $3d_{5/2}$of the g-C_3N_4, CN-CC/FTO, CN-Me/FTO, and CNP/FTO films.

Sample	XPS peak	Peak position (eV)	Attribution
g-C_3N_4	C 1s	284.6	contaminant aromatic carbon
		286.2	carbon linked to amino function (C-NH_x, x=1, 2)
		287.7	sp^2-hybridized carbon in s-triazine ring
	N 1s	398.3	sp^2-hybridized nitrogen in s-triazine rings (C-N=C)
		399.6	tertiary nitrogen N-$(C)_3$ groups
		400.8	amino functions caring hydrogen (-NH_x, x=1, 2)
	O 1s	530-534	adsorbed oxygen species on g-C_3N_4
CN-CC/FTO	C 1s	284.6	contaminant aromatic carbon
		286.3	carbon linked to amino function (C-NH_x, x=1, 2)
		288.3	sp^2-hybridized carbon in s-triazine ring
	N 1s	398.7	sp^2-hybridized nitrogen in s-triazine rings (C-N=C)
		399.9	tertiary nitrogen N-$(C)_3$ groups
		401.1	amino functions caring hydrogen (-NH_x, x=1, 2)
	O 1s	530.8	lattice oxygen of FTO
		532.1	hydroxyl oxygen of FTO or C-OH on CN-CC

		533.4	adsorbed oxygen species
	Cl $2p_{3/2}$	197.7	ionic Cl species
		200.4	C-Cl species
	Sn $2d_{5/2}$	486.7	Sn of FTO
CN-Me/FTO	C 1s	284.6	contaminant aromatic carbon
		286.2	carbon linked to amino function (C-NH_x, x=1, 2)
		288.0	sp^2-hybridized carbon in s-triazine ring
	N 1s	398.6	sp^2-hybridized nitrogen in s-triazine rings (C-N=C)
		399.9	tertiary nitrogen N-$(C)_3$ groups
		401.1	amino functions caring hydrogen (-NH_x, x=1, 2)
	O 1s	530.8	lattice oxygen of FTO
		532.1	hydroxyl oxygen of FTO or C-OH on CN-Me
		533.4	adsorbed oxygen
	Sn $3d_{5/2}$	486.7	Sn of FTO
CNP/FTO	C 1s	284.6	contaminant aromatic carbon
		286.3	carbon linked to amino function (C-NH_x, x=1, 2)
		288.2	sp^2-hybridized carbon in *s*-triazine ring
	N 1s	398.8	sp^2-hybridized nitrogen in *s*-triazine rings (C-N=C)
		399.9	tertiary nitrogen N-$(C)_3$ groups
		401.1	amino functions caring hydrogen (-NH_x, x=1, 2)
	O 1s	530.8	lattice oxygen of FTO
		532.1	hydroxyl oxygen of FTO or C-OH on CNPs
		533.4	adsorbed oxygen species
	Cl $2p_{3/2}$	197.7	ionic Cl species
		200.3	C-Cl species
	Sn $3d_{5/2}$	486.8	Sn of FTO

Table S4 The decay time constants, the corresponding pre-exponential factors, and the mean lifetime for all the samples.

Sample	τ_1 (ns) (Rel.%)	τ_2 (ns) (Rel.%)	τ_m (ns)	Ex (nm)	Em (nm)
g-C_3N_4/FTO	3.44 (47.21)	10.48 (52.79)	7.08	360	450
CN-CC/FTO	1.73(46.19)	7.40 (53.81)	4.61	312	440
CN-Me/FTO	1.67 (52.32)	6.60 (47.68)	4.03	310	450
CNP/FTO	1.07 (61.15)	5.76 (38.85)	2.90	312	470

Table S5 The summary of the preparation and photoelectrochemical performance for O_2 evolution reaction of reported carbon nitride photoanodes.

Entry	Photoanode	Preparation method	Precursor	Preparation temperature	Electrolyte	Light source	Photocurrent density ($\mu A/cm^2$) at 1.23 V vs RHE	reference
1	CNP/FTO	Evaporation polymerization	Melamine and cyanuric chloride	450 °C	0.5 M Na_2SO_4	Xe lamp, simulated solar irradiation (1 sun, AM 1.5)	230	this work
2	PMF-0.8/FTO	Thermal vapor condensation	Melamine and formaldehyde in 2 M H_2SO_4	550 °C	0.2 M Na_2SO_4	Xe lamp, simulated solar irradiation (1 sun, AM 1.5)	228.2	ChemSusChem, 2018, 11, 1-6
3	g-CN600 on FTO	Thermal vapor condensation	Melamine	600 °C	0.1 M Na_2SO_4 containing 0.1 M Na_2SO_3 and 0.01 M Na_2S (pH=11.6)	Xe lamp, simulated solar irradiation (1 sun, AM 1.5), 100 mW/Cm2	130	Nano Energy, 2015, 15, 353-361
4	CMD5 (modified CN films) on FTO	Thermal vapor condensation	Melamine and 2,6-Diaminopyridine	600 °C	0.1 M Na_2SO_4 containing 0.1 M Na_2SO_3 and 0.01 M Na_2S (pH=11.6)	Xe lamp, simulated solar irradiation (1 sun, AM 1.5)	100	Adv. Energy Mater., 2016, 6, 1600263
5	CNBC/FTO	Solvothermal method	Melamine and cyanuric chloride	200 °C	0.5 M Na_2SO_4	Xe lamp, simulated solar irradiation (1 sun, AM 1.5)	4	J. Mater. Chem. A, 2017, 5, 19062-19071
6	CN@FTO-10% on FTO	Microcontact -Printing-Assisted Access	Cyanamide	550 °C	0.1 M Na_2SO_4	Simulated solar light source (AM 1.5)	30.2	Adv. Mater., 2015, 27, 712-718
7	CN-h/FTO	Solvothermal method	Melamine and cyanuric chloride	180 °C	0.2 M Na_2SO_4	Visible light (λ> 420 nm, 200 W Xe lamp)	3.5	RSC Adv., 2016, 6, 9916-9922
8	PCN on FTO	Powder coating	Melamine	-	0.5 M Na_2SO_4	Xe lamp, simulated solar irradiation (1 sun, AM 1.5)	7	Angew. Chem. Int. Ed., 2018,

								57, 1-6
9	Co^{2+}-CN@FTO	Template method and impregnation method	Cyanamide	550 °C	0.2 M Na_2SO_4	50 W white light-emitting diode (λ > 410 nm)	7.5	Chem. Asian J., 2018, 13, 1539-1543
10	g-CN films on FTO	Two-step vapor deposition	Dicyandiamide	500 °C	0.1 M Na_2SO_4	Xe lamp, simulated solar irradiation (1 sun, AM 1.5)	63	Carbon, 2017, 117 (Supplement C), 343-350
11	Ni Embedded CN_x Films on FTO	Liquid-mediated pathway	Cyanuric acid/2,4-diamino-6-phenyl-1,3,5-triazine/nickel chloride	550 °C	0.1 M KOH	Simulated AM 1.5 solar illumination (100 mW cm^{-2}) with a Newport Sol3A Class AAA solarsimulator (94023A-SR3 type)	69.8	ACS Appl. Mater. Interfaces, 2017, 9, 32667-32677
12	Ph-CN thin films on FTO	Liquid-mediated approach	Cyanuric acid/2,4-diamino-6-phenyl-1,3,5-triazine	500 °C	0.1 M KOH	50 W white LED (λ > 410 nm, HLN-60H-24A, Mean Well)	60	Adv. Funct. Mater., 2015, 25, 6265-6271
13	s-BCN on FTO	Rapid thermal vapour deposition	Dicyandiamide and boric Acid	600 °C	0.1 M Na_2SO_4	AM 1.5 illumination at 100 mW/cm	103	Angew. Chem. Int. Ed., 2017, 56, 8221-8225

Table S6 Tafel slopes calculated from current density-voltage (*J*-*V*) curves of samples.

Samples	Tafel slops (mV/dec)	
	pH=7	pH=13
CNP/FTO	154	172
g-C_3N_4/FTO	598	1815
CN-Me/FTO	196	343
CN-CC/FTO	522	1280

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