Electronic Supplementary Information for

Small variation induces big difference: the effect of polymerization kinetics of graphitic carbon nitride on its photocatalytic activity

Tong Li,[a] Bo Lai,[a] Jing Liu,[a] Shuangtao Yuan,[a] Nan Liu,[b] Xiaojia Zhao,[c] Xiaoguang Luo,[d] Dongli Yu*[a] and Yuanchun Zhao*[a]

[a] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

[b] Department of Environmental Sciences, Hebei University of Environmental Engineering, Qinhuangdao 066102, China

[c] Department of Chemistry, Hebei Normal University, Shijiazhuang 050030, China

[d] Department of Electronics, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300071, China

[*] *Corresponding authors E-mail: ydl@ysu.edu.cn, yzhao56@ysu.edu.cn*

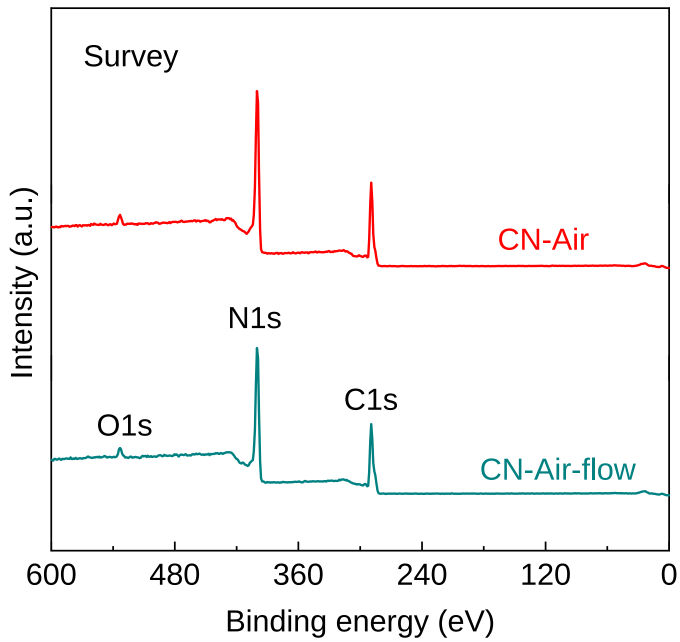

Fig. S1 XPS survey spectra of CN-Air and CN-Air-flow.

Table S1 The relative integrated content of each bonding state determined in the deconvoluted C 1s, N 1s and O 1s XPS spectra of CN-Air and CN-Air-flow.

Sample	C 1s			N 1s				O 1s	
	C_{ad} (%) (284.6 eV)	C_{3N} (%) (288.1 eV)	$C_{C–O}$ (%) (289 eV)	N_{2C} (%) (398.5 eV)	N_A (%) (399.4 eV)	N_B (%) (400.2 eV)	N_{3C} (%) (401 eV)	$O_{C–O}$ (%) (531.1 eV)	O_{ad} (%) (532.3 eV)
CN-Air	16.17	80.41	3.42	70.60	13.72	7.37	8.31	84.40	15.60
CN-Air-flow	21.81	75.09	3.10	73.01	9.89	6.98	10.11	65.46	34.54

Table S2 Compositions and atomic C/N ratios of CN-Air and CN-Air-flow determined by XPS and elemental analysis (EA), respectively.

	XPS				EA			
Sample	C (at %)	N (at %)	O (at %)	C/N	C (at %)	N (at %)	H (at %)	C/N
CN-Air	44.60	53.56	1.84	0.83	32.39	49.10	18.51	0.66
CN-Air-flow	46.12	51.42	2.46	0.89	32.87	49.76	17.37	0.66

Table S3 Fitted PL decay components of CN-Air and CN-Air-flow.

	Decay time (ns)			Relative amplitude (%)			Average lifetime[a] (A_τ, ns)
Sample	τ_1	τ_2	τ_3	a_1	a_2	a_3	
CN-Air	1.47	5.44	30.8	29.91	49.54	20.55	22.22
CN-Air-flow	1.25	4.75	29.1	27.10	50.05	22.85	21.91

[a]Average lifetimes were calculated based on the equation: $A_\tau = (a_1\tau_1^2 + a_2\tau_2^2 + a_3\tau_3^2) / (a_1\tau_1 + a_2\tau_2 + a_3\tau_3)$.

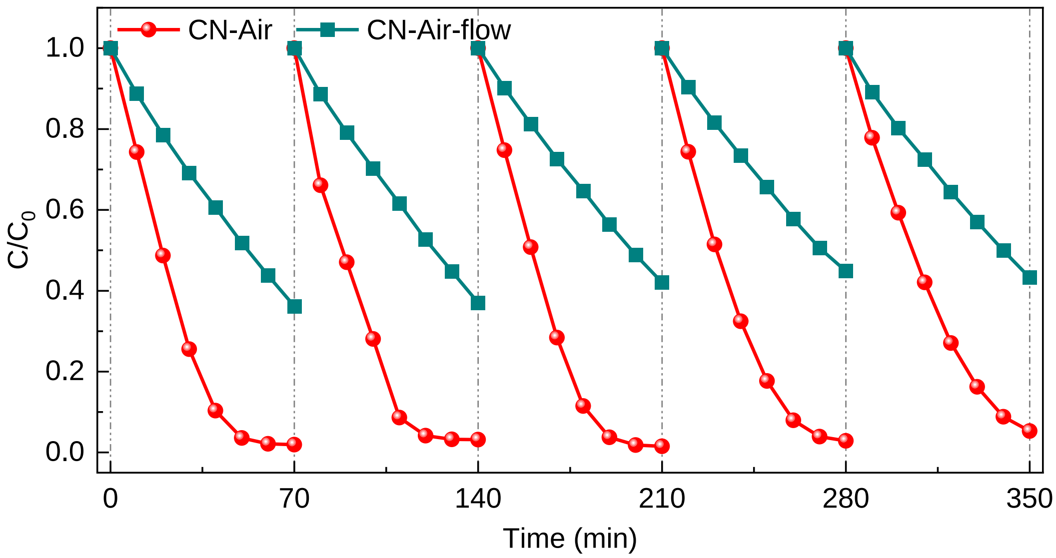

Fig. S2 Recycling RhB degradation tests for CN-Air and CN-Air-flow, respectively.

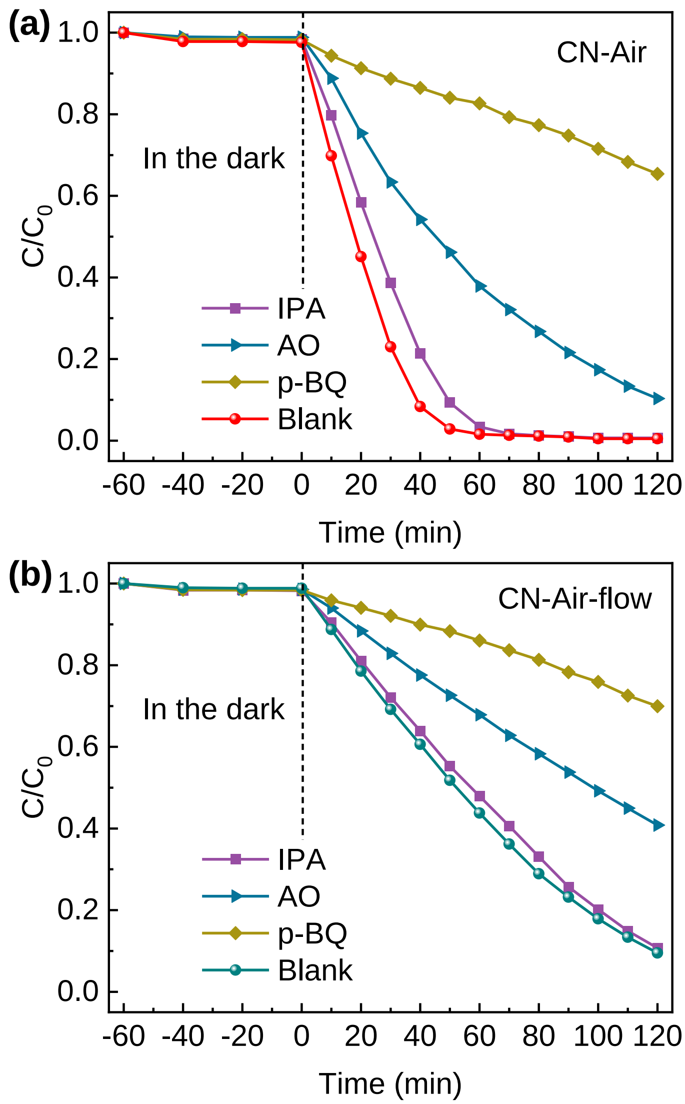

Fig. S3 Trapping experiments for the degradation of RhB under visible light irradiation (λ > 420 nm) without (blank) or with different scavengers catalyzed by (a) CN-Air and (b) CN-Air-flow, respectively.

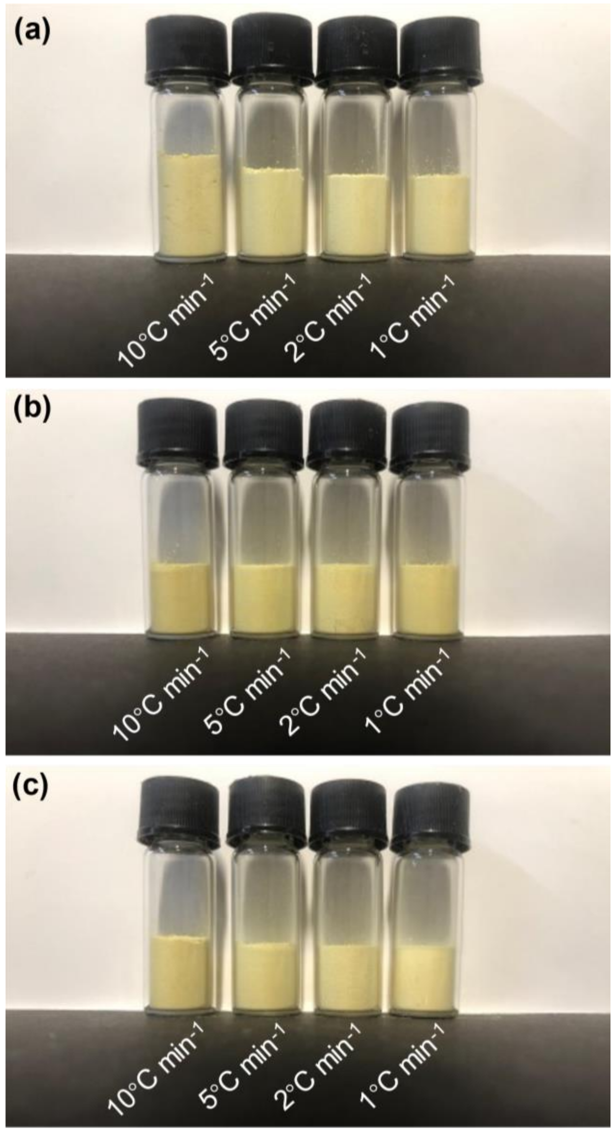

Fig. S4 Photograph of the synthesized samples with an identical weight of 300 mg by changing the ramping rate under different atmospheres (a) in the static air, (b) in the flowing air and (c) in the flowing N_2, respectively. 10 g of melamine was used as precursor for all the g-CN samples.

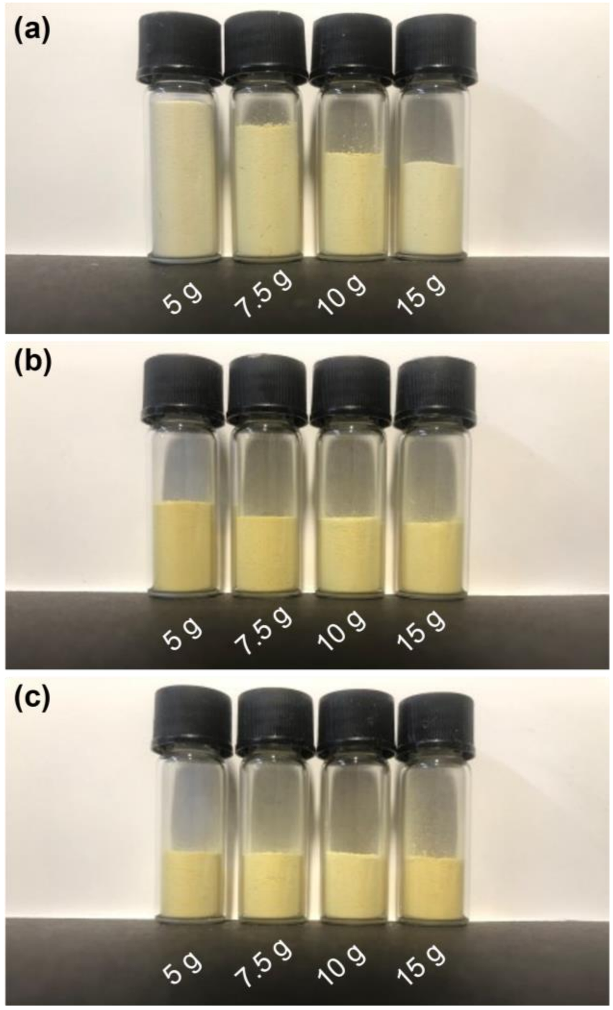

Fig. S5 Photograph of the synthesized samples with an identical weight of 300 mg by changing the loading amount of melamine under different atmospheres (a) in the static air, (b) in the flowing air and (c) in the flowing N_2, respectively. The condensation process was conducted with a ramping rate of 10 ℃ min^{-1}.

Table S4 A summary of the experimental details and PHE performance of conventional bulk g-CN reported in some literatures and this work.

Precursor	Precursor amount (g)	Synthetic atmosphere	Ramping rate (℃ min^{-1})	Condensation procedure	HER[a] (μmol g^{-1} h^{-1})	AQE (%)[b]	Note	Ref.
Melamine	5	Static air	10	550 ℃ × 4 h	415.2	N/A	Production yield: 12.7 %	This work
Melamine	10	Static air	10	550 ℃ × 4 h	229.3	0.33	Production yield: 24.5 %	This work
Melamine	10	Static air	1	550 ℃ × 4 h	157.0	N/A	Production yield: 29.9 %	This work
Melamine	5	Flowing air	10	550 ℃ × 4 h	137.9	N/A	Production yield: 24.8 %	This work
Melamine	10	Flowing air	10	550 ℃ × 4 h	98.9	0.12	Production yield: 33.2 %	This work
Melamine	10	Flowing air	1	550 ℃ × 4 h	67.9	N/A	Production yield: 36.5 %	This work
Melamine	5	Flowing N_2	10	550 ℃ × 4 h	107.1	N/A	Production yield: 27.3 %	This work
Melamine	10	Flowing N_2	10	550 ℃ × 4 h	83.9	N/A	Production yield: 34.8 %	This work
Melamine	10	Flowing N_2	1	550 ℃ × 4 h	58.9	N/A	Production yield: 38.3 %	This work
Cyanamide	1	N/A	2.2	550 ℃ × 4 h	106.9	0.10		S1
Dicyandiamide	1	Static air	2.3	550 ℃ × 4 h	217.0	0.03		S2
Melamine	2	Static air	3	550 ℃ × 4 h	528.0	1.14	Light source: four 3-W LEDs, $\lambda = 420$ nm	S3
Melamine	N/A	Static air	5	550 ℃ × 4 h	437.0	2.1 (405 nm)	Light source: 100 W white LED array, $\lambda > 410$ nm	S4
Melamine	0.126	Flowing N_2	5	550 ℃ × 4 h	270.0	0.24		S5
Melamine	10	Static air	3	550 ℃ × 2 h	150.0	0.86		S6

(continued)

Precursor	Precursor amount (g)	Synthetic atmosphere	Ramping rate (℃ min^{-1})	Condensation procedure	HER (μmol g^{-1} h^{-1})	AQE (%)	Note	Ref.
Melamine	N/A	Static air	3	550 ℃ × 4 h	355.7	0.96 (430 nm)	Light source: 10 W white LED, $\lambda > 420$ nm	S7
Melamine	3	Static air	2.3	550 ℃ × 4 h	160.2	0.65[c]		S8
Dicyandiamide	3	Static air	N/A	550 ℃ × 4 h	180.0	N/A		S9
Melamine	N/A	Static air	5	550 ℃ × 2 h	355.0	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm	S10
Dicyandiamide	3	Static air	N/A	550 ℃ × 4 h	134.0	N/A		S11
Melamine	7	Static air	6.7	550 ℃ × 4 h	98.3	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm	S12
Melamine	N/A	Static air	N/A	550 ℃ × 4 h	98.0	N/A		S13
Melamine	N/A	Static air	5	550 ℃ × 4 h	197.4[c]	N/A		S14
Dicyandiamide	N/A	Static air	N/A	550 ℃ × 4 h	420.0	N/A		S15
Melamine	N/A	Static air	N/A	550 ℃ × 4 h	2355.0	N/A	Catalyst: 0.15 g/L of g-CN	S16
Melamine	2	Static air	3	550 ℃ × 4 h	210.0	N/A		S17
Melamine	1.2	Static air	N/A	550 ℃ × 4 h	4.0	N/A	Scavenger: methanol (10 %)	S18
Dicyandiamide	N/A	Static air	5	550 ℃ × 4 h	290.0	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm	S19
Melamine	2	Static air	3	550 ℃ × 4 h	190.0	N/A		S20
Dicyandiamide	N/A	Static air	N/A	550 ℃ × 4 h	85.0	N/A		S21

(continued)

Precursor	Precursor amount (g)	Synthetic atmosphere	Ramping rate (℃ min^{-1})	Condensation procedure	HER (μmol g^{-1} h^{-1})	AQE (%)	Note	Ref.
Melamine	10	Flowing air	3	550 ℃ × 2 h	63.0	N/A		S22
Melamine	1.2	Static air	N/A	550 ℃ × 4 h	16.0	N/A	Scavenger: methanol (10 %)	S23
Melamine	1	Static air	5	550 ℃ × 4 h	153.9	N/A		S24
Dicyandiamide	N/A	Static air	2.3	550 ℃ × 4 h	13.2	N/A	PHE reactor: 1 bar pressure of inert gas, not in the vacuum	S25
Melamine	5	Static air	5	550 ℃ × 2 h	220.0	N/A		S26
Melamine	10	Static air	2	550 ℃ × 3 h	951.0	N/A		S27
Dicyandiamide	4	Static air	5	550 ℃ × 4 h	125.4	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm	S28
Melamine	5	Static air	5	550 ℃ × 4 h	136.1	N/A		S29
Melamine	10	Static air	5	550 ℃ × 2 h	846.0	N/A	Catalyst: 0.2 g/L of g-CN	S30
Melamine	N/A	Static air	2.3	550 ℃ × 4 h	811.0	N/A	Catalyst: 0.2 g/L of g-CN	S31
Melamine	2	Static air	2	550 ℃ × 4 h	167.3	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm	S32
Melamine	1	Static air	2.5	550 ℃ × 4 h	83.0	N/A		S33
Melamine	N/A	Static air	20	550 ℃ × 4 h	235.9	N/A		S34
Melamine	20	Static air	N/A	550 ℃ × 4 h	80.0	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm	S35
Melamine	5	Static air	5	550 ℃ × 4 h	610.0	N/A		S36

(continued)

Precursor	Precursor amount (g)	Synthetic atmosphere	Ramping rate (℃ min^{-1})	Condensation procedure	HER (μmol g^{-1} h^{-1})	AQE (%)	Note	Ref.
Melamine	10	Static air	10	550 ℃ × 3 h	60.3[c]	N/A		S37
Melamine	2	Static air	N/A	550 ℃ × 3 h	94.0	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm	S38
Melamine	5	Static air	5	550 ℃ × 2 h	1820.0	N/A	Catalyst: 0.1 g /L of g-CN	S39
Melamine	N/A	Static air	5	550 ℃ × 4 h	56.9	N/A		S40
Dicyandiamide	N/A	Static air	N/A	550 ℃ × 4 h	58.0	N/A	Catalyst: 0.125 g/L of g-CN; Scavenger: methanol (50 %)	S41
Melamine	10	Static air	N/A	550 ℃ × 4 h	1130.0	N/A	Catalyst: 0.1 g/L of g-CN	S42
Melamine	5	Static air	2.2	550 ℃ × 4 h	98.0	N/A		S43
Melamine	N/A	Static air	10	550 ℃ × 3 h	450.0	N/A	Light source: 300 W Xe lamp, $\lambda > 400$ nm; Scavenger: methanol (20 %)	S44
Melamine	3	Static air	0.5	550 ℃ × 4 h	150.7	N/A		S45

[a] For conventional PHE tests, 0.5−1 g/L of g-CN powders were used as catalysts and dispersed in deionized water, 0.5−5 wt.% (typically 3 wt.%) of Pt co-catalyst was loaded by in-situ photodeposition, 10−20 vol.% (typically 10 vol.%) of TEOA was used as the scavenger, and the light source was commonly a 300 W Xe lamp with a long-pass cutoff filter ($\lambda > 420$ nm). Using smaller amounts of the catalyst (0.1−0.2 g/L) will lead to much higher HER values, please see the column of "Note" for details.

[b] Unless specifically indicated in the bracket, the AQEs were determined at the wavelength of 420 nm.

[c] The corresponding value was calculated based on the reported details, not directly mentioned in the reference.

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