Supporting Information

Photopolymerization performed under dark condition using long stored electrons in carbon nitride

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Materials:

N, *N*-dimethyl acrylamide (DMA) (Aldrich, 99%) and *N*,*N*-diethyl acrylamide(DEA) (Aldrich, 99%) were de-inhibited by percolating over a column of basic alumina (Sinopharm Chemical Reagent Co., LTD). *N*-isopropylmethacrylamide (NIPAM) (Aldrich, 97%) was purified by recrystallization before use. Melamine (Alfa Aesar, 99%)，diphenyliodonium chloride (DPI) (TCI, 98%), di(p-anisyl)iodonium bromide (DPAI) (Aldrich, 97%), triphenylsulfonium bromide (TPS) (TCI, 98%), tetraphenylphosphonium chloride (TPP) (TCI, 98%) , 4-methylbenzyl alcohol (4-MBA) (TCI, 99%) were used as received. Potassium thiocyanate (98.5%), carbon disulfide (99%), chloroform (99%), acetone (99.5%), tetrabutylammonium hydrogen sulfate (99%), mineral ether (AR), and sodium hydroxide (96%) were obtained from Sinopharm Chemical Reagent Co., LTD. 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized according to literature procedures. Water was deionized to 18 MΩ ·cm resistivity using the nanopure system.

Carbon Nitride Synthesis:

Synthesis of C_3N_4-NH_2: Melamine was added to a porcelain cup and calcined at 560 ^oC for 4 h, with the heating rate of 10.0 K min^{-1}. Grinding of the resultant affords yellow powders of pristine carbon nitride. The pristine carbon nitride was calcined at 400 ^oC for 1.0 h with the heating rate of 20.0 ^oC min^{-1}, and then was calcined at 500 ^oC for 30.0 min with the heating rate of 20.0 ^oC min^{-1}. Grinding of the resultant affords yellow powders of C_3N_4-NH_2.

Synthesis of C_3N_4-NH-CN or C_3N_4-N^--CN: Pristine carbon nitride (400 mg) was thoroughly ground with KSCN (800.0 mg, dried at 60 ^oC in vacuum) and loaded in a quartz boat or a porcelain cup. This mixture was calcined at 400 ^oC for 1.0 h with the heating rate of 20.0 ^oC min^{-1}, and then was calcined at 500 ^oC for 30.0 min with the heating rate of 20.0 ^oC min^{-1}. The resulting yellow product was first washed with water and centrifuged to remove KSCN, then dispersed in a pH=5.0 or pH=13.0 phosphate buffer to obtain the suspension of C_3N_4-NH-CN and C_3N_4-N^--CN, respectively. To obtain the powder product for characterizations, the insoluble product was centrifuged out, then dried at 60 °C under vacuum.

Preparation of ultrathin C_3N_4-NH-CN nanosheets: The C_3N_4-NH-CN nanosheets was obtained by liquid exfoliating of as-prepared bulk C_3N_4-NH-CN in water by an ultrasonic facility (Scientz-II D; Ningbo Scientz biotechnology CO. LTD. China). In detail, 20.0 mL suspension of C_3N_4-NH-CN (2.0 mg/mL) was ultrasonicated for 1.0, 3.0, 10.0 and 30.0 min in an ice bath. The obtained suspension was directly used for characterization and polymerization.

Synthesis of *S,S'*-bis(α, α'-dimethyl-α''-acetic acid) Trithiocarbonate (BDMAT):

BDMAT was synthesised according to literature procedures.[1] Carbon disulfide (13.77g, 0.018 mol), chloroform (58.81 g, 0.45 mol), acetone (26.26 g, 0.45 mol), and tetrabutylammonium hydrogen sulfate (1.21 g, 3.6 mmol) were mixed with 12.0 mL of mineral ether in a 500 mL round bottom. Then NaOH solution (50%, 100.8 g) was added dropwise into the mixture in 1.0 h while maintaining the temperature below 25 °C. After the addition was completed, the reaction was maintained at 22-25 °C for 5.0 h while being stirred with a magnetic stirrer. H_2O (90.0 mL) was added to dissolve the yellow solids, followed by adding hydrochloric acid (12.0 mL) to acidify the aqueous solution and yield crystalline solids. After filtration and washing several times by H_2O, the crude compound was purified by recrystallization in toluene and mineral ether (4:1 v/v). The yield of BDMAT was about 50%. Aliquot of product was diluted in $CDCl_3$ for ^1H NMR measurement.

Characterizations:

Fourier transform infrared (FTIR) spectroscopy was performed on a PerkinElmer UATR TWO spectrometer equipped with a diamond crystal. Static photoluminescence (PL) spectra were acquired at an angle of 90° with respect to the excitation source. The suspension was stirred before the measurement to prevent suspension sedimentation. The UV-vis spectra (DRS) were recorded on a Shimadzu DUV-3700 spectrophotometer. XPS analysis was performed using a Thermo ESCALAB 250Xi spectrometer with Al Kα radiation as the energy source. Transmission electron microscopy (TEM) was performed with a Hitachi-7700K(100kV). Powder X-ray diffraction patterns of samples were recorded using a Rigaku Miniflex-600 with Cu Kα radiation (Cu Kα, λ=0.15406 nm, 40 4kV and 15 mA). ESR spectra were obtained using a JEOL JES-FA200 ESR spectrometer (298 K, 9.058 GHz, X-band). Microwave power employed was 1.0 mW; sweep width ranged from 223 to 423 mT. Modulation frequency and modulation amplitude were 100 kHz and 0.35 mT, respectively. Liquid-state NMR spectra were recorded on a Bruker NMR spectrometer (resonance frequency of 400 MHz for 1H) operated in the Fourier transform mode. Molecular weights and molecular weight distributions were measured by using a Waters 150C gel permeation chromatograph (GPC) equipped with microstyragel columns and an RI 2414 detector at 30 °C. LiBr/DMF (0.1%, w/w) solution with a flow rate of 1.0 mL/min was used as eluent. The molecular weights were calibrated against monodispersed polystyrene standards.

Electron titration experiments:

Methylene blue (MB) was used to perform the electron titration experiments. Suspension of C_3N_4-NH-CN (1.0 mg) and 4-MBA (1.0 mg) in water (1.0 mL) in a photoreactor was irradiated by OSRAM ULTRA-VITALUX (300W) for 60 min under anaerobic conditions. After stopping the irradiation, 2 mL of a deaerated MB solution (5×10^{-5} M) was added into the suspension of C_3N_4-NH-CN with stored electrons. The stored electrons will reduce MB to colorless MB^{2-}, the consumption of MB and the amount of stored electrons can be calculated by detecting the absorption value at 680 nm (one MB molecular corresponding to two electrons).

General Procedure of Photopolymerization under Direct Irradiation：

Photopolymerization 1:

Solution of BDMAT (4.23 mg, 0.015mmol), DMA (296 mg, 3.0 mmol) and DPI (5.0 mg) in water (Total volume: 3.0 mL) were transferred into a polymerization tube, after three freeze-pump-thaw cycles, the tube was sealed. Then, the mixture was irradiated at room temperature. Conversions were recorded by ^{1}HNMR spectra.

Photopolymerization 2:

Suspension of C_3N_4-NH-CN nanosheets (2.0 mg), 4-MBA (2.0 mg), BDMAT (4.23 mg, 0.015mmol), DMA (296.0 mg, 3.0 mmol) and DPI (5.0 mg) in water (Total volume: 3.0 mL) were transferred into a polymerization tube, after three freeze-pump-thaw cycles, the tube was sealed. Then, the mixture was irradiated at room temperature. After reaction, C_3N_4-NH-CN nanosheets was removed by centrifugation and conversions were recorded by ^{1}HNMR spectra.

General Procedure of Storing Electros:

Suspension of C_3N_4-NH-CN nanosheets (2.0 mg) and 4-MBA (2.0 mg) in water (2.0 mL) were transferred into a reaction tube, after three freeze-pump-thaw cycles, the tube was sealed. Then, the mixture was irradiated by OSRAM ULTRA-VITALUX (300W) at room temperature for 1.0 h.

General Procedure of Polymerization Using Stored Electrons under Dark Condtion:

Dark photopolymerization:

The deaerated solution of BDMAT (4.23 mg, 0.015mmol), DMA (296 mg, 3.0 mmol) and DPI (5.0 mg) in water (Total volume: 1.0 mL) was injected into 2.0 mL suspension of C_3N_4-NH-CN with stored electrons. Under the dark polymerization experiments, the reactor was wrapped in aluminium foil to eliminate irradiation by stray light. After reaction, C_3N_4-NH-CN nanosheets was removed by centrifugation and conversions were recorded by ^{1}HNMR spectra.

BDMAT Degradation:

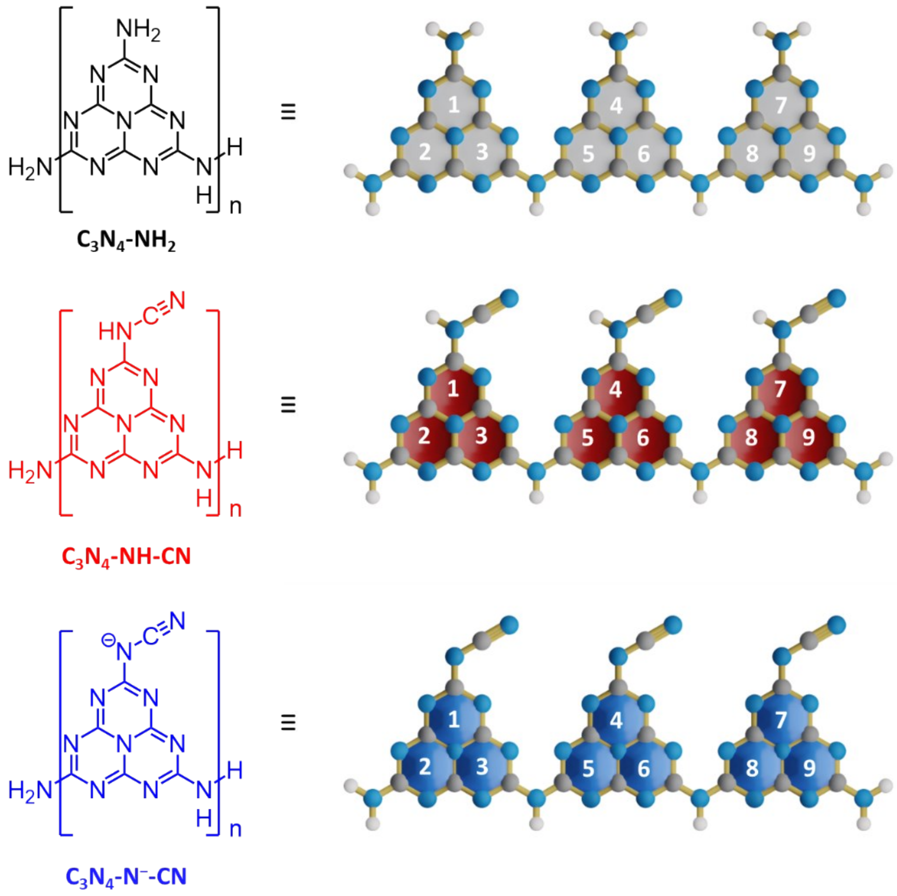
For RAFT polymerization, we verified the occurrence of side reactions during the polymerization process by detecting the degradation of trithiocarbonate (BDAMT). During the polymerization process, 0.3 mL of reaction solution was taken out at 10, 20, 30, 60 and 120 min. The insoluble catalyst is separated by centrifugation, and the absorption of the supernatant at 430 nm is detected by UV-visible absorption spectroscopy.

General Procedure of Chain Extension:

The experiment procedure of chain extension is similar to general procedure of polymerization using stored electron, but using isolated PDMA as a macro-CTA instead of BDMAT.

Computational Details:

The effect of substituent is probed by calculating Hirshfeld charges which has been proven to give quantitative correspondence to the substituent constant.[2] The density functional theory (DFT)[3] has been utilized to calculate the Hirshfeld charges for three compounds. The structures are optimized at the B3LYP/6-311g** theory of level.[4-6] The frequency calculations are also performed to validate that the obtained structures are stationary points on the potential energy surfaces (PES). All calculations are performed by Gaussian 09. The Multiwfn code has been used for post-processing of Hirshfeld charges.[7]



Local charge of each C_3N_3 ring:

	1	2	3	4	5	6	7	8	9
C_3N_4-NH_2	0.021	0.006	0.056	0.049	0.068	0.068	0.021	0.056	0.006
C_3N_4-NH-CN	0.087	0.047	0.100	0.121	0.106	0.114	0.094	0.091	0.056
C_3N_4-N^--CN	-0.064	-0.147	-0.037	-0.020	-0.050	-0.043	-0.050	-0.041	-0.135

Figure S1. Chemical structure and the results for the calculated charge distribution of 'C_3N_3' ring in the trimer of C_3N_4-NH_2, C_3N_4-NH-CN and C_3N_4-N^--CN.

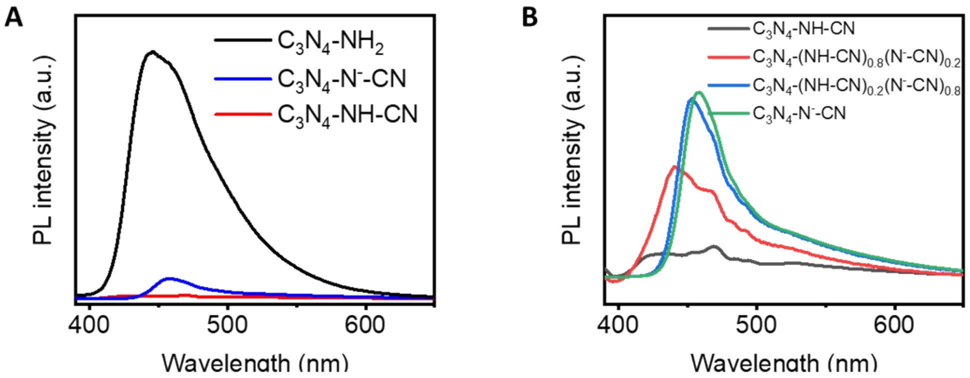


Figure S2. Photoluminescence spectra of different carbon nitride. (A) Photoluminescence spectra of C_3N_4-NH_2, C_3N_4-NH-CN and C_3N_4-N^--CN. (B) Photoluminescence spectra of C_3N_4-NH-CN and C_3N_4-N^--CN with different -NH-CN content.

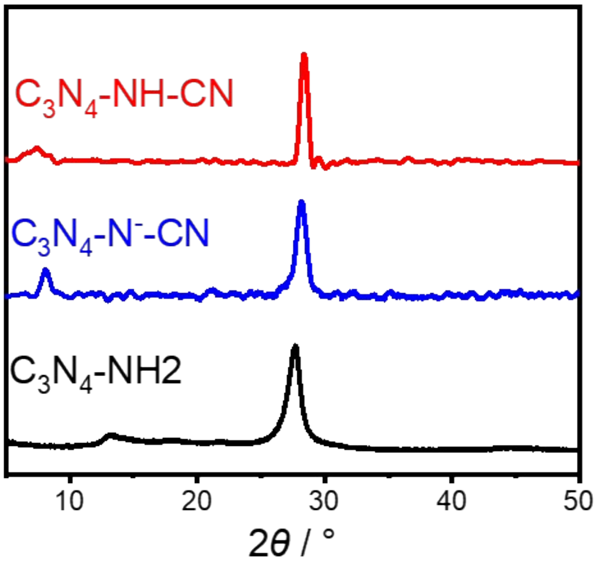


Figure S3. X-ray diffraction patterns of C_3N_4-NH_2, C_3N_4-NH-CN and C_3N_4-N^--CN.

Figure S4. Photographs of the dispersions of C_3N_4-NH-CN in various solvents.

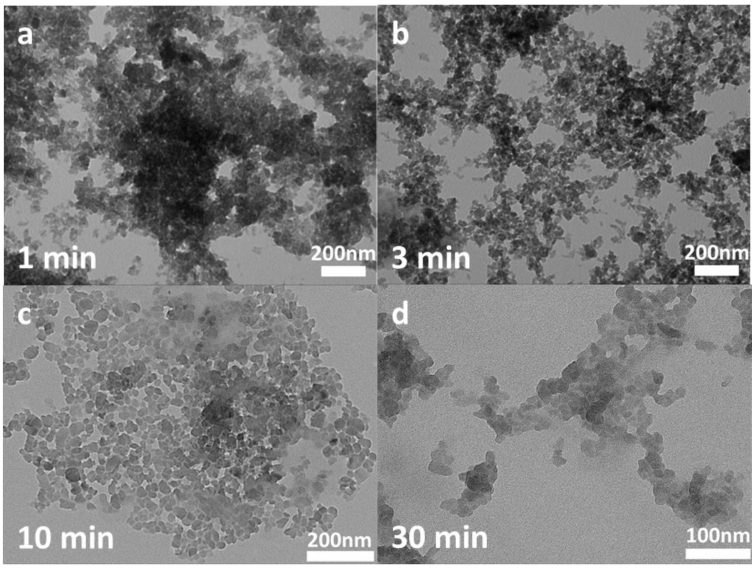


Figure S5. TEM image of C_3N_4-NH-CN after different ultrasonic exfoliation time. (a) 1.0 min, (b) 3.0 min, (c) 10.0 min and (d) 30.0 min.

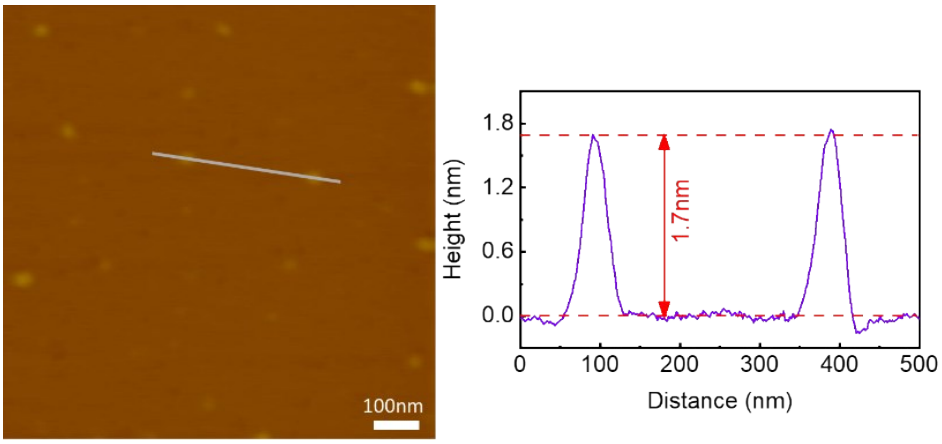


Figure S6. AFM image of the C_3N_4-NH-CN nanosheets (10 min) and the corresponding height image of two random nanosheets.

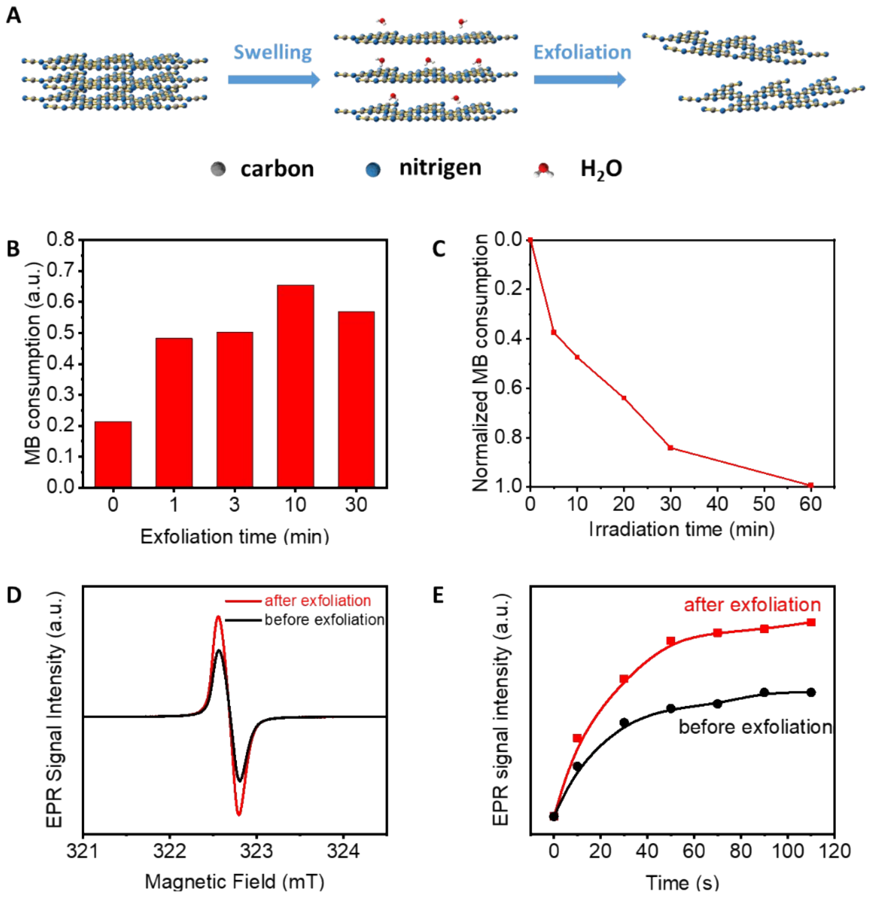


Figure S7. Electron storage performance of C_3N_4-NH-CN with different ultrasonic exfoliation time. (A) Schematic illustration of liquid-exfoliation process from bulk C_3N_4-NH-CN to ultrathin nanosheets. (B) Electron titration of C_3N_4-NH-CN nanosheets with different exfoliation time after 10 min photoirradiation by MB consumption. (C) Normalized concentration of MB consumption of C_3N_4-NH-CN nanosheets with 10min exfoliation after different photoirradiation time. (D) EPR signal intensity of suspension of C_3N_4-NH-CN and C_3N_4-NH-CN nanosheets after 1h irradiation. (E) Growth of EPR signal intensity of suspension of C_3N_4-NH-CN and C_3N_4-NH-CN nanosheets with increasing irradiation time. (The rapid saturation of the EPR signal is due to the smaller amount of sample and stronger light source in the EPR experiment.)

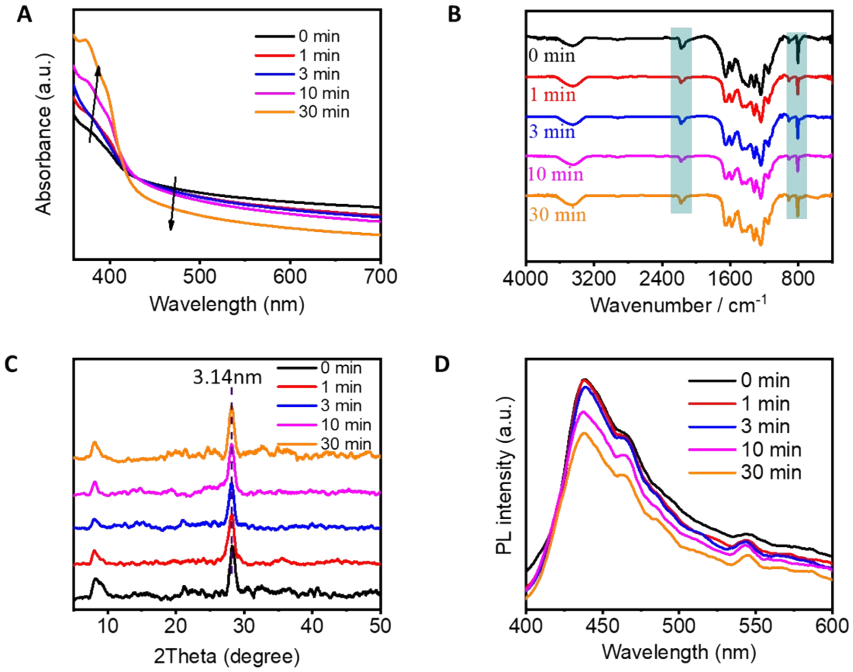


Figure S8. Characterizations of C_3N_4-NH-CN with different ultrasonic exfoliation time. (A) UV-vis absorption spectrum. (B) FT-IR. (C) X-ray diffraction patterns. (D) Photoluminescence spectra.

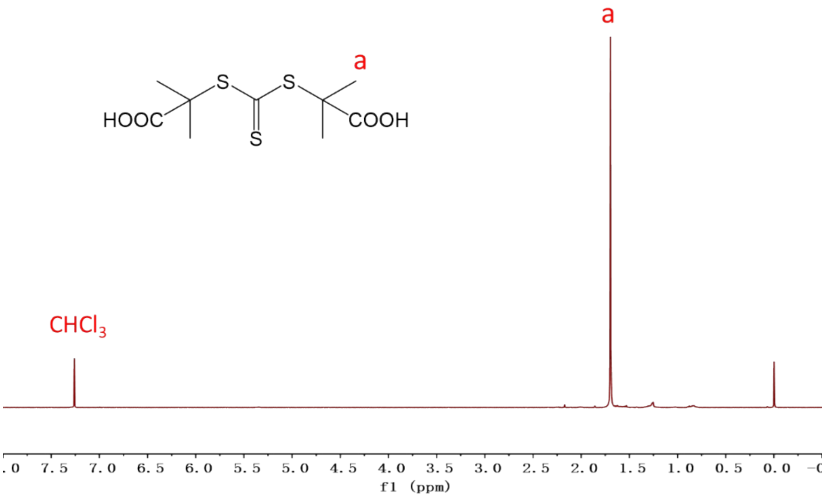


Figure S9. ^{1}H NMR (300 MHz) spectrum of BDMAT in $CDCl_3$.

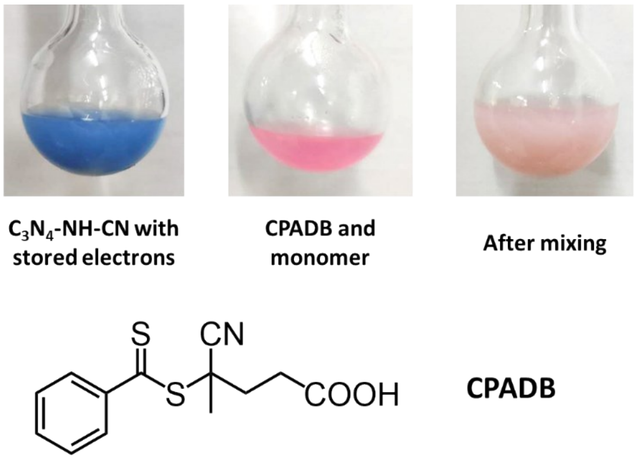


Figure S10. Photo images of color evolution using CPADB as electron acceptor.

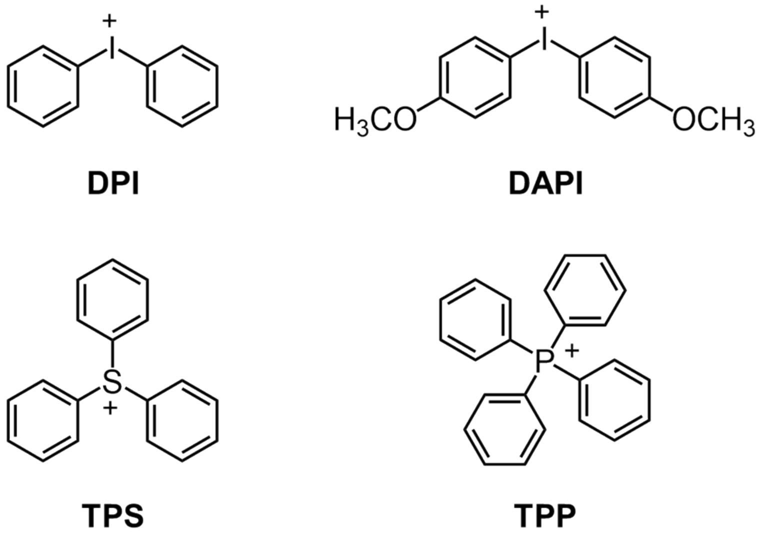


Figure S11. Chemical structure of four kinds of co-catalysis used.

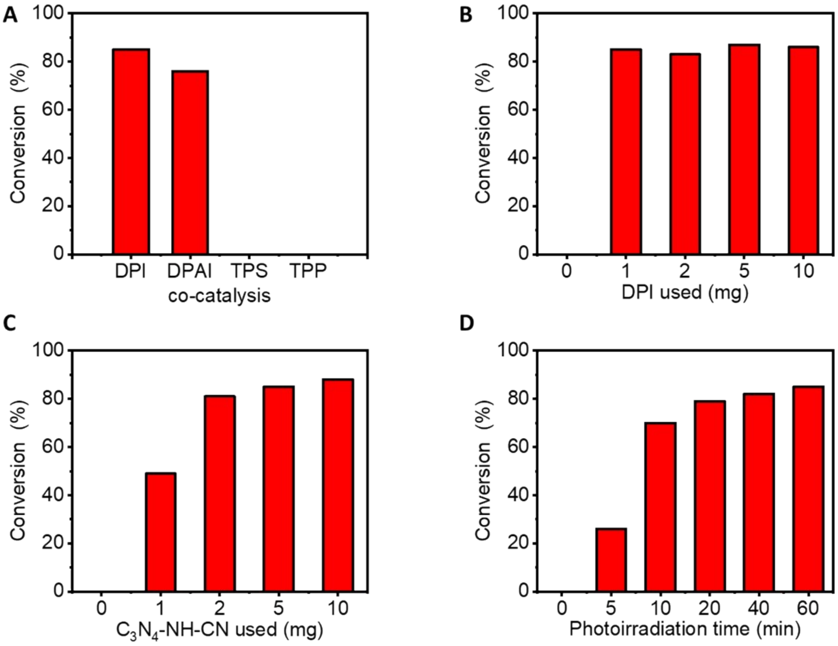


Figure S12. Dark polymerization conversion of DMA with different experimental parameters. (A) Using DPI, DPAI, TPS or TPP as co-catalysis. (B) The amount of DPI used. (C) The amount of C_3N_4-NH-CN nanosheets used for storing electrons. (D) The photoirradiation time for storing electrons.

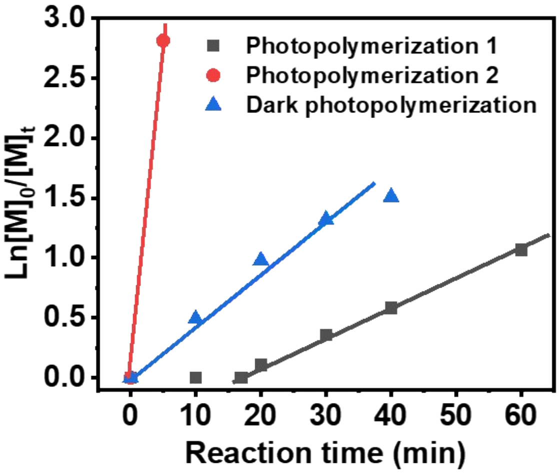


Figure S13. Kinetics plots of polymerization using different method.

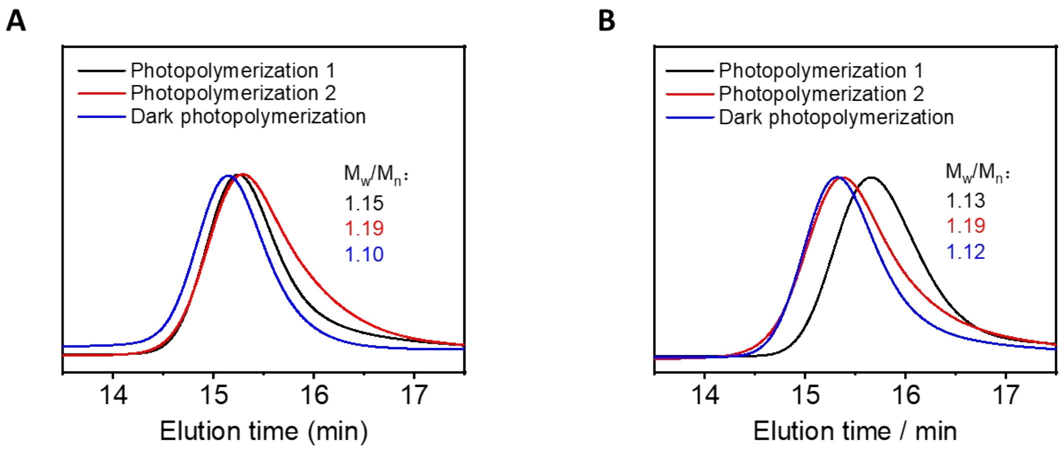


Figure S14. GPC trace of polymers synthesized using different light source. (A) Sun light. (B) UV light. For dark photopolymerization, the sun light and UV light were used for storing electrons.

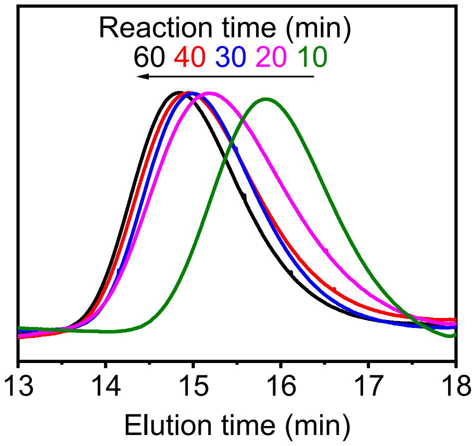


Figure S15. GPC traces of dark photopolymerization at different times corresponding to figure 6B and 6C.

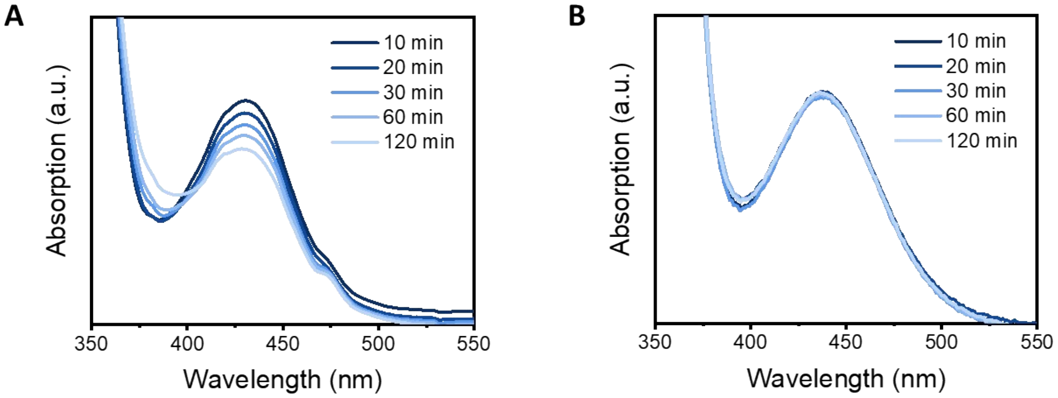


Figure S16. UV-vis spectroscopic evolution of S, S'-bis(α, α'-dimethyl-α''-acetic acid) trithiocarbonate (BDMAT) during polymerization using different polymerization method. (A) polymerization under light condition. (B) polymerization using photo-irradiated C_3N_4-NH-CN under dark condition. (For photopolymerization, the absorption at 430nm decreased significantly with the increase of light time, indicating that BDMAT degraded by uncontrolled radicals during the irradiation process. For polymerization using stored electrons, the absorption at 430 nm did not change with the increase of reaction time, indicating that BDMAT did not degrade during the dark reaction.)

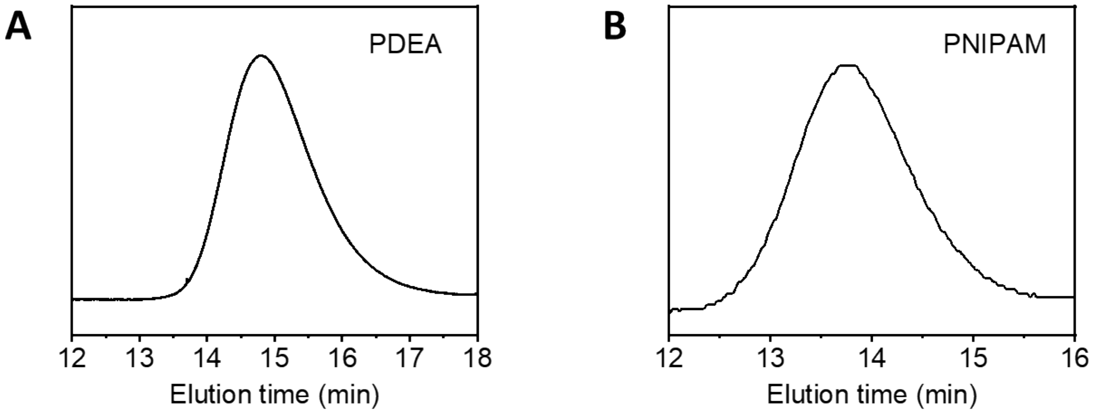


Figure S17. GPC traces of (A) PDEA and (B) PNIPAM.

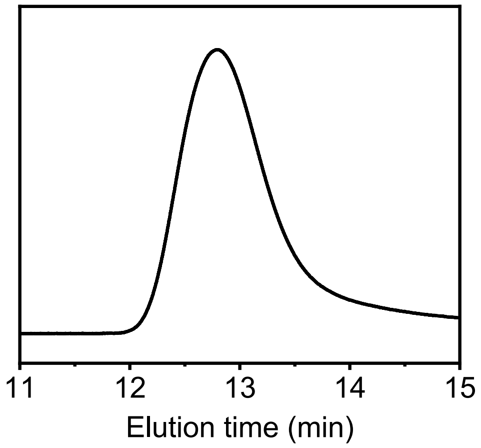


Figure S18. GPC trace of PDEA synthesized from free radical polymerization.

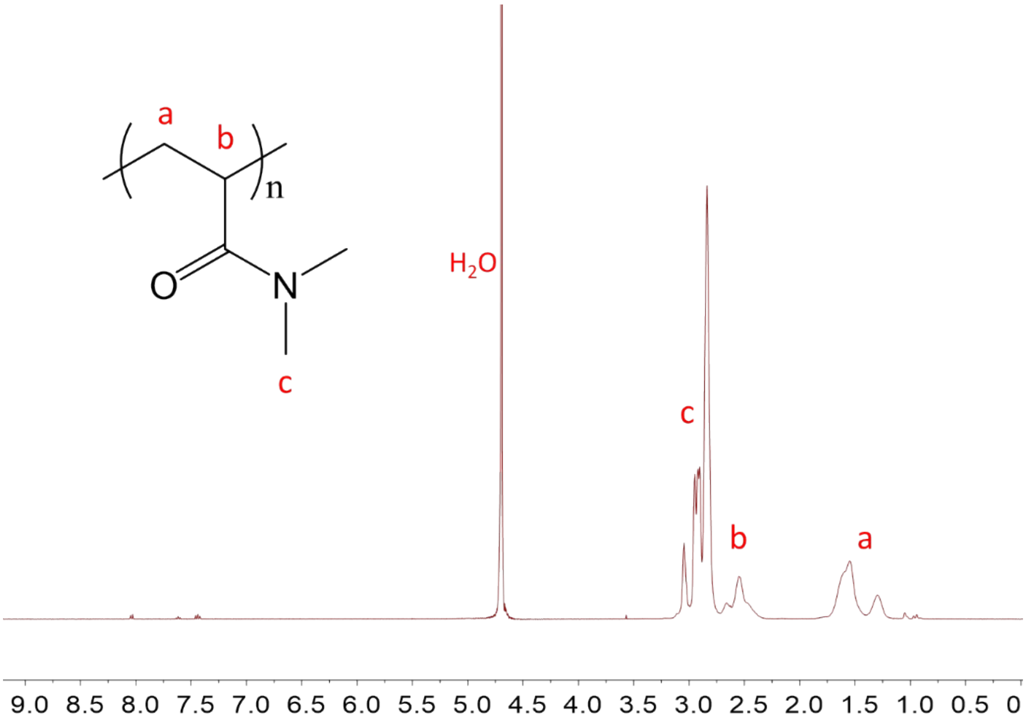


Figure S19. ^{1}H NMR spectrum of isolated PDMA (D_2O).

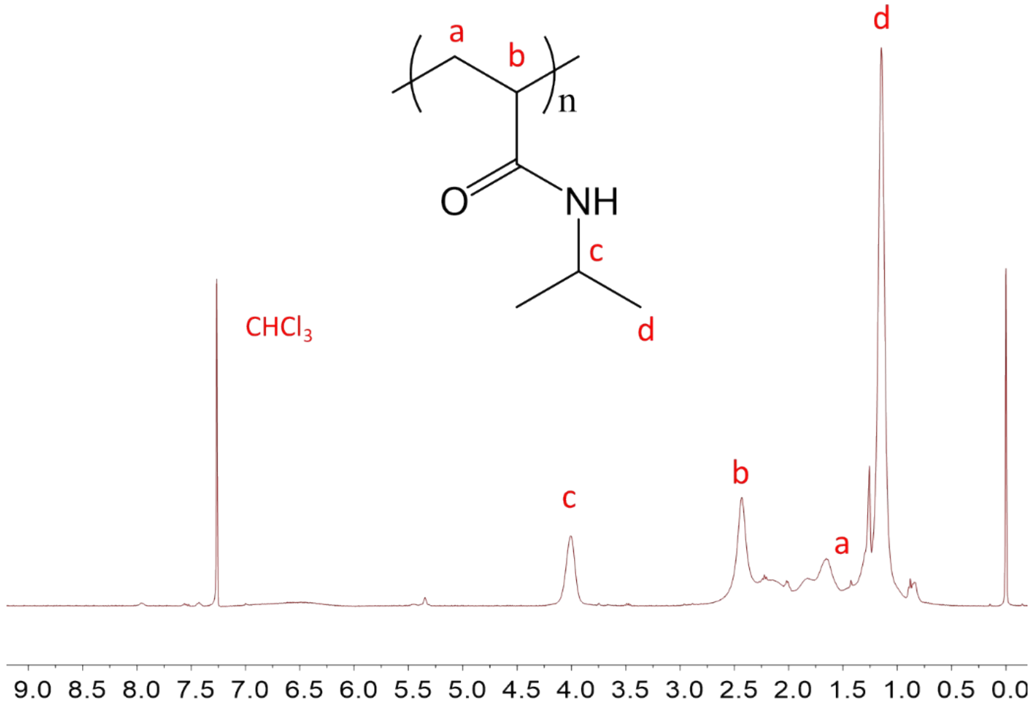


Figure S20. ^{1}H NMR spectrum of isolated PNIPAM ($CDCl_3$).

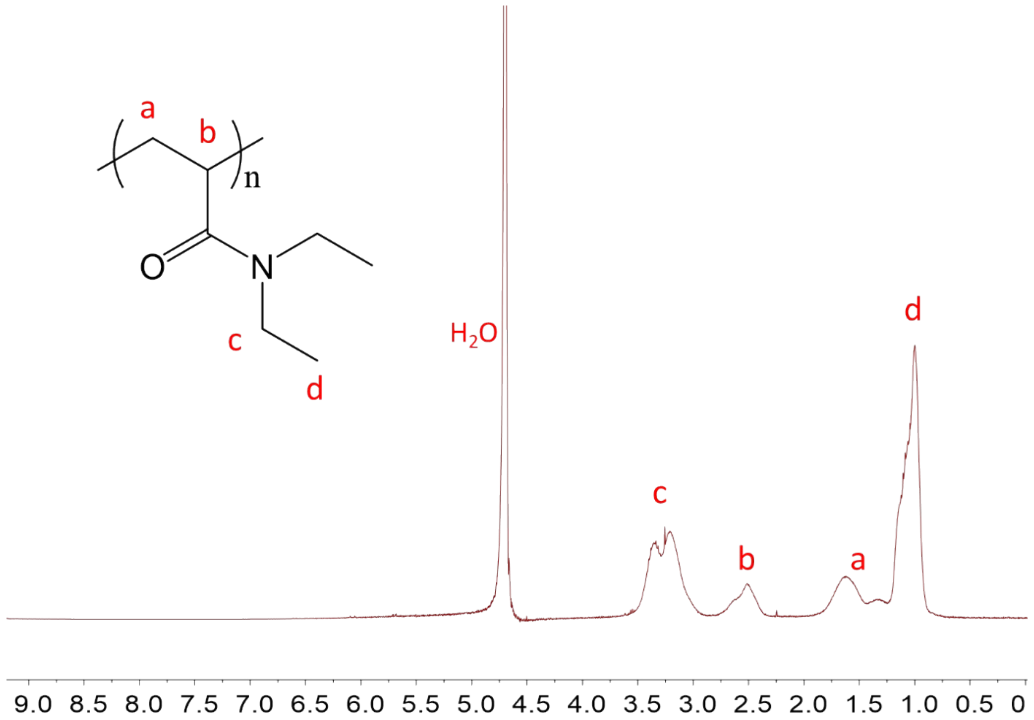


Figure S21. ^{1}H NMR spectrum of isolated PDEA (D_2O).

Table S1. Polymerization of different monomers using stored electrons under dark condition.

	Monomer	RAFT	Time in dark (h)	Con%	$M_{\mathrm{n\ (Theo)}}$	$M_{\mathrm{n\ (GPC)}}$	M_w/M_n
1	DMA	BDMAT	1	83	16600	16500	1.08
2	NIPAM	BDMAT	1	85	21600	25200	1.22
3	DEA	BDMAT	1	78	20100	21000	1.19

Table S2. Polymerization using different polymerization method and light source.

Method	Light source	Irradiation time	Time in dark (h)	Con%	$M_{\mathrm{n\ (Theo)}}$	$M_{\mathrm{n\ (GPC)}}$	M_w/M_n
Photo-polymerization 1	Xe lamp	1	0	60	12200	11800	1.17
	40W UV	1		50	10200	9800	1.13
	Sun light	4		94	19000	18200	1.15
Photo-polymerization 2	Xe lamp	1	0	100	20200	11700	1.25
	40W UV	1		100	20200	16500	1.19
	Sun light	4		100	20200	18000	1.19
Dark Photo-polymerization	Xe lamp	1	1	85	17200	17900	1.08
	40W UV	1		89	18000	17600	1.12
	Sun light	4		86	17400	17600	1.10

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