Supporting Information (SI)

Dual Enhancement of Carrier Generation and Migration on

Au/g-C₃N₄ photocatalysts for High-Efficient Broadband

PET-RAFT Polymerization

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1. Experimental section

Materials

Melamine, urea, hydrogen tetrachloroaurate trihydrate (HAuCl$_4$·3H$_2$O, 99.9%), dimethyl sulfoxide (DMSO, 99.7%, super dry), N,N-dimethyl formamide (DMF, 99%), 4-cyano-4-(thiobenzoylthio)pentanoic acid (CPADB, 99%), 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDTPA, 99%), triethylamine (TEA, AR, 99%), methyl methacrylate (MMA, 99%), methyl acrylate (MA, 99%), benzyl methacrylate (BzMA, 99%), and styrene (St, 99%) were purchased from Aladdin. Toluene (AR) was purchased from Kai Tong. Prior to use, the monomers were passed through basic alumina columns to remove inhibitors. The blue (6W, λ$_{max}$ = 460 nm, 2 mW/cm^2), green (6W, λ$_{max}$ = 532 nm, 1.5 mW/cm^2), red (6W, λ$_{max}$ = 625 nm, 1 mW/cm^2), near-infrared (NIR, λ$_{max}$ = 740 nm, 0.7 mW/cm^2) and white LED (6W, 2 mW/cm^2) were purchased from Rishang Optoelectronics Co. Ltd.

Characterization

Morphology of Au/g-C$_3$N$_4$ was collected on high-resolution TEM with spherical aberration-corrected transmission electron microscope (JEOL, JEM-ARM300F). The monomer conversion was obtained on ^{1}H NMR spectroscopy (Bruker Avance 400 MHz NMR spectrometer), using CDCl$_3$ as the solvent. Gel permeation chromatography (GPC) was performed on SFD2000, using THF as the eluent and calibration with PMMA standards. UV-Vis diffuse-reflectance characterization was conducted on Perkin Elmer Lambda 1050+, with 0.2 g solid samples. Power X-ray diffraction (XRD) were carried out on Pert PRO with a scan step of 2° and the scan range was 20°~80°. And TA thermogravimetric analyzer TGA 55 was utilized for thermal gravimetric

analysis. Photoluminescence (PL) spectra were performed on the Thermo Scientific Lumina fluorescence spectrometer with the excitation wavelength of 380 nm.

Preparation of photocatalyst Au/g-C$_3$N$_4$

Graphite phase carbon nitride (g-C$_3$N$_4$) was prepared according to previous literature report[1]. To be detailed, 20 g melamine was added into the alumina crucible, and calcinated at 550 °C for 3 h (heating rate was 5 °C/min) in a tube furnace to obtain pale yellow solid powder, which was named as g-C$_3$N$_4$.

As for Au/g-C$_3$N$_4$, 100 mL urea solution (0.42 M) and 1 g semiconductor g-C$_3$N$_4$ was filled in a 200 mL flask. 1 mL tetrachloroauric acid solution (HAuCl$_4$, 25.4 mM) was added and stirred for 4 h under 80 °C in the dark. When the flask was cooled to room temperature, the solid matter was collected by centrifugation, washed thrice with distilled water, and dried under vacuum for 12 h. Such solid samples were calcinated at 300 °C for 2 h in a muffle furnace and then grinded properly. The g-C$_3$N$_4$ supported Au NPs heterostructure was obtained, which was named as 1 wt% Au/g-C$_3$N$_4$. Accordingly, by varying the amount of HAuCl$_4$, 6, 10, and 13 wt% Au/g-C$_3$N$_4$ composite photocatalysts were prepared based on the similar procedure.

PET-RAFT polymerization catalyzed by Au/g-C$_3$N$_4$

For a typical PET-RAFT polymerization, photocatalyst Au/g-C$_3$N$_4$ (10 mg), monomer MMA (1 mL, 9.43 mmol, 200 equiv.), chain transfer agent CPADB (13 mg, 0.047 mmol, 1 equiv.), and DMSO (1 mL) were added to 10 mL Schlenk bottle. Then, the system was deaerated through three freeze-pump-thaw cycles and nitrogen was filled. The polymerization was carried out under green light (λ_{max} = 532 nm) at room

temperature. Samples were taken at predetermined timed intervals for GPC and NMR analysis, to measure number-average molecular weight ($M_{n,GPC}$), molecular-weight distribution (PDI = M_w/M_n) and monomer conversion (Conv.).

General procedure for chain extension experiment

The chain extension was performed with 0.85 mL BzMA (884 mg, 5 mmol, 200 equiv.), 10 mg Au/g-C$_3$N$_4$, 210 mg PMMA macroinitiator (0.025 mmol, 1 equiv.) in 1 mL DMSO under nitrogen atomosphere. After stirring for 12 h under green light (λ_{max} = 532 nm), the resulting polymer was precipitated into a large amount of methanol, collected by filtration and washed by methanol. After drying under vacuum at 45 °C for 12 h, block copolymer PMMA-b-PBzMA was obtained.
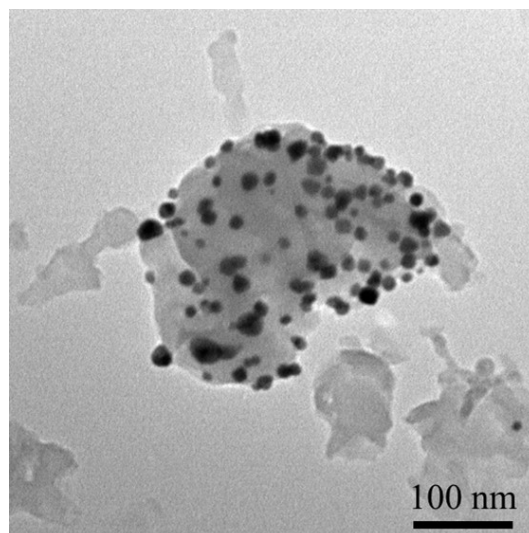
2. TG curves of photocatalysts
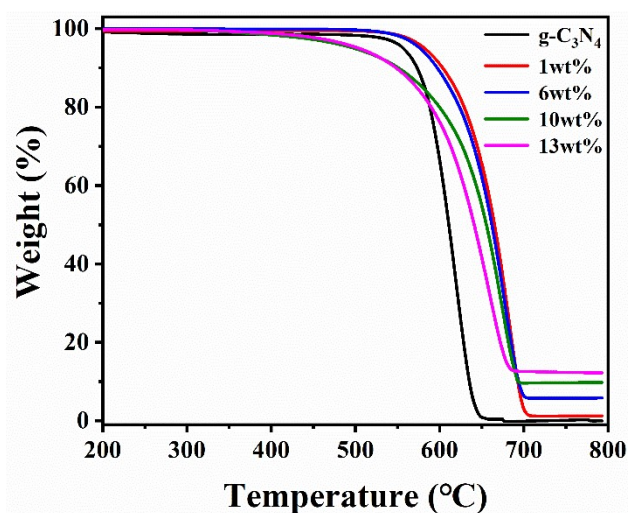
Figure S1. TG curves of g-C$_3$N$_4$ and Au/g-C$_3$N$_4$ with different gold contents at a heating rate of 10 °C/min under N$_2$ atmosphere.
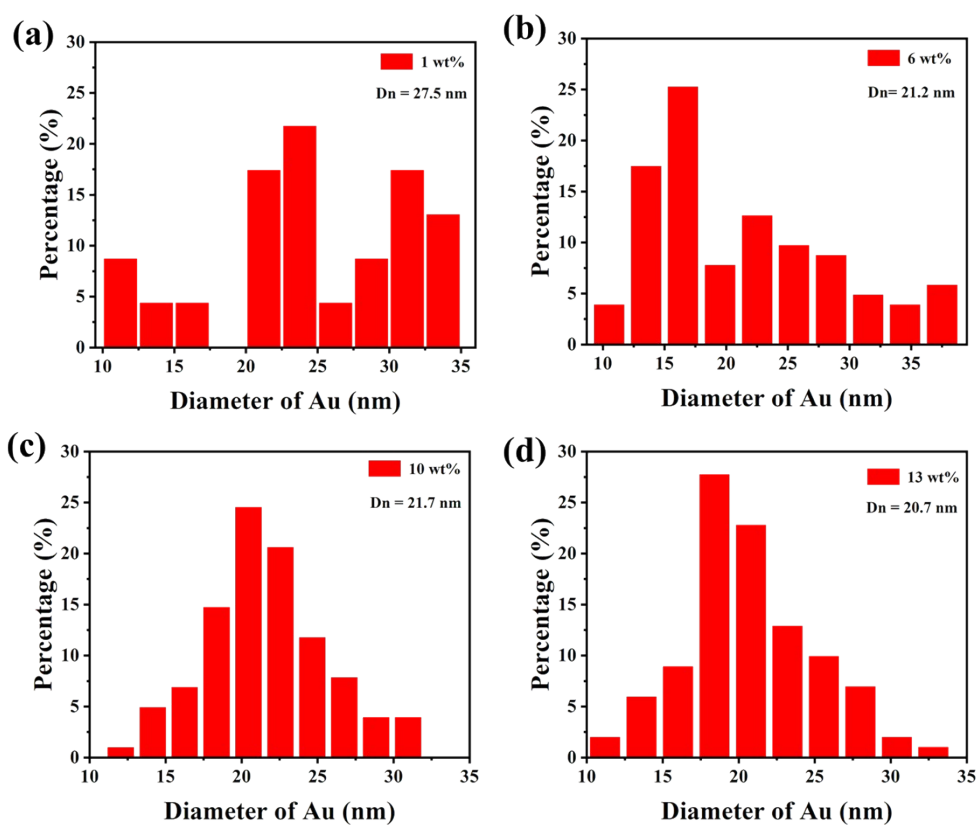
3. TEM images
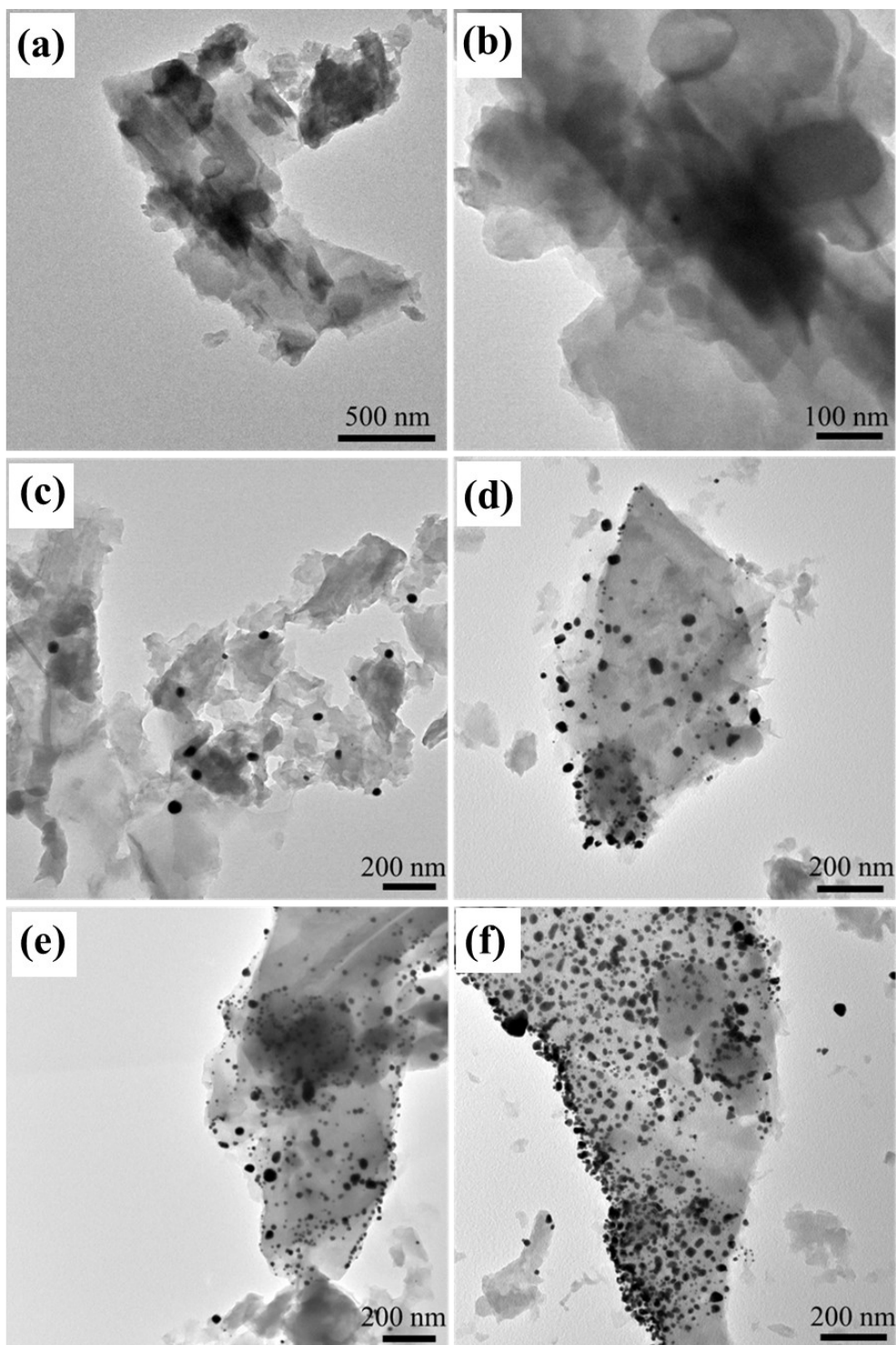
Figure S2. TEM images of g-C$_3$N$_4$ and Au/g-C$_3$N$_4$ with different gold content: (a-b) g-C$_3$N$_4$; (c) 1 wt%, (d) 6 wt%, (e) 10 wt% and (f) 13 wt% Au/g-C$_3$N$_4$.

Figure S3. TEM image of Au/g-C$_3$N$_4$ photocatalyst after PET-RAFT polymerization under green LED light (λ_{max} = 532 nm, 1.5 mW/cm^2) for 20 h in DMSO.

4. Size distribution of Au NPs in Au/g-C$_3$N$_4$

Figure S4. Size distribution of Au NPs in Au/g-C$_3$N$_4$ composites with different gold content: (a) 1 wt%, (b) 6 wt%, (c) 10 wt%, and (d) 13 wt%.
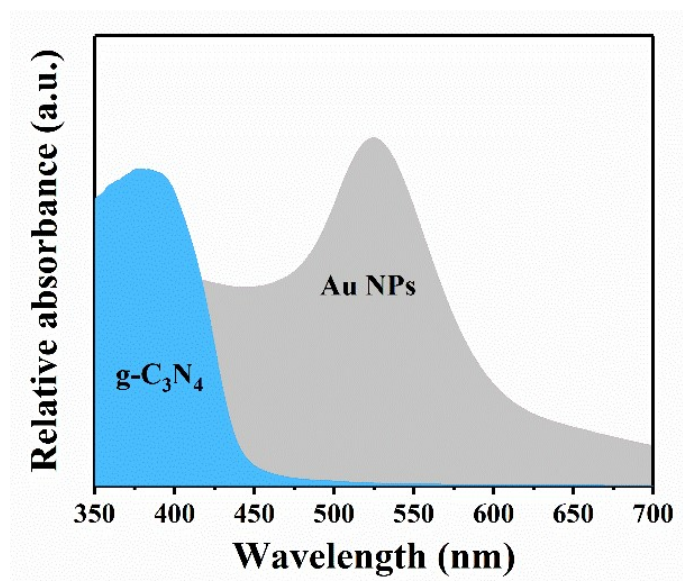
5. Extinction spectra

Figure S5. Extinction spectra of g-C_3N_4 and Au NPs.
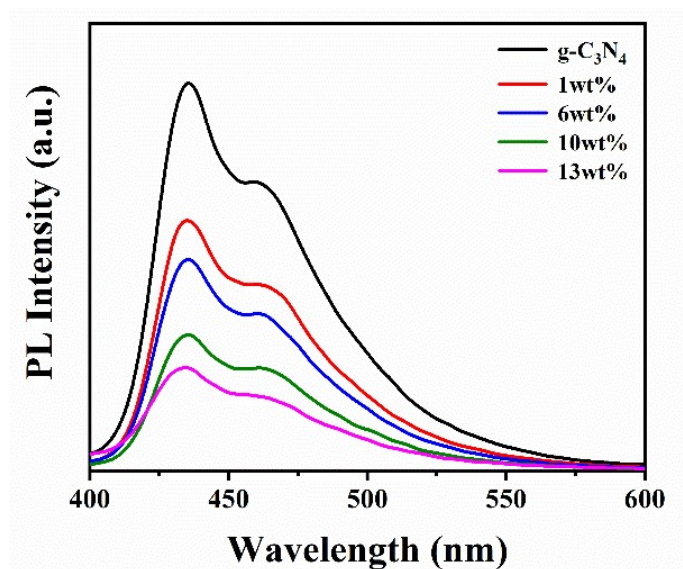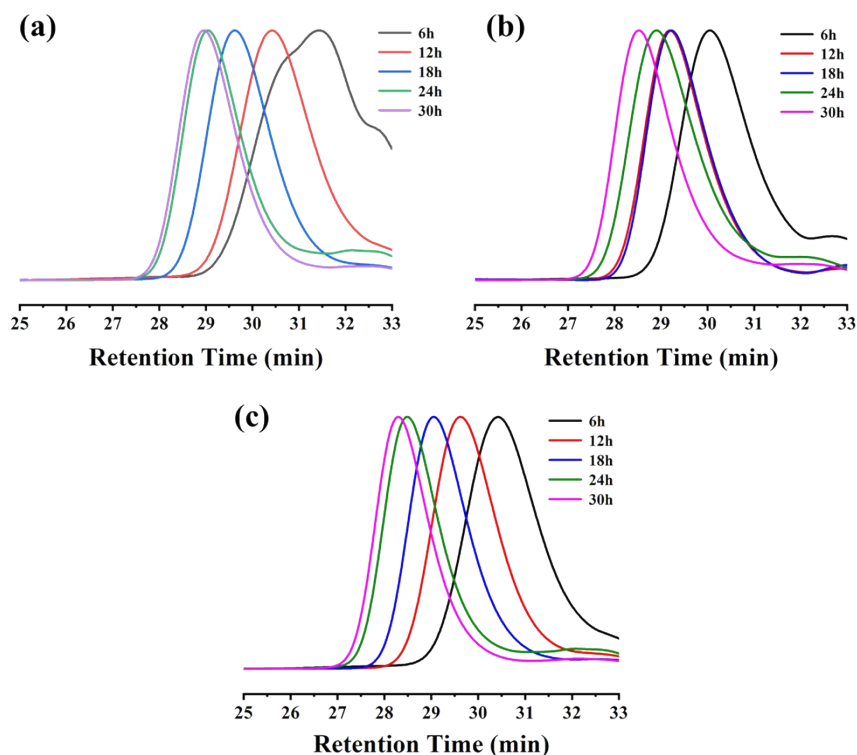
6. Photoluminescence spectroscopy

Figure S6. PL excitation spectra of g-C_3N_4 and Au/g-C_3N_4 with different Au content (0.5 mg/mL in H_2O, λ_{ex} = 380 nm).

7. PET-RAFT polymerization results

Figure S7. GPC traces of PMMA catalyzed by (a) 0.6 mg Au NPs, (b) blending of 0.6 mg Au NPs and 9.4 mg g-C$_3$N$_4$, (c) 10 mg 6 wt% Au/g-C$_3$N$_4$.
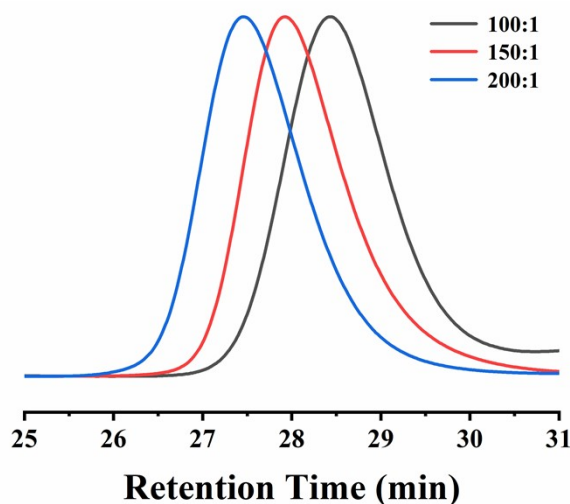
Table S1. 6wt% Au/g-C$_3$N$_4$ catalyzed PET-RAFT polymerization of MMA with different amount of TEA [a].

Entry	[M]:[CTA]:[TEA]	m$_{cat}$(mg)	Time(h)	Conv. [b] (%)	$M_{n,th}$ [c] (kDa)	$M_{n,GPC}$ [d] (kDa)	M_w/M_n [d]
1	200:1:0	10	20	39.9	8.3	5.1	1.23
2	200:1:3	10	20	50.0	10.3	12.1	1.26
3	200:1:6	10	20	68.5	13.8	14.8	1.19
4	200:1:9	10	20	73.6	15.0	19.2	1.24
5	200:1:12	10	20	75.9	15.5	18.5	1.25

[a] Polymerization of MMA was performed in DMSO at room temperature, using CPADB as CTA under green light (λ_{max} = 532 nm, 1.5 mW/cm^2); [b] Monomer conversion was calculated based on ^{1}H-NMR analysis; [c] Theoretical molecular weight was calculated according to the equation: $M_{n,th}$ = [M]$_0$/[CTA]$_0 \times M_W^M \times \alpha + M_W^{CTA}$, where [M]$_0$, [CTA]$_0$, M_W^M, α, and M_W^{CTA} represent the initial

monomer concentration, initial CTA concentration, molar mass of the monomer, conversion, and molar mass of CTA; [d] Molecular weight and dispersity were determined by GPC using THF as eluent.

Figure S8. GPC traces of PMMA catalyzed by 6 wt% Au/g-C$_3$N$_4$ at different feed ration between monomer and RAFT reagent (room temperature, green light).

Table S2. 6 wt% Au/g-C$_3$N$_4$ catalyzed PET-RAFT polymerization of MMA under the absence or presence of oxygen [a].

Entry	[M]:[CTA]:[TEA]	Atmosphere	m_{cat}(mg)	Time (h)	Conv.[b] (%)	$M_{n,th}$[c] (kDa)	$M_{n,GPC}$[d] (kDa)	M_w/M_n[d]
1	200:1:6	N$_2$	10	20	68.5	13.8	14.8	1.19
2	200:1:6	Air	10	20	35.6	7.4	83.8	1.91

[a] The polymerizations were performed in DMSO at room temperature using CPADB as CTA (green light, λ_{max} = 532 nm, 1.5 mW/cm^2); [b] Monomer conversion was calculated based on ^{1}H-NMR analysis; [c] Theoretical molecular weight was calculated according to the equation: $M_{n,th}$ = [M]$_0$/[CTA]$_0$ × M_W^M × α + M_W^{CTA}, where [M]$_0$, [CTA]$_0$, M_W^M, α, and M_W^{CTA} represent the initial monomer concentration, initial CTA concentration, molar mass of the monomer, conversion, and molar mass of CTA; [d] Molecular weight and dispersity were determined by GPC using THF as eluent.

Table S3. 6 wt% Au/g-C$_3$N$_4$ catalyzed PET-RAFT polymerization of MMA with

different RAFT reagents.

Entry	[M]:[CTA]:[TEA]	m_{cat}(mg)	Time(h)	Conv.[c] (%)	$M_{n,th}$[d] (kDa)	$M_{n,GPC}$[e] (kDa)	M_w/M_n[e]
1[a]	200:1:6	10	20	68.5	13.8	14.8	1.19
2[b]	200:1:6	10	3	70.0	14.4	15.5	1.20

[a] The polymerizations were performed in DMSO at room temperature using CPADB as CTA (green light, λ_{max} = 532 nm, 1.5 mW/cm²); [b] The polymerizations were performed in DMSO at room temperature using CDTPA as CTA (green light, λ_{max} = 532 nm, 1.5 mW/cm²); [c] Monomer conversion was calculated based on ¹H-NMR analysis; [d] Theoretical molecular weight was calculated according to the equation: $M_{n,th}$ = [M]$_0$/[CTA]$_0$ × M_W^M × α + M_W^{CTA}, where [M]$_0$, [CTA]$_0$, M_W^M, α, and M_W^{CTA} represent the initial monomer concentration, initial CTA concentration, molar mass of the monomer, conversion, and molar mass of CTA; [e] Molecular weight and dispersity were determined by GPC using THF as eluent.
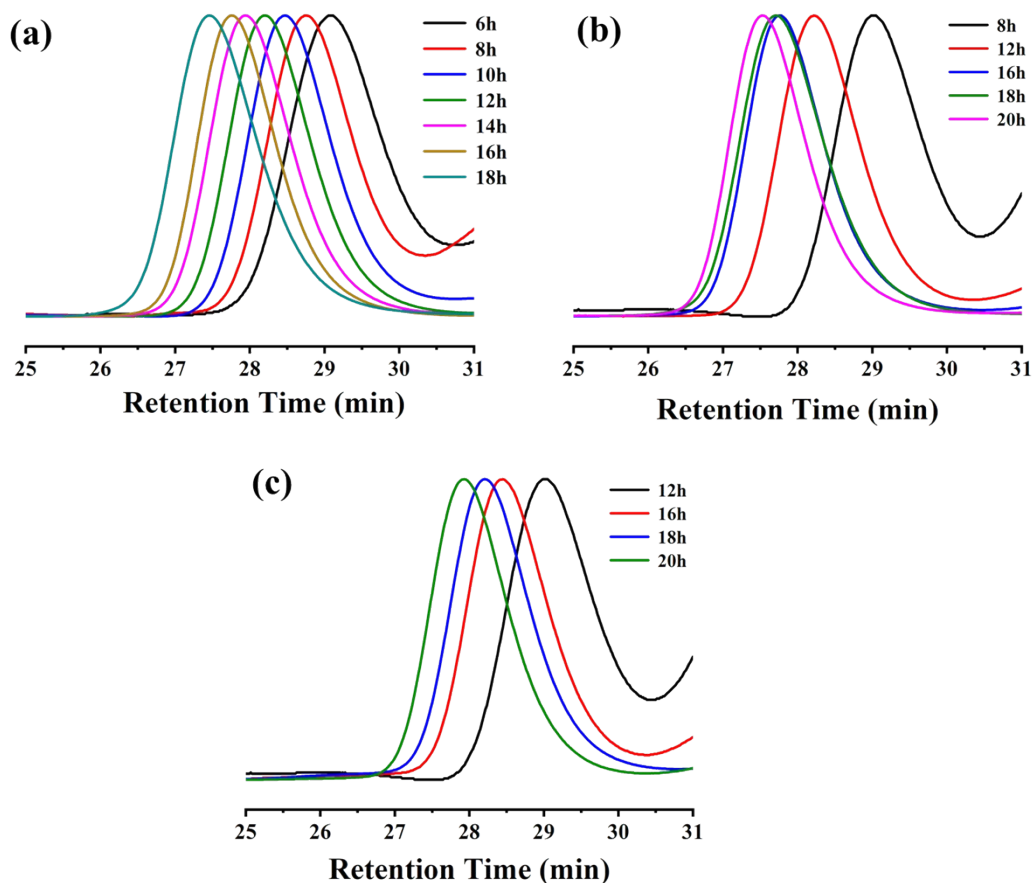
Figure S9. GPC traces of PMMA catalyzed by 6 wt% Au/g-C$_3$N$_4$ in (a) DMSO, (b) DMF and (c) toluene (room temperature, green light).
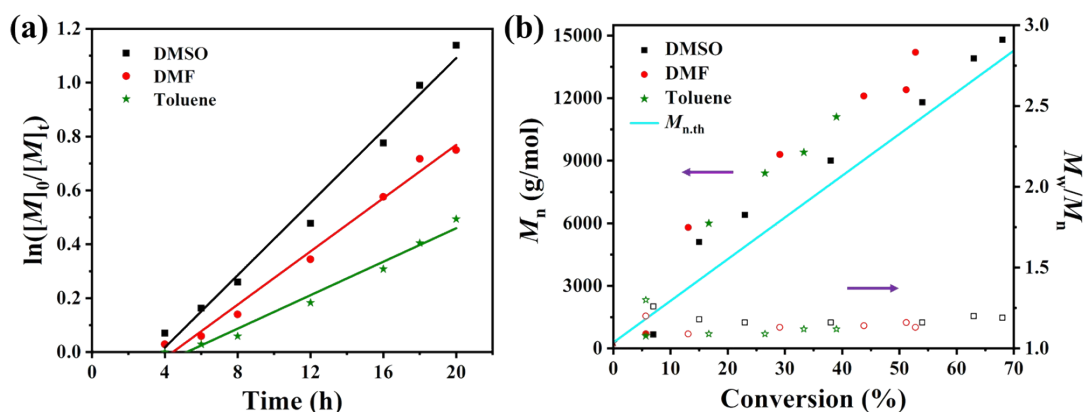
Figure S10. Kinetic plots for PET-RAFT polymerization of MMA catalyzed by 6 wt% Au/g-C$_3$N$_4$ in different solvents: (a) $\ln([M]_0/[M]_t)$ versus time and (b) M_n versus monomer conversion.

Table S4. 6 wt% Au/g-C$_3$N$_4$ catalyzed PET-RAFT polymerization of MMA under different light sources [a].

Entry	λ_{max} (nm)	Time (h)	Conv.[b] (%)	$M_{n,th}$[c] (kDa)	$M_{n,GPC}$[d] (kDa)	M_w/M_n[d]
1	460	20	83.4	16.9	17.1	1.22
2	532	20	68.5	13.8	14.8	1.19
3	625	20	30.9	6.4	6.5	1.21
4	740	20	18.1	3.9	5.7	1.31
5	White	20	63.1	12.9	16.0	1.24

[a] The polymerizations were performed in DMSO at room temperature using CPADB as CTA with 10 mg photocatalyst, [M]:[CTA]:[TEA]=200:1:6; [b] Monomer conversion was calculated based on ^{1}H-NMR analysis; [c] Theoretical molecular weight was calculated according to the equation: $M_{n,th}$ = $[M]_0/[CTA]_0 \times M_W^M \times \alpha + M_W^{CTA}$, where $[M]_0$, $[CTA]_0$, M_W^M, α, and M_W^{CTA} represent the initial monomer concentration, initial CTA concentration, molar mass of the monomer, conversion, and molar mass of CTA; [d] Molecular weight and dispersity were determined by GPC using THF as eluent.

8. Proposed mechanism
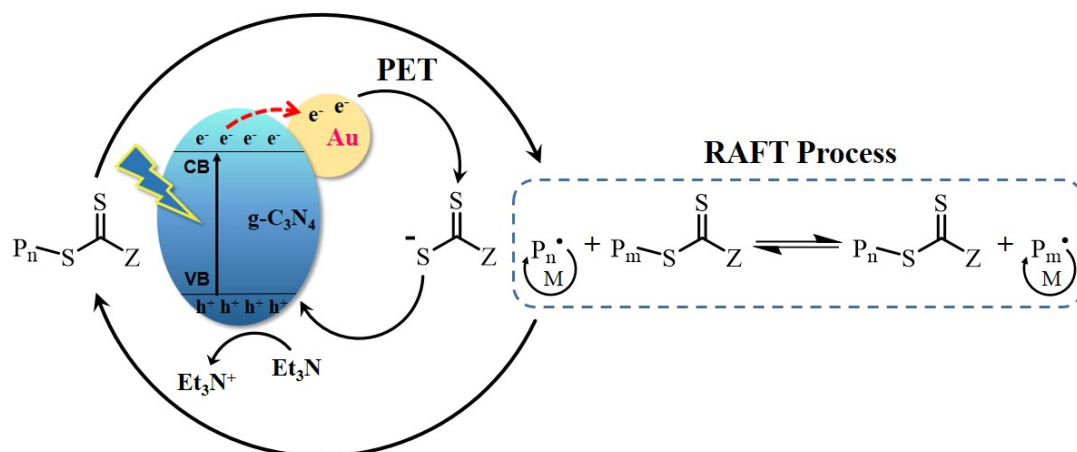
Scheme S1. Proposed mechanism of Au/g-C$_3$N$_4$-catalyzed PET-RAFT

polymerization *via* PIRET-mediation.

9. Reference

(1) Samanta, S.; Martha, S.; Parida, K. Facile Synthesis of Au/g-C$_3$N$_4$ Nanocomposites: An Inorganic/Organic Hybrid Plasmonic Photocatalyst with Enhanced Hydrogen Gas Evolution Under Visible-Light Irradiation. *Chemcatchem* **2014,** *6*, 1453-1462.