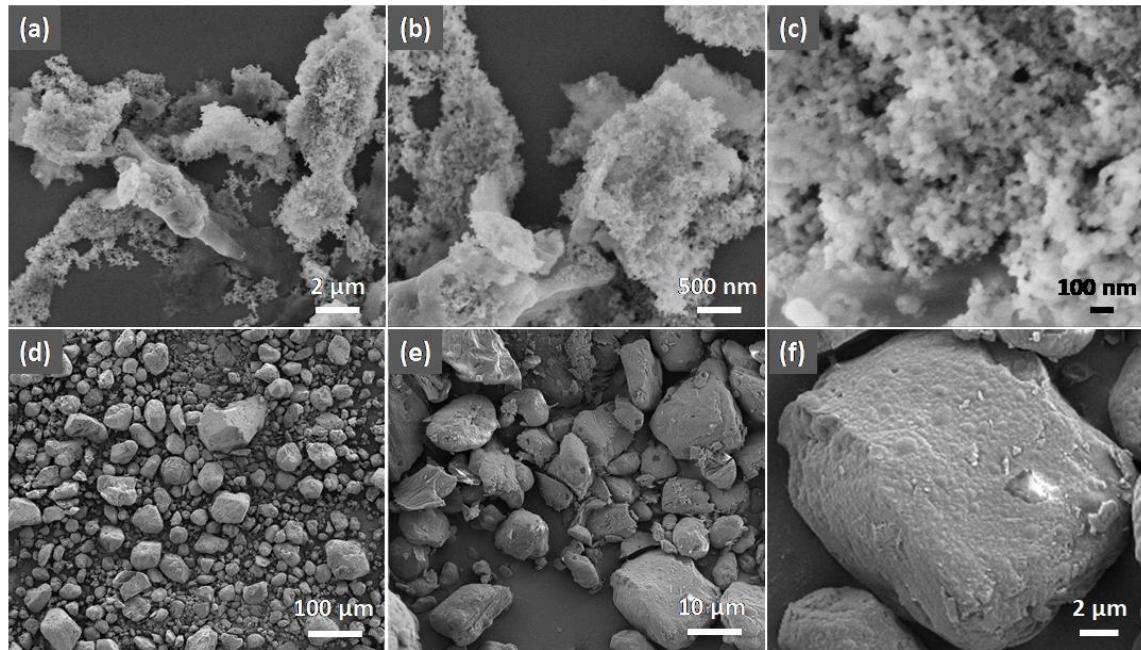


## **Electronic Supplementary Information**

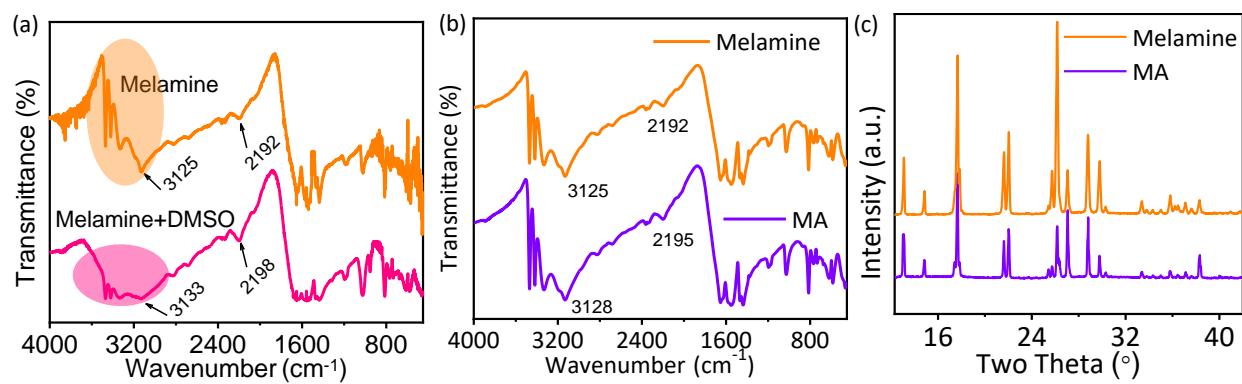
### **Template-free fabrication of hierarchical graphitic carbon nitride via self-assembled aggregates for enhanced photocatalytic hydrogen evolution activity under visible light**

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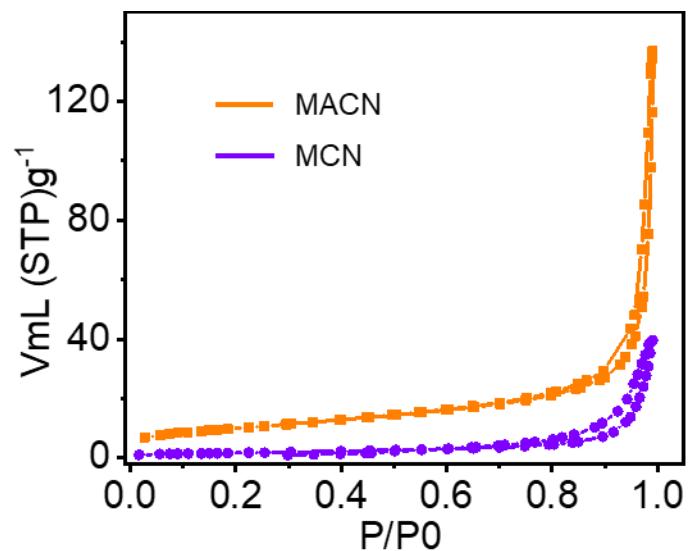
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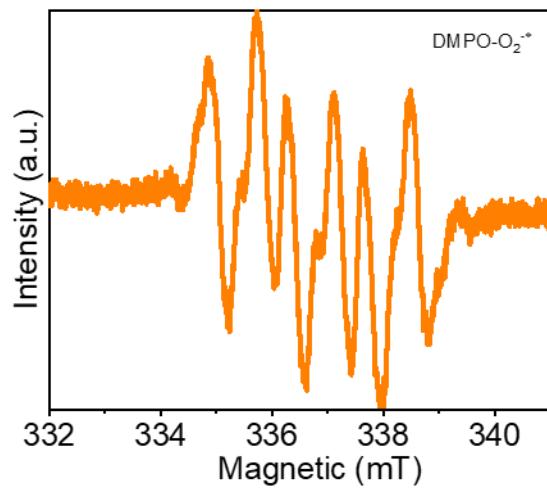
**Fig. S1** Low-resolution (a) and high-resolution (b, c) SEM images of MA; low-resolution (d) and high-resolution (e, f) SEM images of commercial melamine.



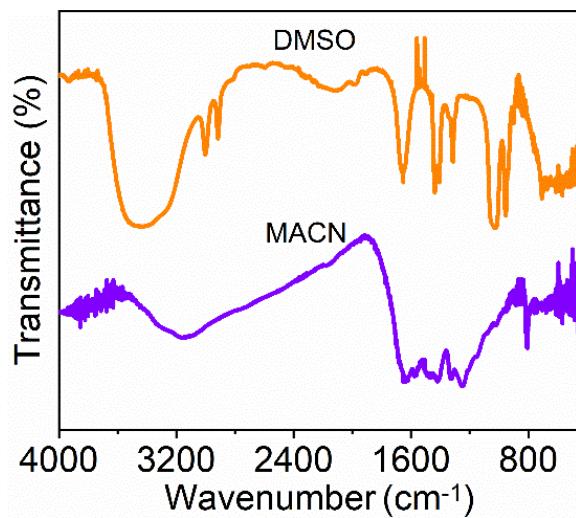
**Fig. S2** (a, b) FT-IR spectra of melamine, “melamine+DMSO”, and MA; (c) XRD pattern of melamine and MA.



**Fig. S3** Brunner Emmet Teller (BET) specific surface area of MCN and MACN.



**Fig. S4** ESR spectrum of DMPO-O<sub>2</sub><sup>-•</sup> for MACN in methanol under light irradiation.



**Fig. S5** FT-IR spectra of DMSO and MACN.

**Table S1** Time-resolved photoluminescence (TR-PL) of MCN and MACN.

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	B <sub>1</sub> (%)	B <sub>2</sub> (%)	$\tau$ (ns)
MACN	1.76	5.86	32.1	67.9	4.84
MCN	2.25	10.2	34.7	65.3	6.04

**Table S2** Comparison of various catalysts for photocatalytic hydrogen evolution reaction.

Photocatalyst	Light source	Co-catalyst	Solution	H <sub>2</sub> /μmol·h <sup>-1</sup> ·g <sup>-1</sup>	AQE /%
g-C <sub>3</sub> N <sub>4</sub> <sup>1</sup>	λ>420 nm	Pt	20 vol% TEOA	5289.9	32.4 (400 nm)
g-C <sub>3</sub> N <sub>4</sub> /In <sub>2</sub> O <sub>3</sub> <sup>2</sup>	λ≥420 nm	Au	10 vol% MeOH	5648	2.5
g-C <sub>3</sub> N <sub>4</sub> / graphdiyne <sup>3</sup>	λ>420 nm	Pt	15 vol% TEOA	792	-
g-C <sub>3</sub> N <sub>4</sub> <sup>4</sup>	λ>420 nm	Ni <sub>2</sub> P	10 vol% TEOA	2849.5	18.8 (420 nm)
g-C <sub>3</sub> N <sub>4</sub> <sup>5</sup>	λ>420 nm	Pt	10 vol% TEOA	1619	-
g-C <sub>3</sub> N <sub>4</sub> <sup>6</sup>	λ>420 nm	Pt	10 vol% TEOA	1540	1.1 (420 nm)
g-C <sub>3</sub> N <sub>4</sub> <sup>7</sup>	λ>400 nm	-	TEOA	28000	23.3 (420 nm)
g-C <sub>3</sub> N <sub>4</sub> <sup>8</sup>	UV-visible	Pt	10 vol% TEOA	66 (0.3 g)	-
g-C <sub>3</sub> N <sub>4</sub> <sup>9</sup>	λ>420 nm	Pt	10 vol% TEOA	13 (0.1 g)	-
g-C <sub>3</sub> N <sub>4</sub> <sup>10</sup>	λ≥420 nm	Pt/CoTPP	10 vol% TEOA	46.9 (0.05 g)	-
g-C <sub>3</sub> N <sub>4</sub> <sup>11</sup>	λ≥400 nm	Fe <sub>2</sub> N	10 vol% TEOA	88.7	-
g-C <sub>3</sub> N <sub>4</sub> <sup>12</sup>	Solar light	Carbon/Pt	5 vol% TEOA	5573	-
g-C <sub>3</sub> N <sub>4</sub> <sup>13</sup>	λ>420 nm	Ni	25 vol% TEOA	2989.5	-
g-C <sub>3</sub> N <sub>4</sub> <sup>14</sup>	UV-visible	Cu/THPP	16.7 vol% TEOA	7.5 (0.01 g)	-
g-C <sub>3</sub> N <sub>4</sub> <sup>15</sup>	λ≥420 nm	NHPI/Pt	10 vol% TEOA	1145.4	4.86 (420 nm)
g-C <sub>3</sub> N <sub>4</sub> <sup>16</sup>	λ≥400 nm	Pt	10 vol% TEOA	793 (2 mg)	-
Our work	λ≥420 nm	Pt	15 vol% TEOA	164 (50 mg)	1.4%

**Table S3** BET surface area of MCN and MACN.

Sample	Specific surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )
MCN	6.0
MACN	35.3

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