Single-crystalline Melem ($C_6N_{10}H_6$) Nanorods: A Novel Stable Molecular Crystal Photocatalyst with Modulated Charge Potentials and Dynamics

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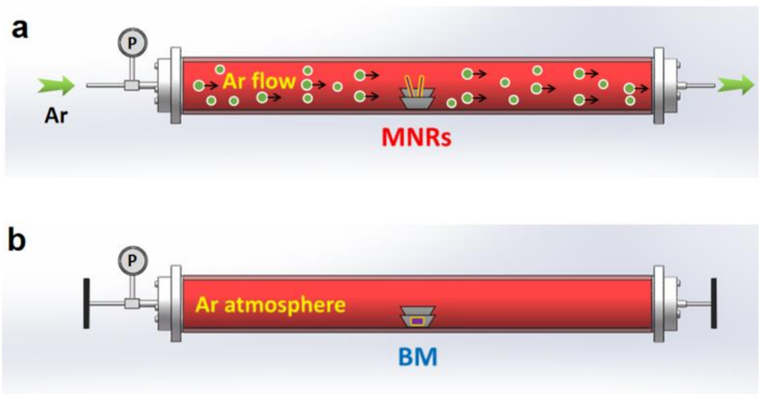


Fig. S1 Schematic illustrations of synthetic routes for (a) MNRs and (b) BM.

Table S1 Observed and calculated distances of crystalline planes of melem nanorods (MNRs). The calculation is based on the CIF file of melem reported in Ref .1.

Formula	$H_6N_7(NH_2)_3$
Space group	$p2_1/c$ (no. 14)

H K L	**DOBS (Å)**	**DCAL (Å)**	**2TH.OBS (degree)**	**2TH.CAL (degree)**
1 0 0	7.3255	7.2887	12.072	12.133
0 1 1	7.1393	7.2336	12.388	12.226
0 0 2	6.6873	6.5909	13.229	13.423
-1 0 2	5.3481	5.3701	16.562	16.494
1 1 1	4.8459	4.9077	18.292	18.061
-1 1 2	4.5415	4.5628	19.53	19.439
1 1 2	4.0373	4.0043	21.998	22.182
1 2 0	3.738	3.7204	23.784	23.899
1 2 1	3.5343	3.501	25.177	25.421
-2 -1 1	3.4049	3.3857	26.15	26.302
0 0 4	3.2821	3.2955	27.147	27.035
1 1 3	3.2361	3.2491	27.54	27.428
-1 1 4	3.0035	3.0161	29.72	29.594
-1 2 3	2.9353	2.971	30.427	30.054
1 0 4	2.8533	2.8257	31.324	31.638
1 2 3	2.716	2.7237	32.952	32.856
-1 -3 1	2.6684	2.6612	33.557	33.65
1 3 1	2.5941	2.5962	34.547	34.52
1 2 4	2.3631	2.3658	38.048	38.003

(* 2Theta < 40°)

Fig. S2a and **S3**e show the SEM images of melamine and g-C_3N_4 synthesized at 550 ℃ for 2 h, respectively. **Fig. S3** also shows the SEM images of carbon nitride samples obtained at different temperatures. When the raw materials were annealed at 300 ℃, massive crystals were obtained. **Fig. S3**a shows that melamine could be stable under 300 ℃. **Fig. S3**b and S3c show that the original morphology of melamine gradually broken at a processing temperature of 350 ℃, which then transformed into thick plates mixed with some rods at 400 ℃. As the annealing temperature was increased to 500 ℃, the nanorods disappeared and micro-sized particles with irregular shape were obtained (**Fig. S3**d).

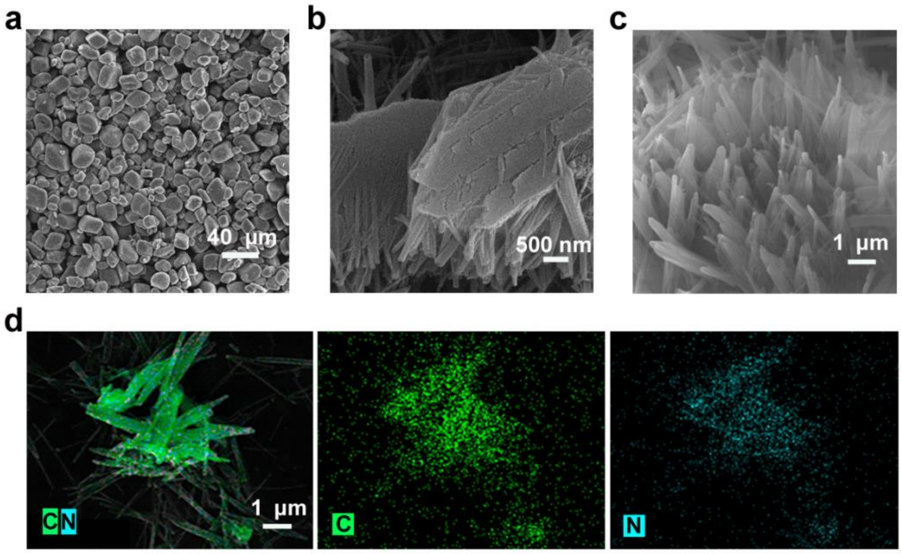


Fig. S2 SEM images of (a) raw material melamine, (b) products synthesized at 450 ℃ for 10 min, and (c) products prepared at 450 ℃ for 120 min. (d) EDS elemental mapping images of MNRs.

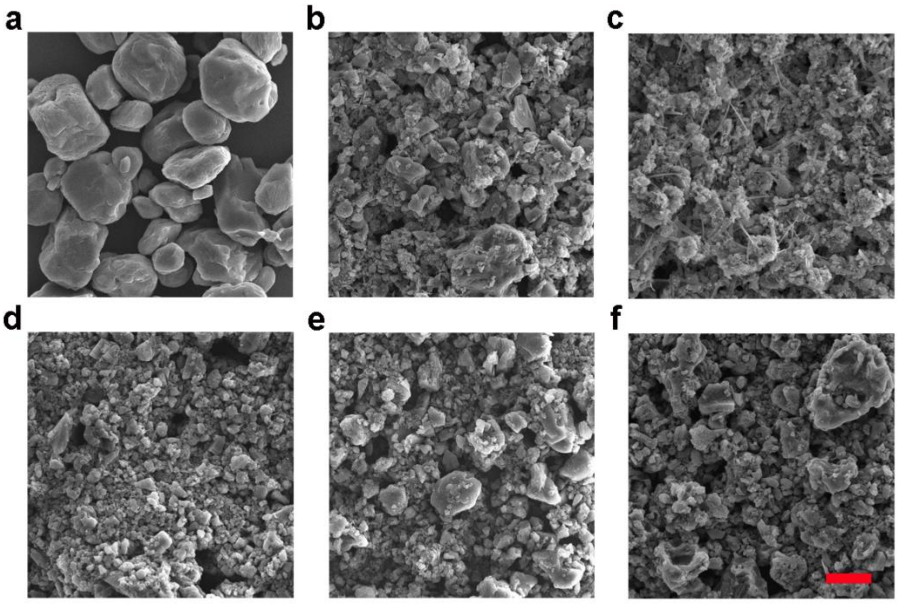
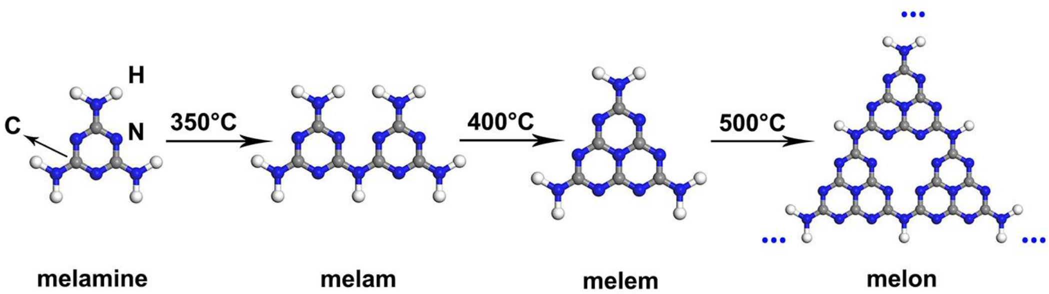


Fig. S3 SEM images of carbon nitride samples obtained at different temperatures, (a) 300 ℃, (b) 350 ℃, (c) 400 ℃, and (d) 500 ℃. SEM images of (e) g-C_3N_4 synthesized at 550 ℃ and (f) BM synthesized at 450 ℃. The scale bar represents 10 μm.



Scheme S1 Formation of carbon nitrides during the thermal polymerization of melamine, proposed by Ref. 2.

The thermal polymerization of melamine is shown in **Scheme S1**,[2] indicating that as the pyrolysis temperature was gradually increased, the C–N rings became connected to yield melam, melem, and melon. However, C–N hexagonal ring remained undestroyed, exhibiting a higher stability.

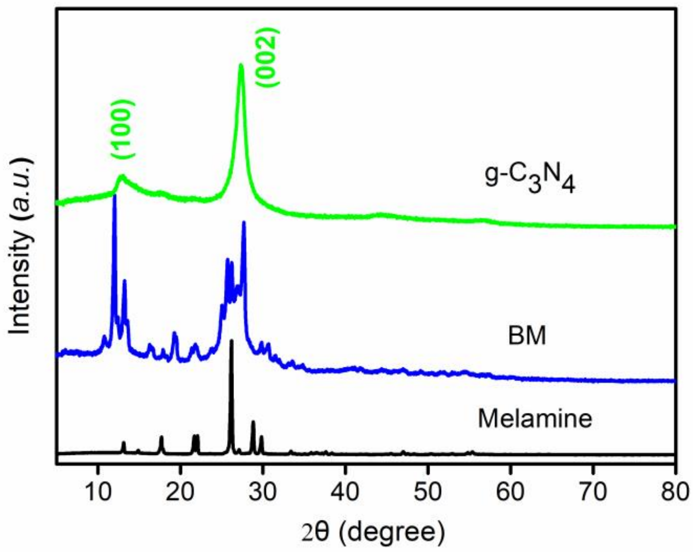


Fig. S4 XRD patterns of the as-synthesized g-C_3N_4, BM, and the raw melamine.

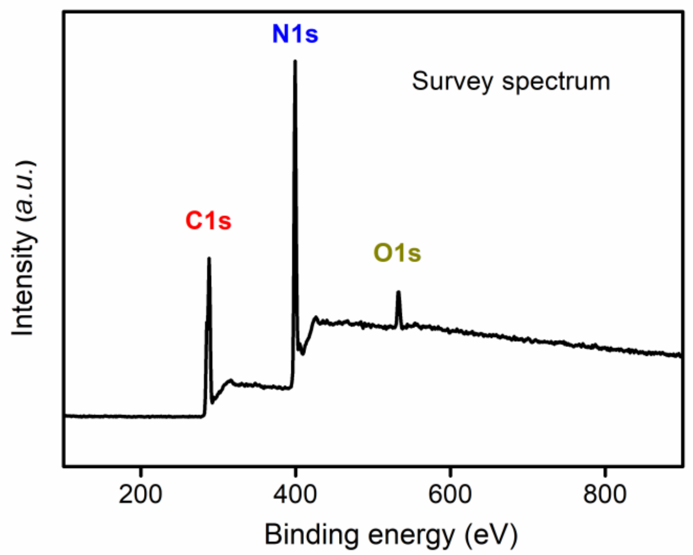


Fig. S5 XPS survey spectrum of MNRs.

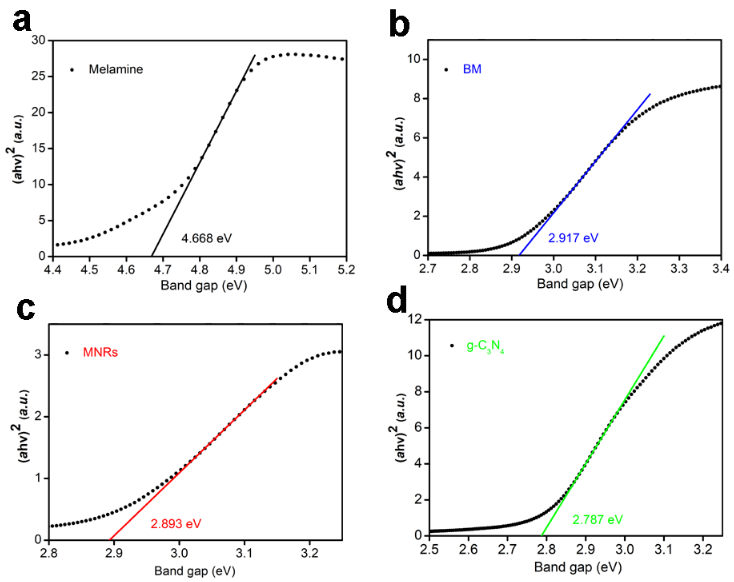


Fig. S6 Fitted Tauc plots of: (a) melamine, (b) BM, (c) MNRs, and (d) $g-C_3N_4$.

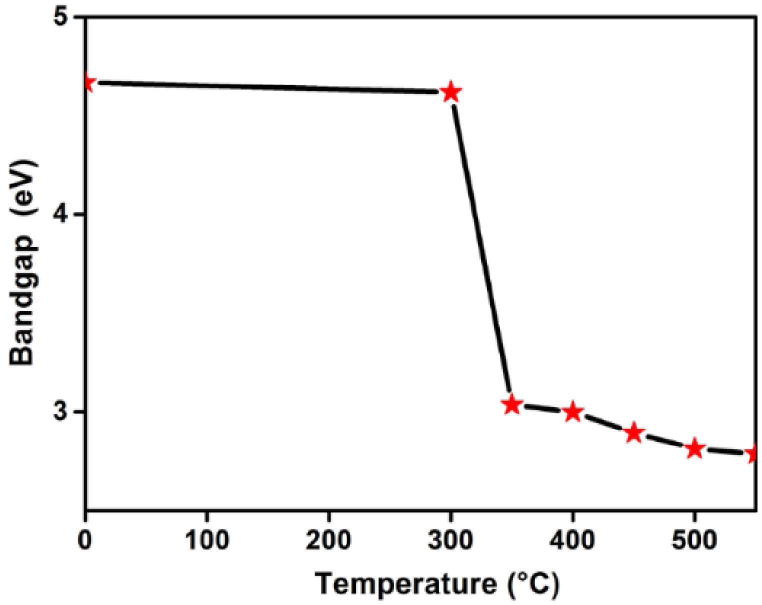


Fig. S7 Temperature-dependent bandgap of carbon nitride products via the pyrolysis of melamine.

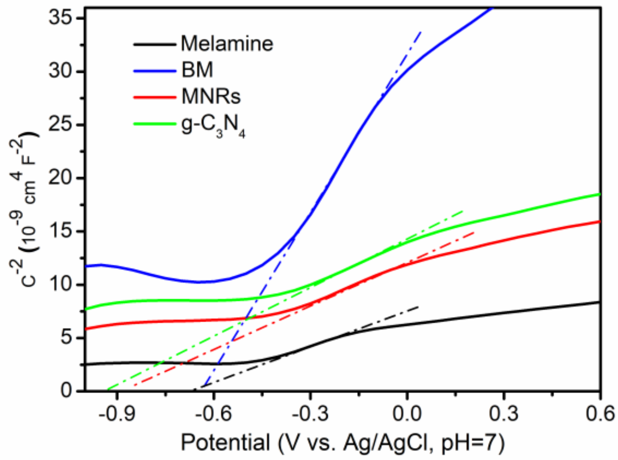


Fig. S8 Mott–Schottky plots of melamine, BM, MNRs, and g-C_3N_4.

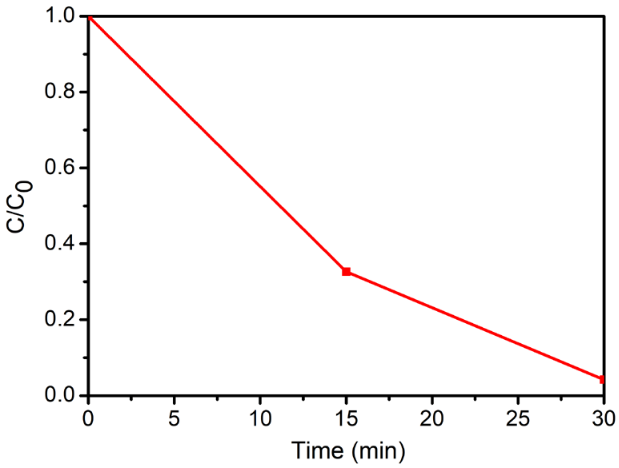


Fig. S9 Time-dependent photocatalytic degradation of RhB on MNR photocatalysts under low-temperature environment (0–3 °C).

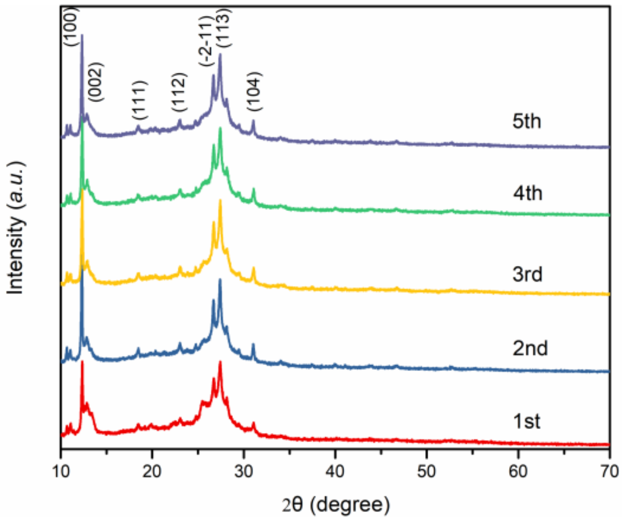


Fig. S10 XRD patterns of MNRs after each cycling test of photocatalytic degradation of RhB.

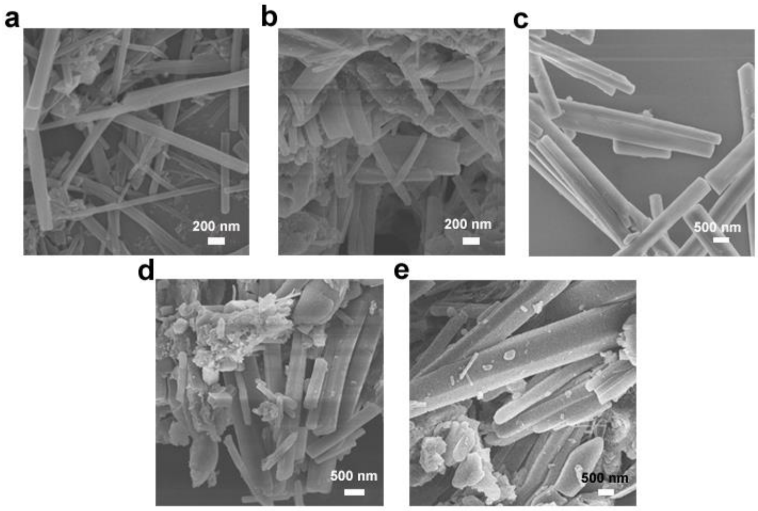


Fig. S11 SEM images of MNRs after each cycling test of photocatalytic degradation of RhB. (a) first, (b) second, (c) third, (d) fourth, and (e) fifth cycle.

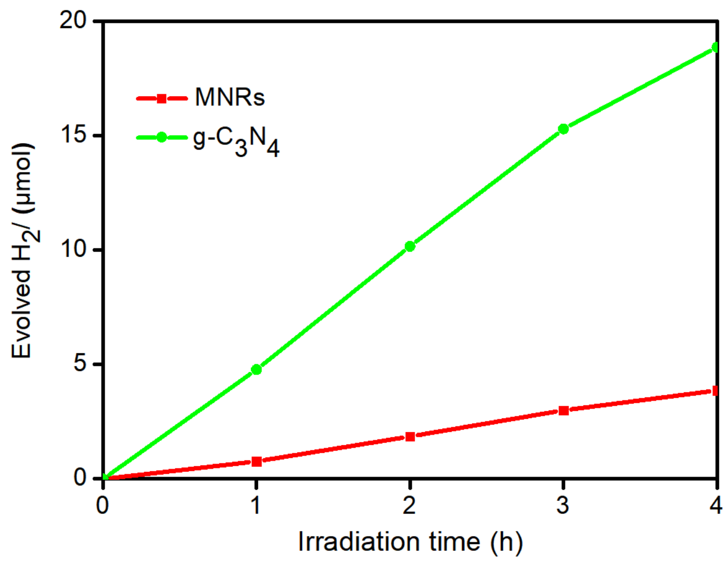


Fig. S12 Time course of H_2 evolution from a 10 vol% aqueous triethanolamine solution by 0.1 wt% Pt-loaded MNRs and g-C_3N_4 under visible-light irradiation.

References

[1] B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller and W. Schnick, *J. Am. Chem. Soc.*, 2013, **125**, 10288-10300.

[2] X.C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76-80.