Electronic Supplementary Information

Accelerated photocatalytic hydrogen evolution over donor-acceptor type graphitic carbon nitride (g-CN) with simultaneous modification of pyrimidine and thiophene rings

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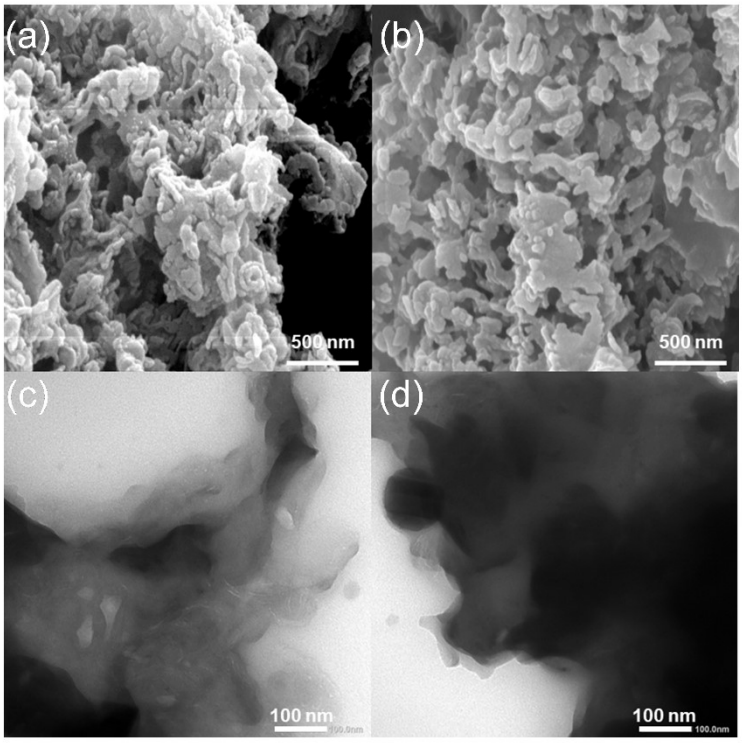

Fig. S1. The SEM images of (a) UPDB-5, and (b) UPDB-30. The TEM images of (c) UPDB-5, and (d) UPDB-30.

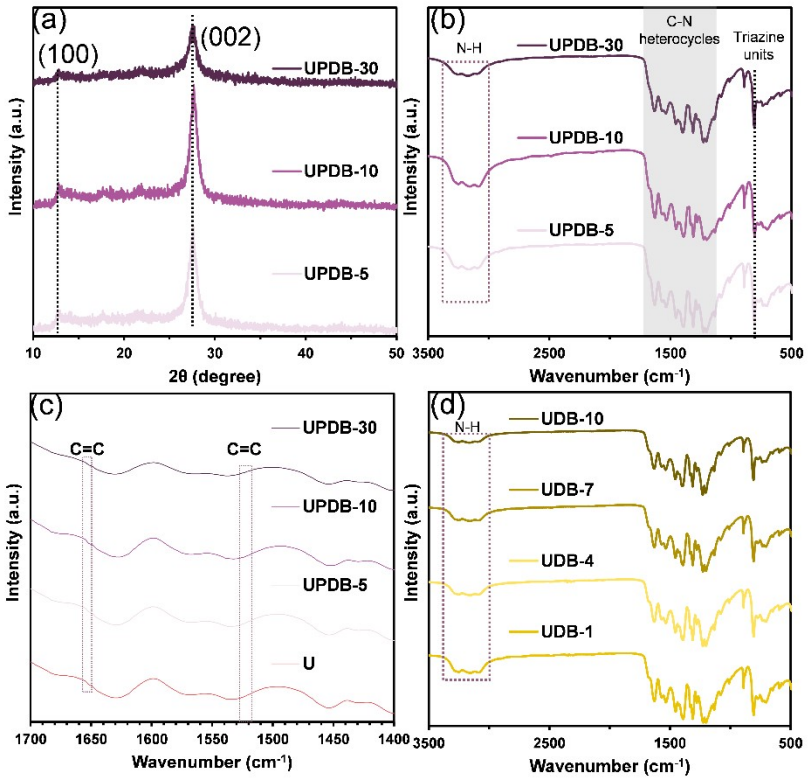

Fig. S2. (a) XRD patterns of each sample. FT-IR spectra of (b) each g-CN, (c) within 1400-1700 cm^{-1} range, and (d) effect of varying DB amounts.

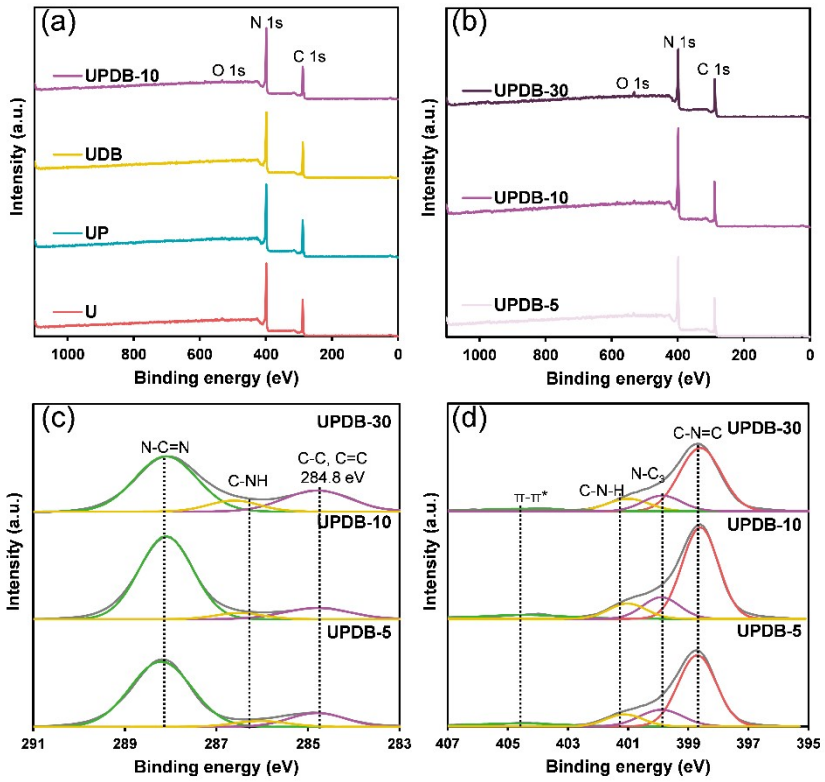

Fig. S3. The XPS survey spectra of (a) each precursor, and (b) amounts of pyrimidine. The XPS narrow spectra of (c) C 1s, and (d) N 1s.

Table S1. Surface atomic ratios of U, UP, UDB, UPDB-5, UPDB-10, and UPDB-30.

Sample	C (%)	N (%)	C/N molar ratio
U	42.0	58.0	0.724
UP	44.0	56.0	0.786
UDB	42.9	57.1	0.751
UPDB-5	44.8	55.2	0.812
UPDB-10	44.7	55.3	0.808
UPDB-30	46.8	53.2	0.880

Table S2. Proportion of each peak in C 1s and N 1s of each sample.

Sample	C 1s (%)	N 1s (%)					
	N=C-N	C=C, C-C	C-NH	π-π^*	C-N=C	C-N-H	N-C_3
U	90.4	3.6	5.9	5.5	70.4	13.8	10.2
UP	82.8	9.6	7.6	4.5	71.2	7.0	17.2

UDB	92.5	4.9	2.6	6.9	67.5	7.4	18.2
UPDB-5	78.8	15.1	6.1	6.3	65.7	10.7	17.3
UPDB-10	81.0	13.7	5.3	6.8	66.1	11.4	15.8
UPDB-30	63.4	26.2	10.4	5.3	66.6	13.1	15.1

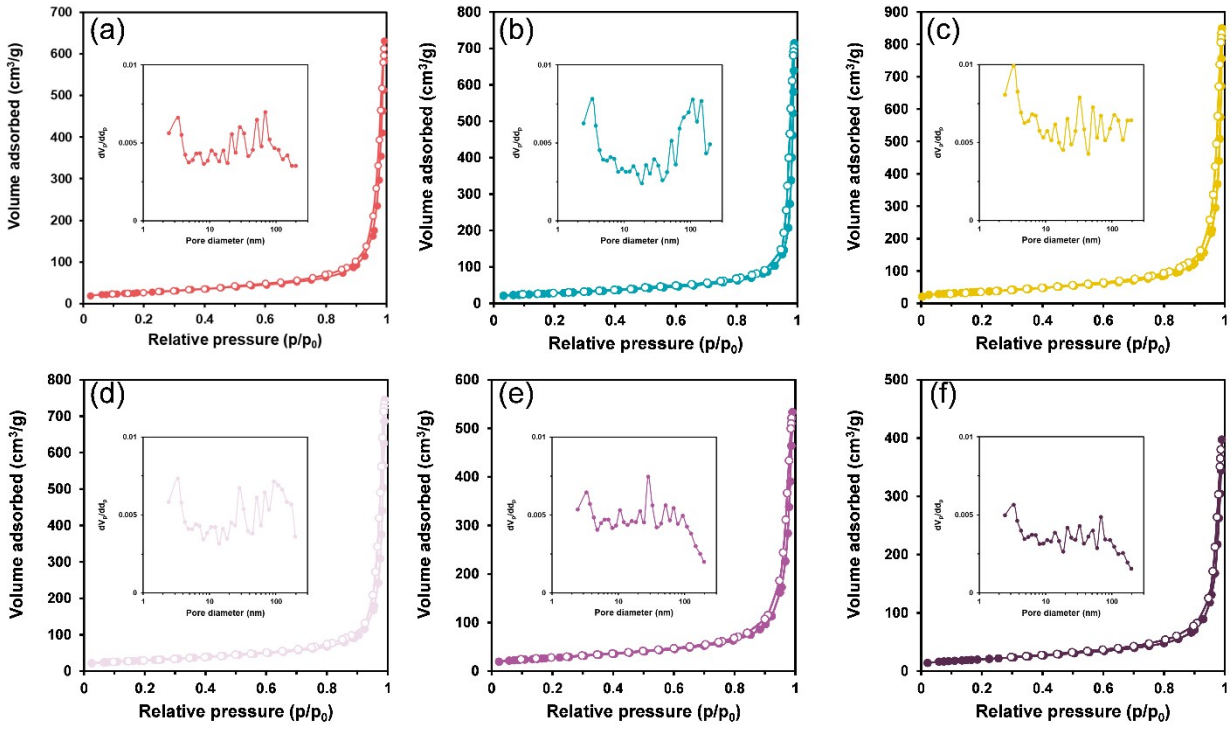

Fig. S4. The BET surface areas from N_2 adsorption-desorption isotherms and the BJH pore diameter distribution plots of (a) U, (b) UP, (c) UDB (d) UPDB-5, (e) UPDB-10, and (f) UPDB-30.

Table S3. BET specific surface area, total pore volume, and average pore diameter of U, UP, UDB, UPDB-5, UPDB-10, and UPDB-30.

Sample	S_{BET} (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
U	96.3	0.92	38.2
UP	97.0	1.10	45.5
UDB	128	1.24	38.8
UPDB-5	105.2	1.13	43.0
UPDB-10	97.0	0.82	33.7
UPDB-30	73.0	0.60	33.0

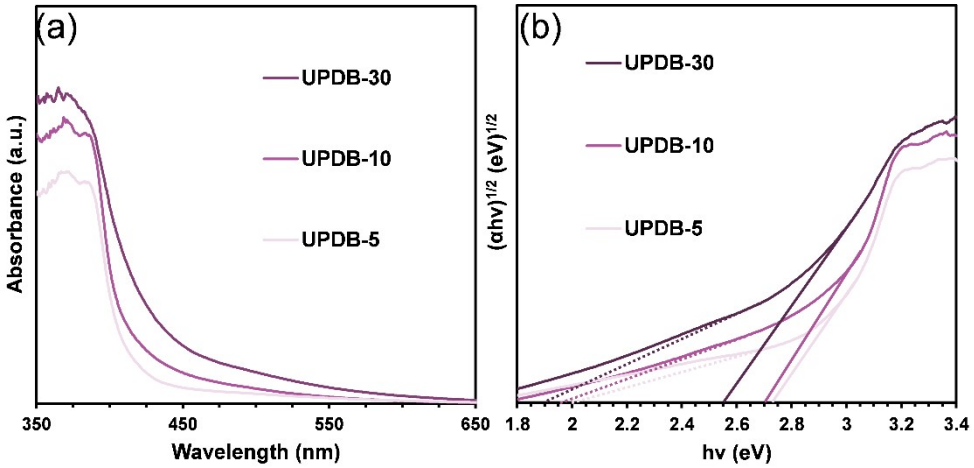

Fig. S5. (a) The Uv-Vis DRS spectra, and (b) tauc plots of each g-CN.

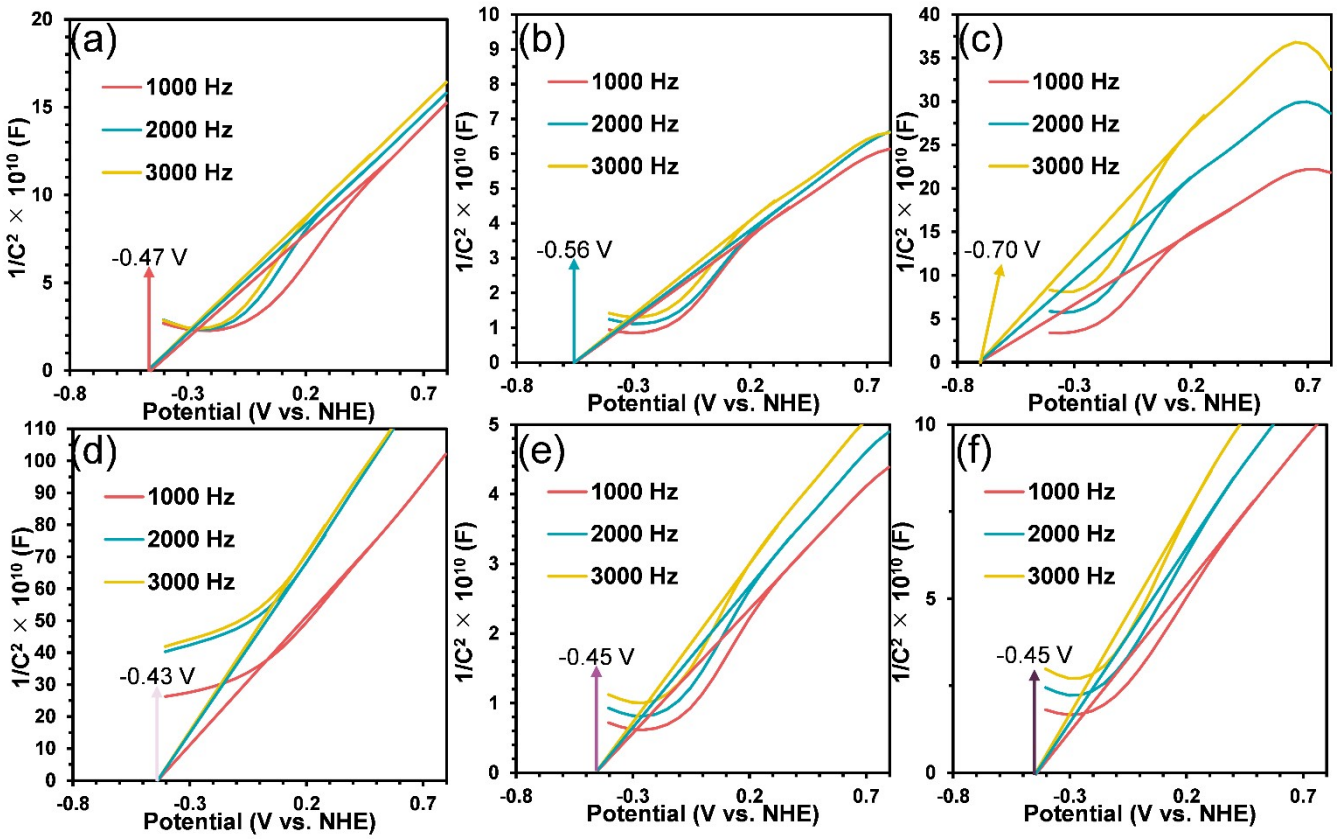

Fig. S6. Mott-Schottky plots of (a) U, (b) UP, (c) UDB (d) UPDB-5, (e) UPDB-10, and (f) UPDB-30.

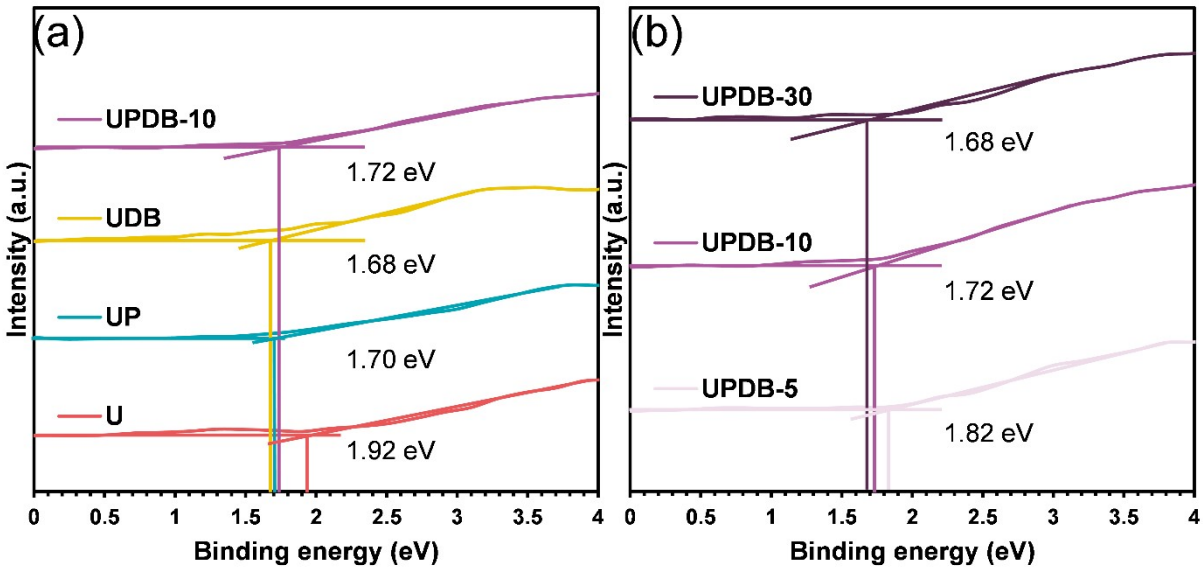

Fig. S7. VBXPS of (a) U, UP, UDB, and UPDB-10, (b) UPDB-5, UPDB-10, and UPDB-30.

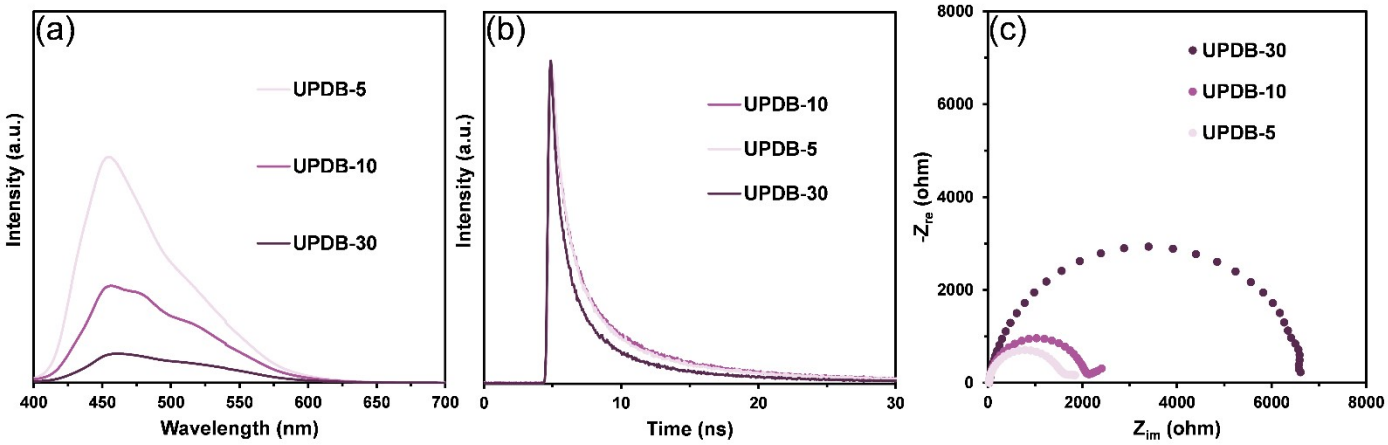

Fig. S8. (a) PL spectra, (b) TRPL spectra and (c) EIS Nyquist plots of UPDB-5, UPDB-10, and UPDB-30.

Table S4. Average lifetimes of U, UP, UDB, UPDB-5, UPDB-10, and UPDB-30.

Sample		Lifetime (ns)	R_A %	Average lifetime (ns)
U	τ1	0.74	21.10	
	τ2	2.51	46.06	4.58
	τ3	9.96	32.85	
UP	τ1	0.21	9.65	

	τ2	2.11	30.61	5.97
	τ3	8.88	59.75	
UDB	τ1	0.33	11.28	
	τ2	1.52	38.28	3.84
	τ3	6.34	50.44	
UPDB-5	τ1	0.33	12.05	
	τ2	2.02	36.99	5.20
	τ3	8.67	50.95	
UPDB-10	τ1	0.23	11.84	
	τ2	2.10	34.29	5.43
	τ3	8.70	53.88	
UPDB-30	τ1	0.33	16.30	
	τ2	1.94	39.89	4.45
	τ3	8.27	43.81	

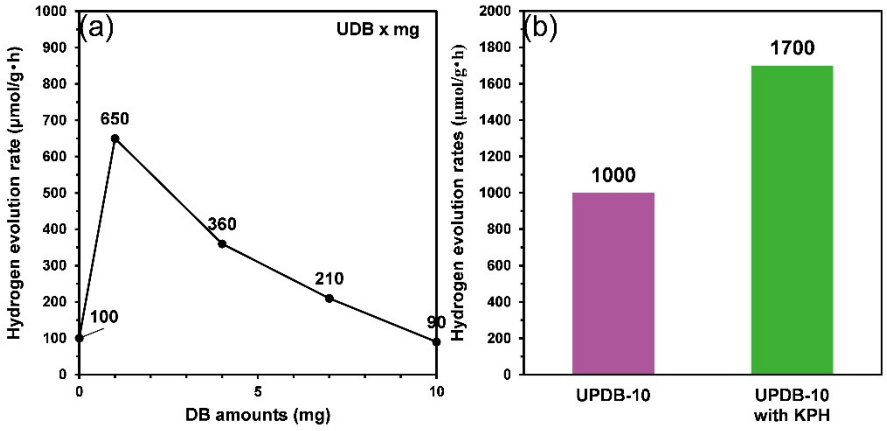

Fig. S9. Photocatalytic hydrogen evolution of (a) amount of DB, and (b) effect of KPH.

Table S5. Comparison of photocatalytic hydrogen evolution activity of carbon nitride-based photocatalysts.

Photocatalysts (mg/mL)	**Co-catalysts**	**Light source**	**H_2 evolution ($\mu mol\ g^{-1}\ h^{-1}$)**	**AQY (%) (420 nm)**	**Ref.**
CNS-H (0.71)	3 wt.% Pt	50 W LED (≧ 380 nm)	17700	16.68 %	[S1]
CuCN (0.5)	3 wt.% Pt	300 W Xe (≧ 420 nm)	2231.8	2.93 %	[S2]
NCN-2AP-X (0.25)	1 wt% Pt	300 W Xe (≧ 420 nm)	2550	9.79 %	[S3]
HCN-EDA (0.25)	0.2 wt% Pt	5 W LED White light	52160	31.6 %	[S4]
PhSO-TCNx (0.4)	3 wt.% Pt	300 W Xe (≧ 420 nm)	8709	12.0 %	[S5]
B,S-TCN (0.1)	3 wt.% Pt	300 W Xe (≧ 400 nm)	9321	5.3 %	[S6]
UPDB-10 (1)	**2 wt.% Pt**	**300 W Xe (≧ 420 nm)**	**1000**	**15.5%**	**This work**

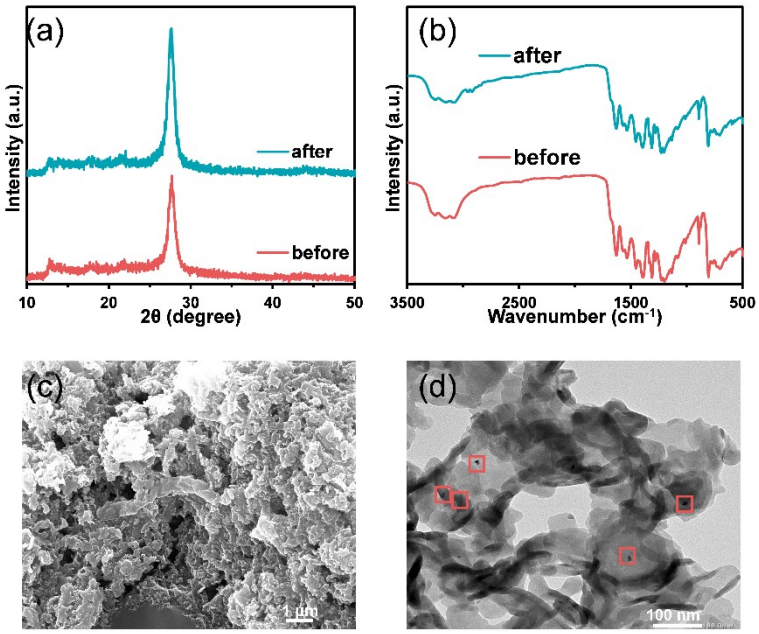

Fig. S10. (a) XRD patterns, (b) FT-IR spectra, (c) SEM image (10K), and (d) TEM image of UPDB-10 (50K) before and after photocatalytic reaction.

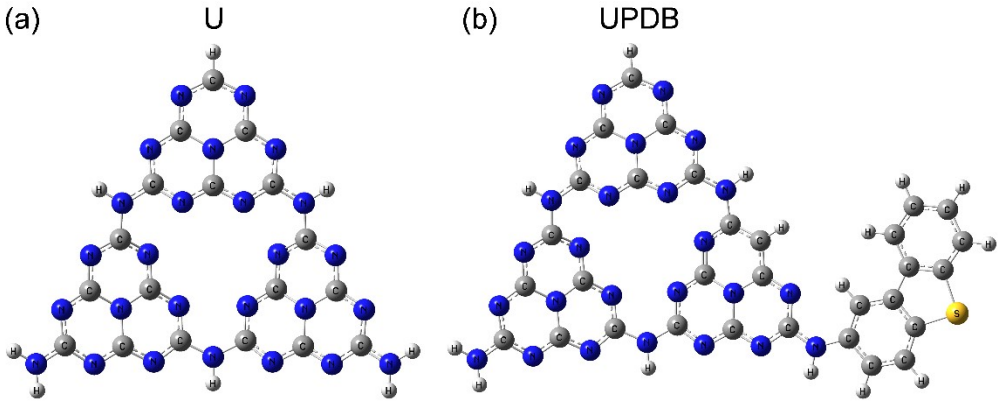

Fig. S11. Most stable optimized structure of (a) U and (b) UPDB, optimized at DFT/B3LYP/6-31g + (d, p) level of theory.

References

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