Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Synergetic Defects Boost Charge Separation in CN for Enhanced Photocatalytic Water Splitting

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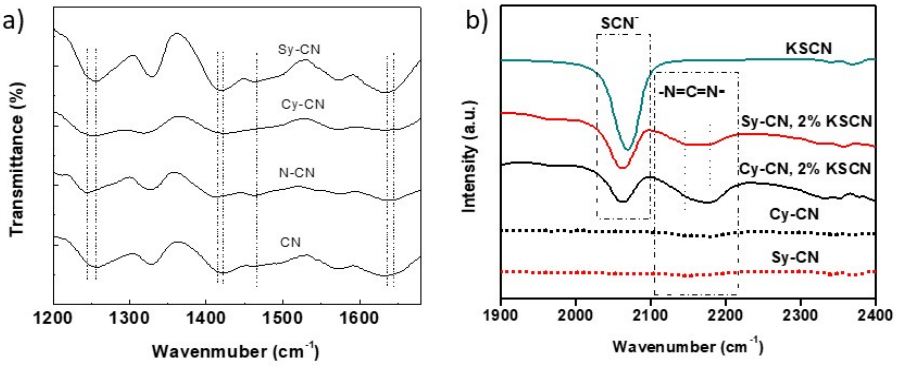
S1. a) The high resolution fourier transform infrared spectra (FTIR) of CN, Cy-CN, Sy-CN, and N-CN; b) FTIR spectra of Cy-CN and Sy-CN taking KSCN as standard.



A certain amount of KSCN was taken as internal standard and mixed with sample to get a mixture containing 2% weight percent of KSCN. Afterwards, the mixture was mixed with a certain amount of KBr and then pressed to get semi-transparent thin wafer suitable for FTIR measurements. The ratio of the area of absorption peaks of SCN^- vs -N=C=N- were used to evaluated the relative amounts -N=C=N- containing. Taking that of KSCN as standard, the contents of the analogue of cyan was evaluated to be 0.35% and 0.87%, which is still semi-quantitative. The amount of analogue of cyan in Sy-CN is about 40% of that in Cy-CN. It is helpful to understand the difference in photocatalytic performance and synergistic effect between the two samples.

S2. C 1s analysis of CN, Sy-CN, N-CN and Cy-CN.

XPS C atom fitting percentage of area fit

Sample	C-C	-N=C=N-	N-C=N
CN	35.48%	2.47%	62.05%
Sy-CN	46.69%	8.44%	44.87%
N-CN	26.30%	4.9%	68.80%

Cy-CN	29.92%	2.5%	67.58%

S3. N 1s analysis of CN, Sy-CN, N-CN and Cy-CN.

XPS N atom fitting percentage of area fit

Sample	N-H	N-(C3)	C=N-C
CN	25.87%	4.31%	69.82%
Sy-CN	25.36%	4.23%	70.41%
N-CN	22.52%	6.79%	70.69%
Cy-CN	23.42%	10.18%	66.40%

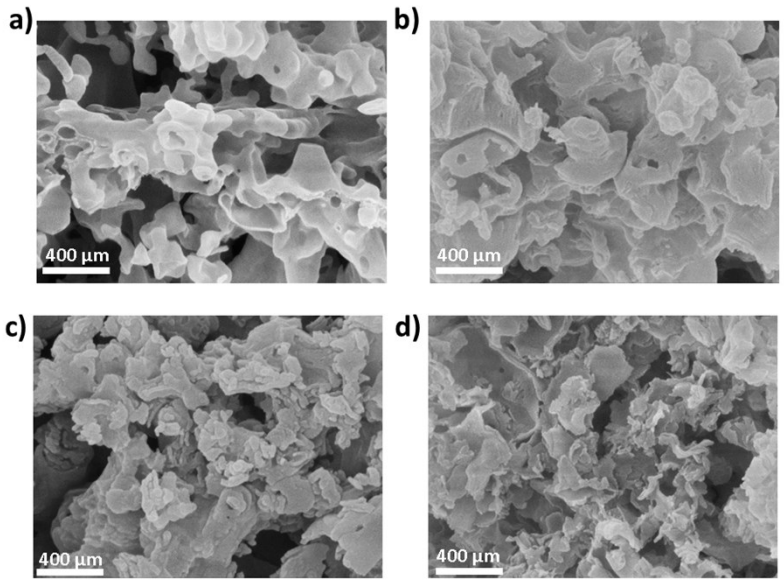
S4. O 1s analysis of CN, Sy-CN, N-CN and Cy-CN.

XPS O atom fitting percentage of area fit

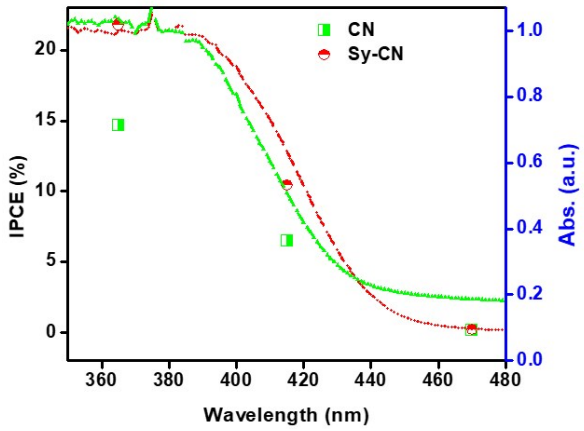
Sample	-OH	C=O
CN	29.91%	70.08%
Sy-CN	38.36%	61.64%
N-CN	25.8%	74.2%
Cy-CN	10.6%	89.4%

By XPS fitting, the hydroxyl content in CN, N-CN, Cy-CN or Sy-CN is estimated to be about 1.42%, 1.08%, 0.65% or 4.28%, respectively.

S5. SEM images of a) Cy-CN, b) CN, c) N-CN, d) Sy-CN.

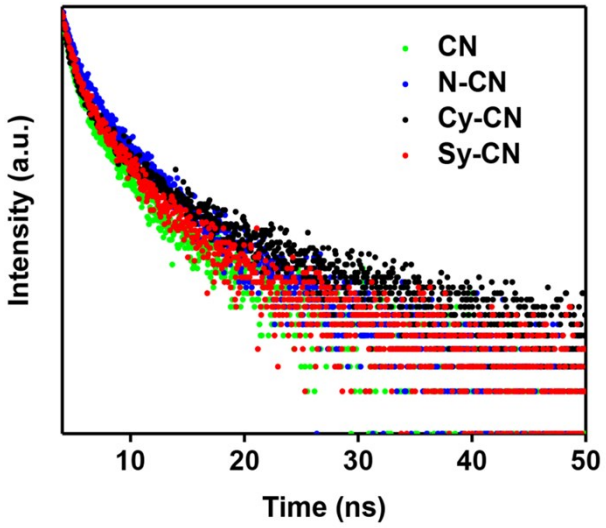


S6. IPCE of the photocatalytic H_2 generation at 390, 415 and 470 nm for Sy-CN and CN.



Photocatalytic reactions and analysis of H2 amounts for IPCE measurements were conducted in the same reactor described in main manuscript. In addition, a LED illuminator (Lampric, China) equipped with 365, 415 and 470 nm monochromatic light lamps was employed as light source, power of which was detected by an optical power meter of (Perfect light PL-MW2000). Scattering power can also be examined by the optical power meter. IPCE data indicated that Sy-CN have superior photoelectric transformation efficiency, in comparison with CN, which is more significant under illumination of higher energy.

S7. Time-resolved photoluminescence decay spectra of the CN, N-CN, Cy-CN and Sy-CN at 455 nm. These spectra were recorded with the excitation of a 405 nm picosecond pulsed light-emitting diode at room temperature.



S8. Fitting results of the photoluminescence decay time (τ) at 438 nm for CN, N-CN, Cy-CN and Sy-CN.

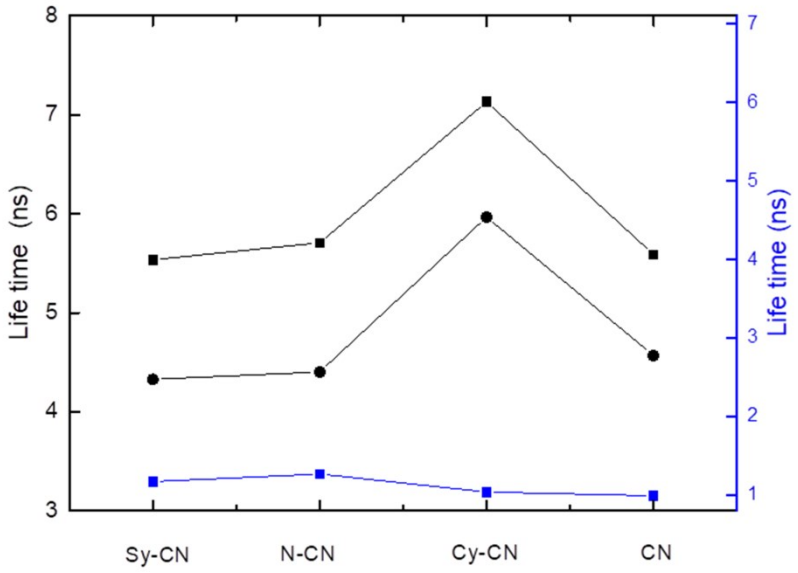
Sample	τ1/ns	Rel%	τ2/ns	Rel%	averge τ/ns
CN	1.1706	42.55%	5.5363	57.45%	3.678695
Sy-CN	1.2668	35.21%	5.708	64.79%	4.144253
N-CN	1.0375	35.31%	7.1329	64.69%	4.980614
Cy-CN	0.9908	47.72%	5.5892	57.28%	3.674304

S9 Fitting results of the photoluminescence decay time (τ) at 455 nm for CN, N-CN, Cy-CN and Sy-CN.

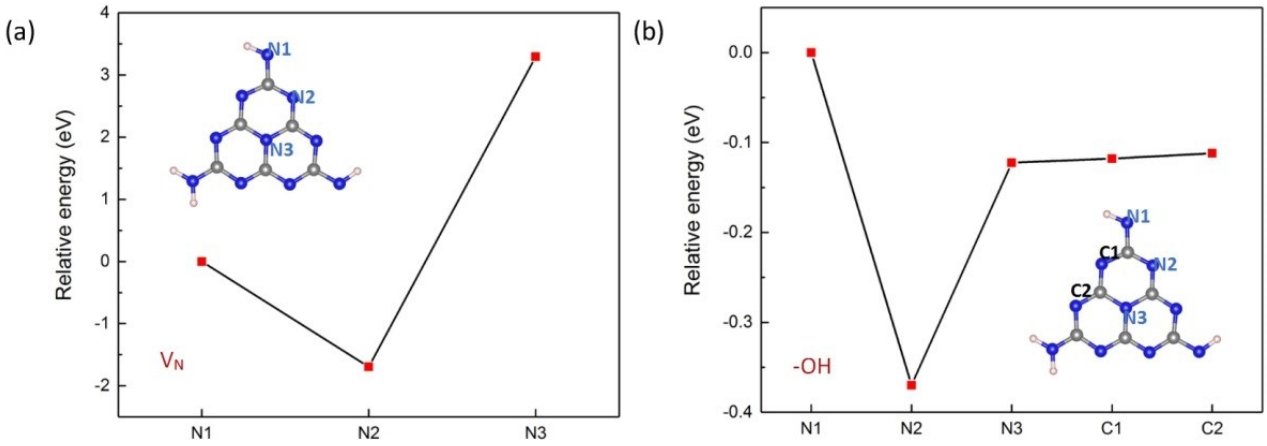
Sample	τ1/ns	Rel%	τ2/ns	Rel%	averge τ/ns
CN	1.2958	40.08%	6.4519	59.02%	4.327268

Sy-CN	1.4998	42.47%	6.5463	57.53%	4.403051
N-CN	1.1589	30.79%	8.1074	69.21%	5.967957
Cy-CN	1.1492	40.19%	6.8648	59.81%	4.5677

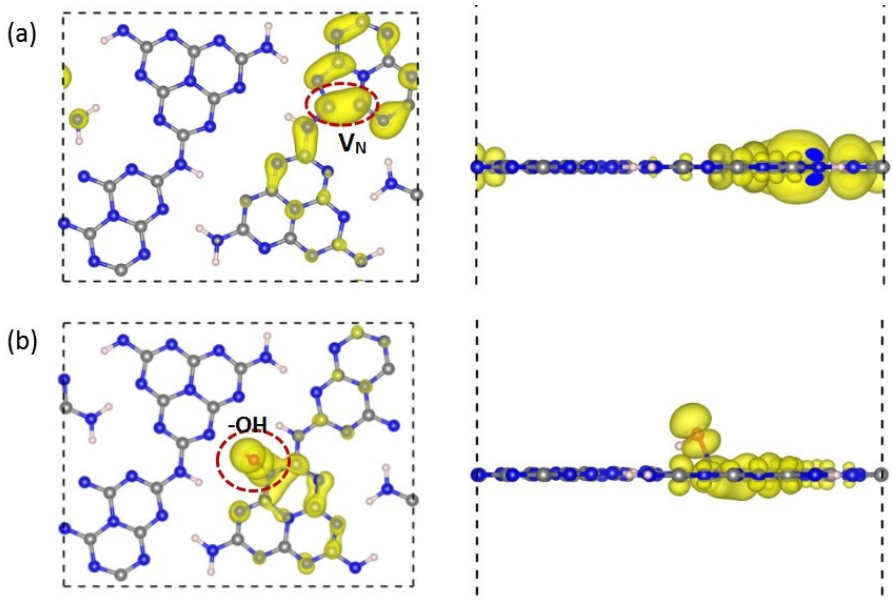
S10. The τ1 (blue solid squares), τ2 (black solid squares) of 438 nm and the average PL life time at 455 nm (solid rounds) for CN, N-CN, Cy-CN and Sy-CN.



S11. Relative energy for (a) CN with nitrogen vacancy and (b) CN with -OH.

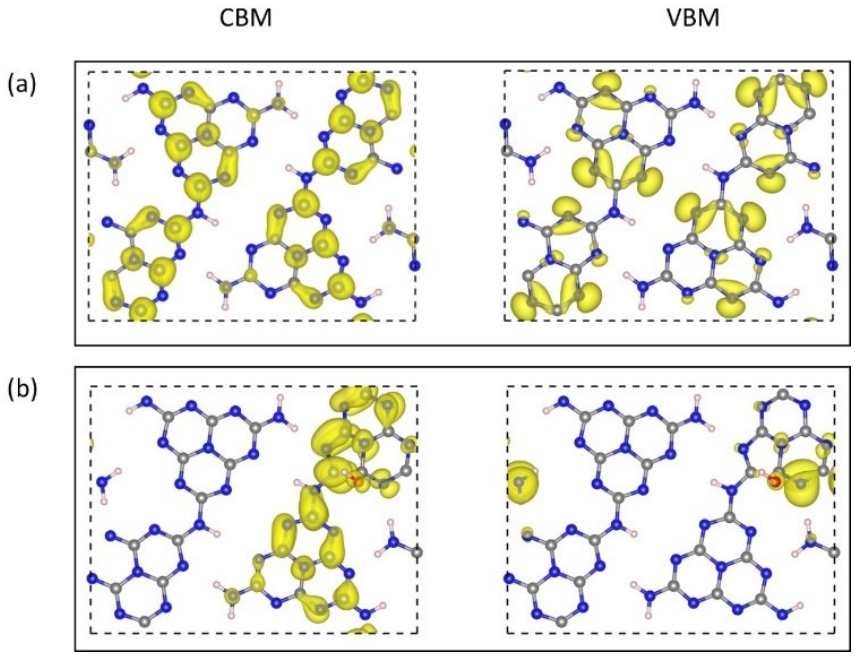


S12. The charge distribution of defect level for (a) CN with nitrogen vacancy and (b) CN with -OH.

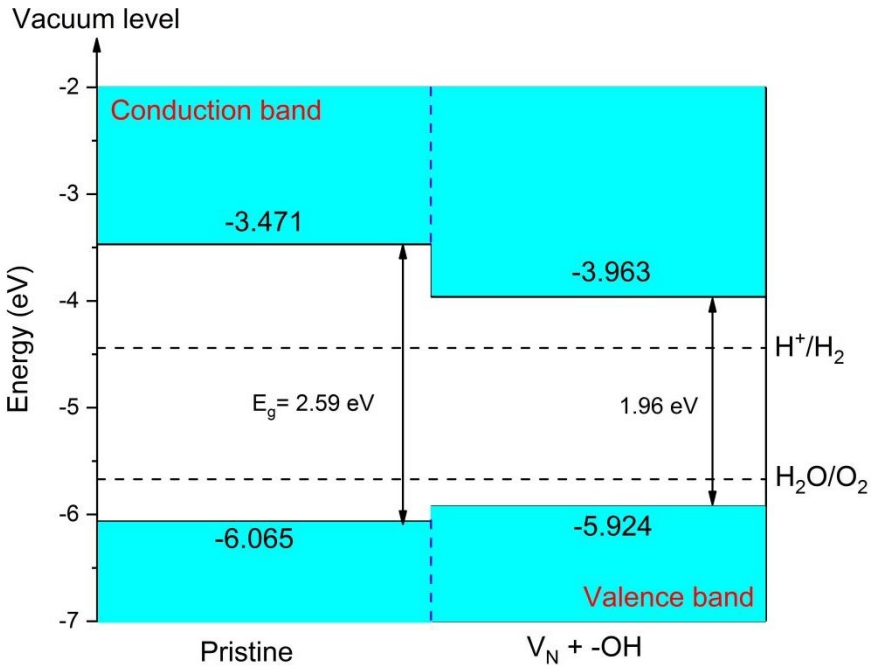


S13. The bond composed charge density of CBM and VBM for (a) pristine CN and (b) CN with functional groups (including nitrogen vacancy and -OH group). Isosurface is taken at a value of 3 × 10^{-3} e/Å^3. As for pure g-C_3N_4, the VBM is mainly distributed on the N2 atoms, and the CBM moderately occupies C and N atoms. In this case, the potogenerated electron-hole pairs are localized in each heptazine unit and their separation is inefficient, resulting in poor

photocatalytic activity. As for CN with functional groups system, the VBM locally distributed at the defect location and the CBM discrete distribution, indicating that defect effective promote the separation process of g-C_3N_4 photo-generated carriers.



S14. Calculated band alignment for pristine CN and CN with functional groups (including nitrogen vacancy and -OH group). The dotted black lines indicate the water reduction (H^+/H_2) and oxidation (H_2O/O_2) potentials. The vacuum level is taken as zero reference. The position of Fermi level and band edges relative to vacuum level could be determined by work function calculations. Then, these levels could be compared directly to the Redox potential energy. The calculation work function for pristine CN and CN with functional groups is 5.128 and 4.916 eV, respectively.


Vacuum level
-2
-3
-4
-5
-6
-7
Energy (eV)
Conduction band
-3.471
-3.963
H+/H2
Eg= 2.59 eV
1.96 eV
H2O/O2
-6.065
-5.924
Valence band
Pristine
VN + -OH