

Supporting Information

Crystalline oxygen-bridged carbon nitride from Self-assembles supramolecular for efficient photocatalytic H₂ evolution

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Synthesis of CMe supramolecular

All reagents in this study were used without additional purification and purchased from Sigma-Aldrich or Macklin. The precursor of melem was obtained through a polymerization process involving the heating of melamine, as previously documented.^[1] Stoichiometric quantities of cyanuric acid (CA) and melem (Me) were dispersed in an ethanol solvent and subjected to ultrasonic agitation for 1 hour. The resulting suspensions were subsequently transferred to a three-necked flask and subjected to reflux at 80 °C for 4 hours. The resulting white suspensions were centrifuged, washed with ethanol, deionized water, and ultimately freeze-dried to yield a white powder. The synthesized supramolecular compounds were denoted as CMe₂₁, CMe₃₂, CMe₆₅, CMe₁₁, and CMe₁₂, with the numerical notations signifying the molar ratios of CA and Me used in the synthesis reaction.

Synthesis of CMe_x-CN

The synthesis of CMe_x-CN involved a conventional thermal polymerization process. Typically, a 1g CMe₃₂ supramolecular intermediate was calcined in an alumina crucible coated with aluminum foil, positioned within a tubular furnace. This calcination was carried out at 550 °C for 4 h, using a heating rate of 2.3 °C/min under nitrogen gas flow. The product was labeled as CMe₃₂-CN. In accordance with the nomenclature established for the supramolecular precursors, the resulting series of samples were named CMe_x-CN (x= 21, 65, 11, 12 respectively). For comparison, the g-C₃N₄, Me-CN and CAME-CN were similarly synthesized under identical condition through the thermal polymerization of melamine, melem and a CA-melem mixture with molar ratio of 3:2, respectively.

Characterizations and photoelectrochemical test

The crystallinity of the samples was assessed by X-ray diffraction utilizing a Smart Lab SE equipped with Cu-K α radiation ($\lambda=1.541 \text{ \AA}$, 40KV, 30 mA). Fourier transforms infrared spectra (FTIR) were recorded using a Bruker VERTEX 700 spectrometer. Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) were carried out on a METTLER TGA/DSC/HT1600 thermal analyzer. X-ray photoelectron spectroscopy (XPS) was performed utilizing the Thermo Fisher Scientific model k-alpha⁺. Quantitative element analysis was conducted using the Vario EL III element analyzer (Germany). The morphology and microstructure were characterized by field emission scanning electron microscopy (SEM, Nova NanoSEM 450) and transmission electron microscopy (TEM, ThermoFisher Talos F200X). The UV-relative diffuse reflectance spectrum (DRS) was obtained using BaSO₄ as a reference on a UV-2600 spectrophotometer. Photoluminescence spectra and transient fluorescence lifetime were recorded on a fluorescence spectrophotometer (FLS920). The photoelectrochemical performance was evaluated using an electrochemical workstation (Wuhan Corrtest, CS2350H) with Ag/AgCl as the reference electrode, platinum flake as the counter electrode, and photocatalyst-coated FTO glass as the working electrode. The working electrode was prepared as followed: 5 mg of samples and 7 mg of iodine were dispersed in 20 mL of acetone and subjected to ultrasonication for 1h to obtain

a suspension. Then, the samples were electrodeposited onto pre-cleaned FTO glass using the electrochemical workstation and then dried for 4 h at 80 °C to yield the working electrode. ¹³C CP/MAS NMR spectra were recorded at room temperature by using a 3.2 mm MAS probe and a MAS spinning rate of 10kHz. A contact time of 20 ms and a recycle delay of 2 s were used for the ¹H–¹³C CP/MAS measurement.

Photocatalytic H₂ evolution experiments

Photocatalytic H₂ evolution experiments were conducted using the Labsolar 6A system, an all-glass automatic closed-cycle setup by Beijing Perfect Light. Specifically, 50 mg of catalyst powder was dispersed in 87 mL of deionized water, with the 10 mL of triethanolamine (TEOA) as a sacrificial agent and 3 mL of an aqueous solution of H₂PtCl₆·6H₂O (1wt% Pt) as cocatalyst. Following ultrasonic treatment for 5 min, the suspension was transferred to a 200 mL quartz glass reactor and continuously stirred via a magnetic agitator. Prior to illumination with a 300 W Xe light source (Beijing Aulight Technology Co.) equipped with a cut-off filter ($\lambda > 420$ nm), the circulatory system underwent a 15 min vacuuming process. The amount of H₂ evolution was analyzed using a gas chromatograph (Zhejiang Fuli 9790 II) equipped with a thermal conductivity detector (TCD) and employing high-purity Ar as the carrier gas. The apparent quantum efficiency (AQE) of the catalyst under monochromatic light at different wavelengths (420 nm, 450 nm, 500 nm) was calculated using the following formula:

$$AQE = \frac{2 \times \text{number of hydrogen molecules}}{\text{number of incident photon}} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where, M is the number of H₂ molecules (mol), N_A denotes Avogadro constant (6.022*10²³ mol⁻¹), h is Planck constant, c is the speed of light (3*10⁸ m·s), S indicates the irradiation area (cm⁻¹), P represents the power density of irradiation light (w·cm⁻²), λ signifies the irradiation wavelength (m), and t (s) is the reaction time.

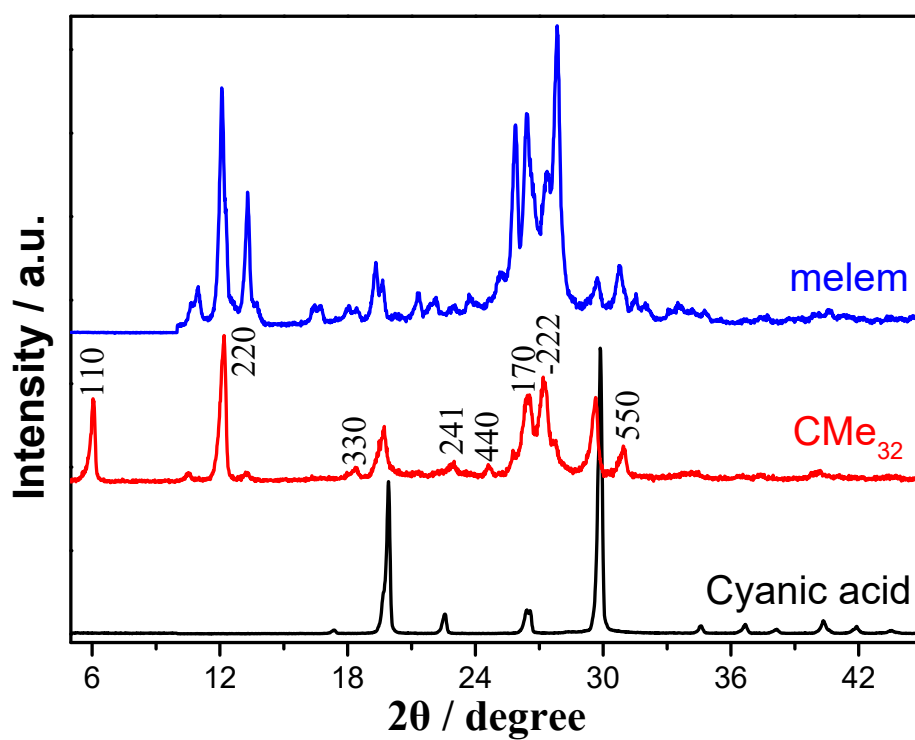


Figure S1. XRD patterns of melem, CMe₃₂, and Cyanic acid (CA).

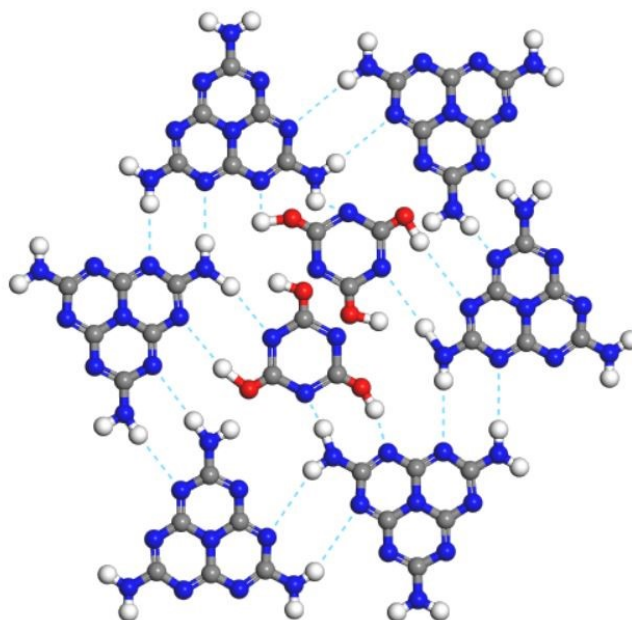


Figure S2. Schematic illustration of CMe₃₂ supramolecular unit assembly of Cyanic acid (CA) with melem via H-bond formation.

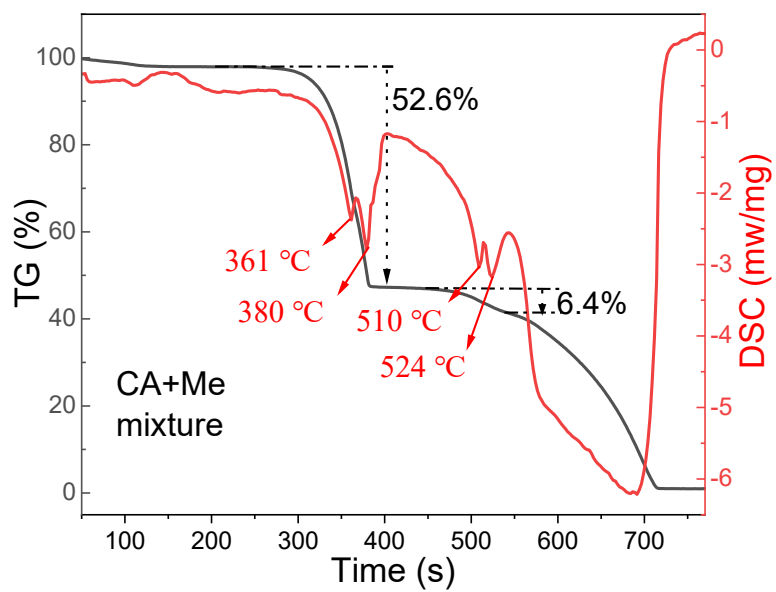


Figure S3. TG-DSC curve of CA-Me mixture.

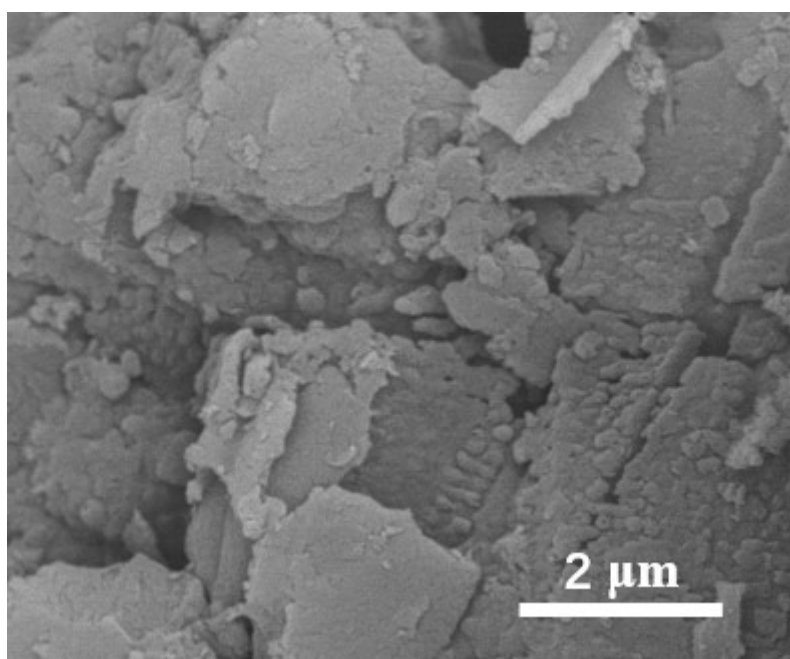


Figure S4. SEM image of pristine g-C₃N₄.

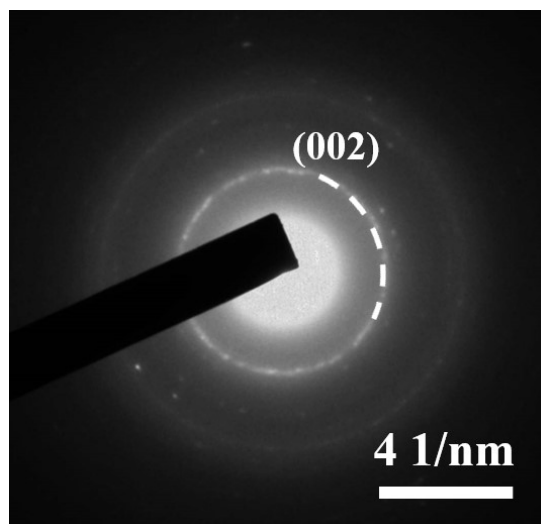


Figure S5. Selected area electron diffraction patterns of CMe₃₂-CN

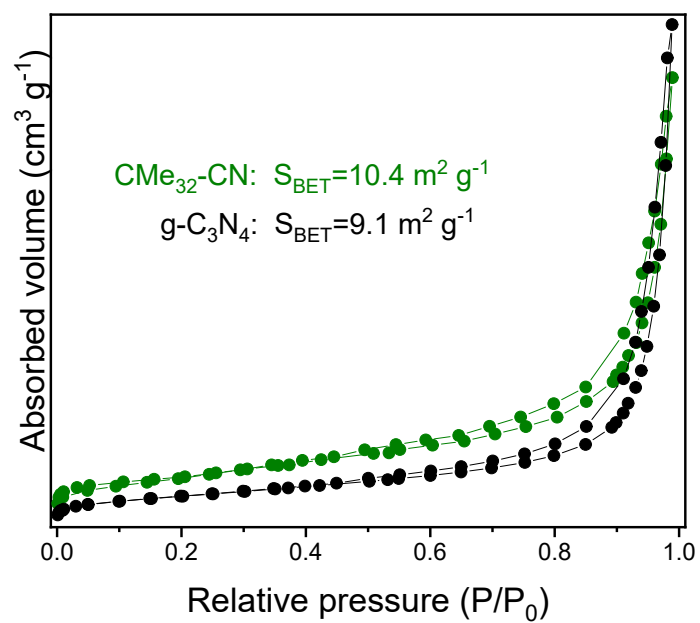


Figure S6. Nitrogen adsorption-desorption isotherms and specific surface area analysis according to the Brunauer–Emmett–Teller (BET) model for g-C₃N₄ and CMe₃₂-CN.

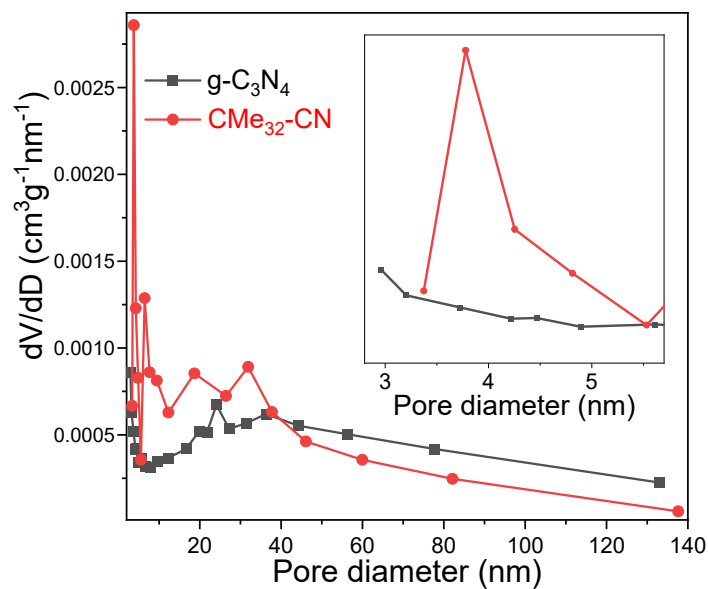


Figure S7. Nitrogen adsorption-desorption isotherms and specific surface area analysis according to the Brunauer–Emmett–Teller (BET) model for $g\text{-C}_3\text{N}_4$ and $\text{CMe}_{32}\text{-CN}$.

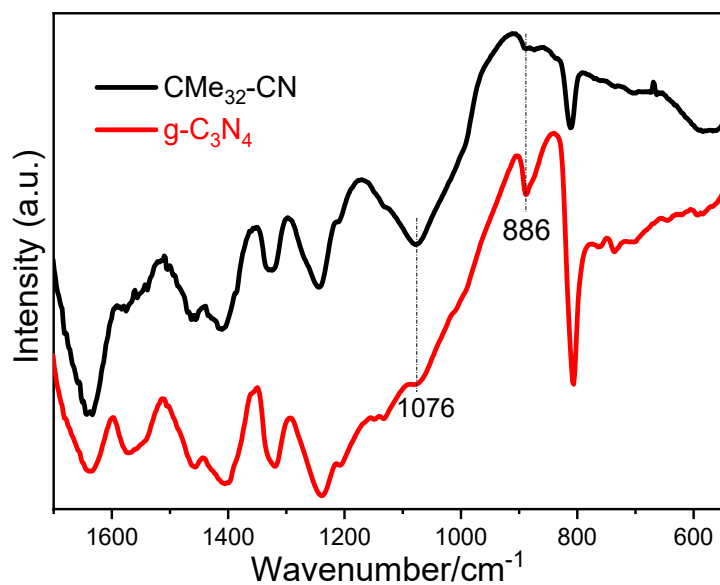


Figure S8. FTIR spectra at $580\text{-}1650\text{ cm}^{-1}$ of $\text{CMe}_{32}\text{-CN}$ and $g\text{-C}_3\text{N}_4$.

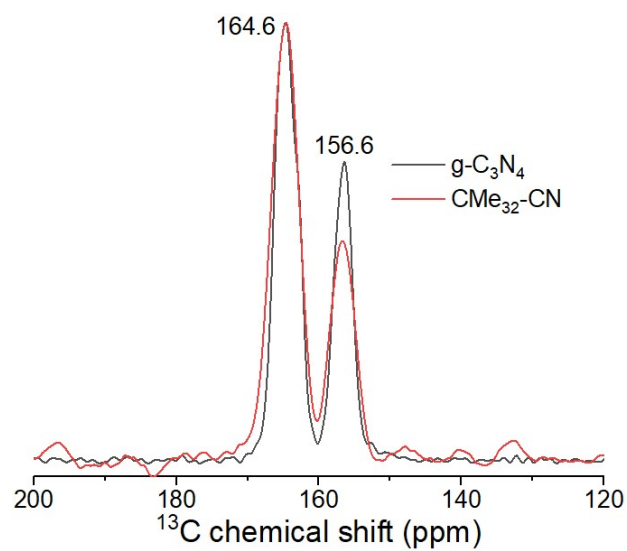


Figure S9. Solid-state NMR ^{13}C spectra of $\text{CMe}_{32}\text{-CN}$ and $\text{g-C}_3\text{N}_4$.

Table S1. $\text{CMe}_{32}\text{-CN}$ and $\text{g-C}_3\text{N}_4$ element analysis results (%).

Sample	C	N	H	O
$\text{g-C}_3\text{N}_4$	35.2	58.7	1.68	4.45
$\text{CMe}_{32}\text{-CN}$	31.1	49.9	1.53	17.43

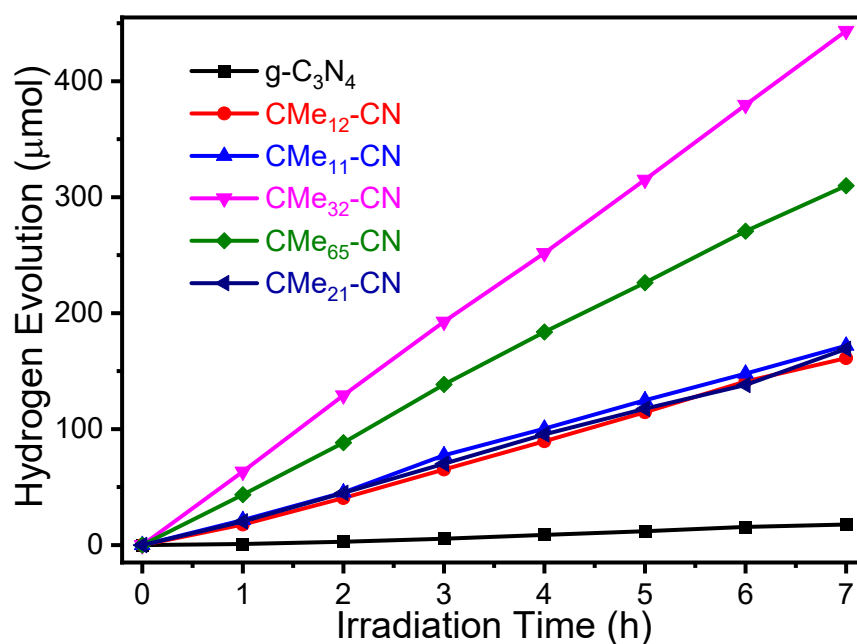


Figure S10. Time course of H₂ evolution for g-C₃N₄ and CMe_x-CN under visible light irradiation.

Table S2. Photocatalytic H₂ evolution activity of partially been reported via facile strategy for doping and crystalline graphitic carbon nitride photocatalysts recently.

Photocatalyst	strategy	HER > 420 nm (sample doses)	AQY /%	Reference
ONLH-600	Oxygen linker OCN	337 μmol/h·g	10.3 at 420 nm	[2]
OCN	Multiple thermal treatment strategy for hollow O-doping CN nanosheet	36 μmol/h	4.28 at 420 nm	[3]
CN-HT	Intramolecular heterostructured with heptazine-triazine	64.88 μmol/h	10.1 at 400 nm	[4]
5% K-PHI/B _{0.8} ST	K ⁺ intercalated act as charge-transfer bridge	87.0 μmol/h	8.05 at 420 nm	[5]
(K)PCN&KTO	multilocal gradient-doping K ⁺ CN	191.5 μmol/h	10.4 at 420 nm	[6]
PTI-Rh/Cr ₂ O ₃ -CoO _x	Bottom-up fabricate single-crystalline PTI nanosheet	λ > 300 nm 610 μmol/h	25 at 365 nm ~1 at 400 nm	[7]
CMe ₃₂ -CN	CA-Me supramolecular synthesize crystalline oxygen-bridged CN	64.7 μmol/h	13.2 at 420 nm	This work

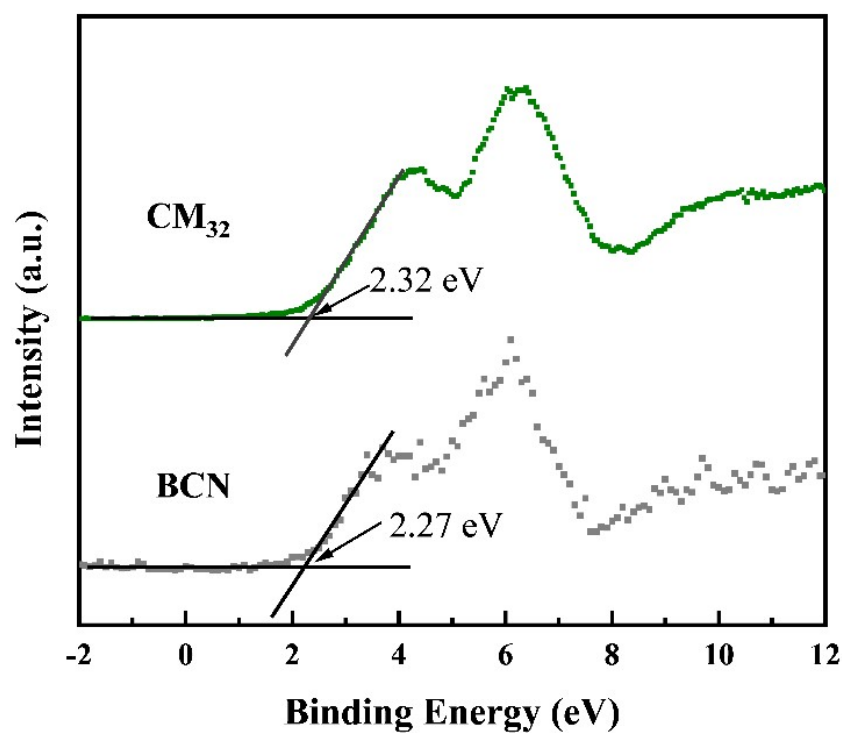


Figure S11. XPS valence band spectra of CM_{e32} -CN and g- C_3N_4 .

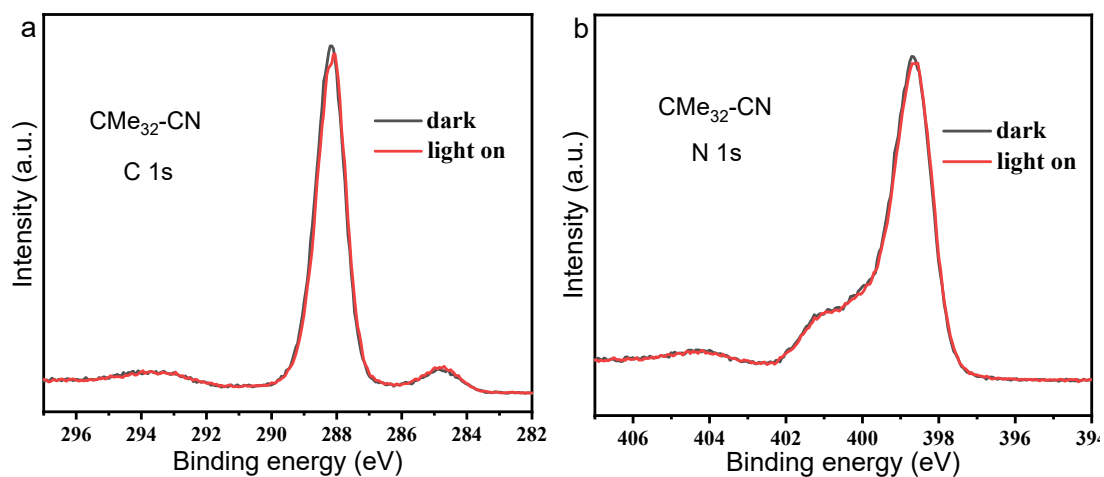


Figure S12. High-resolution in-situ XPS spectra of C 1s (a) and N 1s (b) of CM_{e32} -CN.

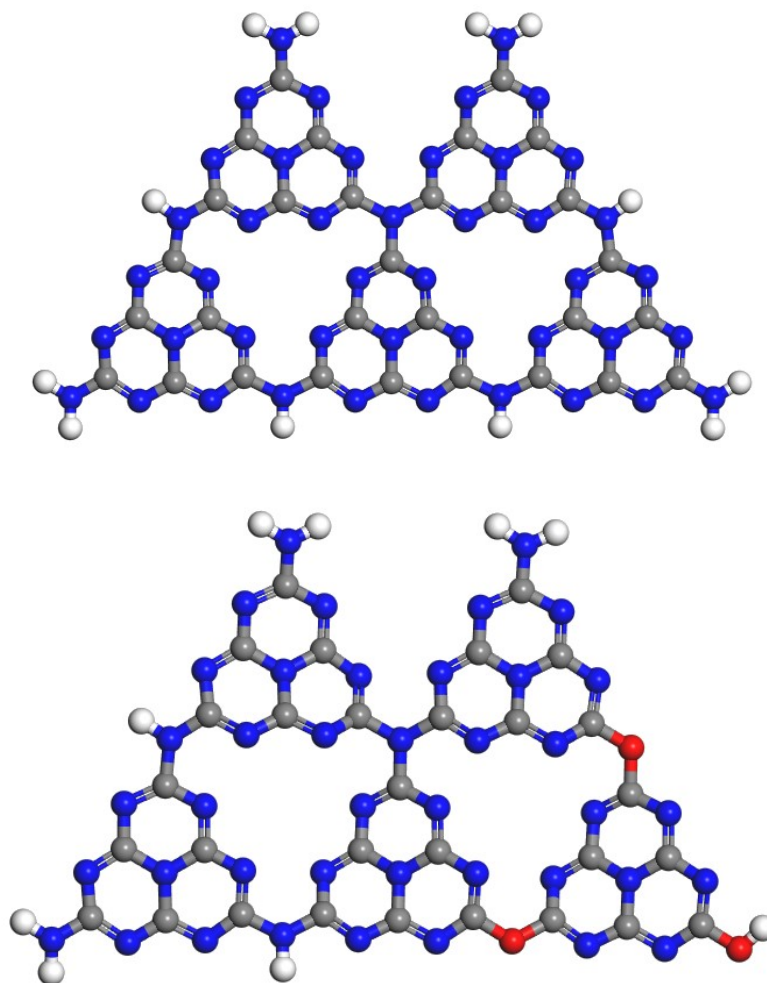


Figure S13. Models of g-C₃N₄ (top) and CMe₃₂-CN (bottom) using in the first-principle calculations.

Reference

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