Energy gap engineering of polymeric carbon nitride Nanosheets for matching with NaYF₄:Yb,Tm: enhanced visible-near infrared

photocatalytic activity

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Experimental Section

Materials: $Y_2O_3 \cdot 6H_2O$ (99.99%), $Yb_2O_3 \cdot 6H_2O$ (99.99%), $Tm_2O_3 \cdot 6H_2O$ (99.99%), were all purchased from Sigma-Aldrich. NaOH (98%), NH_4F (98+%) and oleic acid (OA, 90%), dicyandiamide (DCDA), 2-aminobenzonitrile (ABN). All raw materials were used as starting materials without further purification.

Synthesis of CNX-NSs: Firstly, molecularly grafted bulk CN (CNX) was fabricated by copolymerization of dicyandiamide and 2-aminobenzonitrile (ABN, denoted as X).¹ 3 g of dicyandiamide and different amount of X (0.05g, 0.1g, 0.15g) were mixed in 15 mL of water with stirring at 373 K to remove the solvent. The resultant solids were ground and calcined at 550°C for 4 h in air. The samples thus obtained were denoted

as $CNX_{0.05}$, $CNX_{0.1}$, and $CNX_{0.15}$. CN was synthesized in the same method without adding ABN. Then, the bulk materials were exfoliated to ultrathin nanosheets via an ultrasonication method. 400 mg of bulk CN or CNX powder was ground well with a mortar and a pestle and was then put into 80 mL of 5 M HNO₃ and refluxed for 20 h. After naturally cooling to room temperature, the mixture was filtrated and washed with doubly distilled water until its pH reached 7.0. The products were dispersed in 60 mL of deionized water, followed by sonication for ~4 h. The reaction product was isolated by centrifugation at 3000 rpm for 5 min to remove the residual unexfoliated CN. Generally, 400 mg of bulk CNX powders yield 70~100 mg ultrathin CNX nanosheets.

Synthesis of β -NaYF₄:Yb,Tm/PAA Microrods: The β -NaYF₄ microrods were synthesized by a slightly modified literature procedure via a hydrothermal reaction.² 0.4 mmol of lanthanide oxides Ln₂O₃ (Y/Yb/Tm = 79.5/20/0.05, molar ratio) were dissolved in hot nitride acid (65°C) for several hours to obtain transparent solution. Then the solvent was evaporated to obtain powder Ln(NO₃)₃ followed by diluted with 4 mL of H₂O. In a typical procedure, NaOH (0.6 g; 15 mmol) was first dissolved in 3 mL of water, followed by addition of 10 mL of oleic acid and 10 mL of ethanol under vigorous stirring. The prepared Ln(NO₃)₃ was added to the above solution. Subsequently, an aqueous solution of NH₄F (2 M; 2 mL) was added to form a turbid mixture and the solution was kept stirring for 20 min. The resulting mixture was then transferred into a 40-mL Teflon-lined autoclave and heated to 220 °C for 12 h. After cooling down to room temperature, the reaction product was isolated by centrifugation. Oleic acid capped UCPs (OA-UCPs) were obtained after being washed by ethanol for three times. OA-UCPs were dispersed in 40 mL of acidic ethanol solution (pH=1) and ultrasonicated for 2 h, which protonates the oleate ligand resulting in the release of oleic acid from the surface. The bared UCPs were collected by centrifugation and washed with ethanol and ultrapure water several times, and redispersed in ultrapure water containing 800 mg of PAA, and the solution was vigorously stirred for 24 h. The particles were separated by centrifugation and washed with ultrapure water to obtain β -NaYF₄:Yb,Tm/PAA Microrods.

*Synthesis of UCPs/CNX*_{0.1}-*NSs*: A known quantity of $CNX_{0.1}$ -NSs was dispersed in a certain volume of water, followed by adding a known amount of UCPs-PAA. The obtained suspension was sonicated to disperse uniformly. Then, the suspension was heated to 70 °C and stirred to evaporate water. As time progresses these exfoliated sheets spontaneously coat the UCPs to minimize the surface energy by forming UCPs/CNX_{0.1}-NSs.

Characterization: Transmission electron microscopy (TEM) observation and the linear EDX elemental distribution were carried out with Tecnai G2 F30 (FEI, Holland). Atomic force microscopic (AFM) was performed using an NT-MDT 830 atomic force microscope. Powder X-ray diffraction (XRD) data were recorded by a Bruker D8 Discover X-ray diffractometer using Cu K α irradiation (k =1.5406 Å). The X-ray photoelectron spectroscopy (XPS) spectra were collected on a Kratos Axis Ultra LD spectrometer using a monochromatic Al K α source. FT-IR spectrum was measured on Magan-IR Spectrometer 500 (Nicolet, Madision, WI, USA) with the

KBr pellet technique. The photoluminescence spectra were recorded at room temperature on a RF-5301 PC fluorescence spectrophotometer (Shimadzu, Japan) with excitation of a 980 nm CW laser (Beijing Hi-Tech Optoelectronic Co., China) or 365 nm wavelength. UV–vis diffuse reflectance spectra were conducted on a UV2550 UV-vis spectrophotometer (Shimadzu Scientific Instruments Inc.) with BaSO₄ as the reflectance sample. UV-visible absorption spectroscopy was measured on a Shimadzu UV-2550 UV-vis spectrophotometer.

Photocatalytic performance: Visible irradiation was provided by a 500 W xenon lamp with a 400 nm cutoff filter and the average light intensity was 160.0 mW cm⁻². A 980 nm laser (1W/cm²) was used as the NIR light source. Under Xe lamp irradiation, the photodegradation of RhB was tested using 5 mg of as-prepared catalysts in 5 mL of RhB solution (10 ppm) in water. The suspension was placed in darkness under magnetic stirring for 12 h to reach the absorption/desorption equilibrium. 200 μ L of suspension was taken at certain time intervals (4 min) during the degradation process to record the UV-vis absorption spectra of RhB. The degradation efficiency was determined by calculating *C*/*C*₀, where C is the remained RhB concentration and *C*₀ is the starting concentration of RhB. In the case of 980 nm irradiation, 10 mg of catalyst was added to 1.5 mL of RhB (10 ppm) in a vial and the light beam was placed in the side of vial. The photocatalytic processes of the as-prepared samples were determined by the degradation of RhB under 980 nm NIR light irradiation. At 1.5 h intervals, 100 uL of the suspensions were taken out and centrifuged at 12000 rpm for 10 min. *Electrochemical and photoelectrochemical measurement*: The photocurrents were measured with an electrochemical analyzer (CHI660A, Chen Hua Instruments, Shanghai, China) in a standard three-electrode system, which employed a platinum wire as the counter electrode and saturation calomel electrode (SCE) as the reference electrode. 2 mg of powder was dispersed ultrasonically in1.0 mL of water, and 15 μ L of the resulting colloidal dispersion was drop-cast onto a piece of ITO slice with a fixed area of 0.4 cm² and dried in air at room temperature to form modified ITO electrode. All photocurrent measurements were performed at a constant potential of 0 V (vs. saturated SCE). Na₂SO₄ (0.2 M) was used as the supporting electrolyte for photocurrent measurements. A 500 W Xe lamp was utilized as a light source. The Nyquist plots were recorded within 100 MHz to 100 kHz frequency range. *Calculations*: To account for the copolymerization and exfoliation effects on the electronic structures of the CN structures, we performed electronic structure

calculations with a series of models with various in-plane copolymerization degree and stacking patters. In this work, only the qualitative but not the quantitative results are required to interpret the experimental observations. The structures were fully relaxed by using the self-consistent density functional tight-binding (SCC-DFTB) methods implemented in the package DFTB+ 1.2 with themio-1-1 set of parameters.³⁻⁵ The electronic transitions for each model were calculated with the semiempirical ZINDO method implemented in the Gaussian 09 package, which has been proven to give reliable UV absorption spectra for large conjugated systems.^{6,7} More accurate first-principles methods at the level (TD) B3LYP/6-311++G (d,p) has been used to

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validate the semiempirical results, which shows similar spectroscopic behavior upon copolymerization and stacking.



Figure S1. FT-IR spectra of bulk CN, X-doped CN (CNX_{0.1}), CN-NSs, and X-doped nanosheets (CNX_{0.1}-NSs) (X: 2-Aminobenzonitrile).

The influence of copolymerization as well as exfoliation on the crystal structures of CN and its derivatives can also be analyzed by Fourier transformed infrared (FTIR) spectra. The peaks in the region from 900 to 1800 cm⁻¹ are attributed to the feature-distinctive stretch modes of aromatic CN heterocycles. The sharp peak at around 807 cm⁻¹ corresponds to the breathing mode of the triazine units. The broad peaks between 3000 and 3600 cm⁻¹ are contributed by N–H stretching.



Figure S2. The XPS survey spectra, high-resolution C1s spectra, and high-resolution N1s spectra of $CNX_{0.1}$ and $CNX_{0.1}$ -NSs.

The chemical valence state of the elements was checked by X-ray photoelectron spectroscopy (XPS). According to the survey XPS spectra, both $CNX_{0.1}$ and $CNX_{0.1}$ -NSs contain only C, N and O elements. The binding energies for C 1s, N 1s, O 1s are 285 eV, 399 eV, 533 eV, respectively. The high-resolution C 1s spectra can be divided into two peaks centered at 288.2 eV and 284.8 eV. The major peak at 288.2 eV is identified as the sp²-bonded carbon (N–C=N) in CN network, and the weaker one 284.8 eV is assigned to standard reference carbon (graphitic carbon adsorbed to the surface of CN). The high-resolution N1s spectra can be deconvoluted into three peaks. The main peak at 398.6 eV corresponds to sp² hybridized aromatic N of the triazine rings (C=N–C). The peak at 399.4 eV is attributed to the bridging N bonded to carbon atoms in the form of N–(C)₃ or N bonded with H atoms. As expected, the higher proportion of bridging N is observed in CNX_{0.1}-NSs because of protonation.

The peak at 400.7 eV is derived from quaternary N bonded to three carbon atoms in the aromatic cycles.



Figure S3. UV–visible absorption spectra of (a) bulk CN and (b) CN-NSs with varied doping amount of X (X: 2-Aminobenzonitrile).



Figure S4. Photocatalytic decomposition of Rhodamine B (RhB) by bulk CN and CN-NSs with varied doping amount under visible light irradiation ($\lambda > 400$ nm).



Figure S5. The electrochemical impedance spectroscopy (EIS) response of CN, $CNX_{0.1}$, CN-NSs, and $CNX_{0.1}$ -NSs.

The semicircle at high frequencies in the Nyquist diagrams is in accordance with that in the electron-transfer-limited process and the semicircle diameter is equivalent to the electron-transfer resistance (R_{et}) across the electrode/electrolyte.⁸ In this way, the arc at high frequencies was fitted to a circle so as to measure the diameter. The fitted Ret values for bulk CN, X-doped CN (CNX_{0.1}), CN nanosheets (CN-NSs), and Xdoped CN nanosheets (CNX_{0.1}-NSs) are estimated to be about 96, 80, 67, 46 $\Omega,$ respectively. The slight decrease of $R_{\rm et}$ indicates that phenylene modification improves the electronic conductivity in the non-photoexcited state.¹ Obviously, ultrathin CN nanosheets possess more efficient charge transfer than the bulk CN.9 One possible reason could be the electron-phonon interaction in the material. The lattice photons are different in the low dimension material, which could affect the conductivity of the material. The efficient charge mobility has been observed in low dimension materials, one typical example is graphene, which shows very high electron mobility.¹⁰ Interestingly, the lowest value of R_{et} is obtained in CNX_{0.1}-NSs material, suggesting the most efficient charge transfer across the electrode/electrolyte interface among these materials.



Figure S6. FTIR spectra of PAA-UCP and UCPs/CNX_{0.1}-NSs composite.

For PAA modified UCPs, the typical absorption peaks of C=O stretching vibration (1710 cm⁻¹)), methylene asymmetric C-H stretching (2968 cm⁻¹), -OH bending vibration (1453 cm⁻¹) and carboxylate symmetric COO⁻ stretching (1390 cm⁻¹) in the FT-IR spectrum of PAA-UCPs are observed. For UCPs/CNX_{0.1}-NSs composite, the above signals are indistinctive because of the strong absorption of CN networks.



Figure S7. Zeta potentials of (a) bulk CNX_{0.1}, (b) CNX_{0.1} nanosheets (CNX_{0.1}-NSs),
(c) NaYF₄:Yb,Tm (UCPs), and (d) PAA modified UCPs (PAA-UCPs).

From Zeta potential measurements, protonation by acid makes $CNX_{0.1}$ -NSs carry a positive surface charge in neutral aqueous dispersion.¹¹ Meanwhile, UCPs also carry a positive surface charge due to the large amount of exposed rare earth ions (Yb³⁺ and Tm³⁺). After modified by PAA, the surface charge of UCPs becomes negative.¹²



Figure S8. XRD patterns of NaYF₄:Yb,Tm and NaYF₄:Yb,Tm /CNX_{0.1}-NSs composite.

The position and relative intensity of all diffraction peaks can be readily indexed to the pure hexagonal phase NaYF₄ (β -NaYF₄) according to the JCPDS file NO. 16-0334. No impurity peaks can be identified from the XRD pattern, indicating that the as-synthesized UCPs are single-phased. The broad peak at ~27° in the NaYF₄:Yb,Tm /CNX_{0.1}-NSs composite is assigned to the (002) interlayer diffraction of CN networks.



Figure S9. EDX analysis of NaYF₄:Yb,Tm/CNX_{0.1}-NSs.



Figure S10. Degradation efficiency of RhB after 6h NIR irradiation of different materials.

The influence of different mass ratios between UCPs and $CNX_{0.1}$ -NSs on degradation efficiency of RhB under NIR irradiation was investigated. Pure UCPs and $CNX_{0.1}$ -NSs show nearly no activity. When the mass ratios of UCPs: $CNX_{0.1}$ -NSs were 0.5:1, 1:1, 1.5:1, 2:1, the degradation efficiencies were 39.5%, 52.4%, 57.6%, and 44.8%, respectively.



Figure S11. Comparison of the normalized concentration of RhB decomposed by UCPs-based photocatalysts under Xe lamp (λ >400 nm).



Figure S12. Effects of different scavengers on the degradation of RhB by UCPs/CNX_{0.1}-NSs composite under Xe lamp (λ >400 nm, left) and NIR (right) irradiation.

The degradation efficiency of RhB didn't change upon addition of isopropanol (IPA, a hydroxyl radicals scavenger), suggesting that hydroxyl radicals 'OH are not the active species for the degradation of RhB. While disodium ethylenediaminetetraacetate (EDTA, 1mM, a scavenger for photogenerated holes) or benzoquinone (BQ, 1mM, a scavenger for superoxide radicals O_2^{-}) was added, the degradation is largely prohibited.

Sample	Atom fraction (at %)		
	C	Ν	0
CNX _{0.1}	51.1	45.0	3.9
CNX _{0.1} -NSs	41.5	50.9	7.6

Table S1 The surface elemental stoichiometry calculated from XPS spectrum.

Photocatalyst	dye, volume	light source,	degrading	references
		intensity	efficieny	
YF ₃ :Yb,Tm/TiO ₂ ,	MB, 15mg/L	980nm, 1W	30h: 61%	Chem. Commun. 2010, 46,
				2304.
NaYF ₄ :Yb,Tm/N-TiO ₂	MB, 10mg/L	980nm, 2W	30h: 56%	Adv. Healthcare Mater. 2012,
				1, 470.
NaYF4:Yb,Tm/TiO ₂	MB, 15mg/L	980nm,	14h: 65%	ACS Catal. 2013, 3, 405.
		10W/cm ²		
NaYF ₄ :Yb,Tm/TiO ₂	RhB, 10mg/L	980nm, 1W	24h: 75.7%	Appl. Catal. B: Environ 2013,
				142-143, 377.
NaYF ₄ :Yb,Tm/TiO ₂	RhB, 4.8mg/L	980nm, -	1h:~23%	Appl. Catal. B: Environ 2014,
				144, 379.
NaYF ₄ :Yb,Tm/ZnO	RhB, 20mg/L	980nm,	30h: ~65%	Phys. Chem. Chem. Phys.
		$2W/cm^2$		2013, 15, 14681.
NaYF ₄ :Yb,Tm/CdS	RhB, 10mg/L	980nm, 2W	3h: 24%	Appl. Catal. B: Environ.
				2010, 100, 433.
CaF ₂ :Er,Tm,Yb/	MO, 10mg/L	980nm, 2A	6h: ~10%	Nanoscale 2014, 6, 1362.
BiVO ₄				
YF ₃ :Yb,Tm-P25-GR	MO, 20mg/L	980nm, 4W	3h: ~8%	J. Mater. Chem. 2012, 22,
				11765.
NaYF4:Yb,Tm/CdS/	MB, 15mg/L	980nm,	20h:~70%	Dalton Trans. 2014, 43,1048.
TiO ₂		$2W/cm^2$	(6h:~30%))
Er doped g-C ₃ N ₄	RhB, 10mg/L	640–660nm,	16h: 60%	ACS Appl. Mater. Interfaces
		40W		2014, 6, 16481.
NaYF4:Yb,Tm/ CNX-	RhB, 10mg/L	980nm, 1W	6h: 57.6%	This work
NSs (1.5:1)				

Table S2 Comparison of NIR photocatalytic activity of UCPs/CNX_{0.1}-NSs composite with literature results. MB: methylene blue; RhB: rhodamine B; MO: methyl orange.

Models and calculation details. We selected heptazine as our building block (m0 in Supplementary Figure 13) and copolymerized into dimer (d0) and trimer (t0) to simulate the copolymerization effect. We also functionalized the heptazine blocks with various numbers of X groups, with which relaxed structures depicted in Supplementary Figure 13 (m1, d1, d2, t1, t2, and t3). The inter-layer interactions were modeled by stacking the previous structures into monolayer (L1), bilayer (L2) and trilayer (L3).



Figure S13 Schematic illustration of the fully optimized structures used for the modeling of copolymerization and functionalization of CN. m, d, and t denotes heptazine monomer, dimer and trimer, respectively. The digit following m, d and t denotes the number of grafted benzene rings. Only the in-plane models are shown here, coordinates of multilayer stacking structures can be found in the appendix.

Energy gaps. The energy gaps of the studied models were evaluated as the difference between the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) from SCC-DFTB calculations are listed in Table S3. The correlations between the energy gap values with the concentration of grafted benzene ring is depicted in Fig S14, where the mass concentrations of the benzene ring functional group were given by,

$$C = \frac{W_{bz}}{W_{mol}} \times 100\%$$

Where Wbz and Wmol are the molecular weights of the fragments involved in the benzene ring and of the whole molecule, respectively.

Table S3: Energy gaps of the models used calculated with SCC-DFTB. 'M', 'D' and 'T' denote monomer, dimer and trimer, respectively; The digit followed by M, D, or T denote the number of benzene rings grafted to CN. All gap values in electron volts (eV).

	m0	m1	d0	d1	d2	tO	t1	t2	t3
monolayer	3.883	2.582	3.373	2.823	2.585	3.207	2.500	2.429	2.484
bylayer	3.837	2.499	3.275	2.437	2.428	3.086	2.465	2.315	2.428
trilayer	3.831	2.551	3.314	2.454	2.433	3.074	2.340	2.265	2.389



Figure S14. Energy gap-benzene concentration relationship. The benzene concentrations are taken as the ratio between molecular weights of the fragments involved in the benzene rings and the whole cluster. Red, green, and blue colors represent monolayer, bilayer and trilayer, respectively. Solid circles, squares, and up triangles denote monomers, dimers and trimers, respectively.

Electronic transition calculations: All the electronic transition calculations are performed by using the ZINDO method upon the SCC-DFTB fully relaxed geometries. The degeneracy of the lowest electronic transition depends on the symmetry of the molecule, as listed in Table-NTO. The natural transition orbitals are obtained by a single-value decomposition (SVD) of the single-particle transition matrices.¹³ The UV-Vis absorption spectra for each model were plotted with the ZINDO transition energies and oscillator intensities, with a Lorentzian broadening constant 0.33 eV.¹⁴ All the UV-vis absorption spectra were rescaled by the molecular weight for ease comparison with each other and with experiments.

Table S4: The lowest electronic transitions of the models. The hole and electron states corresponding to each transition are depicted in Column 3 and 4, respectively. Red and blue color denotes positive and negative signs for the real-valued NTOs, respectively. All the isosurfaces are plotted with an isovalue of 0.02 a.u.

Model	Degeneracy	Hole state	Electron state
MO	1		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

M1	1	
D0	2	
D1	1	
D2	2	
то	3	
T1	1	



1. Copolymerization effects:

Doping phenylene group into CN networks will alter the intrinsic electronic structures, resulting in remarkable red shift of the absorption edge. The shift increases with the doping amount.



Figure S15. Calculated UV-Vis absorption spectra of (a) monomers, (b) dimers, and (c) trimers in monolayer.

2. Effects of exfoliation

1) Conjugation length

XRD and AFM characterizations confirm that exfoliation process caused the decrease of conjugation length of CN networks. An obvious blue shift is observed when decreasing the conjugation length from trimers to dimmers and finally to monomers. However, the difference gradually becomes negligible in doped CN networks with increasing doping amount. That is, the influence of decreasing conjugation length on the electronic structure may be less significant in phenylene doped CN system than that in non-doped CN system.



Figure S16. Comparison of calculated UV-Vis absorption spectra of models with different concontration of X: (a) without (b) with one and (c) with two X groups.

2) Interlayer stacking

XRD and AFM characterizations also confirm that exfoliation process destroyed the interlayer stacking of CN networks, generating ultrathin nanosheets with a thickness of 2~5 C-N layers. The decrease of thickness causes an obvious blue shift of the absorption edge in the cases of doped and non-doped systems.



Figure S17. Effects of exfoliation on the UV-Vis absorption spectra of monomers (a) without and (b) with one X group.



Figure S18. Effects of exfoliation on the UV-Vis absorption spectra of dimers (a) without and (b) with one, and (c) with two X groups.



Figure S19. Effects of exfoliation on the UV-Vis absorption spectra of trimers with 0 (a), 1 (b), 2 (c) and 3 (d) X groups.

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