

Electronic Supplementary Information

Ultrastable g-C₃N₄ assemblies with high quantum yield and revisable photoluminescence

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Experimental section

1. Synthesis of precursors

1.1 Synthesis of 650-CN

4g of melamine was added into a quartz boat and calcined at 650 °C for 2 hour in tube furnace under argon atmosphere at a temperature elevation rate of 2 °C/min. After that, obtained sample was washed by deionized water and dried at 60 °C. Finally, the pale yellow powder was obtained as 650 °C (650-CN)

1.2 Synthesis of 750-CN: Collected 4g 600-CN as precursor added into single open quartz tube ($\phi=2$, $L=20$ cm). then the precursor calcined under following process that furnace slowly increased temperature at elevation rate of 2 °C/min to 750 °C under argon atmosphere and kept this temperature for 1 hour. The pale white powder was obtained as crystalline 750 °C g-C₃N₄ (750 CN).

1.3 Preparation of 750@650-CN: Amorphous/crystalline g-C₃N₄ homojunction was synthesized using the way mentioned by Liu et al.^[1] that is, 0.4g of 750-CN was physically mixed with 1.6 g of melamine via an agate mortar for 30 min. after that, above precursor was added in quartz boat and calcined at 650 °C for 2 hours. The temperature elevation rate was 2 °C/min. The resulting sample was named as 20% 750@650 CN (750@650 CN).

1.4 Preparation of gRCN: The experiment was carried out following a alkaline etching method. This is different from an acid etching method.^[2] 0.5 g of 750@650 CN firstly stirred in NaOH solution (8M), and then heated at 70 °C for 24 hours. Obtained light green solution was centrifuged to remove sediment and finally got green-emitting g-C₃N₄ (gRCN).

1.5 Preparation of 750@650-CN with different 750-CN ratios: The synthesis process is similar to process 1.3. The difference is that samples were prepared using different 750-CN ratios in precursor (5, 10, and 50%)

1.6 Preparation of gRCN at different temperature: Samples were prepared using the precursor synthesized by process 1.3 and heated it at different temperature (0, 50, and 90 °C).

2. Characterization:

The morphology analysis of samples was performed on a scanning electron microscopy (SEM) (QUANTA 250 FEG, FEI, America) and transmission electron microscopy (TEM) (JEM-

2010, Japan). High resolution transmission electron microscope (Tecani F20, FEI, America) was used to further observe lattice fringe and obtain selected area electron diffraction (SEAD) results. Atomic force microscope (Multimode 8, Bruker, Germany) was carried out to obtain thickness changes. The X-ray diffraction (XRD) patterns of as-synthesis samples were taken by an X-ray diffract meter (Ultima IV, Japan) with a Cu K α radiation source and recorded in the 2 θ range 10-80°. AUV/visible spectrophotometer (U-4100, Hitachi) was used to make the UV-visible diffuse reflectance spectra of as-synthesis different g-C₃N₄ and absorption spectra of gRCN. The photoluminescence (PL) spectra obtained on Hitachi F-4600 Fluorescence spectrometer at room temperature whose tested wavelength was from 380-700 nm using 453 nm as the excited peak. The data of X-ray photoelectron spectroscopy (XPS) was collected from X-ray photoelectron spectroscopy analyzer (Escalab, Thermo Fisher Scientific, America). The chemical structure of the samples was studied by FTIR spectra (Nicolet 380, Thermo, America). The PL lifetime was obtained from single-photon counting time-resolved spectral fluorescence lifetime instrument (Jobin Yvon IBH, Horiba, Japan, λ_{ex} =374 nm). τ was fitting the decay curve using secondary fitting double-exponential decay function. PL decay dynamics were measured on a timecorrelated single-photon counting spectrofluorometer (Olympus IX 71 fluorescence microscope, Olympus Corporation, Japan) at room temperature, and the gRCN were excited by a 473 nm picosecond laser diode. The data of quantum yield was collected from an Edinburgh FLS920 fluorescence spectrophotometer.

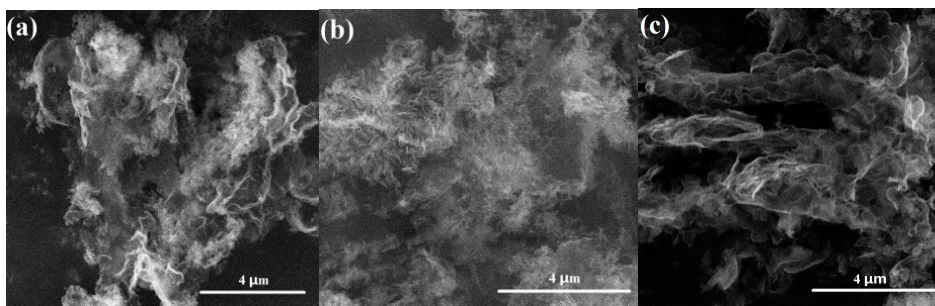


Fig. S1 SEM images of 650-CN (a), 750-CN (b) and 750@650-CN (c).

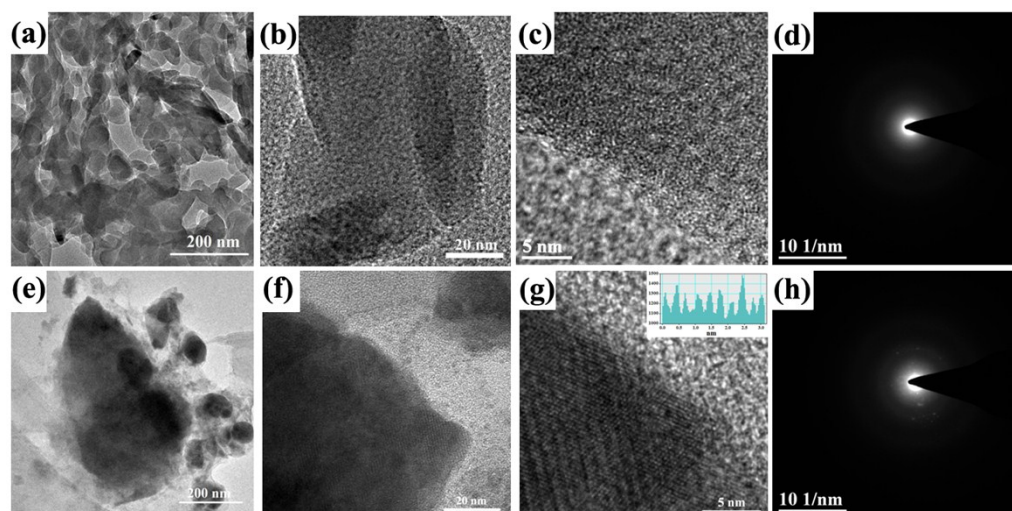


Fig. S2 HRTEM images and SEAD results: HRTEM images of 650-CN (a-c), and 750@650-CN (e-g). The inset in (g) shows the lattice fringe size; SEAD pattern of 650-CN (d) and 750@650-CN (h).

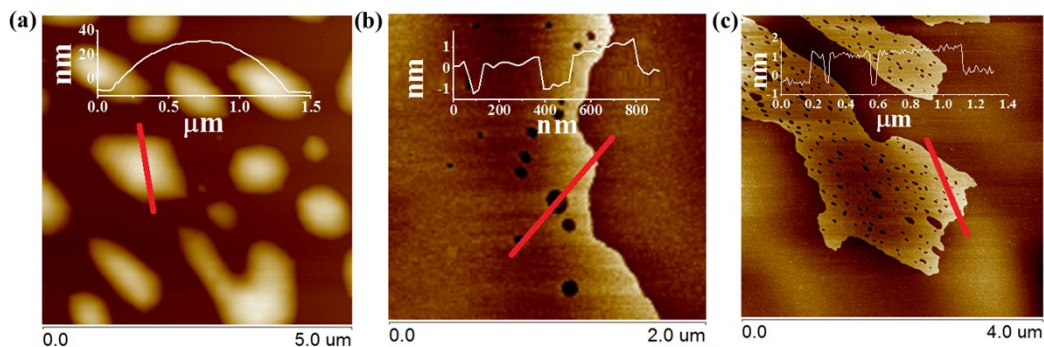


Fig. S3 AFM images of 650-CN (a), 750-CN (b) and 750@650-CN (c). The insets show the height and size of samples.

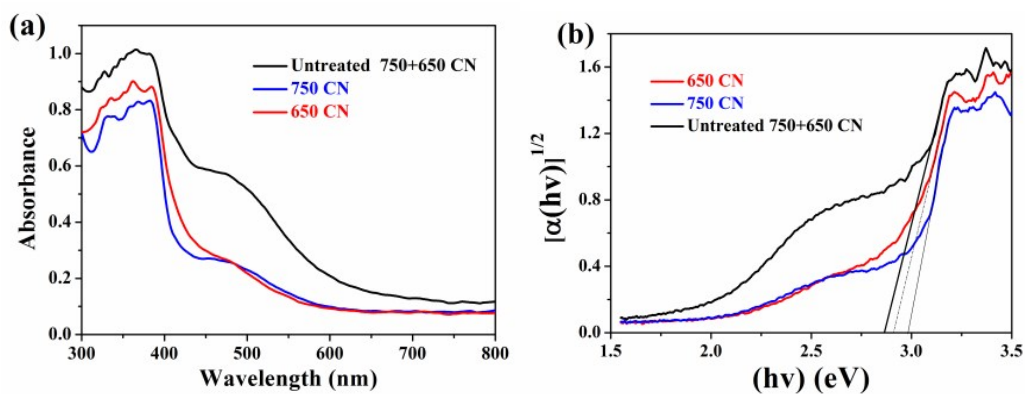
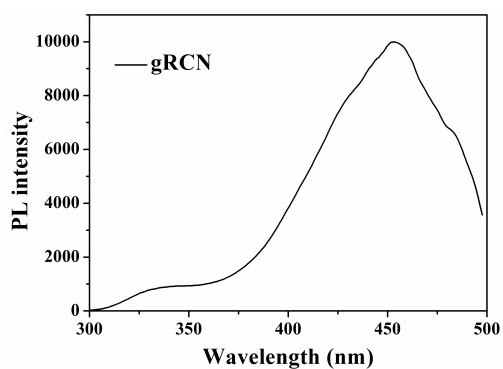


Fig. S4 UV-vis DRS spectra (a) and plots (b) of $[\alpha(h\nu)]^{1/2}$ vs photon energy of 650-CN, 750-CN and 750@650-CN.

Table S1 PLQYs of g-C₃N₄ materials in literature.*

Sample	Size	PLQYs (%)	Ref.
Phenyl-Modified g-C ₃ N ₄ dots	< 100 nm	48.4	4
Ultrathin g-C ₃ N ₄ nanosheets	~120 nm	19.6	5
phenyl-modified g-C ₃ N ₄	100~300 nm	38.1	6
O,S-doped green g-C ₃ N ₄ dots	~2.88 nm	31.7	7
g-C ₃ N ₄ dots	~ 3 nm	46.0	8
Oxygen,sulfur co-doped g-C ₃ N ₄ quantum dots	2.78 nm	14.5	9
g-C ₃ N ₄ dots	2~15 nm	29.0	10
Graphitic g-C ₃ N ₄ quantum dots	~4.3 nm	42.0	11
Fluorine-doped g-C ₃ N ₄ dots	4~10 nm	39.0	12
Nitric acid treated g- C ₃ N ₄	Bulky structure	11.8	13
barbituric acid doped g- C ₃ N ₄	Bulky morphology	17.9	14
This work	~200 nm	78.0	n/a

*All reported materials in literature are pure or doped g-C₃N₄ materials with homogeneity properties. Our sample is homostructures consisted of amorphous/crystalline nanosheets.

**Fig. S5** Excitation spectrum of gRCN

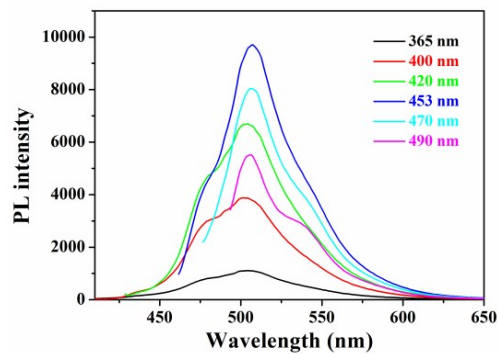


Fig. S6 PL spectra of gRCN at different excitation wavelengths

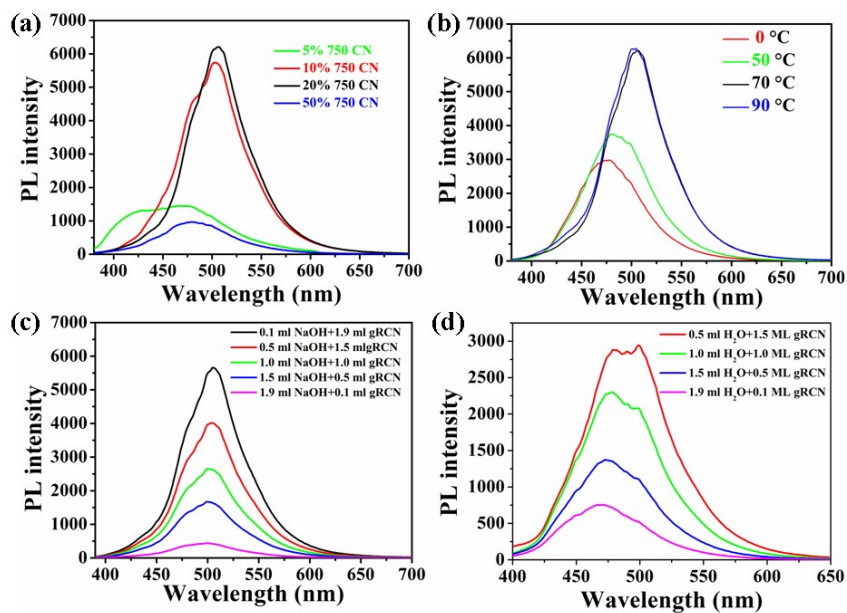


Fig. S7 PL spectra of gRCN: synthesized gRCN with different 750-CN ratios (a), synthesized gRCN at different temperature (b), diluted gRCN using by 8M NaOH (c) and water (d).

As shown in Fig.S7a, The PL peak position of samples prepared using 10 and 20% 750-CN in 750@650-CN is similar. But, The PL peak position of samples prepared using 5 and 50% 750-CN in 750@650-CN is drastically changed and the PL intensity decrease significantly. This phenomenon is attributed to a fact that either excessive or insufficient 750-CN is not suitable to the formation of amorphous/crystalline homojunction with rich $-NH_x$ groups. Although the ratio of 10 % has a similar spectrum, the symmetry of PL spectrum is not good compared with the samples using a ratio of 20%. 20 % is an optimized ratio to get gRCN. Temperature test indicates that samples prepared at 70 and 90 with similar PL property. At relatively low temperature, it is difficult to break g- C_3N_4 for high PL properties.

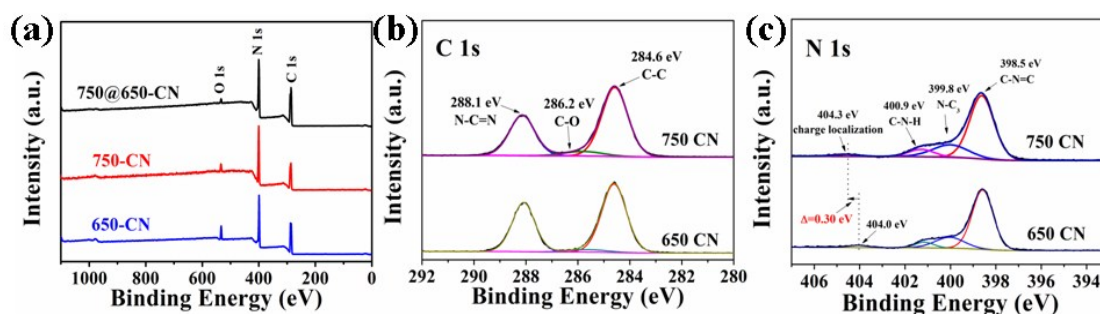


Fig. S8 XPS spectra of sample 650-CN, 750-CN and 750@650CN: survey spectra of 650-CN, 750-CN and 750@650-CN (a), C 1s spectra of 650-CN and 750-CN (b), N 1s spectra of 650-CN and 750-CN (c).

It is clearly that the peak of C 1s and N 1s do not change clearly, except the peaks for N at about 404eV which belongs to charge localization. This difference is attributed to its high crystalline of the sample prepare at high temperature. From the survey spectrum, the ratio of C/N is calculated and the results prove that the C/N ratio of 750-CN is 0.74 while that of 650-CN is about 0.86. As for 750@650-CN, the C/N ratio is about 0.79, which can further prove that both 750-CN and 650-CN contained in amorphous/crystalline homojunction. For calculated $N_3/(N_1+N_2+N_3)$ ratio, the ratio of 650-CN is about 6.32% and that of 750-CN is 8.68%. Both of them have a relatively low N_3 ratios compared with 750@650-CN (10.72%) which is well matched with UV-vis DRS result mentioned in Fig.S4. 750-CN revealed a relatively obvious absorbance around 500 nm which is consistent with $-NH_2$.

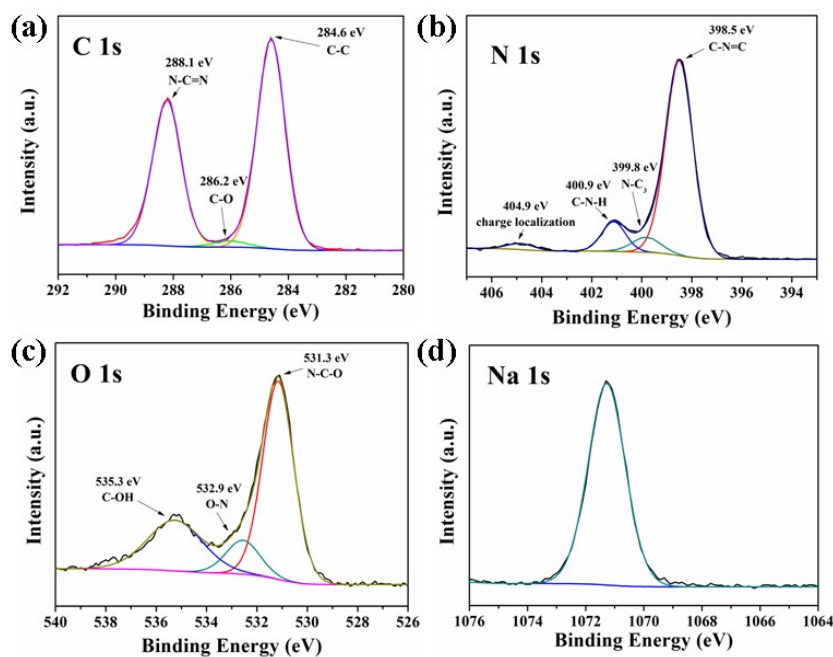


Fig. S9 XPS spectra of NaOH treated 650-CN.

Table S2 Integral area of different carbon in the XPS of different carbon nitride and NaOH treated samples.

Sample	C ₁	C ₂	C ₃
Pure 650 CN	33647.82	22242.18	2006.63
Pure 750 CN	88660.93	50640.12	8745.57
Pure 750@650 CN	90571.05	67581.78	3639.31
NaOH treated 650CN	70255.95	50194.69	2503.74
gRCN	111591.88	48115.74	4363.17

Table S3 Integral area of different nitride in the XPS of different carbon nitride and NaOH treated samples.

Sample	N ₁	N ₂	N ₃
Pure 650 CN	37425.13	9625.16	3175.13
Pure 750 CN	78336.72	22660.30	9596.32
Pure 750@650 CN	117565.30	24157.96	14251.80
NaOH treated 650CN	83082.56	6766.45	11002.07
gRCN	73054.56	7631.42	9681.63

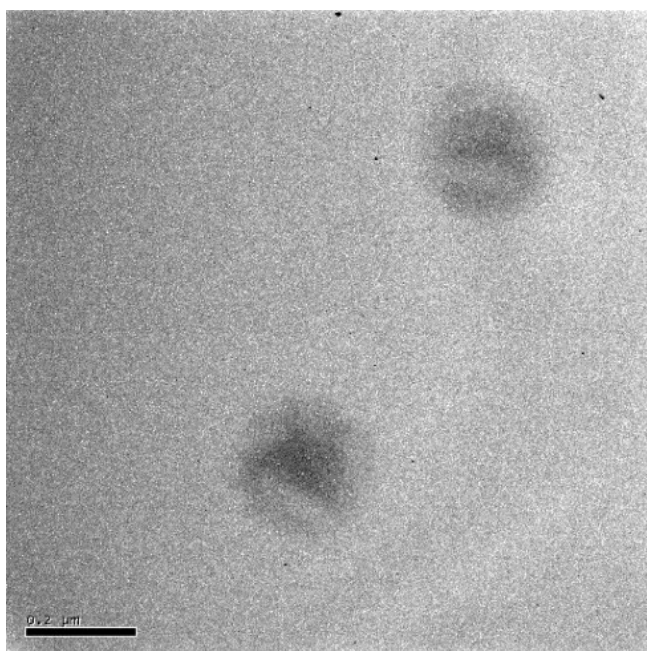


Fig. S10 TEM image of gRCN.

Table S4 Components B_1 and B_2 , time constants τ_1 and τ_2 , and average lifetime τ of gRCN

Sample	B_1	B_2	τ_1	τ_2
gRCN	83.30	16.70	1.86×10^{-9}	5.32×10^{-9}

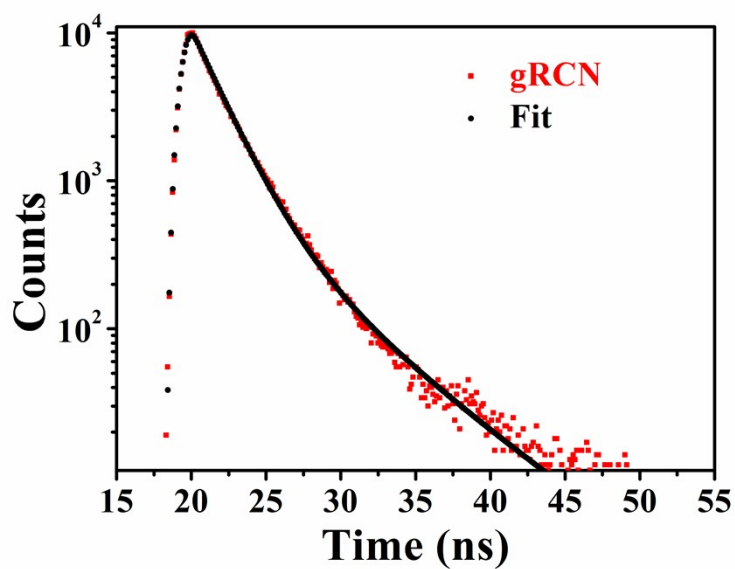


Fig. S11 PL decay curve (measured at maximum emission peak, $\lambda_{\text{ex}} = 374$ nm) of gRCN in colloidal solution. Reproduced curves using the data shown in Table S4 are plotted as thin black line.

The fluorescence decay curve was fitted well to the double exponential model described by the equation:

$$F(t)=A+B_1\exp(-t/\tau_1)+ B_2\exp(-t/\tau_2).$$

The fluorescence lifetime is calculated by the following formula:

$$\tau = (B_1 \times \tau_1^2 + B_2 \times \tau_2^2) / (B_1 \times \tau_1 + B_2 \times \tau_2).^{[3]}$$

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