

Supporting Information

Water-soluble ribbon-like graphitic carbon nitride (g-C₃N₄): green synthesis, self-assembly and unique optical properties

Bo Yuan, Zengyong Chu*, Gongyi Li, Zhenhua Jiang, Tianjiao Hu, Qinghua Wang, and Chunhua Wang

College of Science, National University of Defense Technology, Changsha 410073, P. R. China.

Fax/Tel: 86-731-84574786-811

E-mail: chuzy@nudt.edu.cn

EXPERIMENTAL

Materials

Dicyandiamide (DCDA, AR) was purchased from Xilong Chemical Co. Ltd. (Shantou, China). Sodium chloride (NaCl, AR) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All these chemicals were used without further purification. Deionized water used in the experiment was produced from a Millipore-ELIX water purification system.

Synthesis of bulk and ribbon-like g-C₃N₄

As a typical procedure, DCDA and NaCl with the mass ratio of 1:1 were mixed and ground to fine powders using a mortar and pestle. Then in nitrogen atmosphere, the fine powders were heated from room temperature to 600°C at a rate of 19.3°C•min⁻¹ and kept at 600°C for 60min. After cooling to room temperature, 1g obtained orange sample was grounded, added into 100mL deionized water and sonicated for 30min. The dispersion was centrifuged at 4000rpm for 10min to obtain a homogenous dispersion. After dialyzed by using dialysis bags of 100Da, sodium chloride in the homogenous dispersion was removed. Then the dispersion was freeze-dried, and the target sample was finally obtained. The bulk g-C₃N₄ was prepared as a reference by heating DCDA using the same heating procedure.

Characterization

The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker TENSOR-27 Fourier transform-infrared spectrophotometer. The crystalline structure was investigated by X-ray diffraction (XRD) on a D8ADVANCE type by using Cu K α radiation. X-ray photoelectron spectroscopy (XPS) was investigated using K-Alpha 1063 type with focused monochromatized Al K α radiation. The scanning electron micrographs (SEM) were taken on a JSM-6700F microscope. The transmission electron microscopy (TEM) images were obtained by a JEM-2100F electron microscope at an acceleration voltage of 200kV with a CCD camera. UV-vis diffuse reflectance spectra (DRS) were carried out on a HITACHI U4100 spectrophotometer using BaSO₄ as the reference. The photoluminescence (PL) spectra were recorded by using a FL-3 transient fluorescence spectrometer.

Bulk g-C ₃ N ₄		Ribbon g-C ₃ N ₄	
Name	Atomic %	Name	Atomic %
N1s	48.89	N1s	44.55
C1s:C-O	49.51	Na1s	7.77
O1s	1.02	C1s:C-O	46.31
		Cl2p	0.21
		O1s	1.16

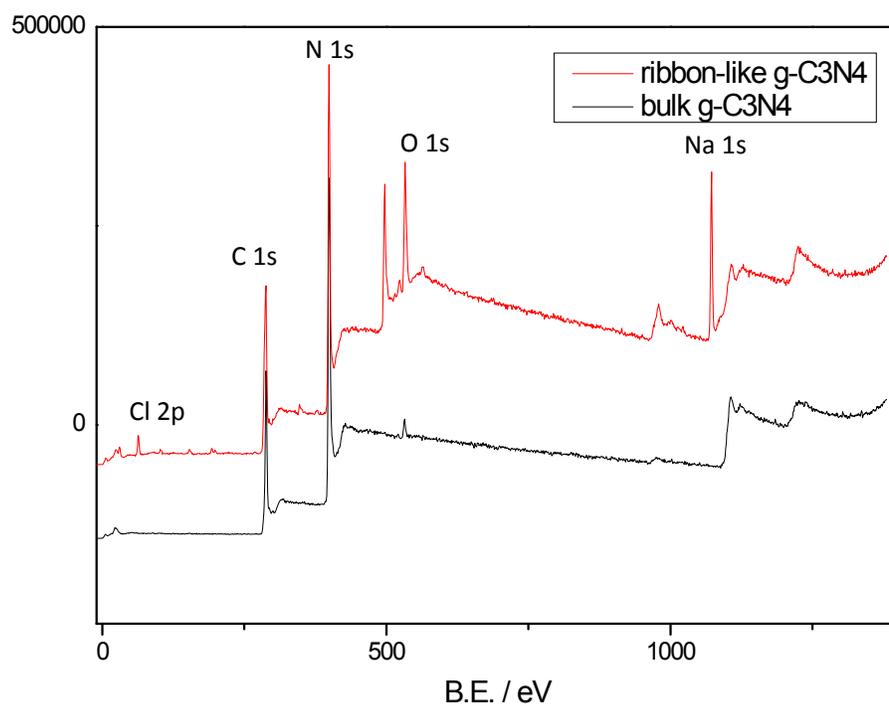


Fig.S1 XPS Full scan of the bulk g-C₃N₄ and ribbon-like g-C₃N₄

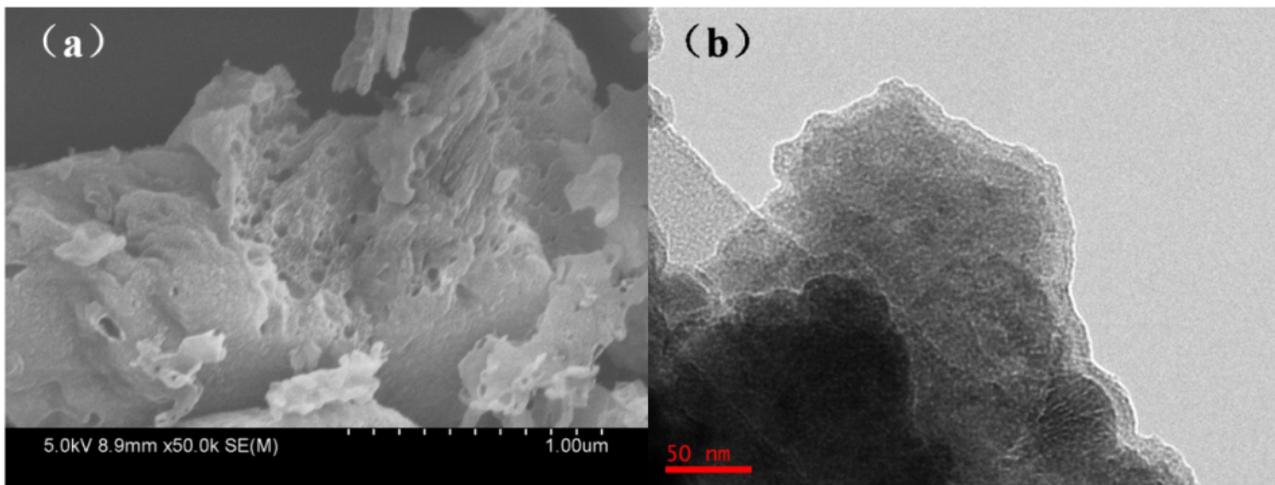


Fig. S2 SEM (a) and TEM (b) images of the bulk g-C₃N₄

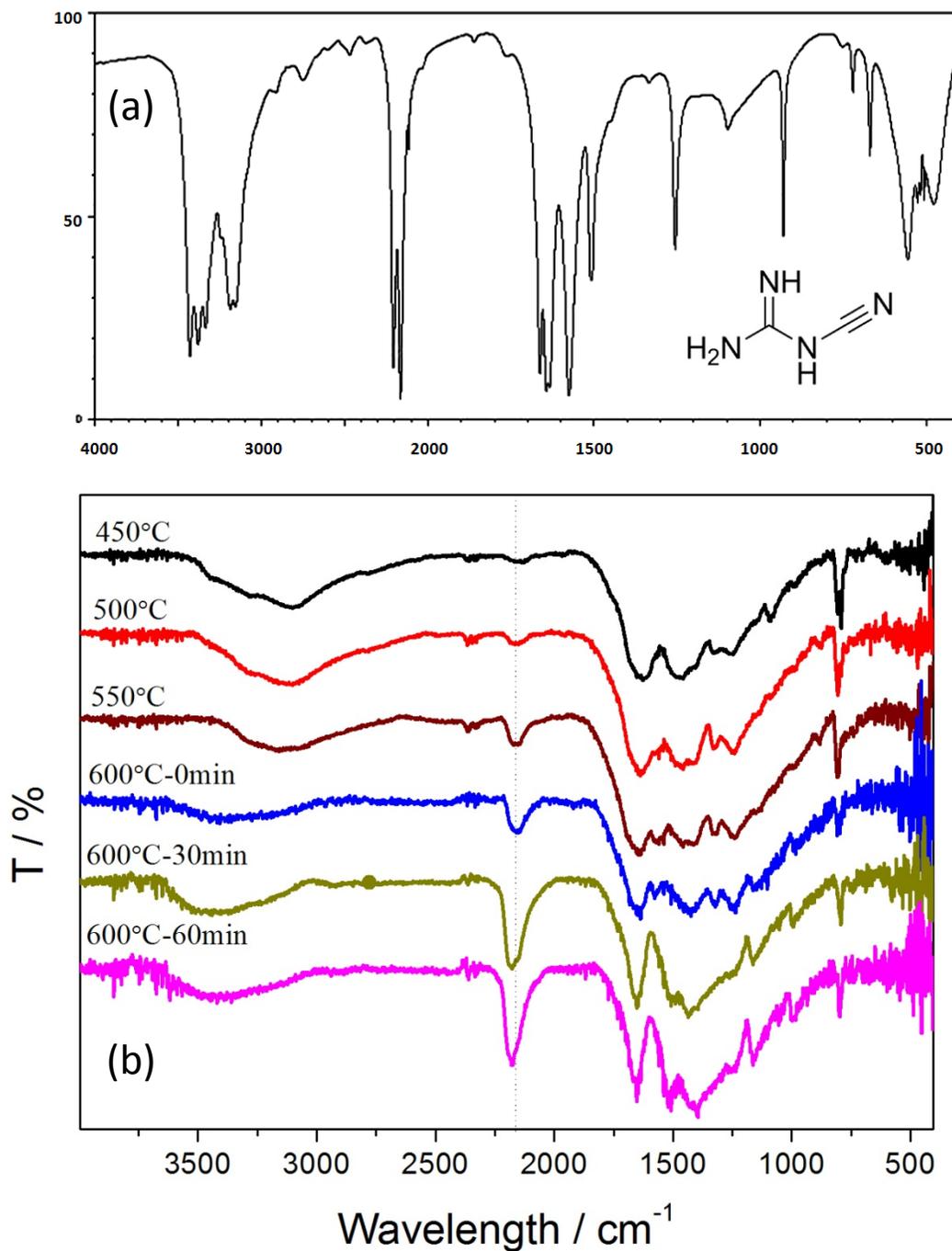


Fig. S3 FT-IR spectra of DCDA (a) and heated samples (b) at different temperatures and times

Comparing FT-IR spectra of the six samples, it can be concluded that cyano group (2200cm^{-1}) emerges in quantity above 550°C . That is to say, cyano group was regenerated by the catalytic pyrolysis of $\text{g-C}_3\text{N}_4$ above 550°C (the raw material DCDA has cyano groups).

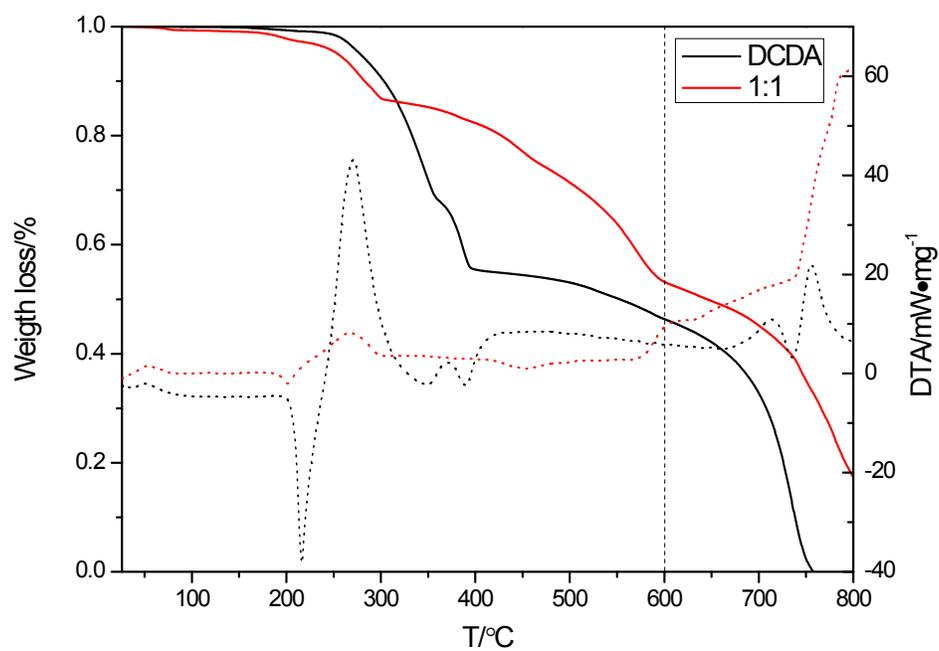


Fig. S4 TGA and DTA curves of the pure DCDA and the mixture of DCDA/NaCl with a mass ratio of 1:1.

Table. S1 Different assemblies associated with different alcohols

Alcohol	Microstructure	Image
None	Ribbons	Fig. 1d-f
Methanol	Belts	Fig. 4a
Ethanol	Belts, Flower clusters	Fig. 4b-f
n-paropropanol	Belts, Flower clusters	Fig. 4b-f
Isopropanol	Rods, Tubes	Fig. 4g-i

Atomic percent, at%

Elements	No.1	No.2	No.3
C K	35.68	40.90	-
N K	44.92	38.67	48.50
O K	8.46	5.01	-
Na K	10.07	11.85	35.93
Cl K	0.87	3.56	15.57

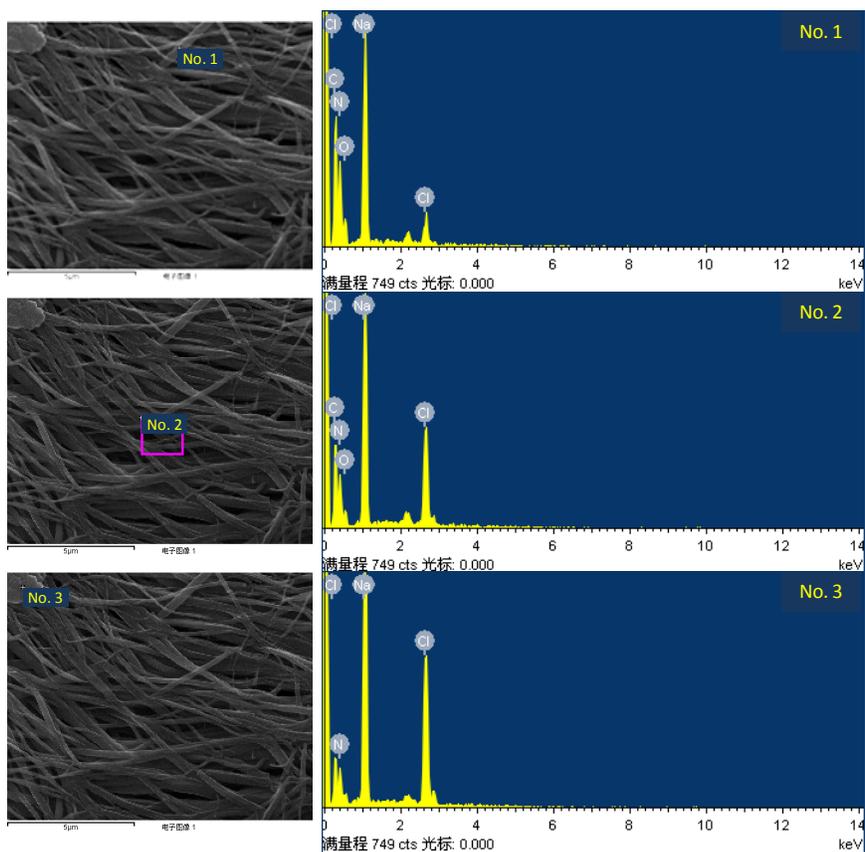


Fig. S5 EDS analysis of the self-assembly belts

Atomic percent, at%

Elements	No.4	No.5	No.6	No.7
C K	32.64	39.15	-	37.31
N K	50.77	38.88	54.65	50.80
O K	6.80	7.25	-	-
Na K	9.27	11.47	32.50	10.27
Cl K	0.52	3.24	12.85	1.62

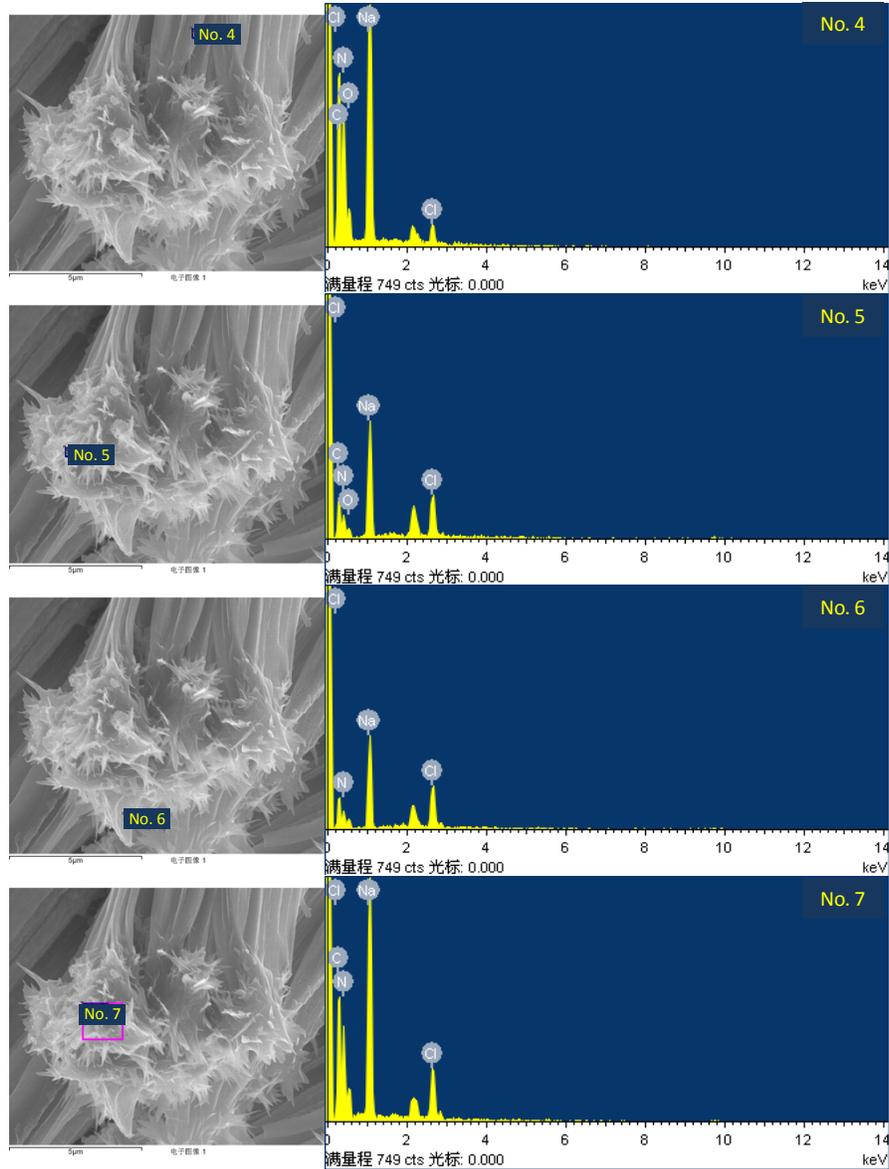


Fig. S6 EDS analysis of the self-assembly flower

Fig. S7 Schematic diagram of the formation of ribbon-like g-C₃N₄ and various special assemblies

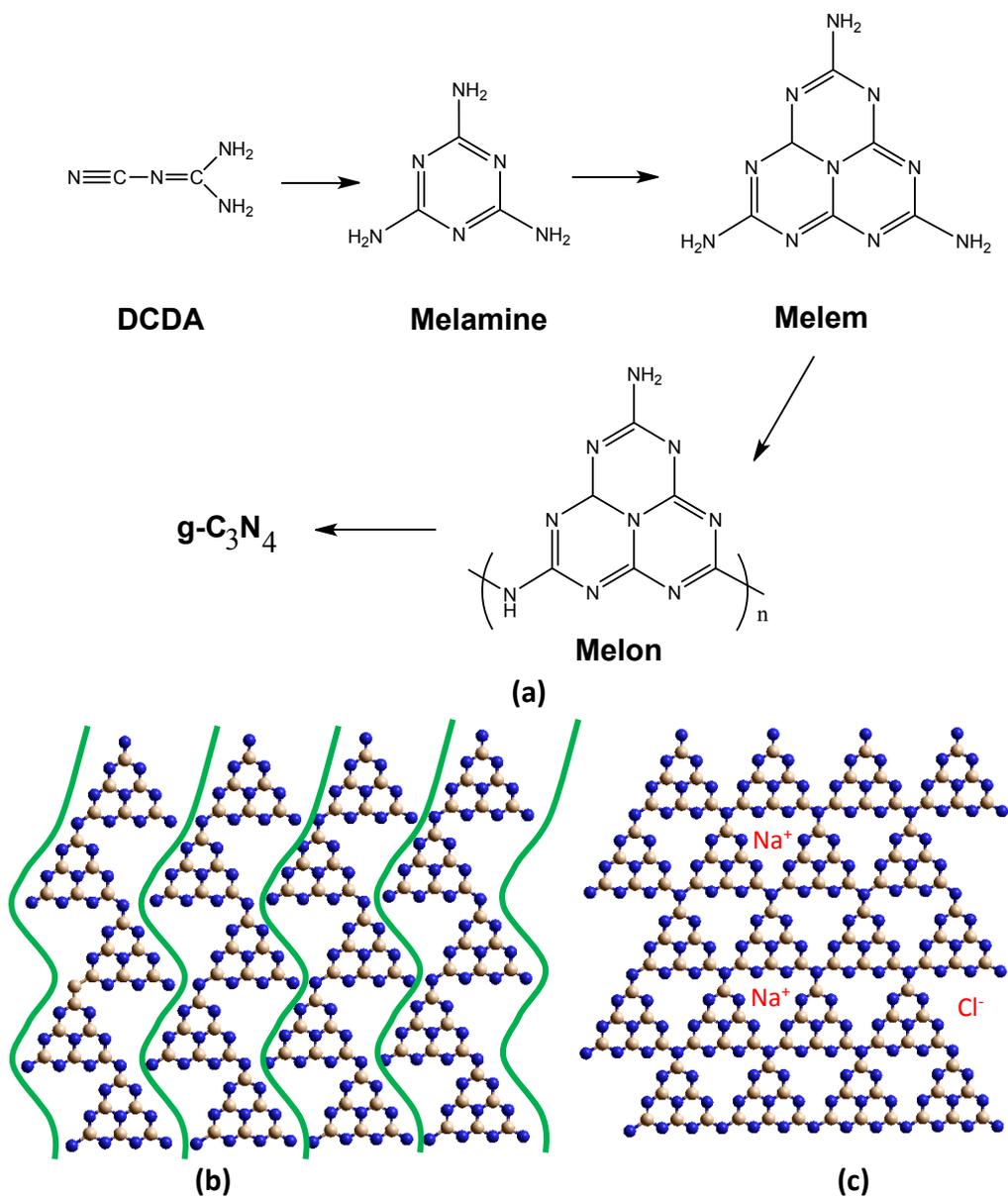


Fig. S8 Polymerization process of DCDA (a), the ball-and-stick models of melon (b) and $\text{g-C}_3\text{N}_4$ (c)