Supporting Information

Dissolution and Liquid Crystals Phase of 2D Polymeric Carbon Nitride

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Experimental

Reagent. Dicyandiamide (DCDA, 99%) and sulfuric acid-d_2 solution (96.0-98.0 wt% in D_2O, 99.5 atom % D) were purchased from Sigma-Aldrich. Tetramethylsilane (TMS) and nitromethane of GC grade for NMR were obtained from TCI (Japan). Concentrated sulfuric acid (H_2SO_4, 95.0-98.0%), methanol (CH_3OH), dimethylformamide (DMF) were of analytic grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Unless otherwise specified, all other regents were of analytical grade and used as received without further purification. Ultrapure water (18.2 MΩ) was obtained through Thermo purification system.

Preparation of bulk graphite-phase polymeric carbon nitride (C/N/H, denoted as GPPCN). The bulk GPPCN was prepared by one-step thermal condensation of dicyandiamide in a crucible with a cover at 550 ^oC for 4 hrs with a 4 hrs ramp time in a muffle furnace (Carbolite, UK). The obtained yellow GPPCN product was ground into powder by agate mortar before use.

Preparation of GPPCN/H_2SO_4 solution. The GPPCN/H_2SO_4 solutions (0-300 mg/mL) was obtained by stirring the mixture of 0-6 g of as-prepared GPPCN and 20 mL H_2SO_4 at 100 ^oC for 2 hrs. The mixture gradually turned into a clear pale yellow solution.

Preparation of GPPCN/H_2SO_4 pastes. To better investigate the mechanism of the dissolution, various GPPCN/H_2SO_4 pastes (600 mg/mL), the intermediate states during the dissolution of GPPCN in H_2SO_4, were prepared by mixing 1.2 g of GPPCN and 2 mL of concentrated sulfuric acid and heating at 100 ^oC for 0, 30, and 120 min, respectively.

Preparation GPPCN that precipitated from GPPCN/H_2SO_4 solution. Since CH_3OH was a poor solvent for GPPCN but dissolvable in H_2SO_4, precipitated GPPCN was prepared by adding CH_3OH into the GPPCN/H_2SO_4 solution, washing the obtained precipitate sufficiently with CH_3OH, and drying at 40 ^oC.

Preparation of g-CN nanosheet suspension. Briefly, 100 mg of bulk g-CN powder was dispersed in 100 mL of water, and then sonicated for about 16 hrs. The initial formed suspension was then centrifuged at about 5,000 rpm to remove large particles.[s1]

Characterization. X-ray powder diffraction (XRD) was characterized with a Bruker D8 Advance diffractometer equipped with high-intensity Cu-Kα radiation (λ = 1.54178 Å). NMR experiments were performed under ambient condition on a Bruker Biospin DRX-600 spectrometer. The chemical shifts in the ^{13}C NMR and ^{15}N NMR

spectra were referenced to TMS and nitromethane, respectively.[s2] X-ray photoelectron spectra (XPS) experiments were carried out on a Theta probe (Thermo Fisher) with monochromated Al Kα X-rays (hv = 1486.6 eV) as the excitation source. UV-vis absorption spectroscopy was measured on Shimadzu UV-2450 spectrophotometer. The Fourier transform infrared (FT-IR) experiment was carried out on a Nicolet 4700 FTIR spectrometer (Thermo, USA), equipped with attenuated total reflectance (ATR). The photoluminescence (PL) spectra were performed by fluorescence spectrometer (Fluoromax-4, Horiba Jobin Yvon, Japan).

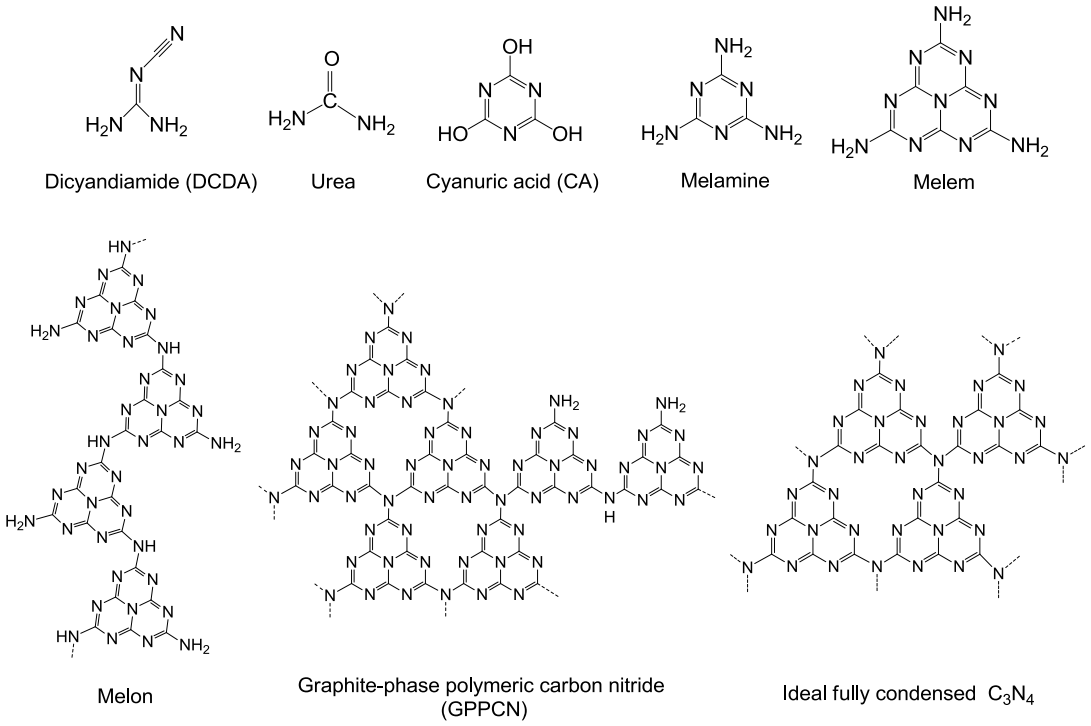

Figure S1. (a) Structure of DCDA, urea, CA, melamine, melem, melon and ideal fully condensed C_3N_4 based on tri-*s*-triazine units, and (b) the proposed structure of GPPCN (cf. NMR results in Fig. 4a and Fig. S11).

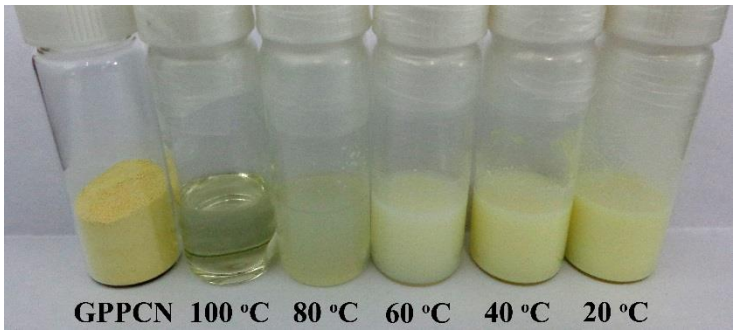

Figure S2. Photo of bulk GPPCN powder and different GPPCN/H_2SO_4 mixtures (50 mg/mL) prepared by heating at 100 °C, 80 °C, 60 °C, 40 °C and 20 °C for 2 hrs.

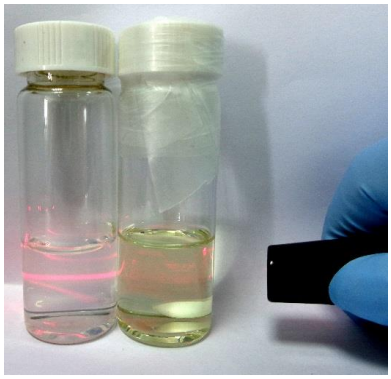

Figure S3. Photo of GPPCN/H_2SO_4 solution (50 mg/mL, right) and GPPCN nanosheet dispersion in water (0.15 mg/mL, left) and evaluation of Tyndall effect.

Carbon nitride can form stable thermodynamic solutions in concentrated sulfuric acid without aggregating upon standing for more than one year and would also be stably co-existed with some polar aprotic solvents such as DMF and NMP. Some protic solvents such as CH_3OH and water would deprotonate carbon nitride and destroy hydrogen bond of the carbon nitride in H_2SO_4 solution. Adding such poor solvents can normally make carbon nitride precipitate. Similar phenomenon was also observed in graphene and carbon nanotube dissolved in concentrated sulfuric acids.[s3]

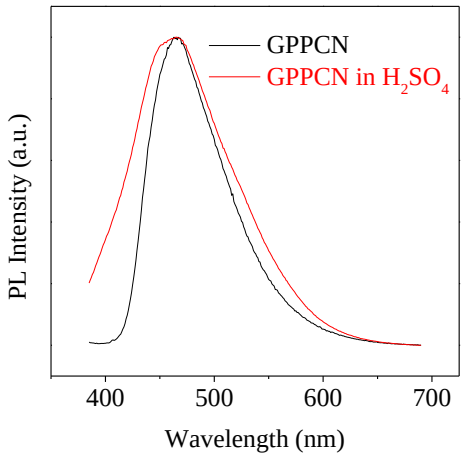

Figure S4. Photoluminescence spectra (E_x = 370 nm) of bulk GPPCN and GPPCN/H_2SO_4 solution (50 mg/mL).

As shown in Fig. S4, the GPPCN/H_2SO_4 solution was found to have the same maximum PL emission peak at 465 nm as the original bulk GPPCN, indicating the preservation of the electronic structure from bulk GPPCN, i.e., the conjugated –C-N- network, was mostly retained after dissolution. It should be noted that the broadening of the PL signal disproportionally to lower wavelength was observed, and could be ascribed to the following two reasons. On the one hand, in general, due to protonation of GPPCN with H_2SO_4, lone pair electron of the "aromatic" nitrogen atoms were prone to interacting with proton, lowering the energy of n nonbonding orbitals. Then, the energy of transition from n nonbonding orbitals to lowest unoccupied molecular orbitals (LUMO) would increase, leading to the blue-shift emission. The similar phenomenon was also observed in the protonation of carbon nitride with HCl.[s4] On the other hand, bulk GPPCN dissolved in sulfuric acids will be exfoliated into a few layered "nanosheets", which may also induce the blue-shift emission due to quantum confinement effect.[s1]

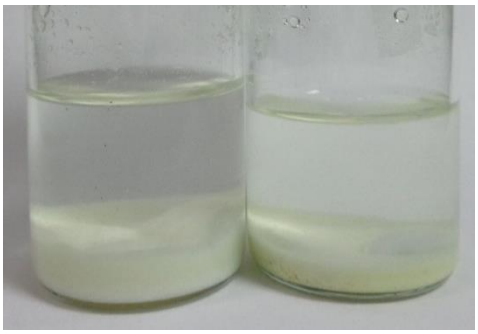

Figure S5. Photo of GPPCN in concentrated HNO_3 (left, 50 mg/mL) and HCl (right, 50 mg/mL) after heating at 100 °C for 2 hrs.

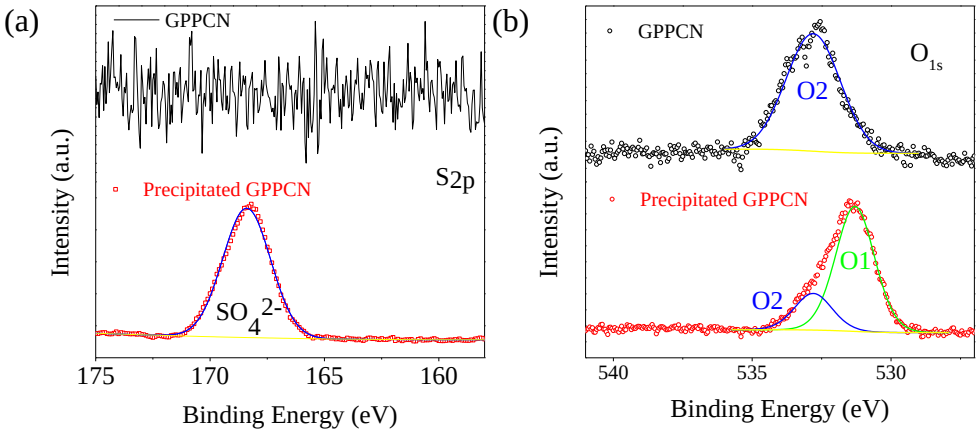

Figure S6. High-resolution S_{2p} and O_{1s} XPS spectra of bulk GPPCN and precipitated GPPCN.

The XPS analysis of the recovered GPPCN sample showed the presence of sulfuric, compared with that of the pristine GPPCN. The new S_{2p} component at binding energy of 168.4 eV which falls within the range of energies characteristic of SO_4^{2-},[s5] strongly indicating the effective protonation of GPPCN in H_2SO_4. It should be noted that such protonation most likely occurred at the same plane of the framework of GPPCN, thus it did not evidently change the interlayer distance (see XRD patterns in Fig. 1b). The similar phenomenon was also observed in the protonation of GPPCN with HCl.[s4] As shown in Fig. S6b, small amounts of oxygen were detected in the

bulk GPPCN, which likely result from water absorption.[s2, 6] Compared with GPPCN, the O_{1s} peaks of the precipitated GPPCN can be deconvoluted into two peaks for the SO_4^{2-} (O1 531.30 eV)[s5] and H_2O (532.80 eV).[s7] Further XPS analysis demonstrated that the molar ratio of S/O1 for precipitated GPPCN is about 0.26 (see Table S2), close to the stoichiometric ratio of SO_4^{2-} about 0.25, indicating the effective protonation of GPPCN in H_2SO_4 and signifying that H_2SO_4 did not destroy the structure of GPPCN. The O_{1s} spectra was consistent with S_{2p} XPS spectra.

Figure S7. Photo of GPPCN/H_2SO_4 paste (600 mg/mL), the intermediate state during the dissolution of GPPCN in H_2SO_4.

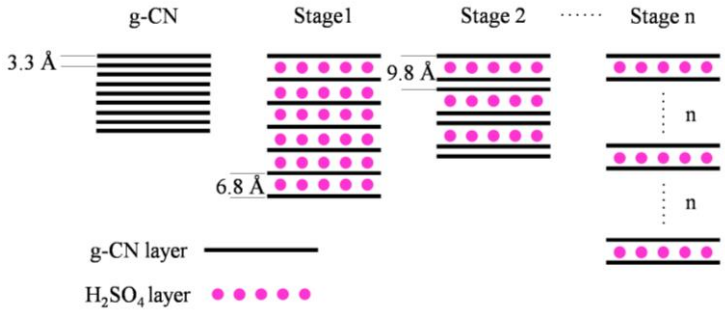

Figure S8. Scheme of the staging phenomenon in GPPCN/sulfuric acid for stage 1 to stage n. The number of GPPCN layers, n, sandwiched between the two intercalant layers is referred to as the stage number.

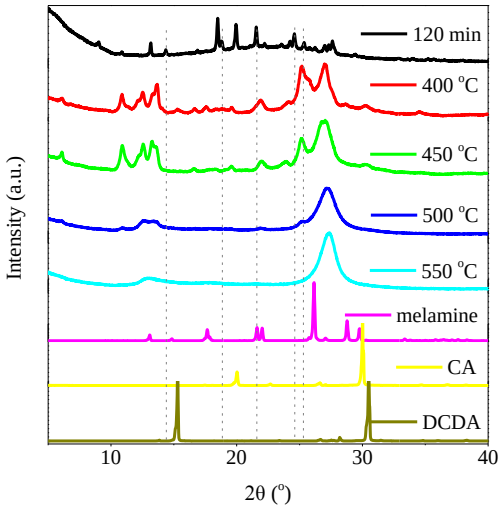

Figure S9. The XRD patterns of intermediated state, carbon nitride synthesized at different temperature, melamine, cyanuric acid (CA) and dicyandiamide (DCDA).

As shown in Fig S9, the XRD patterns of the compounds such as melamine, CA, DCDA and carbon nitride of different degree of polymerization synthesized at different temperature, were quite different to the unassigned peak of GPPCN paste after 120 min of heating, indicating that these molecules could be excluded as the immediate products during the dissolution of polymeric carbon nitride.

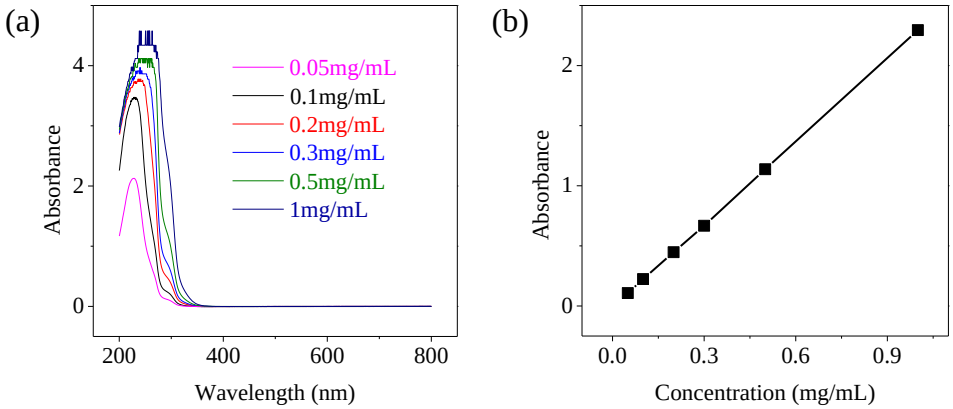

Figure S10. (a) UV-vis absorption spectra for GPPCN/H_2SO_4 solution at different concentrations. (b) The absorbance (λ= 295 nm) as a function of concentration for GPPCN showing Lambert-Beer behavior with an absorption coefficient of ε = 1147.6 L g^{-1} m^{-1}.

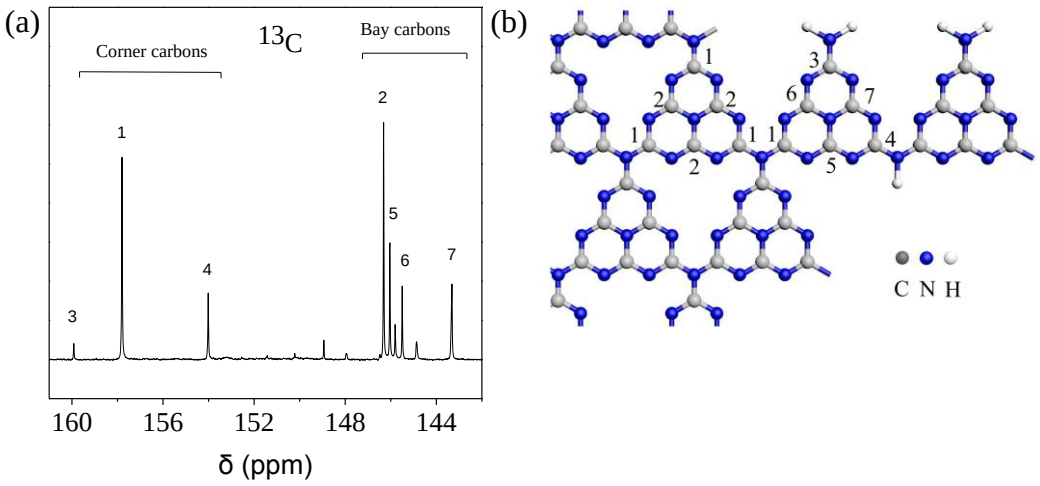

Figure S11. (a) ^{13}C liquid-state NMR spectrum of GPPCN/H_2SO_4 solution, and (b) the proposed structure for GPPCN.

The ^{15}N liquid-state NMR spectrum of GPPCN/H_2SO_4 solution is shown in Fig. 4a. Owing to the protonation and hydrogen bonding environment, the signal slightly shifted to lower ppm similar with protonated melem.[s8] For this, the peaks in the ^{15}N spectra can be assigned as follows: the signal at -196.81 ppm corresponded to the tertiary (N_{tert}) nitrogen atoms in condensed CN network, -228.06 ppm to the protonated tertiary nitrogen atoms, -236.57 ppm to the center nitrogen (N_c) of tri-*s*-triazine, 242.56 ppm to the imino group (NH) and -251.79 ppm to the amino group (NH_2). The values of these shifts coincide with those of solid-state NMR of melon and protonated melem.[s2, 8] In addition, the linking nitrogen (N_l) of fully condensed structure showed a lower ppm compared with center nitrogen of tri-s-triazine according to the calculation of solid-state NMR spectra.[s9] Therefore, the -244.83 ppm could be assigned to the liking nitrogen of fully condensed carbon nitride. The ^{15}N spectra indicated that fully condensed and partially condensed GPPCN network may coexist in as-prepared GPPCN.

It should be noted that intense protonation interaction of polymeric carbon nitride with concentrated sulfuric acids may have a remark effect on the ^{15}N NMR spectrum, presumably resulting in a higher local symmetries or other effect, for example, protonation of graphene in sulfuric acids would alter graphene conformation in solution.[s3b] Therefore, many of the tertiary nitrogen cannot be distinguished. However, the fully condensation structure and partial condensation could be differentiated by ^{13}C NMR spectra. The ^{13}C NMR spectra of GPPCN in Fig. S11 shows multiple resonance signals of the corner (δ=154-160 ppm) and bay carbon (δ=143-147 ppm), also suggesting the incompletely condensed tri-*s*-triazine units in the framework of as-prepared GPPCN. The solid-state ^{13}C NMR spectra of melam, melamine–melem adduct, melem, and melon in previous reports showed that the chemical shift of corner carbons in carbon nitrides were about 10 ppm higher than that of bay carbons.[s2, 10] Thus, the high-field resonances at d = 159.2 (3), 157.8 (1) and 154.0 (4) can be assigned to the corner carbons, and those at 146.3 (2), 146.0 (5) 145.5 (6) and 143.3 (7) ppm to bay carbons. Moreover, the bay carbon resonances of tri-*s*-triazine network would up-shift when the condensation was improved.[s10c] In this sense, resonances at 146.3 (2) ppm can be attributed to bay carbon of fully condensed tri-*s*-triazine network, and the resonances at 146.0 (5), 145.5 (6) and 143.3 (7) ppm may be assigned to partially condensed tri-*s*-triazine network according to computational sequence in previous work.[s2] Since the signals of C-NH_2 often showed ca. 5 ppm higher ppm than C-NH according to experimental and computational data,[s9, 11] the resonance at 159.2 and 154.0 ppm can be assigned to the

C-NH_2 and C-NH of partially condensed tri-*s*-triazine network, and the 157.8 ppm can be ascribed to the corner carbon of fully condensed tri-*s*-triazine network. It should be noted that a clear up-field shift may be assigned to the protonation and hydrogen-bonding environment of carbon nitride in sulfuric acids.[s9] Similar phenomenon was also observed in the protonation of melem with H_2SO_4.[s12] The proposed assignment of ^{13}C NMR spectrum of GPPCN/H_2SO_4 was in agreement with that of ^{15}N NMR spectrum of GPPCN/H_2SO_4 (Fig. 4a).

The proposed structure of both full and partial condensed 2D framework for GPPCN can also be supported by other facts. On the one hand, the C/N ratio of the as-prepared GPPCN (0.71, elemental analysis) fell in the middle of that of the ideal fully condensed carbon nitride (0.75) and melon (0.67). Essentially, it shows that the as-prepared GPPCN is NOT melon, a 1D polymer (Fig. S1). On the other hand, this assumption can also be supported by the successful exfoliation of single-layered or few layered 2D sheets of GPPCN in previous reports.[s1, 13]

Table S1. XPS analysis of bulk GPPCN and precipitated GPPCN.

	Atom (%)		
GPPCN	C1	39.53	C1/N=0.73
	N	54.33	
	O2	6.14	
Precipitated GPPCN	C1	31.69	C1/N=0.73
	N	43.40	
	S	4.21	
	O1	16.14	S/O1=0.26
	O2	4.56	

As shown in Table S2, small amounts of oxygen were detected in the bulk GPPCN, which likely result from water absorption and was pointed out in the literature. [s2, 6] Compared with bulk GPPCN, the oxygen content was increased dramatically, and the molar ratio of the S/O1 is about 0.26, closing to the stoichiometric ratio of SO_4^{2-} about 0.25. Small amouts of water was also absorbed, simlar to the protonated melem.[s8, 14]

Table S2. Elemental analysis of GPPCN and precipitated GPPCN.

entry	C[a]	N[a]	H[a]	S[a]	C/N[b]
GPPCN	35.01	57.60	2.91	0.22	0.71
Precipitated GPPCN	24.03	40.92	3.68	5.59	0.69

[a] wt.%; [b] molar ratio

In order to further study the molar ratio of C/N of the precipitated GPPCN, elemental analysis were performed. The experimental results as displayed in Table S2 show the molar ratio of C/N for the as prepared GPPCN and precipitated GPPCN are about 0.71 and 0.69, respectively, both close to the stoichiometric ratio of C_3N_4. The noticeable increase of hydrogen and sulfur content indicated the protonation of GPPCN with H_2SO_4.

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