



# Synthesis and luminescence mechanism of multicolor-emitting g-C<sub>3</sub>N<sub>4</sub> nanopowders by low temperature thermal condensation of melamine

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Graphite like C<sub>3</sub>N<sub>4</sub> (g-C<sub>3</sub>N<sub>4</sub>) was synthesized facilely via the low temperature thermal condensation of melamine between 300–650 °C. The results showed that the products maintained as melamine when the temperature is below 300 °C. With the increase of temperature, the products were transformed into carbon nitride and amorphous g-C<sub>3</sub>N<sub>4</sub> successively. The morphology of products was changed from spherical nanoparticles of melamine into layer carbon nitride and g-C<sub>3</sub>N<sub>4</sub> with the increase of temperature. The photoluminescence spectra showed that the carbon nitride products have continuous tunable photoluminescence properties in the visible region with increasing temperature. With the help of steady state, transient state time-resolved photoluminescence spectra and Raman microstructural characterization, a novel tunable photoluminescence mechanism was founded systematically, which is mainly related to the two dimensional  $\pi$ -conjugated polymeric network and the lone pair of the carbon nitride.

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Carbon nitride has become a research hot in the field of materials science since Liu and Cohen predicted that the carbon and nitride were the good candidates for the extreme hardness materials<sup>1</sup>. Due to the special electron structures, carbon nitride is a kind of novel organic and metal-free semiconductors, on the other hand, composing by carbon and nitride, as well as its special layer structure make it has better chemically and thermally stable in the ambient conditions<sup>2</sup>. Moreover, the most important is that we can handle the band gap of carbon nitride via doping or modification its morphology<sup>3</sup>. Owing to their special properties such as the super hardness, low density, reliable chemical inertness, water resistivity, wear resistance and biocompatibility<sup>2,3</sup>, carbon nitride was regarded as the promising materials applied in the emission devices, surface modification, medical science and photocatalysis, etc. Wang et al. have reported that using carbon nitride as photocatalysis to acquire the hydrogen from water<sup>2</sup>, and Iwano et al. have reported that the amorphous carbon nitride films can be applied to the white light emitting devices<sup>4</sup>. Among the carbon nitride materials, graphite like carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has attracted considerable attention due to its unique optical and electronic properties, which is promising to be applied as photoelectric nanodevices, chemical sensors, metal free photocatalysis, photovoltaic solar cells, etc.<sup>5–8</sup>.

Up to now, g-C<sub>3</sub>N<sub>4</sub> with several different kinds of morphologies has been fabricated, such as nanoparticles, nanowires, nanobelts, hollow vessels, etc.<sup>5,6,9</sup>. And various techniques and methods, such as chemical vapor deposition (CVD), physical vapor deposition (PVD), solvothermal synthesis, thermal nitridation, etc., have been used to synthesize g-C<sub>3</sub>N<sub>4</sub>. However, most of the traditional techniques and methods need strict synthesized conditions, such as higher temperature, higher pressure or longer time pretreatment. Therefore, a brand new method with simple synthesized process and low cost is eagerly anticipated for the research of g-C<sub>3</sub>N<sub>4</sub>.

Nowadays, several works about the visible photoluminescence (PL) of carbon nitride have been reported<sup>4,10,11</sup>. However, the systematic investigation on the tunable PL of carbon nitride is scarce, and it is much rarer for g-C<sub>3</sub>N<sub>4</sub> compounds. Researchers have tried to propose the explanations about the mechanism of visible PL of carbon nitride<sup>4,10,12,13</sup>. But there is no unambiguous PL mechanism or tunable PL mechanism about carbon nitride, such as g-C<sub>3</sub>N<sub>4</sub>, has been proposed in detail so far, which restricts the preparation and design of carbon nitride with multicolor-emitting and efficient luminescence. Therefore, the mechanism investigation about the luminescence of carbon nitride is extremely important in this research field.

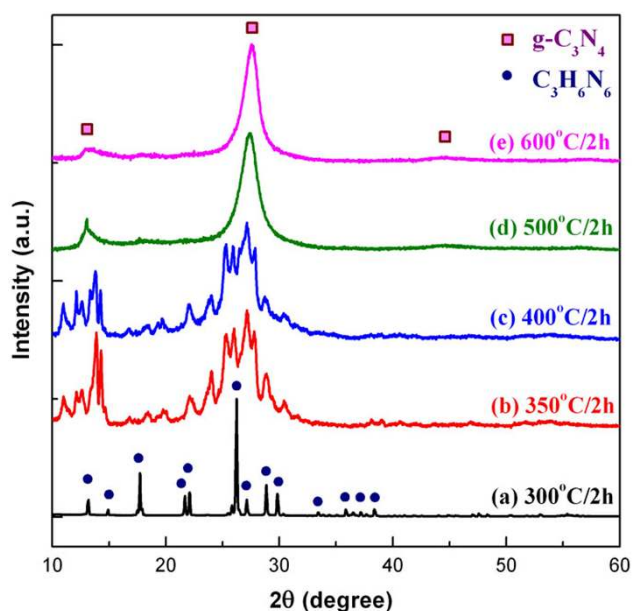


In this work,  $g\text{-C}_3\text{N}_4$  nanopowders were conveniently synthesized through the low temperature thermal condensation of melamine. By changing the temperature of thermal condensation, continuously tunable emissions of  $g\text{-C}_3\text{N}_4$  nanopowders, which are covering the blue to green light region, were obtained. And the tunable PL mechanism of  $g\text{-C}_3\text{N}_4$  nanopowders was also proposed in detail, based on the steady state and transient state time-resolved PL spectra. The  $g\text{-C}_3\text{N}_4$  nanopowders with tunable emissions were expected to extend their applications in photoelectric nanodevices.

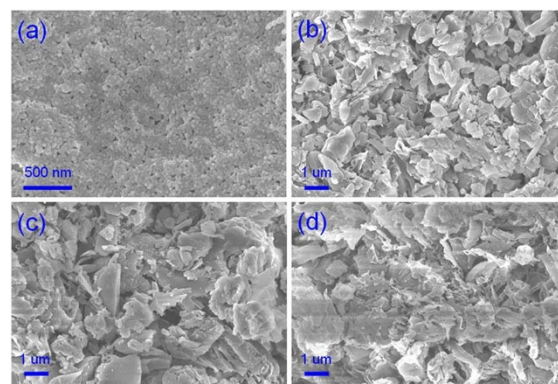
## Results

The normalized XRD patterns of the carbon nitride compounds obtained under different temperatures were shown in Fig. 1. When the raw materials are heated at  $300^\circ\text{C}$  for 2 h, a series of sharp peaks are detected, which are corresponding to the crystalline melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ) phase (JCPDS: 39-1950). The diffraction pattern in Fig. 1(a) indicates that the product maintains as melamine phase, and no other impurity phase is detected. When the processing temperature rises to  $350^\circ\text{C}$  and  $400^\circ\text{C}$ , several new peaks appear and the peaks are broadened compared with those in Fig. 1(a), which indicates that the products have transformed from crystalline to amorphous. With increasing process temperature, three broad distinct diffraction peaks are observed when the processing temperature is higher than  $500^\circ\text{C}$ , which are located at  $27.2^\circ$ ,  $13.1^\circ$ ,  $46.19^\circ$ , respectively. It can be confirmed that all the diffraction peaks are in agreement with the recent reports on the XRD patterns of the amorphous  $g\text{-C}_3\text{N}_4$  prepared via the thermal condensation of the melamine<sup>6,14–16</sup>. The XRD patterns indicate that the products maintained as crystalline melamine phase when the heating temperature is lower than  $300^\circ\text{C}$ . But, when the temperature rises to  $350\text{--}400^\circ\text{C}$ , it is transformed into crystalline or amorphous graphite like carbon nitride compounds, and when the temperature is higher than  $500^\circ\text{C}$ , the products completely forms into amorphous  $g\text{-C}_3\text{N}_4$ .

Figure 2 shows the SEM images of the carbon nitride processed at  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ , respectively. The Fig. 2(a) shows that the morphology of melamine processed at  $300^\circ\text{C}$  is granular with a particle size of  $50\text{--}80\text{ nm}$ . When the processed temperature is higher than  $400^\circ\text{C}$ , the morphology of products have transformed into layer. And with the increase of temperature, the size of the flake is obviously increased. Which can be clearly seen from the results shown in Fig. 2(b) (c) and (d), Fig. 2(b) shows that the size of the



**Figure 1** | XRD patterns of the products synthesized via the thermal condensation of melamine at different temperatures for 2 h.

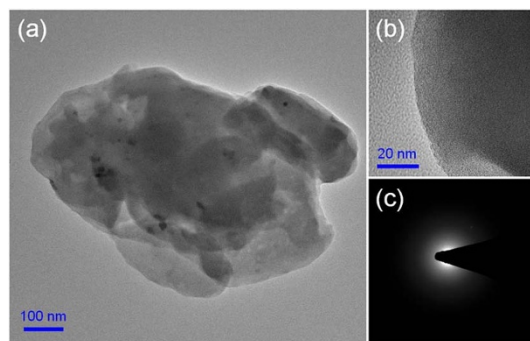


**Figure 2** | SEM images of the products synthesized via the thermal condensation of melamine at different temperatures for 2 h. (a)  $300^\circ\text{C}$ , (b)  $400^\circ\text{C}$ , (c)  $500^\circ\text{C}$ , (d)  $600^\circ\text{C}$ .

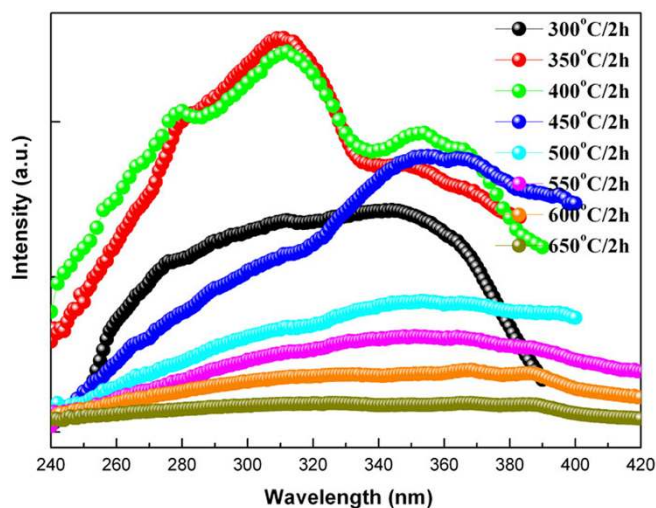
flake is located at a range of  $0.5\text{--}0.8\text{ }\mu\text{m}$  when the temperature is  $400^\circ\text{C}$ . When the processed temperature rises to  $500^\circ\text{C}$  and  $600^\circ\text{C}$ , the size is also increased to  $0.5\text{--}1.0\text{ }\mu\text{m}$  and  $0.5\text{--}1.5\text{ }\mu\text{m}$  (as shown in Fig. 2(c) and (d)), respectively. Obviously, the evolution of the morphology from granular to layer is along with the chemical reaction process, the process of thermal condensation have happened since  $400^\circ\text{C}$  and the increasing temperature promotes this process, so that the degree of the condensation is increased which leads to the grow of the size of flake. In addition, from the SEM images, the size of most carbon nitride particles synthesized in this work is located at the submicron, which makes the products have a bright future in the application of bioengineering and photoelectric fields.

From the TEM image of the carbon nitride processed at  $600^\circ\text{C}$ , as shown in Fig. 3(a), it is obvious that the structure of the product is layer-like structure. The HR-TEM image of the carbon nitride is shown in Fig. 3(b). From the image, no obvious crystal fringe is observed for the product synthesized at  $600^\circ\text{C}$ , which indicates that the product is amorphous. What is more, the mist diffraction ring, shown in the selected area electron diffraction (SEAD) in Fig. 3(c), further confirms that the product synthesized at  $600^\circ\text{C}$  is amorphous. And this result is in good agreement with those of HRTEM and XRD patterns.

Figure 4 shows the PL excitation spectra evolution with increasing process temperature from  $300^\circ\text{C}$  to  $650^\circ\text{C}$  for products and all the excitation spectra are monitored at the emission peak for each specimens. It can be seen that the evolution of the excitation spectra matches well with the phase and microstructure evolution (as shown in Fig. 1). Interestingly, all the excitation spectra exhibit a broad excitation band covering  $250\text{ nm}$  to  $400\text{ nm}$ , which shows a slightly red shift with the increase of process temperature. Moreover, the effect of the processing temperature on the PL emission properties

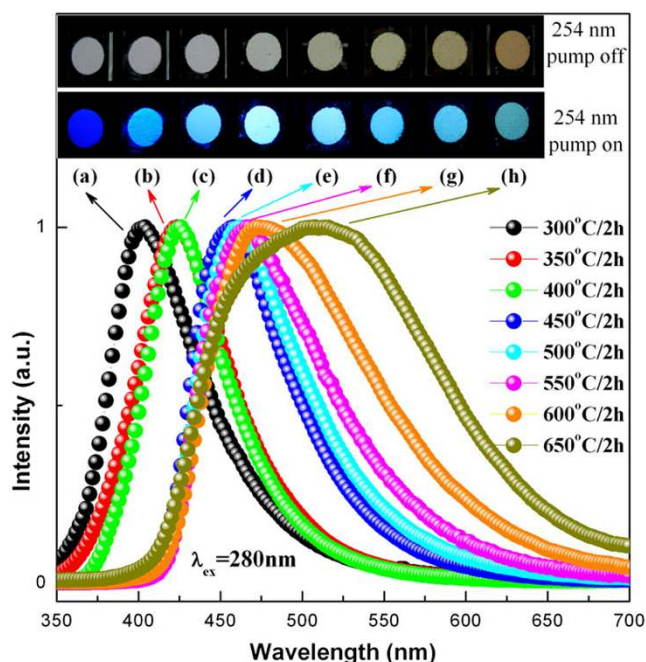


**Figure 3** | (a) TEM, (b) HR-TEM, and (c) SAED images of  $g\text{-C}_3\text{N}_4$  synthesized via the thermal condensation of melamine at  $600^\circ\text{C}$  for 2 h.



**Figure 4** | The PL excitation spectra of the carbon nitride products synthesized via the thermal condensation of melamine at different temperatures for 2 h.

of carbon nitride is studied in this work. To investigate the PL emission properties of specimens under the same excitation, a shorter 280 nm excitation is selected as the excitation wavelength in the following works. Fig. 5 shows the normalized PL spectra of the multicolor-emitting carbon nitride products synthesized at 300, 350, 400, 450, 500, 550, 600 and 650 °C for 2 h under the excitation wavelength at 280 nm, respectively. The peak shape of the PL spectra are similar and the emission peak of PL spectra is located at 405, 425, 426, 458, 462, 475, 480 and 510 nm, respectively. Therefore, from this result, it can be clearly observed that with the processing temperature rising, the center of PL is red shift constantly. The center of PL spectra shifts from 400 nm to 510 nm with the increase of the processing temperatures, which stands for the blue-violet light region to



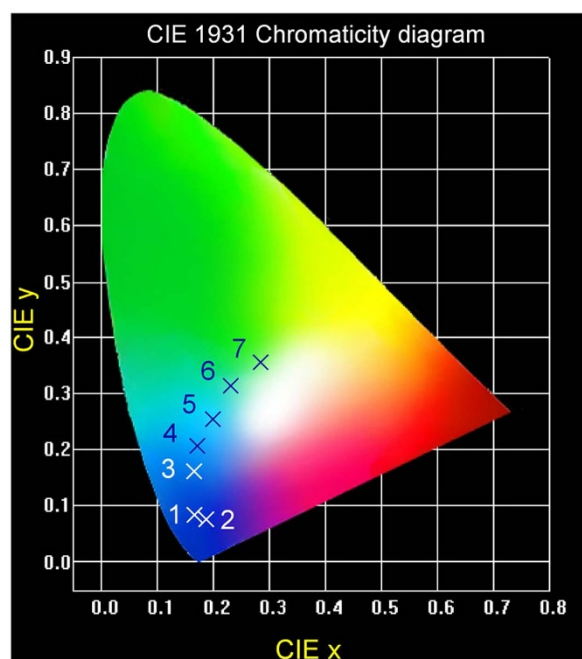
**Figure 5** | The normalized PL emission spectra of the carbon nitride products synthesized via the thermal condensation of melamine at different temperatures for 2 h ( $\lambda_{ex} = 280$  nm). The inset shows the digital photos of carbon nitride products with (bottom) and without (upper) 254 nm excitation.

the green light region. And the digital photos about the multicolor-emitting of carbon nitride products with (bottom) and without (upper) excitation are shown in the inset of Fig. 5, which also confirm that the PL emission is covering the blue-violet to green light region. On the other hand, the full width at half maximum (FWHM) is also became wider with the temperature increasing, which is related to the degree of the thermal condensation and the increase of disorder microstructure of the carbon nitride<sup>17</sup>. For the carbon nitride products synthesized at 650 °C for 2 h, the broad emission band is even extended to the yellow light region.

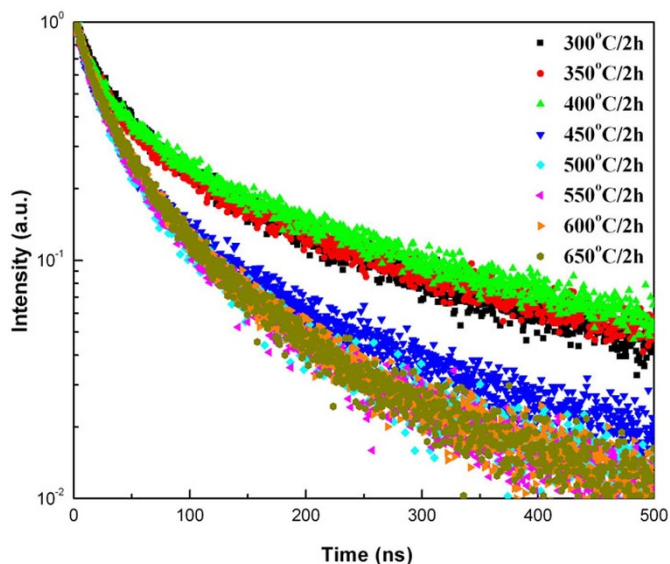
The Commission Internationale de l'Éclairage (CIE) chromaticity diagram of the carbon nitride products synthesized at different temperature is depicted in Fig. 6. The CIE (x, y) coordinate of carbon nitrides synthesized at 300, 350, 400, 450, 500, 550, 600 and 650 °C is located at (0.16, 0.08), (0.18, 0.075), (0.16, 0.16), (0.17, 0.20), (0.2, 0.25), (0.22, 0.31) and (0.28, 0.36), respectively, which further confirm that the PL emission is covering the blue-violet to green light region. Additionally, it is noteworthy that the emission of carbon nitride products obtained at 450–650 °C is located at the edge of the central white-light region. Hence, it is expected to get the white light emitting after introducing red-light emission in the  $g\text{-C}_3\text{N}_4$  products.

Figure 7 shows the decay curves of the carbon nitride products synthesized at different temperature for 2 h, which is measured at the emission peak with the 280 nm excitation. From the decay curves, with the increase of the temperature, the fluorescence lifetime of the products clearly decreases. Moreover, the decay curve of carbon nitride products in Fig. 7 show obvious deviation from the single-exponential decay, which indicates that the multiple processes may be involved during the decay of the emission besides the radiative transition<sup>18</sup>. By the multi-exponential fitting, it can be estimated that the long fluorescence lifetime of carbon nitride products is between 106 ns and 259 ns. The nanosecond level lifetime of the multicolor-emitting carbon nitride products endows their potential application in display, lighting, etc.

The steady-state and transient PL emission spectra of the carbon nitride product synthesized at 400 °C for 2 h are shown in the Fig. 8,



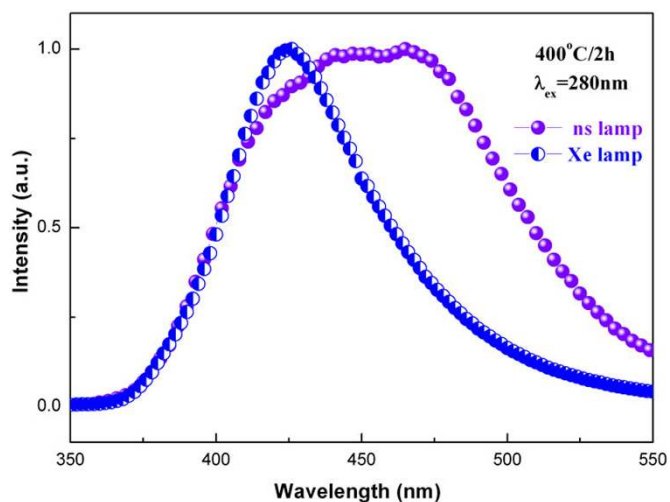
**Figure 6** | The Commission Internationale de L'Éclairage (CIE) chromaticity diagram of the carbon nitride products synthesized at different temperature for 2 h. (1) 350 °C, (2) 400 °C, (3) 450 °C, (4) 500 °C, (5) 550 °C, (6) 600 °C, (7) 650 °C.



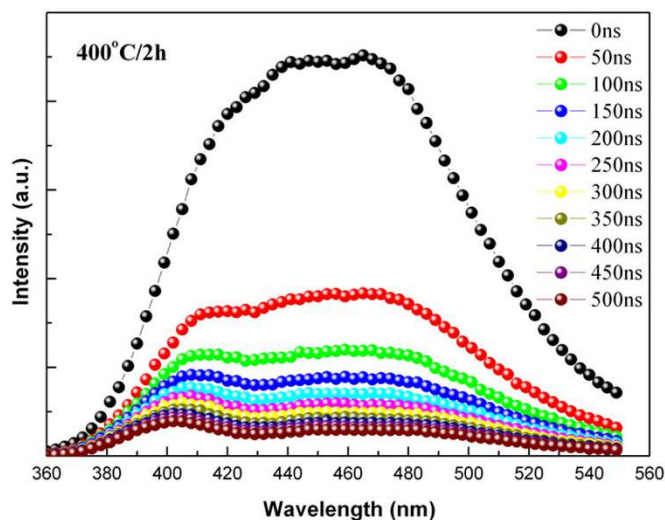
**Figure 7** | The decay curves of the carbon nitride products synthesized via the thermal condensation of melamine at different temperatures for 2 h ( $\lambda_{\text{ex}} = 280$  nm).

which are excited by Xe lamp and ns lamp, respectively. The steady-state PL spectrum exhibits a perfect single speak, while the transient PL spectrum exhibits a board emission band included several peaks. The obvious difference between the steady-state and transient PL emission spectra implies that there is more than one PL emission center during the emission process of carbon nitride products.

Figure 9 shows the time-resolved emission spectra of carbon nitride products synthesized at 400°C for 2 h. It is obvious that there are at least two emission centers at 405 nm and 480 nm, and the emission center located at 480 nm decays faster than that located at 405 nm. What is more, there is a little continuous blue shift for the 405 nm emission with the time decay, which is probably due to the remarkable change of the intensity between 405 nm and 480 nm emission bands<sup>18</sup>. Moreover, another time-resolved emission spectra of the carbon nitride products headed at 600°C for 2 h with the time scale from 0 to 100 ns are shown in Fig. 10. It has a single emission

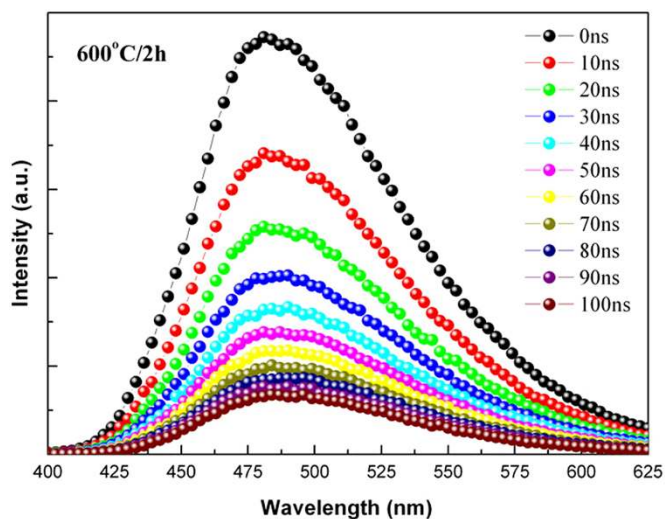


**Figure 8** | The normalized PL emission spectra of the carbon nitride products synthesized via the thermal condensation of melamine at 400°C for 2 h with the ns lamp and Xe lamp excitation ( $\lambda_{\text{ex}} = 280$  nm), respectively.



**Figure 9** | The time-resolve PL spectra for the carbon nitride products synthesized via the thermal condensation of melamine at 400°C for 2 h under ns lamp excitation ( $\lambda_{\text{ex}} = 280$  nm).

peak located at around 485 nm which is consistent to the PL emission peak of the product heated at 600°C obtained in Fig. 5. Compared with the spectra of the product obtained at 400°C, the emission peak located at 405 nm is disappeared or become fairly weak. The reason is listed as follows. From the XRD patterns results (Fig. 1), it is clear that the product obtained at 600°C is g-C<sub>3</sub>N<sub>4</sub> phase has a higher degree of thermal condensation, compared with that obtained at 400°C. So that the structure of g-C<sub>3</sub>N<sub>4</sub> is a plane network consisted of the tri-s-triazine structure<sup>3</sup>, which has a higher degree of disorder and bigger delocalization of electrons. The delocalization of electrons will lead to the overlap of the orbital, so that a bigger overlap of the  $\pi^*$  antibonding state and  $\delta^*$  antibonding state will appear, which makes the transition probability between lone pair (LP) state formed through the LP electron of the nitride and the  $\delta^*$  conduction band becoming weaker. Therefore, this process causes the emission peak located at 405 nm of the carbon nitride disappeared. Furthermore, it can be deduced that the emission peak located at 480 nm is caused by the transition between LP to  $\pi^*$  conduction band.



**Figure 10** | The time-resolve PL spectra for g-C<sub>3</sub>N<sub>4</sub> synthesized via the thermal condensation of melamine at 600°C for 2 h with ns lamp excitation ( $\lambda_{\text{ex}} = 280$  nm).



To investigate the effect of the processing time on the PL properties, the melamine processed at the same temperature for different time are taken. The results of PL spectra are shown in Fig. 11. When the raw materials are processed at the same temperature for different time, the peak shape of the PL spectra is almost similar, which indicates that the PL properties do not change obviously with the increase of processed time. It is noteworthy that, with the processing time increasing, the PL emission spectra of carbon nitride products exhibits a slight red shift as shown in Fig. 11(b). This result can be explained by considering that the longer processing time may cause an increasing of the degree of the thermal condensation, which will lead to the decrease of the optical band gap<sup>19</sup>. Moreover, the PL excitation spectra of the products processed at different temperatures with various treating times are shown in Fig. 11(a), which clearly indicated that the specimen processed at same temperature with different hours have almost the same excitation spectra. With these results, it can be deduced that the processing time have little effect on the PL properties.

To interpretate the PL emission mechanism of carbon nitride and  $g\text{-C}_3\text{N}_4$  products, microstructure evolution of carbon nitride products synthesized at different conditions are investigated by Raman spectra. The normalized Raman spectra of carbon nitride obtained at different temperature is shown in the Fig. 12. The evolution of the Raman spectra shown in Fig. 12(a) is generally due to the structural change of carbon nitride by the thermal condensation. From the spectra, it is confirmed that the products are still melamine crystal when the processing temperature is lower than 300°C. With the processing temperature rising into the region of 350°C to 450°C, a new crystal is formed and the compound phase slowly transforms into amorphous. When the the processing temperature is above 500°C, the products completely transform into amorphous  $g\text{-C}_3\text{N}_4$ . And the above results of Raman spectra is corresponding well with the XRD results (as shown in Fig. 1). What is more, owing to the strong fluorescent backgrounds, some of the structural peaks become inconspicuous. However, there are also two characteristic peaks related to the D and G bands located around 1405  $\text{cm}^{-1}$  and 1570  $\text{cm}^{-1}$  in Fig. 12(b). And the changing of the relative intensity of these two peaks is consistent with a trend that intensity ratio of D ( $I_{\text{D}}$ ) band to G band ( $I_{\text{G}}$ ) becomes grater with the processing temperature rising. According to the equation<sup>20</sup>:

$$I_{\text{D}}/I_{\text{G}} = C''/E_{\text{G}}^2$$

Where  $E_{\text{G}}$  is the band gap of carbon nitride, and  $C''$  is a constant. It can be estimated that the  $E_{\text{G}}$  is becoming narrower with the increase of temperature.

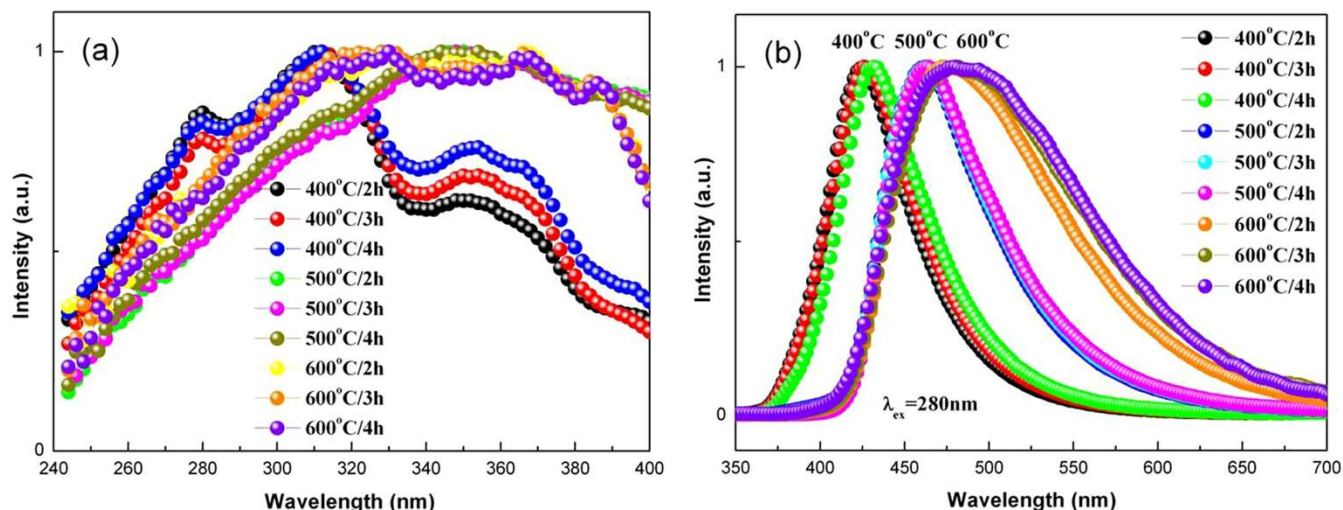
## Discussion

As shown in Fig. 5, the PL emission of the carbon nitride products exhibit continuous red shift with the processing temperature increasing. It is obvious that the PL property of the carbon nitride products synthesized by the thermal condensation of melamine is continuously tunable with the processed temperature rising. Hence, in the following part, the physical mechanism of this interesting tunable PL property of carbon nitride products is discussed in detail.

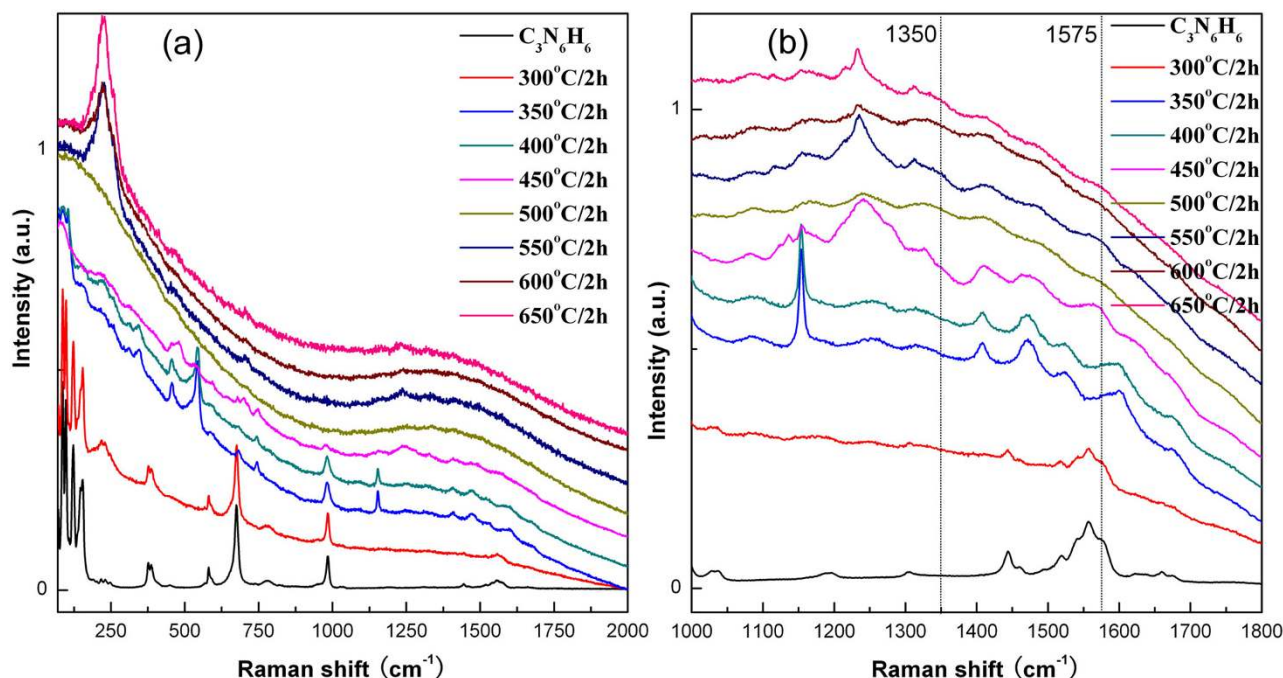
Compared with the results of Fig. 9 and Fig. 10, two emission peaks located at 405 nm and 480 nm are observed in Fig. 9. The emission center at 405 nm is caused by the transition between LP valence band and  $\delta^*$  conduction band which is related to the  $\text{sp}^2$  C-N bond<sup>21</sup>, and the emission band centered at 480 nm is attributed to the transition between the LP valence band and the  $\pi^*$  conduction band. This result is consistent with that reported by Iwano et al., which indicate that the transition is caused by the  $\pi$  valence band and the  $\pi^*$  conduction band, or the LP valence band and the  $\delta^*$  conduction band whose energy is more than 2 eV<sup>4</sup>. These two emission peaks compose the whole PL emission band. Hence, the evolution of these two emissions will alter the PL emission characteristics of the carbon nitride products.

The structure of the melamine and  $g\text{-C}_3\text{N}_4$  is shown in the Fig. 13<sup>22,23</sup>. It is clearly shown that the basic structure of the  $g\text{-C}_3\text{N}_4$  is the tri-*s*-triazine ring structure, which is connected by the N atoms to form a  $\pi$ -conjugated polymeric network. Generally, the optical properties of all the disorder carbon-based materials are related to the  $\pi$  and  $\pi^*$  antibonding states in the visible-near-ultraviolet energy range<sup>12</sup>. And the luminescence property of the carbon nitride materials is considered mainly effected by the size of the  $\text{sp}^2$  C-N clusters and the lone-pair electrons of the nitride<sup>12,21,24,25</sup>. In addition, the formation of the LP state is because the LP electrons of nitride is not hybridization with the carbon and it is located in the  $\text{sp}^2$  C-N  $\pi$  valence band<sup>12,21,26</sup>. Based on the above results and discussion, the tunable PL mechanism of the carbon nitride products are proposed as follows:

- As the processing temperature increasing, the polymeric network of the  $g\text{-C}_3\text{N}_4$  will extend by connecting more tri-*s*-triazine and the bond length of the  $\text{sp}^2$  C-N clusters becomes larger at higher temperature, both of them will increase the size of the  $\text{sp}^2$  C-N clusters. In a typical opinion, the larger size of the  $\text{sp}^2$  clusters has a small optical band gap<sup>4,21,27</sup>.
- The  $g\text{-C}_3\text{N}_4$  is a type kind of extended solid materials condensation by the melamine single molecules, and the thermal condensation increasing at a higher temperature, which will



**Figure 11** | The normalized PL excitation (a) and emission (b) spectra of the carbon nitride products synthesized via the thermal condensation of melamine at different conditions.



**Figure 12** | The Raman spectra of the carbon nitride obtained at different temperatures using the near-infrared (NIR 785 nm) light for excitation. (a) the normalized raman spectra of carbon nitride in the scanning region 50–2000 nm; (b) the normalized raman spectra of carbon nitride in the scanning region 1000–2000 nm.

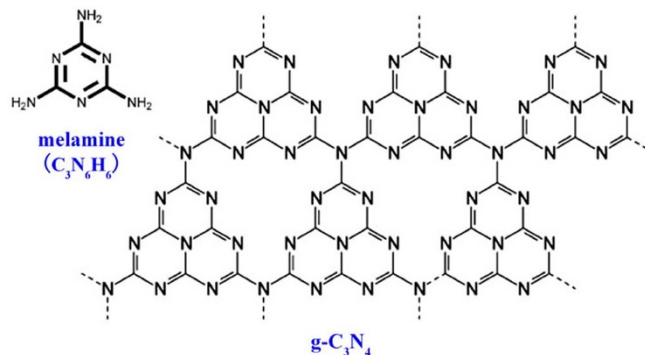
lead to the  $g\text{-C}_3\text{N}_4$  composed by more tri-s-triazine ring. Therefore, the  $\pi$ -conjugated system is enhanced. These effects involve the condensation process and the increasing  $\pi$  states, which will result in the narrowing of band gap<sup>11,28,29</sup>.

- (c) The denser packing of the  $sp^2$  aromatic clusters is formed for the intensity of the thermal condensation. Hence, a stronger overlap of the orbital is appearing, and consequently the band gap of  $g\text{-C}_3\text{N}_4$  decreases.

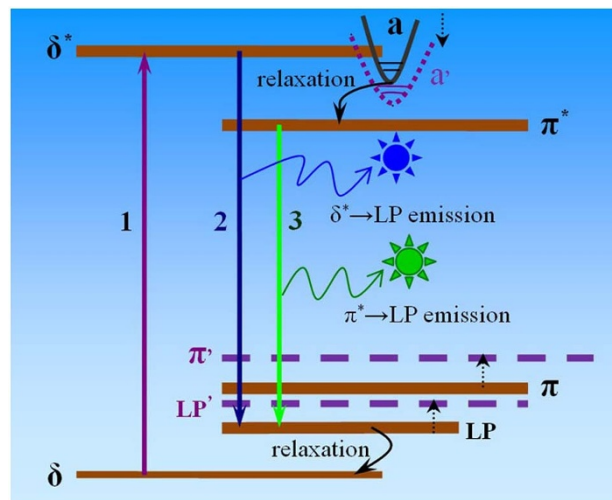
All the above factors are in good agreement with the Raman results, which confirms that the red shift of the PL emission at high temperature is directly caused by the tunable narrowing of band gap.

Herein, for the good insight into the tunable PL mechanism of the carbon nitride, a simple schematic diagram corresponding to the band gap states of the carbon nitride are tentatively founded in Fig. 14. As the excitation spectra exhibit a broad excitation band and it is almost the same for the specimen obtained above 500°C which is nearly forming into  $g\text{-C}_3\text{N}_4$ , we assume that the electronic is excited from the  $\delta$  valence band to the  $\delta^*$  conduction band as the process 1 in Fig. 14. This is because that the degree of thermal condensation has no obvious effect on the  $\delta$  band region<sup>30</sup>. The emission

center located at 405 nm and 480 nm for the carbon nitride obtained at 400°C is corresponded to the process 2 and 3, respectively. The band  $a$  represents the overlap of the  $\delta^*$  and the  $\pi^*$  bands which provides a channel for the excited electrons to relax to the  $\pi^*$  conduction band, and the band  $a$  will be shifted to the direction close to  $\pi^*$  conduction band. So, at the higher processing temperature, the delocalization of the electrons will be increased<sup>24</sup>. Therefore, a stronger overlap is appearing and then the band  $a$  is closer to the  $\pi^*$  state, just as the  $a'$  band in Fig. 14. Hence, the probability for the excited electrons located at  $\delta^*$  conduction band relaxing to the  $\pi^*$  conduction band is increasing, and consequently the  $\pi^* \rightarrow \text{LP}$  emission is slowly dominated the PL emission of the carbon nitride as the processing temperature rising. And this is consistent with the



**Figure 13** | The structure of  $g\text{-C}_3\text{N}_4$  and melamine.



**Figure 14** | Schematic energy level diagram of the PL emission from the carbon nitride products synthesized via the thermal condensation of melamine.



results discussed in Fig. 10. Furthermore, the higher processing temperature enhances the  $\pi$ -conjugated system as higher degree of thermal condensation. Therefore,  $\pi$ -conjugated number is increasing and the packing of the g-C<sub>3</sub>N<sub>4</sub> becomes denser. Owing to all of the above factors will narrow the band gap (just indicated by the  $\pi$  and LP states will continuously move up to the location of  $\pi'$  and LP', respectively), the gap between the LP valence state and the  $\delta^*$  or  $\pi^*$  conduction band is decreasing. Therefore, the PL emission of carbon nitride products is red shift with the increase of processing temperature.

In conclusion, carbon nitride and g-C<sub>3</sub>N<sub>4</sub> nanopowders were synthesized by low temperature thermal condensation of melamine. With the increase of processing temperature, the phase have been transformed from the melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>) phase to amorphous g-C<sub>3</sub>N<sub>4</sub>, and the morphology was also changed from granular to layer structure with different sizes of flakes. Moreover, the PL properties of the carbon nitride products synthesized at different temperatures indicate that there are two PL centers located at 405 nm and 480 nm under the 280 nm excitation. And with the temperature increasing, the carbon nitride products exhibit tunable PL properties, such as the emission peak is red shift from 400 nm to 510 nm, and it can be expand to the range of the green light. The tunable PL mechanism of carbon nitride products is also proposed based on the steady and transient state PL spectroscopy. The PL properties of carbon nitride products are assigned to the change of the optical band gap which is related to the size of the sp<sup>2</sup> clusters. Furthermore, it also has a relationship with the thermal condensation of the carbon nitride products and the LP electrons which can form the LP states. The tunable PL properties of the carbon nitride materials synthesized via convenient low temperature thermal condensation of melamine are expected to expand their applications in displays, lighting, bio-labels, etc.

## Methods

**Materials synthesis.** Analytical grade melamine powders, purchased from Sinopharm Chemical Reagent (SCR) Co., Ltd, Shanghai, China, were first ground for 30 min in agate mortar, and then 2 g ground melamine powders were put into a 20 ml alumina crucible, which was placed in the central region of a quartz tube furnace for heat treatment. High purity nitrogen (99.999%) was introduced into the quartz tube with a rate of 75–150 sccm. The melamine was heated at a designed temperature between 300°C and 650°C for 2–4 h. After cooling to room temperature, the product was taken out and ground into fine powders in the agate mortar.

**Characterization methods.** The structure of the products was studied by X-ray diffraction (XRD) patterns which were obtained by the D8 advance X-ray diffractometer (Bruker, Switzerland) with a Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) and the Raman spectroscopy (Renishaw in Via) using a 785 nm excitation. The morphology of the products was determined by the field emission-scanning electron microscopy (FE-SEM, Nova NanoSEM430, FEI, Netherlands) and high-resolution transmission electron microscopy (HR-TEM, 2100F, JEOL, Japan). The PL properties was investigated using the high resolution spectrofluorometer Edinburgh Instruments FLS 920 equipped with a single photon counting photomultiplier (Hamamatsu R928P) in Peltier air-cooled house for ultraviolet to visible range. All the measurements were carried out at room temperature.

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## Author contributions

G.P.D. proposed and guided the overall project. Y.H.Z., Q.W.P., G.Q.C. and M.R.L. performed all the experiments and analyzed the results. All the authors discussed the results. Y.H.Z. and G.P.D. wrote the manuscript, with discussion from Q.Y.Z. and J.R.Q.



## Additional information

**Competing financial interests:** The authors declare no competing financial interests.

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