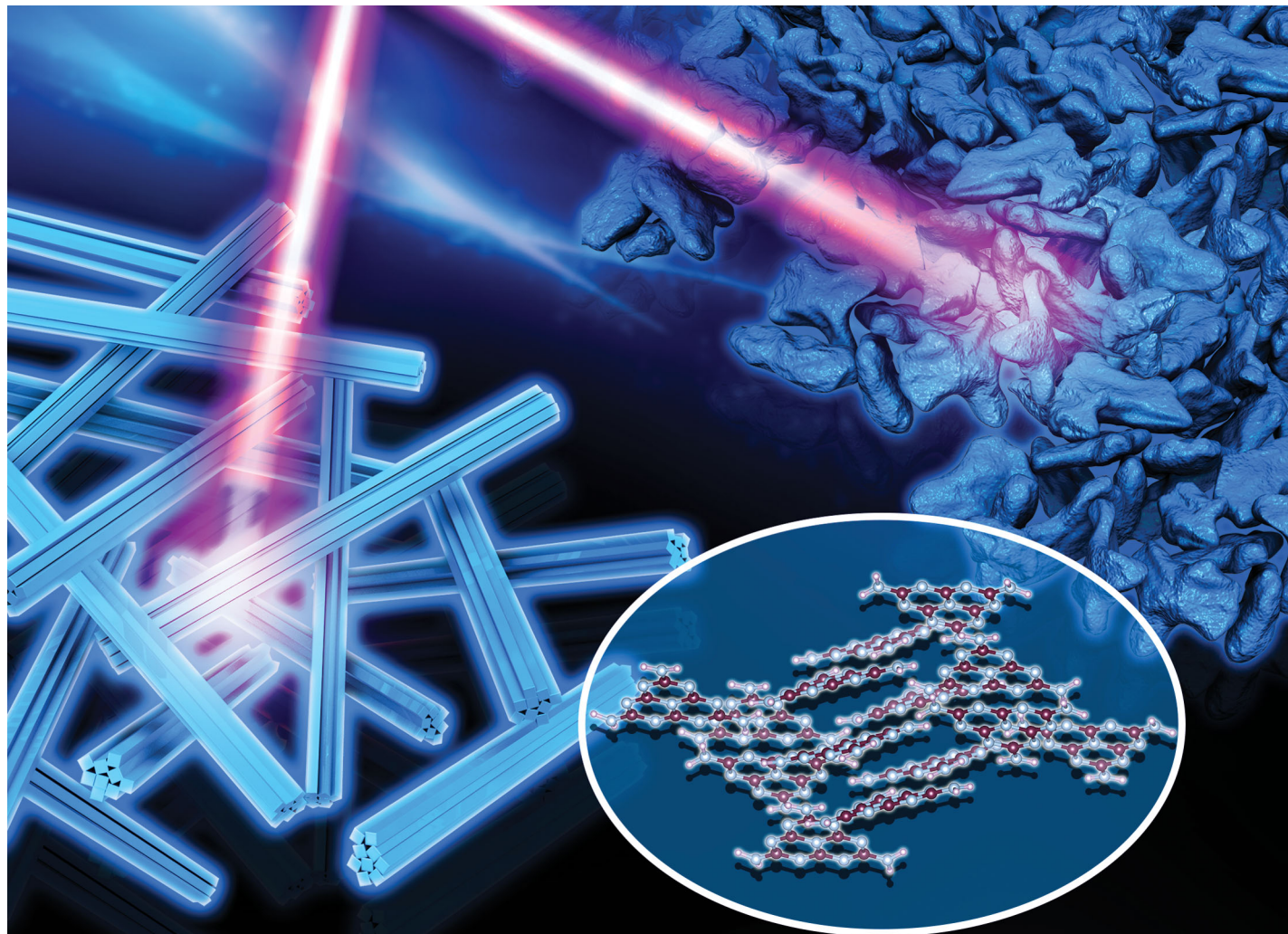




Showcasing research from the group of Prof. Junying Zhang at the Department of Physics, Beihang University.

Melem: an efficient metal-free luminescent material

Metal-free rod-like structured melem was synthesized. The new structured melem powder with a quantum yield as high as 56.9% shows much stronger luminescence than irregular particles. Melem can be synthesized easily at a low cost, which holds great potential for application as an efficient metal-free luminescence material.

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Melem: an efficient metal-free luminescent material†

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Developing efficient metal-free luminescent materials is a challenging topic because their quantum yields are usually quite low. Here, for the first time, we report a new metal-free blue-emitting melem with a high quantum yield of 56.9%. Rod-like structured melem was synthesized by treating a bulk melem with nitric acid and ethylene glycol. The quantum yield of the rod-like melem (56.9%) is about 1.6 times higher than that of the ordinary melem (35.2%) and is substantially higher than that of bulk g-C₃N₄ (4.8%), a well-known metal-free blue emission material. This promising blue phosphor, which is easy to synthesize, abundant on earth and contains no metal elements, has great potential for practical applications.

1. Introduction

Most phosphors are based on metal elements, such as rare-earth activated and self-activated materials.^{1–8} These materials exhibit good luminescence properties, such as high brightness, good color rendering index, and high thermal stability.^{1,9–12} However, they are still restricted by some ineluctable drawbacks. For example, rare earths are expensive and limited in abundance on earth. Also, if they are not disposed and handled properly, they might cause heavy metal pollution to the soil and even poisoning to human beings. Hence, it has always been a hot topic to explore new phosphors that are environmentally friendly, abundant in nature and easy to acquire.^{13–15}

Graphitic carbon nitride (g-C₃N₄) is a layer-structured material with excellent properties.^{16–28} g-C₃N₄ was first found to exhibit excellent photocatalytic properties by Wang *et al.*, and later was found to exhibit excellent luminescence properties as well.^{16,29–32} Among all the outstanding properties of g-C₃N₄, the most valuable one is its biocompatibility. g-C₃N₄ is a metal-free material composed of no other elements but carbon and nitrogen. Hence, they are environmentally friendly. Besides, g-C₃N₄ can be acquired by simply heating melamine, urea, dicyandiamide or cyandiamide in air at temperatures from 480 to 560 °C, which means that g-C₃N₄ is very cheap and can

be synthesized easily and massively.^{30,33–36} g-C₃N₄ meets most of the demands for environmental protection and a lot of work has been done on the luminescence of g-C₃N₄. Zhang *et al.* combined g-C₃N₄ with copper cysteamine Cu₃Cl(SR)₂ to produce a white-emitting composite under single wavelength excitation.⁴ They succeeded in producing a white-emitting diode with the as-obtained composite with a color rendering index as high as 94.3. Xie *et al.* managed to acquire g-C₃N₄ single-layered quantum dots and used them as an economic fluorescent probe for two-photon fluorescence imaging of the cellular nucleus.³⁷ However, as a phosphor, bulk g-C₃N₄ still has some challenging issues. The quantum yield of bulk g-C₃N₄ phosphor reported is only 4.8%, which is very low for self-activated phosphors.³⁷ Therefore, it is important to improve its quantum efficiency.

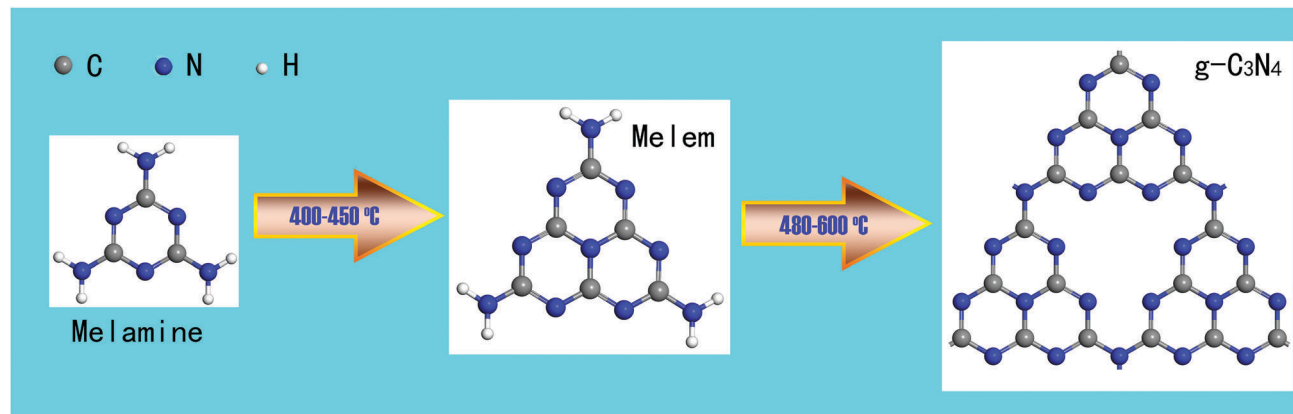
Melem is a trimer of melamine with a molecular formula of C₆N₇(NH₂)₃. Melem can be obtained by condensing melamine in air at temperatures from 400 to 450 °C.^{38–40} It is an intermediate product in the process of heating melamine to produce g-C₃N₄ (Scheme 1).^{41,42} Similar to g-C₃N₄, melem shows excellent photocatalytic properties, which have been extensively investigated.^{38,43} However, to our knowledge, little work has been done on the luminescence behaviours of melem.⁴¹ Melem is composed of carbon, nitrogen and hydrogen, and is a typical metal-free material. Besides, compared with g-C₃N₄, melem can be obtained at a lower condensation temperature, which to some extent means that it is easier to synthesize melem than g-C₃N₄.⁴¹ Furthermore, here we found that, in contrast to the 4.8% quantum yield of bulk g-C₃N₄, the quantum yield of melem condensed directly from melamine (the product is marked as melem AM) is as high as 35.2%. *Via* further treatment with nitric acid and ethylene glycol (the products are marked as melem

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Scheme 1 The condensation process to form melem and g-C₃N₄ from melamine.

AT and melem GT, respectively), we successfully obtained rod-like structured melem with a quantum yield of about 56.9%, which is substantially higher than those of bulk g-C₃N₄ and g-C₃N₄ quantum dots with the quantum yields of 4.8% and 46.0%, respectively.^{44–46} The quantum yield of the present melem could be improved further by forming quantum dots due to the enhanced photoresponsivity.^{46,47} Our observations indicate that melem is a new, efficient and metal-free blue emission phosphor with great potential for practical applications.

2. Experimental section

2.1. Preparation of melem AM, melem AT and melem GT

There are three steps in obtaining the final melem GT from melamine. Firstly, melem AM was obtained by a thermal condensation of 2 g of melamine at 400 °C in air for 2 h with a heating rate of 3 °C min^{−1} in a muffle furnace. The obtained light-grey powder (melem AM) was ground in an agate mortar for further use. Secondly, 0.5 g of melem AM was dispersed in nitric acid solution (25 mL) with a concentration of 40%, and was heated at 90 °C for 20 min with stirring. After that, the suspension was cooled to room temperature and centrifuged at a rate of 12 000 rpm for 5 min. The precipitates were washed with deionized water 5 times and dried in a vacuum oven at 50 °C to obtain melem AT powder. Thirdly, 0.2 g of melem AT powder was dispersed in ethylene glycol (25 mL) and was heated at 90 °C for 2 h with stirring. After that, the powder was centrifuged at a rate of 12 000 rpm and washed 5 times again. After being dried, the powder melem GT was finally obtained.

2.2. Characterization of materials

The morphology and energy dispersive spectra (EDS) of the samples were analyzed using a Zeiss Merlin compact scanning electron microscope (SEM). Specific surface areas were measured using a Micrometer ASAP 2010 accelerated surface area and porosimetry system. The X-ray powder diffraction (XRD) was analyzed using a Bruker D8-Advanced X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 100 mA. Mass spectra were analyzed using a Bruker solariX XR Fourier

Transform Ion Cyclotron Resonance Mass Spectrometer. Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Thermo Fisher Nicolet 50 Fourier transform infrared spectrometer. Solid state nuclear magnetic resonance (NMR) information was recorded using a Bruker Avance III 400 MHz WB solid state NMR spectrometer. Organic elemental analysis (OEA) was performed on a Elementar Analysensysteme GmbH vario EL Elemental Analyzer.

2.3. Luminescence measurements

The luminescence properties of the samples were studied using an Edinburgh Instruments FLS 980 Steady State and Transient State Fluorescence Spectrometer equipped with a 360 W xenon lamp. All tests were performed at room temperature. The quantum yields of the samples were measured with the assistance of an integrating sphere. Decay curves and time-resolved emission spectra (TRES) were measured using a pulsed laser excitation of 255 nm. Decay curves were measured using a single photon counting method. A cathodoluminescence spectrum was measured using an FEI Quanta 200F field emission environmental scanning electron microscope equipped with a Mono CL3+ cathode-fluorometer.

2.4. Calculation details

First-principles calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with the spin polarized Perdew–Burke–Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) and the Heyd–Scuseria–Ernzerhof (HSE) functional to represent the electronic exchange–correlation energy. For a melem unit cell, the cut-off energy and Monkhorst–Pack k -point mesh were 500 eV and $3 \times 3 \times 2$, respectively. The structural relaxations were performed until the self-consistent total energy difference reached 10^{-4} eV and the residual forces on atoms fell below 0.01 eV Å^{−1}. Because of the weak chemical bonding between the melem molecules, a damped van der Waals (optB86b-vdW functional) correction is employed. The effects of spin polarization were considered in energy calculations. The valence atomic configurations of H, C and N were 1s¹, 2s²2p² and 2s²2p³, respectively.

3. Results and discussion

Fig. 1a, c and e show the surface topographies of melem AM, melem AT and melem GT, and Fig. 1b, d and f show the enlarged images of the corresponding areas marked by red frames in Fig. 1a, c and e. Similar to g-C₃N₄, melem AM (Fig. 1a and b) is a layer-structured bulk material. After acid treatment (Fig. 1c and d), the surface of the material becomes rougher and porous, and the average size becomes smaller. It is interesting to see that melem GT becomes well crystallized and shows a rod-like structure after glycol treatment (Fig. 1e and f). The average length of the rods is about 10 μm . To further study the surface characteristics of the samples, the specific surface area was measured using the Brunauer–Emmett–Teller (BET) method. The specific surface areas of the three samples are 4.68 m² g^{−1}, 26.57 m² g^{−1}, and 15.98 m² g^{−1}, which are in accordance with the SEM results. All three samples showed relatively low specific surface areas. Compared with melem AM, melem AT has a higher specific surface area, which is due to its porous structure and smaller particles, as shown in Fig. 1. After melem AT was further treated with ethylene glycol, rod-like melem GT was obtained. Compared with melem AT, the new structured melem GT was well crystallized; herein, the specific surface area of melem GT was reduced, compared with melem AT.

Fig. 2a shows the XRD patterns of g-C₃N₄, melem AM, melem AT and melem GT. In the XRD pattern of melem AM, a series of peaks centered at 12.6, 13.7, 16.8, 18.4, 19.4, 19.8, 22.1, 25.4, 26.2, 27.2, 28.7, 30.6 and 31.2° are observed and the main peak is located at 25.4°. The XRD pattern of melem is in well agreement with that reported in the literature.^{38,41} The result

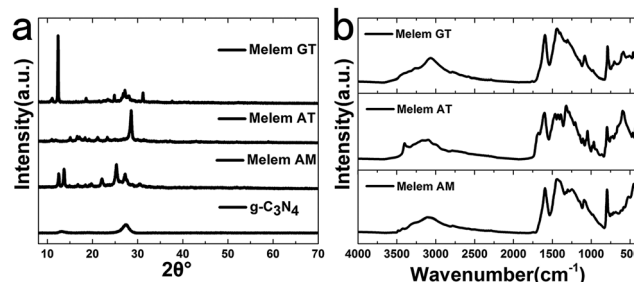


Fig. 2 (a) XRD patterns of g-C₃N₄, melem AM, melem AT and melem GT, and (b) FTIR spectra of melem AM, melem AT and melem GT.

indicates that melem is formed successfully by calcinating melamine at a temperature of 400 °C. The formation of melem is also proved by mass spectral analysis. In the mass spectrum of melem AM (Fig. S1, ESI†), three peaks located at 157, 176 and 219 *m/z* are observed, which are the characteristic peaks for melem. The peak at 219 *m/z* corresponds to C₆N₇(NH₂)₃⁺, and the peaks at 176 and 157 *m/z* correspond to C₆N₇(NH₂)₃–CN(NH₂) and C₆N₇(NH₂)₃–N₄H₆⁺, respectively. Those peaks are the direct proof for the formation of melem. However, after acid treatment, the XRD patterns change greatly. The peak located at 28.7° grows rapidly and becomes the main peak, while the other peaks become weaker in intensity. In addition to the peaks belonging to melem AM, some new peaks at 15.2, 21.2 and 23.4° are observed. These phenomena indicate that after acid treatment the most exposed facet of melem is changed and some new phases may be formed in melem AT. After melem AT is further treated with ethylene glycol, the peak centered at 12.6° becomes the new main peak, and only some weak peaks are seen at 18.4, 24.7, 27.2 and 31.2°. These peaks agree with the peaks of melem AM. As can be identified from Fig. 2a, after melem AM is treated with nitric acid and ethylene glycol, the peaks of melem GT are much sharper and stronger in intensity, indicating an increased particle size and an improved crystallinity, which is consistent with the SEM results.⁴⁸ No new peaks appear in melem GT in comparison with melem AM, indicating that there are no new phases formed during the treatments. According to the SEM images of the samples, melem GT exhibits a rod-like structure, which is different from that of melem AM, indicating a preferential growth. As a result of the preferred orientations, the exposed facets of melem may be different after the treatment. Some facets may become invisible under the X-ray diffraction, while others may become more exposed, which can explain the disappearance of some peaks and the prominence of a peak at 12.6° in the XRD pattern of melem GT. Hence, we may conclude that the melem GT is still a pure melem.

The molecular structures of melem are studied using FTIR spectroscopy. For melem, there are 60 fundamental vibration modes, which can be divided into two groups: 21 vibrations are associated with the three amino groups of melem and 39 vibrations are attributed to the skeletal vibrations of the C₆N₇ nucleus.⁴¹ Fig. 2b shows the FTIR spectra of the three samples. For melem AM, the three characteristic absorption bands centered at 795, 1441 and 1592 cm^{−1} of melem correspond to the stretching and

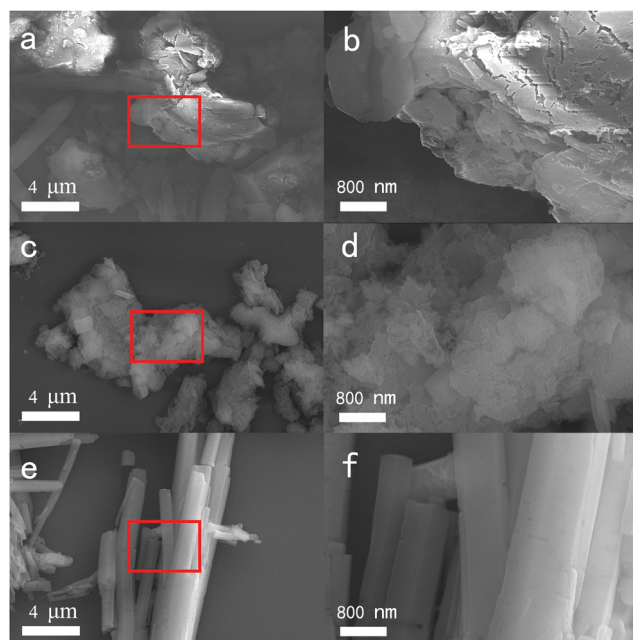


Fig. 1 (a) SEM image of melem AM, (b) the enlarged image of the red frame in (a), (c) SEM image of melem AT, (d) the enlarged image of the red frame in (c), (e) SEM image of melem GT, and (f) the enlarged image of the red frame in (e).

bending vibrations of C–N in the C_6N_7 ring.³⁸ The broad absorbance band from 2800 to 3500 cm^{-1} is ascribed to the N–H stretching vibrations of the NH or NH_2 groups.⁴³ The result verifies the existence of NH_2 groups and the C_6N_7 nucleus in melem AM, which can prove the formation of melem. By comparing the spectrum of melem AM with that of melem GT, we can figure out that the main absorbance bands are well consistent, which proves that their basic molecular structures are the same. This result is a strong support for our verdict that the rod-like products named melem GT are still melem. As for melem AT, a new peak at 3398 cm^{-1} appears and the peaks at 1443 and 1583 cm^{-1} are separated. In the process of acid treatment, the three amino groups may be replaced by some other functional groups, such as hydroxy or nitro groups, and some chemical bonds in the C_6N_7 nucleus may be destroyed by nitric acid treatment, thus leading to the appearances of new peaks.^{42,49–51}

To further verify our conclusion, solid state ^{13}C and 1H nuclear magnetic resonance (NMR) spectra were measured on the samples. The ^{13}C NMR spectrum (Fig. 3a) of melem AM clearly shows two peaks at 164.1 and 154.3 ppm, respectively, indicating that it has only two kinds of carbons. The peak at 164.1 ppm corresponds to the $CN_2(NH_2)$ structure and the peak at 154.3 ppm corresponds to the CN_3 structure.³⁸ These results prove that melem AM is a pure melem. Similarly, for melem GT, only two peaks exist in the ^{13}C NMR spectra, indicating that only two carbon positions exist. However, the peaks shift a bit to 163.2 and 153.2 ppm, respectively. The slight shift is probably due to the change in the microstructure, which may influence the electron cloud distribution, and thus lead to a different shielding effect affecting the NMR signals.⁵² The similarity of the ^{13}C NMR signals of melem AM and melem GT proves that melem GT is a pure melem as well. As for melem AT, two new peaks at 155.8 and 149.9 ppm are observed, indicating a breakage of C–N bonds in the C_6N_7 nucleus. The 1H NMR spectra agree well with the results of ^{13}C NMR spectra. Melem AM and melem GT share the same peak centered at 4.4 ppm, indicating that only one H position exists in these two materials. The peak corresponds to the three NH_2 structure connecting with the C_6N_7 nucleus. The peak of melem AM is broad, while the peak of melem GT is sharp. The broad NMR signal of melem AM is caused by the anisotropy interactions in powder. Melem GT is

better crystallized with a preferred orientation, which can reduce the anisotropy, and thus lead to a sharp NMR signal.⁵³ As for melem AT, similar to the results of ^{13}C NMR spectra, some new peaks appear, indicating that more than one hydrogen position exists. Combining the ^{13}C and 1H NMR spectra of melem AM and GT, we are convinced that only two carbon positions and one hydrogen position exist in melem AM and GT, which can prove that melem GT and melem AM are both pure melem, while melem AT is not. In summary, by heating melamine in air at 400 °C, we successfully synthesized pure melem (melem AM). After melem AM is treated with nitric acid and ethylene glycol, pure rod-like structured melem with better crystallinity (melem GT) is obtained.

The obtained melem shows strong luminescence. Fig. 4 shows the excitation and emission spectra of the as-obtained samples. The results clearly show that melem has a broad excitation band from 240 to 370 nm with a visible emission at around 435 nm in the blue, which can be separated into two peaks at 432 and 454 nm, respectively (see Fig. S2, ESI†). The band structure and density of states of melem calculated based on density functional theory (DFT) are shown in Fig. 5. The crystal structure of melem and the lattice constants are shown in the ESI† (see Fig. S3). The band gap calculated using the GGA-PBE functional based on the completely crystallized structure is 3.24 eV, which is quite close to the measured value of 3.10 eV (see Fig. S4, ESI†). The band gap is also calculated by using the HSE functional taking different AEXX values. For the default AEXX = 0.25, the calculated band gap is 4.39 eV, while the band gap is 3.32 when AEXX = 0.01 (see Fig. S5, ESI†). In this work, the band gap calculated using GGA-PBE is very

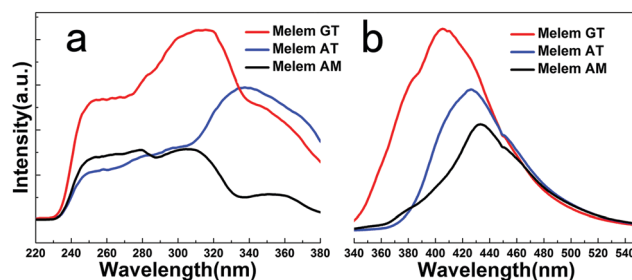


Fig. 4 (a) Excitation spectra of melem AM, melem AT and melem GT by monitoring emission at 405 nm, and (b) emission spectra of melem AM, melem AT and melem GT excited at 320 nm.

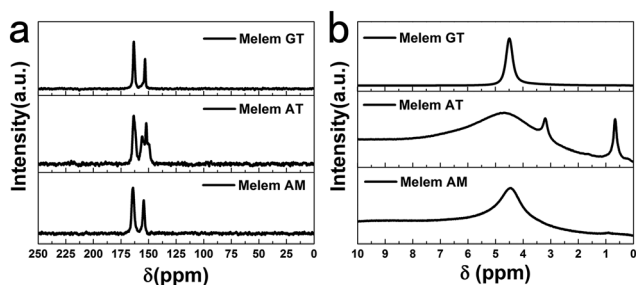


Fig. 3 (a) Solid state ^{13}C NMR spectra of melem AM, melem AT and melem GT, and (b) solid state 1H NMR spectra of melem AM, melem AT and melem GT.

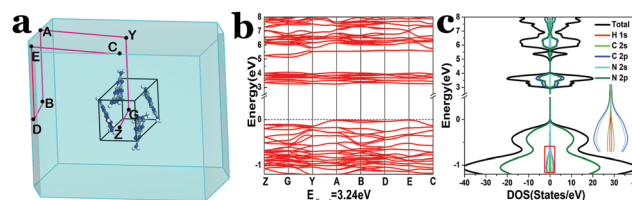


Fig. 5 (a) The first irreducible Brillouin zone, (b) band structure and (c) density of states of total, H 1s, C 2s, C 2p, N 2s and N 2p orbitals in melem calculated by using PBE; the inset shows the enlarged image of the red frame in (c).

close to the experimental value. The main reason is that there is a van der Waals force between melem layers. In addition, melem contains no transition metals.

We also performed the DOS calculations as shown in Fig. 5c and Fig. S5(b) (ESI†). The valence band maximum (VBM) is mainly composed of N 2p states, and the conduction band minimum (CBM) is contributed by N 2p and C 2p states. Hydrogen contributes little to the valence band and the conduction band. The electrons can absorb ultraviolet radiation and transit from the VB to CB, which produces absorption spectra. Similar to $g\text{-C}_3\text{N}_4$, melem has a tri-s-triazine ring structure.^{27,41,54} C and N are sp^2 -hybridized to form C–N clusters, which form the δ^* and π^* states located in the conduction band. The size of the C–N cluster is considered to be the main influence factor of the luminescence properties of carbon nitride.^{30,55} In addition, the unshared electron pairs on the N atoms form the states located in the valence band from -0.7 eV to the VBM.^{30,56} The states below -0.7 eV are the bonding bands composed mainly of the N 2p, N 2s, and C 2p and minorly of C 2s and H 1s orbitals, which can be identified from the inset in Fig. 5c. The two emissions of melem centered at 432 and 454 nm are ascribed to the electron transitions from the δ^* and π^* conduction bands to the unshared electron pair states, respectively.^{30,57,58}

The existence of two emission bands in the samples is also proved by the decay curves and time-resolved emission spectra. Fig. 6a shows the decay curves of melem AM, melem AT and melem GT. As can be identified from Fig. 6a, all three samples show non-exponential decay. Besides, by comparing the decay curves of the three samples, the lifetime of melem GT is the longest among all three samples. The fitted average lifetime of melem AM, melem AT and melem GT is 360 ns, 541 ns and 1409 ns, respectively. The average lifetime was fitted according to the following equation.⁵⁹

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$

The lifetime increase can be explained by the reduction of defects in the samples caused by the improvement in crystallinity.^{60,61} Defects can capture electrons in the δ^* and π^* states located in the conduction band, which would cause luminescence quenching. Electrons in the δ^* state can transit to the valence band to generate visible light, and can also relax to the π^* state, where electrons can transit to the valence band to produce the

second emission band.³⁰ Once the quantity of defects is reduced, fewer electrons would be captured, and more electrons can remain in the excited states, and the possibility of electron transition from both δ^* and π^* states to the valence band is increased, which would cause the increase in the fluorescence lifetime, and simultaneously increase the fluorescence intensity and induce blue shifted emission.⁶³ This result is also evidenced by the TRES measurement. Fig. 6b shows the time-resolved emission spectra of melem GT. As can be identified, a red shift in the fluorescence with time is observed. This is because the δ^* state is a metastable state compared with the π^* state.³⁰ Electrons in the δ^* state would relax to the π^* state rapidly, which corresponds to the fast decay in the decay curves measured.

To further determine the types of defects affecting the luminescence properties of the samples, OEA and EDS measurements were performed to analyze the bulk and surface elemental composition of the samples. Bulk N/C and H/C mass ratios from OEA and surface N/C mass ratios from EDS are listed in Table 1. The N/C mass ratios obtained from OEA of melem AM, melem AT and melem GT were 1.91, 2.00 and 1.94, respectively, which are in a good agreement with the theoretical value of melem. The similarity of the N/C ratios of melem AM and melem GT indicated that they shared the same basic structure of melem. The H/N mass ratios obtained from OEA of melem AM, melem AT and melem GT were 0.042, 0.058 and 0.059, respectively, which are also in a good agreement with the theoretical value of melem. Hydrogen existed in melem in the form of the amino group. The increasing H/N mass ratio indicates an increasing amino group in melem. These results indicate that by treating melem AM with nitric acid and ethylene, the N/C mass ratio is increased, which is believed to be the result of the elimination of nitrogen defects. The OEA results were also reflected by the surface elemental composition analysis from EDS. The N/C mass ratios of melem AM, melem AT and melem GT obtained from EDS were 2.18, 2.21 and 2.36, respectively, which also proves an increasing nitrogen content in the surface area. The nitrogen defects were believed to affect the band structure of carbon nitride,

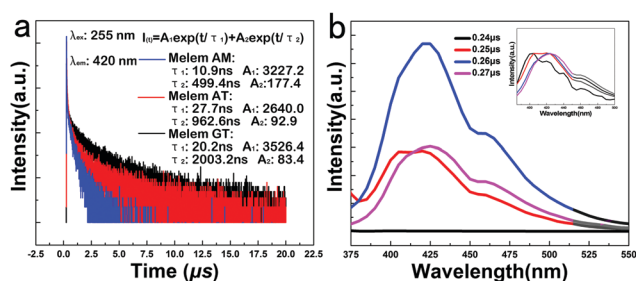


Fig. 6 (a) Decay curves of melem AM, melem AT and melem GT, and (b) time-resolved emission spectra of melem GT; the inset shows the normalized peaks of different times.

Table 1 Elemental composition of melem AM, melem AT and melem GT obtained from OEA and EDS

Sample	OEA		EDS
	N/C	H/N	N/C
Melem AM	1.91	0.042	2.18
Melem AT	2	0.058	2.21
Melem GT	1.94	0.059	2.36

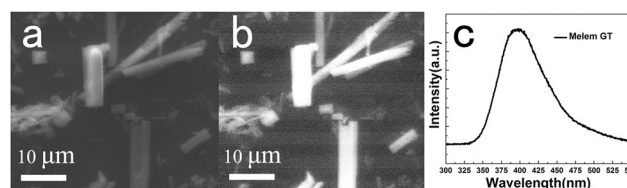


Fig. 7 (a) The secondary electron image, (b) the cathodoluminescence image and (c) the cathodoluminescence spectrum of melem GT.

Table 2 Comparison of the quantum yields of melem AM, melem AT and melem GT with other common metal-free luminescent materials

Luminescent materials	Quantum yield (%)	Sample state	Authors	Ref.
g-C ₃ N ₄	4.80	Bulk material	Zhang <i>et al.</i>	16
g-C ₃ N ₄	46	Quantum dots	Zhou <i>et al.</i>	31
Melem AM	35.16	Bulk material	—	This work
Melem AT	10.49	Bulk material	—	This work
Melem GT	56.85	Bulk material	—	This work
Carbon dots	4–10	Quantum dots	Sun <i>et al.</i>	62
Silicon nanocrystals	60 ± 11	Quantum dots	Jurbergs <i>et al.</i>	65
Graphene	11.40	Quantum dots	Zhu <i>et al.</i>	66

which has been proven in the other literature.⁶³ For example, Yu *et al.* successfully introduced nitrogen defects into g-C₃N₄ by adding alkali compounds during the thermal polymerization process. The obtained nitrogen defect rich g-C₃N₄ exhibits an improved photocatalytic property but a decreased photoluminescence, which is a common phenomenon for photocatalysts with luminescence.⁶³

The influence of crystallinity on the luminescence properties of melem is directly evidenced by cathodoluminescence spectral measurements. Fig. 7a shows the secondary electron image of melem GT and Fig. 7b shows the corresponding cathodoluminescence image. Fig. 7c shows the emission spectrum of the luminescence area in Fig. 7b. From Fig. 7a and b, we can clearly identify that the rod-like structure shows much stronger luminescence than irregular particles.

After acid or/and glycol treatment, the luminescence efficiency of melem was improved greatly. The luminescence intensity of melem GT was much stronger than that of melem AT or melem AM. To quantify the improvement, the quantum yields of melem AM, melem AT and melem GT were measured (see Table 2). Clearly, the quantum yield of melem AM was improved greatly after nitric acid and ethylene glycol treatments. The quantum yields of the as-prepared melem AM and melem GT were 35.16% and 56.85%, respectively. The quantum yield of the as-prepared bulk melem GT was not only tremendously higher than that of bulk g-C₃N₄ or g-C₃N₄ quantum dots, but also higher than the quantum dots of other common metal-free materials and comparable to materials with the highest efficiency.^{16,31,64–66}

4. Conclusion

In summary, we proposed a facile method by chemically treating melem condensed from melamine to synthesize highly efficient rod-like structured phosphor. XRD, FTIR and NMR analyses confirm that chemical treatments do not change the crystal structure of melem, while SEM images show the preferential growth of micro-rods from irregular particles. The photoluminescence spectra show that the rod-like structured melem exhibits stronger luminescence than the bulk melem. Through theoretical first-principles calculations, observations on the fluorescence decay, time-resolved emission spectra, cathodoluminescence spectral measurements, and OEA and

EDS analyses, we unveiled the origin of the luminescence and the luminescence improvement. The two emissions of melem come from electron transition from δ^* and π^* states to the valence band, and the intensity improvement and blue shift of luminescence are ascribed to the elimination of nitrogen defects due to the improved crystallinity. The quantum yield of the as-prepared rod-like structured melem is as high as 56.9% and substantially higher than other bulk metal-free luminescent materials and even higher than or comparable to their quantum dots. The rod-like structured melem is easy to prepare and contains no metal elements. It is a new metal-free efficient and environmentally friendly blue-emitting material with great potential for practical applications.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 T. Matsuzawa, Y. Aoki, N. Takeuchi and Y. Murayama, *J. Electrochem. Soc.*, 1996, **143**, 2670.
- 2 J. S. Kim, P. E. Jeon, J. C. Choi, H. L. Park, S. I. Mho and G. C. Kim, *Appl. Phys. Lett.*, 2004, **84**, 2931.
- 3 R. J. Xie, N. Hirosaki, K. Sakuma, Y. Yamamoto and M. Mitomo, *Appl. Phys. Lett.*, 2004, **84**, 5404.
- 4 H. Guo, J. Zhang, L. Ma, J. L. Chavez, L. Yin, H. Gao, Z. Tang and W. Chen, *Adv. Funct. Mater.*, 2015, **25**, 6833.
- 5 H. Qian, J. Zhang and L. Yin, *RSC Adv.*, 2013, **3**, 9029.
- 6 C. L. Ho, W. Y. Wong, W. Qi, D. Ma, L. Wang and Z. Lin, *Adv. Funct. Mater.*, 2008, **18**, 928.
- 7 Q. Wang, I. W. H. Oswald, M. R. Perez, H. Jia, B. E. Gnade and M. A. Omary, *Adv. Funct. Mater.*, 2013, **23**, 5420.

- 8 Y. C. Kang, H. S. Roh and S. B. Park, *Adv. Mater.*, 2000, **31**, 451.
- 9 P. J. Yadav, C. P. Joshi and S. V. Moharil, *J. Lumin.*, 2013, **136**, 1.
- 10 H. S. Jang, W. B. Im, C. L. Dong, D. Y. Jeon and S. K. Shi, *J. Lumin.*, 2007, **126**, 371.
- 11 Y. S. Tang, S. F. Hu, C. C. Lin and N. C. Bagkar, *Appl. Phys. Lett.*, 2007, **90**, 151108.
- 12 C. Qin, Y. Huang, L. Shi, G. Chen, X. Qiao and H. J. Seo, *J. Phys. D: Appl. Phys.*, 2009, **42**, 185105.
- 13 H. P. Nguyen, K. Cui, S. Zhang, M. Djavid, A. Korinek, G. A. Botton and Z. Mi, *Nano Lett.*, 2012, **12**, 1317.
- 14 D. Lee, O. Bolton, B. C. Kim, J. H. Youk, S. Takayama and J. Kim, *J. Am. Chem. Soc.*, 2013, **135**, 6325.
- 15 S. H. Cho, J. R. Oh, H. K. Park, H. K. Kim, Y. H. Lee, J. G. Lee and Y. R. Do, *Opt. Express*, 2010, **18**, 1099.
- 16 X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 18.
- 17 Y. Wang, R. Shi, J. Lin and Y. Zhu, *Energy Environ. Sci.*, 2011, **4**, 2922.
- 18 S. Cao and J. Yu, *J. Phys. Chem. Lett.*, 2014, **5**, 753.
- 19 Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith and M. Jaroniec, *J. Am. Chem. Soc.*, 2011, **133**, 20116.
- 20 H. Ma, S. Zhao, S. Li and N. Liu, *RSC Adv.*, 2015, **5**, 79585.
- 21 J. Zhang, Y. Wang, J. Jin, J. Zhang, Z. Lin, F. Huang and J. Yu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 10317.
- 22 Y. Hou, Z. Wen, S. Cui, X. Guo and J. Chen, *Adv. Mater.*, 2013, **25**, 6291.
- 23 C. Pan, J. Xu, Y. Wang, D. Li and Y. Zhu, *Adv. Funct. Mater.*, 2012, **22**, 1518.
- 24 Y. J. Chung, B. I. Lee, J. W. Ko and C. B. Park, *Adv. Healthcare Mater.*, 2016, **5**, 1526.
- 25 X. Wang, X. Chen, A. Thomas, X. Fu and M. Antonietti, *Adv. Mater.*, 2009, **21**, 1609.
- 26 H. Yu, L. Shang, T. Bian, R. Shi, G. I. N. Waterhouse, Y. Zhao, C. Zhou, L. Z. Wu, C. H. Tung and T. Zhang, *Adv. Mater.*, 2016, **28**, 5080.
- 27 A. Du, S. Sanvito, Z. Li, D. Wang, Y. Jiao, T. Liao, Q. Sun, H. N. Yun, Z. Zhu and R. Amal, *J. Am. Chem. Soc.*, 2012, **134**, 4393.
- 28 X. Zhang, Z. Meng, D. Rao, Y. Wang, Q. Shi, Y. Liu, H. Wu, K. Deng, H. Liu and R. Lu, *Energy Environ. Sci.*, 2016, **9**, 841.
- 29 J. M. Carlsson, *Nat. Mater.*, 2009, **8**, 76.
- 30 Y. Zhang, Q. Pan, G. Chai, M. Liang, G. Dong, Q. Zhang and J. Qiu, *Sci. Rep.*, 2013, **3**, 1943.
- 31 Z. Zhou, Y. Shen, Y. Li, A. Liu, S. Liu and Y. Zhang, *ACS Nano*, 2015, **9**, 12480.
- 32 J. Zhang, Y. Chen and X. Wang, *Energy Environ. Sci.*, 2015, **8**, 3092.
- 33 J. Liu, T. Zhang, Z. Wang, G. Dawson and W. Chen, *J. Mater. Chem.*, 2011, **21**, 14398.
- 34 Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu and X. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1455.
- 35 Y. Chen, J. Li, Z. Hong, B. Shen, B. Lin and B. Gao, *Phys. Chem. Chem. Phys.*, 2014, **16**, 8106.
- 36 Y. Zhao, L. Zheng, W. Chu, S. Li, Z. Zhang, D. Yu, Y. Tian, S. Xie and L. Sun, *Adv. Mater.*, 2008, **20**, 1777.
- 37 X. Zhang, H. Wang, H. Wang, Q. Zhang, J. Xie, Y. Tian, J. Wang and Y. Xie, *Adv. Mater.*, 2014, **26**, 4438.
- 38 C. Sheng, C. Wang, J. Feng, W. Ying and Z. Zou, *Int. J. Hydrogen Energy*, 2014, **39**, 13519.
- 39 V. L. Bettina and W. Schnick, *Chemistry*, 2007, **13**, 4956.
- 40 V. W. Lau, M. B. Mesch, V. Duppel, V. Blum, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.*, 2014, **137**, 1064.
- 41 B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller and W. Schnick, *J. Am. Chem. Soc.*, 2003, **125**, 10288.
- 42 E. Kroke, M. Schwarz and E. Horath-Bordon, *New J. Chem.*, 2002, **26**, 508.
- 43 S. Liu, H. Sun, K. O'Donnell, H. M. Ang, M. O. Tade and S. Wang, *J. Colloid Interface Sci.*, 2015, 464.
- 44 Z. Zhou, Y. Shen, L. Ying, A. Liu, S. Liu and Y. Zhang, *ACS Nano*, 2015, **9**, 12480.
- 45 S. Barman and M. Sadhukhan, *J. Mater. Chem.*, 2012, **22**, 21832.
- 46 X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2015, **135**, 18.
- 47 J. Zhou, Y. Yang and C. Y. Zhang, *Chem. Commun.*, 2013, **49**, 8605.
- 48 K. Park, H. J. Yu, W. K. Chung, B. J. Kim and S. H. Kim, *J. Mater. Sci.*, 2009, **44**, 4315.
- 49 C. E. Redemann and H. J. Lucas, *J. Am. Chem. Soc.*, 2002, **62**, 842.
- 50 K. Damodaran, G. J. Sanjayan, P. R. Rajamohanam, S. Ganapathy and K. N. Ganesh, *Org. Lett.*, 2001, **3**, 1921.
- 51 E. Kroke, M. Schwarz, E. Horathbordon, P. Kroll, B. Noll and A. D. Norman, *New J. Chem.*, 2002, **26**, 508.
- 52 H. Friebolin, *Basic one- and two-dimensional NMR spectroscopy*, 1991, vol. 87, p. 429.
- 53 C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune and J. R. Salem, *J. Cheminf.*, 1991, **95**, 9.
- 54 Y. Wang and D. X. Wang, *Angew. Chem., Int. Ed.*, 2012, **51**, 68.
- 55 M. Deifallah, P. F. Mcmillan and F. Corà, *J. Phys. Chem. C*, 2008, **112**, 5447.
- 56 L. Ay and C. Ml, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1990, **41**, 621.
- 57 Y. Iwano, T. Kittaka, H. Tabuchi, M. Soukawa, S. Kunitsugu, K. Takarabe and K. Itoh, *Jpn. J. Appl. Phys.*, 2008, **47**, 7842.
- 58 D. Das, S. L. Shinde and K. K. Nanda, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2181.
- 59 M. Shang, G. Li, D. Yang, X. Kang, C. Zhang and J. Lin, *J. Electrochem. Soc.*, 2011, **158**, J125.
- 60 K. K. Kim, J. H. Song, H. J. Jung, W. K. Choi, S. J. Park and J. H. Song, *J. Appl. Phys.*, 2000, **87**, 3573.
- 61 S. S. Kim, S. Y. Choi, C. G. Park and H. W. Jin, *Thin Solid Films*, 1999, **347**, 155.
- 62 Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang,

- H. F. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. M. Veca and S. Y. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756.
- 63 H. Yu, R. Shi, Y. Zhao, T. Bian, Y. Zhao, C. Zhou, G. I. Waterhouse, L. Z. Wu, C. H. Tung and T. Zhang, *Adv. Mater.*, 2017, **29**, 1605148.
- 64 D. Sheila, N. Baker, D. Gary and A. Baker, *Angew. Chem., Int. Ed.*, 2010, **49**, 6726.
- 65 D. Jurbergs, E. Rogojina, L. Mangolini and U. Kortshagen, *Appl. Phys. Lett.*, 2006, **88**, 2915.
- 66 S. Zhu, J. Zhang, C. Qiao, S. Tang, Y. Li, W. Yuan, B. Li, L. Tian, F. Liu and R. Hu, *Chem. Commun.*, 2011, **47**, 6858.