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Photophysics and Photocatalysis of Melem: A Spectroscopic Reinvestigation

Jing Wen, Ruiyu Li, Rong Lu*, and Anchi Yu*[a]

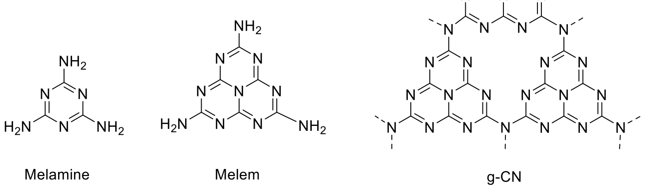
Abstract: Graphitic carbon nitride (g-CN) is one potential metal-free photocatalyst. The photocatalytic mechanism of g-CN is involved with its building unit heptazine ring. Melem is the simplest heptazine-based compound and g-CN is its polymeric product. Thus, studies on the photophysical property of melem will help to understand the photocatalytic mechanism of heptazine-based materials. In this work, we systematically explored the spectroscopic features of melem through measuring its absorption spectrum, fluorescence spectrum and fluorescence decay, respectively. Both fluorescence spectroscopy and fluorescence decay measurements show that the condensation of melamine to melem causes the stronger photoluminescence, while the condensation of melem to g-CN causes the weaker photoluminescence. In addition, all observations reveal that a mixture of monomer melem and its higher condensates is more easily obtained during the preparation of melem, and that the higher condensates of melem affect the photophysical properties of melem dominantly. The photocatalytic hydrogen evolution of melem was also measured and it is found that monomer melem has negligible photoinduced water splitting activity.

Introduction

Graphitic carbon nitride (g-CN) has become the most important and potential visible light responsive metal-free photo-induced water splitting catalyst over past several years.[1-11] However, the mechanism of the photocatalytic water splitting reaction by g-CN is not fully understood yet.[12-14] Recently, Lau *et al.* explored low molecular weight g-CN for solar hydrogen evolution and found that oligomers of melem have higher photocatalytic water-splitting activity than that of g-CN as well as melem monomer.[14] Later, Ehrmaier *et al.* applied first-principle computation and proposed that water splitting with heptazine-based materials can be understood as a molecular excited-state reaction taking place in hydrogen-bonded heptazine-water complexes.[13] g-CN is the polymeric product of melem and heptazine ring is their basic building block (Scheme 1). Since the photocatalytic water-splitting reaction by g-CN is related to the heptazine unit and melem is the simplest heptazine-based compound, the comprehensive investigation of the photophysical properties of melem will help to more deeply understand the mechanism of the photoinduced water splitting reaction of heptazine-based materials.

Melem (2,5,8-triamino-tri-s-triazine, Scheme 1) can be obtained by thermal condensation of melamine, and it is also the intermediate of the further thermal condensation product g-CN at higher calcination temperature.[14-17] Kroke *et al.* have summarized the formation of melem as well as its structure, properties and applications.[15] In 2014, three groups respectively reported the photoinduced water splitting reaction by melem, but they have got different opinions about the photocatalytic activity of melem. Brückner *et al.* systematically explored the structure-activity relationship of g-CN at different calcination temperatures and they found low catalytic activity for melem.[17] Later, Zou *et al.* studied the photocatalytic H_2 evolution of melem and they concluded that melem is a metal-free unit for photocatalytic H_2 evolution.[18] Almost at the same time, Lotsch *et al.* explored the photocatalytic H_2 evolution of melem and its higher condensates and claimed that the oligomers of melem is the most active species.[14] The understanding on the photocatalytic reaction mechanism of a photocatalyst closely depends on the knowledge of its photophysical properties. As for the photophysical properties of melem, there existed inconsistence such as its fluorescence decay lifetime and fluorescence spectrum.[12, 16-20] Therefore, a systematic investigation on the photophysical properties of melem is still in need to correctly understand its photocatalytic mechanism and its related heptazine-based materials.

For comparing with the photophysical data of melem presented in literature[14, 16-19], in this work, purified and unpurified melem were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, element analysis, UV-Vis diffuse reflectance spectroscopy (UVDRS), fluorescence spectroscopy, and fluorescence decay lifetime measurement. The spectroscopic properties of the precursor melamine and its thermal condensation product g-CN were reexamined. The Brunauer-Emmett-Teller (BET) surface areas and the photocatalytic H_2 evolutions of melamine, melem and g-CN were also measured. In addition, the fluorescence feature of melem in aqueous solution was explored for the first time.



Scheme 1. Chemical structures of melamine, melem, and g-CN.

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Results and Discussion

XRD, FTIR and elemental analysis characterization of melem: Figure 1 shows the XRD patterns of the as-synthesized melem, hot-water-washed melem, and melem. In Figure 1, the XRD patterns of melamine and g-CN are also displayed for reference. From Figure 1, it is found that the XRD pattern of the as-synthesized melem in this work is consistent with the reported XRD pattern of the as-synthesized melem,[14, 18-19] and the XRD pattern of the hot-water-washed melem is consistent with that of the DMSO soluble melem[14] and the dehydrated melem[21]. The obvious difference of the XRD patterns between the as-synthesized melem and the hot-water-washed melem indicates that the as-synthesized melem contains a certain amount of melamine and that hot water can remove the non-reacted melamine from the as-synthesized melem. According to the reported method, the hot-water-washed melem was further boiled with HCl and then with NaOH solution,[22] and finally melem power was obtained. The XRD pattern of melem shown in Figure 1 is similar to the calculated pattern based on single-crystal data[21] and the temperature-programmed XRD pattern of melem[23], as well as the observed and calculated XRD pattern of melem[16], indicating that high quality of pure melem is obtained in this work.

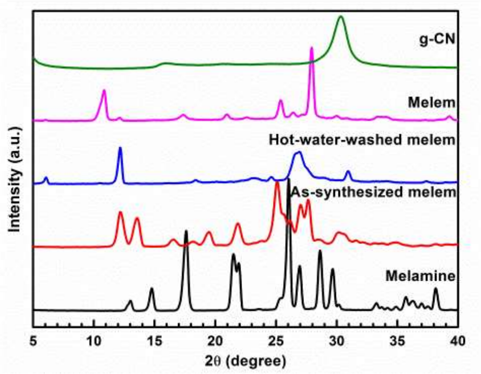

Figure 1. X-ray diffraction patterns of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN.

Figure 2 shows the FTIR spectra of as-synthesized melem, hot-water-washed melem, and melem. In Figure 2, the FTIR spectra of melamine and g-CN are also displayed for reference. As shown in Figure 2, all FTIR spectra of the as-synthesized melem, the hot-water-washed melem and melem present similar features, which agree with the reported FTIR data of melem.[14, 18-19, 21, 23] In general, the FTIR spectra of all melem samples present characteristic bands of aromatic CN heterocycles in the range of 1200 ~ 1700 cm^{-1} and one breathing mode of tri-*s*-triazine unit at 805 cm^{-1}. The broad bands in the range of 3000 ~ 3700 cm^{-1} are attributed to the stretching modes of secondary and primary amines, or their intermolecular hydrogen-bonding interactions.[24] Comparing the FTIR spectra of the as-synthesized melem, the hot-water-washed melem, and melem shown in Figure 2, it is found that the FTIR spectrum of melem is more structured than those of the as-synthesized melem and the hot-water-washed melem in the range of 3000 ~ 3700 cm^{-1}. The elemental analysis data of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN are presented in Table 1. The C:N ratio (0.601) of melem ($C_6N_{10}H_6$) shown in Table 1 is extremely close to the theoretical value, further indicating that the high quality of pure melem is obtained in this work.

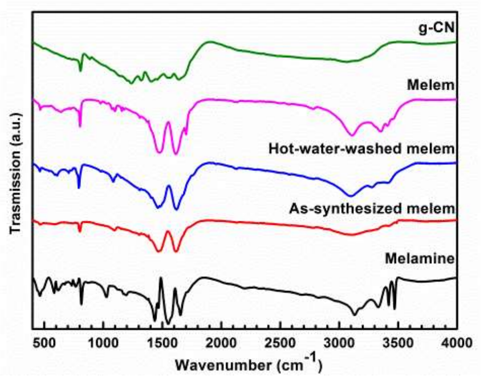

Figure 2. FTIR spectra of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN.

Table 1. Elemental analysis of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN.

Sample	C (ω%)	N (ω%)	C:N atomic ratio
melamine ($C_3N_6H_6$)	28.85±0.01	67.14±0.02	0.501±0.001
as-synthesized melem	32.46±0.09	62.53±0.09	0.605±0.001
hot-water-washed melem	30.67±0.04	59.25±0.08	0.604±0.001
melem ($C_6N_{10}H_6$)	30.28±0.01	58.74±0.02	0.601±0.002
g-CN	34.60±0.12	60.66±0.09	0.665±0.04

UVDRS and fluorescence spectra of melem: Figure 3 displays the normalized UVDRS spectra of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN. As shown in Figure 3, the absorption maximum wavelength of melem locates at around 330 nm. Lotsch *et al.* reported the UVDRS of the DMSO soluble melem powder maximized around 350 nm[14], and Zou *et al.* reported the UVDRS of melem powder maximized at around 390 nm[18]. According to the DRS spectral peaks of the as-synthesized melem, the hot-water-washed melem, and melem shown in Figure 3, the inconsistences among UVDRS data of the obtained melem from different groups are due to the different constitutes of the obtained melem. As shown in Figure 3, the UVDRS spectral band of the prepared melem presents monomer characteristic, indicating that the prepared melem in this work is monomer melem, while the as-synthesized melem as well as the hot-water-washed melem contains both monomer melem and its higher condensates.

Figure 4 shows the fluorescence spectra of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN under 250 nm light excitation. As shown in Figure 4, it is found that the fluorescence emission of melem is peaked at around 395 nm, which is consistent with Shigesato's report but is inconsistent with the Ricci's and Brückner's reports. Shigesato *et al.* reported the emission maximum of melem at 390 nm,[25] Ricci *et al.* reported the emission maximum of melem at 415 nm,[20] and Brückner *et al.* reported the emission maximum of melem at around 420 nm.[17] In Figure 4, we also found that the fluorescence peak positions of the as-synthesized melem, hot-water-washed melem, and g-CN are all red shifted comparing with that of melem. Thus, it is reasonable to suggest that the different emission maxima of melem among Ricci's (415 nm), Brückner's (420 nm) and ours (395 nm) are due to the effect of the higher condensates of melem on melem. In addition, it is also found that the photoluminescence intensities of melamine, melem and g-CN present the decreasing sequence as melem > g-CN > melamine, indicating that the condensation of melamine to melem causes the stronger photoluminescence, while the condensation of melem to g-CN causes the weaker photoluminescence.

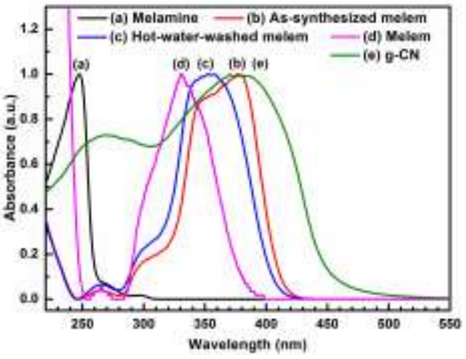

Figure 3. Normalized UVDRS spectra of melamine (a), as-synthesized melem (b), hot-water-washed melem (c), melem (d), and g-CN (e).

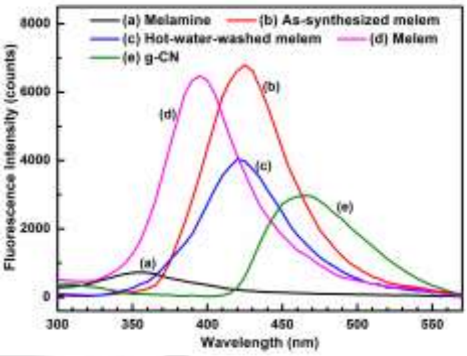

Figure 4. Fluorescence spectra of melamine (a), as-synthesized melem (b), hot-water-washed melem (c), melem (d), and g-CN (e) under 250 nm light excitation.

Fluorescence decay measurement of melem: For further explore the photoluminescence property of melem, the fluorescence decays of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN were measured under 250 nm light excitation by using a home-made time-correlated single photon counting setup, as shown in Figure 5. All the fluorescence decays can be fitted with a two-exponential decay function and their fitting parameters are summarized in Table 2. In Figure 5, the symbols denote the experimental data and the solid lines are their respective fitting curves. The instrumental response function (IRF) curve is also displayed for reference. From Table 2, it is found that the fluorescence lifetimes of melamine, melem and g-CN present the decreasing sequence as melem (9.78 ns) > g-CN (0.89 ns) > melamine (0.20 ns), which is consistent with their respective steady-state fluorescence spectroscopic results shown in Figure 4. Zhang *et al.* reported a more than 300 ns fluorescence lifetime for melem powder,[19] which might be due to the instrument response time limit of their luminescence lifetime setup. The photoluminescence decay lifetime of g-CN measured in this work is close to reported photoluminescence lifetime of g-CN prepared at 550 ºC calcination temperature[26]. In addition, the fluorescence lifetime of melamine is quiet short and close to the IRF time scale, indicating there is almost no fluorescence emission from melamine, which agrees with the reported result from the study of its excited dynamics.[27] Kohler *et al.* explored the excited-state dynamics of melamine in aqueous solution and observed that the excited melamine molecules can decay to its electronic ground state with tens of picoseconds after excitation at 240 nm.[27]

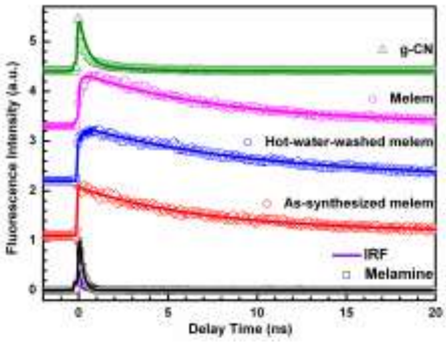

Figure 5. Fluorescence decays of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN. Excitation wavelength: 250 nm; detection wavelength: 420 nm.

Table 2. Fluorescence decay fitting parameters for melamine, as-synthesized melem, hot-water-washed melem, melem, g-CN, and 0.003 mg/ml aqueous melem solution.

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Sample	α_1	τ_1 / ns	α_2	τ_2 / ns	$<\tau>$ / ns [a]
melamine	1.00	0.20			0.20
as-synthesized melem	0.90	7.11	0.10	33.93	9.79
hot-water-washed melem	0.86	9.19	0.14	33.53	12.59
melem	0.89	7.06	0.11	31.78	9.78
g-CN	0.90	0.44	0.10	4.98	0.89
aqueous melem solution	0.41	6.61	0.59	48.29	31.20

[a] $\langle \tau \rangle = (\alpha_1\tau_1 + \alpha_2\tau_2)/(\alpha_1 + \alpha_2)$.

UV-Vis absorption spectra, fluorescence spectra and fluorescence decay of aqueous melem solution: Due to the low solubility of melem in aqueous solution, the photophysical property of melem in aqueous solution is rarely studied in previous report. Figure 6 shows the UV-Vis absorption spectrum of 0.003 mg/ml aqueous melem solution in the wavelength range of 190 - 400 nm. The UV-Vis absorption spectrum of 0.003 mg/ml aqueous melamine solution is also present for reference. In Figure 6, the insert is their respective normalized absorption spectra, which agree with the reported UV-Vis absorption spectra of aqueous solutions of melamine (1.25×10^{-4} M) and melem (2×10^{-5} M).[28] Compared with the UVDRS spectra of melamine and melem shown in Figure 3, both the absorption spectra of their respective aqueous solution present large blue shift, which might be due to the condensed phase characteristic.

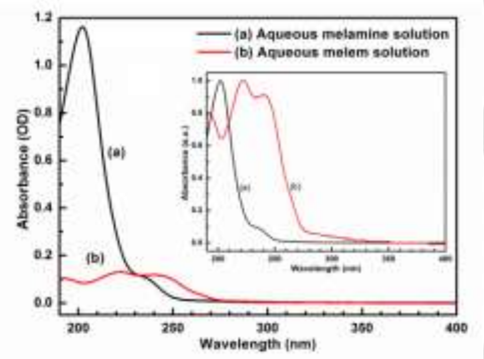

Figure 6. UV-Vis absorption spectra of 0.003 mg/ml aqueous melamine solution (a) and 0.003 mg/ml aqueous melem solution (b). Insert: Normalized UV-Vis absorption spectra of 0.003 mg/ml aqueous melamine solution (a) and 0.003 mg/ml aqueous melem solution (b).

Figure 7A shows the fluorescence emission spectra of 0.003 mg/ml aqueous melem solution under different wavelength light excitation, and the insert is the fluorescence excitation spectrum of 0.003 mg/ml aqueous melem solution under 365 nm light emission. For reference, Figure 7B also displays the fluorescence emission spectra of 0.003 mg/ml aqueous melamine solution under different wavelength light excitation, and the insert is the fluorescence excitation spectrum of 0.003 mg/ml aqueous melamine solution under 365 nm light emission.

From Figure 7A, it is found that the fluorescence maximum excitation wavelength of aqueous melem solution locates at around 250 nm, and the fluorescence maximum emission wavelength of aqueous melem solution locates at around 365 nm. Meanwhile, it is also found that there is no spectral shift of the fluorescence spectra of 0.003 mg/ml aqueous melem solution under different wavelength light excitation, implying that the component of aqueous melem solution is uniform, and thus the component of the prepared melem powder in this work is also uniform. In addition, it is further found that there is very weak fluorescence excitation and fluorescence emission for aqueous melamine solution (Figure 7B), which agrees well with the florescence spectrum of melamine shown in Figure 4 and the fluorescence decay of melamine shown in Figure 5.

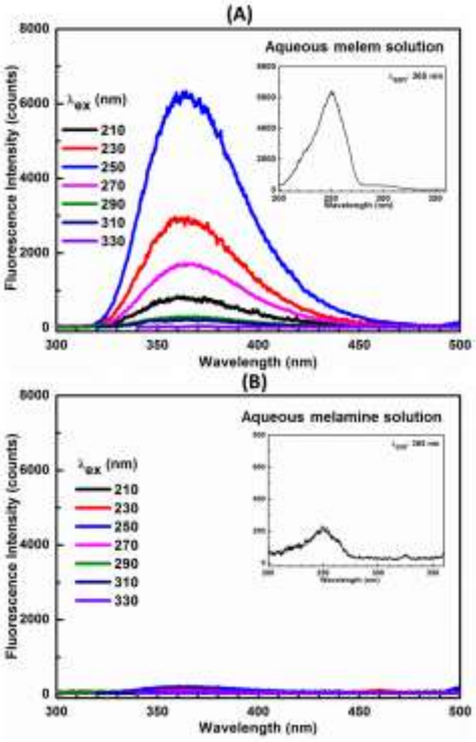

Figure 7. (A) Fluorescence spectra of 0.003 mg/ml aqueous melem solution under different wavelengths light excitation. Insert: fluorescence excitation spectra of 0.003 mg/ml aqueous melem solution at 365 nm light emission. (B) Fluorescence spectra of 0.003 mg/ml aqueous melamine solution under different wavelengths light excitation. Insert: fluorescence excitation spectra of 0.003 mg/ml aqueous melamine solution at 365 nm light emission.

Figure 8A shows the normalized fluorescence spectra of 0.003 mg/ml aqueous melamine solution and 0.003 mg/ml aqueous melem solution, and Figure 8B shows the fluorescence decays of 0.003 mg/ml aqueous melamine solution and 0.003 mg/ml aqueous melem solution. The fluorescence decay fitting parameters are also listed in Table 2. From Figure 8, it is found that both the fluorescence spectrum of 0.003 mg/ml aqueous melamine solution and the fluorescence decay profile of 0.003 mg/ml aqueous melamine solution overlap perfectly with those of 0.003 mg/ml aqueous melem solution. Both the fluorescence spectrum of melamine powder shown in Figure 4 and the fluorescence decay of melamine powder shown in Figure 5 clarify that there is no fluorescence emission from melamine. Therefore, it is reasonable to conclude that the fluorescence emission of 0.003 mg/ml aqueous melamine solution (Figure 7B) originates from the fluorescence emission of the melem impurity containing in melamine. Then, the previous reports about the fluorescence characteristic of melamine [29-30] should be carefully interpreted. Besides, the fluorescence decay lifetime of 0.003 mg/ml aqueous melem is much longer than that of melem powder (Table 2), which is due to the stronger molecular interaction in condensed phase of melem.

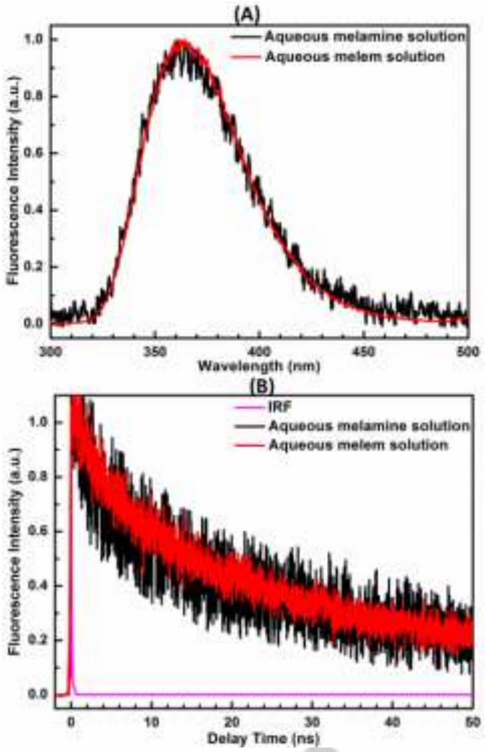

Figure 8. (A) Normalized fluorescence spectra of 0.003 mg/ml aqueous melamine solution (black line) and 0.003 mg/ml aqueous melem solution (red line) under 250 nm light excitation; (B) Fluorescence decays of 0.003 mg/ml aqueous melamine solution (black line) and 0.003 mg/ml aqueous melem solution (red line). Excitation wavelength: 250 nm; detection wavelength: 420 nm.

Photocatalytic H_2 evolution: g-CN is a potential function material for photoinduced water splitting catalyst and its building block heptazine ring is proposed to contribute to its photocatalytic mechanism. In this work, we also measured the photocatalytic H_2 evolutions of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN under Xeon lamp (spectral region around 300 - 700 nm) light irradiation, as shown in Figure 9. The determined photocatalytic H_2 evolution rates for melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN under Xeon lamp light irradiation are all summarized in Table 3. The determined photocatalytic H_2 evolution rate for g-CN under Xeon lamp full light irradiation is consistent with the previous reports.[18, 31] From Figure 9 and Table 3, it is found that the photocatalytic H_2 evolutions of melamine and melem under Xeon lamp light irradiation are almost negligible. Since the photocatalytic H_2 evolution efficiency is related to the surface area of photocatalyst, the BET surface areas of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN are also measured and summarized in Table 3. Table 3 shows that melamine has very low surface area and negligible photocatalytic activity. The negligible photocatalytic activity of melamine is mainly due to its absent absorbance in the Xeon lamp spectral region. As for melem, its surface area is larger than that of g-CN, but its H_2 evolution rate is also negligible compared to g-CN, which is due to the unsuitable oxidation and reduction levels of melem for water splitting reaction.[4, 18] However, the higher photocatalytic activity of the as-synthesized melem as well as the hot-water-washed melem as shown in Table 3 probably originates from the higher condensates of melem in the product.[14]

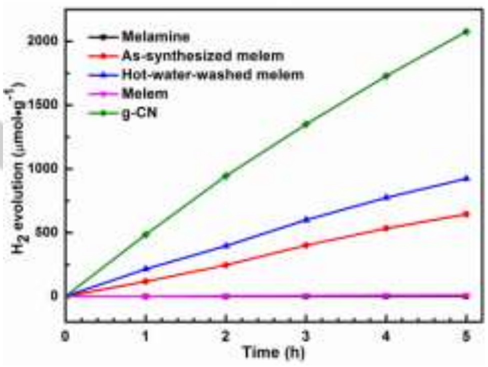

Figure 9. Photocatalytic H_2 evolutions of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN under 300 W Xeon lamp light (300 - 700 nm) irradiation.

Table 1. BET surface areas and photocatalytic H_2 evolution rates of melamine, as-synthesized melem, hot-water-washed melem, melem, and g-CN.

Sample	BET surface area (m^2•g^{-1})	H_2 evolution rate (µmol•g^{-1}•h^{-1})
melamine	0.3±0.01	0
as-synthesized melem	3.9±0.1	135
hot-water-washed melem	13.9±0.1	170
melem	19.4±0.1	1.4
g-CN	7.0±0.1	400

Conclusions

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In conclusion, monomer melem was prepared and characterized by XRD, FTIR and element analysis, as well as by absorption spectroscopy, fluorescence spectroscopy and fluorescence decay measurement. All observations verify that a mixture of monomer melem and its higher condensates is more easily obtained during the preparation of melem, and that the higher condensates of melem in the mixture will affect the spectroscopic feature of melem. The photocatalytic H_2 evolution of melem data indicates that monomer melem has negligible photoinduced water splitting activity under 300 - 700 nm light irradiation, which is due to the unsuitable oxidation and reduction levels of monomer melem for water splitting reaction. In agreement with the literature, the higher condensates of melem will contribute to the photocatalytic water splitting activity. In addition, the photophysical properties of aqueous melem solution and aqueous melamine solution are also explored, and the experimental data reveals that melamine molecule has no fluorescence emission.

Experimental Section

Chemicals

Melamine (99%) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. HCl (36%-38%) and NaOH (96%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Pure water (18 MΩ•cm) was obtained through a Milli-Q water purification system (Millipore, Billerica, MA, USA).

Sample preparation

Melamine (10 g) was heated in an alumina crucible with a cover at 400 ºC for 4 h within a muffle furnace with a heating rate of 2.3 ºC/min to get as-synthesized melem.[17] To remove a certain amount of non-reacted melamine, the obtained as-synthesized melem (500 mg) was placed in 200 ml pure water, and boiled for 1 h under 100 ºC due to that the solubility of melamine in hot water is higher than that of melem,[28] then centrifuged quickly and dried at 70 ºC and hot-water-washed melem was obtained. The yield for the hot-water-washed melem is about 90%. Following the reported method,[22] the obtained hot-water-washed melem (200 mg) was further boiled in 36% HCl (15 ml) solution for 10 min, successively boiled in 2% NaOH solution (20 ml) for 10 min, and then sufficiently washed with water and dried at 70 ºC, and finally melem power was obtained. The obtained melem was fully ground in an agate mortar for further characterization. The yield for melem is about 85%.

According to the reported method,[32] g-CN was prepared by heating melamine in an alumina crucible with a cover at 550 ºC within a muffle furnace for 4 h with a ramping rate of 2.3 ºC /min and then cooled naturally to room temperature. The as-prepared g-CN was washed in hot water and dried at 70 ºC, and then fully ground in an agate mortar for further characterization.

Aqueous solution was prepared as following: first, 3.0 mg melamine or melem was dissolved into 100 ml water as stock solution, then 1 ml stock solution was diluted 10 times with water, and finally 0.003 mg/ml melamine or melem aqueous solution was obtained.

Characterization

The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-7000 diffractometer with Cu-Kα radiation(λ = 1.54056 Å) under 40 KV and 30 mA using a scan rate of 2degree/min. Fourier transform infrared (FTIR) spectra were collected with a Brucker Tensor 27 in a KBr disk in the scan range of between 400 and 4000 cm^{-1}. UV-Vis diffuse reflectance spectrometry (UVDRS) spectra were recorded on a Shimadzu UV-2600 spectrophotometer equipped with a diffuse reflectance accessory with $BaSO_4$ as the reference. UV-Vis absorption spectra were recorded with a Shimadzu UV-3600 spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Hitachi F-4600 spectrophotometer. The chemical compositions of the sample were determined by using an elemental analyzer (Flash-EA-1112). The Brunauer−Emmett−Teller (BET) surface areas of samples were determined with a Belsorp-Mini II equipment through measuring its N_2 adsorption−desorption isotherm at 77 K.

The fluorescence decays were measured using a homemade time-correlated single photon counting (TCSPC) apparatus.[33] Briefly, the second harmonic (250 nm) of the output (500 nm) from an optical parametric amplifier pumped by a Spectral Physics 1 kHz amplified Ti:sapphire laser was used as the excitation source. The emission was collected and sent into a Princeton Instruments SP2358 monochromator and detected with a Hamamatsu R3809U-50 MCP-PMT. The signal from the R3809U-50 MCP-PMT was amplified by a Becher&Hickl GmbH HFAC-26 preamplifier. Then the output of the HFAC-26 preamplifier and the output of a fast PicoQuant TDA 200 photodiode were, respectively, connected to a Becher&Hickl GmbH SPC-130 module as the start and stop pulses. The instrumental response function (IRF) of the TCSPC setup was about 70 ps.

Photocatalytic H_2 evolution

Photocatalytic H_2 evolution reaction was conducted on a Pyrex top-irradiation reaction vessel connected to a closed gas system.[34] In detail, 100 mg catalyst powder was dispersed in 100 ml of aqueous solution, which contains 10% (volume) triethanolamine. A total of 1% (weight) Pt cocatalyst was deposited on the surface of catalyst powder directly adding H_2PtCl_6 in 100 ml of aqueous solution. The air was completely removed before the reaction solution was irradiated with a 300 W LX300F Xeon lamp without any filter. A gas chromatography was used to determine the amount of H_2.

Acknowledgements

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Keywords: melem, melamine, carbon nitride, heptazine ring, photocatalytic hydrogen evolution

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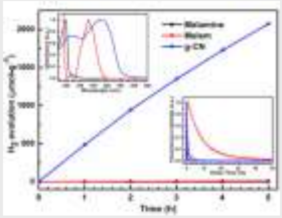
The photophysical properties of monomer melem were reinvestigated. The photocatalytic hydrogen evolution of melem data indicates that monomer melem has negligible photoinduced water splitting activity. The current studies will help to understand the photocatalytic mechanism of heptazine-based materials.



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