High-Yield Synthesis of Carbon Nitride with Improved Photocatalytic Performance

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Carbon nitride (g-C3N4) is synthesized by pyrolysis of urea, thiourea, dicyandiamide and melamine at the temperature ranging from 450 to 600 °C. The photocatalytic performance influenced by different precursors is extensively studied. The yields of carbon nitride pyrolyzed from dicyandiamide and melamine are much higher than that pyrolyzed from urea and thiourea. According to the NO removal efficiency measurement, the optimal fabrication temperature is obtained for four precursors. In addition, carbon nitride prepared from melamine under 500 °C (CNM-500) exhibits the best NO degradation performance compared to samples synthesized from other three precursors with the best fabrication conditions. Scanning electron microscopy, X-ray diffraction, transmission electron microscopy, and degradation ratio of NO results show that the proper mole ratio of g-C3N4 to melem (close to 1:1) is responsible for the highest photocatalytic performance of sample CNM-500. In addition, the specific surface area is another reason for different NO degradation performance. The present work provides new perspectives on selecting suitable precursors and proper synthesis temperature for carbon nitride preparation.

KEYWORDS: Carbon nitride; Melamine; Melem; Photocatalysis; Polymerization

1. Introduction

Carbon nitride has been widely investigated by many researchers in the fields of water treatment,1 lithium ion batteries,2 organic pollutant degradation,3 air purification,4 water splitting5-7 and so on. The tremendous studies on carbon nitride are resulted from the special characteristics of this star material, such as suitable optical band gap 2.6-2.8 eV for visible-light photocatalysis,8-10 its stable photocatalytic performance due to strong covalent bonds between carbon and nitride atoms and facile preparation methods.9,11-12 Compared to traditional photocatalytic material TiO2, carbon nitride can be applied in indoor environment without further treatment with competitive cost.13 Therefore, carbon nitride has been considered as one of the most promising candidate for next generation photocatalyst.14-16 At present, studies on carbon nitride mainly focus on limitations of its high recombination of photogenerated electron-hole pairs,17 relatively small specific surface area and small optical absorption range.18-23

It is documented that carbon nitride sensitized with other materials, such as Bi, CdS, graphene, Fe3O4 and Ag, can effectively improve the photogenerated electron-hole pairs' separation efficiency. For instance, Dong et al. constructed an advanced semimetal-organic Bi spheres-g-C3N4 nanohybrid for enhancing charge separation.24 In his study, carbon nitride was prepared by treating urea at 550 °C. Zhang and his co-investigators synthesized carbon nitride from precursor dicyandiamide and deposited CdS nanoparticles onto carbon nitride for photocatalytic performance improvement.25 Also, Bai XJ et al. constructed Ag@g-C3N4 core–shell nanostructures successfully and the pristine carbon nitride pyrolyzed from dicyandiamide.26 Xiang QJ et al. coupled graphene with g-C3N4 to generate g-C3N4/graphene nanocomposite, and they prepared g-C3N4 from melamine.27 Kumar S et al. prepared g-C3N4–Fe3O4 nanocomposites successfully.28 The charge-separation activities were significantly enhanced, and the experimental g-C3N4 was also derived from melamine. Template method was widely employed to increase the surface area of carbon nitride. Xu et al. investigated the specific surface area effect of carbon nitride on the hydrogen evolution efficiency,21 where carbon nitride was prepared from thiourea based on SiO2 templates. Chen and his co-investigators utilized [Al(NO3)3]-9H2O as a “green template”
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and prepared increased surface area carbon nitride from melamine.\textsuperscript{29} In addition, a number of researchers made tremendous efforts to overcome the small optical absorption range of carbon nitride. Liu Y et al. produced \textsuperscript{g}-C\textsubscript{3}N\textsubscript{4} from melamine under 550 °C and sensitized with CdS quantum dots (CdS QDs).\textsuperscript{30} According to the report, the \textsuperscript{g}-C\textsubscript{3}N\textsubscript{4}-CdS nanocomposites exhibited greatly extended optical absorption range in visible light region. Zhao Y et al. coated graphene onto carbon nitride to increase the absorption range.\textsuperscript{31} The carbon nitride in this study was prepared by melamine mixed with glutaraldehyde.

As mentioned above, the photocatalytic performance studies related to carbon nitride mainly focus on the impacts of external factors, while some original reasons, such as various precursors, synthesis conditions, especially detailed investigations are considered little by researchers which may also have great influence on photocatalytic activity. Zhang WD et al. investigated the effects of precursors on photocatalytic performance of carbon nitride, urea, thiourea, dicyandiamide and melamine were adopted and pyrolyzed and pyrolyzed under the same temperature for 3 h.\textsuperscript{32} In this study, the carbon nitride synthesized from urea exhibited the best NO degradation activity. Martin DJ et al. investigated the hydrogen evolution activities of carbon nitride synthesized from urea, dicyandiamide and thiourea under identical conditions, respectively.\textsuperscript{33} According to the hydrogen evolution measurement, the urea-derived carbon nitride exhibited the highest hydrogen evolution efficiency. However, only the same synthesis condition of the different precursors is considered in these studies.\textsuperscript{12,32–34} In fact, not only the precursors but also the different pyrolysis conditions have great effects on the photocatalytic performance of carbon nitride due to different thermal decomposition temperature of precursors which could lead to various morphology, band gap, surface area and yields.

In present work, we systematically analyze the advantages and disadvantages of carbon nitride prepared from four frequently-used precursors including urea, thiourea, dicyandiamide and melamine, respectively. The yields of carbon nitride from four precursors are demonstrated. NO removal ratio is adopted to measure their photocatalytic performance. Reaction temperatures are adjusted from 450 to 600 °C for each precursor to achieve carbon nitride with best photocatalytic activity, and then comparing their NO removal ratio among the best performance samples from different precursors. Several characteristic tools are adopted to analyze the difference of carbon nitride pyrolyzed from different precursors to discover the important factor for photocatalytic performance. Different reaction temperatures have great effects on the photocatalytic performance, although different precursors possess various best pyrolysis condition. In addition, different cyclic performance of carbon nitride prepared from different precursors are investigated and demonstrated. It will provide a suitable precursor to prepare carbon nitride with appropriate reaction conditions considering the yield, photocatalytic activity and cost.

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2. Experimental

2.1 Materials synthesis

The samples were synthesized according to the steps in the literatures, as shown in Scheme 1.\textsuperscript{1,3} In a typical process, 10 g precursors were put into a semi-closed alumina crucible, treated under temperature from 450 to 600 °C at a heating rate of 15 °C/min and kept for 4 hours in a muffle furnace. After the obtained carbon nitride milled in a mortar, it was collected and washed in a centrifuge for 3-minute-rotation. After that, the ethanol which contained impurities would be poured away. And then, the obtained carbon nitride was centrifugal cleaned twice with water, which was similar to that with ethanol. The carbon nitride which had been centrifugal cleaned with ethanol and water was put into evaporation dishes at 60 °C until moisture removed completely. The obtained yellow powder was collected for further experiment. For investigating the effects of reaction temperatures, other reaction conditions were kept unchanged, while changing the treating temperatures for different precursors. The carbon nitride prepared from urea pyrolyzed at 450, 500, 550, and 600 °C for 240 min are labeled as CNU-450, CNU-500, CNU-550 and CNU-600, respectively. The carbon nitride prepared from thiourea pyrolyzed at 450, 500, 550, and 600 °C for 240 min were labeled as CNT-450, CNT-500, CNT-550 and CNT-600, respectively. The carbon nitride prepared from dicyandiamide pyrolyzed at 450, 500, 550, and 600 °C for 240 min were labeled as CND-450, CND-500, CND-550 and CND-600, respectively. The carbon nitride prepared from melamine pyrolyzed at 450, 500, 550, and 600 °C for 240 min were labeled as CNM-450, CNM-500, CNM-550 and CNM-600, respectively.

2.2 Characterization

The crystal structures of the prepared samples were recorded by an X-ray diffraction with Cu-Kα radiation (XRD, PANalytical X’pert Powder), Thermal gravimetric analysis (TG) and differential scanning calorimetry (DSC) were carried out on Mettler TGA/DSC 1 SF/1382 instrument. Fourier Transform infrared spectroscopy was analyzed by a Nicolet IS10 spectrometer with prepared samples and KBr hybrid tablet. Scan electron microscope (SEM, S-4800) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN) were carried out to analyze the micro structure of samples. The surface areas of the samples were achieved on a Micromeritics ASAP 2020 with all samples degassed at 180 °C for 720 min through obtaining a Nitrogen-absorption-desorption isotherms. The UV-vis diffuse reflection spectra was obtained using a Shimadzu spectrophotometer (UV-vis DRS: UV-2700, Shimadzu, Japan) equipped with an integrating sphere assembly and using BaSO\textsubscript{4} as the blank reflectance. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Scientific Escalab 250Xi.

2.3 Evaluation of visible light photocatalytic performance

For evaluating the photocatalytic performance of the as-prepared
samples, the experiment was processed in a continuous NO flow reactor. The reactor’s volume is 4.5 L (30 cm×15 cm×10 cm). In a typical experiment, a commercial 150 W metal halide lamp was taken as the visible light resource. The prepared samples (0.3 g) were coated onto a diameter 9 cm evaporating dish. NO flow from a compressed gas cylinder with 100 ppm concentration (N₂ balance) was taken as the testing gas resource. For controlling the initial NO concentration in the reactor, we diluted the 100 ppm NO with air stream to about 1000 ppb. The humidity of the gas was controlled at 50% by passing the dry air streams through a humidification chamber. We controlled the gas flow rate at 2.25 L/min by gas flow meter. The metal halide lamp was vertically placed outside the reactor which is 10 cm above the sample dish. Until the system was stable, the concentration of NO can be continuously measured by NO analyzer (Thermo Environment Instruments Inc., 42i-HL), which monitors NO, NO₂, and NOₓ (NOₓ represents NO and NO₂). The removal efficiency was represented by C/C₀ (%), where C₀ was the initial concentration (1000 ppb) of NO and C was the remaining concentration of NO after photocatalytic treatments, respectively.

3. Results and discussion

3.1 Yields of each precursor

As shown in Figure 1, the yields of carbon nitride prepared from the four precursors under 450 to 600 °C are presented. The original weights of urea, thiourea, dicyandiamide and melamine are identically 10 g. The yields of four precursors exhibit decreased trend as elevating pyrolysis temperatures attributed to highly condensed carbon nitride under the higher pyrolyzed temperature. And more hydrogen and ammonia gas will be produced under higher treating temperatures during the process of carbon nitride condensation which can further decrease the yields of carbon nitride. Furthermore, the yields of carbon nitride prepared from urea and thiourea are much lower than that derived from dicyandiamide and melamine at various pyrolysis temperatures, which indicates urea and thiourea are not as suitable as dicyandiamide and melamine to be practically applied for preparing carbon nitride in large scale.

3.2 NO removal efficiency

NO is a kind of harmful gas to human beings which is hard to be purified under the irradiation of visible light without photocatalysis participation. The NO degradation performances of the samples prepared from urea, thiourea, dicyandiamide, and melamine are presented in Figure 2. All samples possess NO purification ability due to its suitable band gap (2.6-2.8 eV) which can be excited under visible light. CNU-550 provides the highest NO removal activity among the samples synthesized from the same precursor under different pyrolyzed temperature as shown in Figure 2 (a). In Figure 2 (b), sample CNT-600 exhibits the highest NO removal ratios, overwhelming other samples. As shown in Figure 2 (c), sample CND-500 possesses the best photocatalytic activities in its group members. In Figure 2 (d), sample CNM-500 demonstrates the most excellent NO removal performance which is 29.26%, overwhelming other samples made from the identical precursor under different treating temperatures. Thus, CNU-550 (27.14%), CNT-600
Examples demonstrated that the NO removal ratio further increased. At last, the NO removal ratio at 27.6° is the highest NO removal ratio observed in all prepared samples.

The highest NO removal ratio in samples prepared from urea and thiourea. The photocatalytic activity of CND is not detected in samples prepared from urea and thiourea. The existence of melam once more is indicated in Figure 3 (f) and (h), the typical diffraction peaks centered at 26.7° disappeared in the XRD spectra of samples CND-550, CND-600, CNM-550 and CNM-600. Moreover, the peaks centered at 12.3° were weakened when increasing pyrolyzed temperatures, as exhibited in Figure 3 (a), (c), (e) and (g). The disappearance of both the peak at 26.7° and the reduced intensity of peak at 12.3° could be attributed to the melam transferred into g-C3N4 completely under elevated treating temperatures. Thus, we can deduce that the precursors (urea, thiourea, dicyandiamide and melamine) can be changed into g-C3N4 when the reaction temperature reached to 550 °C.

DSC and TG are carried out to reveal the thermal dynamic transformation process of four different precursors presented in Figure 4 and Figure S1 (exhibited in Supporting Information).

(21.88%), CND-500 (28.99%) and CNM-500 (29.26%) are the best ones among these samples prepared from each kind of precursor. The good photocatalytic performance of CNU-550, CNT-600, CND-500 and CNM-500 may be attributed to their suitable chemical compositions and crystal structure triggered by the proper pyrolyzed temperatures. Through comparing NO removal ratio of sample CNU-550, CNT-600, CND-500 and CNM-500, CNM-500 shows the highest NO removal ratio (29.26%), overwhelming the other three samples.

3.3 Phase and chemical composition

XRD analysis is applied to explore the differences of chemical compositions and crystal structure in all prepared samples presented in Figure 3. The peak centered at 27.6° exhibiting in each detailed XRD patterns indicates the existence of g-C3N4. The typical peaks centered at 27.6° of the 4 samples (CNU-550, CNT-600, CND-500 and CNM-500) are stronger than that of the other samples in Figure 3 (a), (c), (e) and (g), indicating better crystalline of them which is consistent with the better photocatalytic performance of the 4 samples demonstrated in Figure 2. As shown in Figure 3 (a), (c), (e) and (g), the XRD patterns of these 4 samples possess another typical diffraction peaks located at 12.3° due to the existence of melam. The typical diffraction peaks centered at 12.3° in the spectra of CND-500 and CNM-500 are much higher than that of CNU-550 and CNT-600 implying the existence of more melam in CND-500 and CNM-500 than that in CNU-550 and CNT-600. In addition, a typical diffraction peak centered at 26.7° is detected in CND-450, CND-500, CNM-450 and CNM-500, which indicates the existence of melam once more, while this peak is not detected in samples prepared from urea and thiourea. The photocatalytic activity of CND-450 and CNM-450 are lower than those of CND-500 and CNM-500, because the pyrolyzed temperature 450 °C is too low to prepare sufficient g-C3N4. As presented in Figure 3 (f) and (h), the typical diffraction peaks centered at 26.7° disappeared in the XRD spectra of samples CND-550, CND-600, CNM-550 and CNM-600. Moreover, the peaks centered at 12.3° were weakened when increasing pyrolyzed temperatures, as exhibited in Figure 3 (a), (c), (e) and (g). The disappearance of both the peak at 26.7° and the reduced intensity of peak at 12.3° could be attributed to the melam transferred into g-C3N4 completely under elevated treating temperatures. Thus, we can deduce that the precursors (urea, thiourea, dicyandiamide and melamine) can be changed into melam firstly, Then, melam can be gradually transformed into g-C3N4 as the pyrolyzed temperature further increased. At last, all of the melam is changed into g-C3N4 when the reaction temperature reached to 550 °C.

DSC and TG are carried out to reveal the thermal dynamic transformation process of four different precursors presented in Figure 4 and Figure S1 (exhibited in Supporting Information).
The heating range is from 50 to 800 °C at a heating rate of 15 °C/min. Several phase transformations of these precursors utilized for synthesizing carbon nitride are exhibited in Figure 4.

As shown in Figure 4, the melting point of urea, thiourea, dicyandiamide and melamine is about 135, 175, 210 and 400 °C, respectively. All of these materials were transformed into an undefined phase as the temperature further elevated. Urea, thiourea, dicyandiamide and melamine will be transformed into gas phase when the heating temperature reached 200, 230, 260 and 440 °C, respectively. The strongest endothermal peaks of urea, thiourea, dicyandiamide and melamine appears in the temperature range 200-250, 160-190, 200-240 and 350-420 °C, respectively, which should be ascribed to the decomposition of the precursors. It should be noted that the thermal stability of precursors is different, resulted from the different degrees of condensation between the layers during the polymerization. As demonstrated in Figure S1, most of the weight loss of urea (54%) and thiourea (81%) happened in the range of 150 to 240 °C and 180 to 300 °C, respectively, which are coincide with the strongest DSC exothermal peak appearance respectively. Analogously, a large part of weight loss of dicyandiamide (43%) and melamine (95%) happened in the range of 210 to 390 °C and 340 to 440 °C, respectively, which are consistent with the strongest DSC exothermal peak appearances shown in Figure 4. The main reason of precursors’ weight loss lie in that mass gas (H₂, NH₃ and CO₂) were produced in the condensed process. Moreover, these gas will carry out a part of materials (H, N and C) in all these samples will be disappeared triggered by the transformations to gas phase lastly.

CNU-550, CNT-600, CND-500 and CNM-500 are selected for detailed analysis due to its higher NO degradation activity compared to other samples shown in Figure 2. FT-IR analysis is applied to further investigate the internal chemical structures of CNU-550, CNT-600, CND-500 and CNM-500 presented in Figure 5. The sharp band at around 810 cm⁻¹ appeared in each spectrum is assigned to the characteristic out of plane bending vibration mode of the triazine units. Several strong bands located from 1200 to 1750 cm⁻¹ can be attributed to the typical stretching vibration modes of the heptazine heterocyclic ring (C₇N₇) units. The absorption bands at 1208 cm⁻¹, 1233 cm⁻¹ and 1320 cm⁻¹ account for the existence of C-NH-C unit, which is induced by the bridging secondary amine units. The typical peaks centered at around 3000-3500 cm⁻¹ reveal the incompletely condensed secondary and primary amines of these prepared samples. The peak intensity of CNT-600 at 500-4000 cm⁻¹ is stronger than that of other samples, indicating the highest condensation degree of carbon nitride in CNT-600. However, it should be noted that sample CNT-600 exhibits the lowest NO removal efficiency among them, implying the improved polycondensation of carbon nitride in samples doesn’t account for the highest NO removal efficiency.

### 3.4 Morphology and microstructure

The SEM is applied to investigate the morphology and microstructure of CNU-550, CNT-600, CND-500 and CNM-500, shown in Figure 6. Figure 6 (a, b) and (c, d) show that the morphology and the microstructure of CNU-550 and CNT-600 are disordered with multilayer nanosheets, while the nanorods are not detected in the SEM images of Figure 6 (a, b) or (c, d). And as exhibited in Figure 6 (e, f), two different phase materials including multilayer nanosheets and a great part of long nanorods can be identified in SEM images of CND-500. The size of the nanosheets distributes from 1 to 10 μm, and the length of these nanorods distributes from 20 to 100 μm. As demonstrated in Figure 6 (g) and (h), the SEM images of CNM-500 exhibit the similar morphology to that of CND-500. However, the SEM images of CNM-500 show more multilayer nanosheets and less nanorods than that of CND-500. In addition, the nanorods of CNM-500 are shorter than that of CND-500. The different morphology of the four samples is ascribed to the different condensation process of four precursors.

In order to further investigate the microstructure of CNU-550, CNT-600, CND-500 and CNM-500, the TEM measurements are...
employed to observe the detailed morphology and shown in Figure S2 (exhibited in Supporting Information). As shown in Figure S2 (a) and (b), the TEM images of CNU-550 and CNT-600 exhibit irregular shapes, which are correspondence with their SEM images in Figure 6 (a, b) and (c, d). Both of them are consisted of massive nanosheets with diameters of several micrometers. The nanosheets shown in Figure S2 (a) and Figure S2 (b) are much smaller and thinner than nanosheets shown in Figure S2 (c) and Figure S2 (d), indicating larger surface area of samples prepared from urea and thiourea. And in Figure S2 (c), the nanorod and nanosheet with smooth surface can be identified in the sample CND-500.

The specific surface area of CNU-550, CNT-600, CND-500 and CNM-500 are provided in Figure 7. According to the results, the specific surface area of CNU-550 is 44.0 m²/g, overwhelming the others due to smaller and thinner nanosheets existence in the sample as shown in Figure 6 and Figure S2. And the specific surface area of CND-500 is the minimum one because of more nanorods existed in the sample demonstrated in Figure 6 and Figure S2. Although the specific surface area of CNU-550 and CNT-600 are much larger than that of sample CND-500 and CNM-500, neither the sample CNU-550 nor the sample CNT-600 presents the best NO removal efficiency among the four samples. Thus, we can conclude that the specific surface area is not the critical factor to affect the photocatalytic performance.

3.5 Optical properties and band gap

The UV-vis DRS and plots of (αhυ)¹/² versus photon energy are applied to explore the optical properties and band gap of CNU-550, CNT-600, CND-500 and CNM-500 presented in Figure 8 (a) and (b). As exhibited in Figure 8 (a), the UV-vis DRS diffuse reflectance spectra of these four samples prepared from urea, thiourea, dicyandiamide and melamine reveal their different optical absorption properties. The edge of CNT-600 possesses the strongest light-absorption ability as shown in Figure 8 (a). The reason may lie in that the higher pyrolysis temperature of the precursor (thiourea at 600 °C) will promote the formation of g-C₃N₄ more completely. The NO removal activity is not directly proportionally increased as the light absorption ability enhanced as shown in Figure 2 indicating the optical absorption ability is not the key factor for the different photocatalytic performance. Figure 8 (b) presents the estimated band gap values (Eg) of CNU-550, CNT-600, CND-500 and CNM-500 calculated from UV-vis DRS data. The band gap energy of sample CNU-550, CNT-600, CND-500 and CNM-500 is 2.77, 2.81, 2.72 and 2.71 eV estimated from the intercept of the tangents shown in Figure 8 (b). Diverse band gap energy of these samples reveals that different precursors and different
prepared temperatures may affect the alteration of band gap energies and absorption edge with carbon nitride. Variation of the samples’ band gap is from the different polymerization degree of carbon nitride. The carbon nitride polymerization degree becomes higher and packing of the tri-triazine units becomes denser as the reaction temperature elevated, on account of the enhanced structural connections via gradually raised van der Waals interaction of the tri-s-triazine cores.\textsuperscript{12} In addition, the overlap of molecular orbitals is enhanced by this structural transformation which will lead to the rise of band gap energies of carbon nitride samples.\textsuperscript{12}

As exhibited in Figure 9, XPS is applied to further investigate the surface chemical compositions of four samples. The element of C and N can be observed in CNU-550, CNT-600, CND-500 and CNM-500, which is shown in Figure 9 (a). Obviously, the identification of C and N are derived from the existence of g-C\textsubscript{3}N\textsubscript{4} and melem (C\textsubscript{6}H\textsubscript{4}N\textsubscript{10}) in these samples. As exhibited in Figure 9 (b), two peaks (located around 284.8 eV and 288 eV) can be identified in C 1s spectra. The peak located around 288 eV of CNU-550 exhibits the highest binding energy. Moreover, the peak located around 398.8 eV of CNU-550 exhibits the highest binding energy as well, which can be identified in N 1s spectra in Figure 9 (c). According to the peak fitting result, the peak located around 288 eV in C 1s spectra can be deconvoluted to C4 and C5, which are attributed to N=NC=N and N=NC-NH\textsubscript{2}, respectively.\textsuperscript{42} As reported\textsuperscript{43,44} the condensation ratio of these precursors during the process of carbon nitride synthesis can be suggested by the ratio of C5 to C4. Therefore, the highest ratio of C5 to C4 suggests the lowest ratio of defects and melem intermediates in the sample of CNU-550. Another main peak located around 284.8 eV can be subdivided into C1 and C2, which are induced by the existence of C=CC=C, C-C-N, respectively. And the peak located around 293.9 eV demonstrates the existence of π-π excitation. In Figure 9 (c), two main peaks can be further subdivided into N1 (triggered by C-N=NC), N2 (triggered by C-NH\textsubscript{2}), N3 (triggered by C=N-C-C), N4 (triggered by C≡N), N5, and N6 (triggered by NH\textsubscript{2}), respectively. According to the molecular formulas, the C to N atomic ratio of g-C\textsubscript{3}N\textsubscript{4} and melem (C\textsubscript{6}H\textsubscript{4}N\textsubscript{10}) is 3 : 4 (0.75) and 3 : 5 (0.6). As presented in Figure 9 (d), the atomic ratio of C to N of CNU-550, CNT-600, CND-500 and CNM-500 is 0.745, 0.735, 0.662 and 0.644, respectively. Considering the existences of g-C\textsubscript{3}N\textsubscript{4} and melem (C\textsubscript{6}H\textsubscript{4}N\textsubscript{10}) in these four samples, the atomic ratio of C to N suggests the relative content of g-C\textsubscript{3}N\textsubscript{4} to melem. Thus, relatively lower atomic ratio of C to N of CND-500 and CNM-500 demonstrates more melem in CND-500 and CNM-500 compared the melem amount in CNU-550 and CNT-600.

It has been confirmed that CNU-550, CNT-600, CND-500 and CNM-500 are consisted of g-C\textsubscript{3}N\textsubscript{4} and melem as shown in Figure 9. The hetero-junction is formed between g-C\textsubscript{3}N\textsubscript{4} and melem attributed to the different band potential between melem and g-C\textsubscript{3}N\textsubscript{4} as shown in Figure 10. Firstly, photogenerated electrons and holes are existed under the irradiation of visible light. Then the photogenerated electrons on the conduction band of g-C\textsubscript{3}N\textsubscript{4} will transfer to the conduction band of melem, at the same time, the photogenerated holes on the valence band of melem will transfer to the valence band of g-C\textsubscript{3}N\textsubscript{4}.\textsuperscript{45,46} O\textsubscript{2} are produced through the reaction between photogenerated electrons and O\textsubscript{2}, and •OH are produced through the reaction between photogenerated holes and OH\textsuperscript{-}, both of the O\textsubscript{2} and •OH possess strong oxidation activity in the photocatalytic reactions.\textsuperscript{47} During the reaction process, NO are adsorbed on the active sites of g-C\textsubscript{3}N\textsubscript{4} and reacted with photogenerated active superoxides,\textsuperscript{13,34,47} which will be oxidized into NO\textsubscript{3} (or NO\textsubscript{2}) and HNO\textsubscript{3}. Subsequently, the produced NO\textsubscript{3} (or NO\textsubscript{2}) and HNO\textsubscript{3} can be reacted with photogenerated holes (h\textsuperscript{+}) and NO to generate NO\textsubscript{2}. At last, NO\textsubscript{2} will be transformed into HNO\textsubscript{3} by the effect of photogenerated electrons (e\textsuperscript{-}) and H\textsuperscript{+}. The detailed process of photocatalytic reactions which involved g-C\textsubscript{3}N\textsubscript{4} and
The recycling photocatalytic performance of these samples (CNU-550, CNT-600, CND-500 and CNM-500) is considered to guarantee the practically application in air purification area as presented in Figure 11. All samples exhibit stable photocatalytic performance even being irradiated under visible light for 30 minutes cycled 6 times. However, the performance of CNU-550 and CNT-600 is worse than that of CND-500 and CNM-500. In the recycling test, the NO removal ratio of CND-500 is lower than that of CNM-500. In addition, the cost of CND-500 is much higher than that of CNM-500. As a result, the CND-500 is abandoned to be applied in large scale. And as shown in Figure 11, the photocatalytic performance of CNM-500 is the best one among these four samples lasted from the first cycle to the sixth cycle.

4. Conclusions

The carbon nitride is prepared successfully from the precursors of urea, thiourea, dicyandiamide and melamine at the temperatures from 450 to 600 °C. According to the results of the NO removal efficiency shown in Figure 2, CNU-550, CNT-600, CND-500 and CNM-500 is proved to be more effective in NO degradation among these samples. Specific surface area, amount of melem and band gap energy are the factors to influence the NO removal efficiency of these samples. It should be noted that the amount of melem in the prepared samples is the critical factors according to the research. CNM-500 exhibits the most excellent performance among these samples attributed to the relatively higher amount of melem in it according to the XPS results. Another reason why the photocatalytic performance of CND-500 is not as good as that of CNM-500 may lie in that its relatively smaller specific surface area. Synthetically considering the cost, yields of g-C₃N₄ and the photocatalytic activity, melamine pyrolyzed under 500 °C is proved to be the most suitable approach to produce this kind of photocatalyst in NO degradation field.

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Notes and references

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