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Effect of Calcination Temperature on Synthesis of g-C_3N_4 and its Application in Photocatalytic degradation of Methylene Blue Dye

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Abstract

In this work, graphitic carbon nitride (g-C_3N_4) was synthesized from melamine at different calcination temperatures ranging from 400°C, 450°C, 500°C, 550°C, 600°C, 650°C and 700°C. Structural, morphological, functional and optical properties of synthesized g-C_3N_4 were analyzed by different characterization techniques like XRD, SEM, FT-IR and UV-VIS spectroscopy respectively. XRD results revealed that intensity of peaks increases with increase in the calcination temperature and degree of polymerization increases accordingly. Synthesis of g-C_3N_4 was carried out above 450°C. Diffraction peak observed at 27.6° corresponds to (002) plane at 600°C and corresponding crystalline size is 39.6nm, FWHM is 0.12, d-spacing 3.22 A°, dislocation density is 0.0006nm^{-2} and micro strain is 0.0013. SEM images revealed that g-C_3N_4 has stacked sheet like structure. Vibrational bands shown by FT-IR matches to the standard results. As synthesized g-C_3N_4 was used for photocatalytic degradation of methylene blue (MB) dye.

Keywords: g-C_3N_4, calcination temperature, photocatalytic degradation, methylene blue (MB) dye.

Introduction

In recent years, photocatalysis technology is widely used in different applications such as hydrogen storage by water splitting, water purification, in the elimination of organic pollutants, dye degradation [1-3], self-cleaning coatings and high-efficiency solar cell [4].

Methylene blue is an organic dye used in textile, pharmaceuticals and paper industries is highly toxic and non-biodegradable. To overcome this problem photocatalysis approach have been adopted due to its low cost and reliability [5,6]. Now a days, solar radiation driven semiconducting photocatalyst are widely used for the removal of hazardous dye, water contaminant etc. and it became one of the best promising techniques [7]. Many photocatalyst such as TiO_2 [8], $BiVO_4$ [9], $BiWO_6$ [10], ZnO [11] etc. have been used for degradation of various organic pollutants. Performance of these semiconducting photocatalyst were good to some extent due to low solar energy absorption, high charge recombination rate, slower degradation mechanism restricts to its practical application of photocatalysis [12].

Wide range of semiconductors Bi based, Tio_2 based, ZnO based, C_3N_4 based materials have been used to degrade organic pollutants such as MB [13], RhB [14], AO [15], Phenol [16], ciprofloxacin [17], tetracycline [18] and so on. Among them, graphitic carbon nitride (g-C_3N_4) has received more attention in the area of photocatalysis due to its low cost, medium bandgap(~2.7eV), nontoxic, visible light driven metal free semiconductor having good thermal and chemical stability. Its remarkable applications in the field of waste water treatment, hydrogen evolution, CO_2 reduction [19-21]. g-C_3N_4 can be synthesized from different precursors such as polymerization of urea, cynamide, dicynamide, melamine etc. It has limitation in photocatalysis due to low charge separation, low surface area and poor photon absorption above 450nm. Bulk g-C_3N_4 has thickness around 110nm reported. [22-27].

In current work, g-C_3N_4 was synthesized from melamine at different temperatures ranging from 400℃, 450℃, 500℃, 550℃, 600℃, 650℃, 700℃. From various characterization techniques results were tested. Optimally synthesized g-C_3N_4 powder was used for methylene blue (MB) dye degradation using UV lamp. Degradation efficiency of MB dye at certain time interval was studied.

Methodology

Materials

All chemicals were used without any further purification and of analytical grade (AR). Melamine (99%, Sigma Aldrich), De-ionized water obtained from an ultra-water purification system, Methylene Blue Dye solution.

Preparation of sample

Synthesis of g-C_3N_4 was done by directly heating melamine in muffle furnace. 10 gm of melamine was taken into crucible covered with lid for different temperatures. Samples were calcined from 400℃ to 700℃ at the heating rate of 5℃/min for 3 hours. Prepared yellow bulk g-C_3N_4 was ground by using agate mortar to obtain fine uniform powder.

Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku (Japan) X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm). Scanning electron microscopy (SEM) images were obtained on a JSM-6360 scanning electron microscope (JEOL/EO, Japan). Fourier transform infrared (FT-IR) spectra were obtained using IRA-1S WL(ENG230V) SHIMADZU spectrophotometer. The ultraviolet-visible (UV-vis) absorption spectra were recorded on a UV-1800 UV–Vis spectrometer (Shimadzu, Japan).

Photocatalytic test

Photocatalytic activity was carried out by using Xenon lamp of 300 W Xenon arc lamp with an optical filter ($\lambda > 420$ nm) as the visible light source, 0.5 gm of optimised g- C_3N_4 at 600℃ was dispersed in the 250 ml aqueous solution of Methylene Blue (10 mg/L). The solution was stirred by magnetic stirrer and xenon lamp was fitted above the beaker containing dye solution. Whole assembly was enclosed in wooden box. At certain interval of time, 3.5 mL solution from reaction beaker was collected. Before the light irradiation, the reaction solution was stirred in the dark for 30 min to reach adsorption-desorption equilibrium. The MB concentration was examined by UV-1800 spectrophotometer. Degradation efficiency is given by D (%) as shown below,

$$D\ (\%) = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 is the original absorbance value of MB at time t = 0 min and C_t is the absorbance value for MB at time t.

Result and Discussion

1. XRD Analysis

Structural investigation of synthesized g-C_3N_4 at different temperatures were analysed by XRD study and shown in fig.1. The scanning range of angle 2θ taken from 20˚ to 80˚. Major diffraction peak observed around 27.6˚ which corresponds to (002) plane. This shows that distance between the layers of the graphitic material. Results were matched to standard JCPDS card no.87-1526 [24]. For different temperatures ranging from 400℃ to 650℃, plane (002) shifted to higher angles (27.08˚ to 27.8˚). Corresponding interplanar stacking distance decreases from 0.328nm to 0.319nm. The g-C_3N_4 gives information about layers of triazine units having 3D A-B stacking organization and it has hexagonal unit cell (a = b = 4.7420 Å, c = 6.7205 Å, α = β = 90 °, γ = 120 °) with space group P $\bar{6}$m2 [25]. Crystalline size increases with calcination temperature up to 550℃ and there was sudden decrease in crystalline size at 650℃. Crystalline size for temperatures 400℃ to 550℃ were increased as shown in table (1) and for 600℃ it is 39.6nm. Above 650℃ sample started to decompose and crystalline size were obtained 19nm. FWHM was ranging from (0.432, 0.168, 0.192, 0.336, 0.12, 0.14) for temperatures 400℃ to 650℃.

XRD analysis leads to conclusion that when calcination temperature increases, intensity of peak increases and it becomes narrower at higher temperatures. Also, the degree of polymerization increases with respect to increase in calcination temperature. Higher calcination temperature leads to denser packing of carbon nitride which forms bulk g-C_3N_4. Temperature above 650℃, decomposition of carbon nitride took place. At 700℃, no sample remained in crucible, this confirms that excessive thermal heating leads to decomposition of g-C_3N_4. The optimised range of polycondensation was obtained in between 450℃ to 600℃.

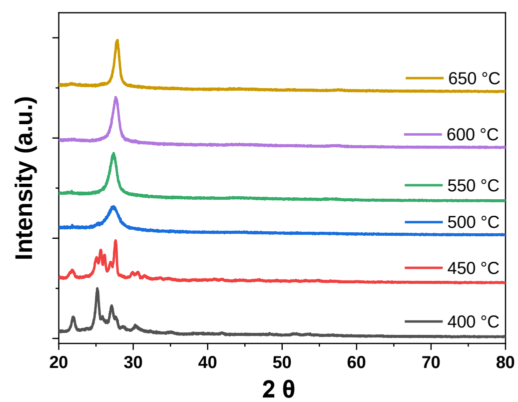


Figure 1. XRD pattern of g- C_3N_4 prepared at different calcination temperatures

Table 1. Calculation from XRD data for various calcination temperature

Sample id	No.	2θ	FWHM	d-spacing [Å]	Crystalline size in nm	Dislocation density nm^{-2}	Micro-Strain
400℃	1	27.0851	0.432	3.28952	15.21	0.004	0.0024
450℃	2	27.7317	0.168	3.21428	22.23	0.002	0.0019
500℃	3	27.1232	0.192	3.28499	24.11	0.001	0.0022
550℃	4	27.4425	0.336	3.24748	47.96	0.0003	0.0014
600℃	5	27.6555	0.12	3.22295	39.6	0.0006	0.0013
650℃	6	27.8798	0.144	3.19753	19	0.0027	0.0032

2. SEM analysis

The morphology of g- C_3N_4 nanoparticles were analysed by using SEM characterization technique. Morphologies at different calcination temperature was shown in fig.2(a-f). The morphologies obtained at 400°C,450°C,500°C shows lumps like structure. Temperature above 550°C images show stacked sheet like morphology.

3. FT-IR Analysis

FT-IR spectroscopy results are shown in the following fig.3 at different calcination temperatures. It gives information about chemical structure of prepared samples at different calcination temperature. For melamine and synthesized g-C_3N_4, principal absorption band was found in between 1200 cm^{-1} to 1650 cm^{-1} which correspond to the stretching modes of C-N heterocycles (absorption band at 1205 cm^{-1},1230 cm^{-1}, 1319 cm^{-1},1405 cm^{-1},1546 cm^{-1} and 1624 cm^{-1}). Another characteristic breathing mode of the triazine units around 804 cm^{-1} was observed. The broad bands observed at 3153 cm^{-1} and most of the bands were fall in the range of 3000 cm^{-1} to 3500 cm^{-1} was indicative of N-H stretching vibration modes [4]. Intensity of peak was increased with increase in calcination temperature shows that there is increase in degree of polymerization. At temperature 400°C the characteristic peaks of g-C_3N_4 was not clearly observed that shows that there might be possibility of the formation of melamine intermediate polymerisation could not be completed [23]. The FTIR analysis gives confirmation that the synthesis of g-C_3N_4 obtained above 450°C which is in agreement of previous results of XRD data analysis.

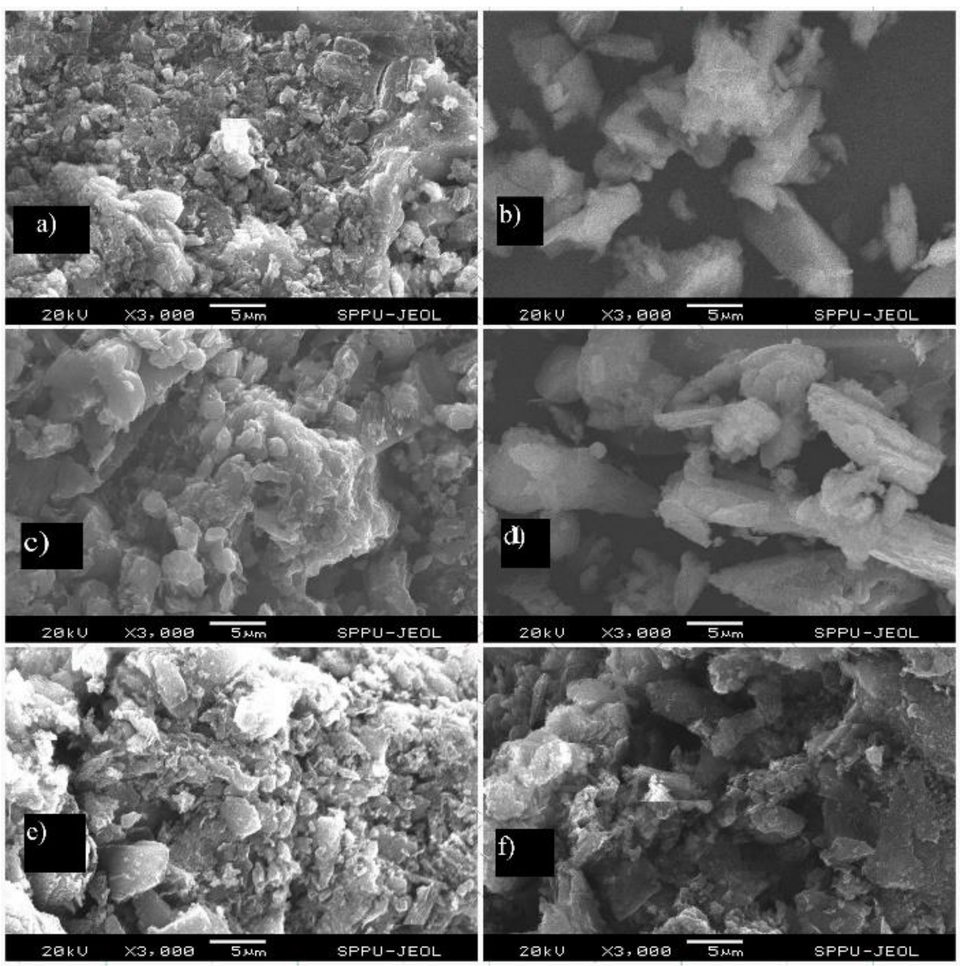


Figure 2. SEM images of g-C_3N_4 prepared at a) 400°C, b) 450°C, c) 500°C, d) 550°C, e) 600°C, f) 650°C

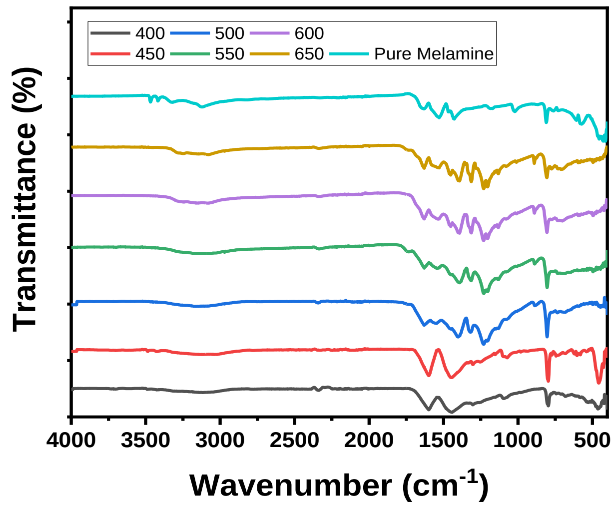


Figure 3. FTIR spectra of pure melamine and synthesized g-C_3N_4 at different calcination temperature

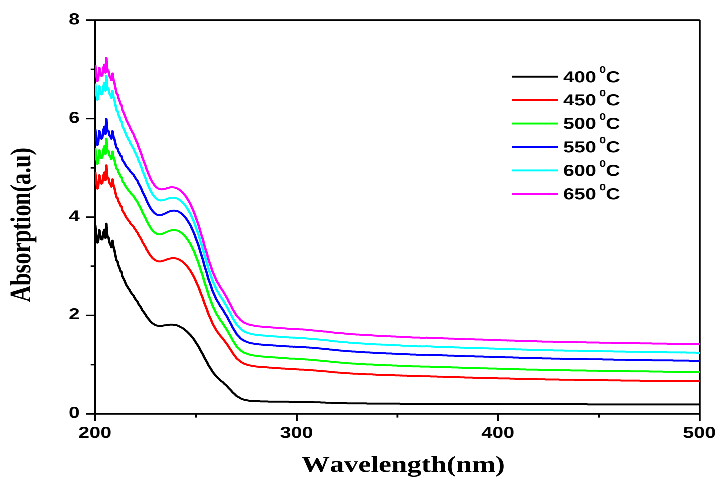


Figure 4. UV-Vis analysis of g-C_3N_4 at different calcination temperature

4. UV-Vis Analysis

Optical properties of g-C_3N_4 were studied by using UV-Vis spectroscopy, the absorption takes place in visible region. Fig.4 shows UV-Vi's spectra of g-C_3N_4 at different calcination temperature. Bandgap of g-C_3N_4 was found around 2.7eV [17].

5. Photocatalytic degradation of Methylene Blue

Photodegradation of Methylene Blue dye was carried out using optimised powder of g-C_3N_4 at 600°C. Graph of absorption (a.u) vs wavelength(nm) at different times for dye degradation was shown in Fig.5. The maximum wavelength was 661.04 A˚ for which absorption increases for time 0 min to 120 min and dye degradation takes place. By using Beer-Amberts law, degradation efficiency was calculated. Concentration C_t/C_0 vs time in min graph plotted and is shown in Fig.6(a)

Degradation efficiency of optimised g-C_3N_4 was achieved up to 51.62%. Graph of $\ln(C_0/C_t)$ vs time in min and degradation (%) vs time in min are shown in fig.6(b). and fig.6(c) respectively. Rate constant of reaction was 0.0064097 min^{-1}. g-C_3N_4 had shown good result for photocatalytic dye degradation of methylene blue.

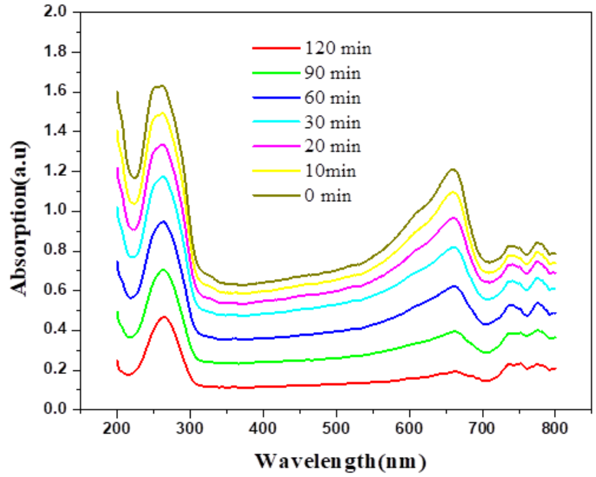
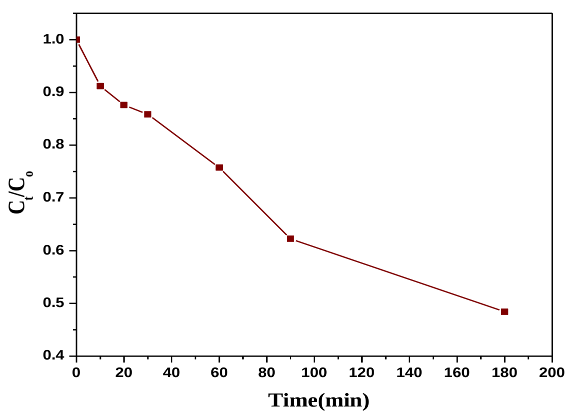


Figure 5.Absorption (a.u) vs wavelength(nm) at different time interval



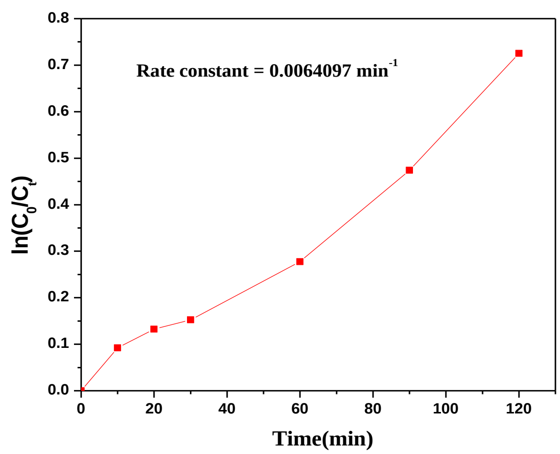


Figure 6(a). graph of C_t/C_0 vs time(min) **Figure 6(b). Graph of $ln(C_t/C_0)$ vs time (min)**

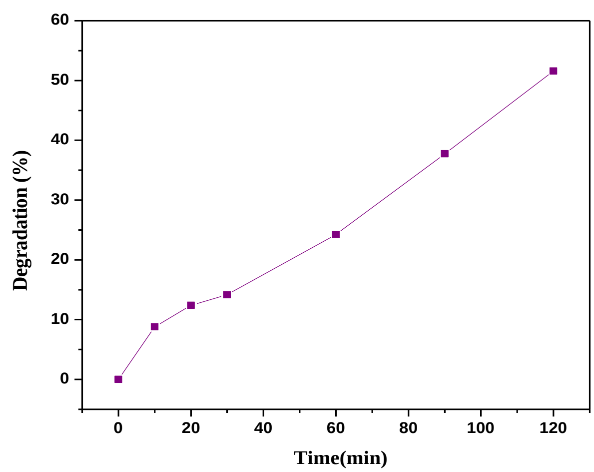


Figure 6(c). Graph of Degradation (%) vs time(min)

Conclusions

In summary, synthesis of g-C_3N_4 from melamine was carried out at different calcination temperatures from 400°C to 650°C. At 700°C sample was decomposed due to high temperature. XRD study revealed that intensity of peak increase with increase in calcination temperature and becomes narrower at highest temperature also polymerization increases with calcination temperature. It was observed that optimised sample was found at 600°C. FTIR study gave information about chemical group present in the sample. There were stretching modes of C-N heterocycles in principal band range 1200 cm^{-1} to 1650 cm^{-1} and the broad bands observed in the range of 3000 cm^{-1} to 3500 cm^{-1} was indicative of N-H stretching vibration modes. The characteristic breathing mode of the triazine units was found around 804 cm^{-1}. Optical study was carried out using UV-Vi's spectroscopy. SEM images shows the stacked sheet like morphology. As temperature increases polymerisation also increases and bulk g-C_3N_4 was prepared. Optimised g-C_3N_4 was used for methylene blue dye degradation. Reaction rate was found to be 0.0064097 min^{-1} and degradation efficiency was 51.62% obtained. So that we can use g-C_3N_4 for different applications of photocatalytic degradation of dyes and organic pollutants.

Conflicts of interest: The authors stated that no conflicts of interest.

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