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STRUCTURAL AND OPTICAL PROPERTY OF GRAPHITIC CARBON NITRIDE THIN FILM USING POLYVINYL ALCOHOL

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Abstract— **Graphitic carbon nitride (g-C_3N_4) nanopowderwas synthesized by thermal decomposition of urea . X-ray diffraction(XRD) spectra confirms the structure of g-C_3N_4.Chemical bonding of the sample has been investigated by Fourier transform infrared spectroscopy (FTIR). The particle size analyser revealed the size is 94nm. g-C_3N_4showed a band gap of 2.72eV which falls in visible light. Synthesized nanomaterial was taken further for thin film fabrication using Poly Vinyl Alcohol(PVA) by dip coating method. The optical property of g-C_3N_4 thin film was analysed. Photoluminescence showed emission spectra at 450nm. The luminescent properties of g-C_3N_4 thin film may have potential application as component of optical nanoscale devices.**

Index terms- **graphitic carbon nitride, Thin film, Photoluminescence.**

I. INTRODUCTION

Visible light-driven semiconductor photocatalytic technology has been the focus of considerable worldwide attention during the past decades because of its great potential in solving current environmental pollution and energy problems [1]. To date, the majority of research is focused on photocatalysts containing metals such as metal oxide, metal sulfide, metal halides, tungstates, niobates, tantalates, and vandates[2]. However, the development of efficient, sustainable, and environmental-friendly photocatalysts remains a significant challenge.

Recently, Wang et al. reported that a new kind of conjugated polymer semiconductor, graphitic carbon nitride (g-C_3N_4), can be used as an attractive metal-free organic photocatalyst that can work in visible light [3].g-C_3N_4possesses a high thermal and chemical stability as well as appealing electronic and optical properties. As a multifunctional catalyst, g-C_3N_4 has been applied in photosynthesis, energy conversion and storage, carbon dioxide storage and reduction, solar cells, and sensing [4]. Nevertheless, the photocatalytic efficiency of bulk g-C_3N_4 is limited because of its low surface area and the fast recombination rate of photogenerated electron–hole pairs. To resolve these problems, numerous strategies have been employed to modify the bulk g-C_3N_4, such as texture tuning by templates, band gap modification by heteroatoms doping, post-functionalization, and semiconductor coupling [5].In our present study we are modifying the property of g-$C_3N_4$by fabricating thin film using Dip coating technique.

g-C_3N_4 can be prepared via facile thermal condensation of nitrogen-rich precursors (such as urea, thiourea, cyanamide, dicyandiamide, and melamine(6)).Urea, a very cheap and abundant industrial agent, was found to be a superior precursor for preparation of g-C_3N_4.The process is free of toxic solvents, templates, and expensive chemicals. .

Here we reportacheap and facile single-source molecular precursor ureawas used to synthesize g-C_3N_4.g-C_3N_4thin film wasfabricated using Polyvinyl alcohol(PVA) by dip coating method and analyzed for its optical properties.

II. MATERIALS AND METHODS

A. Synthesis of g-C_3N_4powder:

The g-C_3N_4 was prepared by calcination with urea as precursor. Typically, 3g of urea was placed in a crucible with a cover, and then heated at 550°C in a muffle furnace for 4h with a heating rate of 10 $°C min^{-1}$. The resultant yellow powder was collected for further use.

B. Synthesis of g-C_3N_4 thin films:

Films of graphitic carbon nitride were synthesized on glass substrate.10% of g-C_3N_4 powderwas dispersed into 3% PVA Solution with the aid of magnetic stirrer. Then the glass slidewere pre-washed with soap solution,Deionized water and methanol and dried at 60°C. The coating was done by Dip coating method. The cleaned glass slide was dipped in g-C_3N_4 solution as mentioned above for 20s and dried under room temperature for 36hrs.

C. Characterization

The powder X-ray diffraction (XRD) patterns were recorded using Bruker AXS D8 advance diffractometer operating with Cu-Ka source to investigate the crystal structure of the samples. FTIR spectra was recorded on JASCO, Model 6300. Optical absorption spectra was recorded using Shimadzu double beam monochromator spectrometer (UV-2540) equipped with an integrated sphere assembly ISR-240A in the range of 190-900 nm. Photoluminescence (PL) spectroscopy was measured at the excitation wavelength of 280nm on JASCO spectrofluorometer8600 at room temperature. The particle size was calculated by particle size analyser.

III. RESULTS AND DISCUSSION

A. Structure

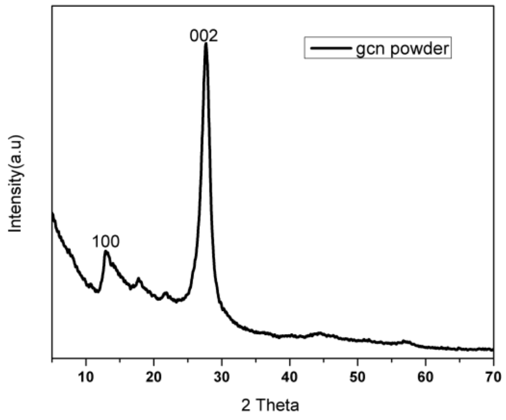


Fig 1 XRD spectra of g-C_3N_4powder

Fig. 1 shows the XRD patterns of the as-prepared samples. The peak observed at around 13.0 is indexed as (100) and represents an in-plane structural packing motif [7]. The strongest XRD peak at around 27.5, which corresponds to an interlayer stacking of aromatic segments is indexed as (002) peak of graphitic materials [7].

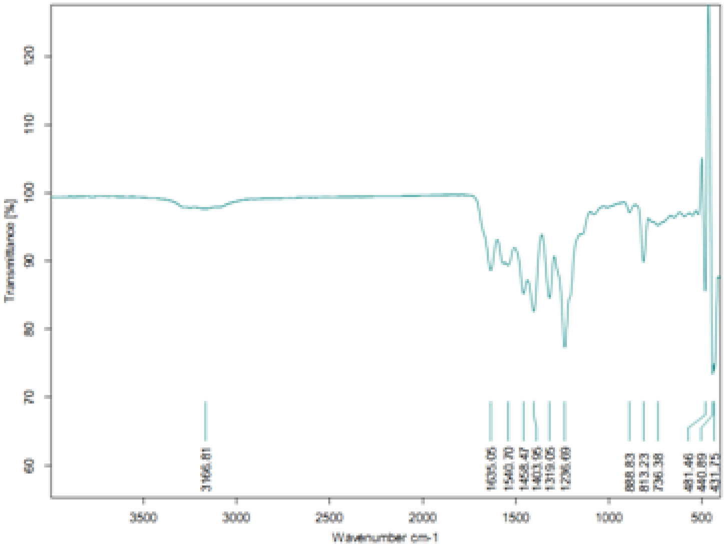


Fig 2 FTIR spectra of g-C_3N_4 powder

Fig 2 shows the FTIR spectrum of g-C_3N_4nanopowder.The spectrum also suggests the existence of graphite-like sp^2 bonded structure . The spectrum of the product shows broad bands of the stretching and deformation modes of -NH_2 groups at 3166cm^{-1}. The peaks at 813 and 1458 cm^{-1} belong to the s-triazine ring modes. The absorption peak at 1635 cm^{-1} is attributed to C=N and the one at 1319cm^{-1}corresponds to C–N[8]. Finally we confirmed the formation g-C_3N_4 through Fourier Transform Infrared Spectroscopy.

B. Particle size analysis

Fig 3 shows the particle size distribution of g-C_3N_4nanopowder. Fig 3 shows the statistics graph for particle size distribution of g-C_3N_4nanopowder. The particle size is 94.68 confirming that synthesized material is in nano form.

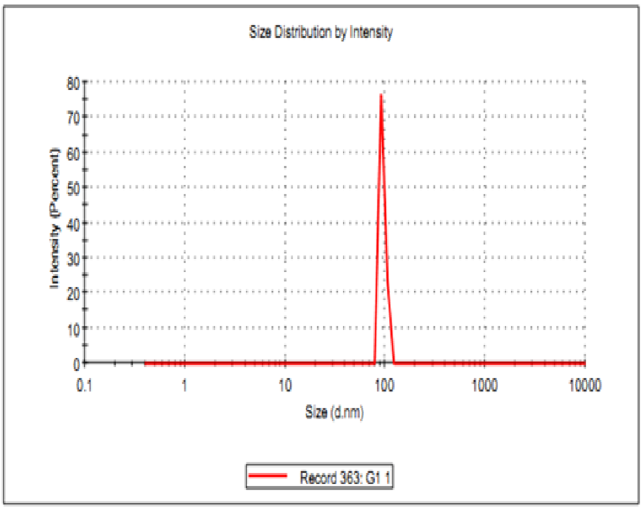
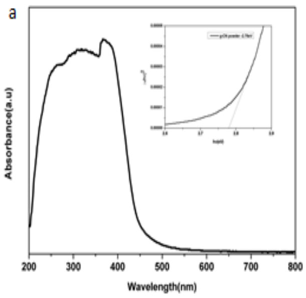


Fig 3 Particle size of g-C_3N_4 powder

C. Optical studies

The absorption spectra of g-C_3N_4powder andg-C_3N_4 thin films was shown in Fig. 4a.and fig 4b.The absorption edge for the graphitic carbon nitride nanopowder is 455 nm which matches well with the literature [9]. The absorption is due to excitation of electron from highest occupied molecular orbital(HOMO) to lowest unoccupied molecular orbital(LUMO). The absorption edge for the graphitic carbon nitride thin film is387nm,when compared to nanoparticle the absorption edge is shifted towards blue region, this is due to the film is two dimension and nanopowder is zero dimension. The band gap for g-C_3N_4nanopowder and g-C_3N_4 thin film is 2.78eV and 3.01eV respectively. The transmission spectra of g-C_3N_4 thin films was shown in Fig. 5. It showed 40% transmittance.



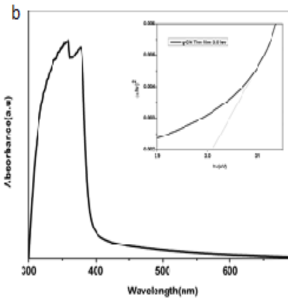


Fig 4a Absorbance spectra of g-C_3N_4nanopowder
Fig 4b Absorbance spectra of g-C_3N_4nanopowder
(inset – band gap energy of g-C_3N_4nanopowder)
(inset – band gap energy of g-C_3N_4thin film)

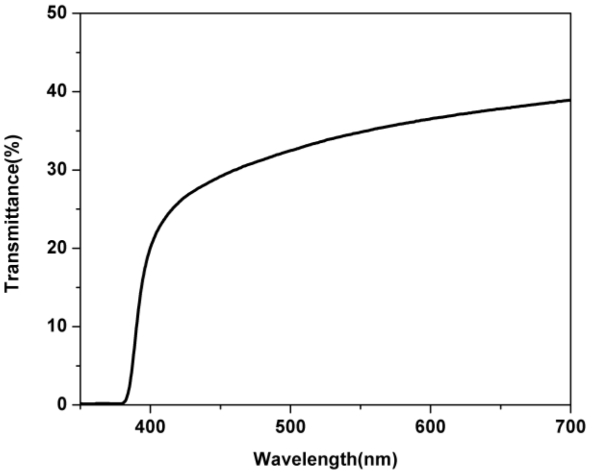


Fig 5Transmittance spectra of g-C_3N_4thin film

It is widely accepted that nitrogen incorporation[9] and $\pi\rightarrow\pi^*$ electronic transitions in the polymericunits[9] play a key role in the PL emission ofcarbon nitride. Owing to the nitrogen-rich characteristicand the existence of s-triazine/tri-s-triazine units inthe products, we studied the PL properties of the graphitic carbon nitride powder and thin film.Fig.6 shows the room temperature PL spectraof the g-C_3N_4nanopowder andg-C_3N_4thin film excited at 280 nm. Boththe samples exhibit blue luminescence properties similarto other carbon nitride morphologies reported[9]. The spectra show broad peaks centered at450 and 470 nm, forg-C_3N_4thin filmandg-C_3N_4nanopowderrespectively. The PL intensity of nanopowder decreased compared with that of thin film. The results indicate that the recombination of electron–hole pairs is moderately inhibited (or the charge separation is significantly accelerated) on thin film when compared to nano powder. This finding implies that the thin film have lower recombination rates of electrons and holes under visible light irradiation, which can be utilised as optical nanoscale devices.

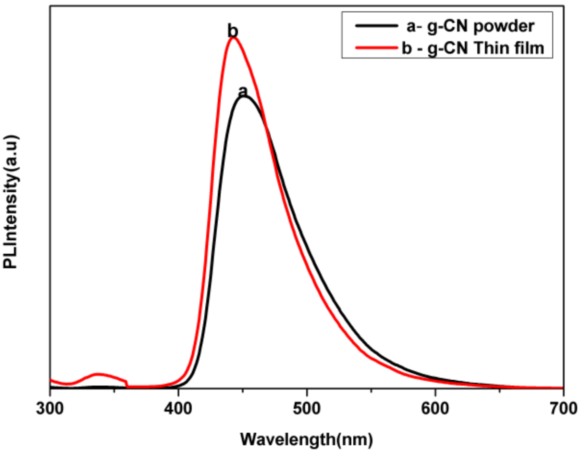


Fig.6Photoluminescence spectra of g-C_3N_4thin film

IV. CONCLUSION

In summary, we demonstrate the synthesis of graphiticcarbon nitride (g-C_3N_4) by simple pyrolysis of urea. The advantages of thismethodinclude the use ofurea as a cheap precursor, easily controlled reaction temperature and simple reactor. The particle size of theg-$C_3N_4$is 94nm showing the synthesized material is in nanorange. g-C_3N_4nanopowder showed a band gap of 2.72eV which falls in visible light. Synthesized nanomaterial was taken further for thin film fabrication using PVA by dip coating method. The optical property of g-C_3N_4thin film was analysed. Photoluminescence of thin film showed emission spectra at 450nm. Band gap of thin filmis 3.01eV. As the band gap of g-C_3N_4thin film falls on visible light, it can be utilized as optical nanoscale devices.

V. ACKNOWLEDGEMENT

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