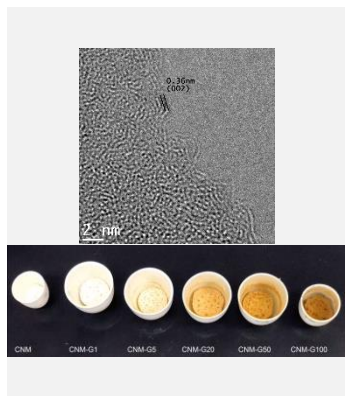


Solar Photocatalytic Activity of g-C₃N₄ for the Decontamination of Pharmaceutical Pollutants

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In this work, the synthesis of g-C₃N₄ by the hydrothermal method is reported, using nitrogen-rich precursors like melamine, urea and thiourea (resulting in CNM, CNU and CNTU samples), analyzing the effect of the usage of glycine as dopant. The g-C₃N₄ samples were characterized by DRX, FTIR, ZPC, DR-UV, PL, SEM, TEM, STEM and XPS for the evaluation of morphology, composition, optical, and structural properties. A series of g-C₃N₄ nanosheets and clusters are prepared by liquid exfoliation using ultrasonic treatment in isopropyl alcohol. The photoactivity of the g-C₃N₄ was examined by the degradation of the ciprofloxacin and paracetamol under solar light irradiation, the samples CNM and CNU presented the higher efficiency in solar photoactivity degradations. This work provides high degradation of pharmaceutical pollutants in water using g-C₃N₄ with solar light.

Introduction

The contamination of water resources by pharmaceutical compounds is a growing environmental concern, (Source of contamination, improper disposal, wastewater treatment limitations, agricultural runoff, industrial discharge). The impact of the pharmaceutical contaminations has a toxic effect on aquatic organisms, even at low concentrations and may potentially lead to a decline in biodiversity, the presence of antibiotics in water can contribute to the development of antibiotic-resistant bacteria, posing a significant threat to human health. While concentrations of pharmaceuticals in drinking water are generally low, concerns remain about potential long-term health effects from chronic exposure. Therefore, the contamination of water by pharmaceuticals is a complex issue that requires a multifaceted approach. Graphitic carbon Nitride (g-C₃N₄) is a promising material for sustainable energy and environmental applications, some photocatalytic applications include but aren't limited to: water splitting, CO₂ reductions, Pollutant Degradations and Organic synthesis; these applications are present in the g-C₃N₄ due to its unique properties, including: 1) two-Dimensional structure (layered structure similar to graphene, consisting of stacked sheets of tris-s-triazine units connected by planar amino groups), 2) Electronic band structure (It has a moderate band gap of around 2.7eV, allowing it to absorb visible light), 3) High thermal and chemical stability (g-C₃N₄ is a thermally stable and resistant to chemical attack), 4) Non-toxicity (it is considered

environmentally friendly and non-toxic), and finally 5) Low cost and easy synthesis (g-C₃N₄ can be synthesized from readily available precursors using relative simple methods). Some disadvantages of g-C₃N₄ include low charge carrier mobility and fast charge recombination, these points limit a photocatalytic efficiency. Today, research focuses on addressing the limitations of g-C₃N₄ and further enhancing its photocatalytic performance through 1) doping with heteroatoms (Introducing elements like nitrogen, sulfur, carbon or phosphorus into the g-C₃N₄ lattice), 2) Creating nanostructures (Fabricating g-C₃N₄ into nanostructures, such as nanosheets, nanotubes, nanorods, clusters), 3) Forming heterojunctions (combining g-C₃N₄ with other semiconductors).

The goal of the present study is to synthesize nitrogen doped g-C₃N₄ in form of nanosheets and clusters nanostructures that can be used in the solar light photocatalytic degradation of ciprofloxacin and paracetamol.

Material and Methods

All chemicals were purchased for direct use without further purification. urea, thiourea, melamine and glycine were purchase from Sigma Aldrich.

To prepare a series of g-C₃N₄ were synthesized using a thermal condensation process, we follow methodology suggested by Li (1), for nitrogen doping in the synthesis method we add some percentage between 0.01 to 0.1% w/w, of glycine for the co-condensation reaction, in general the procedure was as follows: 10g of urea with different amount of glycine (0,1, 5, 20, 50 and 100mg) were

mixed in 10ml deionized water, they were the evaporated at 353 K to remove the water. The resultant mixture was calcined at 550°C for 4Hr using a ramp of 5°C/Min. the samples prepared were collected after the temperature naturally cooled to room temperature and were denoted as CNU-Gx, where x (0,1, 5, 20, 50 and 100mg) is the amount of glycine. In comparison, two other precursors, thiourea and melamine was denoted as CNTU and CNM.

To exfoliate g-C₃N₄ (obtained of nanostructures: nanosheets and clusters), the procedure was it follows: we prepared a dispersion of 10mg by 100ml in water (pH:7) and was ultrasonicated by 24 hours in close system. After we separated the solid of the supernatant by centrifuging (3000 rpm) for 10 min, after that, the solid was washed with deionized water several times, and finally the powder was dried at 60°C by 3 hours.

Results and Discussion

The textural analysis by XDR analysis shown in Fig. 1 (a), the characteristic peaks located around 13.1° (100) and 27°(002) that correspond to the in-plane structural packing of tris-s-triazine units and the typical graphene staking of the conjugated aromatic motif, respectively. As depicted the position of the (002) peaks was constant, illustrating the preservation of the crystalline motif of g-C₃N₄ with the glycine doping, In the Fig 1 (b) PL spectra showed the photo-generated luminescence intensity of the CNTU samples, followed by the PL quenching theory, and the low intensity peak of PL, signifying it has a low recombination probability of photo-excited charges, and high crystallinity nature, it is of great interest to observe that all the g-C₃N₄ samples fabricated with glycine exhibited low values of PL, the nitrogen doped by adding glycine in the synthesis method denoted that the nitrogen atoms were successfully inserted in the g-C₃N₄ network, therefore the high suppressed charge carrier's recombination and facilitate the charger transport

Conclusions

This work provides significant insights into design and synthesis of efficient and stable catalysts for photocatalytic degradation of ciprofloxacin and paracetamol. The nanosheets and clusters morphology of g-C₃N₄ with N dopant increase the visible light absorption and low recombination of photoexcited charges.

Acknowledgments

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References

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across the photocatalysts interface could contribute the enhanced photoactivity performance in the doping samples.

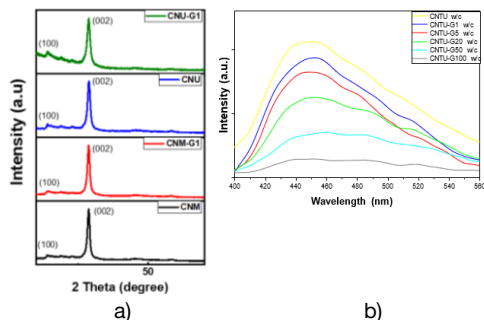


Figure.1 a) X-ray diffraction peaks of CNM, CNM-G1, CNU and, CNU-G1 b) PL spectra of CNTU, CNTU-G1, CNTU-G5, CNTU-G20, CNTU-G50 and CNTU-G100.

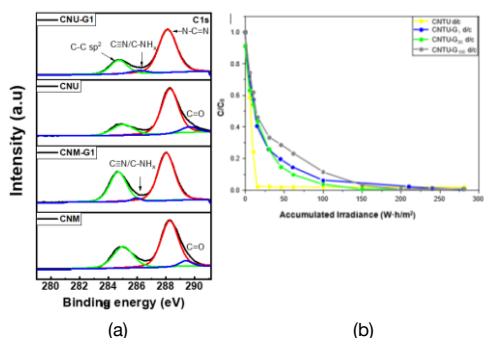


Figure.2 a) XPS spectra of CNU and CNU-G1, CNM and CNM-G1 b) PL spectra of CNTU, CNTU-G1, CNTU-G5, CNTU-G20, CNTU-G50 and CNTU-G100.

The XPS results of the CNU, CNM and CNU-G1, CNM-G1 samples, showed a peak at 286 eV appears when carbon C-NHx group is added and corresponds to the edges of the unitary aromatic rings. These peaks only appear when glycine is added indicating the introduction of -C≡N groups at the g-C₃N₄ network (2).