

Hydrothermal Synthesis of Graphitic Carbon Nitride Nanocluster and Study of its Photoluminescence Properties

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Abstract

In the present scenario of modern urbanization there is an increasing demand of different opto-electronic devices that includes light emitting diodes, photo conductors or many others. From this point of view finding a cheap material with high luminescence efficiency is of extreme important. Along with possessing high radiative recombination efficiency the optoelectronic material should be cost effective as well and at the same time it should be synthesized with high yield. Keeping this in mind, this study presents the synthesis of fractal-like graphitic carbon nitride (GCN) nanostructures via a, low-temperature hydrothermal method. The synthesized material was characterized using various techniques where X-ray diffraction (XRD) confirmed proper phase formation, while field emission scanning electron microscopy (FESEM) revealed its fractal like morphology. UV-Vis reflectance spectra, along with the Kubelka-Munk plot, confirmed that the band gap of the material is around 3 eV and thus comes within the violet-blue range. Fourier-transform infrared (FTIR) spectroscopy provided insights into the different vibrational energy levels present in the sample. Photoluminescence (PL) analysis shows strong PL signal at 431 nm and thus corresponds to band to band transition. The findings indicate this fractal-like GCN has the potential to be used as optoelectronic device.

Keywords- Graphitic carbon nitride, Photoluminescence, Nanostructures, hydrothermal.

1. Introduction

Graphitic carbon nitride (GCN) is carbon-nitrogen based compound and has 2D layered structures analogous to graphene. Here in this material nitrogen is involved in the different position in hexagonal bonded chemical structure of graphene. GCN can be grown with different morphologies that include 0-dimensional quantum dot, 2-dimensional sheets or other all showing enormous potential in different fields of applications like catalysis, sensing, drug delivery, bio-imaging, water splitting, invisible ink, energy storage, solar cells or other (Chand et al., 2024; Liang et al., 2022; Nawaz et al., 2024; Shanbhag et al., 2022; Thomas et al., 2023). Presently, fluorescent GCN nanostructures have gained popularity in sensing applications (Malik et al., 2022; Ye et al., 2022) due to their superior optical behaviour. As mentioned above GCN nanosheets have numerous applications in basic chemical science and technology, including biosensing, bioimaging, ions detection, photocatalysis, optoelectronic devices, carbon dioxide reduction, water splitting, and other (Hasabeldaim et al., 2023; Song et al., 2022; Wang et al., 2021). Researchers have developed pathways to prepare ultrathin GCN nano sheets for bioimaging, as well as for visible-light photocatalytic activity, and developed a fluorescence sensing based approach for the selective determination of Cr(VI) using GCN nanosheets (Xu et al., 2022).

The visible photoluminescence (PL) of graphitic carbon nitride bulk and nano powder has been extensively studied by Zhang et al. (2011) proposing a luminescent mechanism (Zhang et al., 2011). Mubeen et al. (2019) studied the PL features of metal doped GCN (Mubeen et al., 2019).

In 2018, Urakami et al. (2018) were monolithically grown high quality GCN films on the various substrates. PL study revealed enhanced electron injection from the sp^3 hybridized C-N σ conduction band to the sp^2 hybridized C-N π conduction band, with non-radiative recombination becoming dominant at high excitation power density due to phonon interactions and defect capture. In the same year Chaudhary et al. (2018) employed the positron annihilation spectroscopy, steady-state and time-resolved PL spectroscopy to study nitrogen related defects in GCN nanosheets at varying calcination temperatures. This study correlated defect presence with excitonic lifetime, offering insights into tuning the optical properties of GCN. Bayan et al. (2017) demonstrated reduction-dependent modifications in the light emission properties of GCN nanosheets. However, so far, the authors are concern most of the studies have been done on either 2 D sheet like GCN or GCN quantum dots. Thus, study on the PL properties of fractal like GCN cluster would be an effective addition to the existing related literature. Keeping this in mind, in the present work, we have synthesized GCN fractal-like cluster by low temperature hydrothermal approach using urea as precursor. The as-synthesized GCN characterized by different characterization technique has shown excellent luminescence properties in blue-violet emission region.

2. Synthesis and Characterization

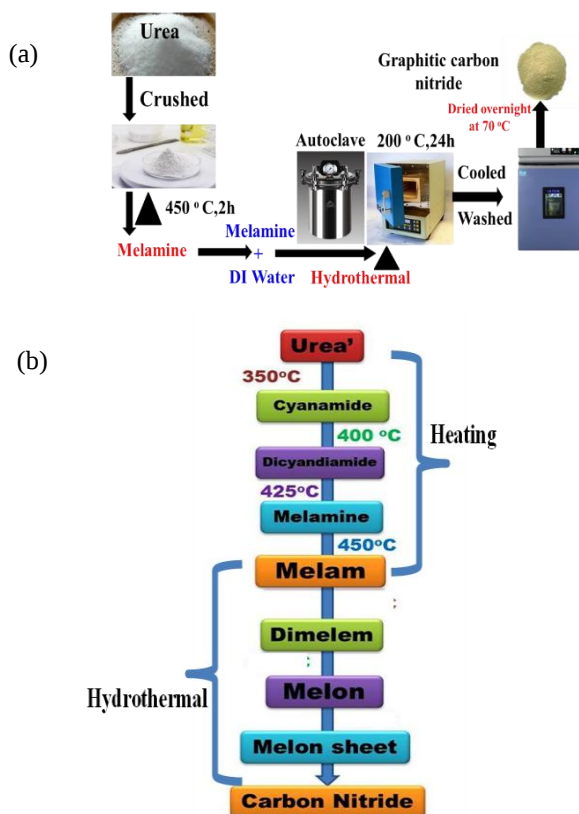


Figure 1. Schematic of various steps for the hydrothermal synthesis of GCN.

Graphitic carbon nitride was synthesized from urea by low temperature hydrothermal synthesis process. Here, in the initial step, appropriate amount of urea was taken and heated up to 450 °C resulting formation of intermediate product melamine. The as synthesized melamine was then stirred in DI water and the aqueous system was then transformed to a Teflon line autoclave where hydrothermal reaction was taken place for 24 hours at 200 °C. After the reaction was over sample was cooled naturally, washed, filtered and the residue was dried overnight at 70 °C to get the final sample. The whole process has been schematically shown in **Figure 1 (a)** and the different intermediate product formed during reaction before formation of final GCN is represented in **Figure 1 (b)**.

The as prepared sample was characterized by x-ray diffraction (XRD BRUKER D8 Advance), field emission scanning electron microscope (FESEM, JEOL 6340F FEG-SEM), Energy Dispersive X-Ray Spectroscopy, Fourier transformed infrared spectrometer (Shimadzu IR Affinity-1S FTIR), UV-Vis spectrophotometer (Shimadzu UV-3600) and Photoluminescence spectrophotometer (PL, Shimadzu RF-5301 Spectro-fluorophotometer).

3. Results and Discussion

3.1 XRD Analysis

Figure 2 shows the XRD pattern of GCN. XRD pattern shows a prominent peak with high intensity centering $2\theta = 27.01^\circ$ that corresponds to the (002) plane of GCN (Chauhan et al., 2024) and the corresponding value of lattice spacing 0.32 nm.

The high intensity peak confirms the good crystalline behavior of the material which shows, the advantage of this process over the commonly used decomposition process of urea where the decomposition temperature is as high as high as 550°C.

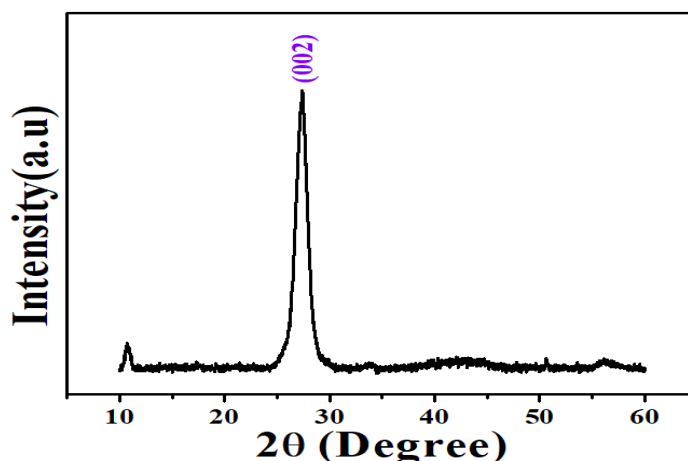


Figure 2. XRD pattern of GCN sample.

3.2 FESEM and EDX Analysis

FESEM micrographs shown in **Figure 3 (a, b)** present the morphology of GCN which confirms the fractal cluster-like structure of the sample developed throughout the entire field of vision. This confirms the uniformity of the sample and thus high yield of the synthesis process. The dimension of each cluster is around 1 μm however careful observation shows that the cluster is composed of tiny particles the morphology of which is beyond the resolution of the FESEM.

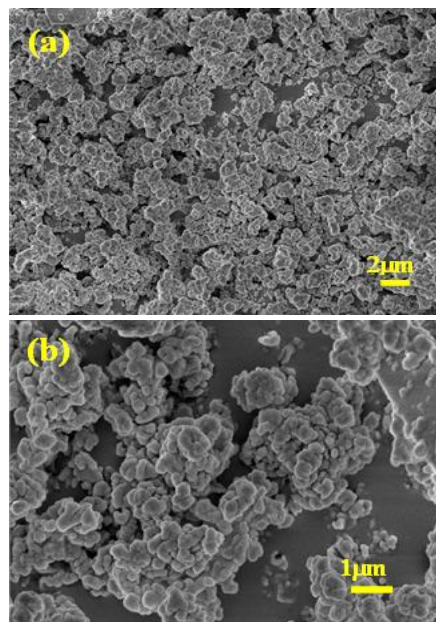


Figure 3. (a, b) FESEM micrographs of GCN with different magnifications.

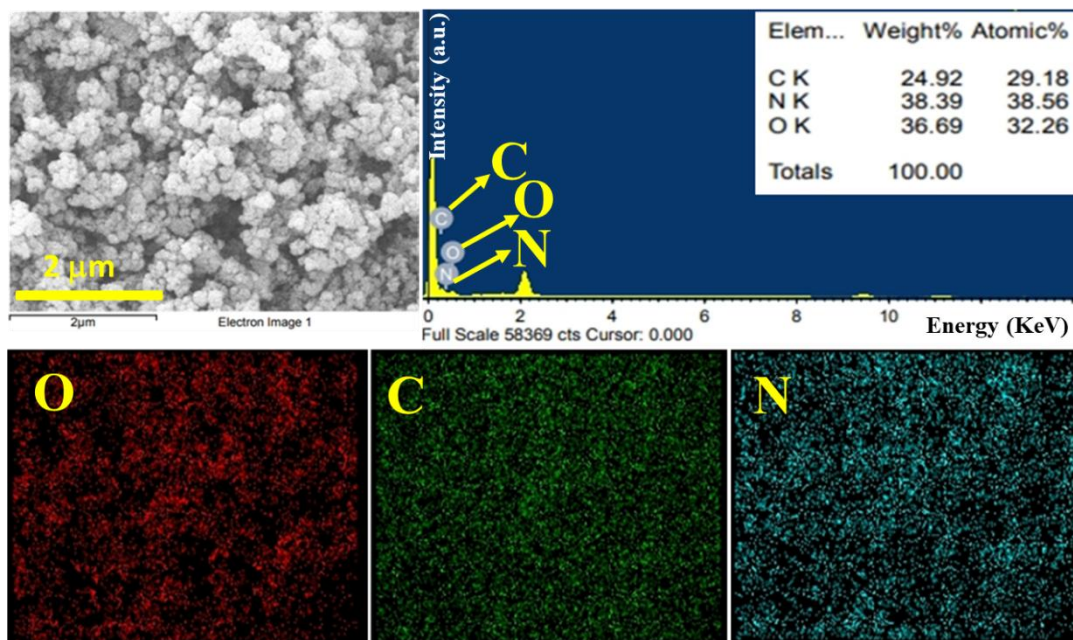


Figure 4. EDX pattern and elemental mapping (O, C and N) of the GCN sample of g-C₃N₄ sample.

EDX was utilized to determine the elemental stoichiometric ratio of the material and the corresponding EDX spectra along with the elemental mapping has been shown in **Figure 4**. It is seen that the material

contains only elements like carbon, oxygen, nitrogen which proves the purity of the sample. Oxygen comes from the environment as mentioned in the coming subsection during FTIR analysis.

3.3 FTIR and Reflectance Spectroscopic Analysis

The FTIR spectra of GCN in transmittance mode **Figure 5 (a)** taken within $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , GCN show two transmittance dips at 807 and 2176 cm^{-1} and two broad bands in the region between $1261\text{--}1633\text{ cm}^{-1}$ and $2089\text{--}3378\text{ cm}^{-1}$ (Chauhan et al., 2024). The dip at 807 cm^{-1} represents the breathing modes of C–N heterocycles ring from the s-triazine building block of GCN. The dip at 2176 cm^{-1} is due to atmospheric CO_2 and the band within $2089\text{--}3378\text{ cm}^{-1}$ (Chauhan et al., 2024) is due to the superposition of C–H_n, OH, and NH_3 groups. The broad band within $1261\text{--}1633\text{ cm}^{-1}$ is the characteristic band of GCN and comes from the C–N stretching vibrational energy level. FTIR pattern of the sample again confirms the purity of the sample with typical feature of the GCN.

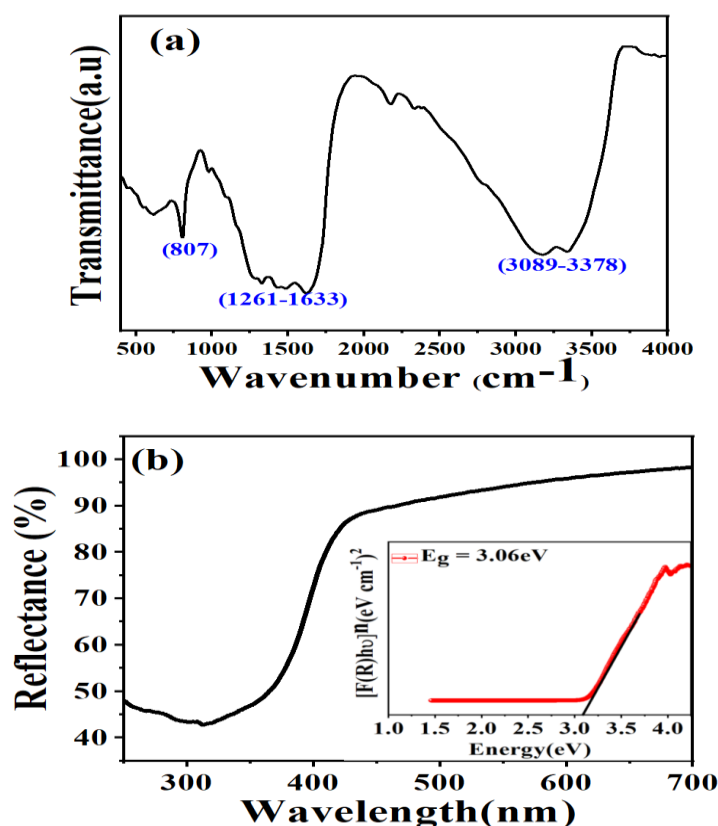


Figure 5. FTIR (a) and UV-Vis reflectance (d) Pattern of GCN; (inset (b) corresponding Kubelka-Munk plot to obtain optical band gap).

The UV-Vis pattern of a GCN sample taken in reflectance mode within the $250\text{--}700\text{ nm}$ wavelength range is shown **Figure 5 (b)**. The Figure shows a high reflectance of the sample up to 400 nm , then a sharp fall to 35% at 300 nm . This highly reflecting feature is expected from a white-coloured sample. The UV-Vis reflectance spectrum is useful for determining band gap using the Kubelka-Munk plot which is shown inset **Figure 5 (b)**. The value of the band gap of the sample comes out to be 3.06 eV , located in the violet-blue region of the visible electromagnetic spectrum.

3.4 PL Study

The PL properties of GCN sample were recorded (**Figure 6 (a)**) under excitation wavelength of 375 nm. The spectra taken between 385 and 650 nm, reveals an intense PL peak around 431 nm. This peak likely originated from the lowest unoccupied molecular orbital and Highest occupied molecular orbital transition. The Lowest unoccupied molecular orbital (LUMO) is formed from sp^2 hybridized aromatic anti-bonding orbitals, while the highest occupied molecular orbital (HOMO) is formed from the lone pair of nitrogen $2p_z$ orbitals triazine units.

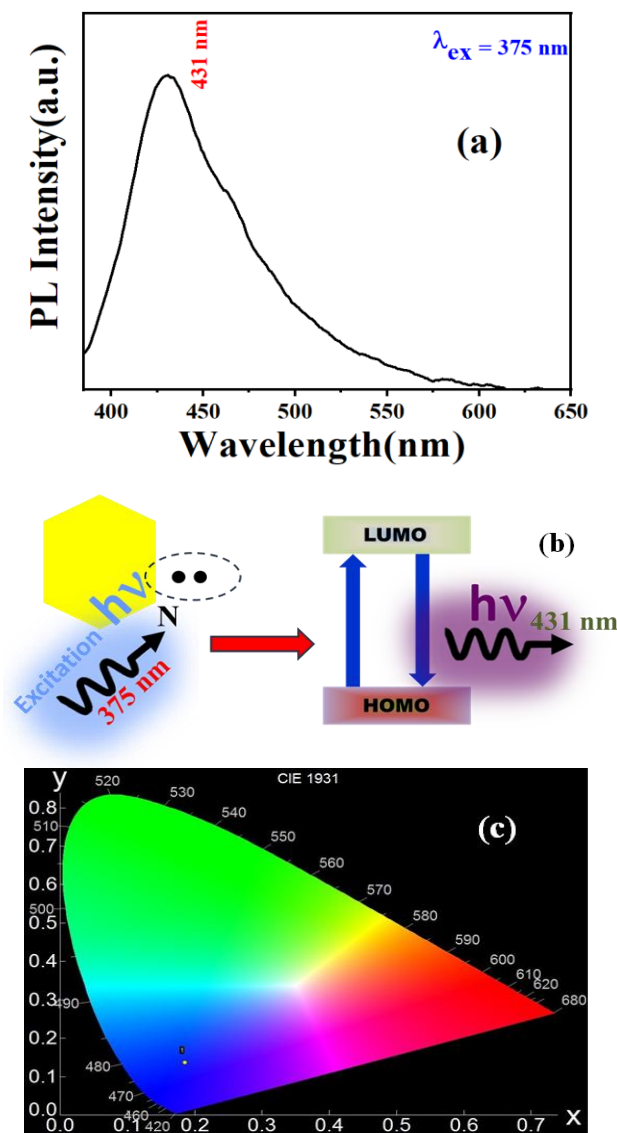


Figure 6. (a) PL characteristics and corresponding (b) band diagram, (c) Chromaticity diagrams of GCN.

Thus, the PL signal that is associated with the band to band transition is actually associated with the HOMO-LUMO transition. The process is schematically shown in **Figure 6 (b)**. The schematic is further justified with the fact that the emission wavelength at 435 nm is associated with an energy around 2.89

eV which is very closed to the band gap obtained from Kubelka-Munk plot. So, this emission signal comes from HOMO-LUMO transition only. The absence of any other emission signal in the lower energy value suggests that the sample is almost free from defects i.e. good crystalline supporting the XRD result.

The high intensity of the PL peak at 431 nm is indicating efficient recombination of photo generated electron-hole pairs, as indicated by the strong emission spectrum. **Figure 6 (c)** shows the associated CIE colour coordinate which also confirms that the emission colour comes in blue-violet region.

4. Conclusions

In summary, we have fabricated GCN by simple two-step hydrothermal method using urea as precursor. The synthesized material was studied by different characterization technique where XRD confirmed good crystallinity of the sample, whereas FESEM shows the small clustered fractal like structure with dimension around 200 nm was formed. FTIR confirmed presence different chemical bond in the sample which may be taken as indirect proof of phase formation. Kubelka-Munk plot drawn from the reflectance spectra show the sample has band gap in the visible blue-violet region and accordingly the sample shows intense PL signal at the same chromatic region.

Conflict of Interest

The author declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Bayan, S., Midya, A., Gogurla, N., Singha, A., & Ray, S.K. (2017). Origin of modified luminescence response in reduced graphitic carbon nitride nanosheets. *The Journal of Physical Chemistry C*, 121(35), 19383-19391.
- Chand, H., Kumar, A., Goswami, S., & Krishnan, V. (2024). Comparison of catalytic activity of graphitic carbon nitrides derived from different precursors for carbon dioxide conversion. *Fuel*, 357, 129757.
- Chauhan, K., Banerjee, D., & Shrivastava, V.P. (2024). Fractal-like graphitic carbon nitride for near-instantaneous removal of rose bengal dye by adsorption. *Journal of The Institution of Engineers (India): Series D*, 1-8. <https://doi.org/10.1007/s40033-024-00806-5>.
- Chauhan, K., Dhariwal, A., Parashar, M., Kumar, P., Prabakar, A.E., Adalder, A., & Banerjee, D. (2024). Photocatalytic removal of rhodamine B by nickel doped graphitic carbon nitride: anomalous dependence of removal efficiency on carrier recombination. *Journal of the Iranian Chemical Society*, 21, 1643-1660. <https://doi.org/10.1007/s13738-024-03024-8>.
- Choudhury, B., Paul, K.K., Sanyal, D., Hazarika, A., & Giri, P.K. (2018). Evolution of nitrogen-related defects in graphitic carbon nitride nanosheets probed by positron annihilation and photoluminescence spectroscopy. *The Journal of Physical Chemistry C*, 122(16), 9209-9219.
- Hasabeldaim, E.H.H., Swart, H.C., Coetsee, E., Kumar, P., & Kroon, R.E. (2023). Degradation and chemical stability of graphitic carbon nitride during ultraviolet light irradiation. *Materials Chemistry and Physics*, 308, 128252.

- Liang, S., Wang, Z., Zhou, Z., Liang, G., & Zhang, Y. (2022). Polymeric carbon nitride-based materials: Rising stars in bioimaging. *Biosensors and Bioelectronics*, 211, 114370.
- Malik, R., Joshi, N., & Tomer, V.K. (2022). Functional graphitic carbon (IV) nitride: a versatile sensing material. *Coordination Chemistry Reviews*, 466, 214611.
- Mubeen, M., Deshmukh, K., Peshwe, D.R., Dhoble, S.J., & Deshmukh, A.D. (2019). Alteration of the electronic structure and the optical properties of graphitic carbon nitride by metal ion doping. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 207, 301-306.
- Nawaz, A., Taj, M.B., & Carabineiro, S.A.C. (2024). Graphitic carbon nitride as an efficient carrier for anti-cancer drug systems: a review. *Next Nanotechnology*, 6, 100074. <https://doi.org/10.1016/j.nxnano.2024.100074>.
- Shanbhag, Y.M., Shanbhag, M.M., Malode, S.J., Dhanalakshmi, S., Mondal, K., & Shetti, N.P. (2022). Direct and sensitive electrochemical evaluation of pramipexole using graphitic carbon nitride (gCN) sensor. *Biosensors*, 12(8), 552. <https://doi.org/10.3390/bios12080552>.
- Song, X., Wang, M., Liu, W., Li, X., Zhu, Z., Huo, P., & Yan, Y. (2022). Thickness regulation of graphitic carbon nitride and its influence on the photocatalytic performance towards CO₂ reduction. *Applied Surface Science*, 577, 151810.
- Thomas, S.A., Pallavolu, M.R., Khan, M.E., & Cherusseri, J. (2023). Graphitic carbon nitride (g-C₃N₄): Futuristic material for rechargeable batteries. *Journal of Energy Storage*, 68, 107673.
- Urakami, N., Kosaka, M., & Hashimoto, Y. (2018). Thermal chemical vapor deposition and luminescence property of graphitic carbon nitride film for carbon-based semiconductor systems. *Japanese Journal of Applied Physics*, 58(1), 010907.
- Wang, Y., Liu, L., Ma, T., Zhang, Y., & Huang, H. (2021). 2D graphitic carbon nitride for energy conversion and storage. *Advanced Functional Materials*, 31(34), 2102540.
- Xu, J., Gao, Q., & Wang, Z. (2022). Porous g-C₃N₄ nanosheets for on-off-on fluorescence detection and elimination of chromium (VI) and sulfite. *ACS Applied Nano Materials*, 6(1), 750-758.
- Ye, M., Yang, C., Sun, Y., Wang, J., Wang, D., Zhao, Y., Zhu, Z., Liu, P., Zhu, J., Li, C., Peng, W., Zhang, N., & Dong, Y. (2022). ZnFe₂O₄/graphitic carbon nitride nano/microcomposites for the enhanced electrochemical sensing of H₂O₂. *ACS Applied Nano Materials*, 5(8), 10922-10932.
- Zhang, J., Li, Y., Zhu, P., Huang, D., Wu, S., Cui, Q., & Zou, G. (2011). Graphitic carbon nitride materials synthesized via reactive pyrolysis routes and their properties. *Diamond and Related Materials*, 20(3), 385-388.



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