ZnO-Modified g-C₃N₄: A Potential Photocatalyst for Environmental Application

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ABSTRACT: Solar energy-driven practices using semiconducting materials is an ideal approach toward wastewater remediation. In order to attain a superior photocatalyst, a composite of g-C₃N₄ and ZnO (GCN−ZnO) has been prepared by one-step thermal polymerization of urea and zinc carbonate basic dihydrate \([\text{Zn(NO}_3\text{)}_2 \cdot \text{Zn(OH)}_2\text{]}_2\). The GCN−ZnO0.4 sample showed an evolved morphology, increased surface area (116 m² g⁻¹), better visible light absorption ability, and reduced band gap in comparison to GCN−pure. The GCN−ZnO0.4 sample also showed enhanced adsorption and photocatalytic activity performance, resulting in an increased reaction rate value up to 3 times that of GCN−pure, which was attributed to the phenomenon of better separation of photogenerated charge carriers resulting because of heterojunction development among interfaces of GCN−pure and ZnO. In addition, the GCN−ZnO0.4 sample showed a decent stability for four cyclic runs and established its potential use for abatement of organic wastewater pollutants in comparison to GCN−pure.

1. INTRODUCTION

Visible light-driven photocatalysis to degrade organic water pollutants is a cheap, clean, and convenient alternative to other water pollution abatement strategies using chemical, biological, and physical methods.¹ A semiconductor material can act as a photocatalyst on absorbing a photon of energy equivalent to the energy of its band gap, producing electron−hole pairs, which are then separated and transferred to the target pollutant for the redox reaction.²−⁴ g-C₃N₄ (GCN) has evidenced as a potential metal-free photocatalytic material having a visible light-responding band gap (2.7 eV) responsive for numerous applications such as chemical sensors, photovoltaic solar cells, water splitting, and pollutant degradation.⁵−¹¹ In addition, it has high chemical and thermal stabilities.¹²,¹³ However, the hindered marginal absorption of light and the low surface area are two major factors, which can lower the efficiency of GCN in visible light.¹⁴,¹⁵ Various studies reported that the morphology of GCN nanostructures plays a vital role in determining the photocatalysis performance. Also, it has been emphasized that the type of precursor used for synthesizing GCN and the molar ratio of the dopant can affect the crystal structure and photocatalytic performance of modified GCN because of distinguished reaction pathways and degrees of condensation between the two. Our previous study reported enhanced photocatalytic degradation efficiency toward the methylene blue (MB) dye on using urea-derived GCN over other precursors.¹⁶ Dong et al. reported that urea-derived GCN showed better interaction with sodium nitrate, over melamine and dicyanamide, as a precursor, leading to the emergence of nanocomposites with a better morphology, surface area, and porosity and better photocatalytic activity of the nanocomposites toward degradation of tylosin.¹⁷ Mishra et al. reported effective interaction among thin GCN nanosheets from the urea precursor over thiourea with TiO₂/bentonite toward photocatalytic degradation of the reactive brilliant red-X3BS dye.¹⁸ Formation of composites among GCN and other metal-oxide semiconductors is one of the most effective and convenient method among other modification techniques as it can overcome the problem of rapid recombination of photogenerated charge carriers and also enhance the response of the photocatalyst toward light.¹⁹−²⁵ Recently, ZnO-modified GCN has been reported to exhibit prominent catalytic properties. Yue et al. has reported dicyandiamide and zinc chloride...
derived ZnO−GCN with improved photoactivity. Liu et al. has reported a GCN/Vo−ZnO hybrid photocatalyst using Zn(OH)F and melamine, which resulted in enhanced photocatalytic activity for organic pollutants. Mohammad et al. has reported a ZnO−CN nanohybrid utilizing urea and [(Zn(hmp-H))2(H2O)(μ-Cl)Zn(μ-Cl)(Cl)]3− with enhanced photocatalytic degradation property toward organic pollutants. Zhu et al. has reported a ZnO−GCN composite has resulted due to the low amount of ZnO in GCN−ZnO composites. In the case of GCN−ZnO0.6, the characteristic peak at 27.3° reduced a lot that it did not appear well. This suggests that when the amount of ZnO precursor added initially was raised to 0.6 mmol, the innate structure of GCN−pure could not be retained well.

2.2. Fourier Transform Infrared Analysis. Fourier transform infrared (FTIR) analysis (Figure 2) revealed C

![Figure 2. FTIR spectra of (a) ZnO, (b) GCN pure, (c) GCN−ZnO0.2, (d) GCN−ZnO0.4, and (e) GCN−ZnO0.6.](http://pubs.acs.org/journal/acso002688)
The above result further indicated that simultaneous crystallization of ZnO could interfere with urea thermal polymerization leading to a partially deteriorated graphitic structure of GCN–pure, which is also consistent with the XRD analysis result. Poor crystallinity observed for GCN–ZnOx composites could result in more defects related to the GCN phase, and such a condition might play a vital role in promoting its activity as a photocatalyst.

2.3. Microscopic Analysis. Morphological and microstructural aspects of samples were analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A distinct morphology was observed in the case of GCN–pure and GCN–ZnO0.4. The SEM image (Figure 3a) of GCN–pure layered structure was found to be identical to the stacked layer morphology of urea-derived GCN reported previously. In Figure 3b, it was observed that after addition of ZnO in GCN–pure, GCN–ZnO0.4 evolved into a slacked interlinked network consisting of elongated fibers with a mean diameter of 20–60 nm. SEM analysis indicated that the interaction of [ZnCO3]2·[Zn(OH)2]3 with urea led to the formation of a loose structure of GCN–ZnO0.4 with an increased surface area and porosity, which probably happened due to the influence of released gases during the thermal polymerization reaction. In addition, Figure 3d presents the high-resolution TEM (HR-TEM) image of GCN-Zn0.4, confirming the simultaneous existence of ZnO and GCN phases, and lattice fringes having a d-spacing of 0.26 nm could be attributed to the (002) plane of hexagonal wurtzite ZnO, whereas Figure 3c shows a single GCN phase in GCN–pure. Energy-dispersive system (EDS) patterns of GCN–pure and GCN–ZnO0.4 are shown in Figure 4c,f respectively. EDS patterns for GCN–pure revealed that it consisted of elements C and N, whereas GCN-ZnO0.4 contained C, N, Zn, and O elements. Further from Table 1 it can be noticed that C/N at. % ratio was 0.85 in the case of GCN–pure, whereas for GCN–ZnO0.4, the ratio was found to be increased to 1.5. This observed change could be a possible representation of the removal of some nitrogen from the GCN–pure framework on addition of [ZnCO3]2·[Zn(OH)2]3 by deamination during the thermal polymerization reaction. Elemental mappings of N, C, Zn, and O shown in Figure 4e were found to be well defined and showed a sharp contrast. Homogenous and effective distribution of ZnO elements could be observed throughout. The results further assured the successful formation of the GCN–ZnO composite.

2.4. X-ray Photoelectron Spectroscopy Analysis. X-ray photoelectron spectroscopy (XPS) analysis was further taken into consideration to assure the presence of ZnO in the prepared sample (Figure 5a–e). A full survey scan (Figure 5a) confirmed the existence of N, C, O, and Zn in the GCN–ZnO0.4 sample. C 1s peaks observed in the short scan (Figure 5b) could be differentiated into four main peaks, with 287.4 eV
depicting C–N–C bonds, 285.8 eV attributed to sp³ C–N bond, 288.1 and 284.7 eV indicating sp²-bonded carbon (N=C–C) and aromatic C atom in the s-triazine ring, respectively.26,29,47 For the N 1s spectrum in Figure 5c, the peak at 398.7 eV originated from C≡N–C, indicating the presence of triazine rings, and a weak peak signal at 400.02 eV depicted tertiary N atoms (N-(C)=C). 29,32 For the O 1s spectrum in Figure 5d, the peak at 529.8 eV correlates with O²⁻ ions in Zn–O bonding and the peak at 531.1 eV corresponds to the OH group adsorbed on the composite surface.31,47 In the case of the Zn 2p spectrum (Figure 5e), the peaks at 1043.9 and 1020.9 eV correlated with Zn 2p¹/₂ and Zn 2p³/₂, respectively, representing typical Zn–O bonds. Also, the binding energy difference between these two peak signals is 23 eV, holding good agreement with the ZnO standard reference value.29 The XPS analysis further confirmed the association of ZnO with GCN.

2.5. Thermogravimetric Analysis. Thermal stability and estimation of the GCN content in the obtained samples were done through the thermogravimetric analysis (TGA) (Figure 6). TGA spectra were found to consist of two stages of weight loss. The major weight loss was observed from about 520–710 °C, which is related to the combustion of the GCN phase.44 Thus, from this weight loss phenomenon, the weight percentage of GCN and ZnO (GCN %/ZnO %) was estimated to be 69.21%/19% in GCN−ZnO0.2, 63.86%/26.9% in GCN−ZnO0.4, and 52.6%/35.4% in GCN−ZnO0.6.29 Based on the above calculation, the corresponding content of ZnO in the total amount of samples obtained (Table 5) was estimated to be 0.098, 0.156, and 0.230 g, which is quite comparable to the expected theoretical value of 0.081, 0.162, and 0.244 g corresponding to the amount of ZnO precursor used for the synthesis of GCN−ZnO0.2, GCN−ZnO0.4, and GCN−ZnO0.6, respectively. A minor weight loss of 11.5–16.4% at the lower temperature range probably resulted because of desorption of surface moisture and other organics present over the surface of samples.31

2.6. Brunauer–Emmett–Teller Analysis. N₂ adsorption–desorption isotherms (Figure 7a,b) were analyzed for GCN−pure and GCN−ZnO0.4 samples. A type III curve with a hysteresis loop was observed for both the samples.48,49 Multipoint Brunauer–Emmett–Teller (BET) plots (Figure 7c) were considered to calculate the specific surface area, and the surface area of GCN−ZnO0.4 (116 m²/g) was nearly 1.5 times greater than that of GCN−pure (74 m²/g). The increased surface area is a clear outcome of morphological evolution caused because of the association of ZnO with GCN−pure, which could have led to the degradation of

| μ | C (wt (%) at. (%)) | N (wt (%) at. (%)) | Zn (wt (%) at. (%)) | O (wt (%) at. (%)) | surface area (m² g⁻¹) | pore vol. (cm³ g⁻¹) | pore radius (nm) |
|---|----------------|----------------|----------------|----------------|-------------------|----------------------|----------------|
| GCN−pure | 42.29 | 46.08 | 57.71 | 53.92 | 74 | 0.133 | 4.13 |
| GCN−ZnO0.4 | 41.46 | 52.20 | 29.41 | 33.58 | 23.70 | 5.80 | 5.43 | 5.42 | 116 | 0.128 | 3.88 |

Figure 5. XPS spectrum of (a) GCNZn0.04 with the elemental composition shown in the inset and short scan for (b) C 1s, (c) N 1s, (d) O 1s, and (e) Zn 2p.

Figure 6. TGA curves of (a) GCN−ZnO0.2, (b) GCN−ZnO0.4, (c) GCN−ZnO0.6, (d) GCN−pure, and (e) ZnO.
graphitic arrangement of the GCN–pure structure because of nitrogen loss, leading to an increased surface area, which is also consistent with the results of SEM and EDS mapping analyses. Further pore size distribution for GCN–ZnO0.4 and GCN–pure, as shown in the inset of Figure 7a,b, was also estimated with the help of the Barrett–Joyner–Halenda method using the isotherm adsorption branch. For both the samples, the pore diameter was estimated to be in the range of 3–10 nm, depicting their mesoporous nature. The specific surface area, pore volume, and size of samples are represented in Table 1.

2.7. Ultraviolet–Visible Spectroscopic Analysis. Optical performance of all samples was analyzed using an ultraviolet–visible (UV–vis) diffuse reflectance spectrometer (Figure 8a). The absorption edge of GCN–pure was found to be getting red-shifted from 456 to 490 nm, and the absorbance intensity got more pronounced with increasing content of [ZnCO$_3$]$_2$$·$[Zn(OH)$_2$]$_3$ added to urea initially. The equation, $\alpha = A(h\nu - E_g)/h\nu$, where $\alpha$ is the absorption coefficient, was applied for band gap calculations. The band gap energy of ZnO, GCN–pure, GCN–ZnO0.2, GCN–ZnO0.4, and GCN–ZnO0.6 was estimated to be 3.28, 2.72, 2.62, 2.56, and 2.52 eV respectively, as shown in Figure 8b. The reduced band gap energy of GCN–ZnO could lead to better absorption of light in the visible region favoring more e–h$^+$ pair formation, thus probably resulting in improved photoactivity.

2.8. Photocatalytic Activity. 2.8.1. Effect of Dopant Concentration. All samples were examined for their photocatalytic potential toward the photodegradation of MB dye solution (Figure 9a,b). GCN–ZnOx samples expressed enhanced photoactivity over GCN–pure and ZnO. The adsorption–desorption equilibrium could reach in 20 min, and adsorption shown by GCN–ZnO0.4, GCN–ZnO0.4, and GCN–ZnO0.6 was 23.6, 49.8, 45.3, and 34% toward MB dye solution. Adsorption could possibly be the result of the mesoporous nature of the samples (GCN–pure and GCN–ZnO0.4), as evident from the results of the BET analysis, and supports the process of heterogeneous photocatalysis. Also, increase in the adsorption percentage for GCN–ZnO0.4 in comparison to GCN–pure is consistent with the results of respective specific surface areas of both the samples. The photodegradation efficiency was calculated by considering the initial amount of dye left after adsorption–desorption equilibrium. Photocatalytic degradation curves of MB dye solution using GCN–ZnO0.2, GCN–ZnO0.4, GCN–ZnO0.6, GCN–pure, and ZnO are shown in Figure 10a–e, where UV–vis absorption peaks for MB for all degradation curves (except for ZnO) are found to show a noticeable blue shift (maximum blue shift of 664–651 nm for GCN–ZnO0.4) after 30 min of irradiation time. This observation also states the difference between the MB absorption curve during adsorption and the photocatalytic degradation process. In the case of ZnO, the photocatalytic...
degradation efficiency was found to be only 12.3%, which is due to its optical property that might show an absorbance potential suitably in the UV spectrum range. GCN−pure showed a good potential and degraded the MB dye up to 53.1%. GCN−ZnO0.2 and GCN−ZnO0.4 composites showed an enhanced degradation potential of 78 and 90%, respectively, in comparison to GCN−pure. The order of photocatalytic activity, GCN−ZnO0.2 > GCN−ZnO0.4 > GCN−pure, was found to be consistent with the order of their calculated band gap energies. In the case of GCN−ZnO0.6, a decrease in photoactivity was observed, which might be due to the existence of surplus defects within the GCN phase of GCN−Zn0.6 acting as the site of e−h+ recombination and thus suppressing the transfer frequency of photo-induced charges. GCN−ZnO0.4 showed the highest value for the apparent rate constant, resulting in an increment of 3.2 times in comparison to GCN−pure, as shown in Table 2. Comparison of GCN−ZnO0.4 with other similar reported systems of GCN−ZnO composites has been discussed in Table 3.

2.8.2. Effect of pH of the Solution. The GCN−ZnO0.4 sample showing the highest photoactivity was further analyzed for the effect of pH of the solution on its photoactivity (Figure 11a,b). Initial pH of the MB dye solution containing the photocatalyst was set from pH 4 to pH 11. When pH of the solution was increased above the normal range to alkaline medium, the photodegradation of MB increased, and it decreased when pH was set to the acidic range below the normal pH condition. Also, it showed the highest photodegradation potential at pH 10, whereas at pH 11, the photodegradation potential showed a decrement. Based on the well-established fact of dependency of surface zeta potential of the photocatalyst on the pH value of the solution, the zeta potential of the GCN−ZnO0.4 sample was measured, as shown in Figure 11d, and was found to be influenced by the MB dye solution pH, as shown in Figure 11c.51,52 The zeta potential value of GCN−ZnO0.4 was found to be 5.91, 3.42, −8.69, −11, −21.7, and −17 mV for solution pH of 4, 5, 7.6, 9, 10, and 11. The increased negative surface charge of the photocatalyst in alkaline medium would enhance the adsorption of positively charged MB dye molecules, which would further facilitate its photodegradation. At an optimum pH condition, degradation of MB reached 97% in 80 min, and the apparent rate constant value increased 1.8 times in comparison to normal pH condition. The apparent rate constant value and the degradation efficiency for GCN−ZnO0.4 measured for all photocatalytic reactions for 80 min at the pH range 4−11 are represented in Table 4.

2.8.3. Reusability Experiment. The stability of the fabricated GCN−ZnO0.4 sample was checked by conducting recyclability and reusability experiments for four cyclic runs as shown in Figure 12. The photocatalyst in use was re-collected at the end of every photocatalytic experimental run and reused for the next cycle by keeping other conditions same. The photocatalytic degradation efficiency was found to be almost the same for all reactions, and a minor decrement in activity with every cyclic run could be attributed to the loss in the amount of photocatalyst during the process of recollection.

Table 2. Degradation Efficiency and Apparent Rate Constant (k) Values Measured for All Prepared Samples

| s. no. | sample      | degradation efficiency (%) | apparent rate constant (k) (min⁻¹) |
|-------|-------------|----------------------------|-----------------------------------|
| 1     | GCN−Zn0.4   | 90                         | 0.01993                           |
| 2     | GCN−Zn0.2   | 77                         | 0.01241                           |
| 3     | GCN−pure    | 53.1                       | 0.00616                           |
| 4     | GCN−Zn0.6   | 55                         | 0.00669                           |
| 5     | Zn0         | 12.3                       | 0.00095                           |
2.8.4. Proposed Mechanism for Enhanced Photocatalytic Activity. As per the above discussion, the GCN−ZnO0.4 composite sample resulted in enhanced adsorption and photoactivity than GCN−pure. This response could be because of two main evolutionary processes between the two variants, that is, increased surface area and smaller band gap, which support the phenomenon of synergism between adsorption and photocatalytic process. Increased surface area in the case of the GCN−ZnO0.4 sample can provide more active sites during the photocatalytic reaction, thus producing more photogenerated electrons, and it can also lead to lower recombination of photogenerated charge carriers.\(^5\) For the demonstration of the role of active species involved in the

| s.-no. | precursor used for synthesizing GCN−ZnO composites | source of illumination | \(C_{\text{photocatalyst}}\) (mg mL\(^{-1}\)) | \(C_{\text{pollutant}}\) (mg L\(^{-1}\)) | time (min) | photocatalytic degradation efficiency (%) | refs. |
|-------|-----------------------------------------------|-----------------------|------------------------------------------|---------------------------------|-------------|---------------------------------|-------|
| 1.    | dicyandiamide and zinc nitrate                  | 300 W Xenon lamp       | 1                                        | 10                              | 120         | 78.6                            | 26    |
| 2.    | urea and Zinc nitrate                           | 500 W tungsten lamp    | 0.33                                     | 3.2                             | 60          | 86                              | 27    |
| 3.    | urea and SSMP                                   | 365 nm UV lamp         | 0.2                                      | 10                              | 150         | >85                             | 25    |
| 4.    | urea and zinc carbonate basic dihydrate         | 200 W tungsten lamp    | 0.1                                      | 10                              | 120         | 90                              | this work |

Figure 11. (a) Comparison of the degradation efficiency. (b) \(\ln(C_0/C(t))\) as a function of visible light irradiation time for MB degradation under different pH conditions using GCN−ZnO0.4. (c) Relation between the surface zeta potential value of GCN−ZnO0.4 and the degradation percentage of the MB dye at different pH values. (d) Zeta potential of GCN−ZnO0.4 at different pH values.

Table 4. Degradation Efficiency and Apparent Rate Constant (\(k\)) Values Calculated for All Photocatalytic Reactions Performed Using GCN−ZnO0.4 for a Duration of 80 min under Different pH Conditions

| s. no. | pH        | efficiency degradation (%) | apparent rate constant (\(k\)) (min\(^{-1}\)) |
|--------|-----------|----------------------------|-----------------------------------------------|
| 1      | 10        | 97                         | 0.0306                                        |
| 2      | 11        | 88                         | 0.0283                                        |
| 3      | 9         | 79                         | 0.0184                                        |
| 4      | 7.6 (normal) | 74                     | 0.0166                                        |
| 5      | 5         | 47.2                       | 0.0083                                        |
| 6      | 4         | 34.5                       | 0.0057                                        |

Figure 12. Recyclability experiment of photocatalytic degradation of MB dye using the GCN−ZnO0.4 sample.
photodegradation of the MB dye, trapping experiments were performed. Ascorbic acid (AA, 0.1 mM), methanol (M, 10 mM), potassium dichromate (K₂Cr₂O₇, 10 mM), and ammonium oxalate (AO, 10 mM) were utilized as superoxide O₂⁻ radicals, hydroxyl *OH radicals, electrons (e⁻), and holes (h⁺) scavengers, respectively, and degradation of MB dye was observed using a UV–vis spectrophotometer after 120 min of visible light irradiation. It can be observed in Figure 13 that AO hindered photoactivity noticeably, suggesting the photoreduction was observed in the presence of K₂Cr₂O₇, in the degradation process. Contrarily, no hindrance in photoredox potential lies at -0.33 eV. The redox potential of "OH/OH⁻" lies at +1.99, and therefore, the photogenerated holes on the GCN surface cannot react with "OH" or H₂O molecules to form "OH radicals. In turn, the holes in the vb of GCN can possibly oxidize the MB dye, as supported by the effect of AO causing hindrance to photoactivity. This improves the transfer of charge carriers, and the recombination of photo-generated e⁻–h⁺ pairs is effectively delayed by ZnO doping. This can be explained with the help of equations below

\[
\text{GCN} - \text{ZnO} + \text{hv} \rightarrow e^- + h^+ \\
e^- + O_2 \rightarrow \cdot O_2^- \\
2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \\
H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + OH^- + O_2 \\
h^+ + H_2O \rightarrow \cdot OH + H^+ \\
\cdot OH + h^+ + \text{MB} \rightarrow \text{degradation products}
\]

Thus, both increased surface area and enhanced visible light absorption ability in the case of the GCN–ZnO0.4 sample can lead to better degradation efficiency toward the MB dye.

3. CONCLUSIONS
The GCN–ZnO composite was prepared in a facile manner and characterized using FTIR, XRD, SEM, energy-dispersive X-ray spectroscopy (EDX), XPS, differential reflectance spectroscopy (DRS), and BET analyses. The strong coordination of ZnO with GCN–pure and partial deterioration of the crystalline structure of GCN–pure on addition of ZnO were indicated by XRD and FTIR analyses. BET and DRS analyses revealed that the GCN–ZnO0.4 composite resulted in an enhanced surface area and visible light absorption ability, leading to increased active sites, photogenerated electron–hole pairs, and reduced frequency of photo-induced charge recombination, which in turn leads to a better photoactivity potential. GCN–ZnO0.4 resulted in an increment in the value of apparent rate constant by 3.2 times over GCN–pure toward degradation of the MB dye and could be further explored for various other environmental applications.

4. EXPERIMENTAL AND CHARACTERIZATION DETAILS
Zinc carbonate basic dihydrate [ZnCO₃]₂[Zn(OH)₂]₃ and urea (CH₄N₂O) were purchased from Sisco Research Laboratories Pvt. Ltd. and Thermo Fisher Scientific India Pvt. Ltd. respectively. A typical procedure to prepare the GCN–ZnO composite has been reported in Figure 15. The yellow-colored solid sample was procured and further processed into a fine powder. The samples were labelled as GCN–ZnOₓ, where x represents the amount of [ZnCO₃]₂[Zn(OH)₂]₃ in mmol put initially in urea (10 g). Table 5 represents the amount of sample obtained in context to synthesized GCN–pure and GCN–ZnOₓ samples. Pristine GCN (GCN–pure) and ZnO were prepared likewise by directly heating their respective precursors.

Further samples were characterized using a Rigaku Ultima IV diffractometer equipped with Cu Kα radiation (1.5406 Å)
for XRD analysis. FTIR analysis was done using a PerkinElmer Frontier FTIR spectrometer. DRS spectra was obtained using a Shimadzu UV-2450 spectrometer from Japan. SEM analysis was done using an EVO LS 10 microscope. TEM was done using a Tecnai G2 20 (FEI) S-Twin (200 kV) transmission electron microscope. XPS analysis was performed on an ESCA + Omicron Nanotechnology Oxford Instrument (1486.6 eV). BET surface area and pore analysis were done using a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). TGA was carried out using a TA SDT Q600 instrument in a N2 atmosphere using α-Al2O3 as the reference and heating @ 10 °C min⁻¹.

Photocatalytic degradation of MB dye solution was carried out at room temperature in a photoreactor containing two tungsten lamps (200 W) (with a 420 nm cutoff filter), fixed on opposite walls, as the visible light source. Light source intensity was determined by a power meter (14.45 mW/cm²). Typically, 0.01 g of the photocatalyst was added to MB dye solution (10 ppm) in a conical glass beaker (250 mL) and kept for stirring in the dark to reach adsorption–desorption equilibrium. During the experiment, 5 mL of suspensions were taken out in intervals of 10 min and centrifuged for photocatalyst separation; then, the suspensions were analyzed for absorbance measurements using a UV–vis spectrophotometer. The photocatalytic degradation efficiency and the apparent rate constant of the degradation process of the dye were estimated following the information given in our previously published work.¹⁶

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D.R.P.: conceptualization, methodology, data curation, formal analysis, investigation, writing—original draft, and writing—review and editing. S.G.: conceptualization, formal analysis, investigation, writing—original draft, and writing—review and editing. P.P.: data curation, formal analysis, investigation, and writing—review and editing. S.P.N.: conceptualization, resources, writing—review and editing, supervision, project administration, and funding acquisition. P.C.: formal analysis, investigation, and data curation. A.S.: conceptualization, resources, and writing—review and editing.

**Notes**

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**Table 5. Amount of Sample Obtained**

| s. no. | sample name | amount obtained (g) |
|-------|-------------|---------------------|
| 1     | GCN–pure    | 0.34                |
| 2     | GCN–Zn0.2   | 0.52                |
| 3     | GCN–Zn0.4   | 0.58                |
| 4     | GCN–Zn0.6   | 0.65                |
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