

RESEARCH ARTICLE

Newly Designed Cutting-Edge GCN@Cd Nanocomposite Catalyst Drives Ultra-Selective Organic Transformations under Solar Light

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ABSTRACT: Transforming nitroarene into value-added chemicals at atmospheric pressure and ambient temperature using environmentally friendly and sustainable energy sources is indeed a challenging but highly desirable task for scientists. We present here the synthesis and development of a visible light active nanocomposite photocatalyst (GCN@Cd) based on graphitic carbon nitride, which was accomplished via thermal polymerization. With GCN@Cd as the photocatalyst, the newly developed nanocomposite photocatalytic system operates with great efficiency, producing a high yield of organic transformation (~95.15%). As a result, we created a GCN@Cd nanocomposite material with superior light-triggeration capabilities for -N=N-bond formation. The current scientific endeavour focuses on the expansion and uses of GCN-based nanocomposite photocatalysts in a variety of domains, including environmental remediation and organic synthesis.

Keywords: Graphitic carbon nitride, GCN@Cd nanocomposite, Solar Light, Organic transformation, Mechanism

Received: 17 January 2024; Revised: 25 February 2024; Accepted: 11 March 2024; Available Online: 21 March 2024

1. INTRODUCTION

The severe environmental pollution crisis and the quick depletion of conventional fossil fuels have spurred the rapid development of renewable energy conversion and storage technologies, including water splitting, fuel cells, and

photocatalysis [1-3]. High catalytic activity for C-H, C-N, and C-S bond activations is currently exhibited by noble metal catalysts such as silver, platinum, ruthenium, and so on [4-6]. However, their broad application is hampered by resource scarcity, high cost, a single catalytic function, and poor stability [7-8]. In order to increase g-C₃N₄ photocatalytic activity, a number of strategies have recently been developed. These primarily consist of controlling g-C₃N₄'s morphology to create nanostructured arrays, combining it with other semiconductors to create heterojunctions, such as Z-scheme photocatalysts [9]. Our group and others have worked extensively on many modified g-C₃N₄ systems in this direction [10-13]. Several researchers have showcased g-C₃N₄ in multiple morphologies, such as leaf-like structures, nanoplates, nanosheets, nanocrystals, and quantum dots. They have also built their heterojunctions using several metal oxides such as BiVO₄, Bi₂MoO₆, and so on [14-16]. The same group has also created BiVO₄ and Bi₂MoO₆ nanocomposites, coated carbon nanotube derivatives with fullerene, and these have demonstrated outstanding photocatalytic activity towards the breakdown of

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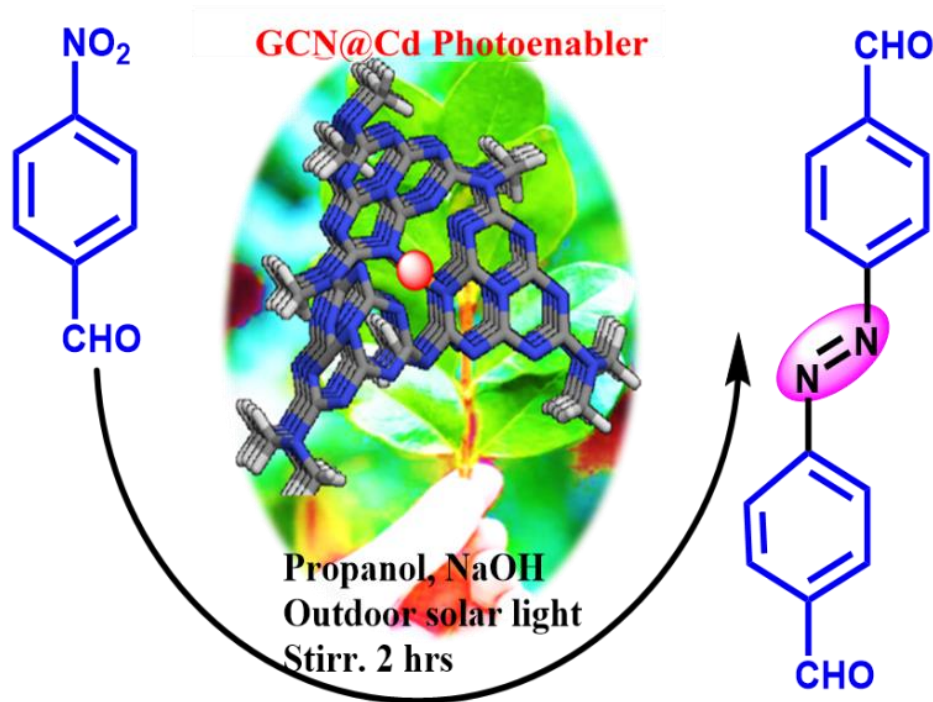
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Rhodamine B [17-19].

In addition, doping g-C₃N₄ with metal and non-metal to modify its surface and lattice electronic structures is thought to be the most effective way to investigate the photocatalytic activity. The electrostatic interaction between the positively charged metal ions and the negatively charged nitrogen atom of the host species causes metal ion doping to typically occur in the g-C₃N₄ lattice, improving charge carrier and migration. Many elements have been doped into g-C₃N₄ up to this point, including transition metals like Ag, Zn, Cu and Ti as well as alkali metals like K and Na. These dopants enhance photocatalytic activity by modifying the electronic structure [20-23]. As an alternative, substitutional doping using nonmetal doping can be used to modify the valance and conduction band positions of g-C₃N₄, increasing the absorption of visible light by substituting N/S/C atoms [24]. Some scientists used trithiocyanuric acid to synthesize highly photoactive sulfur-doped and nitrogen-deficient g-C₃N₄ with a very porous framework, which yields hydrogen about 12 times that of pristine g-C₃N₄ [25]. Similarly, synthesized [26] boron-doped g-C₃N₄ by heating melamine and boron oxide and then subjected to thermal treatment at various temperatures. Wang et al. demonstrated the production of boron-doped carbon nitride with BH₃ as the molecular doping source, avoiding the formation of HF [27]. Thaweesak et al. generated a boron-doped g-C₃N₄ nanosheet using the same process but with a little alteration intriguing ammonium chloride, which displays near about 12 times increased hydrogen evolution under visible light irradiation [28]. The doping heteroatom technique is advantageous for band gap engineering, surface area enhancement, light

trapping, charge separation, and migration, all of which result in more active sites. However, when the photocatalyst's stability is taken into account, suitable photocatalytic and aforementioned qualities cannot be investigated with single heteroatom doping. Co-doping in metal oxides such as TiO₂ and organic materials such as RGO has been thoroughly researched, with co-doping able to combine the properties of both dopants [29-30]. Synthesis of doped ordered mesoporous carbon with heteroatoms such as nitrogen, sulphur, and oxygen. When compared to dual and mono-doped equivalents, triple doped ordered mesoporous carbon demonstrated superior oxygen reduction reaction performance.

There was a remarkable connection between the activity and reaction kinetics of the heteroatoms doped ordered mesoporous carbon [31-32] and the experimentally estimated work function. The shift in work function caused by the dopant inspired the construction of heteroatoms doped g-C₃N₄. However, a few co-doped g-C₃N₄ systems have been developed and their photocatalytic activity investigated. P and S codoped g-C₃N₄, P and O co-doped g-C₃N₄, and I and K co-doped g-C₃N₄ have recently been synthesized, demonstrating outstanding photocatalytic capabilities when compared to single-doped g-C₃N₄ [31-32]. For the first time, we synthesized a newly designed cutting-edge GCN@Cd nanocomposite catalyst that drives ultra-selective organic transformations under solar light using a one-pot in situ calcination technique (Scheme 1, 2, and 3). Cadmium nitrate was employed as a cadmium, glucose and melamine as a raw material for GCN@Cd nanocomposite (Scheme 1).



Scheme 1. Graphitic carbon nitride-based cadmium nanocomposite (GCN@Cd) as a photocatalyst for facile and selective reduction of nitrobenzaldehyde to azo compound.

2. EXPERIMENTAL DETAILS

2.1 Materials and methods

Melamine ($C_3H_6N_6$), glucose ($C_6H_{12}O_6$), cadmium nitrate hexahydrate ($Cd(NO_3)_2 \cdot 6H_2O$), p-nitrobenzaldehyde (4-NBA), 2-propanol, sodium hydroxide (NaOH), ethanol (C_2H_5OH), hydrochloric acid (HCl), ethyl acetate ($CH_3CO_2CH_2CH_3$) and dimethyl sulfoxide (DMSO). All the chemicals are purchased from sigma aldrich and utilized without purification.

2.2 Instruments and measurements

Shimadzu spectrophotometer (UV-visible-1900i), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (FE-SEM~ EDS) JEOL JSM 6490 LV (Japan), X-ray diffraction patterns (XRD) (Bruker D8 Advance Eco, Germany), thermal gravimetric analysis (TGA Q50 V20.13 Build 39) along with DLS (NZS 90) instruments were used for the characterization of the newly designed GCN@Cd nanocomposite photocatalyst

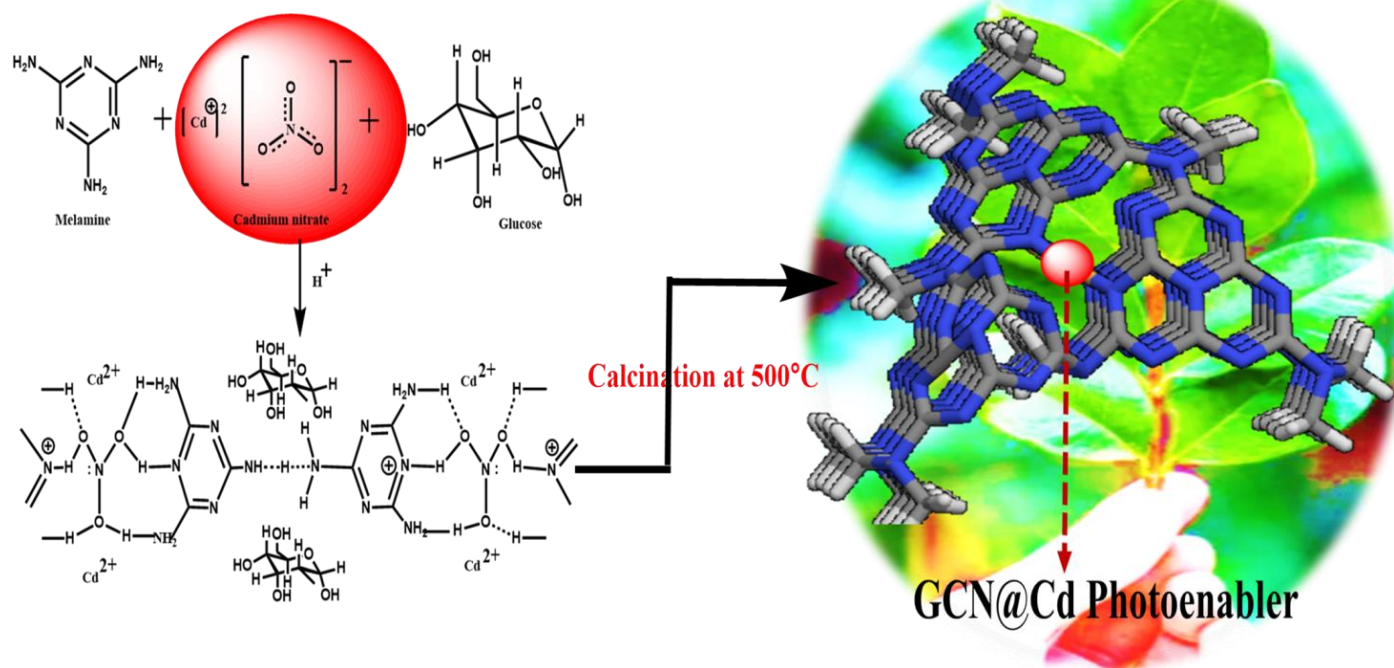
2.3 Synthesis of newly designed GCN@Cd nanocomposite photocatalyst

The GCN@Cd nanocomposite was prepared as per reported method [33-34]. Melamine (5gm) and cadmium nitrate hexahydrate (5gm) precursors were combined to create the GCN@Cd composite photocatalyst, which was

then carbonised at a gradient temperature with glucose acting as a reducing agent. To create a stable gel, the homogenous mixture's pH was brought down to 2.5 using HCl solution. The xerogel formed after the centrifugation and elimination of additional impurities of $Cd(NO_3)_2 \cdot 6H_2O$ was freeze-dried, heated in a muffle furnace, and maintained at $550^\circ C$ for 3 hours. This approach produced a composite catalyst made of Cd nanoparticles and nitrogen-doped carbon nanotubes GCN@Cd that has been shown in Scheme 2.

2.4 Photochemical reduction of nitroarene to azo-compound by newly designed GCN@Cd nanocomposite photocatalyst

To assess the photocatalytic performance of the GCN@Cd nanocomposite photocatalyst, the reduction of nitrobenzaldehyde was selected as the model reaction, as illustrated in Scheme 1. The experimental findings provide evidence for the versatility of the proposed method in achieving the selective and efficient synthesis of azo compounds with high yields. The literature also indicates that the reductive coupling process is significantly influenced by the steric effects of the substituents. When both electron-withdrawing and electron-donating groups are taken into account, selectivity is shown to be higher for para- than for ortho-substituted compounds. Based on this information, we speculate that the surface of GCN@Cd will favour para-substituent than the ortho-substituent because of the steric effects on the phenyl ring and give better yield [35].



Scheme 2. A schematic diagram illustrating the two-step process for the preparation of GCN@Cd is presented. In the first step, protonated melamine self-assembly is initiated in the presence of nitrate anions. In the second step, the composite materials resulting from the self-assembly of melamine are subjected to thermal treatment, leading to the formation of GCN@Cd.

Primarily, 200 mg of 4-NBA, 51 mg of NaOH, and 15 mg of GCN@Cd were taken in 30 mL of dry 2-propanol in a dried vial. Subsequently, the reaction mixture obtained was stirred for duration of 2 hours under solar light within a nitrogen atmosphere. Once the reaction was deemed complete, the mixture was filtered to separate the solid catalyst. The filtrate was then extracted by using a separating funnel with 100 mL of ethyl acetate and 50 mL of distilled water. To obtain a pure azo compound, the residue was further refined using silica gel column chromatography. This chemical appeared as an orange crystalline solid with a 94% yield.

3. RESULTS AND DISCUSSION

3.1. Characterizations and properties

UV-visible spectroscopy measurements were used to characterize the absorption spectrum of the GCN@Cd photocatalyst as shown in Figure 1(a). A strong absorption peak of GCN@Cd composite photocatalyst at 420nm was seen which falls in the visible region. The optical band gap was estimated using the Scherrer equation ($1240/\lambda$) and the result was 2.95eV, indicating its aptness as an active photocatalyst for harvesting solar-light. FTIR was used to analyse the functional groups of graphitic carbon nitride (g-C₃N₄) and its composite with Cd, i.e. GCN@Cd nanocomposite photocatalyst (Figure 1 (b)). The FTIR spectrum of GCN@Cd nanocomposite photocatalyst shows a band in the range of 3200-3500 cm⁻¹ which shows preliminary stretching of the N-H bond associated with uncondensed amino groups [36]. The other peaks in the range of 1200-1700 cm⁻¹ correspond to C-N and C=N stretching vibrations [37]. Furthermore, a sharp peak at 800 cm⁻¹ was attributed to the bending vibration of triazine units, proving that GCN@Cd was successfully synthesized [38-39].

SEM was used to investigate the morphological study of the melamine and GCN@Cd photocatalyst samples. The FE-SEM images of a pure melamine sample and a GCN@Cd nanocomposite photocatalyst, respectively, are shown in Figure 2 (a) and (b). The FE-SEM images of pure melamine showed a hard granular type structure whereas the surface view of GCN@Cd composite showed a mesh-like structure along with the existence of Cd metal, which indicates melamine is polymerized and Cd metal is immobilized to form the GCN@Cd nanocomposite photocatalyst. The uneven surface of the nanocomposite photocatalyst shows that the Cd was boosted to the surface of g-C₃N₄ with good interfacial contact. In fact, doping with cadmium significantly changed the morphology of graphitic carbon nitride (g-C₃N₄) by adding more intrinsic pathways for the photogenerated holes and electrons. This change improved the photocatalytic efficiency of cadmium-doped g-C₃N₄, i.e., GCN@Cd nanocomposite photocatalyst [40-41]. X-ray energy dispersion spectroscopy (EDX) was used to determine the composition of the synthetic Cd-doped graphitic carbon nitride composite material. The GCN@Cd nanocomposite photocatalyst, the presence of Cd along with other elements (C, H, N) indicated the successful incorporation of Cd metal in graphitic carbon nitride to form GCN@Cd composite as a photo catalyt as illustrated in Figure 2 (c) and (d).

X-ray powder diffraction (XRD) was used to investigate the composite structure of g-C₃N₄ i.e. GCN@Cd. The powerful non-destructive technique XRD patterns of melamine and GCN@Cd nanocomposite photocatalyst are displayed in Figure 3(a). The spectra reveal sharp peak in the case of melamine which shows the crystalline nature of the melamine. However, the broad peak reveals the amorphous nature of the GCN@Cd nanocomposite photocatalyst, indicating the polymerization of melamine at 5000C to form the GCN@Cd nanocomposite photocatalyst.

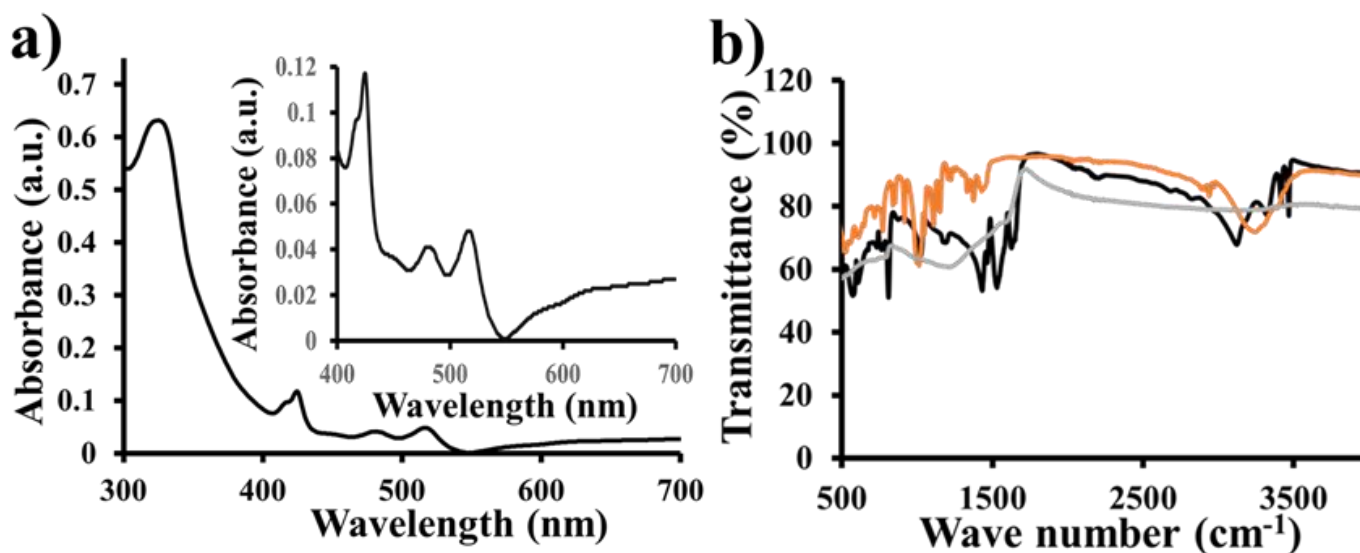


Fig. 1. Optical Characterization using UV-Visible and FTIR spectroscopies. (a) UV-Visible spectra of GCN@Cd nanocomposite photocatalyst. (b) FTIR spectra of melamine (red line), glucose (black line), and GCN@Cd nanocomposite photocatalyst (grey line) respectively.

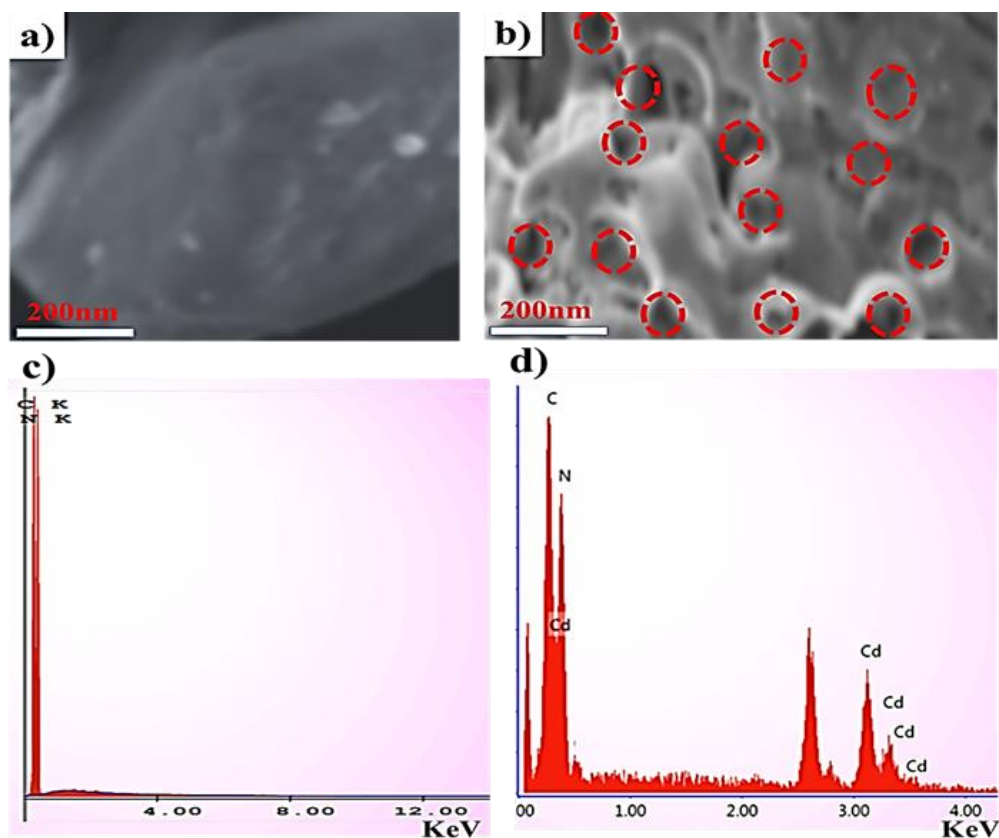


Fig. 2. Field emission scanning electron microscopy (FESEM) images of a) Melamine and b) GCN@Cd nanocomposite photocatalyst and EDX analysis of c) Melamine and d) GCN@Cd nanocomposite photocatalyst, in which Cd indicated by the red circle.

The GCN@Cd nanocomposite photocatalyst sample has two distinct strong diffraction peaks approximately at about 12.7° (diffraction plane 100) and 27.3° (diffraction plane 002) [42]. GCN@Cd does not have a reasonable shift of 002 lines, indicating that the g- C_3N_4 immobilized within Cd, while g- C_3N_4 has a referenced shift of 002 line [43]. This implied that after the incorporation of Cd, the crystallinity of g- C_3N_4 materials diminishes and more edge defects were generated [44]. Moreover, diffraction peaks corresponding to the metallic Cd are scarcely found, which affirms that the state of Cd in GCN@Cd was ionic.

TGA (thermogravimetric analysis) technique was used for the assessment of the thermal properties of materials. Figure 3(b) illustrates the TGA curves of both melamine and the GCN@Cd composite nanocomposite photocatalyst. The thermogravimetric analysis (TGA) was conducted under an inert atmosphere, at a heating rate of $10^\circ\text{C}/\text{min}$, covering a temperature range from 40°C to 800°C . The TGA analysis of the GCN@Cd nanocomposite photocatalyst revealed weight loss occurring in two consecutive steps as the temperature increased up to 800°C . At 100°C , an initial weight loss of approximately 98.7% was observed, which can be attributed to solvent evaporation. Subsequently, a significant and substantial weight loss occurred at 520°C . In contrast, melamine exhibited a sudden weight change at

approximately 300°C . Therefore, the TGA graph verifies that the GCN@Cd nanocomposite photocatalyst possesses superior thermal stability compared with melamine. Consequently, the GCN@Cd nanocomposite photocatalyst is more suitable and practical for organic transformations under solar light conditions than melamine.

The dynamic light-scattering (DLS) technique was used to measure the zeta potential (ζ) values of melamine and GCN@Cd nanocomposite photocatalyst. The zeta potential for the GCN@Cd nanocomposite photocatalyst revealed a greater negative value of -21.2 mV compared to the melamine with a value of -17.1 mV as shown in Figure 4 (a) and (b), which clearly indicated the successful formation of GCN@Cd nanocomposite photocatalyst from melamine. The particle size of melamine and GCN@Cd nanocomposite photocatalyst were also analyzed using the DLS technique as shown in Figure 4 (c) and (d). The particle size of GCN@Cd nanocomposite photocatalyst is 601.7 nm while melamine has a particle size of 1702 nm.

This indicates that the GCN@Cd nanocomposite has greater surface area to volume ratios which further reveals that it is more efficient in organic transformation than melamine. Therefore, GCN@Cd nanocomposite photocatalyst has outstanding photocatalytic ability for the conversion of nitrobenzaldehyde to azo compound.

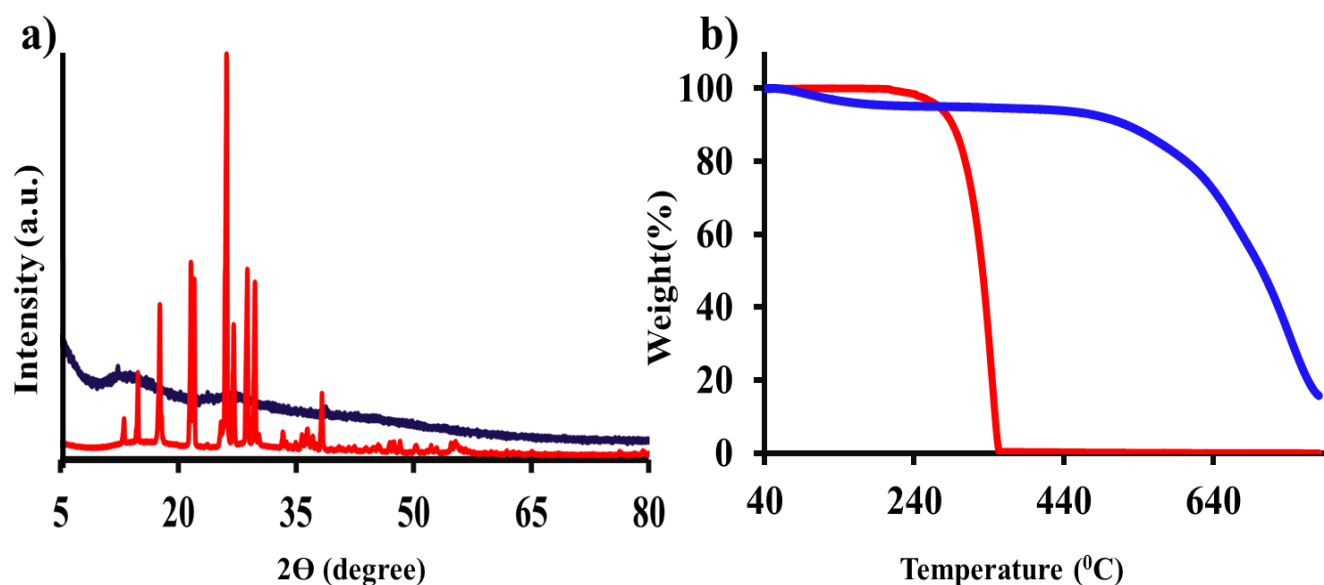


Fig. 3 a) XRD pattern of melamine (red line) and GCN@Cd composite nanocomposite photocatalyst (Blue line) respectively and b) TGA pattern of melamine (red line) and GCN@Cd nanocomposite photocatalyst (blue line).

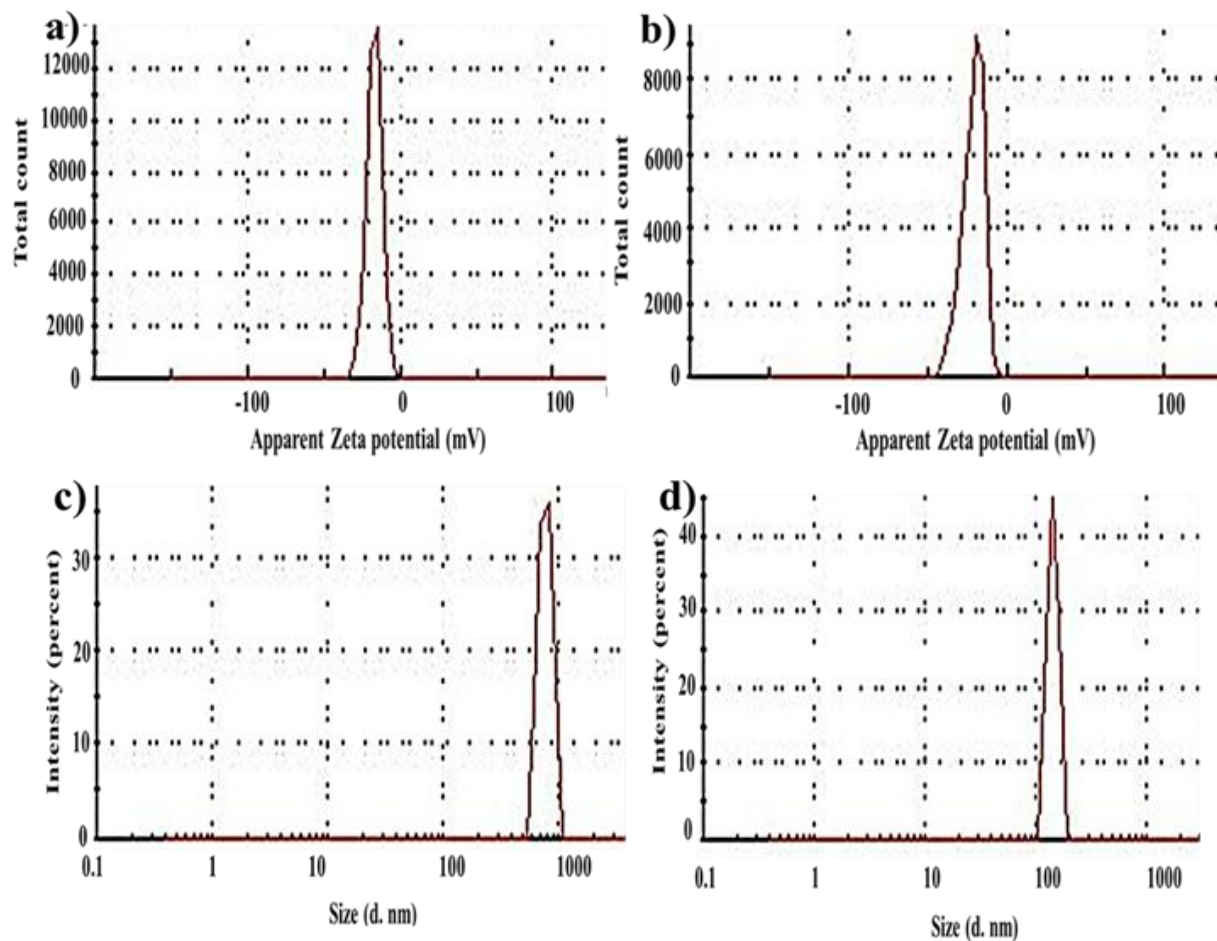
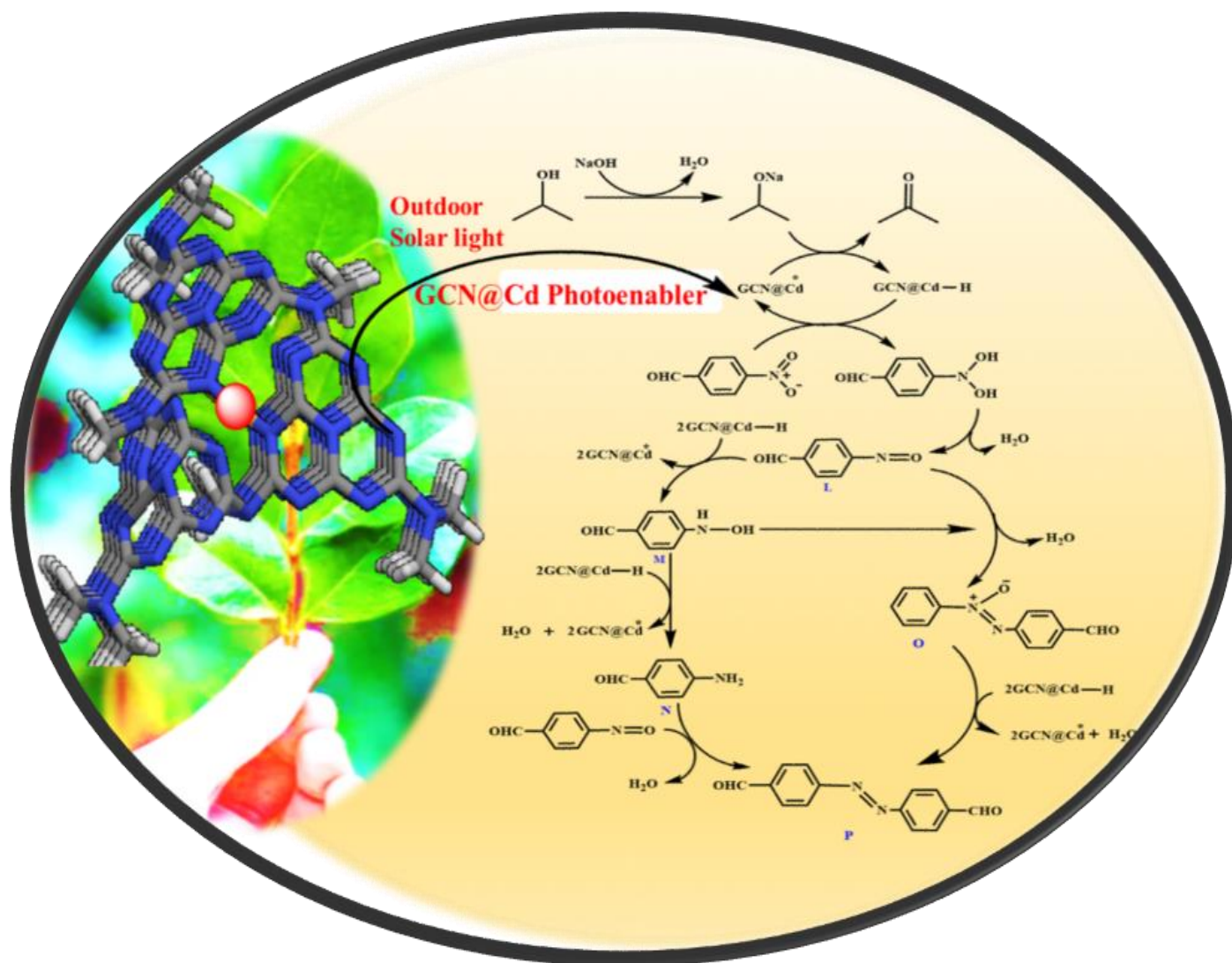


Fig. 4 a) Zeta potential studies of a) melamine (-17.1 mv) b) GCN@Cd nanocomposite photocatalyst (-21.2 mv), c) particle size melamine and d) GCN@Cd nanocomposite photocatalyst.

3.2. Mechanistic route for the reduction of p-nitro benzaldehyde (NBA) to (E)-4, 4'-(Diazene-1,2-diyl) dibenzaldehyde i.e. azo compound

The remarkable performance of the GCN@Cd nanocomposite photocatalyst in the photoreduction of p-nitrobenzaldehyde is hypothesized to be attributed to its efficient utilization of photo-generated electrons in the reduction reaction. This hypothesis is supported by previous studies [45]. Drawing upon patterns from the existing literature, we propose a sequence of reaction steps that are engaged in the photocatalytic reduction process as depicted in Scheme 3. At the outset, it is postulated that NaOH facilitates the extraction of a hydrogen atom from 2-propanol, resulting in the generation of sodium isopropoxide [46]. Upon absorbing solar light, the GCN@Cd photocatalyst generates electrons and holes on its surface, leading to the formation of GCN@Cd-H species through the elimination of hydride from sodium isopropoxide. This process also yields acetone as an oxidized product. The Cd-H bond formed in

this process is relatively stable on the surface of the GCN@Cd catalyst and donates hydride to nitrobenzaldehyde to regenerate the catalyst. Moreover, the donation of two hydride results in the elimination of water and the formation of nitroso-benzaldehyde (L). Nitroso-benzaldehyde serves as a crucial intermediate in this photocatalytic process and can be further transformed into azoarene (P) through two potential pathways. In path A, nitroso-benzaldehyde undergoes conversion to hydroxyamino-arene (M), which is subsequently transformed into aminoarene (N) through a similar hydride transfer process. Moreover, the desired coupling product, azoarene, is formed through the reaction between nitroso-arene and amino-arene, accompanied by the elimination of water. Alternatively, in path B, the formation of azoxy-arene (O) occurs through the reaction between nitroso-arene and hydroxyamino-arene. Subsequently, azoxy-arene is transformed into (E)-4,4'-(Diazene-1,2-diyl) di benzaldehyde (azo compound) through a straightforward hydride transfer process with the removal of water.



Scheme 3. A probable reaction pathway for photocatalytic reduction of p-Nitrobenzaldehyde to Azo Compound.

4. CONCLUSIONS

In summary, a new nanocomposite photocatalyst called GCN@Cd, which involves the in situ doping of Cd into gC₃N₄, has been created for the selective reduction of nitroarene to azo compound. This is the first time such a material has been synthesized using thermal polymerization. Characterization of the GCN@Cd nanocomposite photocatalyst was carried out using various techniques, including UV-visible spectroscopy, Fourier transform infrared spectroscopy, thermal analysis, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, zeta potential, and particle size analysis. The results indicate that the Cd-doped GCN@Cd nanocomposite photocatalyst exhibits excellent performance as a heterogeneous nanocomposite photocatalyst. This catalyst demonstrates remarkable catalytic activity, specifically in the selective photo-reduction of nitroarene to produce azo compounds. Notably, it achieves this at ambient temperature within a very short time frame. This catalyst's remarkable qualities include its excellent product yield and tolerance to a broad variety of functional groups. This simple and targeted nitro reduction technique outperforms the traditional method for nitroarene conversion to azo compounds. This new methodology clearly demonstrates the outstanding efficiency of the GCN@Cd nanocomposite photocatalyst in the conversion of nitroarenes to azo-compounds, in contrast to the previous method that gives product mixes combining azo-oxy amine and different byproducts. Moreover, this method is cost-effective, environmentally friendly, and exhibits excellent photocatalytic stability.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the kind support of the Madan Mohan Malaviya University of Technology, Gorakhpur-273010, Uttar Pradesh, India.

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