Investigation on Cu2O Combined g-C3N4/ZnO Heterostructures For High-Performance Photocatalytic Dye Degradation Under Visible-Light Exposure

Renji Rajendran
Periyar University

Asokan Sasireka
Periyar University

Palanisamy Priya
Periyar University

Shanmugam Vignesh
Periyar University

Sanjeevamuthu Suganthi
Periyar University

Raj Vairamuthu (✉ drrajvchem@gmail.com )
Periyar University  https://orcid.org/0000-0002-3643-8659

Jeyaperumal Kalyana Sundar
Periyar University

Manickam Srinivasan
SSN Research Centre, SSN College of Engineering

P. Ramasamy
SSN Research Centre, SSN College of Engineering

Research Article

Keywords: Nanocomposites, Photocatalytic degradation, Rhodamine B dye, Reusability, Charge separation, Superoxide radicals

DOI: https://doi.org/10.21203/rs.3.rs-206595/v1

License: © This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

To assess a highly effective recyclable for visible-light photocatalysts (PCs), in this work, as-formed a ternary g-C$_3$N$_4$-ZnO/Cu$_2$O nanocomposite PCs which was aimed at the photo-degradation of RhB dye. The essential structural, morphological and optical performance of the nanocomposites (NCs) were categorized by XRD, FT-IR, FE-SEM with EDS, UV-Vis DRS absorption and PL spectra analysis. Photocatalytic actions of the as-obtained g-C$_3$N$_4$-ZnO/Cu$_2$O PCs has remained remarkably upgraded, and those showed greater degradation rate than those of other as-obtained samples. Also, that specified existence of the heterojunction among the interfaces of g-C$_3$N$_4$ and ZnO/Cu$_2$O hence developed the response of visible-light absorptions and separation efficacy of the photo-excited charges which heightened the photocatalytic events of the g-C$_3$N$_4$-ZnO/Cu$_2$O PCs. The photo-degradation efficiency of RhB dye over g-C$_3$N$_4$, g-C$_3$N$_4$/ZnO, g-C$_3$N$_4$/Cu$_2$O and g-C$_3$N$_4$-ZnO/Cu$_2$O PCs were 36.4 %, 53 % and 66 %, and 91.4 % in 100 min, which was owing to the number of dye molecules adsorbed on the PCs under visible-light treatment. The recycling stability test was exposed, the g-C$_3$N$_4$-ZnO/Cu$_2$O PCs exhibit a greater photocatalytic action after five reuses. Therefore, the eco-friendly PCs might be broadly useful to the treatment of dye polluted wastewater.

1. Introduction

As a chief universal ecological concern, a substantial expanse of impurities are discharged into the seawater, waterways, and ground water owed to hasty industrialization, which results in aquatic effluence [1]. It was projected that the organic dyes were discharged, which had poisonous and mutagenic properties on humanoid and living beings [2]. Thus, the organizations that degrade industrialized wastewater, mostly organic dyes, are presently under study by many researchers. Amongst countless approaches, the use of photocatalytic capability through photocatalysts (PCs) to degrade ecological toxins were deliberated by a prospective method. Semiconductor centred nanomaterials (NMs) have concerned extensive considerations for their latent application in photodegradation of organic impurities in aqueous solutions [3]. Sequences of semiconductors (SCs) were used as PCs materials such as TiO$_2$, SnO$_2$, V$_2$O$_5$, WO$_3$, among ZnO and Cu$_2$O are prominent semiconductor PCs owed to their steady and economic benefits. To overcome the low quantum efficacy of unique photocatalyst intended different types of TiO$_2$ and ZnO NMs, to decline the photo-excited electron-hole (e$^-$/h$^+$) recombination rate. Though, simply exploited UV light, which constrained their wide-ranging application [4–6]. The graphitic carbon nitride (g-C$_3$N$_4$) has a metal-free potential photocatalyst owing to the visible-light reaction and proper bandgap position (~ 2.7 eV), chemical and thermal constancies, and fortunate electronic structure, agreed to the durable covalent bonds amid the nitrogen (N) and carbon (C) atoms [7]. However, a high recombination rate of photo-excited (e$^-$/h$^+$) pairs restricted it's improved photocatalytic performance [8, 9]. So, wide-bandgap SCs could be shared with g-C$_3$N$_4$ to attain upgraded charge separation. The combination of g-C$_3$N$_4$ with other SCs based NCs was arranged and investigated to obtain the enlarged visible-light fascination ability and superior quantum proficiency [10].
Moreover, zinc oxide (ZnO) is one of the broadly used supreme photocatalysis, because of its low-cost, great photosensitivity, and ecologically friendly natured material. Also, the ZnO nanoparticles (NPs), it’s one of the multifunctional semiconducting metal-oxides (MOs), owning extensive bandgap of ~ 3.37 eV and great exciton binding energy of ~ 60 meV [11]. Hence, it reveals photo-responsive over the extensive range, since the UV to the visible region also it increases the visible light absorption capacity which evinced to be the utmost appropriate material for photocatalytic application. For pristine g-C₃N₄, the essential weakness for strong photo-excited e⁻/h⁺ pair's recombination rate can be overcome by pairing with Cu₂O [12]. Among those proper SCs for fabricating heterostructures by g-C₃N₄, Cu₂O has been extensively considered as an efficient co-catalyst united with other effective SCs with wide band-structure owed to its direct bandgap (~ 2.0 eV), abundance, chief visible-light response, high stability, nontoxicity and low-cost [13]. Moreover, by modifying and constructing the suitable interface it helps in photocatalytic evolution to an important extent. Hence they have facilitated photo-electron (e⁻) trapping and hinders the recombination of photo-excited h⁺/e⁻ pairs whereas the augmenting charge separation, but also by prolonging its optical absorption to the visible-light responses [14, 15]. Based the above-mentioned ways, and still to the best of our knowledge, to prepare and study the visible-light energetic enrichment of the ZnO/Cu₂O combination by accumulation g-C₃N₄ NMs. In this work, pristine g-C₃N₄ was initially reformed to good nanostructures by acid treatment and further hydrothermal preparation way, and the ZnO/Cu₂O modified g-C₃N₄ nanostructures (NSs) were used in producing sequences of surface coupled hybrids of g-C₃N₄-ZnO/Cu₂O NCs used as PCs. In this study, a novel and efficient photocatalyst of g-C₃N₄-ZnO/Cu₂O NCs was successfully prepared. The crystal structure, chemical states, and optical properties of the PCs were characterized using various techniques. The photocatalytic activity of the as-obtained PCs was explored by RhB dye photo-degradation under visible-light exposure. Moreover, to auxiliary assess the plausible mechanism was also employed.

2. Materials And Methods

2.1 Materials

Melamine (C₃H₆N₆), copper chloride dihydrate (CuCl₂.2H₂O) and zinc acetate dehydrate were purchased from Merck Chemical Reagent Co., Ltd (India). Ethanol absolute (CH₃CH₂OH), sodium hydroxide (NaOH), acetone (C₃H₆O), Isopropanol (IPA), 1,4-benzoquinone (BQ) and Ethylenediamine-tetraacetic acid (EDTA), L-ascorbic acid (C₆H₈O₆) and Polyvinylpyrrolidone (PVP; K-30) were subscribed from Loba Chemical Reagent Co. Ltd (India). All the as-obtained chemical reagents employed in this study were analytical grade (A.R.) and used without further refinement. Deionized water (D.I.) was used in the experimental progression.

2.2. Preparation of g-C₃N₄-ZnO/Cu₂O NCs

Synthesis of g-C₃N₄: Also, to obtain the g-C₃N₄ powder, an applicable dose of melamine in a crucible was thermally decomposed at 550 °C for 2 h, which was described in many reports [16]. Synthesis of ZnO:
ZnO nanomaterials were made by a one-step described method. Briefly, by dissolving 1.47 g zinc acetate dehydrate, 0.05 g of PVP and 0.5 g of NaOH in 100 mL of D.I. water under stirring for 1 h. Finally, this dried powder sample annealed at 400 °C for 3 h [4], and subjected to ultrasonication for 30 mins and then washed with D.I. water and ethanol several times to get a homogeneous mixture. Lastly, it was further dried at 70 °C for 10 h, to get a ZnO NMs. 

**Synthesis of Cu$_2$O:** In a distinctive synthesis procedure, 0.17 g of CuCl$_2$·2H$_2$O and 0.05 g of PVP were dissolved in 50 mL of D.I. water in a 100 mL beaker and heated to 70 °C, at which stage 10 mL (2 M) of NaOH was added dropwise, also the solution color was reformed into black color [12]. At then by an accumulation of 10 mL of L-ascorbic acid (0.2 M) by dropwise to the mixture and stirred for 1 h, hence the black CuO changes into red color, which authorizes the Cu$_2$O. To conclude, the as-obtained product was located in an oven at 60 °C for 24 h [13].

**Synthesis of g-C$_3$N$_4$/ZnO/Cu$_2$O NCs:** Since, the distinct g-C$_3$N$_4$/ZnO/Cu$_2$O NCs with a represented weight ratio of as-obtained g-C$_3$N$_4$, ZnO and Cu$_2$O (1: 0.2: 0.2) NMs were grinded and mixed, and then annealed with a cover at 450 °C for 2 h., and subjected to ultrasonication for 30 mins and then washed with D.I. water and ethanol several times to get a homogeneous mixture [17]. The synthesis procedure to acquire the g-C$_3$N$_4$/ZnO and g-C$_3$N$_4$/Cu$_2$O NCs related to that of the above-defined process with and without resultant ZnO and Cu$_2$O NMs separately which prominent to highly dispersed composite particles.

**Characterization techniques**

Crystalline structure and phase of the as-obtained product were characterized via powder X-ray diffraction (XRD) by PANalytical X-ray diffractometer. Fourier transform-infrared (FT-IR) spectra of the given samples were tested on a Perkin Elmer spectrometer. Surface morphology, in-depth morphology of nanostructures and elemental compositions were analyzed by ((FE-SEM; Carl - ZEISS instrument) Field emission scanning electron microscopy (attached in energy-dispersive X-ray spectroscopy (EDAX) and mapping analysis) and (HR-TEM; FEI Tecnai G2 20 S-TWIN TEM instrument) high-resolution transmission electron microscopy also. Optical behaviours of the given samples were analyzed using UV-Vis diffuse reflectance spectroscopy (DRS) in Shimadzu 2550 spectrometer. The photoluminescence (PL) spectra were exposed via the Perkin Elmer LS45 spectrometer. UV-Visible spectroscopy (Perkin Elmer Lambda 25) was further used to sense the absorptions of RhB dye degradation.

**Photocatalytic activity for RhB Dye**

Rhodamine B (RhB) is most commonly used by dyeing industries purposes, also will cause severe environmental and biological harms. Hence, the elimination of dye from waste-water is an excessive challenge and a persistent task [18]. Photocatalytic activity of as-synthesized PCs (50 mg) appraised by the photo-degradation of RhB aqueous dye, (30 ppm; 5 mg of RhB dye dissolved in 100 mL of D.I. water) under 500 W halogen lamp equipped with being cutoff filter wavelength for $\lambda>$420 nm was performed with double-walled water-cooled vessel setup. Earlier irradiation, the suspension was placed in the darkroom for 60 min to reach the adsorption-desorption equilibrium between the PCs and dye molecules [12]. After visible-light exposure, the 2.5 mL of aliquots RhB aqueous dye solution was collected at
convinced time intervals (20 min.), then filtered to analyze the concentration of RhB dye using a UV-Vis spectrophotometer by the distinctive absorption peak at the range of ~554 nm [19]. The photo-degradation efficiency of the as-given PCs was further extent as ensuing formula, Efficiency (%) = (C₀ - Cₜ)/C₀*100, where C₀ and Cₜ are the absorbance rate of RhB dye solution earlier and afterwards photo-degradation actions [18,20]. Lastly, over the photo-degradation exercise, the PCs was separated by centrifuge from the reaction mixture and dry to succeed for the reusability assessments.

The scavengers assessments elaborated by trapping mechanism by the photo-degradation approach as, disodium ethylenediaminetetraacetate (EDTA; 0.5 mM), isopropyl alcohol (IPA; 0.5 mM) and (BQ; 0.5 mM) benzoquinone utilized to trap the photo-excited holes (h⁺), hydroxyl radicals (OH˙) and superoxide radicals (˙O₂) consistently [21], and hence to discovery the vibrant reactive species for the photocatalytic association.

3. Results And Discussion

3.1. Characterization of the as-synthesized NMs

XRD analysis was used to study the crystalline phase structures and formation of the g-C₃N₄, g-C₃N₄/ZnO and g-C₃N₄/Cu₂O and g-C₃N₄/ZnO/Cu₂O ternary heterostructure composites, with the outcomes of XRD pattern, were presented in Figure. 1 (a-d). The weak and strongest diffraction peak of the g-C₃N₄ sample (Figure. 1 (a)) corresponds to the (100) and (002) crystal plane (JCPDS No. 87-1526) at 2θ = 13.1° and 27.3° which is a typical inter-layer structured stacking peak of aromatic pieces [22]. The peaks into the g-C₃N₄/ZnO sample (Figure. 1 (b)) was located at 2θ = 31.76°, 34.31°, 36.1°, 47.54°, 56.57°, 62.9°, and 67.82° which related to the (100), (002), (101), (102), (110), (103), and (112) crystal planes of the hexagonal wurtzite structure of ZnO [23], besides its good contract with the standard JCPDS No. 36-1451. XRD diffraction peaks appear at 29.61°, 36.38°, 42.41° and 62.3° consistent to (110), (111), (200) and (220) crystal plane (JPCDS No. 65-3288) [24] reflections of Cu₂O NMs in the g-C₃N₄/Cu₂O heterojunction (Figure. 1 (c)). The XRD pattern of g-C₃N₄/ZnO/Cu₂O heterostructure composite (Figure. 1 (d)) which was included all the typical peaks of g-C₃N₄, Cu₂O and ZnO relatively. Hence, the fairly sharp and narrow diffraction peaks which indicate that the as-obtained NMs had high crystallinity and phase pureness. From the XRD analysis results, indicating the coexistence of g-C₃N₄/ZnO, g-C₃N₄/Cu₂O and the chief g-C₃N₄/ZnO/Cu₂O heterostructures and auxiliary elucidating the effective formation of heterostructures. Also, no other characteristic peaks were observed, which thus confirming the high purity phases of the as-obtained samples.

The structural foundations and interface among the components are further confirmed by the FT-IR spectra. Figure. 2 shows the FT-IR spectra of as-obtained samples. The bands at 1650 – 1250 cm⁻¹ are ascribed to the usual C-N-C (C-N and C = N heterocycles) stretching vibrations of the benzene ring of g-C₃N₄. Whereas those at 1385, 3195 and 3430 cm⁻¹ are due to the C-N bending, terminal -NH₂ and N-H
stretching vibrations (amino-groups), individually [25]. Similarly, the -OH bending and stretching vibrations were appear in the range of 3200–3500 cm\(^{-1}\) recognized to the adsorbed water (H\(_2\)O) on Cu\(_2\)O and ZnO materials. The average peaks in 560–720 cm\(^{-1}\) are consigned to the apt bridging of bending/stretching vibrational mode of Zn-O and Cu-O or Zn/Cu-OH bonds in ZnO and Cu\(_2\)O networks [26]. Hence, the FT-IR results are in mark with those of XRD pattern which indicates the formation of ZnO and Cu\(_2\)O on the surface of g-C\(_3\)N\(_4\) nanostructure. All the g-C\(_3\)N\(_4\) based NCs displays a characteristic absorption peak at 809 and 885 cm\(^{-1}\), which matches to the living modes of tris-triazine ring units and the distortion of N-H structured functional group, separately [27]. It could be seen that the g-C\(_3\)N\(_4\)/ZnO, g-C\(_3\)N\(_4\)/Cu\(_2\)O and g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O heterostructure samples have distinctive interaction absorption peaks for both between Cu\(_2\)O, ZnO and g-C\(_3\)N\(_4\), signifying that the effective construction of the NCs.

The microstructure and surface morphological features of g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O nanocomposite were analyzed FE-SEM and HR-TEM analysis. Typical FE-SEM images of (Figure. 3 (a, b) pristine g-C\(_3\)N\(_4\) NMS exhibits porous-like structured rough morphology [28]. The g-C\(_3\)N\(_4\) composite comprising ZnO/Cu\(_2\)O shows a layered structure/wrapped exfoliated with irregular morphology on the smooth surfaces (Figure. 3 (c-e)), which are ascribed to the metal-oxide phases caused by calcination process [29]. The consistent EDX spectra (Figure. 3 (f)) results of the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O has exposed that the composite material which contains the N, O, C, Cu, and Zn elements, designating that the ZnO/Cu\(_2\)O has been effectively loaded onto the g-C\(_3\)N\(_4\) lattice, specifying the construction of the ternary nanocomposite [30]. The corresponding atomic (at. %) and weight (wt. %) percentage of the as-synthesized nanocomposite is publicized in (inset) Figure. 5(f).

To further demonstrate the structural information of as-obtained g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O nanocomposite is attained by HRTEM images. As shown by HR-TEM images in Figure. 4 (a, b) the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O nanocomposite has aggregated g-C\(_3\)N\(_4\) layered like structure and nano-sized ZnO/Cu\(_2\)O (dark colour) NPs are tightly attached and/or deposited on the surface enclosed [28]. Also, the larger amount of spherical shaped NPs was accumulated on the covered structure of g-C\(_3\)N\(_4\). Similarly, the well-recognized that such heterostructures formed among g-C\(_3\)N\(_4\) and the ZnO/Cu\(_2\)O metal-oxide phase, which might give an intense effect also beneficial for the separation/transfer of photo-excited charge carriers, and could facilitate the enhancement of photocatalytic performance of the composite material [31, 32]. Figure. 4 (d) displays a selected area electron diffraction (SAED) pattern of the g-C\(_3\)N\(_4\), ZnO and Cu\(_2\)O major planes (and also the existing of the ring pattern), which were reserved at the interface of the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O composite [33]. Besides, the spots which are distinct with a match to the (002), (101), and (111) planes of as-given samples.

The optical absorbance properties of the as-obtained materials were deliberated by UV-DRS spectroscopy studies, and the outcomes are revealed in Figure. 5(A). It could be seen that the absorption edge of pristine g-C\(_3\)N\(_4\) displays the photo-absorption at ~ 442 nm in the visible-light region, which was owed to the photo-excitation of an electron from the valence band (VB) of N\(_{2p}\) to the conduction band (CB) of the
C$_2p$ orbital. In contrast, the g-C$_3$N$_4$/ZnO displays the photo-absorption band edge at ~ 448 nm in the visible-light region owing to the proper electron transition of n-$\pi^*$ [34]. Also, the absorption spectrum intensity of g-C$_3$N$_4$/ZnO heterostructures exceeds the most solid visible-light absorption region of ~ 518 nm upon the addition of Cu$_2$O NPs. Additionally, a redshift of the absorption bands for g-C$_3$N$_4$/ZnO/Cu$_2$O composite was observed as an effect of coordination bonds fashioned among Cu, Zn, O, C and N elements [35]. The consequences could clear that the g-C$_3$N$_4$/ZnO/Cu$_2$O ternary nanocomposite have higher visible-light activity than as-synthesized other related g-C$_3$N$_4$, g-C$_3$N$_4$/ZnO and g-C$_3$N$_4$/Cu$_2$O NMs. Instead, these results might be owing to the synergistic correlation amid g-C$_3$N$_4$ and ZnO/Cu$_2$O in the composite which loading to the optimum level [12].

As realized in Figure. 5(B), the resultant optical bandgap of g-C$_3$N$_4$, g-C$_3$N$_4$/ZnO, g-C$_3$N$_4$/Cu$_2$O and the chief g-C$_3$N$_4$/ZnO/Cu$_2$O nanocomposite was calculated by Tauc plot via Kubelka-Munk function and the found values are 2.7, 2.91, 2.28 and 2.42 eV individually. The calculated bandgap value of the g-C$_3$N$_4$/ZnO/Cu$_2$O composite was lower than those observed for g-C$_3$N$_4$ and g-C$_3$N$_4$/ZnO NMs [14, 15]. These outcomes demonstrate that the loading of ZnO/Cu$_2$O on g-C$_3$N$_4$ composite reformed the electronic band structure of the graphitic provision, which became capable to absorb light at higher wavelengths in the visible-light range. It also specifies the upgrading of photo-excited electron-hole ($e^-/h^+$) charge carriers, expands the light utilization efficacy, which results in high responsive photocatalytic activity under visible-light exposure [36]. Moreover, the ability of the low bandgap intercept corresponding to Cu$_2$O has relatively considered since it is the key factor contributing to the photoabsorption progression.

An additional feature of to recognize the photo-recombination of the photo-excited electron-hole ($e^-/h^+$) pairs, which are key contributing aspect in the photocatalytic performance [37]. Also, the probability of photo-excited charge carrier recombination, trapping efficiency, charge transfer/separation process and the migration, PL spectra of the as-obtained PCs were verified. Figure. 6 (A) displays the (excited by the light of ~ 337 nm) PL emission spectrum, g-C$_3$N$_4$ illustrates a high PL intensity, which is expressive of fast recombination of the photo-excited charges. Finally, the PL spectra of conforming to the composites have revealed the superficial reduction in the PL intensity of the g-C$_3$N$_4$/ZnO/Cu$_2$O composite, signifying that the charge carriers are efficiently separated with inhibiting the photo-recombination of the electron-hole ($e^-/h^+$) pairs and hence increasing the lifetime of the species [38]. Further, the interfacial blend between ZnO/Cu$_2$O and g-C$_3$N$_4$ in the effective composite making suitable heterojunction formation was also favourable for the charge separation, thus improving the photocatalytic performance.

**Photocatalytic Properties**

The photo-degradation of RhB dye over the as-prepared g-C$_3$N$_4$/ZnO/Cu$_2$O composite PCs was measured in Figure. 6 (B) for the aqueous solution in the existence of visible-light exposure. The declines in the peak intensity (554 nm) which established the photo-degradation of RhB dye and it has proportionate to the exposure time [38]. The g-C$_3$N$_4$, g-C$_3$N$_4$/ZnO and g-C$_3$N$_4$/Cu$_2$O PCs could 36.4 %, 53 % and 66 % of photo-
degradation activity of the RhB dye in 100 min, despite the less utilization of visible-light response, owing to its high photoelectron-hole \((e^-/h^+)\) pair recombination rate of g-C\(_3\)N\(_4\). As exposed in Figure 7(A), the concentration of RhB does not display in the blank test signifying that the self-degradation of RhB dye is negligible degradation under the identical condition [39]. As expected, the sharp reductions in RhB dye absorbance were detected for the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O composite PCs. The photo-degradation efficiency of RhB dye on the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O composite photocatalyst was greater (91.4 % for 100 min.) than that of other as-obtained catalysts (Figure 7 (A)), owing to the most solid visible-light responsive and their absorption range also. Also, the photoelectron-hole \((e^-/h^+)\) pair recombination rate of g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O composite PCs was the lowest as compared to other as-obtained samples [12].

Besides, the pseudo-first-order kinetic model (Figure 7(B)) of the RhB photo-degradation reaction on the as-obtained PCs were could be defined as \(\ln(C/C_0) = -kt\), where \(k\) signifies the pseudo-first-order kinetic rate constant \((\text{min}^{-1})\), \(C_0\) and \(C\) are the primary concentration and at time \(t\) of the RhB dye, individually [40]. The deceptive rate constant \(k\) of g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O ternary nanocomposite \((0.04796 \text{ min}^{-1})\) which was higher results than the degradation rates of as-obtained pristine g-C\(_3\)N\(_4\) \((0.00744 \text{ min}^{-1})\), g-C\(_3\)N\(_4\)/ZnO \((0.01504 \text{ min}^{-1})\) and g-C\(_3\)N\(_4\)/Cu\(_2\)O \((0.02117 \text{ min}^{-1})\) composite PCs materials respectively. Similarly, the outcomes confirmed that the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O ternary nanocomposite had the greater rate constant, which was 6.44, 3.18 and 2.26 folds more eminent than those of as-obtained for pristine g-C\(_3\)N\(_4\), g-C\(_3\)N\(_4\)/ZnO, and g-C\(_3\)N\(_4\)/Cu\(_2\)O NCs, individually [41]. The correlation coefficient \((R^2)\) ideals of g-C\(_3\)N\(_4\), g-C\(_3\)N\(_4\)/ZnO, g-C\(_3\)N\(_4\)/Cu\(_2\)O and g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O ternary nanocomposite materials originated to be 0.9521, 0.9939, 0.9976 and 0.9647, consistently.

Moreover, the stability of the as-obtained PCs is a critical aspect in relative to large-scale technologies practical application [42]. Also, to assess the stability of the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O ternary photocatalyst, recycling tests were directed on the specified photocatalyst for the photo-degradation of RhB aqueous dye under visible-light exposure. When the recycling progression, the photocatalyst was collected by filtering and then washed by D.I. water with auxiliary dried in an oven at 60°C. The catalytic sample was reused for five succeeding degradations, and the stability outcomes plots are obtained in Figure. 8 (A). The composite photocatalyst preserved a great photocatalytic activity, and the removal rate of RhB dye on the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O composite photocatalyst was 80.2 % after five consecutive recycles. It could be seen that g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O nanocomposite has lost ~ 7.5 to 9.5 % of its primary photocatalytic action (91.4 %) towards the dye after the third to five recycles. Besides, there was a slight reduction in the amount of PCs during the recycling progressions [43]. Thus, the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O composite photocatalyst was revealed outstanding catalytic recycling stability under visible-light exposure.

**Photocatalytic recycling stability**

Hence, to additional evaluate the structural steadiness of the g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O samples were collected after five repeated cycles for XRD and FT-IR testing and whereas compared with the XRD pattern and FT-
IR spectra of the samples for before cycling [44]. Also, the outcomes are accessible in Figure. 9 (A and B). No substantial changes were noticed in the structures and active functional groups of the photocatalyst before and after reused, which specifies that the g-C$_3$N$_4$/ZnO/Cu$_2$O heterostructured photocatalyst was greatly stable. The as-obtained photocatalytic activity of this work was better for with the formerly reported photo-degradation [38, 45–47]. Also, the photocatalytic performance of g-C$_3$N$_4$/ZnO/Cu$_2$O composite photocatalyst was greater when compared to the commercial P25 TiO$_2$ NPs [48]. These consequences also further confirmed that the as-obtained g-C$_3$N$_4$/ZnO/Cu$_2$O composite photocatalyst could be recycling process, which is active in the applied application for the effective photo-degradation in various dyes [49].

A Mechanism For Photocatalytic Dye Degradation

To further inspect the mechanism for the photo-degradation of RhB under visible light exposure, radicals and holes scavenging tests were directed to sense the chief active species in the role of photocatalytic progression. Likewise, OH$^\cdot$, $\cdot$O$_2^-$ and h$^+$ were trap reduced using IPA, BQ and EDTA, separately [50]. The photo-degradation efficiencies of RhB dye on the g-C$_3$N$_4$/ZnO/Cu$_2$O PCs in the existence of relative scavengers are obtainable in Figure. 8 (B). In this existent, the removal efficiency of RhB dye was expressively reduced upon an accumulation of BQ, which signifies that the main effect of $\cdot$O$_2^-$ radicals play an energetic part in RhB degradation process. Equally, the removal efficiency of RhB was not considerably reduced in the occurrence of IPA for OH$^\cdot$ radicals have a minor/essential impact on the photocatalytic action [51]. The photo-degradation efficiency has changed slightly by adding EDTA in this identical process, which implies that photo-holes have a minor influence on the RhB dye photo-degradation process [52].

Based on the photo-degradation outcomes, a possible charge transfer mechanism of g-C$_3$N$_4$/ZnO/Cu$_2$O PCs under visible-light exposure has been proposed based on the energy band structure. The effective SCs VB and CB edge potential could be calculated using the resulting formula of (i) $E_{\text{CB}} = \chi - E_e - 0.5 E_g$; and (ii) $E_{\text{VB}} = E_{\text{CB}} + E_g$. Whereas, $\chi$ signifies the absolute electronegativity of the specified semiconductor (g-C$_3$N$_4$ = $\chi$ ~ 4.72 eV; ZnO = $\chi$ ~ 5.79 eV and Cu$_2$O ~ 5.32 eV), $E_{\text{CB}}$ and $E_{\text{VB}}$ are the edge potentials of CB and VB respectively [53] [54]. Also, while the $E_e$ and $E_g$ are the free electron energy (~ 4.5 eV) on the hydrogen scale and the bandgap energy of the as-given semiconductor [55] ($E_g$ = 2.7, 3.29 and 1.98 eV for g-C$_3$N$_4$, ZnO and Cu$_2$O exclusively. The calculated VB and CB edge potentials were; g-C$_3$N$_4$ is at +1.57 eV and −1.13 eV; ZnO is at +2.935 and −0.355 eV; Cu$_2$O is at +1.81 and −0.17 eV; respectively. Figure. 10 displays the probable band configuration of the g-C$_3$N$_4$/ZnO/Cu$_2$O based photocatalysts.

When exposed to visible-light radiation ($\lambda > 400$ nm) of both g-C$_3$N$_4$ and ZnO/Cu$_2$O could adsorb photons and generate e$^-$/h$^+$ pairs under visible-light exposure [6]. While the photo-excited electrons (e$^-$) will transfer under the influence of an interface charges from g-C$_3$N$_4$ to Cu$_2$O, and the photo-excited (h$^+$) holes
will migrate from the VB of ZnO to the VB of Cu$_2$O. Since both VB of ZnO and Cu$_2$O have very higher than g-C$_3$N$_4$, the photo-excited (e$^-$) of g-C$_3$N$_4$ transfer directly to the CB of the ZnO and then Cu$_2$O surface. Consecutively, the photo-excited h$^+$ of ZnO and Cu$_2$O tend to migrate to the VB of g-C$_3$N$_4$ surface [56]. In contrast, photo-holes of ZnO/Cu$_2$O are inserted into the edge potential is fashioned in the charges, which supports the separation of the photo-excited carriers. Also, common facts that g-C$_3$N$_4$ and ZnO are typical n-type SCs, hence the n-n heterojunction was fashioned at the interface among the g-C$_3$N$_4$/ZnO NMs [57]. According to the edge potential heterojunction of g-C$_3$N$_4$ and ZnO/Cu$_2$O, the photo-excited h$^+$ on the VB of g-C$_3$N$_4$ cannot oxidize the adsorbed H$_2$O molecules into OH' / OH% radicals, since the calculated VB potential of g-C$_3$N$_4$ (+ 1.57 eV vs. NHE) is less positive than the standard redox potential E(H$_2$O/ OH') (+ 2.935 eV vs. NHE). The photo-excited e$^-$ on the CB of N-ZnO cannot diminish the physisorbed O$_2$ molecules into $\cdot$O$_2^-$, since the CB potential of Cu$_2$O (-0.17 eV vs. NHE) is further positive than the standard redox potential of E(O$_2$/ $\cdot$O$_2^-$) (-0.355 eV vs. NHE). Then, the photo-electrons stored in CB of g-C$_3$N$_4$ could respond by molecular oxygen dissolved in the solution to yield the responsive either superoxide radicals (\'O$_2^-$), and then \'O$_2^-$ radicals and h$^+$ are capable to openly oxidize the organic impurities (RhB dye) owing to their great oxidative ability reagents for RhB [45] dye to make it degrade eventually. Thus the synergistic separation of photo-excited e$^-$/h$^+$ pairs could be captured on the g-C$_3$N$_4$ surface of the PCs to yield a variety of reactive oxygen species (ROSs) to effect the desired degradation in the aqueous dye solution [58].

Surveyed by the upstairs discussion, it was resolved that the photocatalytic activity of g-C$_3$N$_4$/ZnO/Cu$_2$O composite semiconductor PCs was considerably upgraded. This was because of the resulting in some cases: (i) hetero-structured nature between g-C$_3$N$_4$ and ZnO/Cu$_2$O have enriched the visible-light absorption belongings, (ii) the synergistic effect from the interfacial charge carries and the matched band structure of g-C$_3$N$_4$ and ZnO/Cu$_2$O could increase the separation rate and also effectually inhibit the recombination of photo-excited charge carriers.

**Conclusion**

In this present study, a novel ternary g-C$_3$N$_4$/ZnO/Cu$_2$O recyclable composite PCs were effectively fabricated by facilely calcination and hydrothermal aided preparation way. Various physicochemical systems were used to indorse the as-obtained NMs by XRD, FT-IR, FESEM, HRTEM, UV-Vis absorption and PL spectroscopy relatively. The g-C$_3$N$_4$/ZnO/Cu$_2$O composite photocatalyst revealed the supreme photocatalytic efficiency of RhB dye was 91.4 % in 100 mins, also the maximum photocatalytic reaction rate, which was 6.4 times higher than that of pristine g-C$_3$N$_4$ NMs relatively. Because it’s owing to the upgraded visible-light absorption belongings causes from the synergistic effect for efficient photo-excited charge separation/transfer ability and diminish the electron-hole recombination also. Moreover, g-C$_3$N$_4$/ZnO/Cu$_2$O nanocomposite catalyst has superb recycling stability towards the photo-degradation of RhB aqueous dye under visible-light exposure. Photocatalytic scavenger test was established that the
\( \cdot O_2^- \% \) has the main active radical species liable for the discolouration of RhB under visible-light exposure. As a consequence, the as-synthesized g-C\(_3\)N\(_4\)/ZnO/Cu\(_2\)O nanocomposite provides a reliable photocatalyst might be used as an environmental application for dye wastewater treatment.

**Declarations**

The authors declared no conflict of interest.

**References**

1. R. He, J. Zhou, H. Fu, S. Zhang, C. Jiang, Appl. Surf. Sci. 430, 273 (2018)
2. F. Raziq, C. Li, M. Humayun, Y. Qu, A. Zada, H. Yu, L. Jing, Mater. Res. Bull. 70, 494 (2015)
3. Z. Zhang, X. Li, H. Chen, G. Shao, R. Zhang, H. Lu, Materials Research Express 5, 15021 (2018)
4. P. Yang, J. Wang, G. Yue, R. Yang, P. Zhao, L. Yang, X. Zhao, D. Astruc, J. Photochem. Photobiol., A 388, 112169 (2020)
5. R. Fagan, D. McCormack, S. Hinder, S. Pillai, Materials 9, 286 (2016)
6. D.O. Adekoya, M. Tahir, N.A.S. Amin, Journal of CO2 Utilization 18, 261 (2017)
7. W.J. Ong, L.L. Tan, Y.H. Ng, S.T. Yong, S.P. Chai, Chem. Rev. 116, 7159 (2016)
8. A. Mishra, A. Mehta, S. Basu, N.P. Shetti, K.R. Reddy, T.M. Aminabhavi, Carbon 149, 693 (2019)
9. F. Raziq, M. Humayun, A. Ali, T. Wang, A. Khan, Q. Fu, W. Luo, H. Zeng, Z. Zheng, B. Khan, H. Shen, X. Zu, S. Li, L. Qiao, Appl. Catal. B 237, 1082 (2018)
10. S. Sun, M. Sun, Y. Kong, F. Liu, Z. Yu, S. Anandan, C. Chang, Journal of Materials Science 52, 1183 (2017)
11. Z. Wu, X. Chen, X. Liu, X. Yang, Y. Yang, Nanoscale Res. Lett. 14, 147 (2019)
12. H. Liu, X. Zhu, R. Han, Y. Dai, Y. Sun, Y. Lin, D. Gao, X. Wang, C. Luo, New J. Chem. 44, 1795 (2020)
13. X. Yan, R. Xu, J. Guo, X. Cai, D. Chen, L. Huang, Y. Xiong, S. Tan, Mater. Res. Bull. 96, 18 (2017)
14. H. Li, Y. Gao, X. Wu, P.H. Lee, K. Shih, Appl. Surf. Sci. 402, 198 (2017)
15. S. Liu, J. Chen, D. Xu, X. Zhang, M. Shen, J. Mater. Res. 33, 1391 (2018)
16. Y. Deng, L. Tang, C. Feng, G. Zeng, J. Wang, Y. Zhou, Y. Liu, B. Peng, H. Feng, J. Hazard. Mater. 344, 758 (2018)
17. S. Obregón, Y. Zhang, G. Colón, Appl. Catal. B 184, 96 (2016)
18. D. Zhang, S. Cui, J. Yang, J. Alloy. Compd. 708, 1141 (2017)
19. Y. Yao, Y. Cai, F. Lu, J. Qin, F. Wei, C. Xu, S. Wang, Ind. Eng. Chem. Res. 53, 17294 (2014)
20. Y. Feng, Y. Wang, M. Li, S. Lv, W. Li, Z. Li, Appl. Surf. Sci. 462, 896 (2018)
21. Y. Li, Y. Li, S. Ma, P. Wang, Q. Hou, J. Han, S. Zhan, J. Hazard. Mater. 338, 33 (2017)
22. H. Gao, Y. Liu, L. Wang, J. Zhu, S. Gao, X. Xia, Res. Chem. Intermed. 45, 3687 (2019)
23. S. Kumar, A. Kumar, A. Kumar, R. Balaji, V. Krishnan, ChemistrySelect 3, 1919 (2018)
24. Z. Min, X. Wang, Y. Li, J. Jiang, J. Li, D. Qian, J. Li, Mater. Lett. 193, 18 (2017)
25. D. Monga, S. Basu, Adv. Powder Technol. 30, 1089 (2019)
26. B. Liu, X. Han, Y. Wang, X. Fan, Z. Wang, J. Zhang, H. Shi, J. Mater. Sci.: Mater. Electron. 29, 14300 (2018)
27. M. hong Wu, L. Li, Y. cheng Xue, G. Xu, L. Tang, N. Liu, W. yuan Huang, Applied Catalysis B: Environmental 228, 103 (2018)
28. M. Gao, J. Feng, Z. Zhang, M. Gu, J. Wang, W. Zeng, Y. Lv, Y. Ren, T. Wei, Z. Fan, ACS Applied Nano Materials 1, 6733 (2018)
29. S.P. Adhikari, G.P. Awasthi, J. Lee, C.H. Park, C.S. Kim, RSC Advances 6, 55079 (2016)
30. B. Zhang, Q. Wang, J. Zhuang, S. Guan, B. Li, J. Photochem. Photobiol., A 362, 1 (2018)
31. N. Jiang, H. Geng, Y. Qiao, X. Zhu, C. Li, Q. Cai, New J. Chem. 44, 2303 (2020)
32. X. Xiao, J. Wei, Y. Yang, R. Xiong, C. Pan, J. Shi, ACS Sustainable Chemistry and Engineering 4, 3017 (2016)
33. Q. Tang, X. Meng, Z. Wang, J. Zhou, H. Tang, Appl. Surf. Sci. 430, 253 (2018)
34. A. Akhundi, A. Habibi-Yangjeh, RSC Advances 6, 106572 (2016)
35. Q. Wang, J. Tian, L. Wei, Y. Liu, C. Yang, Opt. Mater. 101, 109769 (2020)
36. D. Jiang, H. Yu, H. Yu, E. Physica, Low-Dimensional Systems and Nanostructures 85, 1 (2017)
37. X. Wang, W. Mao, J. Zhang, Y. Han, C. Quan, Q. Zhang, T. Yang, J. Yang, X. Li, W. Huang, J. Colloid Interface Sci. 448, 17 (2015)
38. T. Fan, C. Chen, Z. Tang, Y. Ni, C. Lu, Mater. Sci. Semicond. Process. 40, 439 (2015)
39. K. Saravanakumar, R. Karthik, S.M. Chen, J. Vinoth Kumar, K. Prakash, V. Muthuraj, J. Colloid Interface Sci. 504, 514 (2017)
40. P.C. Nagajyothi, T.V.M. Sreekanth, R. Ramaraghavulu, K.C. Devarayapalli, K. Yoo, S.V.P. Vattikuti, J. Shim, J. Mater. Sci.: Mater. Electron. 30, 14890 (2019)
41. X. Rong, F. Qiu, Z. Jiang, J. Rong, J. Pan, T. Zhang, D. Yang, Chem. Eng. Res. Des. 111, 253 (2016)
42. Y. Su, P. Chen, F. Wang, Q. Zhang, T. Chen, Y. Wang, K. Yao, W. Lv, G. Liu, RSC Advances 7, 34096 (2017)
43. C. Liu, L. Wang, H. Xu, S. Wang, S. Gao, X. Ji, Q. Xu, W. Lan, Mater. Lett. 164, 567 (2016)
44. J. Zeng, T. Song, M. Lv, T. Wang, J. Qin, H. Zeng, RSC Advances 6, 54964 (2016)
45. G.R. Surikanti, P. Bajaj, M.V. Sunkara, ACS Omega 4, 17301 (2019)
46. L. Qiu, Z. Zhou, M. Ma, P. Li, J. Lu, Y. Hou, X. Chen, S. Duo, Materials 12, 3948 (2019)
47. Z. Zhu, M. Murugananthan, J. Gu, Y. Zhang, Catalysts 8, 112 (2018)
48. H. Liu, Z.G. Zhang, H.W. He, X.X. Wang, J. Zhang, Q.Q. Zhang, Y.F. Tong, H.L. Liu, S. Ramakrishna, S.Y. Yan, Y.Z. Long, Nanomaterials 8, 842 (2018)
49. W. Liang, G. Tang, H. Zhang, C. Li, H. Li, H. Tang, Mater. Technol. 32, 675 (2017)
50. W.K. Jo, S. Kumar, S. Eslava, S. Tonda, Appl. Catal. B 239, 586 (2018)
51. X.N. Wei, H.L. Wang, J. Alloy. Compd. 763, 844 (2018)
52. H. Zhang, W. Wu, Y. Li, Y. Wang, C. Zhang, W. Zhang, L. Wang, L. Niu, Appl. Surf. Sci. 465, 450 (2019)
53. W. Zhao, Z. Wei, H. He, J. Xu, J. Li, S. Yang, C. Sun, Appl. Catal. A 501, 74 (2015)
54. I.M. Sundaram, S. Kalimuthu, G.P. Ponniah, Composites Communications 5, 64 (2017)
55. B. Liu, X. Han, Y. Wang, X. Fan, Z. Wang, J. Zhang, H. Shi, J. Mater. Sci.: Mater. Electron. 29, 14300 (2018)
56. Y. Wang, X. Liu, C. Zheng, Y. Li, S. Jia, Z. Li, Y. Zhao, Advanced Science 5, 1700844 (2018)
57. X. Jia, R. Dai, Y. Sun, H. Song, X. Wu, J. Mater. Sci.: Mater. Electron. 27, 3791 (2016)
58. A. Mitra, P. Howli, D. Sen, B. Das, K.K. Chattopadhyay, Nanoscale 8, 19099 (2016)