

Eco-friendly recovery of ZnO from alkaline batteries for photocatalytic water treatment

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Abstract. One viable solution to the present material shortages is the transformation of old electronics. Through eco-friendly and facile methods, our work demonstrates that old alkaline batteries can be transformed into effective zinc oxide materials. This method promotes a regenerative economic model that can satisfy the rising demand for high-tech materials while simultaneously reducing the negative effects of waste management. Even though reaction durations gradually increased due to surface fouling, ZnO-C₃N₄ demonstrated excellent long-term durability across four successive photocatalytic cycles. It was able to successfully remove over 99.3 % of methylene blue (MB) and over 99 % of crystal violet (CV). This was accomplished despite the fact that surface fouling caused the reaction times to gradually increase. The pH levels had a significant impact on the function of the catalyst, with degrading efficiency increasing from acidic to alkaline conditions. The catalyst reached its greatest effectiveness between pH 9 and 11, when it was able to remove nearly all of both dyes (99.47 to 99.81 % for MB and 99.21 to 99.6 % for CV). These findings underscore the strong reusability and pH adaptability of ZnO-C₃N₄. This study reveals that ZnO-C₃N₄ is a promising application for water remediation, especially dye waste.

Keywords: spent alkaline battery recycling, ZnO nanomaterials, photocatalysis, waste valorization, environmental remediation.

Classification numbers: 1.4, 2.4, 2.5, 2.7.

1. INTRODUCTION

Currently, civilization facing an energy dilemma resulting from the exhaustion of natural resources and global warming primarily caused by electronic waste. Electronic waste refers to electronic devices that have been disposed of and are no longer functional. These devices generally retain precious materials; nonetheless, they are frequently disposed of without undergoing reuse or recycling. The annual increase of electronic waste is attributed to the ongoing trend of innovation in electronic devices, as outdated technologies are supplanted by

more sophisticated models tailored to societal and human requirements. Concerns regarding the excessive quantity of waste being thrown away are raised by this ongoing consumption. Each year, more than 80 billion units of electronic garbage are discarded, and only a fraction of them are recycled [1, 2]. Batteries serve as the principal power source for several devices and constitute a major contributor to overall electronic trash production. The heightened demand for batteries has resulted in a significant quantity of batteries being improperly disposed of in the environment. Efforts to effectively control and manage electronic trash have been constrained by insufficient accountability and the economic feasibility of recycling facilities. A significant percentage of wasted batteries is deposited in landfills and waste sites, where their hazardous constituents are released into the environment such as zinc and manganese, doing considerable damage to ecosystems and human health [3]. At the same time, there is a worldwide demand for novel materials to combat water pollution brought on by pharmaceuticals, dyes, and industrial effluents has increased the importance of finding solutions that are environmentally friendly. This double issue emphasizes the need for waste valorization strategies that promote environmental remediation solutions by using the useful resources from spent batteries like zinc oxide (ZnO) [4–6]. The ecological impact of these common power sources is greatly reduced by efficient collection and recycling systems, which not only reduce soil and water contamination but also recover up to 90% of battery metals for future use [7, 8]. On the other hand, recovering ZnO from spent batteries offers a substantial economic advantage over purchasing commercial ZnO. Additionally, the discharge of dyes from a variety of businesses is the most significant contributor to the formation of waste water through water pollution. Many different businesses are responsible for the pollution of water, including the mining industry, the pharmaceutical industry, and the textile industry. Because it releases chemicals, dyes, and untreated wastewater, the textile sector in particular is a significant polluter [9, 10]. Basic dyes like methylene blue (MB) and crystal violet (CV) are utilized in biological staining and textiles [11]. Nevertheless, CV and MB are resistant to traditional degrading techniques, present health and environmental hazards, and remain stable under extreme circumstances [12]. Taking into consideration the requirement for efficient removal, a number of different approaches, including chemical, physical, and biological practices, have been put into practice [13]. Photocatalysis distinguishes out from other processes because to its ease of use, lack of secondary pollution, and capacity to be recycled [14, 15].

Alkaline batteries constitute a form of electronic waste that contains valuable materials, including manganese oxide (positive electrode) and zinc (negative electrode), as well as additional components such as potassium hydroxide electrolyte, separators, and current collectors, which facilitate the generation of electrical energy. In the discharge process, zinc converts into zinc oxide (ZnO), and manganese dioxide converts to manganese (III) oxide, while electric current is produced by the flow of electrons from the zinc electrode to the manganese dioxide electrode via the external circuit [16]. An other critical concern is that the disposal of alkaline batteries in landfills can lead to the breaking of their steel casings due to moisture and acidic conditions, resulting in the release of a highly alkaline liquid that affects soil pH and mobilizes heavy metals. This liquid then leaches into groundwater and surface waters, posing long-term risks to aquatic ecosystems and drinking water supplies. Fine particle pieces from corroding wasted cells can be carried by rain runoff and bioaccumulate in food chains, where even low quantities of heavy metals are neurotoxic and carcinogenic to wildlife and humans. Incineration or open burning of mixed garbage emits hazardous vapors and particulate-bound metals into the environment, contributing to respiratory dangers and air pollution. Additionally, the amount of alkaline batteries entering waste streams is expected to be in the billions per year in developed countries. Because recycling rates for alkaline cells

continue to be below 20 % in many regions, enormous quantities of zinc, manganese, and steel that are recoverable are lost each year. This forces manufacturers to extract virgin materials, which in turn exacerbates the depletion of resources and the carbon emissions that are associated with mining and refining.

The unique strategy of repurposing spent alkaline batteries to remove dyes from industrial effluent yields waste valorization by recovering zinc and manganese oxides from discarded cells, this method not only diverts hazardous battery components from landfills-thereby mitigating heavy-metal leaching and soil contamination, but also exploits their strong redox reactivity to degrade complex dye molecules in textile wastewater. The use of advanced oxidation processes, often known as AOPs, is an alternate method that can be utilized to reduce the contamination potential of pharmaceuticals and other contaminants [17]. The formation of powerful oxidizing species, most notably the hydroxyl radical ($\bullet\text{OH}$) and the superoxide radical ($\bullet\text{O}_2^-$), is important to the functioning of these processes, which are responsible for the degradation of contaminants. Through the utilization of these highly reactive radicals, advanced organic pollutants (AOPs) are able to effectively degrade pollutants, so making a contribution to the remediation of environmental pollutants and supporting a more sustainable approach to the control of pollution. A semiconductor that is capable of absorbing photons and generating reactive sites that promote the degradation of a variety of pollutants is the defining characteristic of heterogeneous photocatalysis, which is one of the applied optical phenomena (AOPs). According to a number of research, heterogeneous photocatalysis has been a versatile and promising option to trash disposal and environmental matrix remediation [18, 19]. These studies have sought to accomplish economic and environmental viability in heterogeneous photocatalysis by employing solar radiation and waste as inputs. A major improvement in the process's sustainability might be achieved through the synthesis of photocatalysts from electro-electronic waste (e-waste), such as post-consumer alkaline batteries. This would result in a reduction in the costs associated with commercial reagents and an efficient disposal solution for waste items of this kind.

Zinc oxide (ZnO), silver (Ag), and graphitic carbon nitride (g-C₃N₄) have each garnered considerable attention as photocatalytic materials owing to their complementary physicochemical properties, which collectively enhance charge separation, extend light absorption, and improve reactive species generation. ZnO exhibits a wide bandgap (~3.2 eV) and high exciton binding energy, conferring excellent photostability, abundant surface oxygen vacancies, and strong oxidative potential, all of which facilitate efficient generation of hydroxyl radicals under ultraviolet irradiation. Noble-metal Ag nanoparticles, when interfaced with semiconductor matrices, act as electron sinks via localized surface plasmon resonance, enabling visible-light harvesting while suppressing electron/hole recombination; moreover, Ag clusters introduce Schottky barriers at the metal-semiconductor junction, further promoting interfacial charge transfer and prolonging charge-carrier lifetimes. Graphitic carbon nitride, in contrast, possesses a moderate bandgap (~2.7 eV) suitable for absorption in the visible spectrum, abundant tri-s-triazine units that facilitate facile heterojunction formation, and intrinsic nitrogen lone pairs that serve as active sites for molecular oxygen activation. When these three components are synergistically combined, ZnO provides robust oxidative capacity, Ag nanoparticles enhance visible-light utilization and charge separation, and g-C₃N₄ broadens the light-absorption range while furnishing a conjugated framework for rapid electron mobility [17]. This triadic integration yields heterostructured photocatalysts with markedly superior quantum efficiencies, enhanced photogenerated reactive oxygen species production, and

prolonged operational stability, making them highly advantageous for the degradation of persistent organic pollutants and water-splitting applications [20–22].

Numerous metal oxides, such as zinc oxide (ZnO), iron (III) oxide (Fe_2O_3), titanium dioxide (TiO_2), tungsten trioxide (WO_3), zirconia (ZrO_2), and vanadium oxide (V_2O_5), have been studied as heterogeneous photocatalysts for wastewater treatment since 1972 [23]. Due to its exceptional photosensitivity, good pyroelectric and piezoelectric properties as a result of its shape and size, and its potential for simple synthesis using a variety of scalable methods, zinc oxide (ZnO) has demonstrated tremendous promise in recent years among these semiconductors. Zinc oxide also possesses characteristics such as chemical stability, biocompatibility, and a strong ability to withstand oxidation, as well as photocatalytic performance that is considered to be acceptable. However, the unusually wide bandgap (which is around 3.37 eV) necessitates the employment of ultraviolet light, rapid recombination of electron-hole pairs, and low resistance to photocorrosion, all of which make practical use of these materials difficult. The performance of ZnO has been improved thus far using a variety of techniques, such as ion doping, composites, metal loading, coupling with semiconductors, structural design enhancements, and combining it with carbon materials, all in an effort to create visible light-driven photocatalysts or prolong the lifetime of photo-generated electron-hole pairs. By incorporating these recovered ZnO materials into photocatalytic systems for dye degradation and epoxy composites for structural purposes, it is shown that they perform comparably to commercially available substitutes [24, 25]. Particularly noteworthy is the fact that altering ZnO with carbon nitride (g- C_3N_4) or silver (Ag) improves its photocatalytic activity by reducing the occurrence of charge recombination and expanding light absorption into the visible spectrum. In particular, heterostructures material such as ZnO-Ag and ZnO- C_3N_4 have demonstrated superior application potential in wastewater treatment, dye degradation, and the decomposition of toxic organic compounds [26, 27].

2. METHODS & EXPERIMENT

2.1. Chemicals and materials

2.1.1. Chemicals

Ethanol ($\text{C}_2\text{H}_5\text{OH}$), Methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$), Crystal violet ($\text{C}_{25}\text{H}_{30}\text{ClN}_3$), Silver nitrate (AgNO_3), Urea ($\text{CH}_4\text{N}_2\text{O}$, 99 %, Merck), distilled water. These chemicals have all been utilized in the process of synthesis.

2.1.2 Materials

AA-type alkaline batteries that were no longer functioning were collected from a variety of different household sources. To ensure handling safety, all batteries were completely drained prior to disassembly. To remove the substance inside the batteries, the cutting tool will cut the steel shell. The substance consists of a primary white powder, a black powder, and a small amount of electrolyte liquid potassium hydroxide (KOH). The white powder will then be extracted from the batteries. White powders will be the main subject of this effort and will be altered for additional testing.

2.2. Synthesis of ZnO/Ag

2.2.1. Preparation of ZnO

To obtain a fine particle consistency, the powders that are produced after the white powder has been extracted from the batteries should be ground with a mortar and pestle until the desired consistency is reached. The powdered substance must then be mixed with a solvent mixture of ethanol and water in a volumetric ratio of 1:4 and sonicated for 20 minutes. Thereafter, the substance needs to be purified and rinsed several times with distilled water until the pH is between 7 and 8. The final step in the process involves drying the material that has been purified to get it ready for further processing [16].

2.2.2. Synthesis of Ag intergated ZnO (ZnO/Ag)

The ZnO-Ag material was performed by using the chemical and calcination modification method. The process involved first soaking ZnO in an AgNO_3 solution to adsorb Ag^+ ions, using ethanol as the dispersion phase, and then reheating it to fix Ag on the ZnO surface, resulting in the creation of ZnO-Ag material. In detail, a 50 mM AgNO_3 solution was prepared and dispersed in 10 ml of ethanol. The AgNO_3 solution was subsequently stirred magnetically for 2 hours after 400 mg of the previously desiccated ZnO was added. Subsequently, the mixture was centrifuged at 8000 rpm for 10 minutes. Finally, the resultant ZnO-Ag composite was dried at 60 °C and then calcined at 450 °C for 5 hours to eliminate any organic impurities [28].

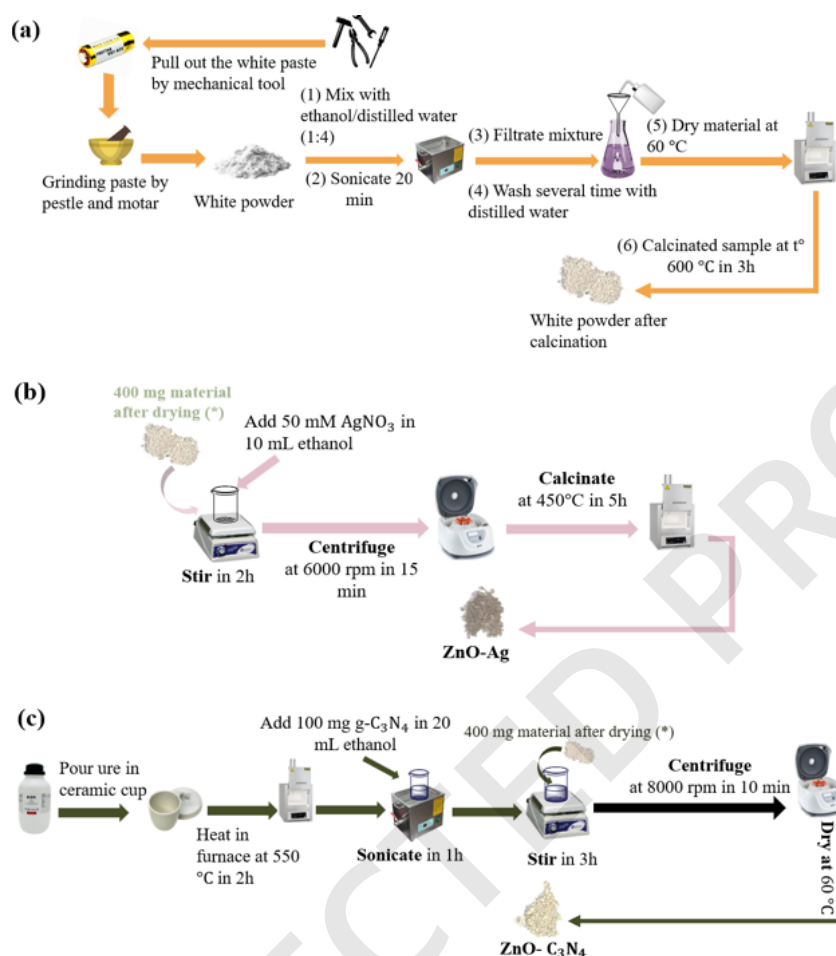
2.3. Synthesis of ZnO- C_3N_4

The process of preparing g- C_3N_4

The creation of graphitic carbon nitride (g- C_3N_4) was accomplished by means of the thermal polycondensation of urea. To mitigate mass loss during the heating process, an exact quantity of urea was meticulously deposited in a ceramic crucible that was covered. Subsequently, the crucible was positioned in a muffle furnace and heated to 550 °C at a rise rate of 10 °C/min. The temperature was maintained for a period of two hours to ensure that the polymerization and thermal decomposition were completed in their entirety. The resulting yellow powder was collected, rinsed with distilled water to remove any remaining impurities, and subsequently dried at 60 °C after natural cooling to ambient temperature. The composite was prepared by precisely grinding the final g- C_3N_4 powder into particles [17].

The g- C_3N_4 modification of ZnO

The process was conducted by wet impregnation combined with thermal treatment method to modify the characterization of material. A homogeneous dispersion was achieved by mixing 100 mg of synthesized g- C_3N_4 with 20 mL of ethanol and then ultrasonically treating the mixture for an hour. After that, 400 mg of dried ZnO powder, which was recovered from used batteries, was gradually added to the g- C_3N_4 suspension while it was being continuously agitated magnetically for three hours at room temperature. This was done in order to enhance robust interfacial contact and composite synthesis. The solid product was isolated by centrifuging the suspension at 8000 rpm for 10 minutes. The ZnO- C_3N_4 composite was subsequently dried in an oven at 60 °C for photocatalytic testing and characterization (Scheme 1).



Scheme 1. Photocatalyst synthesis schematic: (a) ZnO preparation from spent alkaline batteries using ethanol and distilled water, filtration, drying, and calcination; (b) ZnO-Ag composite synthesis with silver nanoparticles, stirring, centrifugation, and calcination; and (c) ZnO- C_3N_4 composite fabrication with ethanol, sonication, stirring, centrifugation, and drying.

2.4. Photocatalytic experiments

Photocatalysis is one of the wastewater treatment methods belonging to the group of advanced oxidation processes (AOPs). The characterization techniques used in this work is UV–Vis spectrophotometry, which was the principal characterization technique employed to monitor pollutant degradation and quantify dye removal. A double-beam UV–Vis spectrometer equipped with quartz cuvettes was used to record absorbance spectra from 200 nm to 800 nm. Prior to photocatalysis tests, the maximum absorbance wavelengths (λ_{max}) for crystal violet and methylene blue were determined by scanning standard dye solutions.

A specialized apparatus was utilized with the intent to evaluate the photocatalytic performance of the solution that was prepared and contained the organic pollutant. A magnetic stirrer and a 60W Luminus L4X were included in this system. The experiment started with the introduction of 200 mg of catalyst into 50 mL of an aqueous solution containing 10 ppm of crystal violet and methylene blue. Subsequently, the catalyst surface was subjected to adsorption equilibrium by stirring the mixture in darkness for thirty mins. The solution was

measured after dark with a UV-Vis spectrometer by withdrawing 3 mL samples. After that, the Luminus visible light lamp was turned on, and the light source was aligned to be directly exposed to the dye solution. Similar to the process of stirring the mixture in the dark, with 3 mL samples being withdrawn at half-hour intervals, the degradation procedure was conducted continuously for 270 minutes. The catalyst particles were filtered from the suspension using nylon syringe filters following extraction, which was conducted during the whole process. Lastly, the solution after filtrating was measured using a UV-Vis spectrometer. The absorbance A_t at $\lambda_{\max}$ was recorded for each time point.

The percentage of dye pollution that is removed is determined by the following equation:

$$\text{Dye removal percent} = \frac{A_0 - A_t}{A_0} \times 100$$

where, A_0 and A_t denote the absorbance measured at the beginning and absorbance observed at a specific time, respectively.

2.5. Battery materials characterization

Fourier Transform Infrared Spectroscopy (FTIR): After the powder samples have been freeze-dried, take a small portion of them and place it directly between two support plates that do not contain any desiccant material (such as KBr or NaCl). The FTIR spectrum was recorded using an FTIR spectrophotometer. This technique show the results for the shift of band of FTIR for ZnO and the exhibition of metal oxides after calcination.

UV-Vis Absorption: The absorption peaks from the UV-Vis spectra of the solution when a catalyst is added and the reaction is exposed to light over time, as determined by the organic dye degradation experiments, are calculated by recording the characteristic maximum absorption of the pollutants.

X-ray diffraction (XRD): Using Cu K α 1 radiation that had been monochromatized with a wavelength of $\lambda = 1.5406 \text{ \AA}$, an automated X-ray diffractometer operating in continuous-scanning 2 θ mode with a voltage of 40 kV and a current of 30 mA was used to generate the XRD patterns of the particles. Demonstrate the characteristic diffraction peaks of g-C₃N₄ and Ag, which clarify the successful modification of the material.

3. RESULTS & DISCUSSION

3.1. Physicochemical properties of nanomaterials

Fourier Transform Infrared Spectra (FTIR)

The heat treatment of ZnO that is obtained from used alkaline batteries results in significant modifications to the FTIR spectra of the material. These modifications are a reflection of the removal of adsorbed species as well as the reorganization of surface and lattice structures. During the process of recovering ZnO from alkaline batteries, the surface of zinc oxide readily adsorbs water molecules and forms Zn-OH bonds. Consequently, the unheated sample exhibits intense absorption bands at approximately 677 cm⁻¹ and 788 cm⁻¹, which are a result of Zn-O lattice vibrations coupled with bending modes of surface hydroxyl groups [29, 30]. The asymmetric stretching of carbonate anions CO₃²⁻ is responsible for the sharp and noticeable band that can be observed at a frequency of 1002 cm⁻¹. This band is a result of the

reaction between the alkaline KOH electrolyte and ambient CO₂ that occurs throughout the process of battery discharge and storage [31]. Further absorptions at 1137 and 1253 cm⁻¹ are associated with the deformation vibrations of adsorbed alkali metal carbonate. On the other hand, large bands centered at 2354, 2953, and 3014 cm⁻¹ are indicative of physisorbed carbon dioxide and the C–H stretching vibrations of trace organic pollutants.

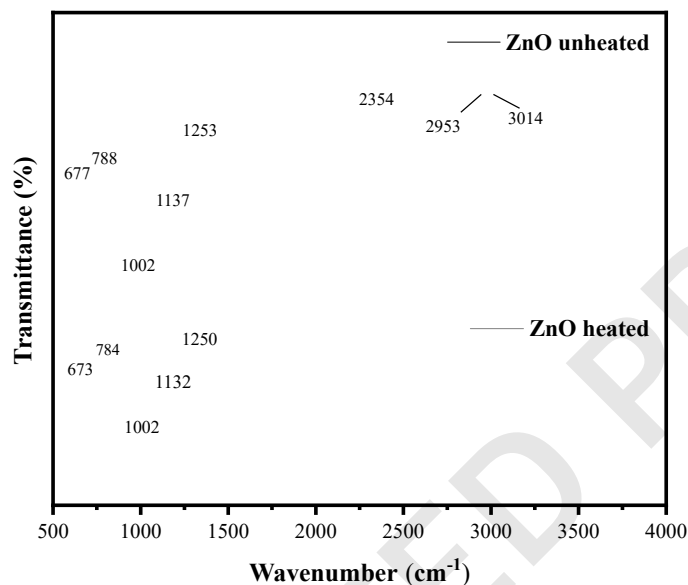


Figure 1. The FTIR spectra of ZnO unheated and heated material from Alkaline Batteries demonstrate the structural features and characteristic functional groups of each material.

The FTIR spectrum endures distinct transformations when heated. The intensity of the hydroxyl-related bands at 677 and 788 cm⁻¹ decreases significantly and marginally shifts to 673 and 784 cm⁻¹, respectively, indicating dehydroxylation of the ZnO surface. The complete eradication of loosely bound organic residues is demonstrated by the complete disappearance of the high-frequency C–H stretching bands (2953 cm⁻¹ and 3014 cm⁻¹). Simultaneously, the heated sample retains the carbonate-associated peak at 1002 cm, albeit with a reduced intensity. This suggests that the firmly bound carbonate anions can withstand complete thermal breakdown under the applied circumstances [34]. As surface anions are largely eliminated and the ZnO lattice achieves more crystallinity, the peaks at 1137 and 1253 cm⁻¹ also experience small downshifts to 1132 and 1250 cm⁻¹. These downshifts are a reflection of subtle changes in bond environment. The cumulative effect of these spectrum changes, which range from peak attenuation and disappearance to marginal wavenumber shifts, demonstrates that heat treatment is effective in removing physisorbed moisture and organic pollutants, while also showing the resilience of electrolyte-derived anions.

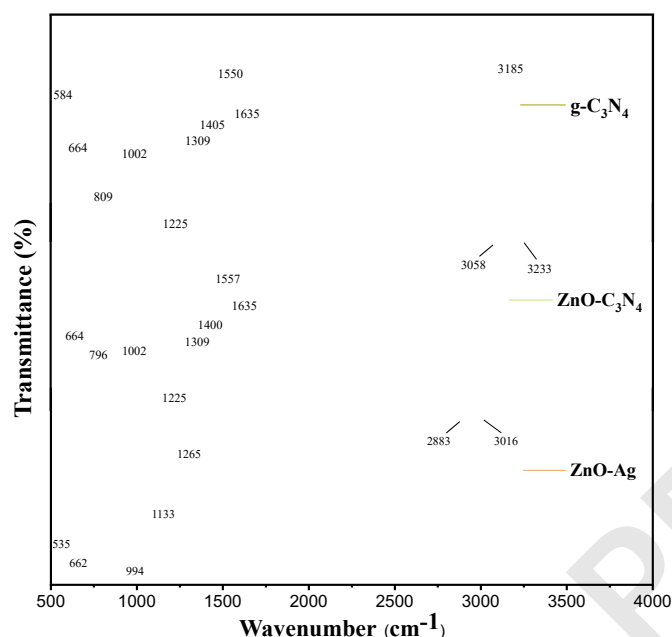


Figure 2. FTIR spectra of g-C₃N₄, ZnO-C₃N₄, and ZnO-Ag materials, illustrating the characteristic functional groups and structural characteristics of each material following modification.

The vibrational signatures of pristine graphitic carbon nitride (g-C₃N₄), the ZnO-C₃N₄ composite, and the ZnO-Ag are varied in the FTIR spectra, which are indicative of their distinct chemical architectures and surface functionalities. The out-of-plane bending mode of tri-s-triazine units is represented by the sharp band at 662 cm⁻¹ in the g-C₃N₄ spectrum. The stretching vibrations of C-N heterocycles and the symmetric and asymmetric modes of C=N bonds within the heptazine network are represented by the series of peaks at 1225, 1309, 1405, 1550, and 1635 cm⁻¹ [32]. A large absorption at 3185 cm⁻¹ is further indication that the N-H stretching of terminal amine groups that are inherent to g-C₃N₄ is occurring. Upon the integration of ZnO onto the g-C₃N₄ framework, the characteristic g-C₃N₄ bands at 1557, 1635 cm⁻¹ (C=N), and 1309 cm⁻¹ (C-N stretches) are retained in the ZnO-C₃N₄ spectrum. Nevertheless, the intensity attenuation and minor shifts are weak, suggesting that electronic interactions and partial charge transfer between ZnO and the conjugated g-C₃N₄ matrix are present. Notably, the ZnO-C₃N₄ composite exhibits emergent absorptions at 3058 and 3233 cm⁻¹, which can be attributed to O-H stretching from surface-adsorbed hydroxyls on ZnO and residual -NH species, respectively. Additionally, a subtle band at 796 cm⁻¹ is observed, which corresponds to Zn-O lattice vibrations interacting with the carbon nitride substrate [32, 33]. Additionally, the FTIR of the ZnO-Ag composite exhibits absorptive features at 535 and 662 cm⁻¹ in comparison to the profiles of ZnO unheated and heated samples. These features may be attributed to Ag-O interactions or altered ZnO lattice distortions caused by the presence of silver nanoparticles. The presence of Ag-O and Zn-O bonds was found at around 470 and 719.45 cm⁻¹ of which indicates the stretching mode for the absorption band, reported in [34]. Further, the C-H stretching bands at 2883 and 3016 cm⁻¹, in conjunction with the emergent peaks at 994, 1133, 1225, and 1265 cm⁻¹, suggest a complicated interaction between silver deposition and surface-bound organic residues. This suggests that the vibrational landscape of ZnO can be modulated by silver incorporation [35, 36].

XRD Spectra

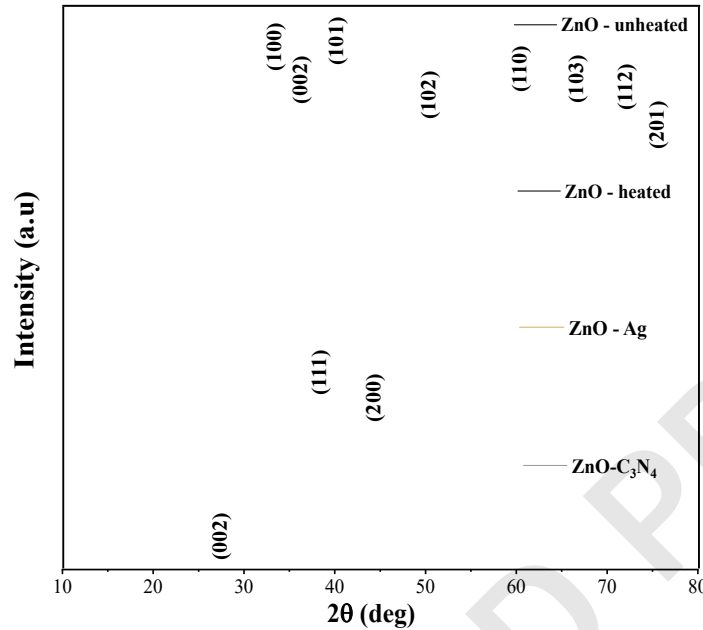


Figure 3. The XRD patterns of ZnO-Ag, ZnO-C₃N₄, and ZnO-unheated samples demonstrate the effective incorporation of Ag and g-C₃N₄ into the ZnO matrix, along with the crystalline phases.

X-ray diffraction (XRD) patterns of zinc oxide (ZnO) and its nanocomposites exhibit particular crystallographic properties that are significantly changed by thermal treatment and compositional alterations. These characteristics contribute to the uniqueness of the XRD patterns. Pristine ZnO nanoparticles exhibit the characteristic hexagonal wurtzite crystal structure, regardless of whether they are unheated or as-synthesized. They exhibit prominent diffraction peaks at 31.82°, 34.46°, 36.3°, 47.58°, 56.66°, 62.92°, 68.04°, and 69.18°, which correspond to the (100), (002), (101), (102), (110), (103), (112), and (201) crystallographic planes of ZnO, respectively [37–39]. According to JCPDS Card No. 36-1451. Larger diffraction peaks with relatively lower intensities are often observed in the XRD patterns of unheated ZnO samples. This indicates that the crystallite sizes are smaller and the lattice strain is higher. These characteristics are typical of nanocrystalline materials that are formed under conditions of low or ambient temperature [38]. On the other hand, as compared with unheated ZnO, the XRD pattern created by heated ZnO exhibits peaks that are much more intense and sharper, as well as a little shift away from the peak. This sharpening and shiftiness are a direct result of thermal annealing, which improves atomic order within the lattice and eliminates defects, thereby increasing the crystallinity of the material and promoting the development of larger crystallites [40]. This transition from an amorphous or inadequately crystalline state to a highly crystalline one is a critical consequence of calcination.

Additional crystallographic features are introduced into the XRD patterns as a result of the incorporation of silver nanoparticles into the ZnO matrix in order to form ZnO-Ag composites. These crystallographic features include the preservation of the hexagonal wurtzite phase of ZnO, as well as the appearance of new diffraction peaks that correspond to the face-centered cubic (FCC) structure of metallic silver. These peaks appear at approximately 38.2° and 44.38°,

respectively, and are attributed to the (111) and (200) planes of silver [41, 42]. The silver particles are successfully integrated into the ZnO-Ag composites without disrupting the fundamental crystal structure of the ZnO host matrix, as indicated by the XRD analysis. However, subtle shifts in the ZnO peak positions may occur as a result of lattice strain from the heterogeneous nucleation and growth of silver particles on the ZnO surface.

When it comes to ZnO-C₃N₄ heterostructures, the XRD patterns display a more complicated diffraction behavior. This is because of the special layered structure of g-C₃N₄ and the way it interacts with the ZnO phase [43, 44]. The (002) planes, which correspond to the in-plane structural packing pattern and the interlayer stacking distance of the graphitic carbon nitride framework, are represented by the characteristic diffraction peaks at 27.36° that the immaculate g-C₃N₄ component contributes [22, 24]. In contrast, the g-C₃N₄ diffraction peaks in ZnO-C₃N₄ composites frequently exhibit diminished intensities or may even fade entirely from the XRD patterns. This phenomenon is ascribed to the robust interfacial bonding between ZnO and g-C₃N₄ phases, which disrupts the van der Waals forces between the carbon nitride layers and results in structural reorganization [45].

The conjugated heterostructure that is produced by the formation of Zn-N bonds at the interface between ZnO and g-C₃N₄ significantly alters the crystallographic ordering of both components. This is demonstrated by the broadening and merging of characteristic peaks and the appearance of new diffraction features at intermediate angles [43, 44].

UV-Vis spectra

The linear region in the Tauc plots of the three specimens under investigation was used to calculate the optical band-gap energies. This calculation correlates the photon energy ($h\nu$) with the squared (for direct allowed transitions) or square-rooted (for indirect transitions) product of the absorption coefficient and photon energy ($\alpha h\nu$). The bandgap of 3.18 eV for the thermally treated ZnO in Figure 4a is consistent with the characteristic direct band gap of bulk wurtzite ZnO and suggests a highly crystalline lattice with minimal defect-mediated sub-band states [46, 47]. It has been demonstrated in research that increased thermal treatment temperatures can influence band gap values through quantum confinement effects and particle size variations. The calcination process causes systematic modifications in the crystalline structure and morphological characteristics, which results in increased crystallinity and decreased defect concentrations. These two factors contribute to the band gap energy that is observed [48].

The band gap is reduced to 3.14 eV as a result of the integration of silver nanoparticles, as shown in Figure 4b by the way. The electrical contact between the conduction band of ZnO is responsible for this slight alteration. This interaction affects the density of states at the band boundaries and promotes interfacial charge transfer, which ultimately results in a narrowing of the effective optical gap [49]. The bandgap in this work also has the same value compared with another report [50], in which the authors said that the E_g is 3.18 eV, 3.15 eV for ZnO and ZnO-Ag, respectively.

For the ZnO-C₃N₄ heterostructure, which has an indirect-transition Tauc fit that results in an E_g of 2.67 eV, a far more pronounced narrowing is observed (Figure 4c). The considerable shift can be attributed to the close interfacial hybridization that occurs between ZnO and the π -conjugated g-C₃N₄ framework. This hybridization results in the production of mid-gap states that originate from N-rich molecules, which in turn generates staggered type-II band alignment [51, 52]. The bandgap for ZnO-C₃N₄ is similar to the result of the literature [50], which is E_g = 2.67 eV. As a consequence, the material's photon absorption extends deep into the visible

spectrum, which increases the potential photo-responsive applications of the material. By modifying the electronic structure, optimizing the optoelectronic performance of ZnO-based nanocomposites, and improving visible-light harvesting through phonon-assisted transition pathways, metallic doping and heterojunction engineering have proven to be effective. This is demonstrated by the progressive decrease in E_g that occurs from ZnO to ZnO-Ag and ZnO- C_3N_4 . As a result of the Tauc studies, the intrinsic wide-bandgap semiconducting capabilities of alkaline-battery-derived ZnO and its Ag-doped form have been confirmed. Furthermore, the potential advantage of g- C_3N_4 integration in regulating the band gap for enhanced visible-spectrum photoreactivity has been highlighted.

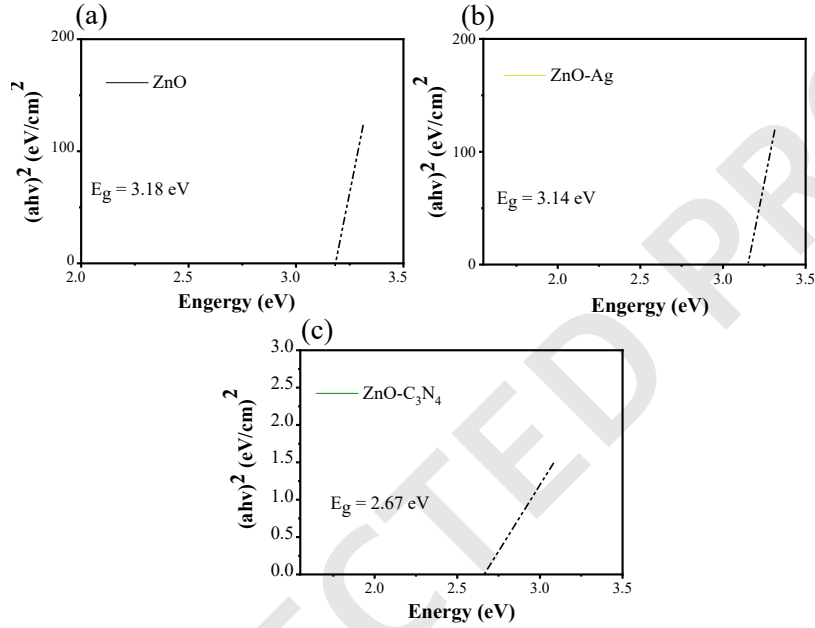


Figure 4. Band gap energy calculation (Tauc plot) of the following samples: (a) ZnO heated, (b) ZnO-Ag, and (c) ZnO- C_3N_4 .

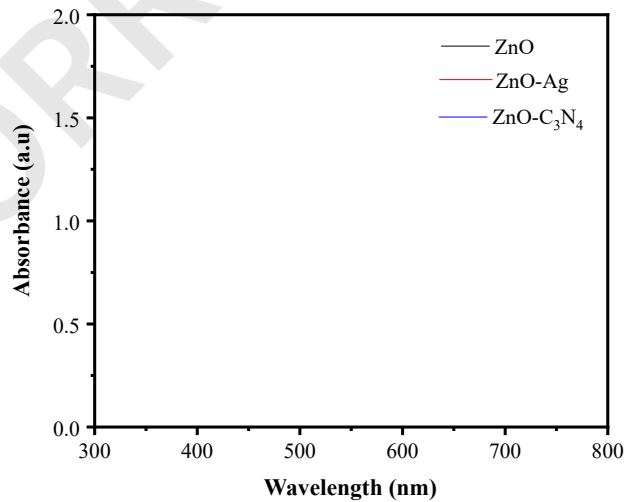


Figure 5. UV-Vis Absorption spectroscopy of ZnO, ZnO-Ag, ZnO- C_3N_4 .

In Figure 5, the UV-Vis diffuse reflectance spectra and corresponding Tauc plots reveal pronounced distinctions in the optical properties of pristine ZnO, ZnO-Ag, and ZnO-C₃N₄ which directly correlate with their photocatalytic efficacies. Pristine ZnO exhibits a steep absorption edge around 390 nm. In ZnO, only ultraviolet light can be absorbed [53], supporting with $E_g = 3.18$ eV in Figure 4a. In addition, a significant decrease in absorbance intensity for the peak of ZnO-Ag have also been observed, which indicates the presence of silver on ZnO surface. Furthermore, Ag²⁺ was present in the nanocomposites' matrix, as evidenced by the decrease in peak intensity in the ZnO-Ag spectrum, which also revealed some degree of agglomeration with irregular morphologies based on the literature [54]. In contrast, the ZnO-C₃N₄ heterostructure displays a dramatically lowered band gap of 2.67 eV along with an expanding absorption band ranging from 390 to 430 nm, which promotes effective photogenerated charge migration from C₃N₄ to ZnO, similar to some literature [53, 55]. Consequently, ZnO-C₃N₄ can utilize a broader spectrum of solar radiation, underpins their superior photocatalytic performance compared to unmodified ZnO.

In conclusion, the photocatalytic systems will maximize photon utilization and minimize recombination losses for ZnO-Ag and ZnO-C₃N₄ by matching the emission spectra of the light sources with their corresponding absorption features.

The SEM image shows that the ZnO-Ag composite consists of agglomerated nanoparticles with irregular shapes. The incorporation of Ag nanoparticles on the ZnO surface generates heterogeneous nucleation sites, which can facilitate charge transfer and suppress electron-hole recombination (Figure 6a). This morphological feature is consistent with the improved photocatalytic performance of ZnO-Ag compared to pristine ZnO. The SEM image reveals a sheet-like and layered structure attributed to g-C₃N₄, with ZnO particles dispersed on its surface. This layered morphology increases the surface area and provides more adsorption and reaction sites for dye molecules (Figure 6b). The intimate contact between ZnO and g-C₃N₄ further favors the formation of heterojunctions, which enhance visible-light absorption and prolong the lifetime of photogenerated charge carriers. The SEM observations confirm the successful incorporation of Ag and g-C₃N₄ into the ZnO matrix. The modified morphologies contribute directly to the enhanced photocatalytic activity observed in MB and CV degradation experiments, as reported in the study.

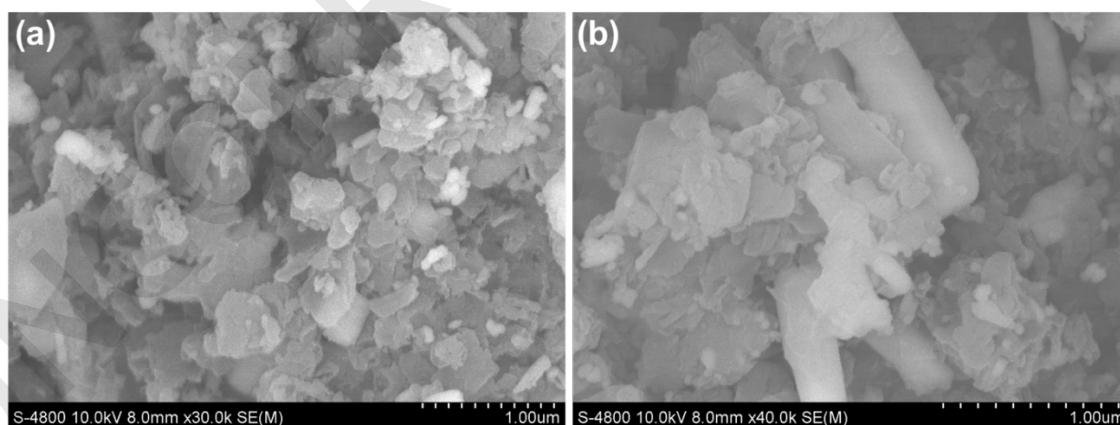


Figure 6. SEM images of the synthesized photocatalysts: (a) ZnO-Ag composite showing aggregated nanoparticles with irregular morphology, and (b) ZnO-C₃N₄ composite displaying layered g-C₃N₄ structures decorated with ZnO particles.

3.2. The adsorption capacity and photocatalytic degradation analysis on MB dyes

Figure 7 presents a comprehensive evaluation of the UV-Vis absorption characteristics and concomitant photocatalytic degradation efficacy of pristine ZnO (Figure 7a), ZnO-Ag (Figure 7b), and ZnO-C₃N₄ heterojunction (Figure 7c) in the context of methylene blue (MB, 10 ppm) abatement, culminating in a comparative kinetic profile (Figure 7d). In the dark adsorption equilibrium, all three catalysts exhibit the characteristic absorbance maxima of MB at 292 nm and 663 nm, with ZnO-C₃N₄ showing slightly elevated baseline adsorption relative to ZnO and ZnO-Ag, indicative of enhanced surface interaction via π - π stacking with the graphitic carbon nitride component. Upon visible-light irradiation, the diminution of the 665 nm spectrum proceeds most rapidly for ZnO-C₃N₄, evidencing near-complete decolorization within 240 min (99.3 %); ZnO-Ag achieves 73.12 % degradation and ZnO attains 75 % removal in the same interval. The progressive attenuation of absorbance across the 200-800 nm range corroborates the synergistic role of Ag nanoparticles in promoting plasmon-induced charge separation for ZnO-Ag and the formation of a type II heterojunction between ZnO and g-C₃N₄, which facilitates efficient electron-hole separation and interfacial charge transfer in ZnO-C₃N₄. The kinetic summary in Figure 7d underscores that ZnO-C₃N₄ surpasses both ZnO and ZnO-Ag in photocatalytic activity under visible irradiation, reflecting its lower band-gap energy and superior suppression of charge recombination.

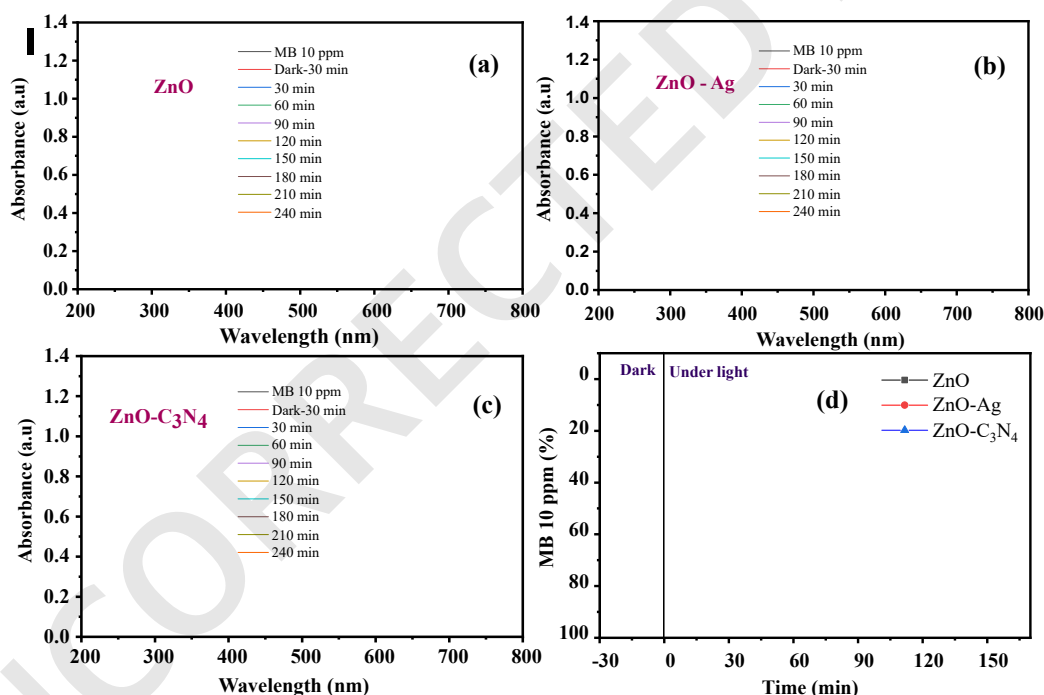


Figure 7. UV-Vis absorption spectra and photocatalytic degradation performance of: (a) ZnO, (b) ZnO-Ag and (c) ZnO-C₃N₄ for the removal of MB 10 ppm; (d) summary of degradation of MB under visible light by ZnO, ZnO-Ag, ZnO-C₃N₄.

3.3. The adsorption capacity and photocatalytic degradation analysis on CV dyes

Figure 8 elucidates the UV-Vis absorption spectra and corresponding photocatalytic degradation kinetics of crystal violet (CV, 10 ppm) mediated by ZnO (Figure 8a), ZnO-Ag

(Figure 8b), and ZnO-C₃N₄ heterojunction composite (Figure 8c), with Figure 8d summarizing the percentage removal of CV over time under visible-light irradiation. In the initial dark adsorption period, all three catalysts display the characteristic CV absorbance peaks at 248 nm, 302 nm, and 590 nm, with ZnO-C₃N₄ exhibiting marginally greater dark-phase uptake, likely due to π - π interactions and increased surface area afforded by the graphitic carbon nitride component. Upon visible-light exposure, ZnO-C₃N₄ demonstrates the most pronounced decline in the 590 nm spectrum, achieving 99 % CV decolorization within 240 min, whereas ZnO-Ag attains 74.37 % removal and ZnO 72.5 % in the same timeframe. The sequential attenuation of absorbance in Figures 8a-c confirms that Ag nanoparticle incorporation enhances light harvesting via localized surface plasmon resonance, improving ZnO-Ag activity, while the type II heterojunction formed between ZnO and g-C₃N₄ in ZnO-C₃N₄ markedly suppresses electron-hole recombination and broadens visible-light absorption. The kinetic summary (Figure 8d) underscores that ZnO-C₃N₄ exhibits superior photocatalytic performance toward CV compared to ZnO-Ag and unmodified ZnO, mirroring the trends observed for methylene blue degradation in Figure 8. Notably, although both dyes follow analogous degradation hierarchies (ZnO-C₃N₄ > ZnO-Ag > ZnO), the absolute removal rates for methylene blue surpass those for crystal violet under identical conditions, suggesting that molecular structure and adsorption affinities modulate photocatalytic efficacy. Consequently, the ZnO-C₃N₄ heterojunction emerges as the most versatile and potent photocatalyst for the remediation of both cationic dyes, with enhanced visible-light utilization and charge-separation dynamics.

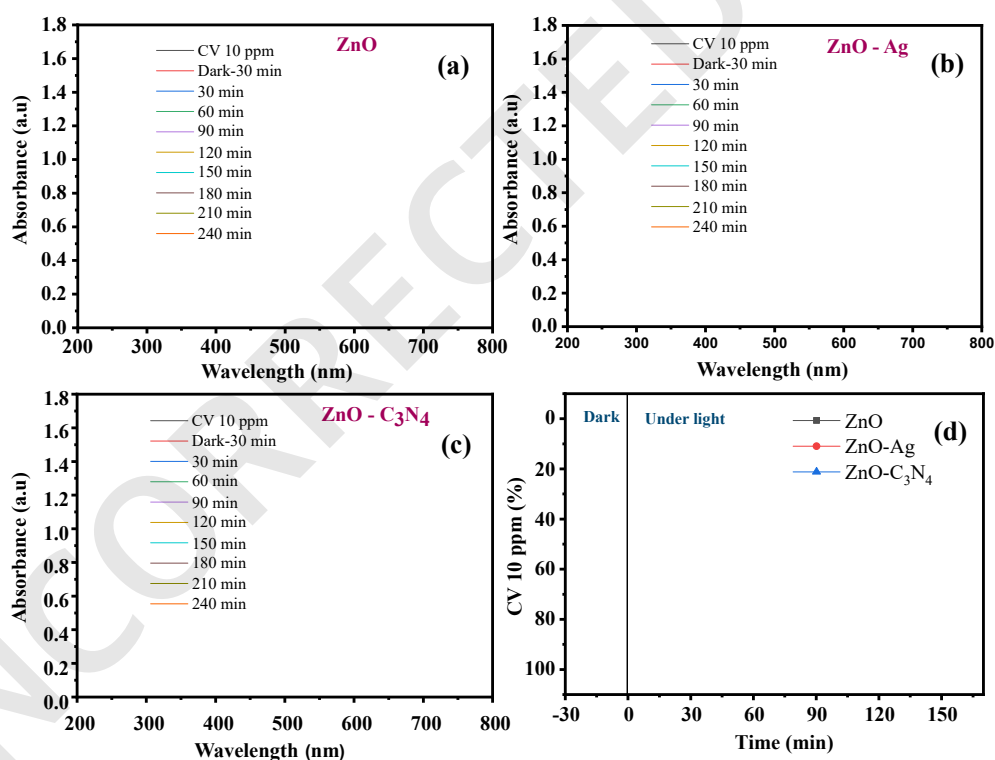


Figure 8. UV-Vis absorption spectra and photocatalytic degradation performance of: (a) ZnO, (b) ZnO-Ag and (c) ZnO-C₃N₄ for the removal of CV 10 ppm; (d) summary of degradation of CV under visible light by ZnO, ZnO-Ag, ZnO-C₃N₄.

For the conclusion on both dyes, MB is more readily degraded than CV across all three photocatalysts under identical visible-light irradiation based on the kinetic profiles. This disparity arises primarily from the distinct molecular structures and electronic properties of the two dyes: methylene blue's lower electron affinity and simpler aromatic framework facilitate more efficient photoinduced electron transfer at the catalyst surface, while the extended conjugation and higher steric hindrance of crystal violet impede both adsorption and interfacial charge transfer. Consequently, methylene blue exhibits faster photon absorption, more facile charge separation, and superior interaction with catalytic active sites, rendering it inherently more susceptible to photocatalytic degradation than crystal violet [12].

3.3. Evaluation of reusability of material on MB

After the first photocatalytic experiment, the sample will be retained by the following method: after the first photocatalytic study, the remaining dye solution and catalyst powder will be poured into a 50 mL centrifuge tube and centrifuged for the first time. Then, the sample will be repeatedly washed again by pouring distilled water into the centrifuge tube, vortexing, and continuing to centrifuge the sample. Finally, the post-centrifugation sample was taken out, dried in a desiccator, and stored. The process will be repeated to evaluate the remaining effectiveness of the material in degrading the dye thru multiple cycles.

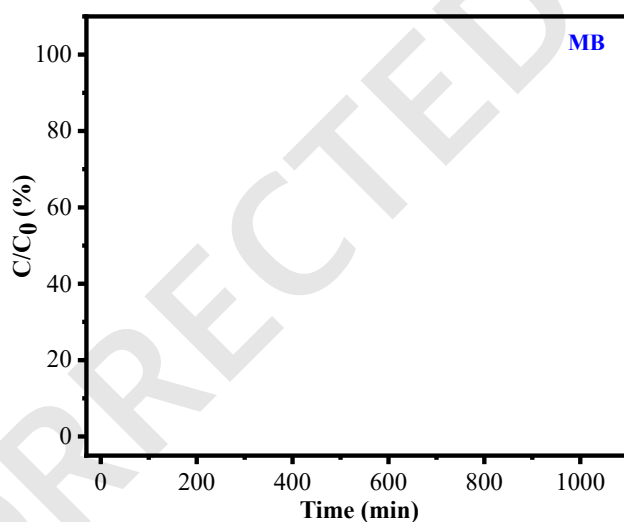


Figure 9. Reusability of material on MB through 4 cycles.

Figure 9 illustrates the exceptional stability and reusability of the ZnO-C₃N₄ photocatalyst during four successive cycles of MB degradation. In the first cycle, the photocatalyst achieves complete MB decolorization in 240 minutes, with the relative concentration C/C_0 dropping steadily from 100 % to 98.94 %. Upon recovery and reuse, the second cycle follows a slightly slower trajectory, yet the catalyst still reaches over 98.45 % removal from 240 to 540 minutes, indicating only a modest loss of activity. The third cycle demonstrates the MB concentration declines from 100 % to 97.87 % from 540 to 810 minutes, highlighting that the photocatalytic sites remain largely intact despite two prior uses. In the fourth cycle, the time for near-complete degradation extends to 810 to 1110 minutes, the ZnO-C₃N₄ composite still accomplishes over 96.62 % MB removal, reflecting remarkable photostability. Across all four cycles, the shape of

each curve-characterized by an initial induction period followed by a rapid degradation phase-remains consistent, which confirms that the fundamental photocatalytic mechanism is preserved after repeated recoveries.

3.4. Evaluation of reusability of material on CV

As shown in Figure 10, the ZnO-C₃N₄ photocatalyst only shows a slow decline in activity, comparable to its performance with MB, and maintains a high degradation efficiency toward CV across four consecutive reuse cycles. During the initial cycle, the CV concentration diminished from 100 % to 97.87 % during 240 minutes, reflecting the fast elimination noted for MB and affirming the catalyst's robust initial efficacy. Following recuperation and redeployment, the second cycle demonstrates a CV elimination rate of 97.49 % from 240 to 540 minutes, accompanied by a slight deceleration in the deterioration rate, analogous to the minor slowdown observed for MB. The third cycle consistently attains over 95.86 % CV elimination from 540 to 810 minutes, demonstrating that the photocatalytic active sites remain predominantly intact after two preceding runs. In the fourth cycle, overall CV decolorization persists at 92.15 %, highlighting exceptional photostability despite repeated applications. Upon comparison of the two dyes, ZnO-C₃N₄ demonstrates slightly accelerated kinetics for MB relative to CV in each respective cycle, presumably attributable to variations in molecular structure and adsorption affinities; nevertheless, in both instances, the catalyst retains removal efficiencies of 96.62 % and 92.15 % by the fourth cycle, respectively. The uniform curve patterns-characterized by an induction period succeeded by a swift degradation phase, which across all cycles and both dyes affirm that the essential photocatalytic mechanism is preserved, highlighting ZnO-C₃N₄ remarkable reusability and extensive applicability for the treatment of various organic pollutants in wastewater.

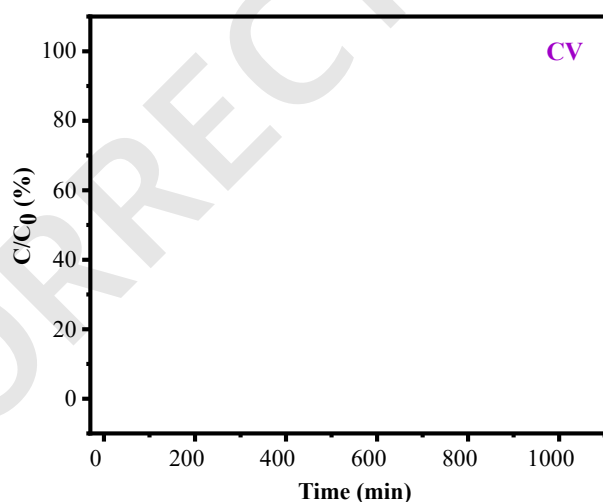


Figure 10. Reusability of material on CV through 4 cycles.

3.5. Evaluation of pHs on ZnO-C₃N₄

Figure 10 illustrates the influence of solution pH on the photocatalytic performance of the ZnO-C₃N₄ composite, evaluated at pH 3, 5, 7, 9, and 11 for both MB and CV. At strongly acidic conditions (pH 3), the degradation efficiencies are lowest which is reached 82.56 % for MB and

80.22 % for CV-likely due to protonation of surface sites on ZnO-C₃N₄, which reduces dye adsorption and limits the generation of reactive oxygen species. As the pH increases to 5, removal rises to around 88.63 % for MB and 87.51 % for CV, reflecting improved catalyst-dye interactions as surface protonation diminishes. At neutral pH (7), both MB and CV achieve 99.3 % and 99 % degradation, respectively, indicating that the catalyst's point of zero charge is approached, optimizing electrostatic attractions and maximizing -OH radical production. Further alkaline conditions (pH 9 and 11) sustain this high activity, both dyes reaching essentially complete removal (99.47 to 99.81 % for MB and 99.21 to 99.6 % for CV), which can be attributed to enhanced generation of hydroxide-derived radicals and deprotonation of the semiconductor surface; these factors together promote stronger dye adsorption and more efficient charge separation. The consistent trend-gradual improvement from acidic to neutral and plateauing under alkaline conditions, which demonstrates that ZnO-C₃N₄ photocatalysis is most effective in neutral to basic environments, a result that informs potential wastewater treatment applications where pH adjustment may further optimize dye removal performance [56, 57].

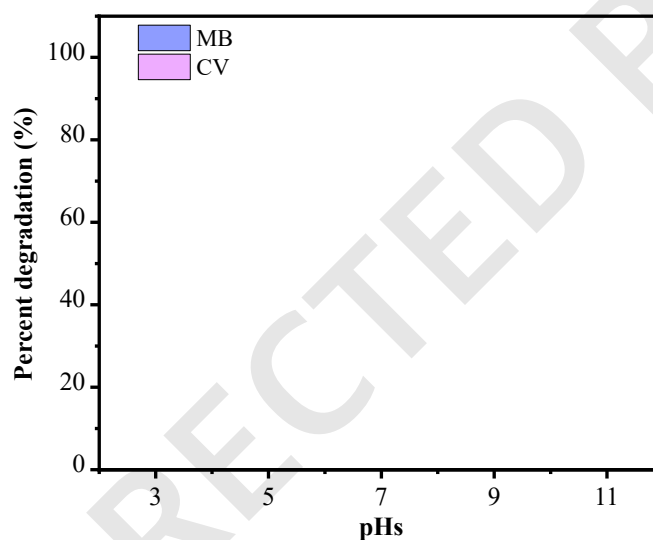


Figure 11. The evaluation of pHs (3, 5, 7, 9, 11) on ZnO-C₃N₄ material.

3.6 Mechanism of ZnO for photocatalytic activity

A type-II heterojunction is created between two semiconductors that have mismatched band alignments. This heterojunction is utilized for the binary g-C₃N₄/ZnO heterojunction. The band gap of graphitic carbon nitride is narrower than that of zinc oxide, which enables it to absorb visible light over a wavelength of 440 nanometers. When both components are lit, electrons that are excited in the conduction band of ZnO move to the higher-lying conduction band of g-C₃N₄. On the other hand, holes that are created in g-C₃N₄ move to the valence band of ZnO. This bidirectional charge flow not only extends the spectrum sensitivity into the visible area, but it also extends the lives of carriers by reducing the amount of interfacial recombination that occurs (Figure 12). An increase in the synthesis of reactive species as a consequence of exposure to visible light results in a significant acceleration of the breakdown of dyes like methylene blue, with removal efficiencies that are significantly higher than those of the constituents individually [52, 58].

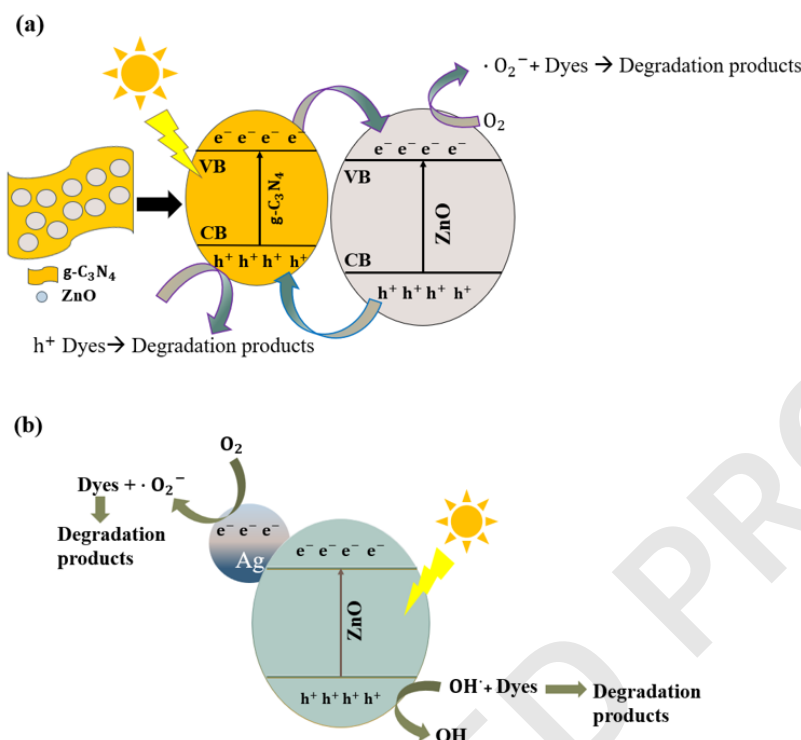


Figure 12. This diagram depicts two different mechanisms: (a) the binary ZnO-C₃N₄ composites, and (b) the proposed photodegradation pathway for ZnO-Ag.

As a result of light stimulation of ZnO, electrons in its conduction band migrate to the lower-energy Fermi level of Ag, which serves as an effective electron sink in the Ag-doped ZnO system (Figure 10b). Recombination between electrons and holes is significantly reduced as a result of the spatial separation of electrons on Ag from holes that are still present in ZnO. As electrons collect on the surface of silver, they convert dissolved oxygen into superoxide radicals (·O₂⁻). On the other hand, holes in zinc oxide (ZnO) oxidize water or hydrogen peroxide into hydroxyl radicals (·OH on the Ag surface) [59, 60].

Through intentional charge separation, ZnO-Ag and ZnO-C₃N₄ heterostructures both produce greater photocatalytic performance. However, they do so through fundamentally distinct paths. In conclusion, both of these heterostructures achieve this superior performance. Under the influence of ultraviolet light, ZnO-Ag is able to increase the production of oxygen-based radicals because it is dependent on the Schottky junction-mediated electron trapping conducted by metal nanoparticles. In contrast, ZnO-C₃N₄ is able to harness visible light and orchestrate the transfer of directed charge across the interface. The final products after the degradation of MB, CV are described by the reactive species, which are specifically hydroxyl (·OH) and superoxide anion (·O₂⁻) have powerful oxidizing capabilities that allow them to attack dye molecules by targeting the chemical bonds that are the most vulnerable. In the end, the photocatalytic process results in the mineralization of dye molecules, which are then converted into chemicals that do not pose any threat, such as water, carbon dioxide and inorganic ion such as NH₄⁺ and SO₄²⁻ for MB, NO₃⁻ for CV based on some literature [27, 61].

Having an understanding of these mechanistic distinctions is essential for the rational design of photocatalysts of the next generation, which are specifically designed for suitable light-driven sources in laboratory and industrial settings.

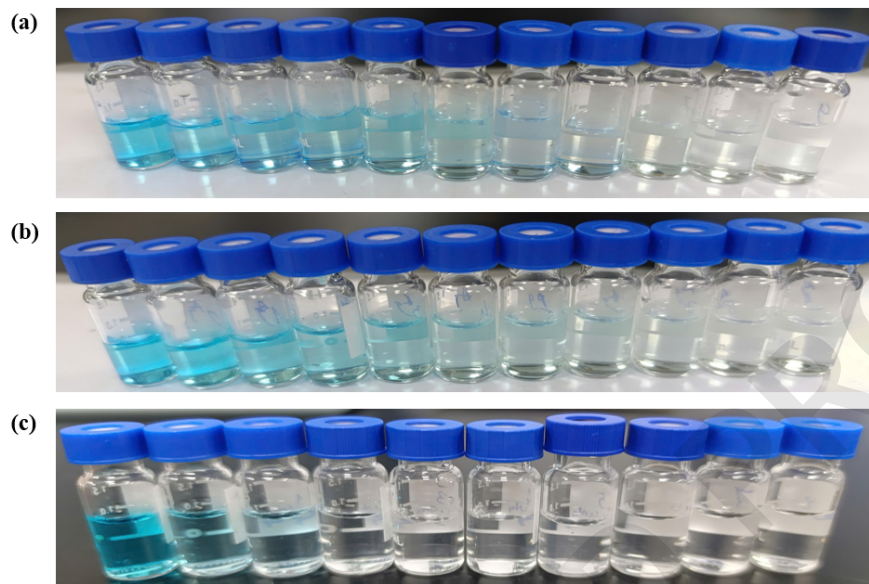


Figure 13. The color-change images of the MB solutions at each interval: (a) ZnO, (b) ZnO-Ag, (c) ZnO-C₃N₄ samples.

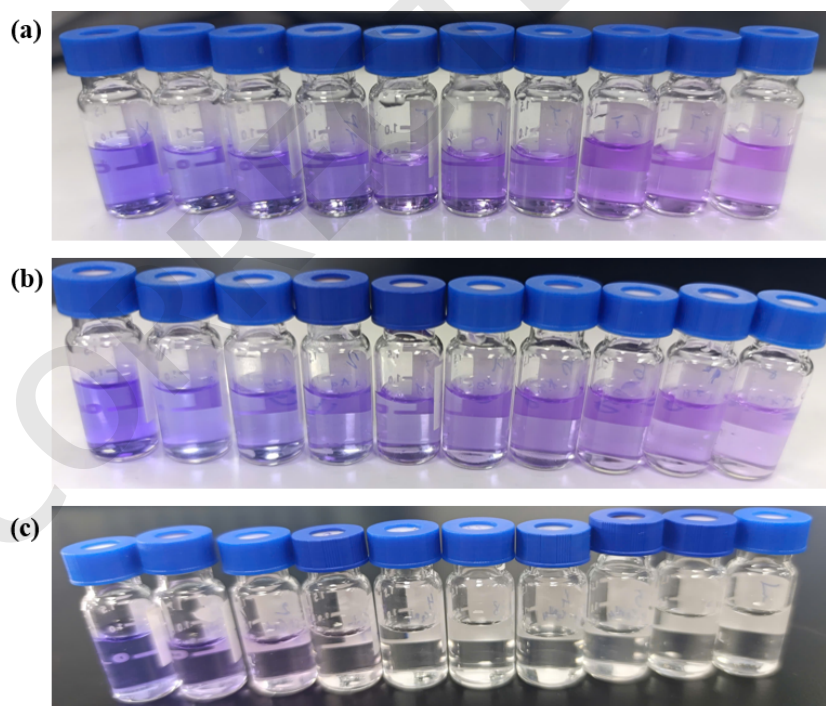


Figure 14. The color-change images of the CV solutions at each interval: (a) ZnO, (b) ZnO-Ag, (c) ZnO-C₃N₄ samples.

3.7. Comparison of ZnO-C₃N₄ with previous works for photocatalytic activity

Table 1 summarizes the photocatalytic performance of ZnO-C₃N₄ reported in this work compared with previous studies employing different synthesis methods. It can be observed that the degradation efficiencies in earlier reports range from 85 % to 97 %, depending on the synthesis approach and experimental conditions. For instance, the solvothermal method achieved 85 % degradation of MB after 100 minutes under a fluorescent visible lamp, while the hydrothermal method reached 97 % degradation of CV under solar light within 4 hours. Similarly, the solid-state method yielded 92 % MB degradation after 120 minutes under direct sunlight. In contrast, the ZnO-C₃N₄ synthesized in this work via a wet impregnation method exhibited superior performance, achieving 99.47 % degradation of MB and 99.21 % degradation of CV within 270 minutes under a 60 W visible-light source. Although the reaction time was relatively longer, the near-complete degradation and the consistent performance for both MB and CV dyes highlight the remarkable photocatalytic efficiency of the material prepared in this study. These results clearly demonstrate that the strategy employed here not only competes favorably with previously reported methods but also offers enhanced applicability for practical wastewater treatment.

Table 1. Comparison for the results of the material in this paper with the previous works.

Synthesis method	Experimental conditions					Photocatalytic evaluation	
	Heating	ZnO-C ₃ N ₄ (mg)	Dyes	Time (min)	Irradiation Source	Degradation (%)	Refs.
Solvothermal	Microwave, 160 °C, 30 min	50	MB (10 mg/L)	100	23 W fluorescent visible lamp, 400–1050 nm, 10 W/m ²	85	[62]
Hydrothermal	Autoclave, 97 °C, 4h	25	CV (20 mg/L)		Solar light	97	[63]
Solid-state	Electric furnace 550 °C 2 h	50	MB (10 mg/L)	120	Direct sunlight	92	[64]
Wet impregnation	Dry in desiccator at 60 °C, 6h	200	MB and CV (10 mg/L)	270	60W Luminus L4X (visible light)	99.47 (MB), 99.21 (CV)	This work

4. CONCLUSIONS

The transformation of spent AA-type alkaline batteries into ZnO-based photocatalysts offers a sustainable route to valorize electronic waste while addressing dye-polluted water. Through a simple extraction, purification, and thermal treatment process, ZnO was recovered and further engineered into Ag-doped ZnO and ZnO-C₃N₄ composites. The Ag-ZnO heterostructure exhibited enhanced light harvesting via localized surface plasmon resonance, delivering superior photocatalytic activity compared to unmodified ZnO. The ZnO-C₃N₄ composite demonstrated a pronounced band-gap narrowing to 2.90 eV, enabling visible-light responsiveness and forming a type-II heterojunction that markedly suppressed electron-hole recombination.

In photocatalytic experiments with 10 ppm methylene blue and crystal violet, ZnO-C₃N₄ outperforming both ZnO-Ag and ZnO. The ZnO-C₃N₄ catalyst maintained high degradation efficiencies across four reuse cycles, underscoring its robust stability. Moreover, its photocatalytic performance improved from acidic (pH 3) to alkaline (pH 11) conditions, reaching near-complete dye removal under neutral to basic pH, thus demonstrating adaptability to varied wastewater environments.

In general, the ZnO-C₃N₄ heterojunction, provide a viable and environmentally benign solution for water cleanup procedures. This particular approach not only reduces the impact that wasted batteries have on the environment, but it also results in the production of photocatalysts that are not only cost-effective but also reusable, and they are able to effectively remove persistent organic dyes when exposed to visible light.

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CrediT authorship contribution statement. Huynh Chi Hieu: Investigation, Writing – original draft. Van Thuan Le: Formal analysis, Investigation. Vy Anh Tran: Investigation, Writing – original draft, Writing – review & editing, Supervision.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that influence the work reported in this paper.

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