

Synergistic effect of plasmonic Au nanostar and Cu₂O/TiO₂ heterojunctions toward highly efficient photocatalytic degradation of MB dye under visible light irradiation

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ABSTRACT

In this work, a series of the visible-light-active Au nanostar-loaded Cu₂O/TiO₂ nanocomposite were synthesized for the photocatalytic degradation of methylene blue dye as water pollutant. The incorporation of Au nanostars induced strong localized surface plasmon resonance (LSPR), enhancing visible-light absorption and facilitating charge carrier generation, while the Cu₂O/TiO₂ heterojunction (band gap ~2.3 eV) significantly improved charge separation and extended the optical response into the visible region based on the DRS analysis. DLS and TEM analysis confirmed uniform nanoscale dispersion, while zeta potential indicated good colloidal stability. XRD patterns verified the crystalline phases of Cu₂O, anatase TiO₂, and Au nanostars. Enhanced photocatalytic performance was attributed to efficient interfacial charge transfer and suppressed electron-hole recombination, leading to the generation of reactive oxygen species (•OH and O₂•⁻) responsible for dye degradation. The effects of Au nanostar loading and catalyst dosage were systematically optimized, showing an initial increase in degradation efficiency followed by a decline at higher levels due to active site shielding and light scattering. The high efficiency was observed (~97%) with good reusability, decreasing to ~84% after ten cycles. Overall, the synergistic effect of Au nanostars, Cu₂O/TiO₂ heterojunction, and plasmonic enhancement resulted in excellent visible-light photocatalytic activity for wastewater treatment applications.

KEYWORDS: Nanophotocatalyst, Au nanostar, Cu₂O/TiO₂, Dye photodegradation

1. Introduction

The rapid expansion of industrial activities has resulted in the continuous release of hazardous contaminants into aquatic environments, posing serious threats to ecosystems and human health. Among various industrial sectors, the textile industry is considered one of the major sources of water pollution due to the extensive use of synthetic dyes, surfactants, finishing agents, and auxiliary chemicals during manufacturing processes [1]. It has been reported that approximately 10–15% of the dyes employed in textile processing are discharged into wastewater streams, leading to severe environmental concerns [2]. These dye-containing effluents are characterized

by high color intensity, elevated chemical oxygen demand (COD), toxicity, and poor biodegradability. Furthermore, many textile dyes and their degradation intermediates exhibit carcinogenic, mutagenic, and teratogenic properties, which may adversely affect both aquatic organisms and human health [3]. Various physicochemical and biological techniques have been developed for the treatment of dye-contaminated wastewater, including adsorption, coagulation–flocculation, membrane filtration, ion exchange, biological degradation, and advanced oxidation processes (AOPs) [4]. Although these treatment methods can achieve acceptable pollutant removal efficiencies, they frequently suffer from

limitations such as high operating costs, sludge generation, membrane fouling, incomplete mineralization, and reduced effectiveness toward persistent organic contaminants [5]. Consequently, the development of environmentally sustainable and highly efficient treatment technologies remains a critical challenge.

Among the available treatment technologies, semiconductor photocatalysis has emerged as one of the most promising approaches for environmental remediation because it can utilize solar energy to generate highly reactive oxygen species capable of mineralizing organic pollutants into harmless products [6]. The photocatalytic process is mainly driven by the formation of hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$), which possess strong oxidation potential and can effectively degrade a wide variety of organic contaminants [7]. Since the pioneering work of Fujishima and Honda on photoelectrochemical water splitting using TiO_2 electrodes, photocatalysis has attracted extensive attention for wastewater treatment, air purification, hydrogen production, and self-cleaning applications [8]. Titanium dioxide (TiO_2) is among the most extensively investigated photocatalytic materials owing to its excellent chemical stability, low toxicity, strong oxidative power, and cost-effectiveness [9]. Nevertheless, the practical application of TiO_2 is limited by its wide band gap (~ 3.2 eV), which restricts its photoresponse to the ultraviolet region of the solar spectrum, accounting for less than 5% of the total solar irradiation reaching the Earth's surface [10]. In addition, the rapid recombination of photogenerated electron-hole pairs substantially decrease its photocatalytic efficiency [11]. Therefore, significant research efforts have focused on developing visible-light-responsive photocatalysts with improved charge separation characteristics.

Copper(I) oxide (Cu_2O) has attracted considerable interest as a visible-light-active semiconductor because of its narrow band gap (~ 2.0 eV), abundance, low cost, and environmental compatibility [12]. Owing to its strong absorption in the visible-light region, Cu_2O has been widely investigated for photocatalytic degradation, photoelectrochemical applications, and solar energy conversion [13]. However, Cu_2O suffers from photocorrosion and rapid charge carrier recombination, which limit its long-term photocatalytic performance [14]. To address these challenges, the construction of $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunctions has been proposed as an effective

strategy to enhance charge separation and suppress recombination through the formation of an internal electric field at the semiconductor interface [15].

In recent years, noble metal nanoparticles have been incorporated into semiconductor heterostructures to further improve photocatalytic activity. Among them, gold nanoparticles (Au NPs) are particularly attractive because of their high electrical conductivity, electron trapping capability, and localized surface plasmon resonance (LSPR) effect [16]. The incorporation of Au nanoparticles into semiconductor photocatalysts can facilitate interfacial electron transfer, enhance visible-light absorption, and suppress charge recombination [17]. Several studies have demonstrated the superior performance of Au-modified $\text{Cu}_2\text{O}/\text{TiO}_2$ photocatalysts in environmental and energy-related applications. For instance, Shao et al. reported that Au-mediated charge transfer significantly improved the photoelectrochemical performance of $\text{Cu}_2\text{O}/\text{Au}/\text{TiO}_2$ nanoheterostructures [18]. Similarly, Lee and Choi developed a $\text{Cu}_2\text{O}-\text{Au}-\text{TiO}_2$ heterostructure that exhibited enhanced photocatalytic degradation of volatile organic compounds under visible-light irradiation [19]. Despite the considerable progress achieved with Au nanoparticle-modified photocatalysts, most previous studies have focused on conventional spherical Au nanoparticles. Compared with spherical nanoparticles, gold nanostars possess a unique branched morphology characterized by multiple sharp tips capable of generating intense localized electromagnetic fields [20]. Such structural features significantly enhance the localized surface plasmon resonance effect and broaden the optical absorption range from the visible to the near-infrared region [21]. Furthermore, the anisotropic geometry of gold nanostars can promote hot-electron generation and facilitate interfacial charge transfer, resulting in improved photocatalytic efficiency [22].

Therefore, in the present work, a novel Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ ternary heterostructure was designed and synthesized as an efficient visible-light-responsive photocatalyst for methylene blue degradation. The incorporation of Au nanostars is expected to improve solar light harvesting, enhance charge separation, and promote the generation of reactive oxygen species through plasmon-assisted photocatalytic processes. To the best of our knowledge, the application of Au nanostars as plasmonic mediators in $\text{Cu}_2\text{O}/\text{TiO}_2$ photocatalytic systems has received limited attention. Accordingly, this work provides a new strategy for the development of advanced plasmonic photocatalysts

with superior visible-light photocatalytic performance for environmental remediation applications. The prepared nanophotocatalyst was characterized with Diffuse reflectance spectroscopy (DRS), Transmittance electron microscopy (TEM), XRD, Dynamic light scattering (DLS) and zeta potential analysis. As an application in the field of wastewater treatment the methylene blue photodegradation under visible light irradiation was studied and the effect of Au nanostar loaded in the $\text{Cu}_2\text{O}/\text{TiO}_2$ matrix, the amount of nanophotocatalyst and reusability as operational parameter were investigated.

2. Experimental Section

2.1. Materials and method

Titanium(IV) isopropoxide (TTIP, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, $\geq 97\%$, Sigma-Aldrich) was used as the titanium precursor for the synthesis of spherical TiO_2 nanoparticles. Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\geq 99\%$, Merck) was used as the copper source for Cu_2O synthesis. Sodium hydroxide (NaOH , $\geq 98\%$, Merck) and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, $\geq 99.5\%$, Merck) were used as precipitating and reducing agents, respectively. Hydrochloric acid (HCl , 37%, Merck) was used for pH adjustment. Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$, Sigma-Aldrich) was used as the gold precursor for Au nanostar synthesis. Cetyltrimethylammonium bromide (CTAB, $\text{C}_{16}\text{H}_{33}\text{BrN}$, $\geq 99\%$, Sigma-Aldrich) was used as a surfactant. Sodium borohydride (NaBH_4 , $\geq 98\%$, Merck) was used as a strong reducing agent, while ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, $\geq 99\%$, Merck) was used as a mild reducing agent. Silver nitrate (AgNO_3 , $\geq 99\%$, Merck) was used as a shape-directing agent. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.8%, Merck) and deionized water ($0.05 \mu\text{S}\cdot\text{cm}$) were used as solvents throughout all experiments. All chemicals were used as received without further purification.

2.2. Synthesis of Spherical TiO_2 Nanoparticles

Spherical TiO_2 nanoparticles were synthesized via a controlled sol-gel method using titanium isopropoxide as precursor [23]. Briefly, certain amount of titanium isopropoxide was dissolved in absolute ethanol under vigorous magnetic stirring to form solution A. In parallel, a mixture of deionized water, ethanol, and hydrochloric acid ($\text{pH} \approx 1-2$) was prepared as solution B. Solution B was slowly added dropwise into solution A under continuous

stirring at room temperature to control hydrolysis and condensation reactions. This process led to the formation of a homogeneous TiO_2 sol, which gradually transformed into a gel. The controlled hydrolysis rate favored the formation of spherical morphology. The obtained gel was aged for 12–24 h, dried at 80°C , and calcined at 450°C for 2 h to obtain crystalline spherical anatase TiO_2 nanoparticles [23].

2.3. Synthesis of Cu_2O Nanoparticles

Cu_2O nanoparticles were prepared via a chemical reduction route. Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was dissolved in deionized water under stirring. Sodium hydroxide solution was added to form a $\text{Cu}(\text{OH})_2$ precipitate. Then, glucose (or hydrazine hydrate) was introduced as a reducing agent at $60-80^\circ\text{C}$, leading to the reduction of Cu^{2+} to Cu^+ and formation of Cu_2O nanoparticles. The product was centrifuged, washed with water and ethanol, and dried at 60°C [24].

2.4. Preparation of the $\text{Cu}_2\text{O}/\text{TiO}_2$ Nanocomposite

Spherical TiO_2 nanoparticles were first dispersed in ethanol under ultrasonication for 20 min. Cu_2O nanoparticles were added and stirred to form a $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction system. Then, the $\text{Cu}_2\text{O}/\text{TiO}_2$ product is centrifuged and washed several times with distilled water and ethanol to remove residual ions. The obtained $\text{Cu}_2\text{O}/\text{TiO}_2$ powder is dried at $60-80^\circ\text{C}$ overnight and optionally annealed at 200°C for 1 h in inert atmosphere to strengthen interfacial contact without oxidizing Cu_2O to CuO . The weight percentage ratio of $\text{Cu}_2\text{O}/\text{TiO}_2$ was adjusted at 1:1. The formation of $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction is based on a p-n junction structure, where: TiO_2 = n-type semiconductor and, Cu_2O = p-type semiconductor. This interface enhances charge separation and suppresses electron-hole recombination, significantly improving photocatalytic efficiency under visible light irradiation. This mechanism and synthesis strategy are consistent with recent reports on $\text{Cu}_2\text{O}/\text{TiO}_2$ heterostructures for environmental and energy applications [24,25].

2.5. Synthesis of Au nanostars (seed-mediated growth method)

Gold nanostars were synthesized using a modified seed-mediated method. First, spherical gold seeds were prepared by reducing chloroauric acid

($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) with sodium citrate. In a typical procedure, 100 mL of HAuCl_4 solution (0.25 mM) was brought to boiling under vigorous stirring, followed by rapid injection of 10 mL trisodium citrate (1 wt%). The solution gradually turned wine-red, indicating formation of Au seeds (~10–15 nm). For nanostar growth, 0.1 mM HAuCl_4 was mixed with a growth solution containing ascorbic acid (AA, 0.1–0.2 mM) as a mild reducing agent and AgNO_3 (10–50 μM) as a shape-directing agent. A small amount of Au seed solution (0.5–1 mL) was added under gentle stirring. The mixture was kept at room temperature for 15–30 min, during which star-shaped Au nanoparticles with sharp branches were formed due to anisotropic growth driven by Ag^+ ions and kinetic control of reduction. This method is widely reported for producing Au nanostars with strong localized surface plasmon resonance (LSPR) in the near-infrared region [26].

2.6. Decoration of Au nanostars on $\text{Cu}_2\text{O}/\text{TiO}_2$ composite

The previously prepared $\text{Cu}_2\text{O}/\text{TiO}_2$ powder (1 g) was dispersed in 200 mL water under ultrasonication for 30 min. Then, a calculated amount of Au nanostar colloid (typically corresponding to 0.5–2 wt% Au loading) was added dropwise under continuous stirring. To enhance anchoring, the pH was adjusted to ~6–7 using dilute NaOH or HCl. The suspension was stirred for 6 h at room temperature, followed by mild thermal treatment at 60–80 °C overnight to ensure strong physical adsorption and partial chemical interaction between Au nanostars and the $\text{Cu}_2\text{O}/\text{TiO}_2$ surface. In some cases, a very low-temperature annealing step (150 °C, 1 h under Ar) is applied to improve interfacial contact without destroying Cu_2O or reshaping Au nanostars [28].

2.7. Characterization

The hydrodynamic particle size distribution and colloidal properties of the synthesized Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite were evaluated using a Dynamic Light Scattering (DLS) analyzer (Better size). DLS is a widely employed technique for determining the hydrodynamic diameter and particle size distribution of nanomaterials dispersed in liquid media, providing valuable insight into dispersion quality, colloidal stability, and aggregation behavior. The surface charge characteristics and colloidal

stability of the synthesized Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite were investigated using a zeta potential analyzer (CAD instrument). Zeta potential analysis is one of the most important characterization techniques for evaluating the electrostatic properties of nanomaterials dispersed in liquid media. This parameter reflects the magnitude of electrostatic repulsion or attraction between suspended particles and is widely used to assess colloidal stability, aggregation tendency, surface charge behavior, and dispersion quality. The crystalline structure, phase composition, and crystallographic properties of the synthesized Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite were investigated using X-ray diffraction (XRD) analysis performed on a Philips (X'Pert- MPD PRO- PW3040/60) equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Furthermore, XRD analysis plays a crucial role in confirming the successful formation of heterostructured nanocomposites and evaluating structural modifications induced by the incorporation of different functional components. Therefore, XRD measurements were employed to verify the coexistence of TiO_2 , Cu_2O , and Au phases and to assess the crystallographic integrity of the synthesized photocatalyst based on the standard reference peaks (JCPDS/PDF cards) for TiO_2 , Cu_2O , and Au beneath the diffraction patterns. The optical properties and light-harvesting capability of the synthesized Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite were investigated using a UV–Vis diffuse reflectance spectrophotometer using a UV/Vis/NIR spectrophotometer (JASCO, V-670 (190–2700nm)). DRS is one of the most important characterization techniques for semiconductor photocatalysts because it provides valuable information regarding optical absorption behavior, absorption edge position, band-gap energy, and the capability of a material to utilize solar radiation. TEM analysis was used to improve the morphology of the prepared Au nanostar and also the Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite using (Zeiss-EM10C-80 kV).

2.8. Photocatalytic study

The photocatalytic activity of the synthesized Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite was evaluated through the degradation of methylene blue (MB) aqueous solution (10 mg/L) under visible-light irradiation. Methylene blue was selected as a model organic pollutant due to its high stability, distinct absorption peak, and widespread use as a

standard probe molecule in photocatalytic studies. The photocatalytic experiments were carried out in a cylindrical batch photoreactor fabricated from borosilicate glass with a total working volume of 250 mL. The reactor was equipped with a visible-light source consisting of a 300 W LED lamp fitted with a UV cut-off filter ($\lambda > 420$ nm) positioned vertically above the reaction vessel. The distance between the light source and the reactor was maintained at approximately 15 cm to ensure uniform light irradiation throughout the reaction medium. To minimize thermal effects, the reactor was surrounded by a circulating water-cooling jacket, maintaining the reaction temperature at 25 ± 2 °C during the photocatalytic experiments. Typically, certain amount of the photocatalyst was dispersed in 100 mL of methylene blue solution with an initial concentration of 10 mg L^{-1} . Prior to light irradiation, the suspension was magnetically stirred in the dark for 30 min to establish adsorption–desorption equilibrium between the dye molecules and the nanophotocatalyst surface. This step is essential for distinguishing the contribution of photocatalytic degradation from simple adsorption phenomena. Following dark equilibration, the visible-light source was switched on and the photocatalytic degradation of MB was initiated. After 90 min of photocatalytic procedure, approximately 3 mL aliquots were withdrawn from the reactor. The sample solution was immediately centrifuged to remove suspended nanophotocatalyst particles. The residual concentration of MB was determined using a UV–Vis spectrophotometer by monitoring the characteristic absorption peak of MB at $\lambda_{\text{max}} = 664$ nm. The MB photocatalytic degradation efficiency was calculated according to:

$$\text{Photodegradation Efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 and C_t represent the initial concentration and the concentration of methylene blue at irradiation time t , respectively. The superior photocatalytic performance of the Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite can be attributed to the synergistic effects of the $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction and the plasmonic properties of Au nanostars. During the photocatalytic procedure the p–n heterojunction facilitates efficient separation of photogenerated electron–hole pairs, while the localized surface plasmon resonance (LSPR) effect of Au nanostars enhances visible-light harvesting and promotes hot-electron injection into the TiO_2 conduction band.

These processes increase the generation of reactive oxygen species, including superoxide radicals ($\bullet\text{O}_2^-$) and hydroxyl radicals ($\bullet\text{OH}$), which are primarily responsible for the oxidative degradation of methylene blue molecules [29]. In this section, the effect of gold nanostar loading in $\text{Cu}_2\text{O}/\text{TiO}_2$ matrix, the effect of catalyst amount (g/L) and reusability of nanophotocatalyst in MB photodegradation under visible light irradiation were considered. The photocatalytic degradation kinetics of methylene blue over the best sample of Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ photocatalyst in the MB photodegradation was analyzed using the pseudo-first-order kinetic model based on the Langmuir–Hinshelwood equation. A linear relationship between $\ln(C_0/C_t)$ and irradiation time was obtained at interval of 10 min to measure the C_t using UV-vis spectrophotometer

3. Results and discussion

3.1.DLS Analysis

Fig.1 presents the DLS analysis for the Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ (1.0GS) as typical sample in photocatalytic study. The DLS analysis revealed an average hydrodynamic particle size of approximately 120 nm with a polydispersity index (PDI) of 0.31. The obtained particle size confirms the successful fabrication of the nanocomposite within the nanoscale regime and indicates the formation of finely dispersed particles in suspension. It should be emphasized that the hydrodynamic diameter measured by DLS is generally large because the DLS measures the effective diameter of nanoparticles together with their surrounding solvation layer and any adsorbed species present at the particle–liquid interface. The measured PDI value of 0.31 indicates a relatively narrow particle size distribution and an acceptable degree of colloidal homogeneity and monodispersity. The DLS profile exhibited no evidence of pronounced multimodal distributions or large aggregated populations, suggesting that the synthesis procedure provided effective control over nucleation, growth, and surface modification processes [30]. Consequently, the resulting nanocomposite consists predominantly of uniformly distributed nanoparticles with only a limited tendency toward agglomeration. The observed size distribution further demonstrates that the incorporation of Au nanostars onto the $\text{Cu}_2\text{O}/\text{TiO}_2$ heterostructure did not induce significant particle clustering, indicating

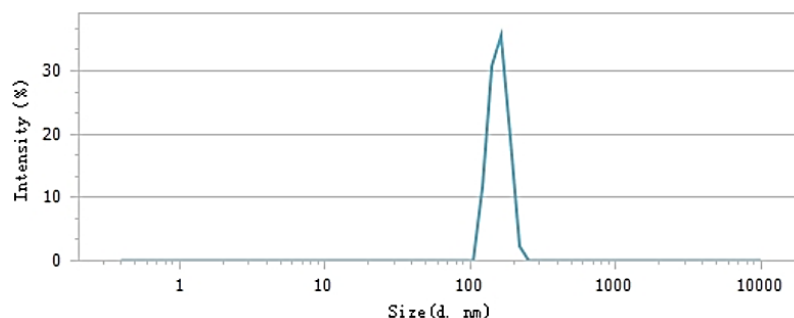


Fig.1. DLS analysis for the Au nanostar/Cu₂O/TiO₂ (1.0GS)

strong interfacial compatibility among the individual components. Such a homogeneous distribution is particularly important for photocatalytic applications because it ensures a more uniform exposure of active sites, enhances catalyst–pollutant interactions, and promotes efficient utilization of incident light throughout the photocatalyst suspension. Moreover, nanoparticles with dimensions in the range of approximately 120 nm provide a favorable balance between colloidal stability and surface activity. Overall, the DLS results confirm that the synthesized Au nanostar/Cu₂O/TiO₂ nanocomposite possesses a homogeneous nanoscale particle distribution, good dispersion behavior, and satisfactory colloidal stability. The absence of severe aggregation together with the relatively narrow particle size distribution indicates the successful preparation of a well-dispersed photocatalyst, which is highly desirable for maximizing photocatalytic activity and ensuring reproducible performance in aqueous environments.

3.2. Zeta potential analysis

In photocatalytic systems, zeta potential plays a crucial role in determining particle–particle interactions, adsorption behavior toward charged pollutants, suspension stability, and ultimately the accessibility of active surface sites [31]. Therefore, zeta potential measurements provide valuable information regarding the physicochemical properties of nanocatalysts and their expected performance in aqueous photocatalytic processes for dye degradation. The zeta potential of the Au nanostar/Cu₂O/TiO₂ nanocomposite was found to be approximately −25 mV, indicating good colloidal stability and effective electrostatic repulsion among suspended particles. The negative surface charge can be attributed to the abundance of surface hydroxyl groups on TiO₂ as well as the negatively charged surface of Au

nanostars. Such a zeta potential value is sufficiently high to prevent severe particle agglomeration and maintain a stable colloidal suspension. The observed electrostatic stabilization is beneficial for preserving a high accessible surface area, ensuring homogeneous dispersion of photocatalyst particles throughout the reaction medium, and facilitating efficient interaction between the catalyst surface and target pollutants. Furthermore, the negative surface charge may enhance the adsorption of positively charged species and contribute to improved photocatalytic activity through increased availability of reactive surface sites. Overall, the obtained zeta potential value demonstrates that the synthesized nanocomposite possesses favorable colloidal characteristics and adequate suspension stability, which are essential prerequisites for achieving efficient photocatalytic performance and reproducible catalytic behavior in aqueous environments.

3.4. XRD analysis

The crystal structure and phase composition of the synthesized Au nanostar/Cu₂O/TiO₂ photocatalyst were investigated by X-ray diffraction (XRD). As shown in Fig. 2, the diffraction peak located at $2\theta = 25.3^\circ$ corresponds to the (101) plane of anatase TiO₂, which represents the characteristic and most intense reflection of the anatase phase. Additional diffraction peaks observed at 37.8° , 48.0° , 53.9° , 55.1° , and 62.7° were indexed to the (004), (200), (105), (211), and (204) crystal planes of anatase TiO₂, respectively, confirming the successful formation of highly crystalline TiO₂ nanoparticles [32]. Besides the diffraction peaks associated with TiO₂, several additional reflections appeared at 29.6° , 36.4° , 42.3° , 61.3° , and 73.5° , corresponding to the (110), (111), (200), (220), and (311) lattice planes of cubic Cu₂O. The presence of these diffraction peaks

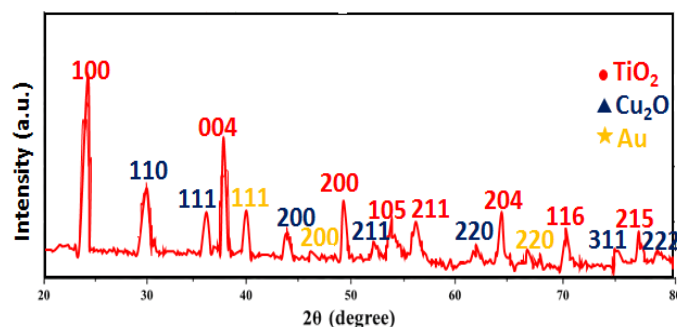


Fig.2. The XRD of the synthesized Au nanostar/Cu₂O/TiO₂ (1.0 GS) photocatalyst

demonstrates the successful deposition of Cu₂O onto the TiO₂ surface and confirms the formation of a Cu₂O/TiO₂ heterojunction without detectable impurity phases such as CuO or metallic copper [33]. Furthermore, weak but distinguishable diffraction peaks located at approximately 38.2°, 44.4°, 64.6°, and 77.5° can be assigned to the (111), (200), (220), and (311) crystal planes of face-centered cubic (fcc) metallic gold, respectively. The relatively low intensity of these peaks is attributed to the small loading amount and nanoscale dimensions of the Au nanostars. The appearance of these reflections confirms the successful incorporation of crystalline Au nanostars into the Cu₂O/TiO₂ matrix [34]. Notably, no additional diffraction peaks related to secondary phases or undesired by-products were detected, indicating the high purity of the synthesized nanocomposite. In addition, slight peak broadening observed for the Au and Cu₂O phases suggests the formation of nanocrystalline domains, which is consistent with the nanoscale particle size obtained from DLS analysis. The coexistence of diffraction peaks belonging to TiO₂, Cu₂O, and metallic Au demonstrates the successful construction of a ternary plasmonic heterostructure. Such a heterostructure is expected to facilitate efficient interfacial charge separation, suppress electron–hole recombination, and enhance visible-light harvesting owing to the localized surface plasmon resonance effect of Au nanostars [35].

2.4. DRS Analysis

In photocatalytic systems, the band-gap energy directly governs the wavelength range that can be absorbed and determines the efficiency of photogenerated charge carrier production. Therefore, DRS analysis is essential for evaluating the potential of

newly developed photocatalysts for visible-light-driven applications. The diffuse reflectance spectra revealed a significant red shift in the absorption edge of the Au nanostar/Cu₂O/TiO₂ nanocomposite compared with pristine TiO₂. Pure anatase TiO₂ generally exhibits a band-gap energy of approximately 3.2 eV and can only absorb ultraviolet light below 390 nm. In contrast, the synthesized ternary nanocomposite demonstrated strong optical absorption throughout the visible-light region, indicating a substantial enhancement in solar light utilization. The optical band-gap energy estimated from the Kubelka–Munk transformed reflectance data and Tauc plot analysis was approximately 2.3 eV, confirming the successful modification of the electronic structure of TiO₂ through the incorporation of Cu₂O and Au nanostars. A band-gap value of 2.3 eV corresponds to an absorption edge of approximately 539 nm, indicating that the photocatalyst can efficiently harvest a significant fraction of visible light. The reduction in band-gap energy can be primarily attributed to the formation of a Cu₂O/TiO₂ heterojunction. Cu₂O possesses a narrower band gap (approximately 2.0–2.2 eV) than TiO₂ and introduces additional electronic states that facilitate visible-light absorption. Upon coupling with TiO₂, the electronic interaction between the two semiconductors promotes band structure modulation and extends the absorption range toward longer wavelengths. Consequently, the heterostructure exhibits improved photoresponse under visible-light irradiation compared with pure TiO₂. Furthermore, the incorporation of Au nanostars plays a crucial role in enhancing optical absorption through the localized surface plasmon resonance (LSPR) effect. Due to their anisotropic morphology and multiple sharp branches, Au nanostars exhibit intense plasmonic resonance

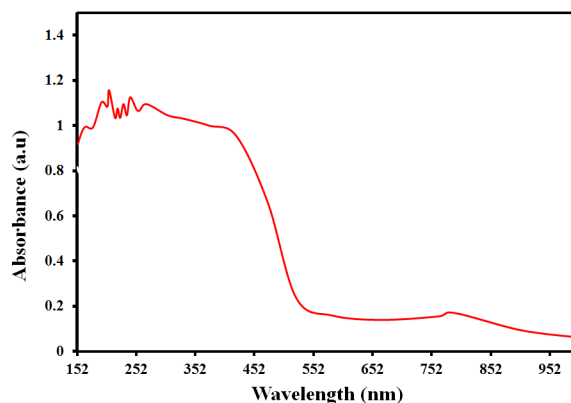


Fig.3. The DRS analysis of the synthesized Au nanostar/ Cu_2O / TiO_2 (1.0 GS) photocatalyst

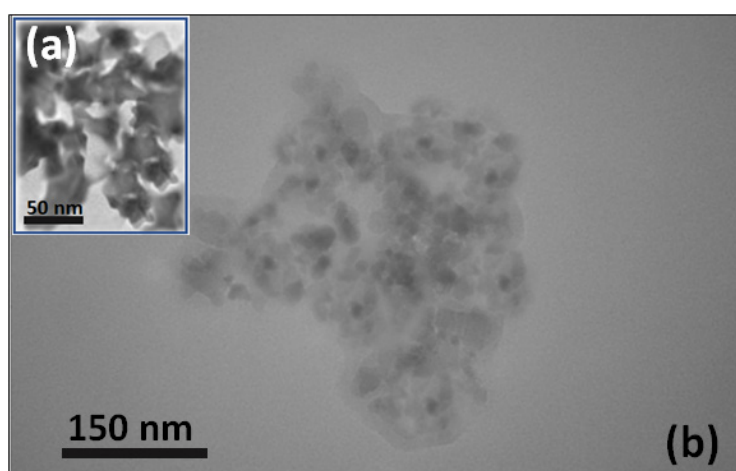


Fig. 4. TEM images of the (a) Au nanostar, and (b) Au nanostar/ Cu_2O / TiO_2 1.0 GS nanophotocatalyst

within the visible and near-infrared regions. The sharp tips act as electromagnetic field concentrators, generating highly localized plasmonic hot spots that significantly amplify light absorption. This plasmonic effect not only broadens the optical response of the nanocomposite but also facilitates hot-electron generation and transfer across the semiconductor interfaces, thereby improving photocatalytic efficiency under visible-light irradiation. The synergistic interaction between TiO_2 , Cu_2O , and Au nanostars results in a substantial extension of the absorption spectrum from the ultraviolet region into the visible domain. The observed red shift and reduced band-gap energy indicate that the synthesized nanocomposite possesses superior solar-light harvesting capability compared with conventional TiO_2 -based photocatalysts. Enhanced visible-light absorption is expected to increase the generation

of electron–hole pairs, improve charge separation efficiency, and ultimately promote the formation of reactive oxygen species responsible for photocatalytic degradation reactions [36–38].

3.5. TEM images

The morphology of the synthesized Au nanostructures and the final Au nanostar/ Cu_2O / TiO_2 1.0 GS was investigated by TEM. As shown in Fig. 4-(a), the synthesized Au nanoparticles exhibit a well-defined star-shaped morphology. This morphology is consistent with previous reports describing the successful formation of Au nanostars prepared via seed-mediated growth methods [26]. The sharp protrusions are known to generate strong localized surface plasmon resonance (LSPR), leading to enhanced visible-light absorption and more efficient charge separation. The TEM image

of the Au nanostar/Cu₂O/TiO₂ nanocomposite (Fig. 4 (b)) demonstrates that the Au nanostars are uniformly dispersed throughout the Cu₂O/TiO₂ matrix without noticeable aggregation. The intimate interfacial contact between the Au nanostars and the semiconductor particles is expected to facilitate rapid electron transfer and suppress the recombination of photogenerated electron–hole pairs. The homogeneous distribution of plasmonic Au nanostars within the heterostructure provides abundant active sites and contributes significantly to the superior photocatalytic performance observed under visible-light irradiation.

3.5. Effect of Catalyst Composition on Photocatalytic Activity

In the photocatalytic degradation of methylene blue (MB), as can be seen from Fig. 5, the catalytic performance strongly depends on the amount of gold nanostars (Au NSs) incorporated into the TiO₂/Cu₂O (1:1 molar ratio) composite. Among the prepared samples, the sample of 1.0 GS catalyst exhibited the highest photocatalytic efficiency after 90 min, indicating an optimal Au nanostar loading for maximizing the MB degradation rate. This enhancement at 1.0 wt% Au nanostar can be attributed to the synergistic effects between TiO₂, Cu₂O, and plasmonic Au nanostars. In particular Au nanostar improve visible-light absorption via localized surface plasmon resonance (LSPR) and facilitate effective charge carrier separation at the heterojunction interface, thereby suppressing electron–hole recombination and promoting the formation of reactive oxygen species responsible for

MB dye degradation. However, when the Au nanostar content was increased beyond 1.0 wt%, no significant improvement in photocatalytic activity was observed. This behavior can be explained by the excessive coverage of active sites on the semiconductor surface and the possible role of Au aggregates as recombination centers, which counteract the beneficial effects of plasmonic enhancement. Therefore, the sample of 1.0 GS nanophotocatalyst represents the optimal catalyst composition, achieving a balance between light harvesting, charge separation efficiency, and surface accessibility, while higher loadings do not contribute further to photocatalytic performance. The photocatalytic degradation kinetics of methylene blue over the Au nanostar/Cu₂O/TiO₂ (1.0 GS) photocatalyst were analyzed using the pseudo-first-order kinetic model based on the Langmuir–Hinshelwood equation. A linear relationship between $\ln(C_0/C_t)$ and irradiation time was obtained, indicating that the degradation process follows pseudo-first-order kinetics. The apparent reaction rate constant (k) was calculated to be 0.0384 min^{-1} , with a correlation coefficient ($R^2 = 0.926$). These results demonstrate the high photocatalytic activity of the synthesized Au nanostar/Cu₂O/TiO₂ composite under visible-light irradiation. To further evaluate the photocatalytic performance of the proposed Au nanostar/Cu₂O/TiO₂ photocatalyst, its activity was compared with previously reported Cu₂O/TiO₂- and Au/Cu₂O/TiO₂-based photocatalysts. As summarized and compared with previous reports in Tab. 1, the present photocatalyst exhibited a degradation efficiency of 97.62% together with an apparent pseudo-first-order rate constant of 0.0384 min^{-1} ,

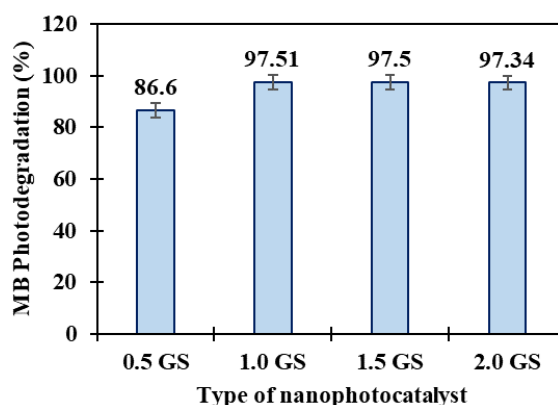
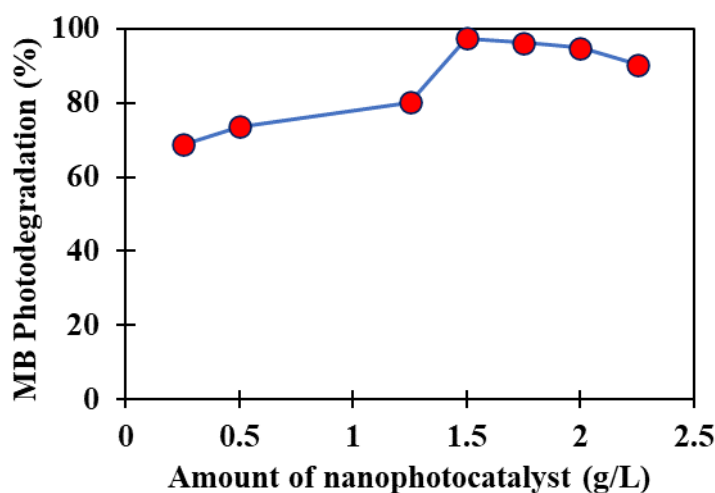


Fig. 5. The effect of type of nanophotocatalyst for photocatalytic degradation of MB with Au nanostar/Cu₂O/TiO₂ at different Au loading after 90min

Tabl. 1. A comparative study between this study and previous work

Photocatalyst	Pollutant	Light source	Degradation (%)	k (min ⁻¹)	Reference
Cu ₂ O/TiO ₂	Organic dye	Visible	88–92	0.020–0.028	[39]
Cu ₂ O/TiO ₂ (oxygen vacancy)	RhB	Visible	94–96	0.030–0.034	[40]
Au/Cu ₂ O/TiO ₂ (spherical Au)	Organic dye	Visible	95–96	0.031–0.036	[41]
Au nanostar/Cu ₂ O/TiO ₂ (1.0 GS)	Methylene blue	Visible	97.62	0.0384	(This work)

Fig. 6. The effect of amount nanophotocatalyst under photocatalytic degradation of MB with Au nanostar/Cu₂O/TiO₂ after 90 min

which is higher than those reported for conventional Cu₂O/TiO₂ heterojunctions and slightly superior to Au/Cu₂O/TiO₂ systems employing spherical Au nanoparticles. As summarized in Tab. 1, the improved performance can be attributed to the unique star-shaped morphology of the Au nanostructures, which generates multiple sharp tips capable of producing stronger localized surface plasmon resonance (LSPR), enhancing visible-light harvesting and facilitating the separation and migration of photogenerated charge carriers. Consequently, the Au nanostar/Cu₂O/TiO₂ nanocomposite demonstrates enhanced photocatalytic efficiency under visible-light irradiation compared with previously reported counterparts. So, compared with previously reported Cu₂O/TiO₂ heterojunctions and conventional Au/Cu₂O/TiO₂ photocatalysts, the synthesized Au nanostar/Cu₂O/TiO₂ photocatalyst exhibited a higher degradation efficiency (97.62%) and a larger apparent pseudo-first-order rate constant (0.0384 min⁻¹). The superior performance is mainly attributed to the unique star-shaped Au nanostructures, which

provide stronger localized surface plasmon resonance (LSPR), enhanced visible-light harvesting, and more efficient separation of photogenerated charge carriers [39–42].

3.6. Effect of Photocatalyst Dosage on Methylene Blue Degradation

The effect of photocatalyst dosage on the degradation of methylene blue (MB) was investigated by varying the amount of nanophotocatalyst in the reaction system and shown in Fig. 6. As shown in the corresponding figure, the degradation efficiency increased with increasing catalyst loading up to 1.5 g L⁻¹ after 90 min, where the maximum photocatalytic activity was observed. This improvement can be attributed to the higher availability of active sites and increased generation of reactive oxygen species (ROS), such as •OH and O₂•⁻ radicals, which enhance the degradation rate of MB molecules. However, further increase in catalyst dosage beyond 1.5 g L⁻¹ did not lead to any significant improvement in photocatalytic performance. This phenomenon

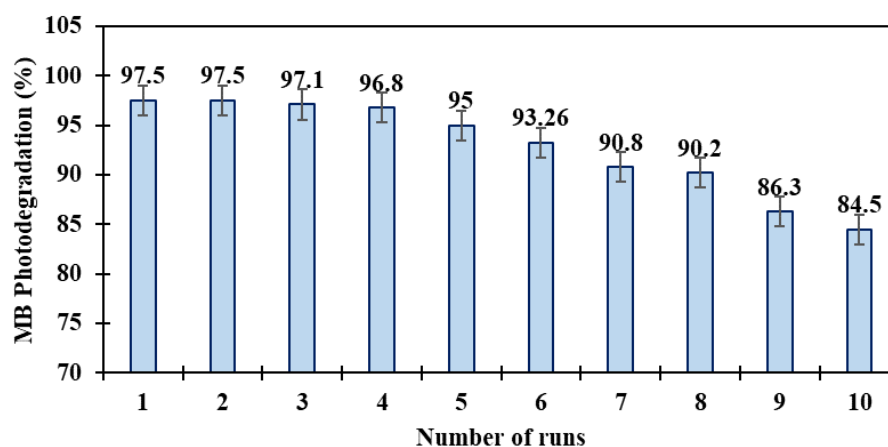


Fig. 7. The reusability and stability of the synthesized nanophotocatalyst under photocatalytic degradation cycles of MB with Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$

is commonly attributed to light scattering and shielding effects at higher solid concentrations, which reduce light penetration into the reaction medium. In addition, excessive catalyst particles can lead to agglomeration, decreasing the effective surface area available for photocatalytic reactions and promoting recombination of photogenerated electron-hole pairs. Therefore, 1.5 g L^{-1} was identified as the optimum catalyst loading, providing a balance between sufficient active surface area and efficient light utilization in the reaction system. This behavior is consistent with previous studies reporting an optimal catalyst dosage beyond which photocatalytic efficiency reaches a plateau or decreases due to mass transfer limitations and photon shielding effects [39].

3.7. Reusability and Stability of the Nanophotocatalyst

The reusability and stability of the synthesized nanophotocatalyst were evaluated through successive photocatalytic degradation cycles of methylene blue (MB). As illustrated in the corresponding Fig. 7, the prepared nanophotocatalyst exhibited high initial stability, maintaining a degradation efficiency of approximately 97% in the first run after 90 min. A slight decrease in photocatalytic performance was observed over repeated cycles, reaching about 93% after the 6th run. This minor decline in activity during the initial cycles can be attributed to partial surface fouling by intermediate degradation products, possible adsorption of reaction by-products on active sites, and slight agglomeration of nanoparticles, which

may reduce the availability of surface reactive centers. Nevertheless, the catalyst still retained a high level of activity up to this stage, indicating good structural stability and resistance to deactivation. From the sixth to the tenth cycle, a more pronounced decrease in photocatalytic efficiency was observed, with the degradation rate gradually declining to approximately 84%. This further reduction is likely due to cumulative surface blockage, gradual loss of active surface area, and possible minor photocorrosion effects, particularly in semiconductor-based heterojunction systems under prolonged irradiation. Despite this gradual deactivation, the catalyst maintained acceptable photocatalytic performance even after ten consecutive cycles, demonstrating reasonable reusability and stability, which are crucial parameters for practical wastewater treatment applications. This trend is in good agreement with previous reports, where a progressive decline in photocatalytic efficiency over multiple cycles is commonly observed due to surface poisoning and structural/chemical changes in the catalyst during repeated use [44].

3.8. Photocatalytic Mechanism

The remarkable photocatalytic performance of the Au nanostar/ $\text{Cu}_2\text{O}/\text{TiO}_2$ ternary heterostructure can be attributed to the synergistic coupling of a p-n heterojunction and plasmon-induced charge transfer processes which can be seen in Fig. 8. Upon contact between p-type Cu_2O and n-type TiO_2 , the difference in their Fermi levels induces interfacial charge redistribution, resulting in the formation of

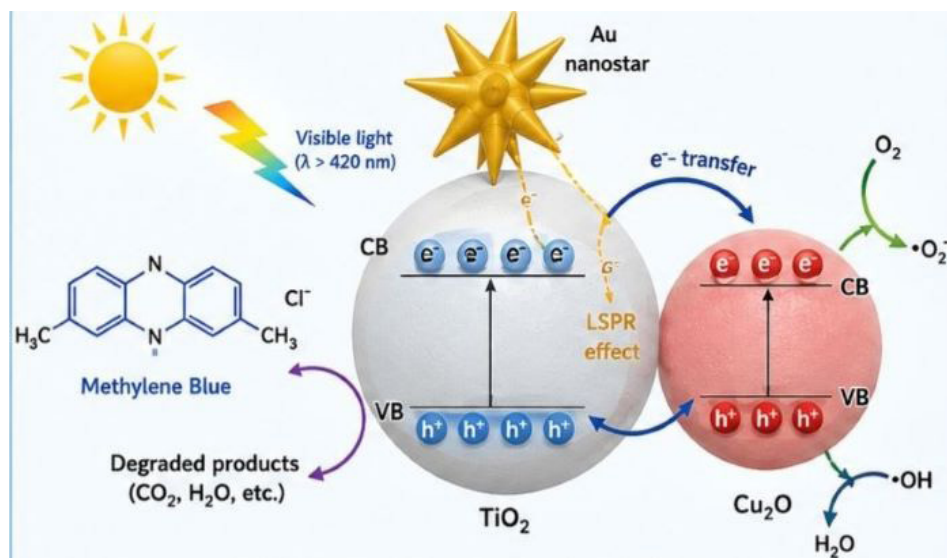


Fig. 8. The suggested mechanism for photocatalytic performance of the Au nanostar/ Cu_2O / TiO_2 ternary heterostructure based on the synergistic coupling of a p–n heterojunction and plasmon-induced charge transfer processes

a built-in electric field at the $\text{Cu}_2\text{O}/\text{TiO}_2$ interface. This internal electric field facilitates the migration of photogenerated electrons and holes in opposite directions, thereby suppressing charge recombination and improving carrier separation efficiency [40]. Under visible-light irradiation, Cu_2O acts as the primary photoactive component owing to its narrow band gap (~ 2.0 eV), generating a large number of electron–hole pairs, while TiO_2 provides a chemically stable platform for charge transport and surface redox reactions [38]. However, the binary $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction alone suffers from limited charge-transfer kinetics and incomplete utilization of the solar spectrum. To overcome these limitations, Au nanostars are introduced as plasmonic sensitizers. The unique anisotropic morphology of Au nanostars, characterized by multiple sharp branches, gives rise to an intense localized surface plasmon resonance (LSPR) effect. Upon illumination with visible and near-infrared light, collective oscillation of conduction electrons occurs within the Au nanostars, generating highly concentrated electromagnetic fields at the tip regions. These plasmonic “hot spots” significantly enhance local light absorption and promote the generation of energetic hot electrons [38]. A fraction of these hot electrons possesses sufficient energy to overcome the Schottky barrier formed at the Au/ TiO_2 interface and is subsequently injected into the conduction band of TiO_2 , leading to a substantial increase in the density of reactive electrons available

for photocatalytic reduction reactions [38,40]. Simultaneously, Au nanostars serve as electron reservoirs and charge-transfer mediators. Electrons photogenerated in the conduction band of Cu_2O can migrate to the metallic Au nanostars and subsequently transfer to TiO_2 through energetically favorable pathways. This directional migration pathway effectively suppresses electron–hole recombination and prolongs the lifetime of charge carriers [4]. As a consequence, electrons accumulate predominantly on the TiO_2 surface, where they react with dissolved oxygen molecules to generate superoxide radicals ($\bullet\text{O}_2^-$), whereas photogenerated holes remain in the valence band of Cu_2O and participate in oxidation reactions, producing hydroxyl radicals ($\bullet\text{OH}$) either directly or through interaction with adsorbed water molecules [40]. Moreover, the sharp tips of Au nanostars induce a pronounced lightning-rod effect, which amplifies the local electromagnetic field intensity compared with conventional spherical Au nanoparticles. This phenomenon broadens the optical response of the composite toward the visible and near-infrared regions and further improves solar energy harvesting efficiency [40–43]. Therefore, the combined effects of the $\text{Cu}_2\text{O}/\text{TiO}_2$ p–n heterojunction, Schottky junction formation at the Au/ TiO_2 interface, plasmon-induced hot electron injection, and enhanced light absorption result in efficient charge separation and accelerated interfacial charge transfer. Consequently, the Au nanostar/

Cu₂O/TiO₂ nanocomposite exhibits superior photocatalytic activity through enhanced reactive oxygen species generation and improved utilization of the solar spectrum [44].

4. Conclusion

In this study, a highly efficient visible-light-driven Au nanostar-loaded Cu₂O/TiO₂ nanocomposite was successfully synthesized and evaluated for the photocatalytic degradation of methylene blue. The presence of Au nanostars significantly enhanced visible-light absorption through localized surface plasmon resonance (LSPR), while the Cu₂O/TiO₂ heterojunction facilitated efficient charge separation and suppressed electron-hole recombination. Systematic optimization of Au loading and catalyst dosage demonstrated that both parameters critically influence photocatalytic performance, with excessive amounts leading to reduced efficiency due to light shielding and mass transfer limitations. Structural and surface analyses (XRD, DLS, and zeta potential) confirmed the successful formation of a crystalline, well-dispersed, and stable nanocomposite system. The photocatalyst exhibited excellent degradation efficiency (~97%) and good reusability over multiple cycles, maintaining acceptable stability (~84% after ten cycles). The enhanced performance is attributed to the synergistic interaction between plasmonic Au nanostars, Cu₂O/TiO₂ heterojunction, and efficient reactive oxygen species (ROS) generation. Overall, the developed nanocomposite shows strong potential as a promising photocatalyst for wastewater treatment and environmental remediation under visible-light irradiation.

Conflict of Interest

The authors declare that they have no known conflicts of interest.

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