https://doi.org/10.30799/jnst.380.26110510 J. Nanosci. Tech. - Volume 11 Issue 5 (2026) 1205–1207

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ISSN: 2455-0191

Photocatalytic Activity of Undoped, Cu-, N-, and (Cu, N) Co-Doped TiO_2 Nanomaterials Synthesized via Sol–Gel Method

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ARTICLEDETAILS

Article history:
Received 13 October 2026
Accepted 24 October 2026
Available online 04 November 2026

Keywords:
Sol-Gel
Photocatalytic Material
Cu-Doped TiO_2
N-Doped TiO_2
UV Irradiation

ABSTRACT

Titanium dioxide (TiO_2), Cu-doped TiO_2, N-doped TiO_2 and Cu-N co-doped TiO_2 nanomaterials were successfully synthesized using sol-gel method and investigated for their structural, morphological, compositional and photocatalytic activity. The synthesized materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). XRD analysis confirmed the crystalline nature of the prepared TiO_2-based nanoparticles and revealed the formation of mixed phase of TiO_2 crystalline. The average crystallite size of co-doped nanomaterial, estimated from the XRD data using the Scherrer equation was approximately 9.25 nm. SEM analysis showed the formation of nanosized particles with relatively homogeneous morphology, although some degree of particle agglomeration was observed. EDX analysis confirmed the presence of the titanium and oxygen in the prepared TiO_2 samples and verified the purity of the synthesized materials. The photocatalytic performance of the prepared samples was evaluated through the degradation of methylene blue (MB) dye under UV irradiation. Among the investigated materials, the pristine TiO_2 exhibited highest photocatalytic degradation efficiency (91.30%) under 30 min UV light irradiation.

1. Introduction

The discovery of the photocatalytic behavior of titanium-based materials by Fujishima and co-workers in the early 1970s initiated extensive research into semiconductor photocatalysis [1]. Since then, substantial efforts have been directed toward designing photocatalytic materials with improved activity, stability and practical applicability. Among the various semiconductor materials investigated, titanium dioxide (TiO_2) has attracted particular attention because of its physical and chemical properties and broad range of application.

TiO_2 possesses relatively low toxicity, good chemical and thermal stability, resistance to corrosion, high photostability, and good environmental compatibility. TiO_2 based photocatalysts have been explored extensively for the treatment of environmental pollutants, particularly for the removal and degradation of organic contaminants present in wastewater and gaseous pollutants in air [2].

Beyond environmental remediation, these materials have also been investigated for applications in solar energy conversion, photocatalytic water spitting for hydrogen generation, self-cleaning coatings and anti-fogging technologies [2-5].

Among the various strategies developed for pollutant removal photocatalytic degradation has emerged as particularly promising and sustainable and efficient methods for pollutant removal. In recent years, this method has been widely used for the remediation of waste water and industrial discharge, particularly for the degradation of persistent organic pollutants such as methyl blue (MB) dye. Improving the light driven photocatalytic performance of TiO_2 remains a critical objective in photocatalysis research. Despite its numerous advantages, TiO_2 exhibits limited photocatalytic efficiency under different light source because of its wide band gap (3.2eV).

To overcome this limitation, various modification strategies have been investigated to improve its photocatalytic performance. These approaches include metal doping with elements such as Cu, Ag, Cr, Fe, Zn and nonmetal doping with C, N, S and P. In particular, transition metal doping has attracted considerable research interest because it can modify the electronic structure of TiO_2 [6-10]. These modifications can promote charge-carrier separation and improve photocatalytic activity depending on dopant type concentration and synthesis conditions. Various synthesis approaches have been reported for the fabrication of pristine and doped TiO_2 nanoparticles including sol-gel, hydrothermal, chemical vapor methods.

Among these techniques, the sol-gel method is widely recognized for its versatility and suitability for producing nanostructured materials with controlled properties [11]. Its major advantages include precise control over chemical composition and particle growth, high product purity, relatively low processing temperatures, improved compositional homogeneity and cost –effectiveness. Furthermore, this method facilitates the incorporation of dopant elements into TiO_2 structure, making it particularly suitable for tailoring the structural, optical and functional properties of TiO_2 nanoparticles [12].

In this study, the photocatalytic performance of pristine TiO_2, Cu-doped TiO_2, N-doped TiO_2 and Cu-N co-doped TiO_2 nanomaterials in powder form were investigated for degradation of methylene blue (MB) dye under UV irradiation. The photocatalytic activity of Cu-N co-doped TiO_2 was evaluated by comparing it with those of pristine TiO_2, Cu-doped TiO_2 and N-doped TiO_2 to assess the influence of individual and combined doping on dye degradation efficiency.

2. Experimental Methods

2.1 Synthesis of Pristine and Doped TiO_2 Nanoparticles

Pristine TiO_2, Cu-doped TiO_2, N-doped TiO_2, and Cu-N co-doped TiO_2 nanoparticles were synthesized through a conventional sol-gel method using titanium isopropoxide (TTIP) as the titanium precursor without further purification. Urea and copper nitrate trihydrate [$Cu(NO_3)_2.3H_2O$] were employed as the nitrogen and copper sources respectively.

In the typical synthesis, 50 mL of titanium isopropoxide (TTIP) was slowly added to 500 mL of deionized water under continuous magnetic stirring. 2 mL of HNO_3 was added to the reaction mixture to control the hydrolysis and condensation processes. The resulting suspension was stirred until a homogeneous sol was obtained. The sol was subsequently aged 20 h at room temperature to promote further hydrolysis, polymerization and condensation of the containing species. After aging, the sol was heated at 100 °C for 4 h to remove physically adsorbed water and volatile components and to obtain a dry precursor. The dried material

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https://doi.org/10.30799/jnst.380.26110510

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Cite this Article as: Rajesh Kumar, Vishal Shukla, Mahendra Kumar, Photocatalytic activity of undoped, Cu-, N-, and (Cu, N) co-doped TiO_2 nanomaterials synthesized via sol–gel method, J. Nanosci. Tech. 11(5) (2026) 1205–1207.

was carefully ground using an agate mortar and pestle to obtain a homogeneous powder. The resulting precursor as finally calcined at 450 °C for 2 h to remove residual organic species and promote crystallization of TiO_2.

For the preparation of Cu-doped TiO_2, the same sol-gel procedure was followed with the incorporation of copper precursor. Copper nitrate trihydrate [Cu $(NO_3)_2.3H_2O$] was used as the Cu dopant. For a nominal Cu concentration of 1wt %, 0.51 g of Cu $(NO_3)_2.3H_2O$ was used for the 50 mL TTIP. The calculated amount of Cu $(NO_3)_2.3H_2O$ was dissolved in 100 mL of deionized water and stirred in a magnetic stirrer for 1 h to obtain a homogeneous solution. The copper precursor solution was then added gradually to the TTIP sol under continuous stirring to achieve uniform dispersion of the Cu species. The resulting sol was aged 20 h, followed by heating at 100 °C for 3 h to obtain the dried precursor. The dried powder was finely ground and subsequently calcined at 450 °C for 2 h.

Nitrogen- doped TiO_2 was synthesized using urea as the nitrogen precursor while maintaining the same sol-gel conditions used for pristine TiO_2. For 1 wt% N-doping 0.29 g urea was mixed in 50 mL TTIP. The calculated amount of urea was dissolved in deionized water under continuous stirring to form a homogeneous solution. The urea solution was then introduced gradually into the TTIP based sol. The resulting mixture was continuously stirred to promote uniform interaction between the nitrogen precursor and the hydrolyzed titanium species. The sol was subsequently aged for 20 h. After aging, the material was heated at 100 °C for 3 h and the resulting dry precursor was ground thoroughly. The powdered precursor was then calcined at 450 °C for 2 h to obtain the nitrogen-doped TiO_2 nanoparticles.

Cu-N co-doped TiO_2 was synthesized by simultaneously incorporating Cu $(NO_3)_2.3H_2O$ and urea into the TTIP. The copper nitrate trihydrate and urea were separately dissolved in appropriate amounts of deionized water under continuous stirring. The two precursor solutions were subsequently combined and added gradually to the TTIP based sol while maintaining vigorous stirring. Continuous stirring was maintained to promote homogeneous distribution of Cu and N –containing species throughout the titanium precursor. The resulting Cu-N containing sol was allowed to age for 20 h. Following aging, the sol was heated at 100 °C for 3 h to remove water and volatile components and calcined at 450 °C for 2 h.

2.2 Characterization Techniques

The structural properties of the synthesized TiO_2 nanoparticles were investigated by X-ray diffraction (XRD) (PANalytical X'Pert PRO diffractometer) Cu Kα radiation (λ = 1.5406 Å) at an operating voltage of 40 kV and a current of 40 mA. The crystallite size of the samples was estimated from the characteristic diffraction peaks using the Debye–Scherrer equation.

The morphological characteristics of the synthesized powders were examined by JEOL field-emission scanning electron microscopy (FESEM) at an accelerating voltage of 25 kV. Energy-dispersive X-ray spectroscopy (EDS) was employed to determine the elemental composition of the samples and to confirm the presence of the incorporated dopant elements.

2.3 Photodegradation Experiments

Methylene blue (MB) is a widely used dye in photocatalytic studies. In this work methylene blue (MB) was selected as a representative organic pollutant to assess the photocatalytic performance of the synthesized TiO_2 upon irradiation with ultraviolet and visible light. Photocatalytic degradation studies were performed using 100 mL of 10 ppm aqueous methylene blue (MB) solution. To each solution an amount of 0.5 g of the TiO_2 was added. To ensure adsorption -desorption equilibrium, the reaction mixture was magnetically stirred under dark conditions for 1 hour before light exposure.

Blank experiments confirmed that no significant change in dye concentration occurred in the absence of the photocatalyst under identical irradiation conditions. After adsorption equilibrium, the initial dye concentration (C_0) was recorded, and the suspension was irradiated with a 30 W mercury lamp for UV light. The photocatalytic experiments carried out in a 10 cm diameter reaction vessel below 10 cm of the lamp. At regular time intervals, 5 mL aliquots were withdrawn and the photocatalyst was removed by centrifugation. The concentration of MB in the supernatant was measured using a UV-Vis spectrophotometer (Jasco V-550, Japan) at λ = 662 nm.

The percentage degradation of the pollutant was evaluated using the Eq.(1):

$$\%\text{Degradation efficiency} = \frac{C(0) - C(t)}{C(0)} \times 100 \quad (1)$$

where C(0) and C(t) represents the dye concentrations at initial stage and after an irradiation time of t respectively.

3. Results and Discussion

3.1 XRD Analysis

The XRD patterns of investigated samples pristine TiO_2, Cu-doped TiO_2, N-doped TiO_2 and Cu-N co-doped TiO_2 are shown in Fig. 1. The diffraction peaks are labeled as A and R corresponding to the anatase and rutile phases of TiO_2 respectively. The diffraction peaks observed at 2θ values of approximately 25.5°, 37.3° and 48.2° are assigned to the (101), (004), (200) planes of anatase TiO_2 respectively in accordance with JCPDS card no. 21-1272.

In addition, some low intensity diffraction peaks appearing at approximately 27°, 35.1°, 43° and 53.3° are consistent to crystallographic planes (110), (101), (111) and (211) for rutile TiO_2. The XRD patterns shows mixed phase of TiO_2 structure. Furthermore, no distinct diffraction peaks corresponding to crystalline copper containing phases were observed in the XRD patterns. This may indicate that Cu species are highly dispersed within the TiO_2 structure and incorporated into the TiO_2 lattice. These observations are consistent with previous studies on copper-modified TiO_2 materials [13]. The ratio of rutile to anatase phase can be calculated by using Eq.(2).

$$\%\ \text{Rutile} = \frac{R}{0.866A+R} \times 100 \quad (2)$$

where A and R is intensities of the anatase peaks (101) and rutile peaks (110) respectively.

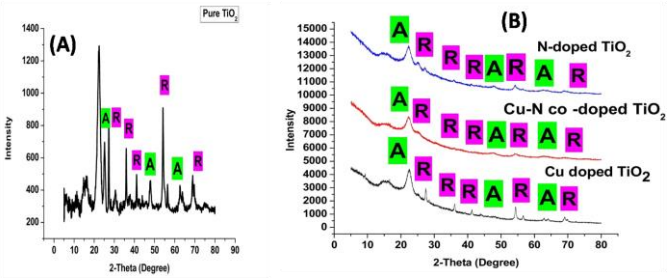


Fig. 1 XRD for Pure TiO_2, Cu-doped TiO_2, N-doped TiO_2 and Cu-N co-doped TiO_2

The crystalline size of each prepared sample was estimated from broadening of the XRD diffraction peaks by measuring their full width at half maximum (FWHM) as shown in Figure (1), using the Debye- Scherrer equation, $D = \frac{K\lambda}{\beta COS\theta}$, where D is the average crystalline (nm), λ is the wave length of the X-ray radiation (Cu Kα= 0.15406 nm), β is the value of half width and θ is the Bragg angle. The ratio of rutile to anatase phase and average crystallite sizes calculated for the prepared samples are presented in Table 1. The results show that the doped TiO_2 samples exhibit smaller average crystallite sizes than pure TiO_2 [14, 15].

Table 1 Comparison of the rutile to anatase phase ratio and average crystallite size of pure TiO_2, Cu-doped TiO_2, N-doped TiO_2, and Cu-N co-doped TiO_2 nanoparticles

S.No.	Samples	Ratio of rutile to anatase (%)	Average crystallite sizes (nm)
1.	Pure TiO_2	57.27	26.80
2.	Cu-doped TiO_2	48.37	12.22
3.	N-doped TiO_2	73.60	25.8
4.	Cu-N co-doped TiO_2	48.33	9.35

3.2 SEM and EDX Analysis

The surface morphology of pristine TiO_2, Cu-doped TiO_2, N-doped TiO_2 and Cu-N co-doped TiO_2 nanoparticles was examined using scanning electron microscopy (SEM) as shown in Fig. 2 [16].

The pristine TiO_2 sample exhibits irregularly distributed closely packed particles with notable agglomeration. The Cu-doped and N-doped samples display larger irregularly shaped aggregates, indicating pronounced particle agglomeration. In contract, the Cu-N co-doped TiO_2 sample exhibits a comparatively uniform, fine grained surface texture with relatively small particles distributed across the observed area and a few larger agglomerates.

The elemental composition of TiO_2-based samples was examined using energy-dispersive X-ray spectroscopy (EDX) as shown in Fig. 3. The spectra of all samples exhibit characteristic signals associated with titanium and oxygen, confirming that these elements are the principal constituents of the TiO_2-based materials. For Cu-doped, N-doped and Cu-N co-doped TiO_2 samples, additional peaks attributed to copper and n supporting the presence of Cu and N in the prepared materials [17].

https://doi.org/10.30799/jnst.380.26110510

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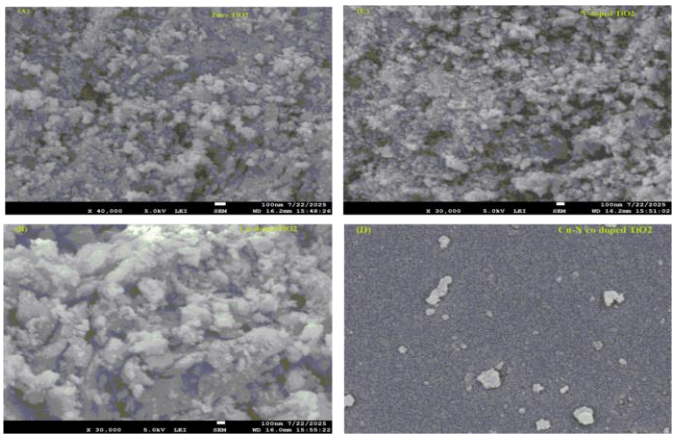


Fig. 2 SEM images of (A) Pure TiO_2 (B) Cu-doped TiO_2 (c) N-doped TiO_2 and (D) Cu-N co-doped TiO_2

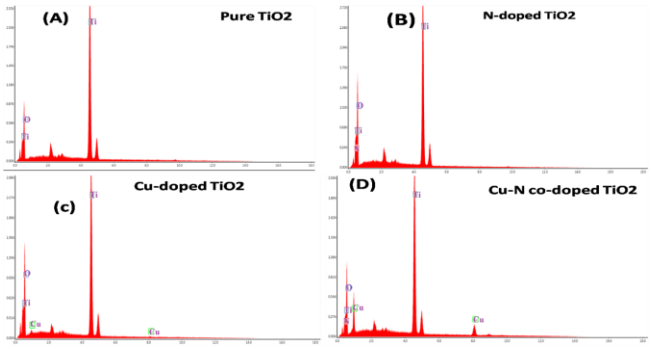


Fig. 3 EDX spectrum of pure TiO_2, N-doped TiO_2, Cu-doped TiO_2 and Cu-N co-doped TiO_2

3.3 Photocatalytic Degradation

The photocatalytic performance of pure and doped TiO_2 nanoparticles was evaluated through the degradation of methylene blue (MB) under UV light irradiation within 30 minutes after dark absorption (Fig. 4). Prior to illumination, the mixture of catalyst and dye solution was continuously stirred in the dark to establish adsorption–desorption equilibrium for 30 minutes. The temporal degradation behavior was tracked by recording the concentration value (C_o/C_t) at regular intervals. The degradation efficiency changes with irradiation time for all samples [18]. Among the investigated materials, the pristine TiO_2 exhibited highest photocatalytic degradation efficiency (91.30 %) under 30 min UV- light irradiation.

Table 2 Comparative photocatalytic degradation performances

Samples	TiO_2	Cu-doped TiO_2	N-doped TiO_2	Cu-N co-doped TiO_2
% Degradation	91.30	59.64	85.56	48.59
Degr. Ratio(C_o/C_t)	11.494	2.478	6.929	1.946

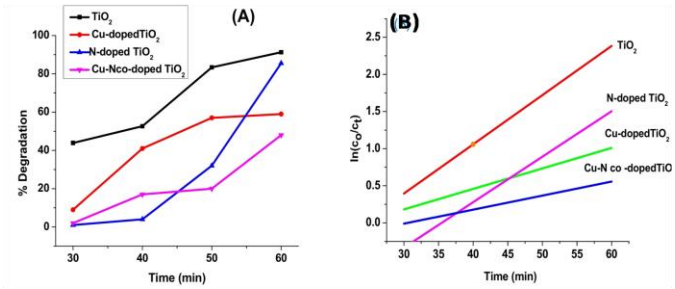


Fig. 4 (A) Photocatalytic % degradation vs. irradiation time (B) Pseudo-first-order kinetics plot

3.4 Kinetic Analysis

The photocatalytic degradation kinetics was analyzed using the pseudo-first-order model, $-\ln\frac{c_o}{c_t} = kt$. The linear relationship between ln (C_0/C_t) and irradiation time confirms that the degradation process follows pseudo-first-order kinetics. The pseudo-first order rate constants are estimated from the slope of the fitted straight line corresponds to the apparent rate constant (k) versus irradiation time plots [19]. Under UV-irradiation pristine TiO_2 nanoparticles exhibit a higher reaction rate constant than Cu-doped, N-doped and Cu-N co-doped TiO_2 nanoparticles.

4. Conclusion

Titanium dioxide (TiO_2), Cu-doped TiO_2, N-doped TiO_2 and Cu-N co-doped TiO_2 nanomaterials were successfully synthesized using sol-gel method and evaluated for their photocatalytic performance toward methylene blue (MB) degradation under UV irradiation. Morphological analysis revealed that the synthesized nanoparticles exhibited a spherical shape with noticeable agglomeration. Structural characterization indicated that the incorporation of the copper and nitrogen influenced the phase composition of TiO_2 promoting the formation of rutile phase. Among the investigated materials, the pristine TiO_2 exhibited highest photocatalytic degradation efficiency approximately 91.30% under 30 min UV light irradiation. This result indicates that pristine TiO_2 was more effective in degradation methylene blue (MB) under the experimental conditions employed. The comparatively lower degradation efficiency of the doped samples may be associated with changes in the crystal phase, defect distribution and charge-carrier dynamics induced by Cu and N incorporation.

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https://doi.org/10.30799/jnst.380.26110510

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