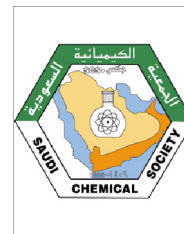




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ORIGINAL ARTICLE

Efficient photocatalysis of Cu doped $\text{TiO}_2/\text{g-C}_3\text{N}_4$ for the photodegradation of methylene blue



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Abstract The release of dyes into normal water reservoirs has become a tremendous environmental problem and the development of methods to remove such dyes is essential. A novel photocatalyst was fabricated in which Cu doped TiO_2 was coupled with $\text{g-C}_3\text{N}_4$ ($\text{Cu-TiO}_2/\text{g-C}_3\text{N}_4$) in different weight percentages as 10, 30 and 50%, hydrothermally. Pure TiO_2 consisted of both Anatase and Rutile phases where slight lattice distortions were observed in the Cu-doped TiO_2 as evidenced by the XRD and Raman analysis. Cu was present at 1.7% by weight respective to TiO_2 according to the XRF analysis. Spherical and irregularly shaped aggregated Cu-doped TiO_2 nanoparticles in the range of 15–55 nm were heterogeneously distributed on the $\text{g-C}_3\text{N}_4$ matrix as observed by TEM and SEM. The band gap of TiO_2 (3.0 eV) was reduced to 2.67 upon doping with Cu. The band gap of $\text{g-C}_3\text{N}_4$ was found to be 2.81 eV and that of $\text{Cu-TiO}_2/\text{g-C}_3\text{N}_4$ in different weight percentages were in the range of 2.82 to 2.88 eV. Synthesized photocatalysts were tested on the ability to degrade methylene blue under UV and Visible light. $\text{Cu-TiO}_2/50\% \text{ g-C}_3\text{N}_4$ showed the highest rate constant ($4.4 \times 10^{-3} \text{ min}^{-1}$) which is 5 and 9.8 times greater than TiO_2 and $\text{g-C}_3\text{N}_4$, respectively. The rate constant decreased with the introduction of EDTA and Isopropyl alcohol as they scavenge holes and hydroxyl radicals, respectively. The photocatalytic activity of all the nanomaterials increased with the increasing concentration of persulfate due to the increasing concentration of $\text{SO}_4^{\bullet-}$ and $\text{OH}^{\bullet}$ produced. Synthesized nanomaterials effectively adsorb methylene blue under dark conditions following the pseudo-second-order kinetics suggesting that methylene blue molecules were chemisorbed to the adsorbents. The adsorption rate constant resulting in the

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best-performing photocatalyst was $0.122 \text{ g mg}^{-1} \text{ min}^{-1}$. Hence, it is evident that $\text{Cu-TiO}_2/\text{g-C}_3\text{N}_4$ can effectively degrade methylene blue.

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1. Introduction

Water pollution is a tremendous problem being emerged in the last few decades due to industrialization, urbanization and economic revolution. Organic pollutants including but not limited to dyes, pesticides, and pharmaceuticals are released to water reservoirs and cause severe hazardous effects because they persist in the environment as they are resistant to degradation. Therefore, water purification is eliciting attracting scientists to mitigate the severe effects resulting from the pollutants. Among the many organic pollutants that are being discharged into water, dyes which are released from textile, paper, paint (Al-Tohamy et al., 2022; Parmar et al., 2022; Silva et al., 2021) etc. industries play a major role as they are constituted of heavy metals (Singha et al., 2021) and aromatic compounds (Faria et al., 2008) in addition to the dye molecules. Dyes in aquatic environments cause health risks to living organisms, reduce the light penetration into the water body and hence reduce the photosynthetic efficiency of aquatic plants which also leads to producing anoxic conditions that impact the aquatic fauna and flora (Dutta & Bhattacharjee, 2022). They degrade the aesthetic value of the water bodies due to the persistent colours and increase the biological and chemical oxygen demand (Azanaw et al., 2022). Further, they get accumulated in the food chain and promote toxicity leading to many severe health conditions (Lellis et al., 2019). Therefore, it is vital to remove the dyes from normal water reservoirs. Many methods including membrane filtration (Ramutshatsha-Makhwedzha & Nomngongo, 2022), adsorption (Birniwa et al., 2022; Gunathilaka et al., 2021), ion exchange (Lu et al., 2022), coagulation (Ihaddaden et al., 2022), oxidation (Javanbakht & Mohammadian, 2021), hydrogenation catalysis (J. Thambiliyagodage et al., 2016) etc. have been employed to remove dyes from contaminated water. However, these methods possess different disadvantages such as sludge production, high cost, incomplete removal, poor mass transfer, low permeability, unsuitable for larger volumes, formation of toxic byproducts etc. despite their advantages of being effective in a wide range of dyes, eco-friendliness, effective decolourization etc (Moosavi et al., 2020). Hence, it is necessary to develop a new technique to alleviate the existing problem which could overcome the drawbacks shown by the established methods and be more advantageous including being efficient.

The advanced oxidation process (AOP) involves the generation of reactive oxygen species such as $\text{OH}^\bullet$, $\text{O}_2^\bullet$, H_2O_2 , and O_3 which degrade the pollutant molecules into harmless products. Degradation of methylene blue by many AOP methods including ozonation (Babar et al., 2022), photocatalysis (Thambiliyagodage, Kumara, et al., 2022), Fenton (Kirchon et al., 2020), sonolysis (Bezzerrouk et al., 2021), and electrochemical oxidation (Samarghandi et al., 2020) have been reported. However, these methods possess disadvantages such as toxicity of by products, the requirement of large quantities of H_2O_2 , effective in low pH, the requirement of sophisticated equipment, highly expensive etc. (X. Li et al., 2021; Lyu et al., 2016; Pirsaeheb & Moradi, 2021). Photocatalysis is advantageous over the other methods because methylene blue is degraded into harmless products such as CO_2 , H_2O , NH_4^+ , SO_4^{2-} and NO_3^- (Charitha et al., 2021).

Semiconductors are employed in mineralizing organic molecules via AOP and the most widely used semiconductor is TiO_2 due to its stability, non-toxicity and low cost (Guo et al., 2019). However, TiO_2 bearing a band gap of 3.2 eV in general is active only in the UV range limiting its applicability in the visible range (Sharma et al., 2019). TiO_2 has been doped with metals like Fe (Thambiliyagodage & Mirihana, 2021), Cu (Lee et al., 2021), and Mn (Lee et al., 2021), and non-metals such as N (Thambiliyagodage

& Usgodaarachchi, 2021), C (Pandi et al., 2022), and S (T. Li et al., 2021) to reduce the band gap to increase the visible light sensitivity. However, the photocatalytic activity is reduced due to the electron-hole pair recombination even though in general the photocatalytic activity in visible light is enhanced via reducing the band gap. Therefore, to enhance the charge separation TiO_2 has been coupled with other semiconductors forming type I and type II heterojunctions. Semiconductors including WO_3 (H. Li et al., 2021), Fe_2O_3 (Fawzi Suleiman Khasawneh & Palaniandy, 2021), BiOI (Liao et al., 2022), and MoS_2 (Y. Wu et al., 2022) form type I heterojunctions with TiO_2 while semiconductors like CuO (Shi et al., 2019), CdSe (M. Yang et al., 2018), V_2O_5 (Ghosh et al., 2018), CeO_2 (Tuyen et al., 2018), Bi_2S_3 (Z. Wu et al., 2020), WS_2 (Jing & Guo, 2007), Bi_2O_3 (Lakshmana Reddy et al., 2017) form type II heterojunctions.

$\text{g-C}_3\text{N}_4$ is a metal-free semiconductor which is normally synthesized by precursors such as urea, melamine, cyanamide etc. It is comprised of s-triazine or tri-s-triazine units as the structural monomers where the sheets resemble the structure of the honeycomb. Atoms of one sheet are interconnected via covalent bonds and the sheets are held together by Vander Waals forces (Yu et al., 2023). $\text{g-C}_3\text{N}_4$ has been coupled with other materials including TiO_2 (Kobkeattawin et al., 2022), ZnO (Geng et al., 2021), Fe_2O_3 (Pham et al., 2022), SnO_2 (Van et al., 2022), V_2O_5 (Preeyanghaa et al., 2022), Bi_2O_4 (J. Yang et al., 2020), $\alpha\text{-MoCl-x}$ quantum dots (Zhu et al., 2022), charcoal (Yu et al., 2020) etc. and also with to maximize the charge separation as $\text{g-C}_3\text{N}_4$ is taken individually electron-hole pair recombination was found to be a problem which leads to lower photocatalytic activity.

According to our knowledge coupling of $\text{g-C}_3\text{N}_4$ with TiO_2 doped with metals has not been reported in detail. Metal-doped TiO_2 possess a reduced band gap being active in the visible range but shows low photocatalytic activity due to electron-hole pair recombination while as discussed above $\text{g-C}_3\text{N}_4$ also exhibits the same disadvantage. Therefore, coupling such two semiconductors would be advantageous as both the semiconductors are visible active. Hence, Cu doped TiO_2 was coupled with $\text{g-C}_3\text{N}_4$ to form a z-scheme heterojunction and the photocatalytic activity of the synthesized nanocomposite was evaluated in the photodegradation of methylene blue.

2. Materials and methods

2.1. Materials

P25 TiO_2 (99.5%) and Urea (99.5%) were purchased from Sigma Aldrich, German. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99%) was procured from Sisco Research Laboratories (Pvt) Ltd, India. Methylene blue (98%) was purchased from Himedia Laboratories (Pvt) Ltd, India. All the chemicals were used as it is without further purification. Distilled water was used for all the experiments.

2.2. Procedure

2.2.1. Synthesis of Cu-TiO_2

P25 TiO_2 was dispersed in distilled water. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in distilled water where the molar percentage of Cu was maintained at 1% with respect to Ti and the obtained solution was added dropwise to the solution containing P25 while stirring. Stirring continued for 24 h and the obtained pre-

precipitate was washed with distilled water until the filtrate was negative for Cl⁻ ions for the AgNO₃ test. Then the temperature was increased and maintained at 80 °C until all water evaporates. The resulting solid was ground and calcined at 450 °C for 2 h. The product is denoted as Cu-TiO₂ in the text.

2.2.2. Synthesis of g-C₃N₄

The urea was annealed in a tube furnace at 550 °C for 4 h under N₂ atmosphere and the resulting yellow colour product was washed with distilled water and ethanol, followed by drying at 80 °C.

2.2.3. Synthesis of Cu-TiO₂/C₃N₄

g-C₃N₄ was mixed with Cu-TiO₂ in different weight percentages as 10, 30 and 50 % and the product was sonicated for 1 h. The resulting mixture was hydrothermally treated at 180 °C for 15 h. The product obtained was washed with distilled water and ethanol and dried at 80 °C.

2.3. Characterization techniques

X-ray diffraction (XRD) patterns were collected using an Advance Bruker system using CuKα ($\lambda = 0.154$ nm) radiation and 2θ varying from 5°–80° at a scan speed of 2°/min. Raman spectra were acquired by a Bruker Senterra Raman microscope spectrometer. The morphology of the nanomaterials was observed by both scanning electron microscope (SEM) and transmission electron microscope (TEM). The transmission electron microscope was operated at 200 kV (JEOL - JEM – 2100). The sample (1 μ l) was mounted on a holey carbon copper grid and allowed to dry at room temperature before TEM analysis. SEM images were collected by Hitachi SU6600 Analytical Variable Pressure FE-SEM (Field Emission Scanning Electron Microscope). Samples were mounted on a carbon tape pasted on a stub and the samples were sputtered with gold to neutralize the charge. The chemical composition of the samples was analyzed by X-ray fluorescence (XRF) using a HORIBA Scientific XGT-5200 X-ray analytical microscope equipped with a Rh anode X-ray tube operated at a maximum voltage of 50 kV. The surface chemistry of the nanomaterials was analyzed by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific™ ESCALAB Xi + X-ray Photoelectron Spectrometer. Shimadzu 1800 UV/Visible spectrophotometer utilizing a precision Czerny-Turner optical system was used to analyze diffuse reflectance spectra of the prepared powder samples. The measurements were carried out through the range of 400 to 750 nm with a bandwidth of 1.0 nm (wavelength accuracy $\pm$ 0.1 nm). The absorbance of MB samples was measured by a Shimadzu UV-1990 double-beam UV–Visible spectrophotometer.

2.4. Photocatalysis

Each synthesized photocatalyst (200 mg) was shaken with 100 ml of 10 mg/L MB solution in dark for 1 h to reach the adsorption and desorption equilibrium during which aliquots were taken in different time intervals to study the adsorption kinetics. After that, the samples were exposed to a UV–Visible source operated with a 100 W mercury lamp (253 nm) and 100 W LED (589 nm) light and aliquots were withdrawn in

15 min time intervals to study the photocatalytic performance. To study the effect of scavengers EDTA (4 mM) and IPA (4 mM) were added just before exposing them to the light source. Similarly, to study the effect of persulfate on photocatalysis persulfate was added to the reaction mixture in different concentrations as 2, 4 and 8 mM and the photocatalysis experiments were carried out as described above.

3. Results and discussion

3.1. XRD analysis

XRD analysis was performed to determine the crystal structure of the synthesized nanomaterials. The XRD pattern of g-C₃N₄ shows two peaks at 13.00° and 27.04° which correspond to (100) and (002), respectively. XRD pattern of P25 TiO₂ shows peaks at 27.57°, 36.18°, 41.37° and 56.73° which are attributed to (110), (101), (111) and (220) planes of the Rutile phase and the peaks at 25.46°, 37.95°, 38.72°, 39.31°, 48.17°, 54.07°, 55.18°, 62.83°, 68.94°, 70.34° and 75.21° assigned to (101), (103), (004), (112), (002), (105), (211), (204), (115), (220) and (215) the Anatase phase (Fig. 1 (a)). The same peaks were observed in Cu-TiO₂ and Cu-TiO₂ composited with g-C₃N₄. The Interlayer distance (d) and the crystallite size (L) of the synthesized nanomaterial were calculated by equations 1 and 2, respectively, where,

- λ - wavelength of the X-ray source
- θ - diffraction angle
- L - crystallite size
- β - half maximum of the peak in radians
- K - Scherer's constant (0.9)

$$\lambda = 2d\sin(\theta). \quad (1)$$

$$L = K\lambda/\beta\cos\theta. \quad (2)$$

The interlayer distance and the crystallite size of g-C₃N₄ were 0.3293 nm and 2.591 nm and the number of planes in the synthesized g-C₃N₄ was 8. (101) plane of the Anatase phase and (110) of Rutile phase was considered for the calculation of the interlayer distance and crystallite size of those phases in P25 TiO₂ and they were calculated to be 0.3495 nm and 18.622 nm, respectively, for Anatase phase and 0.3232 nm and 29.263 nm, respectively, for Rutile phase. The number of planes in the Anatase phase is 53 and in the Rutile phase is 90.

Peaks corresponding to the same planes were considered for calculations of the same parameters in Cu-TiO₂ and Cu-TiO₂ composited with g-C₃N₄. Table 1 summarizes all the data calculated relative to the crystalline structure of the synthesized nanomaterials. But peak positions of the (101) plane of Anatase and (110) plane of Rutile reduced in Cu doped sample than that of P25 suggesting the lattice distortion which may have occurred during doping of Cu (Fig. 1 (b)). No crystal peaks corresponding to Cu or oxide of Cu were observed suggesting that Cu has successfully doped to the P25 lattice. Generally, the crystallite size of the Anatase phase increased with the doping of Cu and compositing with g-C₃N₄. However, no such trend in crystallite size was observed with the Rutile

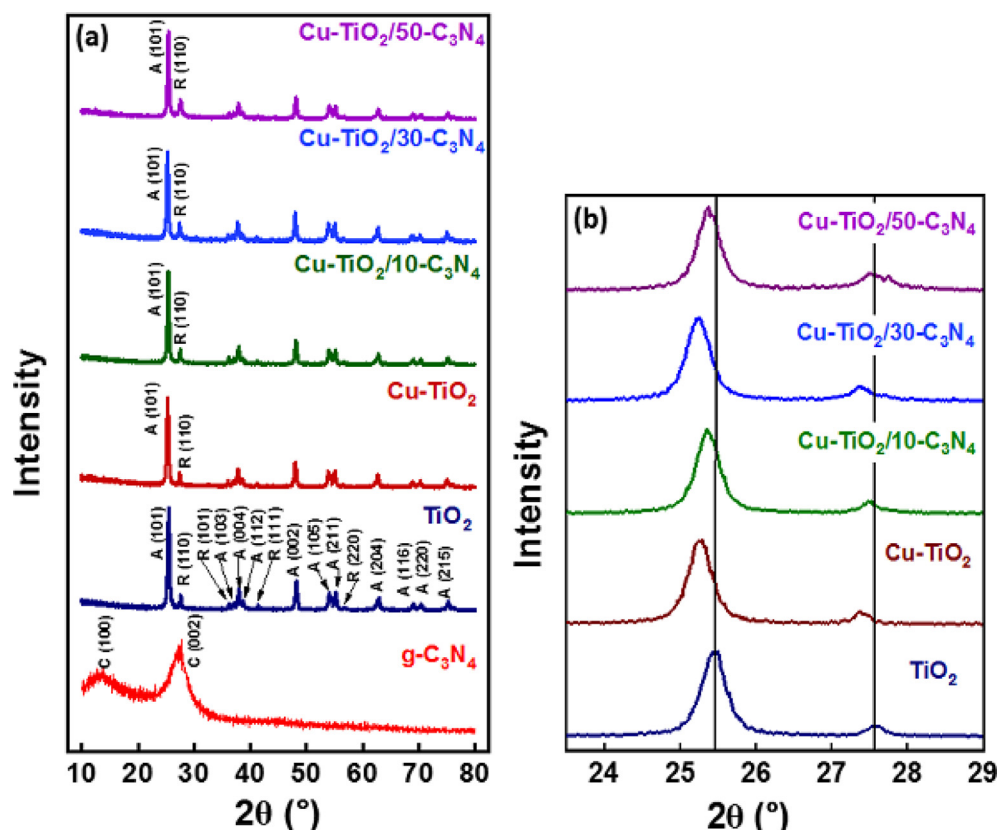


Fig. 1 (a) XRD pattern of the synthesized nanomaterials (b) partially enlarged XRD patterns between 24° and 29°.

Table 1 Crystallographic parameters of the synthesized nanomaterials.

Sample	Crystal Plane	2θ (°)	L (nm)	d (nm)	L/d
g-C ₃ N ₄	C (002)	27.05	2.591	0.3293	8
TiO ₂	A (101)	25.45	18.622	0.3495	53
	R (110)	27.57	29.263	0.3232	90
Cu-TiO ₂	A (101)	25.26	18.995	0.3521	54
	R (110)	27.37	21.240	0.3254	65
Cu-TiO ₂ /10- C ₃ N ₄	A (101)	25.36	19.317	0.3508	55
	R (110)	27.49	27.816	0.3240	85
Cu-TiO ₂ /30- C ₃ N ₄	A (101)	25.24	18.996	0.3525	54
	R (110)	27.37	21.240	0.3255	65
Cu-TiO ₂ /50- C ₃ N ₄	A (101)	25.36	19.456	0.3507	55
	R (110)	27.57	14.907	0.3232	46

phase. The interlayer distance of both Anatase and Rutile did not change upon doping with Cu or g-C₃N₄. This suggests that Cu²⁺ ions have been doped to the Anatase crystal structure of P25. The ionic radius of Cu²⁺ (73 pm) is quite similar to the ionic radius of Ti⁴⁺ (74 pm). Metal ions could be doped to TiO₂ interstitially or substitutionally and as the cationic radii of both are quite similar it is suggested that Cu²⁺ have replaced Ti⁴⁺ in the Anatase phase of TiO₂ lattice. Further, the absence of peaks attributed to Cu or oxide of Cu could be due to the good dispersion of those compounds if they have formed at the low concentration of Cu (1%) introduced during the synthesis.

3.2. Raman analysis

Raman analyses were performed to confirm the crystal structure suggested by XRD analysis (Fig. 2). The Raman spectrum of P25 TiO₂ shows peaks at 143 cm⁻¹, 196 cm⁻¹, 396.5 cm⁻¹, 515 cm⁻¹ and 638.5 cm⁻¹ which are attributed to E_g, E_g, B_{1g}, A_{1g} and E_g vibrational modes of Anatase phase (Balachandran & Eror, 1982; Hardcastle, 2011). Peaks relevant to the vibrational modes of the Rutile phase were absent. The Raman spectrum of Cu-TiO₂ is identical to that of P25. However, the peak corresponding to the E_g band appeared in P25 at 143 cm⁻¹ while that in Cu-TiO₂ appeared at 144 cm⁻¹ suggest-

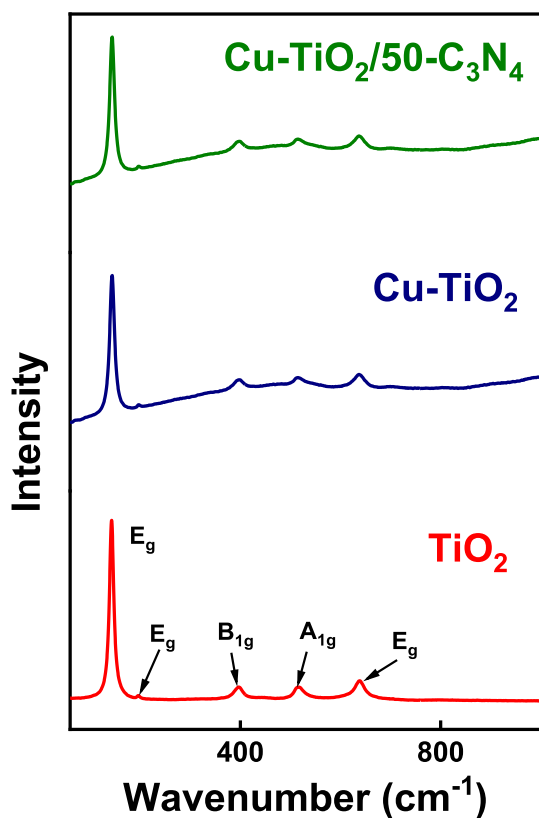


Fig. 2 Raman spectra of TiO_2 , Cu-TiO_2 and $\text{Cu-TiO}_2/50\text{-C}_3\text{N}_4$.

ing a lattice distortion upon doping with Cu being consistent with the XRD analysis. The Raman spectrum of $\text{Cu-TiO}_2/50\text{-C}_3\text{N}_4$ is also identical to that of P25 and no peaks corresponding to $\text{g-C}_3\text{N}_4$ were observed.

3.3. TEM analysis

Transmission Electron Microscopy (TEM) is used to study the morphology of nanomaterials synthesized at the nanoscale. TEM image of $\text{g-C}_3\text{N}_4$ (Fig. 3 (a)) shows that thin and fluffy $\text{g-C}_3\text{N}_4$ nanosheets are arranged as tremella-like layers. Further, a mesoporous network has been formed in the nanosheets of $\text{g-C}_3\text{N}_4$ as revealed in Fig. 3 (b) due to the polymerization and the elimination of gas molecules during the annealing process. Nitrogen and oxygen in the reaction system can generate gas bubbles splitting the polymer when it polymerizes resulting in stripping $\text{g-C}_3\text{N}_4$ layers into small layers producing a fluffy structure. TEM image of P25 TiO_2 (Fig. 3 (c)) shows spherical homogeneously distributed nanoparticles along with some aggregated irregular shape particles. The crystalline plane arrangement of P25 TiO_2 is exhibited in the Higher resolution TEM (HRTEM) image (Fig. 3 (d)). Calculated interlayer distances, 0.23 nm and 0.35 nm correspond to the (103) plane and (101) plane of the Anatase phase, respectively. Cu-TiO_2 nanoparticles show spherical and irregular shape nanoparticles with some agglomerations (Fig. 3 (e)). HRTEM of Cu-TiO_2 (Fig. 3 (f)) clearly shows crystalline plane arrangements with interlayer distances of 0.35 nm and 0.32 nm, corresponding to the (110) plane of Anatase and (101) plane of the Rutile phase, respectively. TEM image of $\text{Cu-TiO}_2/50\text{-C}_3\text{N}_4$ (Fig. 3 (g)) shows spherical and aggregated nanoparticles heteroge-

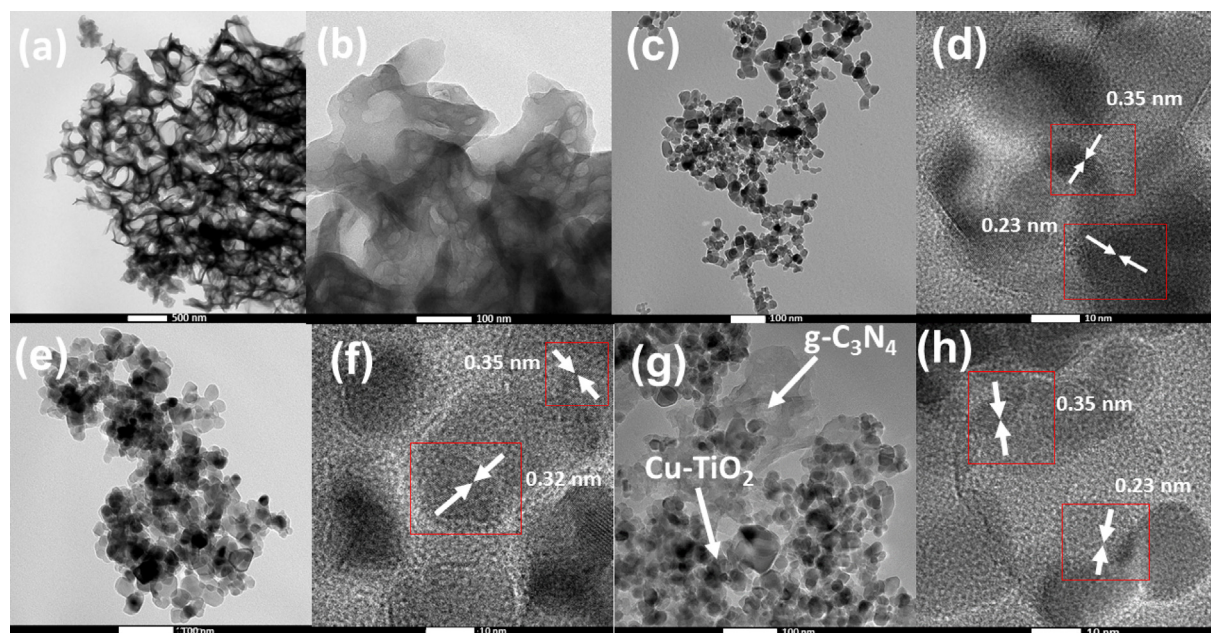


Fig. 3 TEM images of (a) $\text{g-C}_3\text{N}_4$ at low magnification (b) $\text{g-C}_3\text{N}_4$ at high magnification (c) P25 TiO_2 (d) HRTEM image of P25 TiO_2 (e) TEM image of Cu-TiO_2 (f) HRTEM image of Cu-TiO_2 (g) TEM image of $\text{Cu-TiO}_2/50\text{-C}_3\text{N}_4$ (h) HRTEM image of $\text{Cu-TiO}_2/50\text{-C}_3\text{N}_4$.

neously distributed on a fluffy nanosheet mesoporous network. HRTEM image of Cu-TiO₂/50-C₃N₄ (Fig. 3 (h)) shows the interlayer distances 0.35 nm and 0.23 nm corresponding to (101) and (103) planes of Anatase phase, respectively further supporting the crystal nature of the nanoparticles in the composite.

3.4. SEM analysis

SEM images were collected to study the morphology of the synthesized nanomaterials. SEM image of P25 TiO₂ (Fig. 4 (a)) shows the spherical and irregularly shaped nanoparticles with some agglomerations. Upon doping with Cu further agglomerations were observed which could have occurred during the synthesis and annealing (Fig. 4 (b)). SEM image of g-C₃N₄ (Fig. 4 (c)) exhibited a properly developed macropore structure where ligaments are interconnected to form a disordered macropore network and the insert of Fig. 4 (c) shows the irregularity of the macropores in high magnification. g-C₃N₄ possesses a well-established mesopore structure as shown in the TEM image (Fig. 3 (b)). These mesopores and macropores together form a hierarchical porous system where the two porous systems are interconnected forming channels for the reagents and products to pass through which is an important characteristic in catalysis. However, such porous structure has been disturbed upon coupling with Cu-TiO₂ as shown in Fig. 4 (d) in Cu-TiO₂/50-C₃N₄, as the nanoparticles which are high in weight proportion of the composite, mask and block the porous system. Further, Cu-TiO₂ nanoparticles are properly distributed on the g-C₃N₄ matrix which would

facilitate the physical connection of the two materials, Cu-TiO₂ and g-C₃N₄, making them ideal candidates in catalysis.

Brunauer-Emmett-Teller (BET) surface area analysis was performed to study the surface area and the pore size distribution of the samples. Adsorption desorption isotherms and the pore size distribution curves of TiO₂, Cu-TiO₂, and Cu-TiO₂/50-C₃N₄ are shown in Supplementary Figure 1 (a) and (b), respectively. Isotherms exhibited type IV behaviour indicating the mesoporous structure. The surface area of Cu-TiO₂ (82.76 m²/g) is lesser than that of TiO₂ (110.99 m²/g) indicating the agglomeration resulted during doping while the surface area of Cu-TiO₂/50-C₃N₄ (35.46 m²/g) is lesser than both. No significant change was found in the total pore volume of Cu-TiO₂ (0.38 cc/g) and TiO₂ (0.37 cc/g), and that of Cu-TiO₂/50-C₃N₄ (0.08 cc/g) was very low. The pore radius of Cu-TiO₂ (9.12 nm) is greater than that of TiO₂ (6.66 nm) indicating the generation of more meso and micropores while doping and the pore radius of Cu-TiO₂/50-C₃N₄ is 4.38 nm.

3.5. XPS analysis

X-ray photoelectron spectra were collected to study the surface of the synthesized catalysts. The survey spectrum of P25 TiO₂ (Fig. 5 (a)) shows the presence of C, Ti and O and the survey spectrum of Cu-TiO₂ (Fig. 5 (b)) exhibits the presence of Cu in addition to C, Ti and O. The presence of C, N and O was revealed in the survey spectrum of g-C₃N₄ (Fig. 5 (c)) while the survey spectrum of Cu-TiO₂/50-C₃N₄ (Fig. 5 (d)) indicates the presence of all C, O, N, Ti and Cu. The higher-resolution spectra of the synthesized materials were collected to study sur-

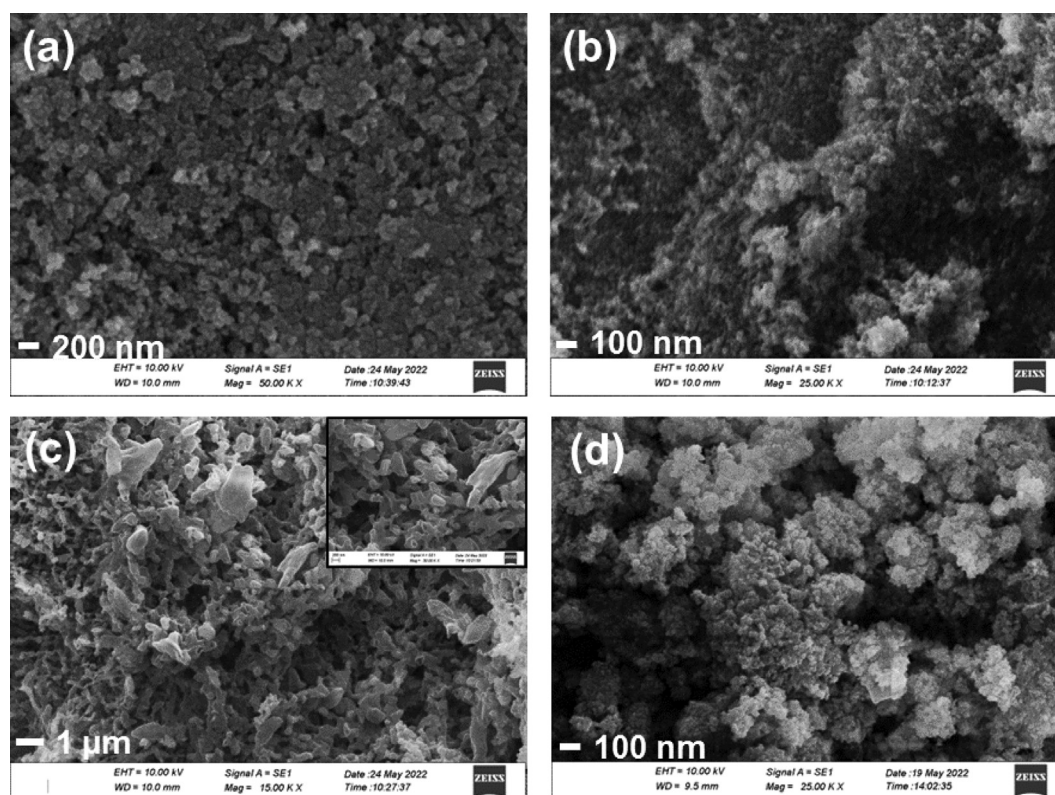


Fig. 4 SEM images of (a) P25 TiO₂ (b) Cu-TiO₂ (c) g-C₃N₄ (d) Cu-TiO₂/50-C₃N₄.

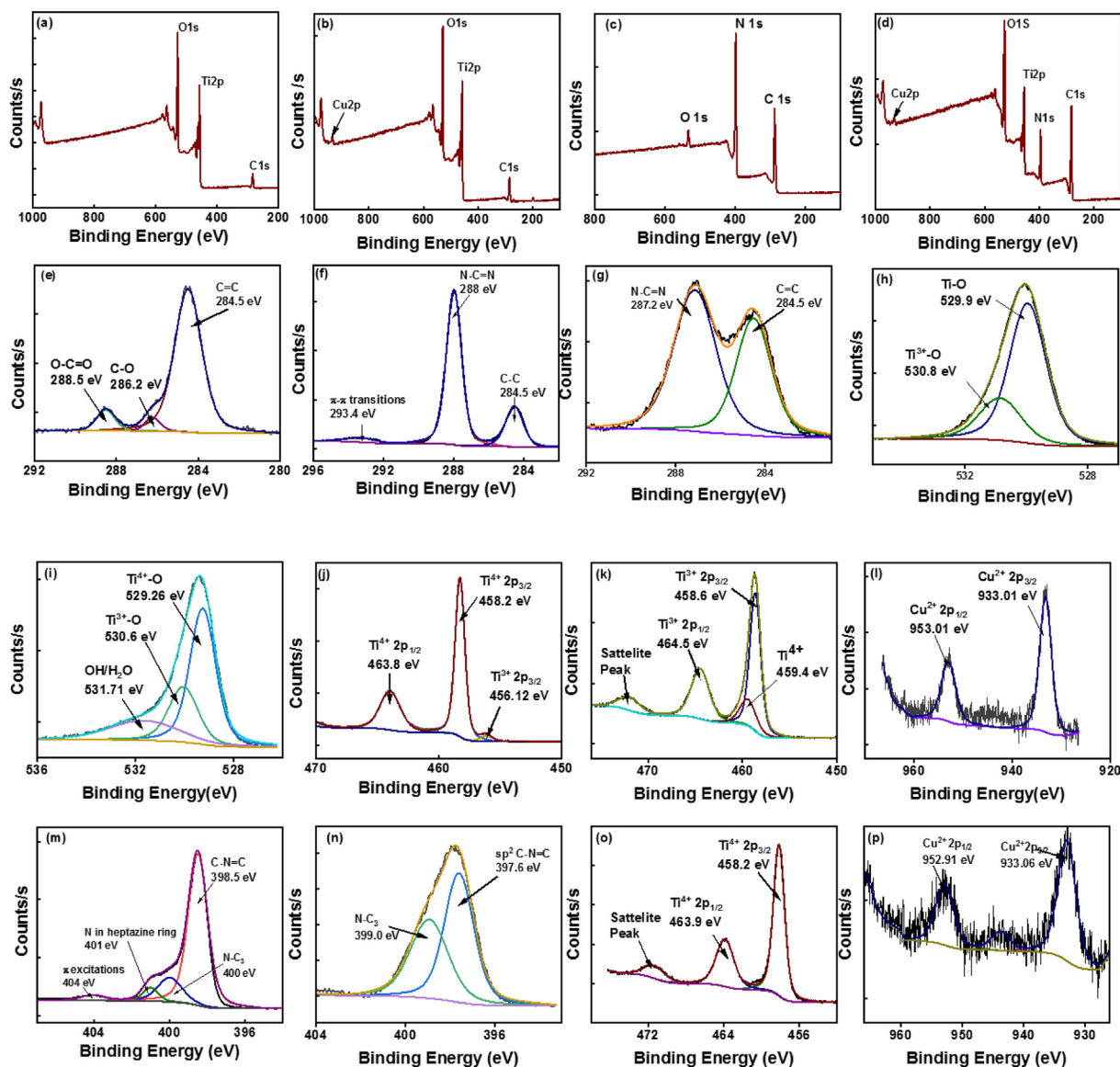


Fig. 5 Survey spectra of (a) P25 TiO₂ (b) Cu-TiO₂ (c) g-C₃N₄ (d) Cu-TiO₂/50-C₃N₄, C 1 s higher resolution spectrum of (e) P25 TiO₂ (f) g-C₃N₄ (g) Cu-TiO₂/50-C₃N₄, O 1 s higher resolution spectrum of (h) P25 TiO₂ (i) Cu-TiO₂, Ti 2p higher resolution spectrum of (j) P25 TiO₂ (k) Cu-TiO₂, of (l) Cu 2p higher resolution spectrum Cu-TiO₂, N 1 s higher resolution spectrum of (m) g-C₃N₄ (n) Cu-TiO₂/50-C₃N₄ (o) Ti 2p higher resolution spectrum of Cu-TiO₂/50-C₃N₄ (p) Cu 2p higher resolution spectrum of Cu-TiO₂/50-C₃N₄.

face chemistry in detail. The higher resolution spectrum of C 1 s of P25 TiO₂ (Fig. 5 (e)) was deconvoluted to three peaks centered at 284.5, 286.2 and 288.5 eV which are attributed to sp² hybridized C=C, C-O and O-C=O, respectively. The higher resolution spectrum of C 1 s of g-C₃N₄ is given in Fig. 4 (f) and is deconvoluted to three main peaks centered at 284.5, 288 and 293.4 eV, which are attributed to the sp² hybridized graphitic C (C-C), sp² hybridized carbon in N-C=N and π - π transitions, respectively. Interestingly the two peaks appeared at 284.5 and 287.16 eV in the higher resolution spectrum of C 1 s of Cu-TiO₂/50-C₃N₄ (Fig. 5 (g)) which were assigned to C=C and N-C=N, respectively. The binding energy of the peak corresponding to N-C=N has shifted to lower binding energy due to the interfacial interactions of g-C₃N₄ with Cu-TiO₂. The higher resolution spectrum of O 1 s of P25 TiO₂ (Fig. 5 (h)) is deconvoluted to two peaks at

529.95 and 530.85 eV. The peak at 529.95 eV is assigned to oxygen bound to Ti while the peak at 530.85 eV represents Ti₂O₃ further revealing the presence of both Ti⁴⁺ and Ti³⁺ in P25 TiO₂. The higher resolution spectrum of O 1 s of Cu-TiO₂ (Fig. 5 (i)) is deconvoluted into three peaks at 529.26, 530.6 and 531.71 eV where the third new peak is attributed to the oxygen present in the hydroxyl group or physisorbed water. The higher resolution spectrum of Ti 2p of P25 TiO₂ (Fig. 5 (j)) shows the spin-orbital coupling where the 2p_{3/2} and 2p_{1/2} peaks of Ti⁴⁺ appeared at 458.2 and 463.8 eV, respectively, while the peak at 456.12 eV with low intensity corresponds to the 2p_{3/2} of Ti³⁺. The appearance of Ti 2p peaks in the higher resolution spectrum of Ti 2p of Cu-TiO₂ (Fig. 5 (k)) is different to that of P25 TiO₂. The peak that appeared at 458.6 eV could be attributed to the Ti³⁺ and the peak at 459.4 eV could be assigned to the Ti⁴⁺ of TiO₂ and

the binding energy has shifted to higher values upon doping of Cu. As described in the XRD section Cu^{2+} replaces Ti^{4+} when Cu is doped to TiO_2 because the cationic radii are quite similar. However, once Cu^{2+} replaces the Ti^{4+} , it creates a charge imbalance where an oxygen atom is also removed creating an oxygen vacancy to compensate for the balance. The most stable site to create the oxygen vacancy is the oxygen site neighbouring to the Cu dopant. Once an oxygen atom is removed the adjacent Cu and Ti ions to which the removed oxygen atom was bound would have five-fold coordination and thus produce the Ti^{3+} state (Mathew et al., 2018). The higher resolution spectrum of Cu 2p of Cu-TiO₂ (Fig. 5 (l)) shows the spin-orbital coupling where the 2p_{3/2} and 2p_{1/2} appeared at 933.26 and 953.01 eV, respectively, indicates the presence of Cu^{2+} . The higher resolution spectrum of N 1 s of g-C₃N₄ (Fig. 5 (m)) shows four sub-peaks at 398.5, 400, 401 and 404 eV, which are assigned to sp^2 hybridized N in s-triazine rings (C-N=C), N-C₃, N atoms in the heptazine ring and as bridging atom, and π -excitations, respectively. The higher resolution spectrum of N 1 s of Cu-TiO₂/50-C₃N₄ (Fig. 5 (n)) shows only two peaks at 397.6 and 399 eV in which the binding energies have decreased due to the interfacial linkage occurs between g-C₃N₄ and Cu-TiO₂ during the formation of the composite (Tan et al., 2015). The higher resolution spectrum of Ti 2p (Fig. 5 (o)) and Cu 2p (Fig. 5 (p)) of Cu-TiO₂/50-C₃N₄ shows the presence of Ti^{4+} (458.2 eV) and Cu^{2+} (933.06 eV), respectively, indicating that unstable Ti^{3+} has oxidized to Ti^{4+} in coupling with g-C₃N₄ during hydrothermal synthesis.

3.6. XRF analysis

XRF analysis was performed to understand the elemental composition. Six spots were chosen from each sample to perform the analysis to study the elemental distribution throughout the sample. TiO_2 purely contain only Ti as shown in Table 2. Cu-TiO₂ sample contains an average of 98.35 wt% of Ti and an average of 1.65 wt% of Cu where both the elements are uniformly distributed in all six places analyzed suggesting the homogeneous distribution of Cu on Ti. Therefore, it is evident that Cu has homogeneously doped to TiO_2 lattice.

3.7. UV-Visible diffuse reflectance spectroscopy

The optical absorption behaviours of the synthesized photocatalysts were evaluated by UV-Visible diffuse reflectance spectroscopy (Supplementary Figure 2 (a)). It could be seen that the TiO_2 exhibits the UV range with an absorption edge at 400 nm. The absorption edge of g-C₃N₄ appeared at 425 nm indicating the visible range absorption while that of Cu/TiO₂ is further shifted towards the visible range suggesting

high visible light absorption. The behaviours of the absorption spectra of Cu-TiO₂/g-C₃N₄ were quite similar where they indicate visible light sensitivity of the heterojunctions. Tauc plots were constructed using the formula shown in equation 3 to determine the band gap of the synthesized nanomaterials.

$$(ah\nu)^n = A(h\nu - E_g) \quad (3)$$

Where $h\nu$, A , E_g and a represent the photon energy, absorption coefficient, band gap energy and a constant, respectively (Q. Li et al., 2007). $n = 2$ denotes the direct transitions and $n = 1/2$ indicates indirect transitions, and the plots corresponding to indirect and direct transitions are shown in Fig. 6 and Supplementary Figure 2 (b), respectively.

The behaviours of the plots suggest that the indirect transition is more feasible in the synthesized nanomaterials. The band gap of TiO_2 was 3.00 eV while that of g-C₃N₄ is 2.81 eV. The band gap of Cu-TiO₂ is found to be 2.67 eV exhibiting prominently visible absorption. A new energy level is created below the CB of TiO_2 narrowing down the band gap and further enhancing the visible light absorption. However, the band gap values of g-C₃N₄ coupled Cu-TiO₂ were higher than that of Cu-TiO₂ and were similar to each other and to that of g-C₃N₄. This could be due to the sample used for the analysis being more concentrated with g-C₃N₄. Further, the particle size directly contributes to the band gap whereas in general particle size is inversely proportional to the band gap. The size of the nanoparticles greatly affects the band gap where the band gap values increase as the particle size decreases. Holes in the valence band and electrons in the conduction band become confined with decreasing particle size and due to this confinement in the electrons and holes the band gap between the valence and conduction bands increases. The shape of the nanomaterials contributes to the band gap values. Volume to surface area ratio varies as the size and shape of the nanomaterials change which contributes to the variation in the number of surface atoms and hence the cohesive energy. Therefore, the band gap varies at the nanoscale due to the change in size and shape (Singh et al., 2018). Therefore, the obtained band gap values are a result of collective factors. It is evident that the coupled heterojunction composites are visible active for photocatalysis. All the calculated band gap values are tabulated in Table 3.

3.8. Photocatalysis

The photocatalytic activity of the synthesized nanomaterials was evaluated on the degradation of methylene blue under the exposure of UV and visible light. Before exposure to the light, source catalysts were shaken in dark for one hour to reach the adsorption-desorption equilibrium. Adsorption kinetics were studied using pseudo-first-order and

Table 2 XRF analysis of P25 TiO_2 and Cu-TiO₂.

Sample	Element	Spot 1 Mass %	Spot 2 Mass %	Spot 3 Mass %	Spot 4 Mass %	Spot 5 Mass %	Spot 6 Mass %
P25 TiO_2	Ti	100	100	100	100	100	100
Cu-TiO ₂	Ti	98.38	98.31	98.38	98.38	98.31	98.31
	Cu	1.62	1.69	1.62	1.62	1.69	1.69

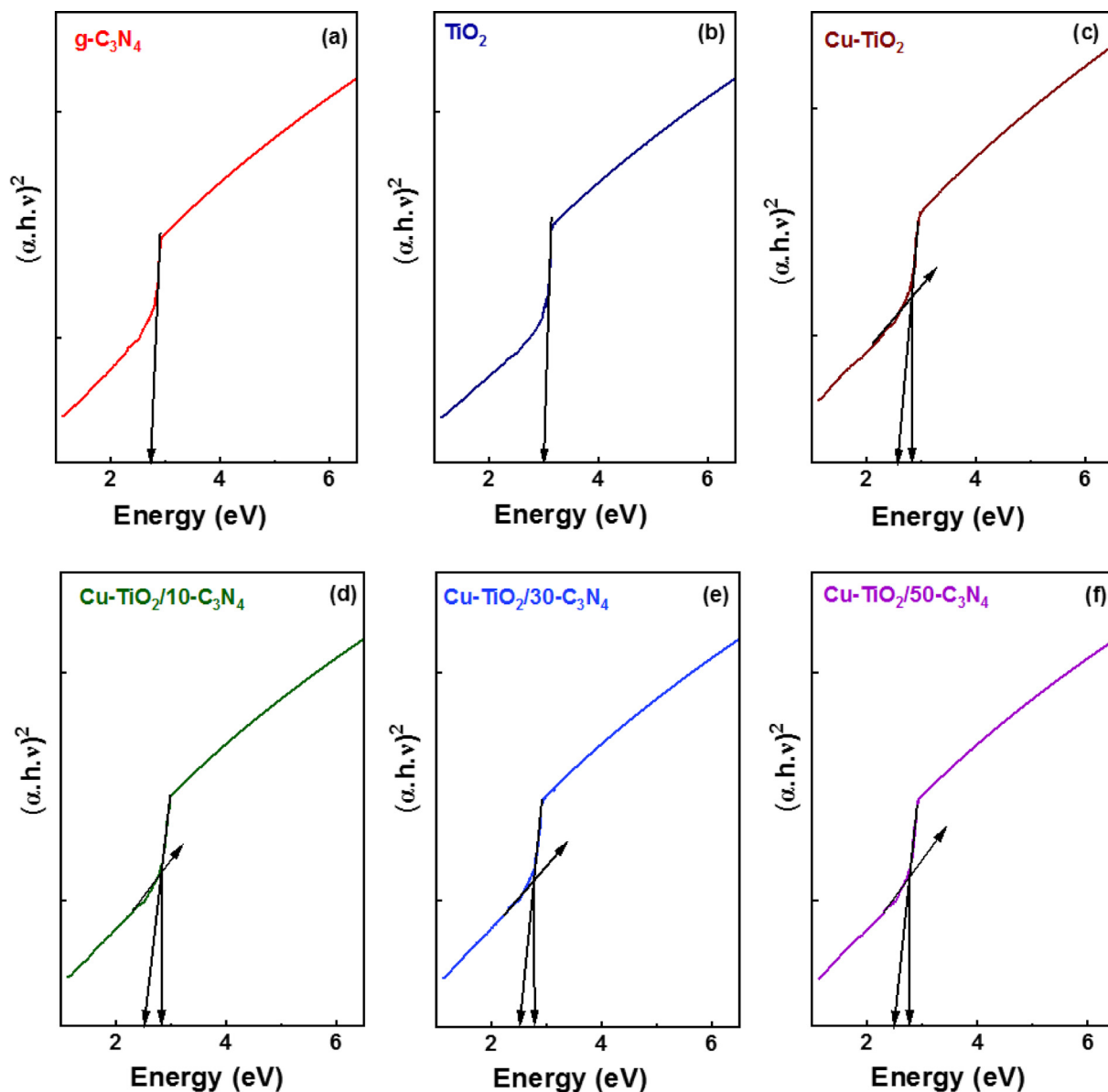


Fig. 6 Tauc plots indicating the indirect transitions of (a) g-C₃N₄ (b) TiO₂ (c) Cu-TiO₂ (d) Cu-TiO₂/10-C₃N₄ (e) Cu-TiO₂/30-C₃N₄ (f) Cu-TiO₂/50-C₃N₄.

pseudo-second-order kinetics models as shown in Fig. 7 (a) and (b). The respective rate constants and the correlation coefficient values are tabulated in Table 4. It is evident that the adsorption followed pseudo-second-order kinetics with a high R^2 value suggesting chemisorption of MB to the catalysts. Then the samples were exposed to the light source and the aliquots were withdrawn in 15 min time intervals (Fig. 8). Obtained data were fitted to the first-order kinetics model and the obtained data are tabulated in Table 5. Cu-TiO₂/50-C₃N₄ showed the highest rate constant ($4.4 \times 10^{-3} \text{ min}^{-1}$) for the photodegradation of MB followed by Cu-TiO₂/30-C₃N₄ ($4.1 \times 10^{-3} \text{ min}^{-1}$). The photocatalytic activity of Cu-TiO₂/50-C₃N₄ is 9.8 times greater than that of g-C₃N₄, 4 times greater than Cu-TiO₂ and 5 times greater than that of TiO₂. g-C₃N₄ is a visible active photocatalyst and the least photocatalytic activity was observed with

g-C₃N₄ due to the electron-hole pair recombination. Pure TiO₂ is only active in the UV range leading to lower photocatalytic activity. Upon doping with Cu, the band gap reduces as a new energy level is constructed below the CB of TiO₂ increasing the visible light sensitivity. Therefore, the photocatalytic activity of Cu-TiO₂ is higher than that of TiO₂. Cu-TiO₂/C₃N₄ composites showed comparatively higher photocatalytic activity due to the proper band alignment which enhances the charge separation and the presence of two visibly active semiconductors, Cu-TiO₂ and g-C₃N₄. Photocatalytic activity of Cu-TiO₂/30-C₃N₄ and Cu-TiO₂/10-C₃N₄ was lower due to the low weight ratio between Cu-TiO₂ and g-C₃N₄ which leads to improper formation of the heterojunction. Therefore, it could be concluded that Cu-TiO₂/50-C₃N₄ is the most sustaining photocatalyst among the nanomaterials synthesized for the

Table 3 Band gap energies calculated for direct and indirect transitions of the synthesized nanomaterials.

Sample	Band Gap (eV) for direct transitions ($n = 2$)	Band Gap (eV) for indirect transitions ($n = 1/2$)
g-C ₃ N ₄	2.73	2.81
TiO ₂	3	3
Cu-TiO ₂	2.59	2.67
Cu-TiO ₂ /10-C ₃ N ₄	2.84	2.88
Cu-TiO ₂ /30-C ₃ N ₄	2.78	2.84
Cu-TiO ₂ /50-C ₃ N ₄	2.76	2.82

degradation of MB. MB was not degraded upon exposure to the light source without any catalyst as shown in the [supplementary figure 3](#).

Mechanism of Photocatalysis

The engineering of the structure of the heterostructure is important to determine the mechanism of photocatalysis. The band gap values of Cu-TiO₂ and g-C₃N₄ calculated from the Tauc plots are 2.67 and 2.80 eV, respectively. The band edge potentials of the conduction band (E_{CB}) and the valence band (E_{VB}) of the above semiconductors were calculated by the formula (4) and (5), respectively.

$$ECB = X - EC - 0.5 E_g. \quad (4)$$

$$EVB = X - EC + 0.5 E_g. \quad (5)$$

where X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, and E^C is the energy of the free electrons on the hydrogen scale which is approximately 4.5. X value for Cu-TiO₂ is assumed to be similar to that of TiO₂ (5.81) as the percentage of Cu incorporated is low compared to Ti (1%) and that of g-C₃N₄ is 4.73. E_{CB} calculated for TiO₂ (Rutile), TiO₂ (Anatase) Cu-TiO₂ and g-C₃N₄ are -0.19, -0.39, -0.03 and -1.18 eV/normal hydrogen electrode

(NHE), respectively, and the E_{VB} calculated are 2.81, 2.81, 2.65, and 1.64 eV/normal hydrogen electrode (NHE), respectively. A homojunction was established between the Rutile and Anatase phases of P25 TiO₂ as shown in [Fig. 9](#) (a) where the CB band of Rutile lies below that of Anatase facilitating the migration of electrons from the CB of Anatase to that of Rutile. The potential of the VB of both TiO₂ Rutile and Anatase (2.81 eV) is greater than that of the standard potential of OH[•]/OH⁻ (1.99 eV) and OH[•]/H₂O (2.68 eV) facilitating the oxidation of both OH⁻ and H₂O to produce OH[•]. Further, the potential of the CB of TiO₂ (Anatase) (-0.39 eV) is greater than that of the standard potential of O₂/O₂^{•-} (-0.33 eV) favouring the reduction of O₂ to O₂^{•-}. However, the potential of the CB of TiO₂ (Rutile) (-0.19 eV) is smaller than the standard potential of O₂/O₂^{•-} and hence prohibits the reduction of O₂ to O₂^{•-}. Further, as the potential of the CB of TiO₂ (Rutile) is lower than that of TiO₂ (Anatase) there is a net electron transfer from the CB of TiO₂ (Anatase) to the CB of TiO₂ (Rutile). Hence, the probability of the reduction of O₂ to O₂^{•-} is lower than expected. Therefore, such produced OH[•] and O₂^{•-} degrade the MB molecules in the presence of UV light. As discussed in the XRD analysis Cu²⁺ ions have been mainly doped to the TiO₂ (Anatase) phase of P25 TiO₂ lowering the band gap to 2.67 eV and the CB of Cu-TiO₂ lies at -0.03 eV while the VB would be located at 2.64 eV creating a type I heterojunction. Further, the electrons will travel from the CB of TiO₂ (Rutile) to the CB band of Cu-TiO₂ while the holes will migrate from the VB of the TiO₂ (Rutile) to the VB of Cu-TiO₂ and hence cause electron hole pair recombination leading to poor charge separation. The oxidation of H₂O to OH[•] is feasible at the VB of TiO₂ (Rutile) but would occurrence be limited as the holes are migrated to the VB of Cu-TiO₂ due to the favourable potential difference as shown in [Fig. 9](#) (b). The oxidation of OH⁻ to OH[•] is favourable and occurs at high probability at the VB of Cu-TiO₂ due to the flow of holes to the VB of Cu-TiO₂. Hence, OH[•] contribute to the degradation of MB by Cu-TiO₂. The photocatalytic activity of this photocatalyst is comparatively higher than that of both pure TiO₂ and g-C₃N₄ due to its high visible activity. The electrons which migrated to the CB of the Cu-TiO₂ from TiO₂ (Rutile) then travelled to the VB of g-C₃N₄ of Cu-TiO₂/C₃N₄ as the z-scheme band alignment created due to the potential difference of the CB of Cu-TiO₂ and the VB of g-C₃N₄

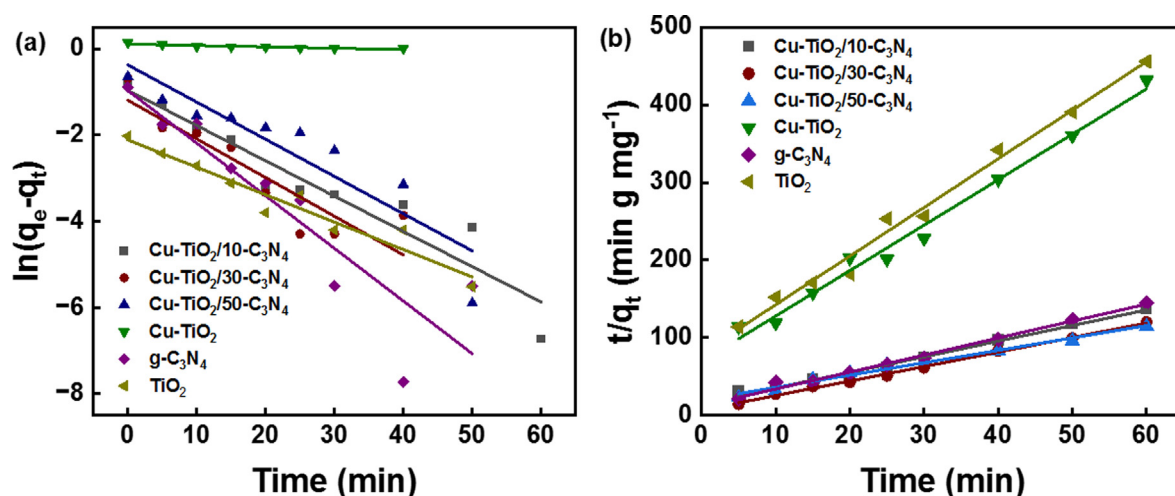


Fig. 7 (a) Pseudo-first-order (b) Pseudo-second-order adsorption kinetic model for adsorption of MB to the synthesized nanomaterials.

Table 4 Kinetics parameters for adsorption of MB to the synthesized nanomaterials.

Sample	1st order rate constant (min ⁻¹)	R ²	2nd Order rate Constant (mg g ⁻¹ min ⁻¹)	R ²
Cu-TiO ₂ /10-C ₃ N ₄	0.091	0.89	0.243	0.99
Cu-TiO ₂ /30-C ₃ N ₄	0.107	0.79	0.436	0.99
Cu-TiO ₂ /50-C ₃ N ₄	0.100	0.82	0.122	0.98
Cu-TiO ₂	0.004	0.8	0.479	0.99
g-C ₃ N ₄	0.144	0.79	0.345	0.99
TiO ₂	0.070	0.93	0.481	0.99

Table 5 Kinetics parameters for photocatalytic degradation of MB in the presence of the synthesized catalysts.

Sample	1st Order rate constant (min ⁻¹)	R ²	1st Order rate constant in the presence of 4 mM persulfate (min ⁻¹)
Cu-TiO ₂ /10-C ₃ N ₄	3.9×10^{-3}	0.99	4.9×10^{-2}
Cu-TiO ₂ /30-C ₃ N ₄	4.1×10^{-3}	0.99	1.3×10^{-1}
Cu-TiO ₂ /50-C ₃ N ₄	4.4×10^{-3}	0.99	7.9×10^{-2}
Cu-TiO ₂	1.1×10^{-3}	0.99	5.6×10^{-2}
g-C ₃ N ₄	4.5×10^{-4}	0.97	6.3×10^{-2}
TiO ₂	8.7×10^{-4}	0.99	4.9×10^{-2}

favour the electron transfer. Additional to the reactions occurred at Cu-TiO₂ electrons at the VB of g-C₃N₄ get excited to the CB and the reduction of O₂ to O₂^{•-} happens at the CB of g-C₃N₄ as the potential of the CB of g-C₃N₄ (-1.18 eV) is greater than the reduction potential of O₂/O₂^{•-}. Hence, both OH[•] and O₂^{•-} are responsible for the degradation of MB in the presence of Cu-TiO₂/C₃N₄ as the photocatalyst.

Cu-TiO₂/50 g-C₃N₄ showed the highest rate constant (4.4×10^{-3} min⁻¹) due to the proper ratio of mixing Cu-TiO₂ with g-C₃N₄. Composites made with other ratios where 10% and 30% g-C₃N₄ were coupled with Cu-TiO₂ also effectively contributed to the photodegradation of MB but with lesser activity as the heterojunctions with the proper ratio were not formed. The rate constant per surface area of Cu-

TiO₂/50 g-C₃N₄ (1.24×10^{-4} min⁻¹/m².g⁻¹) is greater than that of Cu-TiO₂ (1.3×10^{-5} min⁻¹/m².g⁻¹) and TiO₂ (7.8×10^{-6} min⁻¹/m².g⁻¹) further indicate that the coupling of Cu-TiO₂ with g-C₃N₄ has greatly enhanced the photocatalytic activity.

XPS analysis further supports the above-proposed mechanism. The higher resolution spectrum of N1s of Cu-TiO₂/50-C₃N₄ showed 0.9 eV and 1.0 eV downshifts of the binding energy of the peaks corresponding to C-N = C and N-C₃, respectively, compared to those of pure g-C₃N₄ indicating an increase in the electron density. Hence, those electrons present in the CB of g-C₃N₄ of Cu-TiO₂/50-C₃N₄ are taken by the O₂ and get reduced to O₂^{•-} which converts MB to harmless products (Thambiliyagodage, Usgodaarachchi, et al., 2022). Further, the binding energy of Ti 2p of Ti⁴⁺ of Cu-TiO₂/50-

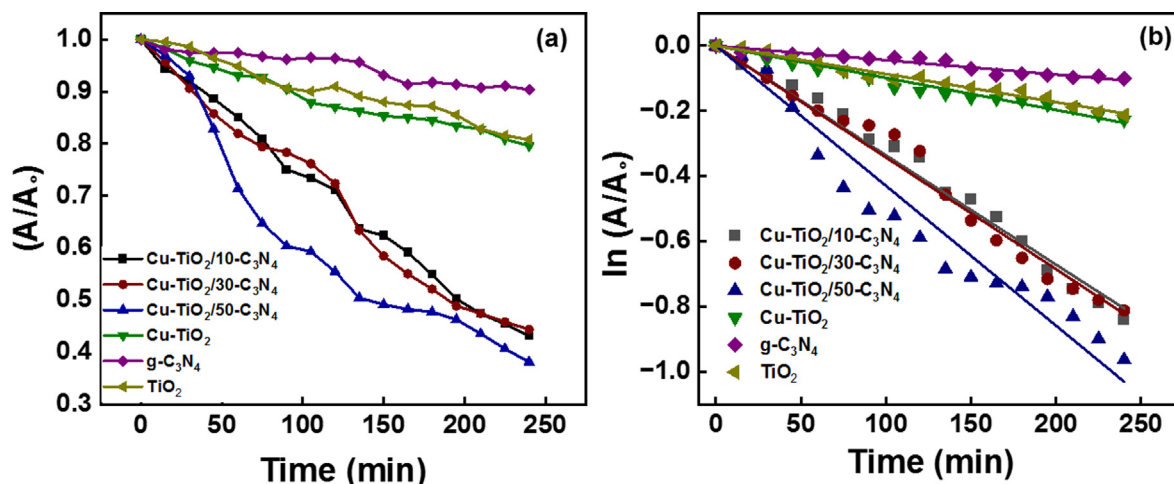


Fig. 8 Photocatalytic degradation of MB in the presence of the synthesized photocatalysts following (a) photocatalytic degradation (b) pseudo-first-order kinetics model.

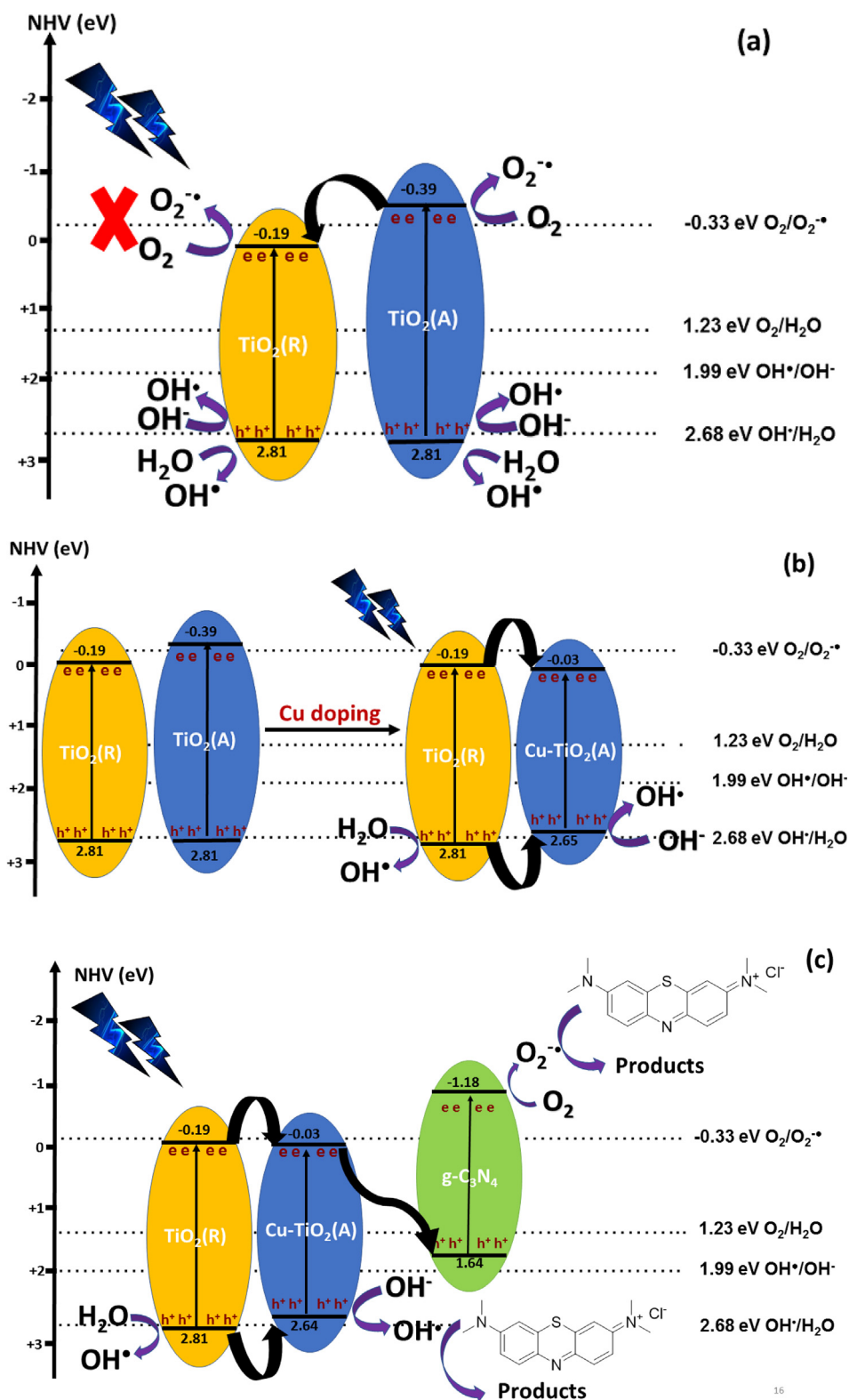


Fig. 9 Band alignment of (a) P25 TiO₂ (b) Cu-TiO₂ (c) Cu-TiO₂/g-C₃N₄.

C₃N₄ shows a 1.2 eV downshift compared to that of Cu-TiO₂, while a 0.2 eV downshift in the Cu 2p was also observed in Cu-TiO₂/50-C₃N₄ compared to Cu-TiO₂. This indicates an increase in the electron density in the CB of Cu-TiO₂ of Cu-TiO₂/50-C₃N₄ which is due to the electron flow from g-C₃N₄

as suggested by described band alignment. Higher resolution spectra of Cu-TiO₂/50-C₃N₄ used for the photocatalytic reaction (Cu-TiO₂/50-C₃N₄ – L) were acquired to further support the charge transfer mechanism. The higher resolution spectrum of Ti 2p Cu-TiO₂/50-C₃N₄ – L was deconvoluted into five

peaks as shown in supplementary figure 4 (a). The peak at 458.7 eV is attributed to the Ti³⁺ while the peak at 460.9 eV is ascribed to Ti⁴⁺ of Ti 2p_{3/2}. The peaks at 464.4 and 466.5 eV correspond to the 2p_{1/2} of the Ti³⁺ and Ti⁴⁺, respectively. Though only Ti⁴⁺ was present in the Cu-TiO₂/50-C₃N₄ interestingly both Ti³⁺ and Ti⁴⁺ were present in the same catalyst which was exposed to the photocatalytic reaction. As shown in Fig. 9 photogenerated electrons in the VB band of TiO₂ (Rutile) are transferred to the VB of TiO₂ (Anatase) and hence the Ti⁴⁺ of anatase reduced to Ti³⁺ greatly where the ratio of Ti⁴⁺/Ti³⁺ is 1:2 indicating that 2/3 of Ti⁴⁺ have been reduced to Ti³⁺ when exposed to the reaction in the presence of the light source. The higher resolution spectrum of N 1s of Cu-TiO₂/50-C₃N₄ - L (supplementary figure 4 (b)) was deconvoluted to three peaks where an additional peak at 398.5 eV corresponding to N in the pyridine ring appeared which indicates the adsorption of MB molecules to the catalyst surface during the catalytic reaction as the MB molecule possesses a pyridine ring in its structure (supplementary figure 5).

To identify the reactive species, the study was conducted in the presence of EDTA and IPA as they scavenge the holes and OH[•], respectively. The rate constant for the photodegradation of MB decreased to 3.2×10^{-4} and $2.9 \times 10^{-3} \text{ min}^{-1}$, respectively, in the presence of EDTA and IPA which are 13.8 and 1.5 times lesser than the rate constant when no scavenger is used ($4.4 \times 10^{-3} \text{ min}^{-1}$) (Fig. 10 (a)). The percentage conver-

sion of MB in the presence of EDTA and IPA reduced to 8 and 48 %, respectively, indicating that both holes and OH[•] have contributed to the photodegradation of MB where the effect from holes for the photocatalysis is 9.1 times greater than that from OH[•] (Fig. 10 (b)).

The rate constant was increased to $7.9 \times 10^{-2} \text{ min}^{-1}$ with the addition of persulfate (S₂O₈²⁻) ions to the medium which increased the rate by 18 times because the SO₄^{•-} and OH[•] produced by the reduction of S₂O₈²⁻ readily degrade MB increasing the conversion of MB to 98% compared to 62 % resulted when persulfate was not used. S₂O₈²⁻ ions are reduced to SO₄^{•-} as shown in reaction 1 by the photogenerated electrons and such produced SO₄^{•-} reacts with OH⁻ in the medium to produce SO₄²⁻ and OH[•] (reaction 2). Further, in the presence of UV light S₂O₈²⁻ degrades to produce 2SO₄^{•-} (reaction 3) which would react with OH⁻ to produce OH[•]. Moreover, in the presence of O₂^{•-}, S₂O₈²⁻ produce SO₄²⁻, SO₄^{•-} and O₂ as shown in reaction 4. Additionally, the standard reduction potential of S₂O₈²⁻/2SO₄^{•-} (2.01 eV) is lesser than E_{VB} of Cu-TiO₂, the longer O-O bond (1.497 Å) and easiness to break the O-O bond with less energy to produce OH[•], making S₂O₈²⁻ a better candidate to improve the reaction rate. The concentration of S₂O₈²⁻ was varied as 2, 4 and 8 mM to study the optimum concentration of S₂O₈²⁻ and the rate constants for the photodegradation of MB were calculated to be 5.6×10^{-2} , 7.9×10^{-2} and $1.2 \times 10^{-1} \text{ min}^{-1}$, respectively (Fig. 10 (c)).

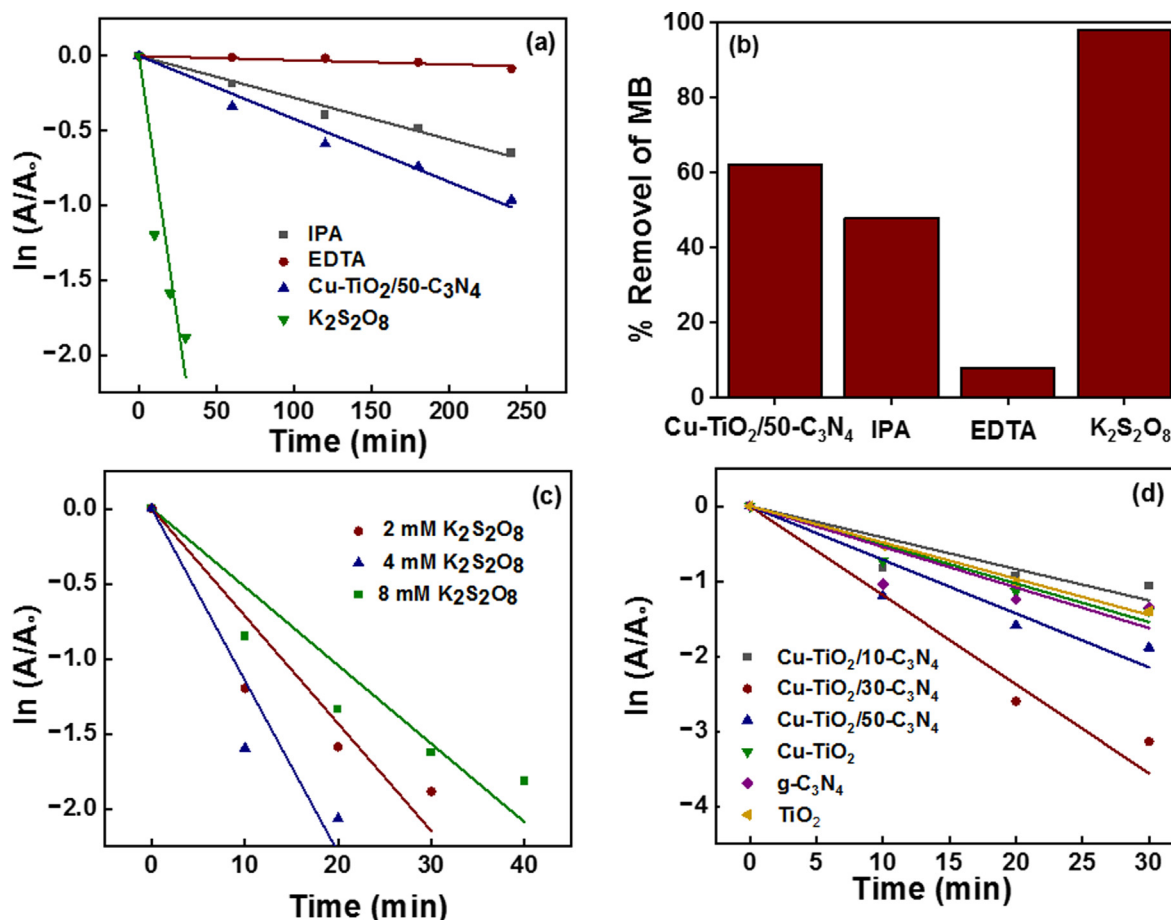
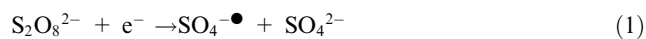


Fig. 10 (a) First order kinetics model for the catalytic system with additives; IPA, EDTA, K₂S₂O₈, and no additive (b) % removal of MB with the additives (c) First order kinetics model for the catalytic system with varying concentrations of K₂S₂O₈, (d) effect of K₂S₂O₈ on all the catalytic systems.

The rate constant increased with increasing concentration of $S_2O_8^{2-}$ as the concentrations of produced $SO_4^{\bullet-}$ and $OH^{\bullet}$ increase with increasing concentration of $S_2O_8^{2-}$.



Moreover, the effect of $S_2O_8^{2-}$ on the photocatalytic activity in the presence of all the synthesized photocatalysts was determined using 4 mM $S_2O_8^{2-}$ solution and the obtained rate constants are tabulated in Table 5. It is observed that the rate constants increased by 13, 32, 51, 140 and 56 times in the presence of Cu-TiO₂/10-C₃N₄, Cu-TiO₂/30-C₃N₄, Cu-TiO₂, g-C₃N₄ and TiO₂, respectively, suggesting that the photocatalysis is greatly increased due to two reasons mainly, which are the production of $SO_4^{\bullet-}$ and $OH^{\bullet}$ which readily degrade MB molecules and the prevention of electron-hole pair recombination due to rapid capture of the photogenerated electrons by $S_2O_8^{2-}$ (Fig. 10 (d)). A drastic increase in the reaction rate in the presence of Cu-TiO₂/10-C₃N₄, Cu-TiO₂/30-C₃N₄, Cu-TiO₂, g-C₃N₄ and TiO₂ catalysts was observed in the presence of $S_2O_8^{2-}$ because the rate constants without $S_2O_8^{2-}$ were very low. The rate constants for the degradation of MB in the presence of all the composites are higher than that of Cu-TiO₂/50-C₃N₄ reported without $S_2O_8^{2-}$. Further, with the addition of $S_2O_8^{2-}$ the photocatalytic activity of Cu-TiO₂/30-C₃N₄ resulted to be higher than that of Cu-TiO₂/50-C₃N₄ which showed the highest photocatalytic activity without $S_2O_8^{2-}$. This suggests that the proper amount of g-C₃N₄ was not available in Cu-TiO₂/30-C₃N₄ to couple with Cu-TiO₂ and a low photocatalytic activity next to Cu-TiO₂/50-C₃N₄ was obtained due to the possible electron-hole pair recombination resulted due to the reduced band gap of Cu-TiO₂ (2.67 eV). However, $S_2O_8^{2-}$ readily captures the photogenerated electrons, and thus prevents the electron-hole pair recombination leading to a higher photocatalytic activity.

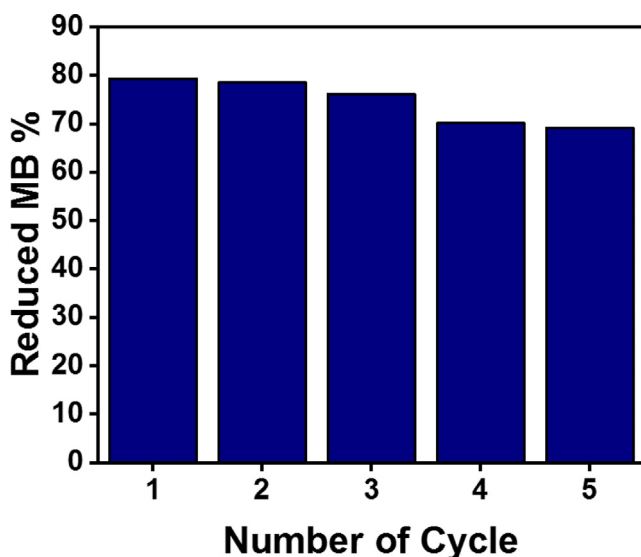


Fig. 11 Reusability of Cu-TiO₂/50-C₃N₄.

The reusability of Cu-TiO₂/50-C₃N₄ was tested to study the stability of the photocatalysts (Fig. 11). The total removal of MB in the first cycle (79%) decreased to 69% by the fifth cycle. Positively charged MB molecules have a strong affinity to the negatively charged catalyst surface triggering the chemisorption of MB. Therefore, the catalyst surface could have been saturated by the chemisorbed MB molecules limiting the available surface for the new MB molecules though the catalyst surface was washed with distilled water and ethanol because such washing would mainly remove the physisorbed MB molecules. The porous structure of the catalyst could have been blocked with the chemisorbed MB molecules reducing the surface area and the total pore volume limiting the MB adsorption. Moreover, it was observed that the catalyst particles were agglomerated with prolonged use reducing the surface area and restricting the access of MB molecules to the active sites. Further, there could be a loss in the weight of the catalyst moving from one cycle to the other resulting in a reduction in the total removal of MB.

4. Conclusions

Cu-TiO₂ nanoparticles were successfully coupled to g-C₃N₄ in different weight ratios hydrothermally to synthesize Cu-TiO₂/g-C₃N₄ nanocomposites. Cu has been doped to the Anatase phase of TiO₂ which possess both Anatase and Rutile phases without causing significant lattice distortions. Cu-TiO₂ nanoparticles were heterogeneously distributed on the g-C₃N₄ matrix. Adsorption of methylene blue molecules followed second-order kinetics indicating chemisorption of methylene blue molecules to the catalyst surface. The photocatalytic activity of the synthesized nanocomposites was evaluated on the photodegradation of methylene blue and Cu-TiO₂/50-C₃N₄ showed the highest rate constant ($4.4 \times 10^{-3} \text{ min}^{-1}$) which was 5 and 9.8 times greater the activity of TiO₂ and g-C₃N₄, respectively. The z-scheme band alignment of Cu-TiO₂/C₃N₄ facilitates the charge separation minimizing the electron-hole pair recombination and leading to higher photocatalytic activity. Superoxide radicals, hydroxyl radicals and holes are responsible for the photodegradation of methylene blue as exhibited by the study performed with scavengers. Persulfate ions greatly enhanced the photocatalytic activity where the rate constant of Cu-TiO₂/50-C₃N₄ was increased by 18 times as they generate $SO_4^{\bullet-}$ and $OH^{\bullet}$ and prevent the electron-hole pair recombination. Therefore, it could be concluded that the fabricated Cu-TiO₂/C₃N₄ nanocomposites are effective in degrading methylene blue and could be used for environmental remediation effectively.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.arabjc.2023.104749>.

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