

Photocatalytic Degradation of Methylene Blue by $\text{XyTi}_{1-y}\text{O}_2$ (X = Zn, Cu, Mg) Thin Films: Structural, Optical, Kinetic, and Mechanistic Insights.

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Photocatalytic Degradation of Methylene Blue by $X_y\text{Ti}_{1-y}\text{O}_2$ ($X = \text{Zn, Cu, Mg}$) Thin Films: Structural, Optical, Kinetic, and Mechanistic Insights.

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Abstract

Undoped and X-doped TiO_2 thin films ($X = \text{Zn, Cu, Mg}$; $y = 0.03, 0.06, 0.09$, and 0.12) were deposited on glass substrates by ultrasonic spray pyrolysis and evaluated for the photocatalytic degradation of methylene blue (MB). X-ray diffraction confirmed that anatase TiO_2 remained the dominant phase for all films, while dopant incorporation induced peak shifts, peak broadening, and a reduction in crystallite size. Raman spectroscopy corroborated retention of the anatase framework, and EDX confirmed the presence of the corresponding dopant elements. SEM observations showed that doping progressively increased surface roughness, grain coalescence, and agglomeration. Optical measurements revealed dopant-dependent behavior. Zn and Mg doping increased the optical band gap from 2.95 eV for TiO_2 to 3.36 and 3.55 eV for $\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$ and $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$, respectively, whereas Cu doping reduced the band gap to 2.82 eV for $\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$. Photocatalytic testing showed that all doped films outperformed undoped TiO_2 . Kinetic parameters were determined by nonlinear least-squares fitting of the original untransformed pseudo-first-order model. The highest apparent rate constant was obtained for $\text{Cu}_{0.09}\text{Ti}_{0.91}\text{O}_2$, with $k = 0.010455 \pm 0.000047 \text{ min}^{-1}$, a degradation efficiency of $84.77 \pm 0.13 \%$, and the shortest half-life time. $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$ ranked second with $k = 0.009814 \pm 0.000106 \text{ min}^{-1}$ and $82.91 \pm 0.33 \%$ degradation, whereas $\text{Zn}_{0.09}\text{Ti}_{0.91}\text{O}_2$ was the optimum composition within the Zn-doped series ($k = 0.007875 \pm 0.000038 \text{ min}^{-1}$; $75.77 \pm 0.17 \%$). Overall, the combined structural, optical, morphological, and kinetic results indicate that controlled doping is an effective strategy for tuning TiO_2 thin-film photocatalysts for dye-removal applications.

Keywords: TiO_2 thin films; ultrasonic spray pyrolysis; metal-ion doping; methylene blue degradation; photocatalysis; optical band gap; apparent pseudo-first-order kinetics.

1. Introduction

Titanium dioxide (TiO_2) remains a benchmark semiconductor photocatalyst for environmental remediation due to its chemical stability, low toxicity, abundance, and high photo-oxidative capacity [1, 2]. However, the practical application of pristine TiO_2 is severely limited by its wide band gap (~ 3.2 eV for anatase), restricting light absorption to the ultraviolet region, and the rapid recombination of photogenerated electron-hole pairs [3-6]. To overcome these bottlenecks, extensive research focuses on systematically modifying TiO_2 to improve charge separation, expand visible-light utilization, and optimize surface reactivity for the mineralization of persistent organic pollutants like methylene blue [7-11].

Metal-ion doping is a robust strategy for precisely tuning the physicochemical properties of the TiO_2 matrix [12-14]. Incorporating foreign metal ions can alter crystallite growth mechanisms, introduce tailored lattice microstrain, and modulate internal defect density, creating localized states that extend carrier lifetimes [15-19]. Zinc, copper, and magnesium offer a fascinating comparison as they influence TiO_2 through distinct physical and chemical pathways. Zn modifies crystallinity and oxygen vacancy defect chemistry, enhancing structural stability without severely altering intrinsic bulk features [20-22]. Conversely, Cu doping introduces discrete impurity bands inducing a red shift in optical absorption, enabling visible-light activation and efficient interfacial charge transfer [23-25]. Meanwhile, Mg distinctly modifies crystallite growth and surface basicity, expanding the band gap through quantum-confinement effects without establishing traditional transition-metal recombination centers [26-30].

Immobilized thin-film photocatalysts offer practical advantages for continuous water purification by eliminating costly post-treatment filtration and preventing catalyst aggregation [31]. Ultrasonic spray pyrolysis is an attractive deposition technique for fabricating these films, offering a simple, cost-effective, and scalable process with precise control over film stoichiometry, thickness, and morphology [32].

The main gap addressed in the present work is the lack of a direct, comprehensive side-by-side comparison of Zn-, Cu-, and Mg-doped TiO_2 thin films prepared under strictly identical deposition conditions and systematically evaluated through the exact same set of advanced structural, compositional, optical, kinetic, and mechanistic analyses.

2. Materials and Methods

2.1 Materials and Precursor Preparation

Titanium(IV) isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 98%, Sigma-Aldrich) was used as the titanium precursor. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), copper acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), and magnesium acetate tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were used as dopant precursors. A 0.15 M TiO_2 precursor solution was prepared in an ethanol/deionized water mixture (1:1, v/v). Dopant precursor solutions were prepared at the same molar concentration in the same solvent system.

For each composition, the total precursor volume was fixed at 100 mL. The undoped sample was prepared from 100 mL of TiO_2 precursor solution, whereas doped samples were prepared by replacing part of the TiO_2 precursor solution with the corresponding dopant precursor solution to obtain nominal compositions $\text{X}_y\text{Ti}_{1-y}\text{O}_2$ with $y = 0.03, 0.06, 0.09$, and 0.12 . The pH of the precursor solutions was approximately 4.5 and was not adjusted further. All solutions were filtered through a $0.45 \mu\text{m}$ membrane before deposition.

Table 1. Consolidated precursor-volume ratios and nominal film compositions used for the Zn-, Cu-, and Mg-doped TiO_2 thin-film series.

Series	y	TiO_2 precursor (mL)	Dopant precursor (mL)	Nominal composition
Zn-doped	0.03	97	3	$\text{Zn}_{0.03}\text{Ti}_{0.97}\text{O}_2$
Zn-doped	0.06	94	6	$\text{Zn}_{0.06}\text{Ti}_{0.94}\text{O}_2$
Zn-doped	0.09	91	9	$\text{Zn}_{0.09}\text{Ti}_{0.91}\text{O}_2$
Zn-doped	0.12	88	12	$\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$
Cu-doped	0.03	97	3	$\text{Cu}_{0.03}\text{Ti}_{0.97}\text{O}_2$
Cu-doped	0.06	94	6	$\text{Cu}_{0.06}\text{Ti}_{0.94}\text{O}_2$
Cu-doped	0.09	91	9	$\text{Cu}_{0.09}\text{Ti}_{0.91}\text{O}_2$
Cu-doped	0.12	88	12	$\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$
Mg-doped	0.03	97	3	$\text{Mg}_{0.03}\text{Ti}_{0.97}\text{O}_2$
Mg-doped	0.06	94	6	$\text{Mg}_{0.06}\text{Ti}_{0.94}\text{O}_2$
Mg-doped	0.09	91	9	$\text{Mg}_{0.09}\text{Ti}_{0.91}\text{O}_2$
Mg-doped	0.12	88	12	$\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$

2.2 Thin-Film Deposition by Ultrasonic Spray Pyrolysis

Glass substrates were rigorously cleaned prior to deposition and maintained at a steady temperature of 450 °C during film growth to ensure optimal precursor decomposition [33]. The aerosol flow rate of the ultrasonic sprayer was set to 5 mL min⁻¹, utilizing compressed air as the carrier gas at a flow rate of 6 L min⁻¹, and the nozzle-to-substrate distance was fixed at 25 cm [34]. Each film was deposited using exactly eight spray cycles, with each active spray duration lasting 12 s followed by a 30 s pause interval to allow for proper solvent evaporation and layer consolidation [35]. These deposition parameters were kept strictly constant for all undoped and doped films to ensure that any observed morphological or optical differences exclusively reflected the dopant type and concentration rather than synthesis variations [36]. After deposition, the films were allowed to naturally cool to room temperature under ambient conditions prior to structural, optical, and photocatalytic characterization.

2.3 Characterization

X-ray diffraction (XRD) patterns were recorded over the 2θ range of 15°–90° using Cu Kα radiation (λ = 1.5406 Å) to analyze the crystallographic structure and phase purity [37]. Raman spectroscopy was utilized to verify phase retention and assess the local structural disorder induced by dopant incorporation [38]. The surface morphology and elemental composition of the films were examined by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) [39, 40]. Finally, UV-Vis spectroscopy measurements were conducted to determine the optical transmittance and to accurately estimate the optical band gap energies derived from Tauc plots [41, 42].

2.4 Photocatalytic Testing and Kinetic Treatment

Photocatalytic activity was evaluated using 50 mL of methylene blue (MB) solution at 10 mg L⁻¹. Thin-film samples with an approximate area of 2 cm × 2 cm were immersed in the dye solution and stirred in the dark for 30 min to establish adsorption-desorption equilibrium. Irradiation was provided by a 15 W UV-visible lamp (350–800 nm) with an irradiance of about 10 mW cm⁻² measured at the sample surface. The lamp-sample distance was 20 cm, and the suspension was continuously stirred during the test. [42-46]

Aliquots were collected at selected time intervals, and the MB concentration was monitored by UV-Vis spectrophotometry at 664 nm. The degradation efficiency was calculated from the decrease in concentration with irradiation time. The kinetic parameters were determined by nonlinear least-squares fitting of the original untransformed pseudo-first-order model to the experimental concentration-time data. Depending on the form of the dataset, the fitting was performed using either $C_t = C_0 e^{-kt}$ or the equivalent normalized form $\frac{C_t}{C_0} = e^{-kt}$, where C_0 is the initial MB concentration, C_t is the MB concentration at irradiation time t , and k is the apparent pseudo-first-order rate constant. The apparent half-life was

calculated from $t_{1/2} = \frac{\ln 2}{k}$. The standard errors of k were obtained from the nonlinear regression, whereas the uncertainties in $t_{1/2}$ and the degradation efficiency at 180 min were estimated by error propagation from the fitted value of k . [47-50]

3. Results and Discussion

3.1 Structural Analysis by XRD

As shown in Figure 1 and summarized in Table 2, all samples retained the anatase structure, with the dominant (101) reflection remaining near 25.3° . A comprehensive view of the XRD patterns for all individual compositions across the three doping series is provided in Figure S1. Doping induced small but systematic changes in peak position and peak broadening, confirming that Zn, Cu, and Mg incorporation affected the TiO_2 lattice. Zn and Mg doping caused slight shifts of the (101) peak toward lower 2θ values, whereas Cu doping produced a shift toward higher angles, indicating a different lattice interaction for Cu compared with Zn and Mg. At the same time, the full width at half maximum increased progressively with dopant concentration, accompanied by a reduction in crystallite size. The crystallite size decreased from 18.31 nm for undoped TiO_2 to 12.06 nm for $\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$, 10.29 nm for $\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$, and 14.40 nm for $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$. Among the investigated dopants, Cu caused the strongest crystallite-size reduction, while Mg-doped films maintained comparatively larger crystallites [33-36]

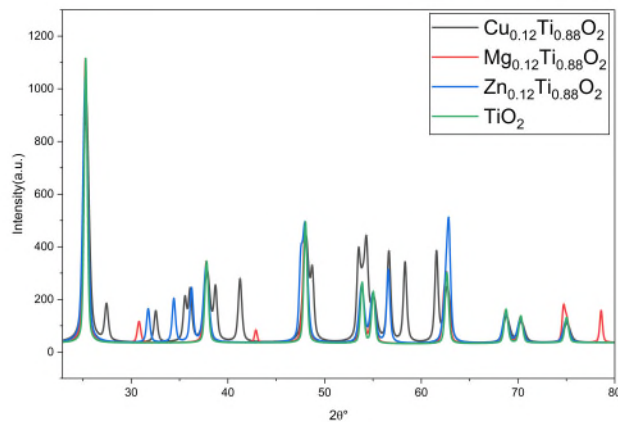


Figure 1. X-ray diffraction (XRD) patterns of undoped TiO_2 and metal-doped $\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$, $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$, and $\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$ thin films. Experimental conditions: The films were deposited on glass substrates via ultrasonic spray pyrolysis at a constant substrate temperature of 450°C . The 0.15M precursor solutions were prepared in a 1:1 (v/v) ethanol/deionized water mixture. Deposition was performed using 8 spray cycles (12s spray duration, 30s pause), with an aerosol flow rate of 5mLmin^{-1} , a compressed air carrier gas flow of 6Lmin^{-1} , and a nozzle-to-substrate distance of 25cm.

XRD measurements were conducted using Cu K α radiation ($\lambda = 1.5406\text{\AA}$) over a 2θ range of $15^\circ - 90^\circ$. The diffraction peaks correspond to the anatase TiO₂ phase (main (101) reflection near 25.3°), where dopant-induced peak shifts and broadening indicate lattice distortion and changes in crystallite size.

Table 2. Structural parameters of undoped and Zn-, Cu-, and Mg-doped TiO₂ thin films derived from the anatase (101) XRD reflection, including 2theta, d-spacing, full width at half maximum (FWHM), and Scherrer crystallite size.

Sample	y	Plane	2theta (deg)	d (Å)	FWHM (deg)	Crystallite size (nm)
TiO ₂	0.00	(101)	25.300	3.52	0.445	18.31
Zn-TiO ₂	0.03	(101)	25.281	3.52	0.542	15.02
Zn-TiO ₂	0.06	(101)	25.273	3.52	0.586	13.90
Zn-TiO ₂	0.09	(101)	25.265	3.52	0.630	12.92
Zn-TiO ₂	0.12	(101)	25.258	3.53	0.675	12.06
Cu-TiO ₂	0.03	(101)	25.320	3.51	0.598	13.61
Cu-TiO ₂	0.06	(101)	25.330	3.51	0.661	12.32
Cu-TiO ₂	0.09	(101)	25.340	3.51	0.726	11.22
Cu-TiO ₂	0.12	(101)	25.350	3.51	0.791	10.29
Mg-TiO ₂	0.03	(101)	25.289	3.52	0.495	16.45
Mg-TiO ₂	0.06	(101)	25.285	3.52	0.518	15.73
Mg-TiO ₂	0.09	(101)	25.280	3.52	0.541	15.04
Mg-TiO ₂	0.12	(101)	25.276	3.52	0.565	14.40

3.2 Raman Analysis

Raman spectroscopy, shown in Figure 2 (and detailed for all doping concentrations in Figure S2), confirmed retention of the anatase framework in all samples. The characteristic anatase modes remained visible after doping, although changes in peak position and intensity indicated increased structural disorder and dopant-induced lattice perturbation [33-36]. In the Zn-doped series, the main E_g mode decreased in intensity and shifted slightly to a lower wavenumber, and a shoulder near 438.5 cm^{-1} was attributed to Zn-related vibrations. In the Cu-doped films, the strongest E_g band weakened substantially, and additional bands near 299.5 and 346.5 cm^{-1} were assigned to Cu–O or CuO-related vibrations at higher Cu loadings. In the Mg-doped series, the anatase modes remained dominant, with only modest shifts and reduced intensity [12-14].

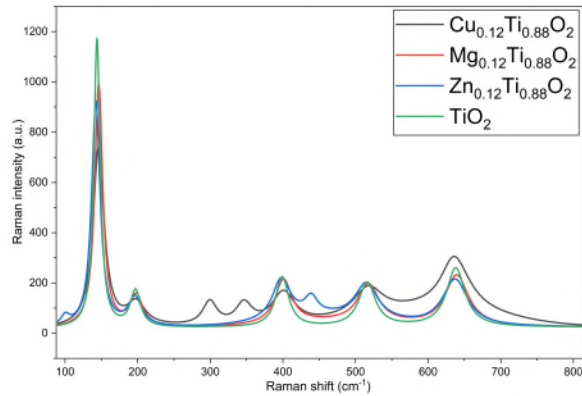


Figure 2. Raman spectra of undoped TiO₂ and metal-doped Cu_{0.12}Ti_{0.88}O₂, Mg_{0.12}Ti_{0.88}O₂, and Zn_{0.12}Ti_{0.88}O₂ thin films. Experimental conditions: The films were deposited on glass substrates via ultrasonic spray pyrolysis at a constant substrate temperature of 450 °C. Precursor solutions (0.15 M) were prepared in a 1:1 (v/v) ethanol/deionized water mixture. The deposition process consisted of 8 spray cycles (12 s spray duration, 30 s pause interval) maintaining an aerosol flow rate of 5 mL/min, a compressed air carrier gas flow of 6 L/min, and a nozzle-to-substrate distance of 25 cm. Raman scattering measurements were recorded at room temperature over a Raman shift range of 100–800 cm⁻¹. The spectra display the characteristic active vibrational modes (E_g , B_{1g} , and A_{1g}) of the anatase TiO₂ phase. Variations in peak intensity, position, and band shape reflect dopant-induced lattice distortion and structural disorder within the host matrix.

3.3 EDX Analysis

As shown in Figure 3, the EDX spectra of the undoped and selected doped TiO₂ thin films confirm the presence of Ti and O as the main constituent elements [43]. The complete set of EDX spectra corresponding to all dopant concentrations is presented in Figure S3. In the Zn-, Cu-, and Mg-doped series, additional signals corresponding to the respective dopant elements are clearly observed, and their intensities increase progressively with increasing nominal dopant concentration [44]. This trend indicates successful incorporation of Zn, Cu, and Mg into the TiO₂ films at the elemental level. The Ti and O signals remain dominant in all spectra, showing that the TiO₂ matrix is preserved after doping [45], while the gradual increase in the dopant-related peaks reflects the systematic change in film composition with dopant loading [46].

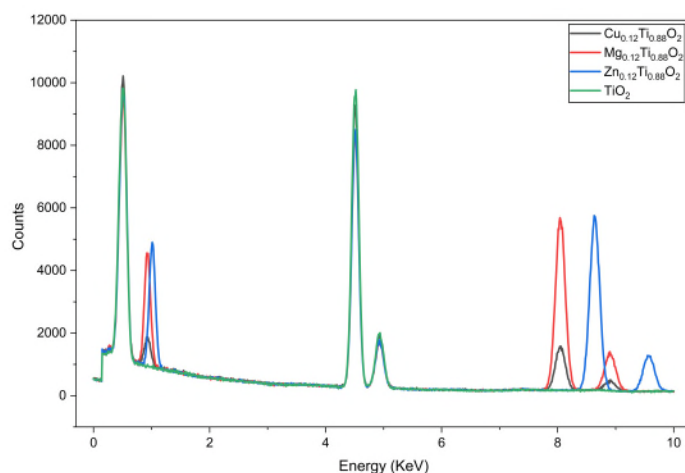


Figure 3. Energy-dispersive X-ray (EDX) spectra of undoped TiO_2 and metal-doped $\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$, $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$, and $\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$ thin films. Experimental conditions: The films were deposited on glass substrates via ultrasonic spray pyrolysis at a constant substrate temperature of 450°C . Precursor solutions (0.15M) were prepared in a 1:1 (v/v) ethanol/deionized water mixture. The deposition process consisted of 8 spray cycles (12s spray duration, 30s pause interval) maintaining an aerosol flow rate of 5mLmin^{-1} , a compressed air carrier gas flow of 6Lmin^{-1} , and a nozzle-to-substrate distance of 25cm. The spectra confirm the presence of Ti and O as the primary matrix elements across all samples. The distinct elemental peaks for Cu, Mg, and Zn validate the successful incorporation of the respective dopants into the host TiO_2 lattice at the targeted concentrations.

3.4 Surface Morphology by SEM

The SEM micrograph of the undoped TiO_2 film, compared with the optimal Cu-doped sample in Figure 4, revealed a relatively homogeneous and compact surface with fine grains and no obvious large cracks or voids [47]. The detailed morphological evolution across all dopant concentrations is comprehensively illustrated in the Supplementary Information (Figures S4, S5, and S6). Doping progressively increased roughness, grain coalescence, and surface heterogeneity [48]. The Zn-doped films (Figure S4) evolved from relatively uniform grains at low Zn loading to rougher and more agglomerated surfaces at higher Zn content. The Cu-doped series (Figure S5) displayed the most pronounced surface irregularity and clustering, consistent with the stronger crystallite-size reduction observed by XRD [49]. Mg doping (Figure S6) led to a more gradual morphological evolution, but high Mg loading still produced coarse agglomerated features and an irregular texture [50].

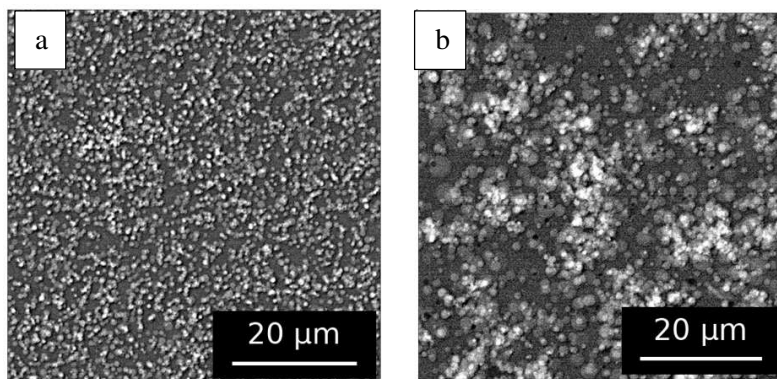


Figure 4. Scanning electron microscopy (SEM) micrographs comparing the surface morphologies of (a) the undoped TiO_2 thin film and (b) the optimum $\text{Cu}_{0.09}\text{Ti}_{0.91}\text{O}_2$ thin film deposited on glass substrates via ultrasonic spray pyrolysis at a constant substrate temperature of 450°C . The 0.15M precursor solutions were prepared in a 1:1 (v/v) ethanol/deionized water mixture. The deposition parameters were strictly maintained at 8 spray cycles (12s spray duration, 30s pause interval), an aerosol flow rate of 5mLmin^{-1} , a carrier gas (compressed air) flow of 6Lmin^{-1} , and a nozzle-to-substrate distance of 25cm. Panel (a) reveals a relatively homogeneous and compact pristine surface composed of uniformly distributed fine grains. In contrast, panel (b) demonstrates increased surface roughness, distinct grain coalescence, and microstructural agglomeration induced by optimal copper incorporation. This modified morphology in the best-performing sample enhances the active surface area and interfacial contact, which is highly favorable for photocatalytic reactions. Scale bars represent $20\mu\text{m}$.

3.5 Optical Properties

As shown in Figure 5, the optical response changed markedly with dopant type and concentration. The detailed UV-Vis transmittance spectra and the corresponding Tauc plots for all series are presented in Figures S7, S8, and S9. Zn and Mg doping increased the visible transmittance and shifted the absorption edge toward shorter wavelengths, indicating a widening of the optical band gap [51]. For the Zn-doped series (Figure S7), the average visible transmittance increased from 87.80% for undoped TiO_2 to 90.37% for $\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$, while the band gap increased from 2.95 to 3.36 eV. Mg doping (Figure S9) produced an even stronger effect, with the transmittance reaching 93.82% for $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$ and the band gap increasing to 3.55 eV. This behavior indicates suppression of low-energy absorption and improved transparency, which is favorable for transparent coatings, window layers, and optoelectronic devices requiring high visible-light transmission [52]. In contrast, Cu doping (Figure S8) produced the opposite trend in Figure 5. The average visible transmittance decreased from 87.80% for undoped TiO_2 to 64.86% for $\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$, while the band gap decreased to 2.82 eV at the highest Cu loading [53].

The red shift of the absorption edge and the reduced transparency indicate the formation of additional electronic states that promote absorption in the longer-wavelength region [13]. From a functional point of view, this behavior is less favorable for transparent optoelectronic applications but more suitable for visible-light-responsive photocatalytic and photoactive coatings, where enhanced light harvesting is desirable [54].

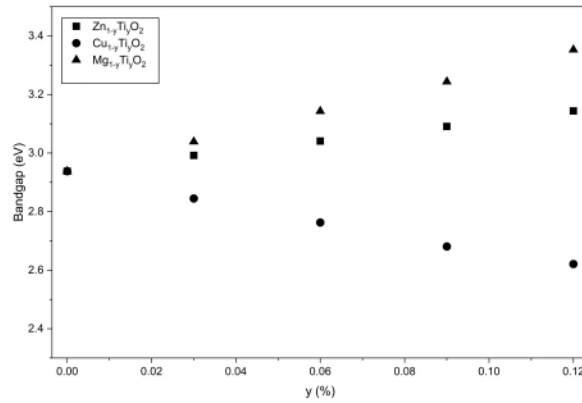


Figure 5. Comparative variation of the optical band gap energy (E_g) as a function of the nominal dopant concentration (y) for undoped TiO_2 and metal-doped $\text{Zn}_y\text{Ti}_{1-y}\text{O}_2$, $\text{Cu}_y\text{Ti}_{1-y}\text{O}_2$, and $\text{Mg}_y\text{Ti}_{1-y}\text{O}_2$ thin films deposited on glass substrates via ultrasonic spray pyrolysis at a constant substrate temperature of 450°C . Precursor solutions (0.15M) were formulated in a 1:1 (v/v) ethanol/deionized water mixture. The deposition parameters were strictly maintained at 8 spray cycles (12s spray duration, 30s pause interval), an aerosol flow rate of 5mLmin^{-1} , a carrier gas (compressed air) flow of 6Lmin^{-1} , and a nozzle-to-substrate distance of 25cm . The optical band gap values were estimated via Tauc plot analysis derived from UV-Vis transmittance spectra. The plotted trends reveal distinct dopant-dependent electronic modifications: Zn and Mg incorporation progressively widens the band gap, whereas Cu doping leads to significant band gap narrowing at higher dopant loadings, thereby enhancing visible-light absorption.

3.6 Photocatalytic Degradation of Methylene Blue

The photocatalytic behavior of the films was evaluated from the decrease in methylene blue (MB) concentration under irradiation, using the absorbance at 664 nm as the analytical signal. In the revised analysis, the kinetic parameters were determined by nonlinear least-squares fitting of the original untransformed pseudo-first-order model to the experimental concentration-time data rather than by linear regression of transformed equations. Depending on the form of the dataset, the fitting was performed using either $C_t = C_0 e^{-kt}$ or the equivalent normalized form $\frac{C_t}{C_0} = e^{-kt}$, where C_0 is the initial methylene blue concentration, C_t is the concentration at irradiation time t , and k is the apparent pseudo-first-order rate

constant. The degradation efficiency was calculated as $\eta(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100$, and the apparent half-life was obtained from $t_{1/2} = \frac{\ln 2}{k}$. [45-54]

3.6.1 Zn-Doped TiO₂ Films

The temporal evolution of the UV-Vis absorption spectra during the degradation process is presented in Figure S10. Figure 6 shows the photocatalytic kinetic curves (C_0 / C_t versus irradiation time) of methylene blue over undoped and Zn-doped TiO₂ thin films under irradiation. The Zn-doped films exhibited a faster increase in C_0 / C_t and a higher degradation efficiency (as clearly illustrated in Figure S11) than undoped TiO₂, confirming that Zn incorporation improved the photocatalytic performance [20, 21]. The kinetic parameters were obtained by nonlinear least-squares fitting of the original untransformed pseudo-first-order model, $C_0 / C_t = e^{kt}$, which is a well-established approach for evaluating dye degradation kinetics [7, 9, 11]. As summarized in Table 3, the apparent rate constant increased from $0.003812 \pm 0.000033 \text{ min}^{-1}$ for TiO₂ to 0.005175 ± 0.000040 , 0.006618 ± 0.000044 , and $0.007875 \pm 0.000038 \text{ min}^{-1}$ for Zn_{0.03}Ti_{0.97}O₂, Zn_{0.06}Ti_{0.94}O₂, and Zn_{0.09}Ti_{0.91}O₂, respectively, followed by a slight decrease to $0.007224 \pm 0.000038 \text{ min}^{-1}$ for Zn_{0.12}Ti_{0.88}O₂. The degradation efficiency at 180 min followed the same trend, increasing from $49.65 \pm 0.30\%$ for TiO₂ to $60.60 \pm 0.28\%$, $69.61 \pm 0.24\%$, and $75.77 \pm 0.17\%$, then decreasing slightly to $72.75 \pm 0.19\%$ at the highest Zn loading. The corresponding half-life values decreased from $181.8 \pm 1.6 \text{ min}$ for TiO₂ to $88.0 \pm 0.4 \text{ min}$ for Zn_{0.09}Ti_{0.91}O₂, then increased to $96.0 \pm 0.5 \text{ min}$ for Zn_{0.12}Ti_{0.88}O₂. These results identify Zn_{0.09}Ti_{0.91}O₂ as the optimum composition within the investigated Zn-doped series.

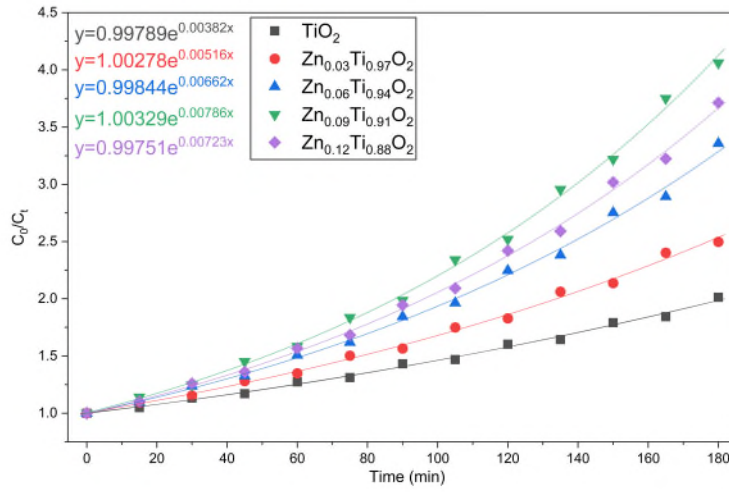


Figure 6. Time-dependent photocatalytic kinetic curves (C_0 / C_t versus irradiation time) of methylene blue over undoped and Zn-doped TiO_2 ($\text{Zn}_{0.03}\text{Ti}_{0.97}\text{O}_2$, $\text{Zn}_{0.06}\text{Ti}_{0.94}\text{O}_2$, $\text{Zn}_{0.09}\text{Ti}_{0.91}\text{O}_2$, and $\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$) thin films the catalyst films ($2\text{cm} \times 2\text{cm}$) were deposited on glass substrates by ultrasonic spray pyrolysis at 450°C . The photocatalytic tests were conducted using 50mL of dye solution (10mgL^{-1}) under continuous stirring at $25 \pm 2^\circ\text{C}$, and irradiated by a 15W UV-visible lamp ($350 - 800\text{nm}$). The solid lines represent the fitted kinetic behavior obtained directly from the non-linear least-squares fitting of the original pseudo-first-order model.

Table 3. Kinetic parameters obtained by nonlinear least-squares fitting of the original pseudo-first-order model for methylene blue degradation over undoped and Zn-doped TiO_2 thin films, including the apparent rate constant k , its standard error, the coefficient of determination R^2 , the degradation efficiency after 180 min, and the apparent half-life

Sample	k (min^{-1})	R^2	Degradation efficiency at 180 min (%)	$t_{1/2}$ (min)
TiO_2	0.003812 ± 0.000033	0.9953	49.65 ± 0.30	181.8 ± 1.6
$\text{Zn}_{0.03}\text{Ti}_{0.97}\text{O}_2$	0.005175 ± 0.000040	0.9957	60.60 ± 0.28	133.9 ± 1.0
$\text{Zn}_{0.06}\text{Ti}_{0.94}\text{O}_2$	0.006618 ± 0.000044	0.9964	69.61 ± 0.24	104.7 ± 0.7
$\text{Zn}_{0.09}\text{Ti}_{0.91}\text{O}_2$	0.007875 ± 0.000038	0.9978	75.77 ± 0.17	88.0 ± 0.4
$\text{Zn}_{0.12}\text{Ti}_{0.88}\text{O}_2$	0.007224 ± 0.000038	0.9976	72.75 ± 0.19	96.0 ± 0.5

3.6.2 Cu-Doped TiO₂ Films

The time-dependent UV-Vis absorption spectra recorded during the degradation process for this series are provided in Figure S12. Figure 7 illustrates the photocatalytic kinetic curves (C_0/C_t versus irradiation time) of methylene blue over undoped and Cu-doped TiO₂ thin films.

Compared with undoped TiO₂, all Cu-doped films showed a more pronounced increase in C_0/C_t with irradiation time and markedly higher degradation efficiencies (as detailed in Figure S13), indicating a substantial enhancement in photocatalytic activity after Cu incorporation [23, 24]. The kinetic parameters were determined by nonlinear least-squares fitting of the original pseudo-first-order expression, $C_0/C_t = e^{kt}$, a standard procedure for evaluating such catalytic systems [8, 10, 13]. The values listed in Table 4 show that the apparent rate constant increased from $0.003836 \pm 0.000039 \text{ min}^{-1}$ for TiO₂ to 0.006650 ± 0.000053 , 0.008529 ± 0.000048 , and $0.010455 \pm 0.000047 \text{ min}^{-1}$ for Cu_{0.03}Ti_{0.97}O₂, Cu_{0.06}Ti_{0.94}O₂, and Cu_{0.09}Ti_{0.91}O₂, respectively, before decreasing to $0.009085 \pm 0.000046 \text{ min}^{-1}$ for Cu_{0.12}Ti_{0.88}O₂.

The degradation efficiency at 180 min increased from $49.87 \pm 0.35\%$ for undoped TiO₂ to $69.79 \pm 0.29\%$, $78.46 \pm 0.19\%$, and $84.77 \pm 0.13\%$, followed by a slight decrease to $80.51 \pm 0.16\%$ at the highest Cu content. The corresponding half-life values decreased from $180.7 \pm 1.8 \text{ min}$ for TiO₂ to $66.3 \pm 0.3 \text{ min}$ for Cu_{0.09}Ti_{0.91}O₂, then rose to $76.3 \pm 0.4 \text{ min}$ for Cu_{0.12}Ti_{0.88}O₂. These results indicate that Cu_{0.09}Ti_{0.91}O₂ is the optimum composition in the Cu-doped series.

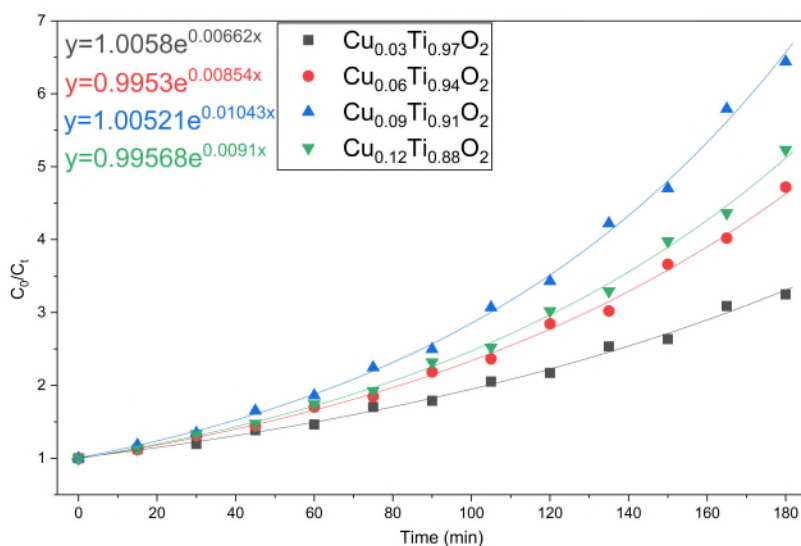


Figure 7. Time-dependent photocatalytic kinetic curves (C_0 / C_t versus irradiation time) of methylene blue over Cu-doped TiO_2 ($\text{Cu}_{0.03}\text{Ti}_{0.97}\text{O}_2$, $\text{Cu}_{0.06}\text{Ti}_{0.94}\text{O}_2$, $\text{Cu}_{0.09}\text{Ti}_{0.91}\text{O}_2$, and $\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$) thin films the catalyst films ($2\text{cm} \times 2\text{cm}$) were deposited on glass substrates by ultrasonic spray pyrolysis at 450°C . The photocatalytic tests were conducted using 50mL of dye solution (10mgL^{-1}) under continuous stirring at $25 \pm 2^\circ\text{C}$, and irradiated by a 15W UV-visible lamp ($350 - 800\text{nm}$). The solid lines represent the fitted kinetic behavior obtained directly from the non-linear least-squares fitting of the original pseudo-first-order model.

Table 4. Kinetic parameters obtained by nonlinear least-squares fitting of the original pseudo-first-order model for methylene blue degradation over undoped and Cu-doped TiO_2 thin films, including the apparent rate constant k , its standard error, the coefficient of determination R^2 , the degradation efficiency after 180 min, and the apparent half-life.

Sample	k (min^{-1})	R^2	Degradation efficiency at 180 min (%)	$t_{1/2}$ (min)
$\text{Cu}_{0.03}\text{Ti}_{0.97}\text{O}_2$	0.006650 ± 0.000053	0.9946	69.79 ± 0.29	104.2 ± 0.8
$\text{Cu}_{0.06}\text{Ti}_{0.94}\text{O}_2$	0.008529 ± 0.000048	0.9969	78.46 ± 0.19	81.3 ± 0.5
$\text{Cu}_{0.09}\text{Ti}_{0.91}\text{O}_2$	0.010455 ± 0.000047	0.9976	84.77 ± 0.13	66.3 ± 0.3
$\text{Cu}_{0.12}\text{Ti}_{0.88}\text{O}_2$	0.009085 ± 0.000046	0.9974	80.51 ± 0.16	76.3 ± 0.4

3.6.3 Mg-Doped TiO_2 Films

The time-dependent UV-Vis absorption spectra recorded during the degradation process for this series are provided in Figure S14. Figure 8 presents the photocatalytic kinetic curves (C_0 / C_t versus irradiation time) of methylene blue over undoped and Mg-doped TiO_2 thin films. The Mg-doped samples displayed a progressive increase in C_0 / C_t and a corresponding improvement in degradation efficiency (as detailed in Figure S15) with increasing Mg content. The kinetic analysis was performed by nonlinear least-squares fitting of the original pseudo-first-order model, $C_0 / C_t = e^{kt}$, a methodology extensively validated in similar degradation studies [9, 11, 28]. As shown in Table 5, the apparent rate constant increased steadily from $0.003812 \pm 0.000033\text{min}^{-1}$ for undoped TiO_2 to 0.005615 ± 0.000040 , 0.007628 ± 0.000045 , 0.008821 ± 0.000032 , and $0.009814 \pm 0.000106\text{min}^{-1}$ for $\text{Mg}_{0.03}\text{Ti}_{0.97}\text{O}_2$, $\text{Mg}_{0.06}\text{Ti}_{0.94}\text{O}_2$, $\text{Mg}_{0.09}\text{Ti}_{0.91}\text{O}_2$, and $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$, respectively.

The degradation efficiency at 180 min increased monotonically from $49.65 \pm 0.30\%$ for TiO_2 to $63.85 \pm 0.32\%$, $75.39 \pm 0.27\%$, $79.58 \pm 0.17\%$, and $82.91 \pm 0.33\%$ for the Mg-doped films.

In parallel, the half-life values decreased from 181.8 ± 1.6 min for TiO_2 to 123.4 ± 0.9 , 90.9 ± 0.5 , 78.6 ± 0.3 , and 70.6 ± 0.8 min with increasing Mg content. Unlike the Zn- and Cu-doped series, no decline in activity was observed at the highest Mg concentration, which aligns with the distinct electronic behavior of Mg acting predominantly through morphological and surface basicity modifications rather than forming discrete mid-gap recombination centers [29, 30]. These findings indicate that $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$ is the optimum composition within the investigated Mg-doped series.

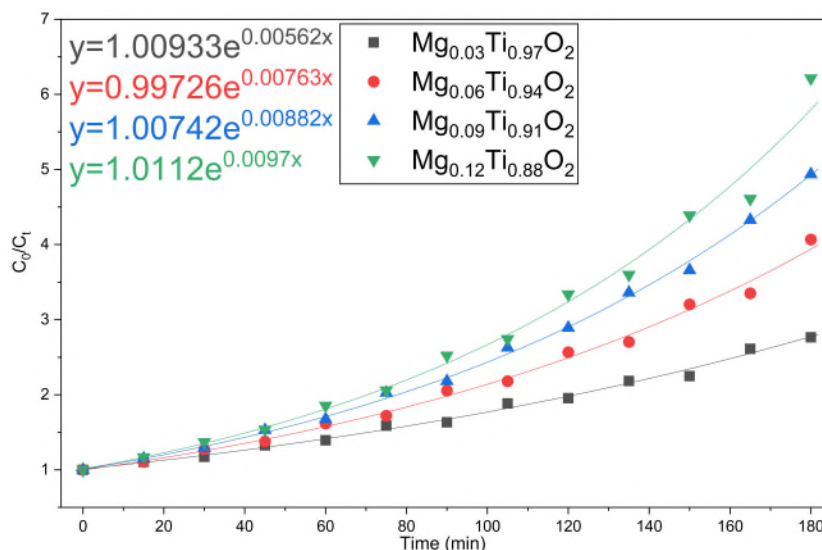


Figure 8. Time-dependent photocatalytic kinetic curves (C_0 / C_t versus irradiation time) of methylene blue over Mg-doped TiO_2 ($\text{Mg}_{0.03}\text{Ti}_{0.97}\text{O}_2$, $\text{Mg}_{0.06}\text{Ti}_{0.94}\text{O}_2$, $\text{Mg}_{0.09}\text{Ti}_{0.91}\text{O}_2$, and $\text{Mg}_{0.12}\text{Ti}_{0.88}\text{O}_2$) thin films. The catalyst films ($2\text{cm} \times 2\text{cm}$) were deposited on glass substrates by ultrasonic spray pyrolysis at 450°C . The photocatalytic tests were conducted using 50mL of dye solution (10mgL^{-1}) under continuous stirring at $25 \pm 2^\circ\text{C}$, and irradiated by a 15W UV-visible lamp ($350 - 800\text{nm}$). The solid lines represent the fitted kinetic behavior obtained directly from the non-linear least-squares fitting of the original pseudo-first-order model.

Table 5. Kinetic parameters obtained by nonlinear least-squares fitting of the original pseudo-first-order model for methylene blue degradation over undoped and Mg-doped TiO₂ thin films, including the apparent rate constant k , its standard error, the coefficient of determination R^2 , the degradation efficiency after 180 min, and the apparent half-life.

Sample	k (min ⁻¹)	R^2	Degradation efficiency at 180 min (%)	$t_{1/2}$ (min)
Mg _{0.03} Ti _{0.97} O ₂	0.005682 ± 0.000052	0.9936	64.04 ± 0.33	122.0 ± 1.1
Mg _{0.06} Ti _{0.94} O ₂	0.007625 ± 0.000066	0.9932	74.65 ± 0.30	90.9 ± 0.8
Mg _{0.09} Ti _{0.91} O ₂	0.008860 ± 0.000038	0.9981	79.71 ± 0.14	78.2 ± 0.3
Mg _{0.12} Ti _{0.88} O ₂	0.009814 ± 0.000106	0.9871	82.91 ± 0.33	70.6 ± 0.8

3.6.4 Structure-Property-Performance Correlation

Taken Comprehensive analysis of the XRD, Raman, SEM, optical, and nonlinear kinetic-fitting results indicates that the photocatalytic response is profoundly influenced by the synergistic effects of crystallite-size evolution, structural disorder, surface morphology, and dopant-dependent band-gap modifications [12, 15, 51]. Among the investigated films, Cu doping produced the highest apparent rate constant at the optimum composition, Cu_{0.09}Ti_{0.91}O₂, which can be attributed to the efficient narrowing of the band gap and the creation of beneficial interfacial charge-transfer states [23, 24]. Conversely, Mg doping showed a progressive, monotonic enhancement in photocatalytic performance across the entire studied composition range, predominantly driven by morphological improvements and surface basicity without creating excessive mid-gap recombination centers [27, 28]. In the Zn-doped series, the photocatalytic activity increased up to Zn_{0.09}Ti_{0.91}O₂ and then decreased slightly at the highest Zn loading [20].

These trends collectively suggest that the overall photocatalytic performance heavily depends on a critical balance between the beneficial effects of dopant incorporation (such as extended light harvesting and carrier separation) and the adverse effects (such as the formation of recombination centers or severe lattice distortion) that inevitably arise at excessive dopant concentrations [4, 18, 54].

3.7 Proposed Photocatalytic Mechanism

Based on the combined structural, optical, and kinetic results, a plausible photocatalytic degradation pathway for methylene blue over undoped and doped TiO₂ thin films is proposed [45, 46]. Under irradiation, TiO₂ generates conduction-band electrons (e_{CB}^-) and valence-band holes (h_{VB}^+) according to the standard photoexcitation process ($h\nu \rightarrow e_{CB}^- + h_{VB}^+$) [3, 4]. The photogenerated holes can react with adsorbed water molecules or surface hydroxyl groups to produce hydroxyl radicals (OH[•]), while

conduction-band electrons can reduce dissolved oxygen to superoxide radical species ($O_2^{\bullet-}$). These reactive oxygen species, particularly $OH^\bullet$ and $O_2^{\bullet-}$, are considered the main oxidizing species responsible for the degradation of methylene blue into intermediate products [7, 47, 48], followed by further oxidation toward complete mineralization products such as CO_2 and H_2O [49-51]. The present results suggest that dopant incorporation affects the photocatalytic response through combined changes in light absorption, charge separation, crystallite size, and surface reactivity [12, 18, 52].

Within the investigated compositions, Cu doping produced the strongest enhancement [23, 24], Mg doping showed a progressive improvement across the studied range [28, 29], and Zn doping exhibited an optimum composition at intermediate loading [20, 21]. This mechanistic interpretation is proposed as a plausible explanation of the comparative photocatalytic behavior observed in the present study and should not be interpreted as direct proof of a single dominant reaction pathway [53, 54].

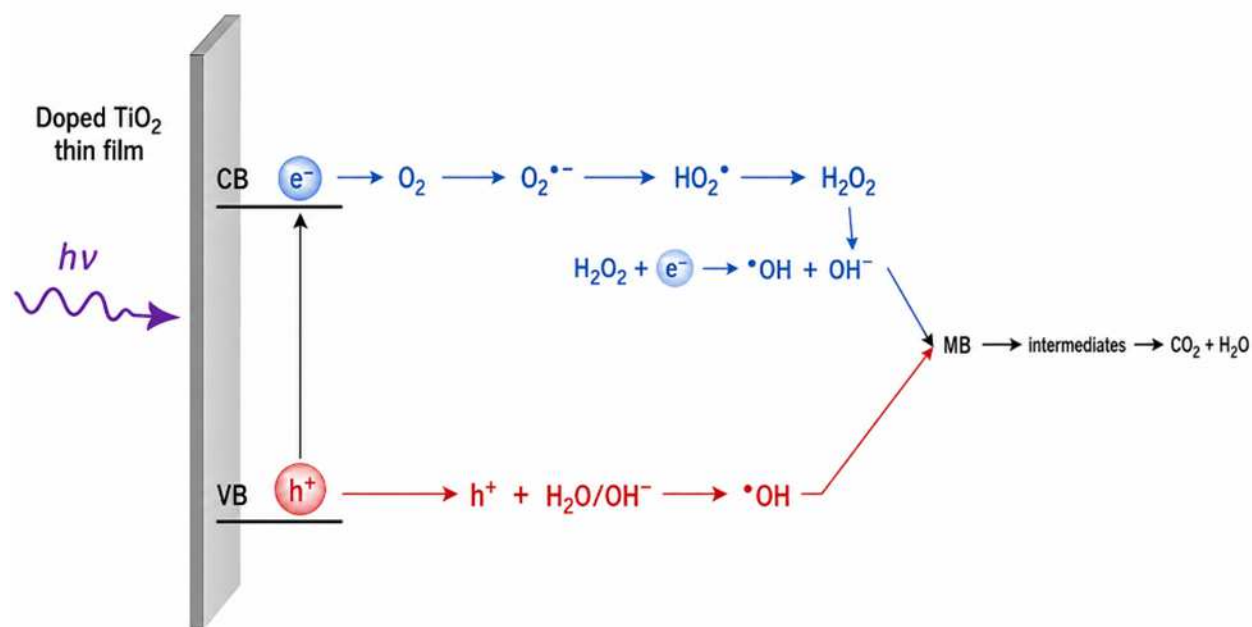


Figure 9. Schematic illustration of a plausible photocatalytic degradation pathway of methylene blue over doped TiO_2 thin films under UV-visible irradiation, showing photogenerated charge separation, reactive oxygen species formation, and the subsequent transformation of methylene blue into intermediate compounds and final mineralization products.

4. Conclusion

Undoped and Zn-, Cu-, and Mg-doped TiO₂ thin films were successfully prepared by ultrasonic spray pyrolysis and systematically evaluated as photocatalysts for the degradation of methylene blue in aqueous solution. This comparative study allowed evaluation of how dopant type and concentration influence the structural, optical, morphological, and photocatalytic properties of TiO₂ thin films.

The structural characterization showed that anatase TiO₂ remained the dominant crystalline phase after doping for all investigated compositions. Nevertheless, dopant incorporation produced measurable changes in peak position, peak broadening, and crystallite size, indicating that Zn, Cu, and Mg affected the TiO₂ lattice in different ways. Raman analysis further confirmed the preservation of the anatase framework, while also reflecting dopant-dependent changes in structural disorder. Surface and compositional analyses revealed that doping modified the film morphology and surface texture, which are expected to influence adsorption behavior, active-site accessibility, and interfacial charge-transfer processes during photocatalysis.

The optical results demonstrated a clear dopant-dependent response. Zn and Mg incorporation increased the optical band gap and generally preserved or improved the transparency of the films, whereas Cu incorporation reduced the band gap and promoted stronger visible-light absorption. These findings indicate that the electronic structure of TiO₂ can be tuned effectively through controlled doping, although the direction and magnitude of the modification depend strongly on the dopant species and concentration.

The photocatalytic experiments showed that all doped films outperformed undoped TiO₂ in methylene blue degradation. The kinetic parameters were determined by nonlinear least-squares fitting of the original untransformed pseudo-first-order model rather than by linear regression of transformed equations. On this basis, the highest apparent rate constant was obtained for Cu_{0.09}Ti_{0.91}O₂ ($0.010455 \pm 0.000047 \text{ min}^{-1}$), which also exhibited the highest degradation efficiency after 180 min ($84.77 \pm 0.13\%$). Mg_{0.12}Ti_{0.88}O₂ showed the next-best performance, with an apparent rate constant of $0.009814 \pm 0.000106 \text{ min}^{-1}$ and a degradation efficiency of $82.91 \pm 0.33\%$. Within the Zn-doped series, the optimum composition was Zn_{0.09}Ti_{0.91}O₂, with $k = 0.007875 \pm 0.000038 \text{ min}^{-1}$ and a degradation efficiency of $75.77 \pm 0.17\%$.

The comparative behavior of the three-dopant series suggests that photocatalytic performance is governed by a combination of factors rather than by a single structural or optical parameter. The enhanced activity appears to result from the interplay between crystallite-size evolution, surface morphology, dopant-induced modifications of the band structure, and the resulting changes in charge separation and reactive-species generation. Cu doping provided the strongest enhancement, likely because its effect on visible-light absorption and charge-transfer behavior was particularly favorable at intermediate concentration. Mg

doping produced a progressive improvement across the investigated composition range, whereas Zn doping showed an optimum at intermediate loading followed by a slight decline at the highest Zn content, indicating that excessive dopant incorporation may partially offset the beneficial effects achieved at lower concentration.

Overall, the present results show that controlled metal-ion doping is an effective strategy for tuning the physicochemical and photocatalytic properties of TiO₂ thin films. Among the investigated samples, Cu_{0.09}Ti_{0.91}O₂ emerged as the most efficient photocatalyst for methylene blue degradation under the applied experimental conditions. These findings indicate that doped TiO₂ thin films are promising photocatalytic materials for dye-removal applications, while also highlighting the importance of optimizing both dopant identity and dopant concentration.

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