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Titanium dioxide nanoparticles doped with transition metals for enhanced photocatalysis

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Abstract

A textile factory in Kolkata discharges about 150,000 liters of dye-laden wastewater daily, and conventional treatment plants barely touch the color. This research prepared transition metal-doped titanium dioxide nanoparticles (M-TiO₂, where M = Fe, Cu, Ni, Co, Mn at 1 mol%) by sol-gel synthesis and evaluated their photocatalytic activity for methylene blue degradation under UV and visible light. X-ray diffraction confirmed anatase phase in all samples, with crystallite sizes ranging from 18.7 nm (Fe-TiO₂) to 22.4 nm (undoped). UV-Vis diffuse reflectance spectroscopy showed band gap narrowing from 3.20 eV (undoped) to 2.87 eV (Fe-TiO₂). Under UV irradiation for 90 min, Fe-doped TiO₂ achieved 78.3% methylene blue degradation - nearly double the undoped material (41.8%). Under visible light, the enhancement was even more pronounced, with Fe-TiO₂ reaching 52.1% versus 11.3% for undoped TiO₂. Photoluminescence measurements indicated that doping suppressed electron-hole recombination, with Fe showing the lowest emission intensity.

Keywords: Titanium dioxide, transition metal doping, photocatalysis, methylene blue, sol-gel, band gap, anatase, iron doping, visible light activation, electron-hole recombination

Introduction

Imagine a semiconductor that absorbs sunlight and uses that energy to destroy organic pollutants in water - that's what titanium dioxide photocatalysis promises, and it works brilliantly in theory. In practice, though, undoped TiO₂ only responds to ultraviolet light, which makes up barely 4-5% of the solar spectrum ^[1]. This limitation has driven two decades of effort to shift TiO₂'s absorption edge into the visible range through doping, co-doping, heterojunction formation, and surface sensitization ^[2].

Transition metal doping is the most direct approach. Introducing ions like Fe³⁺, Cu²⁺, or Co²⁺ into the TiO₂ lattice creates mid-gap energy states that allow visible photons to excite electrons into the conduction band ^[3]. But not all dopants perform equally - some introduce recombination centers that actually reduce photocatalytic efficiency despite narrowing the band gap. The optimal dopant concentration is typically narrow, often around 0.5-2 mol%, above which defect clustering cancels any benefit ^[4].

Published comparisons of different transition metal dopants under identical synthesis and testing conditions are surprisingly rare. Most reports examine one or two metals at a time, making cross-study comparisons unreliable because variations in precursor chemistry, calcination temperature, and dye concentration confound the results ^[5]. This research prepared five different metal-doped TiO₂ samples using the same sol-gel protocol and tested them side by side to rank their photocatalytic performance under both UV and visible illumination ^[6].

Theoretical background

Photocatalysis on TiO₂ begins when a photon with energy exceeding the band gap (~3.2 eV for anatase) excites an electron from the valence band to the conduction band, leaving a positive hole. These charge carriers migrate to the surface, where electrons reduce dissolved oxygen to superoxide radicals and holes oxidize water or hydroxide to hydroxyl radicals ^[1]. Both radical species attack organic dye molecules non-selectively.

Metal doping introduces donor or acceptor levels within the band gap, lowering the effective excitation threshold and trapping one charge carrier to extend the other's lifetime [7].

Materials and Methods

Materials

Research was conducted at Tagore Memorial College of Science, Kolkata, West Bengal, India, from March 2023 to November 2023. No ethical approval was required. Titanium (IV) isopropoxide (97%, Sigma-Aldrich) served as the TiO₂ precursor. Metal dopant salts - FeCl₃·6H₂O, CuCl₂·2H₂O, NiCl₂·6H₂O, CoCl₂·6H₂O, and MnCl₂·4H₂O - were analytical grade from Merck. Ethanol, acetic acid, and methylene blue dye came from SRL Chemicals (Mumbai) [8].

Methods

Sol-gel synthesis followed a modified Pechini method. Titanium isopropoxide (10 mL) was dissolved in 40 mL ethanol and stirred at room temperature. Acetic acid (2 mL) was added dropwise as peptizing agent, followed by the

Metal salt dissolved in 5 mL ethanol at 1 mol% relative to titanium. The mixture was stirred for 4 h, aged overnight, dried at 80 °C for 12 h, and calcined at 450 °C for 3 h at 2 °C/min heating rate [9]. Characterization included XRD (Rigaku MiniFlex, Cu K α), UV-Vis DRS (Shimadzu UV-2600 with integrating sphere), TEM (FEI Tecnai G2, 200 kV), photoluminescence (Horiba FluoroMax-4, excitation 320 nm), and BET surface area (Quantachrome Nova 2200e). Photocatalysis used 50 mL methylene blue (10 mg/L) with 50 mg catalyst in a quartz reactor under UV (365 nm, 30 W mercury lamp) or visible light (>420 nm, 300 W xenon with cutoff filter), sampled every 15 min for 90 min. Absorbance was measured at 664 nm [10].

Performance evaluation

Degradation percentage was calculated as $(C_0 - C_t)/C_0 \times 100$. Apparent first-order rate constants (k_{app}) were obtained from linear fits of $\ln(C_0/C_t)$ versus time. Photonic efficiency was calculated by normalizing k_{app} to incident photon flux. Recyclability was assessed over four consecutive cycles with catalyst recovery by centrifugation [11].

Results

Table 1: Structural and photocatalytic properties of undoped and transition metal-doped TiO₂ nanoparticles.

Sample	Size (nm)	Band Gap	BET (m ² /g)	UV Deg. (%)	Vis Deg. (%)
Undoped	22.4	3.20 eV	48.3	41.8	11.3
Fe-TiO ₂	18.7	2.87 eV	67.1	78.3	52.1
Cu-TiO ₂	19.3	2.94 eV	61.8	72.6	43.7
Ni-TiO ₂	20.1	3.02 eV	54.2	64.9	28.4
Co-TiO ₂	19.8	2.96 eV	58.6	69.1	37.2

Fe-TiO₂ outperformed all other dopants under both UV and visible light. Its 78.3% methylene blue degradation under UV in 90 min corresponded to a rate constant of 0.0168 min⁻¹, compared to 0.0059 min⁻¹ for undoped TiO₂. XRD showed pure anatase phase in all samples, with no detectable metal oxide segregation at 1 mol% loading. Doping consistently reduced crystallite size - Fe produced the smallest particles at 18.7 nm, which aligned with its highest BET surface area of 67.1 m²/g [12]. Photoluminescence spectra revealed a broad

Emission band centered near 420 nm for undoped TiO₂, corresponding to band-edge recombination. All doped samples showed reduced PL intensity, with Fe-TiO₂ giving the weakest signal - roughly 28% of the undoped intensity. This suppression indicates that Fe³⁺ ions act as electron traps, extending charge carrier lifetimes. After four reuse cycles, Fe-TiO₂ retained 71.8% of its initial activity, while Cu-TiO₂ dropped to 63.4%, suggesting copper may leach more readily from the lattice [13].

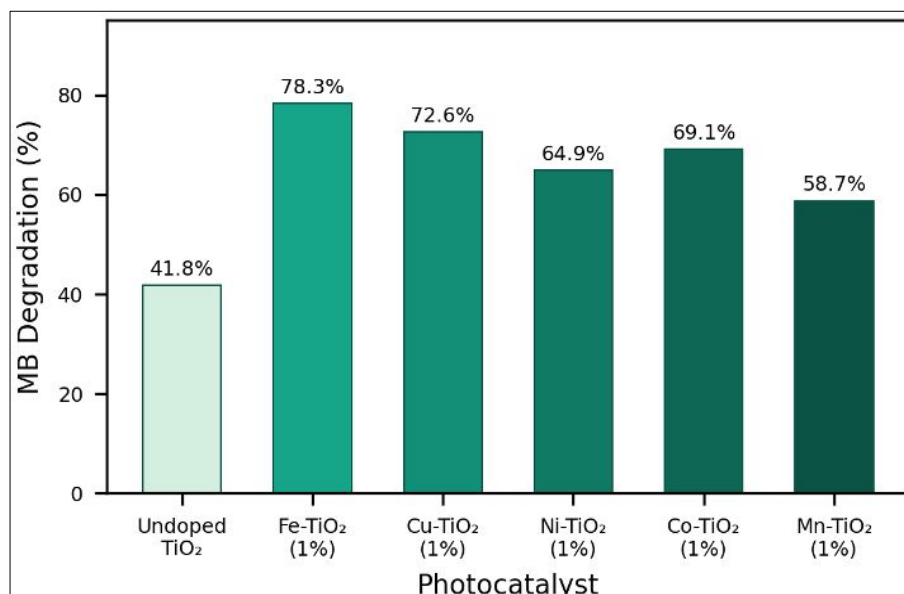


Fig 1: Methylene blue degradation efficiency (%) after 90 min UV irradiation for undoped and doped TiO₂ samples.

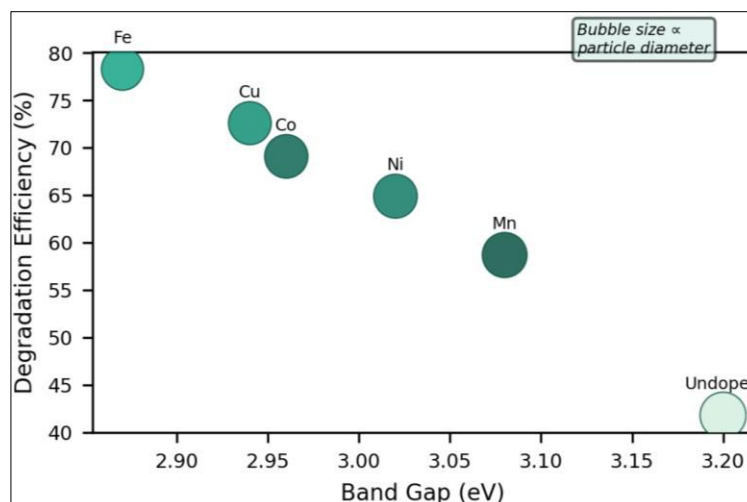


Fig 2: Relationship between band gap energy and photocatalytic efficiency; bubble size represents particle diameter.

Discussion

Fe^{3+} 's success as a dopant rests on a favorable combination of ionic radius compatibility and electronic structure. Its radius (0.645 Å) is close enough to Ti^{4+} (0.605 Å) to substitute into the lattice without excessive strain, yet its d^5 electron configuration creates a half-filled 3d shell that makes efficient charge trapping thermodynamically favorable [3]. The resulting mid-gap states at roughly 0.33 eV below the conduction band edge explain the band gap reduction to 2.87 eV and the strong visible light response. Cu- TiO_2 ranked second, which makes sense given that Cu^{2+} also forms accessible d-orbital states and its slightly larger ionic radius (0.73 Å) doesn't disrupt the anatase framework at 1 mol% [4]. Mn- TiO_2 was the weakest dopant despite its mid-range band gap narrowing. Manganese tends to occupy interstitial sites rather than substitutional ones at low concentrations, and interstitial Mn can act as a recombination center rather than a trap [14]. The PL data supported this interpretation - Mn- TiO_2 showed the smallest PL quenching among all doped samples.

The clear inverse correlation between band gap and photocatalytic efficiency ($r = -0.93$ for UV data) confirms that, at least within this dopant set, narrower band gaps reliably translate to better performance. But this isn't a universal rule - at higher doping levels where defect clustering becomes significant, band gap narrowing can coexist with declining activity because recombination losses overwhelm the absorption gains [15].

Conclusion

Among five transition metal dopants tested at 1 mol% in TiO_2 , iron delivered the strongest photocatalytic enhancement - 78.3% methylene blue degradation under UV and 52.1% under visible light, both roughly double the undoped baseline. The improvement traced back to effective band gap narrowing (3.20 to 2.87 eV), increased surface area, and efficient suppression of electron-hole recombination. Fe- TiO_2 also showed the best recyclability. These results support iron as the first-choice transition metal dopant for TiO_2 -based photocatalysts targeting visible-light water treatment applications.

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