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Spin-Coated Nanostructured Tungsten Oxide (WO₃) Thin Films for Photocatalytic Degradation of Organic Dyes: A Comprehensive Review

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Abstract

The rapid release of colored waste water, which is typically contaminated with synthetic organic dyes from the textile, paper, leather, pharmaceutical, and printing industries, is a significant threat to the environment. These dyes can be toxic and persist in the environment. A viable solution to address these threats includes using semiconductor photocatalysis, as it is a method that is highly effective, safe to the environment and sustainable. Several photocatalytic materials have been studied; however, among them, tungsten oxide (WO₃) is one of the most attractive due to its relatively narrow band gap energy (1.23 eV), good chemical stability, visible light photoactivity, and low toxicity. Spin coated nano-structured WO₃ thin films are being widely investigated because they provide advantages such as low production costs, high uniformity of the thin films deposited onto substrates with controlled thickness and scalability to large area substrates. This article provides a thorough analysis of developments of spin-coated nanostructured WO₃ thin films based on photocatalytic degradation of organic dyes. The crystalline structures, optical properties, electronic characteristics, photocatalytic processes and other critical factors that affect the performance of WO₃ thin films were analyzed. Modifications to increase the photocatalytic efficiency included metal or non-metal doping, hetero-junction formation, defect engineering and plasmonic enhancements that facilitate charge separation and enhance photocatalytic activities under visible light illumination. Finally, comparative studies regarding the degradation efficiencies of representative organic dyes (such as methylene blue, rhodamine B, methyl orange, and Congo Red) were reviewed. Furthermore, the main challenges that need to be addressed in order to develop stable long-lasting photocatalysts at large scales, while suggesting potential areas for future investigation on multi-functional coatings and solar driven photocatalytic systems.

Keywords: Tungsten oxide (WO₃), Spin coating, Thin-film photocatalyst, Nanostructured materials, Photocatalysis, Organic dye degradation, Visible-light photocatalysis, Wastewater treatment, Semiconductor photocatalysts, Environmental remediation.

1. Introduction

Water pollution is today considered one of the biggest environmental problems all over the world due to fast development of industry and cities, and increasing number of people. Synthetic organic dyes from textile, paper, leather, pharmaceutical, cosmetic, food-processing and printing industries represent persistent pollutants among other contaminants. Due to their large aromatic molecular structure, good chemical resistance, bad biodegradability, and potential harmfulness for ecosystems and humans, they present a danger for both aquatic ecosystems and human life [1]. According to estimates, there are more than 100,000 commercially available dyes produced all around the world. Each year alone, more than 7×10^5 tones of dyes are produced. It is estimated that up to 90% of them end up in waste-water during the dye-making process and dyeing processes [2, 3]. In addition, even if present in small amounts, dyes may block sunlight penetrating through aquatic

environment, diminish photosynthesis activity, increase the amount of chemical oxygen demand and biochemical oxygen demand, and also generate mutagenic, teratogenic and carcinogenic compounds in the same way producing a threat to ecosystem and human health. To eliminate dyes from wastewater several traditional removal technologies have been used, including adsorption, coagulation-flocculation, membrane filtration, ion exchange, biological treatments, ozonations and chemical oxidation. While each technology may be efficient for its own purposes under certain conditions, they all suffer from significant disadvantages. Those include inadequate mineralization; elevated operational expenses; creation of secondary sewage sludges; clogging of membranes; and inefficiency to degrade resistant organics [3-6]. For this reason, advanced oxidation processes have gained much interest as a new method to remove organic pollutants from wastewater sustainably because they allow the full mineralization of organic pollutants into harmless substances

like CO₂, H₂O and inorganic ions when illuminated by light [8]. The basic principle behind photocatalysis is the ability of semiconductors to generate electrons-holes by illuminating the material using wavelengths smaller than the bandgap of the semiconductor. Once generated, the electron-hole pair migrates toward the surface of the semiconductor where it participates in redox reaction. The result of this process is the formation of ROS which include •OH radicals, •O₂⁻ radicals, singlet oxygen, and H₂O₂. The ROS then effectively degrades complex organic pollutants [5, 9]. During last two decades considerable research efforts have been made to develop semiconductor-based photocatalytic materials. Some examples of those are TiO₂, ZnO, WO₃, SnO₂, Fe₂O₃, BiVO₄ and g-C₃N₄. Nevertheless, many of those materials show some drawbacks regarding the too large band gap energy, too little use of visible light, rapid decay of charge carriers and too short lifetime [10].

There are many types of semiconductors that react to light in the visible spectrum; among them, Tungsten Trioxide (WO₃), as a photocatalyst due to its relatively small energy band gap and excellent chemical-thermal stabilities under acidic and oxidizing conditions, as well as being naturally abundant, low toxic, and exhibiting beneficial photoelectrochemical properties [11]. Unlike titanium dioxide, which absorbs mostly UV light, only 5% of the total solar spectrum, WO₃ effectively uses visible light down to around 480 nm, thus especially useful for solar powered environmental remediation [12]. Furthermore, WO₃ shows high quality electrochromic, photochromic, gasochromic, and catalytic properties that provide potential use outside of photocatalysis to include smart windows, gas sensors, photoelectrochemical water splitting, lithium ion battery and electrochemical devices [13 – 14]. WO₃ is an n-type transition-metal oxide semiconductor that exists in multiple crystallographic forms including monoclinic, triclinic, orthorhombic, tetragonal, hexagonal, and cubic. Its crystal structure, degree of crystallinity, shape/morphology, O vacancy density, exposure of facets and surface chemistry all significantly affect how WO₃ absorbs light optically, transports charges and performs as a photocatalyst [5, 15].

A few reviews have covered WO₃-based photocatalysts but most of those reviews addressed either all photocatalytic

materials broadly speaking, powder catalysts or broadly-speaking environmental applications rather than reviewing spin-coated nanostructure WO₃ thin film photocatalysts specifically addressing their structural-property relations in dye-degradation. Moreover, this review aims to evaluate the role that process-related parameters play in determining the photodegradation performance of WO₃ thin films and discuss recent approaches to modify the photocatalytic properties of WO₃ thin films including doping and defect engineering in addition to creating hetero-junctions. The last part of this review outlines the existing major obstacles to developing stable-durable-scalable-solar driven photocatalysts for water treatment that could meet the needs of sustainable technologies [11, 16].

2. Fundamentals of Tungsten Oxide (WO₃) Photocatalysts

2.1. Crystal Structure and Phase Transition of WO₃

Tungsten Trioxide (WO₃) is an n- type semiconducting material known for having excellent chemical durability, strong light absorbing ability within the visible region, and possessing many useful physical/chemical characteristics. As such, WO₃ has been identified as a very promising photocatalytic material for use in environmental cleanup processes and photo-electrochemical systems [17]. The primary factors affecting how well WO₃ performs as a photocatalyst are the structure of the crystals present, the extent of crystallization, the shape/morphology of the crystals, and the amount of defects present. Crystallographically, WO₃ is comprised of corner sharing WO₆-octahedral units which form a distorted ReO₃ type perovskite framework. WO₃ can exist in a variety of polymorphic forms depending upon the reaction temperature and other synthesis parameters. There have been reports of six different polymorphic forms of WO₃; monoclinic, triclinic, orthorhombic, tetragonal, hexagonal and cubic. Although moderate levels of oxygen deficiency will typically enhance photocatalytic activity via improved light absorbency, extremely high vacancy densities may result in decreased activity from promoting recombination sites for charge carriers. Therefore, maintaining strict control over vacancy density is critical to balancing light harvesting and charge carrier transport [18].

Table 1: Crystal phases, structural characteristics, and photocatalytic significance of WO₃ polymorphs.

Crystal Phase	Crystal System	Stability	Characteristics	Photocatalytic Significance	Reference
Triclinic (δ-WO ₃)	Triclinic	Low temperature	Distorted crystal lattice	Limited photocatalytic application	[2, 3]
Monoclinic (γ-WO ₃)	Monoclinic	Stable at room temperature	Thermodynamically stable and highly crystalline	Excellent visible-light photocatalytic activity	[2, 3]
Orthorhombic (β-WO ₃)	Orthorhombic	Intermediate temperature	Transitional crystal phase	Moderate photocatalytic performance	[3, 4]
Tetragonal (α-WO ₃)	Tetragonal	High temperature	High crystal symmetry	Improved charge transport at elevated temperatures	[3, 17]
Cubic WO ₃	Cubic	Very high temperature	Highly symmetrical crystal structure	Limited ambient stability	[2, 4]
Hexagonal WO ₃	Hexagonal	Metastable	Tunnel-like open framework with large channels	High surface area and enhanced adsorption capability	[2, 17]

Table 1 lists the various polymorphic forms of WO₃ along with their structural attributes, thermal stability, and catalytic properties related to photocatalysis. Monoclinic WO₃ is the most thermally stable form of WO₃ at room temperature and has been extensively used in many different types of visible light photocatalytic applications. WO₃'s phase (crystal) and

morphological structures are greatly affected by both synthesis procedures and heat treatments. Sol-gel processing, spin coating, hydrothermal synthesis and sputtering have all proven useful in controlling the degree of crystallinity as well as nano-structure of a material [40].

2.2. Electronic Structure and Optical Properties of WO₃

The photocatalytic performance of WO₃ is primarily determined by its electronic structure. Since it acts like an n-type semiconductor with a band gap of approximately 2.4 – 2.8 eV, WO₃ can absorb visible light at wavelengths up to approximately 480 nm [11, 17, 19] and thus be used more efficiently for solar energy harvesting. In the valence band of WO₃, orbitals predominantly composed of o 2p are present. The conduction band of WO₃ is predominantly comprised of W 5d orbitals. When irradiated using visible-light, electrons from the valence band are promoted into the conduction band. Upon promotion of these electrons, electron-hole pairs are formed which drive oxidation-reduction reactions involving photocatalysis [20]. Additionally, sub-stoichiometric states of WO₃ that include oxygen vacancies further modify this band structure by introducing defect levels below the minimum energy level within the conduction band. This facilitates lower-energy excitations. In comparison to traditional photocatalysts such as TiO₂, the narrower band-gap of WO₃ allows it to utilize visible light more effectively. Therefore, the use of WO₃ offers enhanced solar-energy harvesting capabilities and improved photocatalytic activity under natural sunlight. However, due to the relatively positive potential of the conduction-band of WO₃, the reduction capability of WO₃ is limited. Additionally, rapid recombination between the photo-generated electron hole-pairs decreases quantum efficiency. To overcome these limitations, several modification strategies including elemental doping, engineering of oxygen-vacancy concentration, construction of heterojunctions, and deposition of plasmonic metals have been developed to enhance charge carrier separation and extend the range of visible light absorption [11, 21].

2.3. Photocatalytic Mechanism of WO₃

Photocatalysis in tungsten trioxide (WO₃) results from the potential of absorbing visible light and creating an electron hole pair that participates in redox reactions. Due to a relatively small bandgap, WO₃ has the capability of utilizing the majority of the visible light spectrum; therefore, it may be utilized as a promising photocatalyst for environmental remediation [13, 22]. When exposed to photons having an energy greater than or equal to the band gap energy of WO₃, electrons are transferred from the valence band to the conduction band and positive holes remain in the valence band. As a result, the photo-generated electrons and holes travel to the surface of the photocatalyst. At the surface, these photo-generated species interact with adsorbed oxygen and water molecules. Holes within the valence band oxidize water molecules or hydroxide ions to create highly oxidative hydroxyl radical species while electrons within the conduction band reduce dissolved oxygen to form superoxide radical species. Both types of reactive oxygen species are capable of reacting with large molecular weight organic dyes; first breaking down these complex molecules into smaller intermediate products, then eventually mineralizing these products into carbon dioxide, water, and other inorganic ions [23]. As shown in fig 1, when a WO₃ material is exposed to visible light it causes electrons to be transferred from the valence band to the conduction band of the material creating "electron-hole" pairs that allow for the generation of reactive oxygen species. The reactive oxygen species then react with the organic dyes and oxidatively degrade them by converting the dyes into CO₂, H₂O, and inorganic ions. Therefore, WO₃ is an attractive choice as a photocatalyst for the degradation of organic dyes and treatment of wastewater due to its ability to operate under visible light, its chemical stability and its ability to produce reactive oxygen species [24].

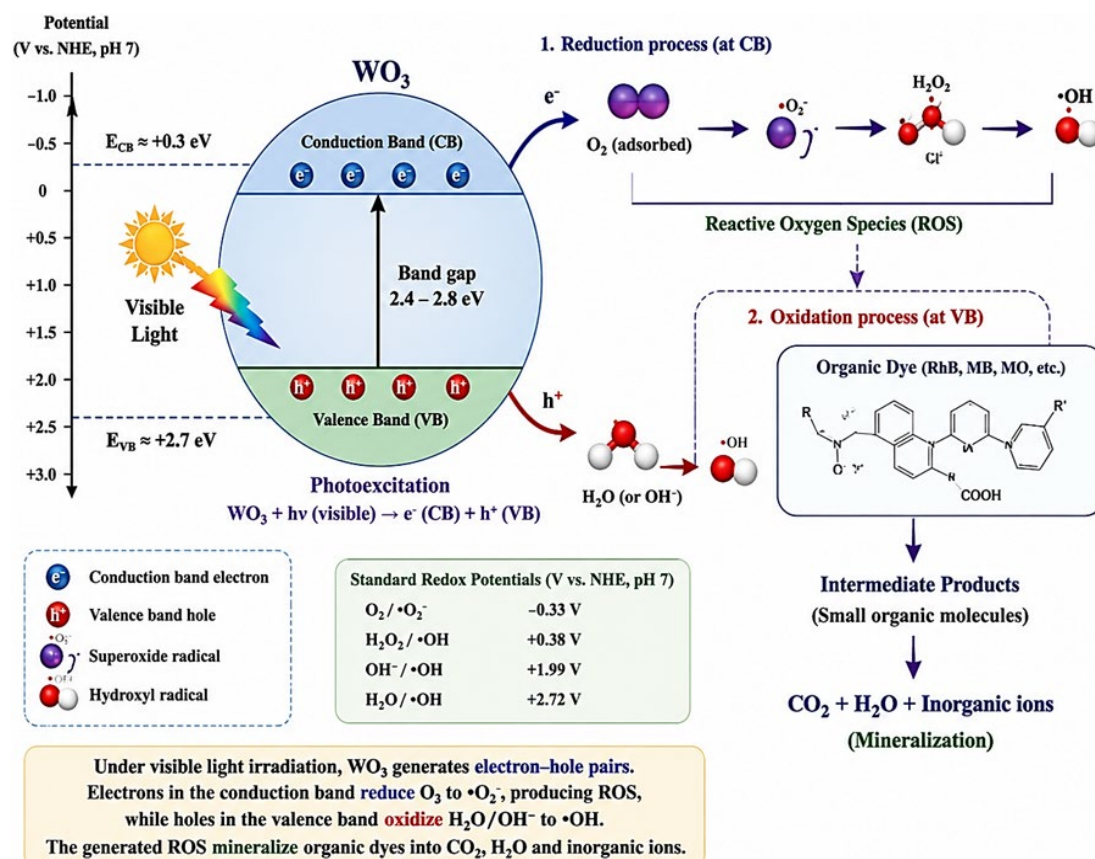


Fig 1: Energy band structure and visible-light photocatalytic mechanism of WO₃ showing electron-hole pair generation, reactive oxygen species (ROS) formation, and degradation of organic dyes under visible-light irradiation.

2.4. Advantages and Limitations of WO₃ Photocatalysts

Tungsten trioxide (WO₃) has been viewed as one of the most prominent candidates among visible-light responsive semiconductor photocatalysts due to the advantageous properties of this compound. The band gap of WO₃ is relatively narrower than other common photocatalysts like ZnO and TiO₂. This means that WO₃ will absorb much of the sun's light in the visible spectrum. In turn, the amount of sunlight absorbed allows for a much better use of solar radiation. Additionally, WO₃ has demonstrated high chemical stability and thermal stability. It possesses good resistance to corrosion from photoinduced reactions in acidic environments. Because WO₃ is non-toxic and mechanically stable, it has great potential for continuous use over many years in environmental remediation. As well, fabricating thin-film forms of WO₃ facilitates easy separation of the film after completion of the reaction. Thus, problems inherent in recovering catalyst particles from powdered photocatalysts are eliminated [25]. Nanoengineering of WO₃, defect manipulation, doped elements into WO₃, and heterophotocatalyst formation may all contribute to improvements in the photocatalytic performance of WO₃. For example, thin films of nanostructured WO₃ have increased surface area per unit volume, more active sites for reaction and reduced path lengths for charge carriers to diffuse before being captured. These factors enhance the rate at which organic pollutants degrade. Also, manipulating the oxygen vacancies within WO₃ or combining WO₃ with another semiconductor material that provides charge separation can reduce electron-hole pair recombination and increase activity toward photocatalysis under visible light illumination [18].

2.5. Comparison of WO₃ with Other Semiconductor Photocatalysts

Semiconductor photocatalysts including TiO₂, ZnO, BiVO₄, Fe₂O₃, and graphitic carbon nitride (g-C₃N₄) have been studied extensively for the degradation of organic contaminants. WO₃ has garnered significant attention due to its ability to absorb visible light through its narrow band gap enabling it to utilize more of the sun's energy compared to TiO₂ and ZnO. Both TiO₂ and ZnO are limited in their ability to use sunlight for photocatalysis due to large band gaps limiting them primarily to ultraviolet radiation. Additionally, WO₃ demonstrates excellent chemical durability and low toxicity along with stable operation under acidic conditions making it a viable candidate for water purification [17]. While

TiO₂ continues to serve as a benchmark photocatalyst due to its high stability and high oxidative power, the material suffers from a wide band gap which limits its ability to utilize visible light. Although ZnO displays similar levels of photocatalytic activity when compared to TiO₂, ZnO suffers from photo-corrosion which greatly diminishes its long-term stability. BiVO₄ and Fe₂O₃ display good visible light absorption capabilities, yet suffer from poor carrier transport and high rates of e-h pair recombination resulting in less than optimal application for most practical uses. Similar to BiVO₄ and Fe₂O₃, g-C₃N₄ is also a metal-free semiconductor with acceptable visible light sensitivity, but typically exhibits lower specific surface areas and less efficient photocatalysis compared to single phase semiconductors [26].

3. Section 3: Fabrication of Nanostructured WO₃ Thin Films

3.1. Spin-Coating Technique

Spin Coating has been one of the most common means of preparing uniform, quality Tungsten Trioxide (WO₃) thin films due to its relatively simple nature, and because the method allows for control over both film thickness and surface morphology. The technique lends itself well to the preparation of nano-structured photocatalytic films on surfaces such as; glass, quartz, silicon and fluorine doped tin oxide and is therefore very useful in applications involving photo-electrochemical reactions and environmental remediation [27]. The general procedure for spin coating involves placing a solution containing tungsten salt or alkoxide precursors onto a clean substrate that is then subjected to high-speed rotation. During this time centrifugal force distributes the solution evenly over the substrate. As the solution continues to dry through solvent evaporation during the continued rotation of the substrate, a thin layer of precursor material will have formed on the substrate. Following drying, the deposited film is heated in an oven to remove excess solvents from the precursor, to break down organic components within the precursor, and to promote crystallization of the WO₃. The final properties of the thin film are dependent upon numerous processing parameters such as precursor concentration, solution viscosity, speed of rotation, time of rotation, number of coats applied and heating conditions used for drying and thermal decomposition [12]. Figure 2 presents the fabrication sequence for WO₃ thin films, including precursor preparation, substrate cleaning, spin coating, drying, and annealing.

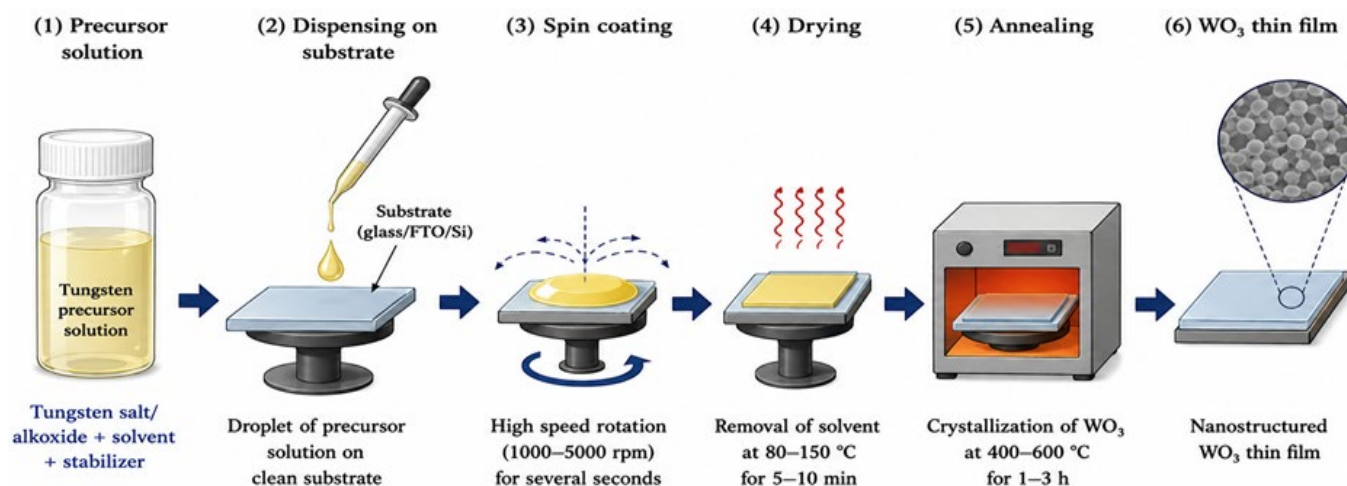


Fig 2: Schematic illustration of the spin-coating process for the fabrication of nanostructured WO₃ thin-film photocatalysts.

3.2. Effect of Spin-Coating Parameters on WO₃ Thin-Film Properties

When you create WO₃ thin films via spin-coating, your structural, optical, and photocatalytic characteristics will be affected by how you process them. Parameters such as the amount of precursors (e.g. tungsten oxide) per liter of water you use in your coating solution (the concentration), the rate at which you spin the coated substrate (spin speed), the number of times you coat the substrate (coating cycle(s)), and the temperature at which you heat it after coating (annealing temperature) all impact your final film thickness, crystal structure, topography, and the ability of the film to effectively degrade organic dyes when exposed to light. In terms of coating parameters, one of the most important factors in determining film thickness and uniformity is the spin speed. As a general rule, increasing your spin speed will produce thinner and more even films due to increased centrifugal

forces and faster solvent evaporation rates. Conversely, using slower spin speeds will tend to produce thicker coatings that could have surface irregularities or cracks. Solution viscosity is impacted by precursor concentration. Generally, higher precursor concentrations lead to thicker films with better light absorption. However, excessive film thickness can impede carrier movement and cause an increase in electron-hole recombination, thus decreasing photocatalytic activity [28]. The spin-coating process strongly influences the thickness, morphology, crystallinity, and photocatalytic performance of WO₃ thin films. As illustrated in Fig 3, spin speed, precursor concentration, coating cycles, and annealing temperature determine the final film characteristics. Proper optimization of these parameters produces uniform, well-adhered and highly crystalline WO₃ films with improved visible-light photocatalytic activity.

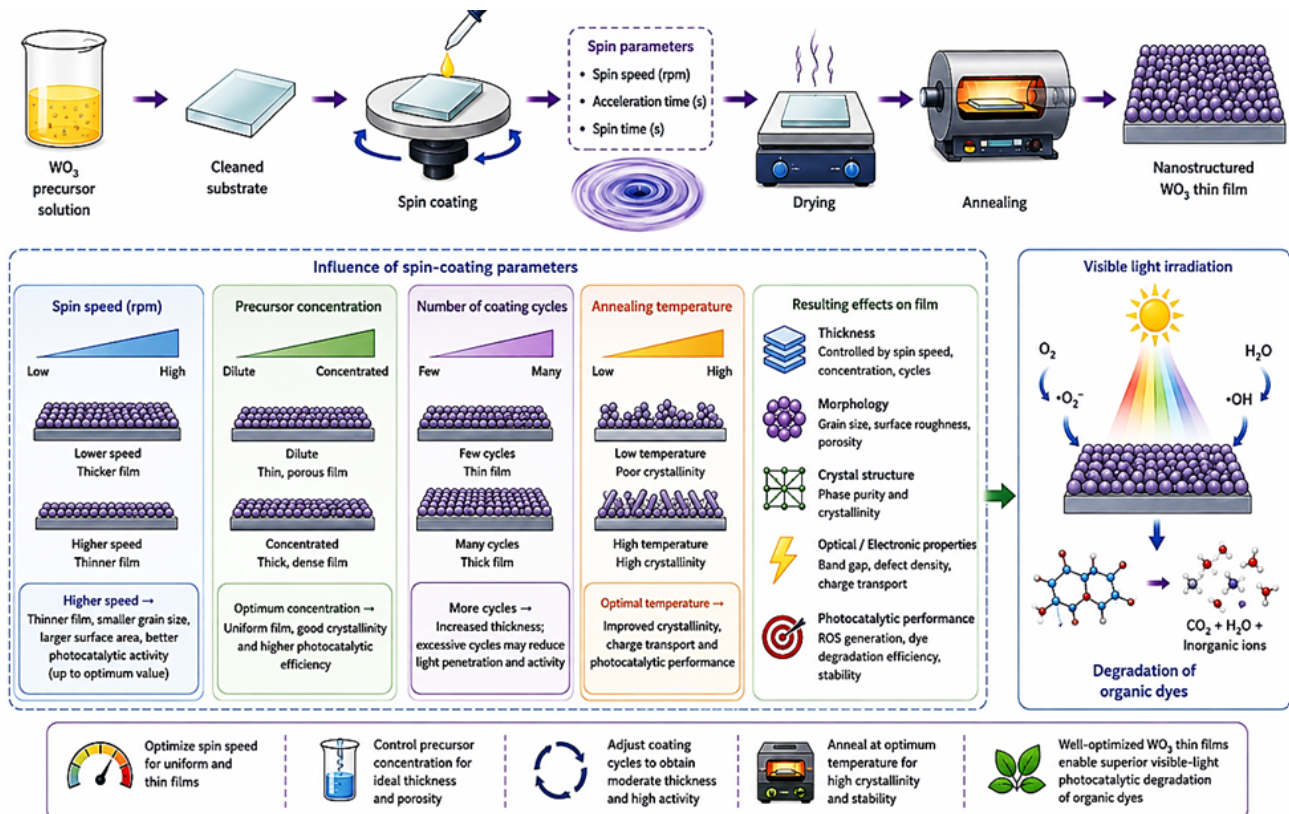


Fig 3: Schematic illustration of the spin-coating process and the influence of key processing parameters on the thickness, morphology, and photocatalytic performance of nanostructured WO₃ thin films.

3.3. Characterization of Spin-Coated WO₃ Thin Films

Comprehensive characterization of spin-coated WO₃ thin films is essential for developing an understanding of how process conditions effect structural features and photocatalytic performance. A variety of techniques are used to provide information on crystalline structure, morphology, chemical composition, optical properties and surface characteristics of these films. Atomic force microscopy provides fundamental insight into the surface roughness and topography at the nanoscale level. In addition to this it may be possible to identify physical defects that could impact charge transfer. X-ray diffraction is widely employed to determine the crystalline phase, estimate particle size and determine the degree of crystallinity. When heat-treated at appropriate temperatures, spin-coated WO₃ films generally exhibit monoclinic crystalline phase which is favorable for photocatalysis using visible light. Scanning electron microscopy and

atomic force microscopy provide information on surface morphology, particle distribution, grain size, film thickness and surface roughness. Transmission electron microscopy provides details on the nanostructure and lattice fringes of WO₃ particles. Furthermore, the FTIR analysis shows the presence of W-O and W-O-W bond vibrational modes and the Raman analysis will provide additional structural lattice vibration data to support further determination of the overall structure-property relationship in the spin coated WO₃ thin film samples. The combination of both the aforementioned analytical methods will allow us to achieve a full understanding of the relationships among structure, properties and efficiency for photocatalytic materials as applied to environmental remediation [29].

3.4. Nanostructure Engineering of WO₃ Thin Films

Nanostructure engineering is a method used to optimize the

photocatalytic performance of WO₃ thin films as well as to increase light absorption, increase the specific surface area, and separate charges generated during light exposure. As a result of varying synthesis routes and processing conditions, WO₃ has been formed into a wide range of nanostructures (nanoparticles; nanorods; nanowires; nanosheets; nanotubes; nanoflower; porous thin films) which allow for increased site availability for photocatalytic reaction processes and shorter distances for charge carrier diffusion resulting in reduced electron-hole recombination^[30]. Due to their one-dimensional structure, both nanorod and nanowire configurations provide efficient electron transport while nanosheet configurations provide larger surface areas than other configurations exposing more reactive surfaces toward pollutants for adsorption. In addition, porous WO₃ thin film configurations are capable of improving photocatalytic activity through improved reactant molecule diffusion and improved light harvesting via multiple internal reflections. Hierarchically structured nanoconfigurations that include two or more types of nanostructures have demonstrated the ability to improve photocatalytic activities by creating interconnective paths for charge transport and increasing visible light use.

4. Photocatalytic Degradation of Organic Dyes Using Spin-Coated WO₃ Thin Films

The growing number of dye-laden effluent discharges originating from textile and leather processing, as well as from paper manufacturing, pharmaceuticals and print production processes are necessitating the development of new treatment solutions that can efficiently remove harmful pollutants while being both economically viable and environmentally safe. Thin-film WO₃ spin coated on glass or other surfaces represent one of the most advanced forms of visible-light responsive photocatalysts presently available. In comparison to particulate photocatalysts, thin-films are also significantly easier to recover and reuse. Upon exposure to visible light (which represents approximately 45% of all sunlight) electrons will be produced within the WO₃ material through a process known as photo-excitation. These electrons then form an electron-hole pair; once formed, they will rapidly react with dissolved O₂ and H₂O to produce very reactive free radical species known as superoxides and hydroxyl radicals. These highly reactive species can break down large complex dye molecules into numerous intermediate products, which are typically eventually oxidized into CO₂, H₂O and inorganic salts^[31].

Table 2: Representative studies on WO₃ thin-film photocatalysts for the degradation of organic dyes.

WO ₃ Photocatalyst	Target Dye	Light Source	Key Finding	Reference
Spin-coated WO ₃ thin film	Rhodamine B (RhB)	Visible light	Efficient degradation due to high crystallinity and uniform film morphology	[19]
Nanostructured WO ₃ thin film	Methylene Blue (MB)	Simulated solar light	Enhanced photocatalytic activity through increased surface area	[32]
WO ₃ thin film	Methyl Orange (MO)	Visible light	Improved degradation efficiency with optimized film thickness	[19]
Oxygen vacancy-rich WO ₃	Congo Red (CR)	Visible light	Oxygen vacancies promoted charge separation and ROS generation	[33, 34]
WO ₃ heterojunction thin film	Crystal Violet (CV)	Visible light	Heterojunction formation significantly suppressed electron-hole recombination	[35, 36]
Doped WO ₃ thin film	Malachite Green (MG)	Solar light	Metal doping enhanced visible-light absorption and photocatalytic stability	[37, 38]

Table 2 is a selection of literature to illustrate how WO₃ thin film photocatalysts are used to degrade a wide variety of organic dyes. Overall results indicate that nanostructured design (the size and shape of the nanoparticles), defects within those nanoparticles, and creating heterojunctions all contribute to increased photocatalysis at wavelengths corresponding to "visible light". Recent research has even optimized WO₃ thin film photocatalysis by using dopants as well as forming heterojunctions and modifying defects. These methods improve the ability of charges to separate from one another, prevent electron-hole pairs from recombining, and increase production of ROS.

4.1. Factors Affecting Photocatalytic Degradation Efficiency

Photocatalytic degradation efficiency of WO₃ thin film (prepared using the spin coating technique) is largely influenced by numerous process parameters and properties of materials which are responsible for absorption of light, separating charges of carriers and generating reactive oxygen species. Film thickness is one of the key variables since the excessive thinness of the film may result in limited availability of catalytically active sites while over-thickness may prevent light from penetrating into the film and thus

increase recombination rate of electrons and holes. Therefore, there exists an optimal thickness of the film which allows maximum activity of photodegradation. In addition to the film thickness solution pH affects the photocatalytic activity by changing surface charge density of WO₃ and degree of ionization of dye molecule which in turn influences its adsorption and further degradation. Nature and intensity of light used for activation also significantly affect photocatalytic activity. As WO₃ is visible-light responsive semiconductor, light sources emitting visible light (or simulating solar irradiance) are generally better suited to activate WO₃ than UV radiation alone. Additionally, crystallinity, oxygen vacancy concentration, and structural characteristics of nanostructure of WO₃ thin films substantially determine separation of charge carriers and reactive oxygen species production. Therefore, nanostructured WO₃ thin films having optimized defect structures allow to achieve greater visible light absorption and enhanced kinetic constants of degradation. Optimization of above-mentioned reaction parameters is crucial to achieve maximum photocatalytic activity of spin coated WO₃ thin films, and consequently enable their practical application in water treatment technologies^[39].

4.2. Recent Advances in WO₃ Thin-Film Photocatalyst for Organic Dye Degradation

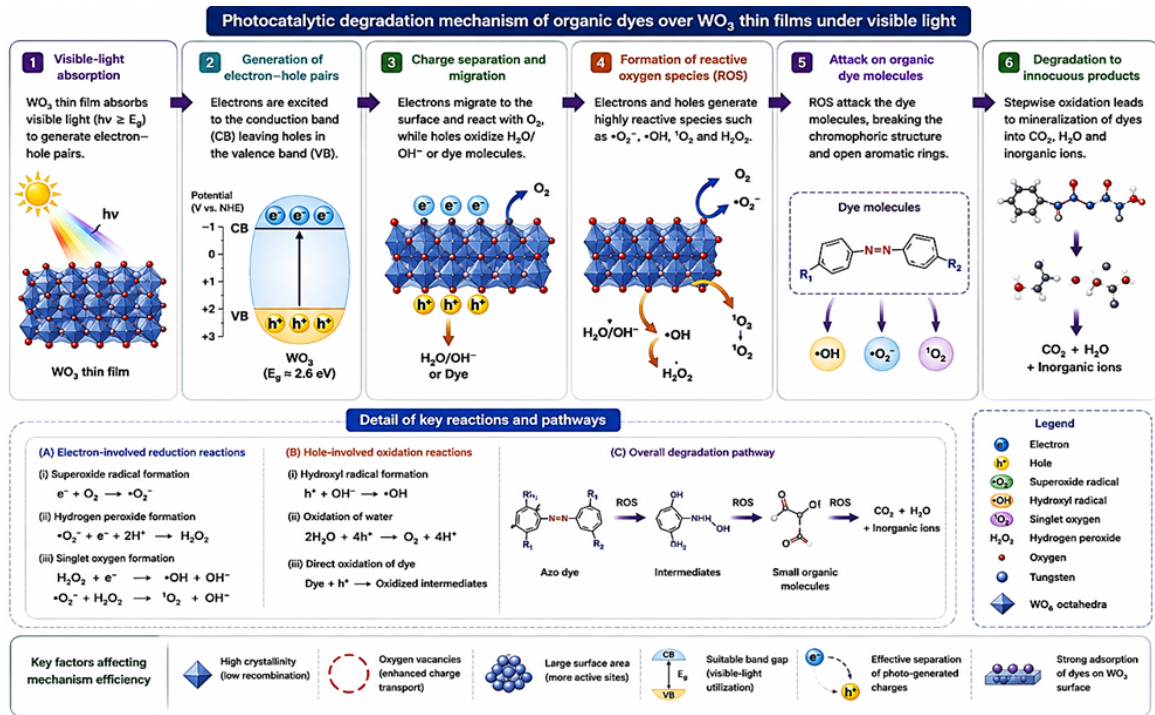


Fig 5: Photocatalytic degradation mechanism of organic dyes over WO₃ thin films under visible-light irradiation, showing charge generation, reactive oxygen species formation, and stepwise degradation of dye molecules.

Recent findings suggest that photo-catalytically active nano-structured thin film WO₃ (titanium dioxide) are stable and can be reused many times without significant loss of catalytic ability. Because these thin films are attached or "immobilized" on a surface, there is no need to remove and/or recycle loose particulate catalysts following treatment, which makes them more suited for use as continuous flow systems for water treatment than other types of powdered catalysts. Alongside this, developments in chemical precursors and optimized coating procedures have made it possible to produce films of titanium dioxide having excellent uniformity, crack free surfaces, higher crystalline structure,

good adhesion to the substrate and improved catalytic properties. Nevertheless, despite advancements, several additional challenges remain to increase the quantum efficiency, improve the long-term durability of the material's structure and develop methods to fabricate the materials at a larger scale. Therefore, future research will focus on developing multi-functional hetero-junctions, precisely engineered defects and solar driven photo-catalysis using titanium dioxide thin film photo-catalysts to enable their use in environmental remediation [20]. Table 3 represents an important comparison of key approaches used for enhancing photocatalysis of WO₃ thin film.

Table 3: Critical comparison of modification strategies for WO₃ thin-film photocatalysts.

Modification Strategy	Advantages	Major Limitations	Research Gap/Future Need	References
Pristine WO ₃	Good visible-light absorption, high chemical stability, reusable thin films	Rapid electron-hole recombination and low quantum efficiency	Improve charge separation without sacrificing stability	[40]
Metal-ion Doping (Ag, Fe, Cu, Mo, etc.)	Enhances visible-light absorption and charge transport	Dopant concentration must be optimized; excess dopants become recombination centers	Develop stable, low-cost dopants with long-term durability	[41]
Non-metal Doping (N, C, S, B)	Narrows band gap and improves solar-light utilization	Limited thermal stability and possible lattice distortion	Control dopant distribution and defect formation	[42]
Oxygen Vacancy Engineering	Increases active sites and promotes charge separation	Excess vacancies may decrease structural stability	Optimize vacancy concentration for maximum activity	[43]
Heterojunction Formation (WO ₃ /TiO ₂ , WO ₃ /g-C ₃ N ₄ , WO ₃ /BiVO ₄)	Efficient charge separation and broader light absorption	Complex synthesis and interfacial instability	Design robust Z-scheme and S-scheme heterojunctions	[44]
Plasmonic Metal Decoration (Ag, Au)	Localized surface plasmon resonance enhances visible-light harvesting	High material cost and possible nanoparticle agglomeration	Develop low-cost plasmonic alternatives	[45]

5. Conclusion

The use of spin coated nano-structured thin film of WO₃ has been widely studied as an efficient material for the

photodegradation of organic dyes through its high light absorbency, low toxicity and good chemical stability. The spin coating method is one of the most commonly used

methods for producing uniform thin films of WO₃ due to it being relatively inexpensive, easy to scale up, and allows for controlling the film's thickness, structure and crystalline phase. The structural, optical and photocatalytic characteristics of WO₃ thin films are strongly dependent upon process conditions such as precursor concentration, spin speed, number of coatings and heat treatment temperature. The modification of nano structures, oxygen vacancies and dopant elements in addition to forming hetero-junctions are some recent approaches that improve photocatalytic performance of WO₃ thin films by enhancing the ability to absorb visible light and reduce the rate of electron-hole pair recombination. Using spin coated thin films, the photocatalytic activity of WO₃ can be utilized efficiently for the removal of a broad variety of organic dyes (methylene blue, rhodamine B, methyl orange, congo red) which demonstrate the applicability of WO₃ thin films for wastewater treatments. Additionally, immobilizing the thin films facilitates reusing them without needing additional steps to separate the catalyst from treated solution and enables scaling-up to integrate into continuous flow water treatment systems.

Although significant advancements have been made in utilizing WO₃ based materials for photocatalysis; there are still significant issues associated with recombining charges carriers during operation, stability over time and practicality for large scale implementations. Therefore, future work should be focused on developing multi-functional heterostructures composed of WO₃ and other materials; defect engineered thin films; and photo catalytic systems driven by sunlight with improved efficiencies and stabilities. Furthermore, investigating experimental data using simulations models combined with reactor scale experiments would expedite the transition from laboratory to practical application of WO₃ photocatalyst.

Credit authorship contribution statement

Prafulla S. Patil: Writing–Original draft, review & editing, Conceptualisation, Formal analysis and Data curation.

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Abbreviations

(Fe₂O₃) iron(III) oxide, (BiVO₄) bismuth vanadate, (g-C₃N₄) graphitic carbon nitride, (ROS) reactive oxygen species, (•OH) hydroxyl radical, (•O₂⁻) superoxide radical, (UV) ultraviolet, (Vis) visible, (NIR) near-infrared, (XRD) X-ray diffraction, (SEM) scanning electron microscopy, (TEM) transmission electron microscopy, (AFM) atomic force microscopy, (FTIR) Fourier-transform infrared spectroscopy, (UV–Vis) ultraviolet–visible spectroscopy, (PL) photoluminescence, (BET) Brunauer–Emmett–Teller, (PEC) photoelectrochemical, (AOPs) advanced oxidation processes, (COD) chemical oxygen demand, (BOD) biochemical oxygen demand, (MB) methylene blue, (RhB) rhodamine B, (CR) Congo red, (CV) crystal violet, (LSPR) localized surface plasmon resonance, (PVD) physical vapor deposition, (PLD) pulsed laser deposition, (CVD) chemical vapor deposition,

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