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Recent Advances in Sol–Gel Dip-Coated TiO_2 Thin Films: Defect-Mediated Photoluminescence and Photocatalytic Performance

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Abstract Titanium dioxide (TiO_2) thin films are widely explored for optical and photocatalytic applications due to their stability, non-toxicity, and tunable electronic structure. This review clearly explains a complete analysis of recent advances in sol–gel dip-coated TiO_2 thin films, with special focus on defect-mediated photoluminescence (PL) and its interrelationship with photocatalytic performance. The sol–gel dip-coating technique allow good/specific control over film thickness, crystal structure, and defect density, which collectively control charge-carrier recombination dynamics and surface reactivity. Rather than a coincidental observation, a principal outcome of this review is the identification of the inverse PL–photocatalysis relationship as a practical materials design principle. Key challenges, unresolved issues, and future research directions for rational defect and interface engineering are discussed, and also highlighting pathways how to better control toward optimized TiO_2 thin films for environmental remediation and optoelectronic applications. This review explains annealing-temperature effects, film thickness control, atmospheric processing, and dopant-induced defect modulation, and how these factors are important for environmental remediation and optoelectronic device integration.

Keywords
Titanium dioxide (TiO_2); Sol–gel dip-coated thin films; Photoluminescence (PL); Defect engineering; Charge-carrier recombination; Photocatalysis; Electronic and optoelectronic applications.

I. INTRODUCTION

Titanium dioxide (TiO_2) remains a cornerstone semiconductor for photocatalysis and optoelectronic applications due to its natural abundance, chemical stability, and favourable band-edge positions. In thin-film form, TiO_2 provides several advantages over powders, including mechanical robustness, reusability, and better compatibility with device fabrication. However, its functional performance of TiO_2 is highly sensitive to fabrication parameters and defect chemistry.

Among different deposition techniques, the sol–gel dip-coating method is distinguished for its simplicity, low cost, and large-scale production. More importantly, this approach allows controlled tuning of defect states that regulate both photoluminescence (PL) emission and photocatalytic activity. Despite significant prior research, many studies treat PL as a qualitative characterization tool rather than a descriptor of recombination dynamics. This review clearly connects sol–gel processing parameters, defect-induced PL behaviour, and photocatalytic performance, establishing the inverse PL–photocatalysis relationship as a rational materials design principle rather than a descriptive observation. This review is based on peer-reviewed journal articles published mainly between 2010 and 2025, which retrieved from databases such as Scopus, Web of Science, and ScienceDirect using keywords including ‘sol–gel dip-coated TiO_2 thin films’, ‘photoluminescence’, ‘defect states’, and ‘photocatalysis’. Priority was given to studies reporting both photoluminescence and photocatalytic performance to enable correlation analysis.

Accordingly, this review is structured with primary emphasis on the electronic and defect-related origins of photoluminescence in sol–gel dip-coated TiO_2 thin films. Photocatalytic activity is intentionally treated as a secondary outcome, discussed only insofar as it reflects underlying charge-carrier recombination dynamics rather than application-driven performance metrics.

II. SOL-GEL DIP-COATING: KEY PROCESSING CONSIDERATIONS

Sol–gel dip coating offers a versatile and scalable route for fabricating uniform TiO_2 thin films with **tunable defect chemistry**, and subtle variations in precursor formulation and processing parameters critically influence the resulting **optoelectronic and photocatalytic properties**. Rather than reiterating textbook-level reaction chemistry, this section focuses on the **processing–structure–property relationships** that are central to defect engineering in sol–gel-derived TiO_2 films.

Sol–gel dip coating is a flexible and scalable method for preparing uniform TiO_2 thin films, where even small changes in precursor composition or processing conditions can noticeably affect defect formation and, in turn, the optoelectronic and photocatalytic behaviour. Rather than repeating standard reaction chemistry, this section highlights how processing conditions shape the film structure and properties, which is crucial for defect engineering in sol–gel-derived TiO_2 thin films. In a typical sol–gel process, titanium alkoxide precursors undergo controlled hydrolysis and condensation to build up a polymeric Ti–O–Ti network. Chelating agents are often added to slow the hydrolysis process and keep the sol stable. This helps avoid early-stage precipitation and produce crack-free and compositionally uniform films. During the dip-coating process, the final thickness and uniformity of the deposited film are mostly controlled by the substrate withdrawal speed, because it controls the balance between viscous drag and solvent evaporation at the coating surface. Subsequent thermal annealing then promotes further densification of the film and drives its crystallization.

Importantly, the combined effects of sol composition, withdrawal speed, and annealing temperature determine not only the crystallinity and grain size of the TiO_2 films along with the density and spatial distribution of defect states, such as oxygen vacancies and Ti^{3+} centers. These sub-bandgap states exhibit a dual role: they can act as non-radiative recombination centers that suppress photoluminescence (PL) emission, or as charge-trapping sites which helps to sustain the carrier lifetime and facilitate interfacial redox reactions under photo excitation. As a result, variations in defect density directly influence the observed PL intensity and photocatalytic reaction kinetics."

Therefore, careful control of the annealing conditions is essential to achieve a balance between enhanced crystallinity and controlled defect concentration. Insufficient thermal treatment, the films may lead to poor crystallinity and excessive structural disorder. Whereas overly aggressive annealing temperature can reduce defect density or induce undesirable phase transformations, which can ultimately diminish photocatalytic performance. Together, these linked relationships between processing conditions, film structure, defect states, and activity provide the basis for correlating PL behavior with photocatalytic efficiency in sol–gel dip-coated TiO_2 thin films.

Figure 1: Schematic of the sol–gel dip-coating process, defect formation, and resulting functional properties of TiO_2 thin films.

Fig. 1 presents a schematic overview of the sol–gel dip-coating process, showing sol preparation, substrate dipping and withdrawal, gel formation, drying, and annealing. The figure also indicates how changes in processing parameters affect the film thickness, crystal structure, defect density, and associated photoluminescence and photocatalytic behaviour of the films. (Original schematic by the authors)

III. STRUCTURAL AND MORPHOLOGICAL CHARACTERISTICS

Sol–gel dip-coated TiO_2 thin films are typically amorphous in the as-deposited state and transform into the anatase phase after annealing in the range of 350–450 °C. Increasing the annealing temperature improves crystallinity but simultaneously it also reduces the concentration of structural defects. At excessively high temperatures (>600 °C), partial conversion to the rutile phase may occur. Therefore, choosing an appropriate annealing temperature is important to achieve an optimal balance between good crystallinity and defect-related activity.

Surface morphology with factors such as withdrawal speed, number of coating cycles, and thermal treatment. Moderately rough, nanocrystalline surface is usually beneficial for enhanced active surface area and light scattering, whereas surface becomes excessively rough introduce recombination-prone grain boundaries. ***Morphological optimization is*** is essential ***to charge-carrier utilization efficiency.***

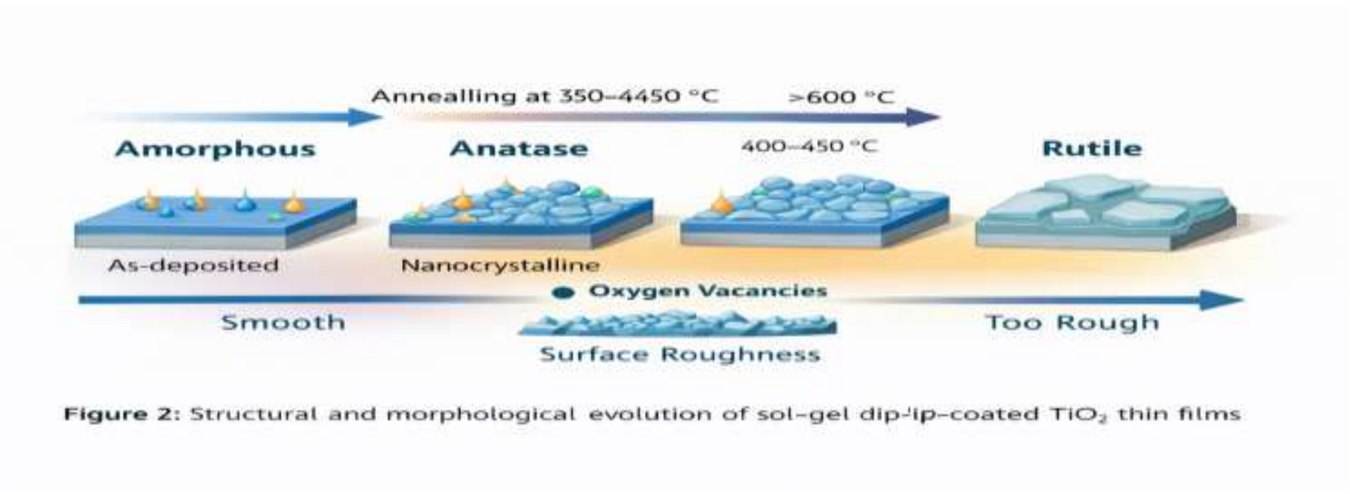


Fig. 2 Representative surface morphology and cross-sectional view of sol–gel dip-coated TiO_2 thin films annealed at different temperatures and also showing the evolution of grain size and roughness with thermal treatment. (Original schematic created by authors)

Table I, Summary of the effects of annealing temperature on phase evolution, grain size, defect density, photoluminescence (PL), and photocatalytic performance of sol–gel dip-coated TiO_2 thin films.

Annealing Temperature (°C)	Phase	Grain Size	Defect Density	PL Emission	Photo catalytic Performance
As-deposited	Amorphous	<10 nm	High	Strong visible PL	Low activity
350–450	Anatase	10–25 nm	Moderate	Moderate PL	Optimal activity
450–600	Anatase/ Rutile mix	20–50 nm	Low to moderate	Weak PL	Moderate activity
>600	Rutile	>50 nm	Low	Very weak PL	Reduced activity

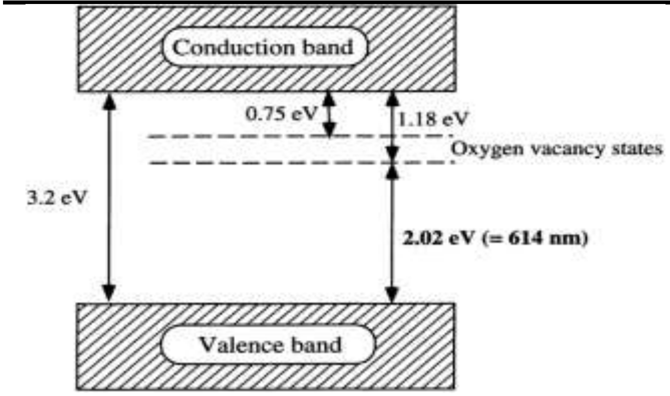
As summarized in Table I, annealing temperature significantly influences on structural, optical, and photocatalytic properties of sol–gel dip-coated TiO_2 thin films. Moderate annealing temperature (350–450 °C) yields anatase phase flim with optimal defect concentration, balancing crystallinity and surface reactivity. At higher temperatures, reduce defect-related recombination but it may trigger rutile phase formation. This phase typically exhibits lower photocatalytic activity under UV irradiation.

IV. PHOTOLUMINESCENCE PROPERTIES AND DEFECT STATES

In TiO_2 thin films photoluminescence (PL) emission originates from near-band-edge (NBE) excitonic recombination typically observed in the ultraviolet region (~380 nm), and from defect-related radiative transitions in the visible region (450–550 nm). Oxygen vacancies and Ti^{3+} ions are the primary intrinsic defects responsible for blue–green emission and these defects serve as dominant carrier recombination centres. As a result, films with high defect density exhibit strong visible PL intensity but reduced charge-carrier lifetimes.

Annealing temperature and processing atmosphere strongly influence the PL intensity and spectrum of TiO_2 thin films. Lower annealing temperatures or oxygen-deficient environments promote oxygen vacancies and also enhancing visible PL emission. In contrast, higher annealing temperatures improve crystal quality and reduce defect density, which resulting in PL quenching. . Time-resolved PL studies in the literature reported which further confirm that suppressed PL intensity corresponds to longer charge-carrier lifetimes and reduced recombination losses.

Dopant incorporation (metal or non-metal) creates extra defect states within the band gap, which changes PL behaviour by introducing new radiative pathways or by facilitating non-radiative recombination. However, excessive dopant concentration often causes concentration quenching due to increased defect clustering and enhanced non-radiative decay channels. The general trend of decreasing PL intensity with increasing annealing temperature, arising from defect annihilation and improved crystallinity. This trend is schematically illustrated in Fig. 3 & Fig. 4



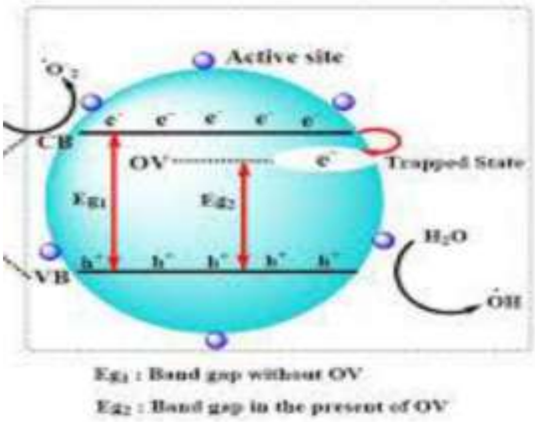


Fig. 3 and Fig. 4 Schematic band diagram of TiO_2 showing sub-bandgap defect states (oxygen vacancies and Ti^{3+} centers) responsible for visible-range photoluminescence and charge trapping/recombination. (Adapted from RSC Advances, DOI:10.1039/C8RA05117H)

These diagrams (Fig. 3 and Fig. 4) show **band-gap defect levels and how oxygen vacancy states lie between the conduction band (CB) and valence band (VB)**

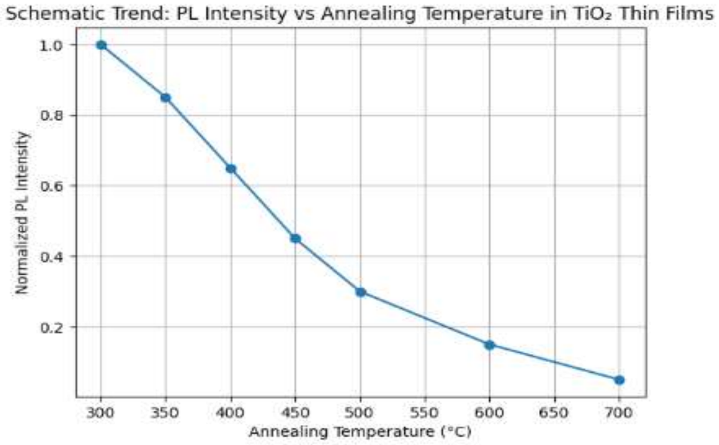
The band diagram clarifies that shallow oxygen vacancy states near the conduction band can temporarily trap photogenerated electrons, whereas deep-level Ti^{3+} states act as recombination centers. Radiative transitions from these defect states to the valence band are highly responsible for the observed

Table II Assignment of photoluminescence (PL) emission peaks to defect states in TiO_2 thin films and their implications for charge recombination behavior.

PL Peak Position (nm)	Emission Region	Defect / Transition Type	Physical Origin	Implication for Carrier Dynamics
~370–390	UV	Near-band-edge (NBE)	Excitonic recombination between conduction band (CB) and valence band (VB)	Indicates good crystallinity and low defect density
420–450	Violet–Blue	Shallow oxygen vacancies (V_O)	Radiative recombination via shallow donor levels near CB	Moderate recombination; may assist charge separation if controlled
450–480	Blue	Oxygen vacancies (V_O)	Electron recombination from V_O states to VB	Strong visible PL; shortened carrier lifetime
500–530	Green	Ti^{3+} centers	Deep trap states associated with Ti^{3+} ions	Dominant non-radiative losses; detrimental to photocatalysis
530–560	Green–Yellow	Surface defect states / hydroxyl-related defects	Surface-localized recombination pathways	Indicates high surface defect density
>560	Yellow–Red	Deep defect clusters / dopant-induced states	Defect clustering or excessive dopant concentration	Concentration quenching and reduced photocatalytic efficiency

Table II, Assignment of visible-range photoluminescence (PL) emission peaks in TiO_2 thin films to specific defect states. Shallow oxygen vacancies (420–480 nm) temporarily trap carriers, while deep Ti^{3+}-related states (500–530 nm) act as strong non-radiative recombination centers. The position and intensity of PL peaks provide indirect information of defect density and carrier recombination dynamics, which directly influence photocatalytic performance.

Fig. 5 Schematic representation of the dependence of photoluminescence (PL) intensity on annealing temperature in sol–gel dip-coated TiO_2 thin films. Increasing annealing temperatures improved crystallinity and reduces defect density, suppresses defect-mediated PL emission. (Original schematic by authors)



As shown in Fig. 5, PL intensity systematically decreases with increasing annealing temperature due to/ beacuase progressive annihilation of oxygen-vacancy-related defects. The strong PL quenching above ~450 °C indicates reduced radiative recombination and longer charge-carrier lifetimes, which benefit photocatalytic reactions.

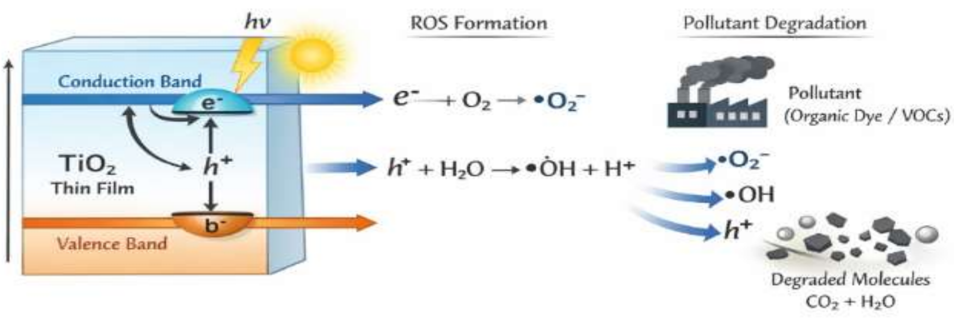
V. PHOTOCATALYTIC RESPONSE: A CONSEQUENCE OF ELECTRONIC CHARGE SEPARATION

While photocatalysis represents a technologically relevant application of TiO_2 thin films, it is discussed here primarily as a consequence of electronic charge separation and recombination behavior. The purpose of this section is not to provide a comprehensive treatment of photocatalytic chemistry, but rather to illustrate how defect-mediated electronic processes influence surface redox activity.

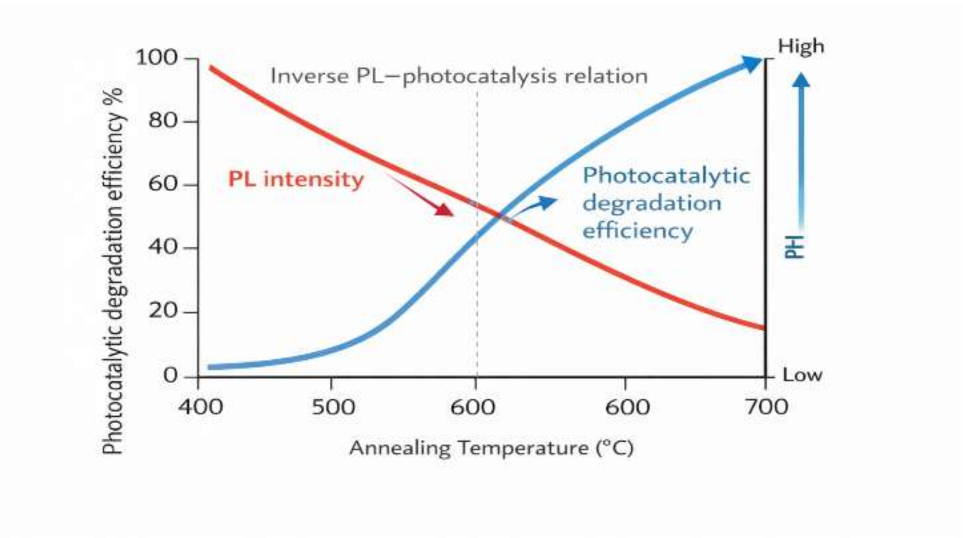
Photocatalytic activity in TiO_2 thin films starts with the generation of electron–hole pairs under light exposure. These electrons participate in surface redox reactions that produce reactive oxygen species (ROS), such as hydroxyl radicals (•OH), superoxide radicals ($•O_2^-$), and photogenerated holes (h^+). The overall photocatalytic efficiency is mainly controlled by capability of light absorption, charge separation efficiency, and suppression of electron–hole recombination.

Photocatalytic performance is commonly evaluated through the degradation of model organic pollutants, such as methylene blue and rhodamine B, under UV or visible-light illumination. The apparent first-order reaction rate constant (k) is generally used to compare photocatalytic efficiencies of different thin-film systems indicating how quickly the pollutant is broken down.

Defect engineering, controlled doping, and heterojunction formation are common strategies to enhance photocatalytic activity. While surface defects can help by providing reactive adsorption sites, but excessive defect density promotes carrier recombination. Heterojunctions and conductive additives facilitate/ improve interfacial charge transfer and charge separation, which often accompanied by photoluminescence (PL) quenching. This lower PL emission serves as an indirect indicator of reduced radiative recombination and enhanced photocatalytic performance.



Schematic illustration of the photocatalytic mechanism in TiO_2 thin films showing charge generation, reactive oxygen species formation, and pollutant degradation.



VI. CORRELATION BETWEEN PHOTOLUMINESCE AND PHOTOCATALYSIS: A DEFECT-RECOMBINATION-ACTIVITY FRAMEWORK

In this context, photocatalytic reaction rates should be interpreted not as independent performance metrics, but as functional indicators of recombination kinetics and charge-carrier lifetime within the TiO_2 thin films.
A consistent inverse correlation between photoluminescence (PL) intensity and photocatalytic performance has been observed in sol–gel dip-coated TiO_2 thin films. To explain this relationship beyond phenomenological observation, a simple three-step defect–recombination–activity framework is proposed, that connect processing conditions to defect formation, charge-carrier dynamics and photocatalytic efficiency. This inverse relationship is schematically summarized in Fig. 8

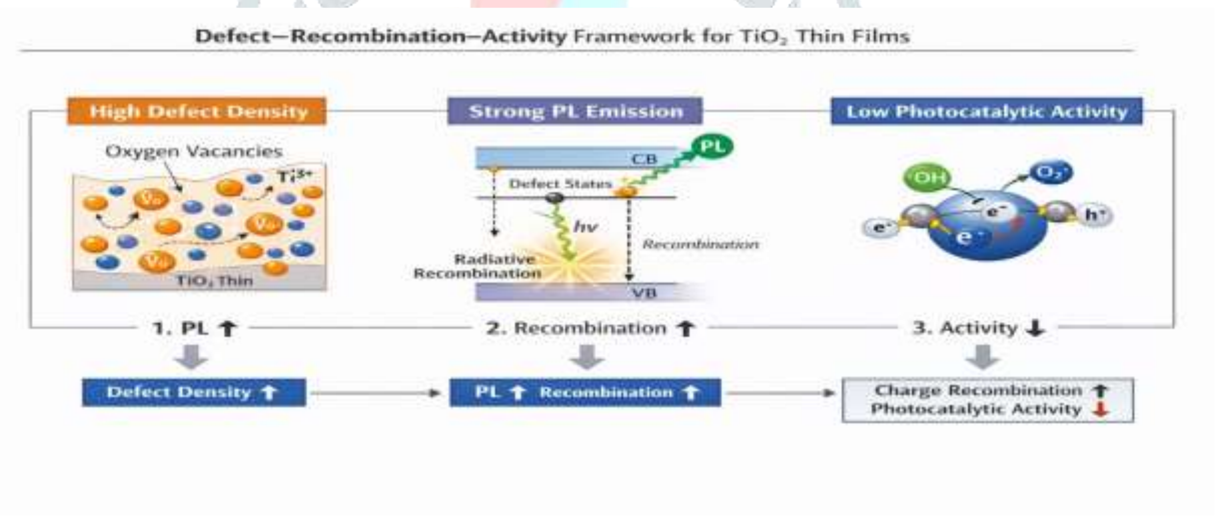


Fig. 8: Schematic shows how the defect–recombination–activity framework related in photoluminescence (PL) intensity with photocatalytic performance in sol–gel dip-coated TiO_2 thin films. Increasing the number of defect such as oxygen vacancies and Ti^{3+} defect-assisted radiative recombination becomes more prominent, resulting in stronger PL emission. However, a Strong PL intensity reflects accelerated charge recombination and shortened carrier lifetimes, thereby suppressing photocatalytic activity. On the other hand, proper optimization reduces PL emission, promotes efficiency of charge separation, and enhances photocatalytic performance. (Conceptual schematic, not to scale.) (Original schematic by authors)
Step 1: Increased Defect Density → Higher Photoluminescence Intensity ↑
Sol–gel processing parameters such as low annealing temperature, oxygen-deficient atmosphere, or too much dopant incorporation increase the concentration density of intrinsic defects, especially oxygen vacancies and Ti^{3+} centers. These defects create localized electronic states within the band gap, which act as sites where electrons and holes recombine and emit light. As a result, films with higher defect density show stronger visible photoluminescence, particularly in the blue–green spectral region. Therefore, strong PL emission is sign of indirect indicator of abundant defect-mediated radiative pathways. On the other hand, proper optimization reduces PL emission, promotes efficiency of charge separation, and enhances photocatalytic performance. (Conceptual schematic, not to scale.) (Original schematic by authors)
Step 2: Higher Photoluminescence Intensity → Faster Charge Recombination Rate

An increasing PL intensity shows an increased probability of electron–hole recombination through defect states. While radiative recombination produces PL emission, at the same time it also reduces the effective lifetime of photogenerated charge carriers.

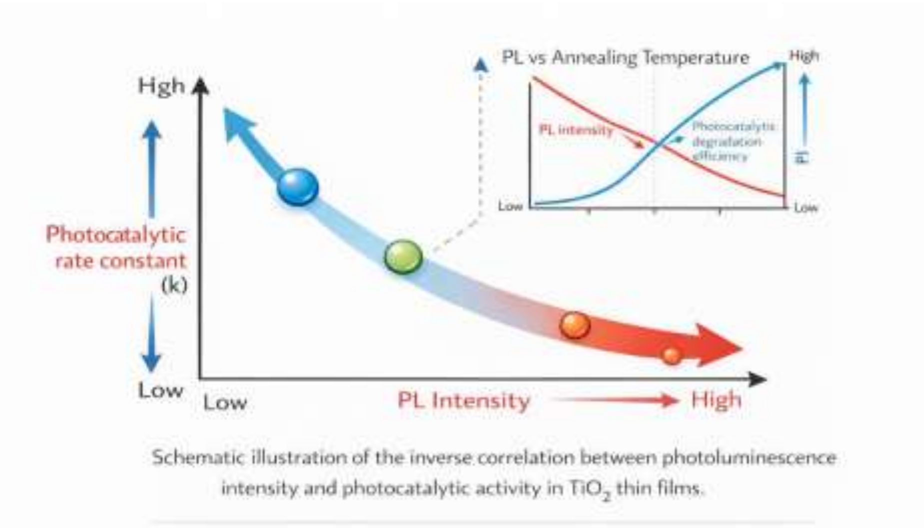
Time-resolved PL studies clearly show that reduced carrier lifetimes in high-PL films, clearly showing that intense PL emission is a sign of fast recombination processes rather than efficient charge separation.

Step 3: Charge Recombination Rate ↑ → Photocatalytic Activity ↓

Photocatalytic reactions depend on the availability of long-lived electrons and holes, these charges participate in surface redox processes and generate reactive oxygen species. For faster charge recombination lead to strong PL emission, reduces the number of charge carriers reaching the surface, which reduce the photocatalytic reaction rates. Due to optimized crystallinity and reduced deep defects, or effective interfacial charge transfer in TiO_2 thin films exhibiting quenched PL intensity. As a result, these films demonstrate superior photocatalytic performance.

This inverse relationship, schematically illustrated in the figure, demonstrates that PL quenching can provide a qualitative indicator of efficient charge separation and higher performing photocatalytic activity in TiO_2 thin films.

This three-step framework explains why stronger PL emission is typically associated with reduced photocatalytic activity. This clearly shows a direct cause-and-effect relationship, rather than a mere coincidence. However, the relationship is not absolute. A moderate concentration of shallow defect can trap charge carriers which help them move to the surface and actually improve photocatalysis without causing too much recombination. Therefore, the optical photocatalytic performance is achieved from carefully controlling defects engineering, which reducing PL but not completely eliminating it.



Schematic illustration of the inverse correlation between photoluminescence intensity and photocatalytic activity in TiO_2 thin films.

Fig. 9 (Original schematic by authors)

Table III, summarizes key enhancement strategies and their effects on PL and photocatalytic performance.

Strategy	Role	Effect on PL	Impact on Photocatalysis
Defect engineering	Adsorption sites	PL increase	Optimal at moderate defects
Doping	Band-gap tuning	PL modification	Enhanced visible response
Heterojunctions	Charge separation	PL quenching	Strong enhancement

Table III Summary of key enhancement strategies for TiO_2 thin films and their contrasting effects on photoluminescence (PL) and photocatalytic performance. Defect engineering and doping can initially increase PL intensity by introducing additional radiative pathways, In conform heterojunction formation typically reduce PL performance by enhancing charge separation. Optimal photocatalytic activity is achieved when PL is suppressed but not completely eliminated, showing that defect state not to be carefully controlled.

VII. CHALLENGE AND FUTURE PERSPECTIVES

Despite significant progress, several challenges still need to be addressed:

1. **Defect Control:** It is very to hard to Achieving reliable and controllable defect densities. Too many defects increase electron holes recombination, while insufficient of defects reduce surface reactivity.

2. **Long-Term Stability:** Sustained light exposure and environmental conditions can reduce in quality of film performance, so giving importance to the need for more stable and durable photocatalytic structures.

3. **Scalability:** To fabricate uniform, large-area TiO_2 thin films with well-controlled thickness and surface morphology remains challenging, which limits large-scale practical applications.

Future research should focus on the following directions:

1. **Operando PL studies:** To directly connect defect states with charge separation and recombination dynamics under real working conditions.

2. **Computational defect modelling:** To understand and predict defect concentrations and suitable dopant configurations for improved performance.

3. **Device integration:** To incorporate TiO_2 thin films into practical photocatalytic and optoelectronic devices while preserving their functional performance.

VIII. CONCLUSION

Sol–gel dip-coated TiO_2 thin films act as a flexible and acceptable platform for multifunctional optical and photocatalytic applications. By establishing the inverse relationship between photoluminescence and photocatalytic activity as a guiding design principle, this review highlights some effective strategies like defect engineering, heterojunction formation, and improving interfaces help enhance performance. Continue improvement in control processing method, advanced characterization, and successful device integration are expected to speed up the use of TiO_2 thin films in environmental remediation and next-generation optoelectronic technologies. Overall, this framework summarizes current understanding and provides a practical roadmap for the efficient design and scalable application of TiO_2 thin-film systems. Throughout this review, photocatalytic behavior has been deliberately treated as a secondary functional outcome, employed primarily to validate defect-mediated electronic recombination dynamics rather than application-driven performance.

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