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EXPERIMENTAL INVESTIGATION OF TIO_2-MODIFIED CONCRETE: MICROSTRUCTURAL BEHAVIOR, MECHANICAL PERFORMANCE, DURABILITY CHARACTERISTICS, AND ENVIRONMENTAL IMPLICATIONS

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ABSTRACT

Titanium dioxide (TiO_2) has attracted considerable scholarly and industrial attention as a functional additive for cementitious composites, owing to its photocatalytic activity, chemical inertness, and the potential it holds for improving both the engineering performance and environmental credentials of concrete structures. This review synthesizes and critically evaluates experimental evidence from more than three decades of research concerning the incorporation of TiO_2 into ordinary Portland cement (OPC)-based systems, encompassing anatase and rutile polymorphs at dosages typically ranging from 1% to 10% by mass of binder. The paper examines the microstructural modifications induced by TiO_2 addition, including pozzolanic reactivity, pore size refinement, and interfacial transition zone (ITZ) densification. Mechanical performance data drawn from diverse studies consistently demonstrate compressive strength gains of 10–25% at optimal dosages (typically 2–5 wt.%), alongside improvements in tensile and flexural capacity. Durability assessments reveal reduced water absorption, lower chloride penetration depth, and enhanced resistance to sulfate attack and carbonation. The photocatalytic properties of TiO_2-modified concrete are evaluated in the context of air purification, de-pollution of nitrogen oxides (NOx) and volatile organic compounds, and self-cleaning surface behavior. Contradictory findings in the literature are critically addressed, particularly concerning the effects of high TiO_2 dosages and particle size on workability and long-term hydration kinetics. Environmental implications, including embodied energy trade-offs, lifecycle considerations, and urban heat island mitigation, are also discussed. Future research directions and practical challenges associated with large-scale deployment are identified, providing a nuanced foundation for material scientists, structural engineers, and sustainability researchers.

KEYWORDS: TiO_2 Nanoparticles, Photocatalytic Concrete, Durability And Sustainability, Self-Cleaning Construction Materials

1. INTRODUCTION

Concrete remains the most extensively manufactured construction material in the world, with annual production exceeding 10 billion tonnes and projected demand continuing to rise in tandem with rapid urbanization across developing economies (Mehta & Monteiro, 2014). Despite its ubiquity and structural versatility, conventional Portland cement concrete is susceptible to numerous deterioration mechanisms, including chloride-induced corrosion of embedded reinforcement, carbonation-driven depassivation, sulfate attack, and alkali–silica reaction, all of which diminish structural service life and impose substantial economic burdens on maintenance and rehabilitation (Neville, 2011; Aïtcin & Flatt, 2016). Concurrently, the built environment is increasingly expected to contribute to broader environmental objectives, including the mitigation of air pollution, reduction in urban heat island intensity, and diminished reliance on chemical cleaning cycles for exposed surfaces. These dual

imperatives — enhanced engineering performance and reduced ecological impact — have catalyzed intensive research into multifunctional concrete additives.

Among the various nano- and micro-scale additives that have been investigated as performance enhancers and functional modifiers for cementitious systems, titanium dioxide (TiO_2) occupies a particularly prominent position. This white, wide-bandgap semiconductor exists predominantly in three crystalline polymorphs — anatase, rutile, and brookite — of which anatase and rutile are commercially significant (Chen & Mao, 2007). The photocatalytic activity of TiO_2, first documented by Fujishima and Honda (1972) and later extended to environmental remediation applications by Hashimoto et al. (2005), constitutes its most distinctive functional attribute. Under ultraviolet (UV) illumination, TiO_2 generates electron–hole pairs capable of oxidizing organic pollutants, decomposing nitrogen oxides, and imparting self-cleaning characteristics to surfaces, properties that carry obvious appeal when the host material is exposed infrastructure in polluted urban environments.

Beyond photocatalytic functionality, TiO_2 particles exert physicochemical influence on cement hydration reactions, pore network geometry, and microstructural development. Several researchers have documented accelerated cement hydration in the presence of TiO_2 nanoparticles, attributing this effect to nucleation seeding of calcium silicate hydrate (C–S–H) phases (Chen & Poon, 2009; Jalal et al., 2013). The resulting microstructural densification tends to reduce effective porosity and enhance both mechanical strength and transport resistance. These outcomes are highly desirable from a durability standpoint and have motivated efforts to deploy TiO_2-modified concrete in pavements, facades, bridge decks, and tunnel linings.

Notwithstanding these reported benefits, the literature contains numerous inconsistencies and unresolved questions. The magnitude and direction of TiO_2's influence on concrete properties depend strongly on particle size, crystal phase, dosage level, water-to-cement ratio, supplementary cementitious material (SCM) content, and curing conditions, rendering broad generalizations hazardous. Moreover, the economic premium associated with TiO_2 nanoparticles and the energy intensity of their synthesis impose practical constraints that necessitate careful cost–benefit analysis before large-scale adoption. This review aims to provide a structured and critical synthesis of experimental findings across the full spectrum of TiO_2-modified concrete research, from fresh-state behavior and hydration chemistry through mechanical characterization, durability performance, photocatalytic efficacy, and environmental assessment.

2. PHYSICOCHEMICAL PROPERTIES OF TIO_2 AND MECHANISMS OF INTERACTION WITH CEMENT

2.1 Crystal Structure and Surface Chemistry

Titanium dioxide is a transition metal oxide with a molecular weight of 79.87 g/mol and a density ranging from 3.78 g/cm³ (anatase) to 4.26 g/cm³ (rutile) (Diebold, 2003). The anatase polymorph adopts a body-centered tetragonal structure and exhibits superior photocatalytic activity relative to rutile owing to its higher surface area and elevated conduction band potential, which facilitate efficient electron–hole pair generation and slower recombination rates. Rutile, the thermodynamically stable phase at ambient conditions, possesses greater refractive index (2.72 versus 2.54 for anatase) and is widely employed as a white pigment in the construction industry. Commercial photocatalytic applications frequently employ the mixed-phase Degussa P25, which contains approximately 75% anatase and 25% rutile and exhibits synergistic photocatalytic performance attributed to favorable charge transfer between the two phases (Ohno et al., 2001).

The surface chemistry of TiO_2 in aqueous alkaline environments is particularly relevant to its interaction with Portland cement pore solution, which typically exhibits pH values in the range of 12.5–13.5. Under these conditions, TiO_2 surfaces carry a net negative charge (the point of zero charge of anatase is approximately pH 5.8–6.2), which influences particle agglomeration tendencies and adsorption of ionic species such as Ca^{2+} and Al^{3+} (Guo et al., 2020). These electrostatic interactions can modify the dispersion of TiO_2 within the cement paste matrix and affect

the uniformity of its distribution throughout the hardened microstructure, a factor with significant implications for both photocatalytic surface availability and volumetric mechanical performance.

2.2 Photocatalytic Mechanism

The photocatalytic action of TiO_2 under UV irradiation involves the absorption of photons with energy exceeding its bandgap (~3.2 eV for anatase, ~3.0 eV for rutile), generating electrons in the conduction band and holes in the valence band. These charge carriers participate in a cascade of redox reactions with adsorbed water molecules and dissolved oxygen to produce reactive oxygen species (ROS), including hydroxyl radicals (•OH), superoxide anion radicals ($O_2•^-$), and hydrogen peroxide (H_2O_2), which are potent oxidizing agents capable of mineralizing organic pollutants to CO_2 and water (Herrmann, 1999; Fujishima et al., 2008).

In the context of concrete surfaces exposed to atmospheric pollution, the most practically significant reactions involve the oxidation of nitric oxide (NO) to nitrate (NO_3^-), which is then washed away by rain, and the degradation of organic soiling agents such as carbonaceous particulates and biological films. Several field and laboratory studies have quantified NOx removal efficiencies of TiO_2-treated concrete pavements at 20–70% under simulated or natural UV exposure, depending on flux intensity, airflow velocity, and surface TiO_2 concentration (Guerrini & Peccati, 2007; Ballari & Brouwers, 2013). The incorporation of visible-light-active TiO_2 through nitrogen or carbon doping has been explored as a means of extending photocatalytic activity to the broader solar spectrum (Asahi et al., 2001), though concrete applications of such modifications remain at the laboratory stage.

2.3 Effects on Cement Hydration and Microstructure

When TiO_2 particles are dispersed within a fresh cement paste, their primary mechanistic role in the early hydration stage is as nucleation sites that accelerate the precipitation of C–S–H gel. This seeding effect, well documented for nanosilica and analogous for TiO_2, shortens the induction period of cement hydration and advances the timing of heat evolution peaks, as detected by isothermal calorimetry (Nazari & Riahi, 2011a; Li et al., 2017). The increased number of nucleation sites distributes C–S–H precipitation more uniformly throughout the paste volume, yielding a finer and more homogeneous gel network with reduced mean pore diameter and narrower pore size distribution as confirmed by mercury intrusion porosimetry (MIP) and nitrogen adsorption analysis.

At later ages, TiO_2 may participate in pozzolanic-type reactions, consuming portlandite (CH) produced during cement hydration to form additional C–S–H. However, the pozzolanic reactivity of TiO_2 is generally considered modest relative to high-reactivity pozzolans such as silica fume or metakaolin, because its siliceous content is absent and its reaction with CH proceeds primarily through surface adsorption and physical filling rather than chemical conversion (Chen & Poon, 2009). The filler effect of fine TiO_2 particles in densifying the paste and the interfacial transition zone (ITZ) between aggregate and paste is thus considered a more quantitatively significant contributor to strength and transport property improvements than pozzolanic chemistry per se.

3. EXPERIMENTAL METHODOLOGIES AND MIX DESIGN PARAMETERS

A diversity of experimental approaches has been employed across the TiO_2 concrete literature, reflecting varying research objectives, available raw materials, and testing standards. The following subsections synthesize the principal variables that have been systematically investigated, with Table 1 providing a comparative summary of representative mix designs from key studies.

Table 1. Summary of Representative Mix Design Parameters in TiO_2-Modified Concrete Studies

Reference	w/c Ratio	TiO_2 (wt.%)	TiO_2 Type	Particle Size	SCM Used	Cement Type	Age (d)
Chen & Poon (2009)	0.45	2.5–10	P25	~21 nm	None	OPC	28
Nazari & Riahi (2011a)	0.40	1–4	Anatase	15 nm	None	OPC	28, 90
Jalal et al. (2013)	0.40	2–6	Anatase	10–25 nm	SF, GGBS	OPC	28, 90

Mohseni et al. (2015)	0.45	0–5	Rutile	~200 nm	SF	OPC	7, 28
Rahim et al. (2016)	0.50	1–3	Anatase	~100 nm	None	OPC	28
Guo et al. (2020)	0.38	0–4	P25	21 nm	FA	OPC	28, 56
Oner & Akyuz (2021)	0.42	2–8	Anatase	50 nm	None	OPC	28, 90
Singh et al. (2022)	0.45	1–5	Anatase	20 nm	RHA	OPC	28

Note: *P25 = Degussa P25 (75% anatase/25% rutile); SF = silica fume; GGBS = ground granulated blast-furnace slag; FA = fly ash; RHA = rice husk ash; OPC = ordinary Portland cement; w/c = water-to-cement ratio.*

3.1 TiO_2 Dosage and Particle Size

The dosage of TiO_2 as a replacement or addition to cement binder has been the most universally varied parameter in experimental programmes, with tested ranges typically spanning 0.5 to 15% by weight of cement. The preponderance of evidence indicates that the relationship between TiO_2 content and mechanical performance is non-monotonic, with strength and durability benefits peaking at intermediate dosages (generally 2–5 wt.%) before declining at higher substitution levels (Nazari & Riahi, 2011b; Mohseni et al., 2015). This non-linearity is attributed to the increased difficulty of achieving uniform particle dispersion at elevated concentrations, leading to agglomeration clusters that function as stress concentrators within the hardened matrix. The particle size of TiO_2 governs both its specific surface area, and consequently its nucleation seeding capacity, and its photocatalytic efficiency, which is maximized at the nanoscale owing to quantum confinement effects and reduced bulk recombination. Nanoparticles in the 10–50 nm range have demonstrated superior mechanical performance enhancements relative to micro-scale counterparts, though they also present greater handling and dispersion challenges (Li et al., 2017).

3.2 Crystal Phase and Commercial Sources

The choice between anatase and rutile TiO_2, and the use of mixed-phase commercial products such as Degussa P25, substantially influences experimental outcomes. Studies comparing anatase and rutile additions at equivalent dosages have generally found anatase to yield greater improvements in compressive strength, consistent with its higher specific surface area (BET surface area: anatase ~100 m^2/g; rutile ~10–50 m^2/g) and stronger nucleation seeding capacity (Chen & Poon, 2009). However, rutile's greater density and optical opacity contribute disproportionately to reflectivity in white cement applications, and its superior chemical stability under alkaline conditions may confer longer-term durability advantages in highly aggressive exposure classes (Ohno et al., 2001).

3.3 Supplementary Cementitious Materials and Binary Blends

A growing body of research has explored synergistic interactions between TiO_2 and supplementary cementitious materials including silica fume, fly ash, ground granulated blast-furnace slag (GGBS), and metakaolin. Jalal et al. (2013) found that binary blends of TiO_2 with silica fume in self-compacting concrete yielded super additive strength improvements compared with either additive used alone, attributing the synergy to complementary action: TiO_2 accelerates early hydration through nucleation seeding while silica fume densifies the microstructure through its high pozzolanic reactivity at later ages. Similar cooperative effects have been documented in TiO_2–fly ash blends, where the dilution of early hydration provided by fly ash is offset by TiO_2's nucleation acceleration, yielding superior 90-day strength compared with either single-component addition (Guo et al., 2020). These combinatorial strategies have particular relevance for the construction industry's decarbonization agenda, as they enable partial replacement of clinker-intensive OPC while maintaining or improving performance.

4. FRESH-STATE BEHAVIOR AND WORKABILITY

The incorporation of TiO_2 particles into concrete mixtures consistently produces a measurable reduction in workability as quantified by slump, flow diameter, and Vebe time tests, an effect that becomes more pronounced with increasing dosage and decreasing particle size. Reductions in slump of 15–40% relative to plain concrete controls have been reported at TiO_2 additions of 5% or higher, attributed primarily to the substantially increased surface area

of the nanoscale particles competing for the available free water necessary for lubrication of aggregates and paste flow (Mohseni et al., 2015; Li et al., 2017). The high specific surface energy of TiO_2 nanoparticles also promotes particle agglomeration in the absence of effective dispersion protocols, further impeding flow.

Several research groups have implemented superplasticizer dosage adjustments to restore target workability in TiO_2-modified mixtures at constant w/c ratio, a strategy that also mitigates the water-demand penalty associated with high specific surface area additions (Jalal et al., 2013). Ultrasonic dispersion and high-shear mixing protocols have been shown to substantially improve particle distribution within the cement paste, reducing agglomerate size and producing more uniform fresh-state rheology. Sonebi et al. (2015) demonstrated that incorporating TiO_2 as a pre-dispersed aqueous suspension rather than dry powder significantly reduced slump loss and improved 28-day compressive strength compared with dry addition at the same nominal dosage, underscoring the critical importance of dispersion methodology on performance outcomes.

Regarding setting time, TiO_2 additions have been reported to accelerate both initial and final setting times, consistent with the nucleation seeding effect on cement hydration kinetics. Accelerations of 10–30 minutes in initial setting have been documented at 3–5% TiO_2 addition, which may have practical implications for hot weather concreting or for admixture scheduling where extended open time is required (Nazari & Riahi, 2011a). Air entrainment in TiO_2-modified mixtures has been found to be somewhat reduced relative to plain concrete, possibly owing to the hydrophilic surface of TiO_2 altering bubble stability, a consideration relevant to freeze–thaw durability design.

5. MECHANICAL PROPERTIES OF TIO_2-MODIFIED CONCRETE

5.1 Compressive Strength

Compressive strength is the most widely reported mechanical property in TiO_2 concrete studies, and the literature reveals a consistent trend of dose-dependent strength enhancement followed by deterioration at excessive addition levels. Table 2 summarizes compressive strength results from selected studies across a range of TiO_2 contents and testing ages.

Table 2. Compressive Strength of TiO_2-Modified Concrete at 28 Days from Selected Studies

Reference	TiO_2 (%)	Control (MPa)	Optimum (MPa)	Optimal Dosage	% Gain
Chen & Poon (2009)	2.5–10	42.1	52.6	5%	+25%
Nazari & Riahi (2011a)	1–4	38.4	46.8	3%	+22%
Jalal et al. (2013)	2–6	55.2	64.8	4%	+17%
Mohseni et al. (2015)	0–5	39.7	47.1	3%	+19%
Rahim et al. (2016)	1–3	36.5	42.8	2%	+17%
Guo et al. (2020)	0–4	48.0	56.4	3%	+17.5%
Singh et al. (2022)	1–5	34.2	41.6	3%	+21.6%

The consistently reported optimum TiO_2 dosage in the range of 2–5 wt.% across diverse mix designs and cement sources reflects the balance between beneficial microstructural densification and the deleterious effects of particle agglomeration and dilution of cementite content that manifest at higher dosages. At the microstructural level, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies consistently reveal denser C–S–H morphology, reduced portlandite crystal size, and diminished ITZ thickness in optimally dosed TiO_2 concretes compared with control specimens (Li et al., 2017; Guo et al., 2020). X-ray diffraction (XRD) analysis corroborates reduced CH content in TiO_2-modified pastes, consistent with accelerated consumption of portlandite through nucleation-induced recrystallization rather than pozzolanic reaction per se.

5.2 Tensile and Flexural Strength

While tensile and flexural properties have received less exhaustive experimental attention than compressive strength, the available data broadly support the finding that TiO_2 additions improve these properties in a manner broadly proportional to, but somewhat exceeding, the enhancement in compressive strength. Splitting tensile strength improvements of 10–28% at optimal dosages have been reported, with flexural strength gains typically

in the range of 8–20% (Nazari & Riahi, 2011b; Jalal et al., 2013). The disproportionate enhancement in tensile and flexural properties relative to compressive strength suggests that TiO_2 addition may exert a beneficial influence on crack propagation resistance, possibly through the creation of a more tortuous crack path in the denser microstructure or through enhanced bonding at the aggregate–paste interface. Mohseni et al. (2015) reported that TiO_2-modified concrete exhibited higher modulus of rupture values compared with silica fume concrete at equivalent w/cm ratios, suggesting complementary rather than competing roles for the two additives in a binary blend.

5.3 Modulus of Elasticity

Limited but consistent data indicate that TiO_2 addition increases the static modulus of elasticity of concrete, reflecting the increased stiffness of a denser and less porous matrix (Rahim et al., 2016). Reported elastic modulus gains range from 5 to 15% at optimal dosages, somewhat lower in proportional terms than the corresponding compressive strength gains, consistent with the well-established weaker dependence of elastic modulus on porosity relative to strength. Dynamic modulus measurements by ultrasonic pulse velocity (UPV) have also been employed as a non-destructive indicator of microstructural quality in TiO_2 studies, with pulse velocity increases of 3–7% reported at optimum dosages, corroborating the microstructural densification inferred from MIP and SEM analysis (Oner & Akyuz, 2021).

6. DURABILITY PERFORMANCE

6.1 Water Absorption and Porosity

The reduced capillary porosity and refined pore size distribution characteristic of TiO_2-modified concrete translate directly into diminished water absorption capacity, a fundamental indicator of resistance to multiple deterioration mechanisms. Total water absorption reductions of 15–35% relative to control mixes have been reported at optimal TiO_2 additions across diverse experimental programmes (Chen & Poon, 2009; Guo et al., 2020). MIP measurements consistently reveal decreases in the volume fraction of pores in the macropore range (>50 nm diameter), which are primarily responsible for capillary suction and moisture transport, while the finer gel pore network is comparatively less affected. Sorptivity coefficients, which characterize the rate of capillary absorption under unsaturated conditions, have been found to decrease by 20–40% in TiO_2-modified concretes, a finding with direct relevance to structures exposed to cyclic wetting and drying in aggressive marine or industrial environments (Mohseni et al., 2015).

6.2 Chloride Ion Penetration Resistance

Chloride-induced corrosion of steel reinforcement is the primary cause of premature deterioration in reinforced concrete infrastructure in coastal and de-iced road environments. The rapid chloride permeability test (RCPT, ASTM C1202) and the non-steady-state migration coefficient (NT BUILD 492) have been widely used to assess chloride transport resistance in TiO_2 concrete. Jalal et al. (2013) reported RCPT charge passed reductions of 40–60% in TiO_2-modified self-compacting concrete relative to plain controls, attributing this improvement to pore refinement and the blocking of chloride transport pathways by physically adsorbed TiO_2 particles. Similar findings were reported by Guo et al. (2020) for binary TiO_2–fly ash systems, where the combined effect of the two additions on pore network connectivity produced chloride diffusion coefficients approximately 50% lower than the fly ash control. These results suggest that TiO_2 addition offers a meaningful contribution to the durability of concrete elements in chloride-laden service environments.

6.3 Sulfate Attack Resistance

Sulfate attack involves the reaction of sulfate ions penetrating from external sources with cement hydration products, particularly aluminate phases, to form expansive ettringite and gypsum, leading to cracking and loss of cohesion. The denser microstructure of TiO_2-modified concrete provides a physical barrier to sulfate ingress, while the reduced portlandite content in TiO_2-modified paste limits the availability of calcium ions for gypsum formation (Singh et al., 2022). Studies subjecting TiO_2-modified concrete specimens to sulfate immersion for 90–180 days have documented lower mass loss, smaller expansion values, and superior residual compressive strength retention compared with plain controls, with protection efficiency increasing with TiO_2 content up to the optimal dosage (Oner & Akyuz,

2021). The combination of TiO_2 with slag cement, which further reduces the C_3A content of the binder, has been identified as a particularly effective strategy for sulfate-resistant concrete in foundations and wastewater infrastructure.

6.4 Carbonation Resistance

Carbonation involves the reaction of atmospheric CO_2 with calcium hydroxide and C–S–H in the concrete cover zone, progressively reducing the pH of the pore solution and depassivating the steel reinforcement. The higher density and lower effective porosity of TiO_2-modified concrete slow the CO_2 diffusion front, resulting in reduced carbonation depths as measured by phenolphthalein spray indicator after accelerated carbonation exposure. Rahim et al. (2016) reported 28-day accelerated carbonation depths approximately 20–35% lower in TiO_2-modified concrete than in comparable OPC controls, with the benefit concentrated at the 2–4% dosage range. This improvement is consistent with the role of reduced connected porosity in limiting gaseous diffusion, and is further supported by reductions in oxygen permeability coefficient measured by the Torrent permeability tester.

Table 3. Durability Performance Summary for TiO_2-Modified Concrete from Representative Studies

Reference	TiO_2 (%)	Water Absorption	RCPT (Coulo-mbs)	Carbonation Depth	Sulfate Resistance
Chen & Poon (2009)	5	–28%	1820 (Low)	Not reported	Improved
Jalal et al. (2013)	4	–32%	1240 (Very Low)	–30%	Superior
Mohseni et al. (2015)	3	–25%	2100 (Low)	Not tested	Improved
Rahim et al. (2016)	2	–19%	Not reported	–25%	Moderate
Guo et al. (2020)	3	–30%	980 (Very Low)	–28%	Superior
Oner & Akyuz (2021)	4	–27%	1560 (Low)	–32%	Excellent
Singh et al. (2022)	3	–24%	1780 (Low)	–22%	Good

Note: *RCPT = Rapid Chloride Permeability Test; values are relative changes from respective control specimens.*

6.5 Freeze–Thaw Resistance

Freeze–thaw cycling induces hydraulic and osmotic pressure within the pore network of concrete, progressively degrading surface integrity and diminishing residual mechanical properties. While TiO_2 addition reduces total porosity, the effect on the critical air void system that governs freeze–thaw performance in air-entrained concrete is not straightforwardly beneficial; some studies have reported reduced air void spacing factors in TiO_2-modified mixtures without air entrainment, potentially increasing vulnerability to frost damage (Sonebi et al., 2015). Conversely, the reduced capillary absorption of TiO_2-modified concrete limits the degree of saturation achieved in freeze–thaw cycles, which is the fundamental precondition for hydraulic pressure development. Singh et al. (2022) found that TiO_2-modified concrete exhibited superior relative dynamic modulus after 300 freeze–thaw cycles compared with OPC controls when both were prepared without air entrainment, suggesting that the reduced saturation effect outweighed any adverse change in void geometry.

7. PHOTOCATALYTIC PROPERTIES AND ENVIRONMENTAL FUNCTIONALITY

7.1 Self-Cleaning Behavior

The photocatalytic oxidation of organic soiling agents on TiO_2-modified concrete surfaces under UV irradiation imparts a self-cleaning functionality that has attracted commercial application in façade elements, pavements, and roofing materials. The UV-driven generation of hydroxyl radicals at the surface decomposes hydrophobic organic films, while the concurrent photoinduced superhydrophilicity of TiO_2 causes water to spread uniformly over the surface rather than forming discrete droplets, facilitating the runoff of loosened soiling particles during rainfall (Hashimoto et al., 2005). Laboratory assessments employing methylene blue (MB) degradation as a standardized proxy for organic decomposition activity have shown rhodamine B and MB discoloration rates substantially higher for TiO_2-modified concrete specimens than for plain concrete controls, with activity proportional to the available surface TiO_2 content rather than the bulk dosage (Guerrini & Peccati, 2007). This distinction between surface availability and bulk content is critical for mix design optimization: ensuring that TiO_2 particles are concentrated near the exposed surface, through mix proportioning or surface treatment techniques,

maximizes photocatalytic efficiency for a given total TiO_2 mass.

7.2 Atmospheric Depollution: NOx Removal

The depollution of nitrogen oxides (NO and NO_2, collectively NOx) from urban air represents the most environmentally significant and best-documented application of TiO_2-modified concrete in field conditions. NOx are byproducts of vehicular combustion and industrial processes that contribute to photochemical smog formation, respiratory disease, and acidic deposition. Photocatalytic concrete surfaces oxidize NO to NO_2 and ultimately to water-soluble nitrate, which is washed from the surface by precipitation and enters the stormwater system as a dilute nitrate solution (Ballari & Brouwers, 2013). Field trials of TiO_2-treated concrete pavements in street canyon environments in Milan, Antwerp, and London have demonstrated NOx concentration reductions of 20–50% in the near-surface air layer under daytime conditions, though actual depollution efficiency depends strongly on traffic volume, pavement surface area, UV irradiance, and ambient humidity (Beeldens et al., 2011; Hunger et al., 2010). A critical challenge in evaluating field NOx removal performance is the potential for released nitrate to contribute to nutrient loading of receiving water bodies, representing an environmental trade-off that lifecycle assessment (LCA) studies must account for. Ballari and Brouwers (2013) performed a comprehensive modeling analysis and concluded that NOx removal benefits outweigh nitrate load concerns when photocatalytic pavements are deployed in areas with high vehicular NOx emission density, but that benefits diminish substantially under low UV conditions such as those prevailing in northern European winters.

7.3 Volatile Organic Compound (VOC) Degradation

Beyond NOx, TiO_2-modified concrete has demonstrated photocatalytic activity toward a broad range of VOCs including benzene, toluene, ethylbenzene, xylene (BTEX compounds), formaldehyde, and acetaldehyde, which are emitted by traffic, industrial processes, and building materials. Laboratory chamber tests have quantified degradation efficiencies of 30–80% for individual VOC species on TiO_2-modified mortar and concrete specimens under controlled UV irradiation, with performance depending on compound polarity, molecular weight, and competitive adsorption effects when multiple species are present simultaneously (Hunger et al., 2010). The application of TiO_2-modified concrete in indoor environments, where VOC concentrations are often higher than outdoors, is an emerging area of investigation with implications for indoor air quality improvement in schools, hospitals, and residential buildings.

8. MICROSTRUCTURAL CHARACTERIZATION

8.1 Scanning Electron Microscopy and Energy Dispersive Spectroscopy

SEM investigations of TiO_2-modified concrete fracture surfaces and polished sections consistently reveal a morphological transformation of the hydrated microstructure characterized by denser C–S–H morphology, reduced visible porosity, and more intimate contact between hydration products and aggregate surfaces compared with plain concrete controls. At optimal TiO_2 dosages, the ITZ, which in conventional concrete is typically wider (15–50 μm) and more porous than the bulk paste due to the wall effect and water film accumulation at aggregate surfaces, appears markedly densified, with fewer visible portlandite crystals and a smoother textural appearance (Li et al., 2017). Energy dispersive spectroscopy (EDS) mapping has been employed to confirm the distribution of titanium throughout the paste matrix and to verify the absence of discrete unreacted TiO_2 clusters at optimal dosages, while confirming their presence and spatial extent when higher dosages lead to agglomeration (Guo et al., 2020).

8.2 X-ray Diffraction Analysis

XRD patterns of TiO_2-modified cement pastes at progressive hydration ages reveal characteristic features consistent with the nucleation seeding hypothesis. The intensity of the portlandite (calcium hydroxide) diffraction peaks at $2\theta \approx 18°$ and 34° is consistently reduced in TiO_2-modified samples compared with controls at equivalent ages, suggesting either accelerated consumption of CH through the densification of the C–S–H network or redistribution of crystallization sites (Nazari & Riahi, 2011a). The anatase and rutile TiO_2 peaks remain detectable in XRD patterns of hardened pastes even at late ages,

confirming that TiO_2 does not fully dissolve or react chemically with cement hydration products under normal curing conditions, consistent with its role as a physical modifier and nucleation template rather than a pozzolanic reactant in the conventional sense.

8.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of TiO_2-modified cement pastes provide quantitative information on bound water content and portlandite mass fraction as functions of curing age and TiO_2 dosage. Studies employing TGA have generally found lower CH content in TiO_2-modified pastes compared with controls at ages of 28 and 90 days, with CH reduction proportional to TiO_2 dosage up to approximately 5%, beyond which CH reduction plateaus or reverses slightly, possibly owing to retarded hydration caused by excessive particle loading (Singh et al., 2022). The degree of hydration, as inferred from the non-evaporable water content, is consistently higher in TiO_2-modified pastes at early ages (3–7 days), confirming the accelerating effect of TiO_2 on cement hydration kinetics, while the difference narrows at 90 days as the untreated paste hydration approaches completion.

9. ENVIRONMENTAL IMPLICATIONS AND SUSTAINABILITY ASSESSMENT

9.1 Lifecycle Assessment Considerations

The environmental credentials of TiO_2-modified concrete must be assessed not only on the basis of its functional performance but also through a comprehensive lifecycle assessment (LCA) framework that accounts for the embodied impacts of TiO_2 production, transportation, and end-of-life scenarios. The synthesis of TiO_2 nanoparticles via the sulphate or chloride process involves substantial energy consumption, chemical inputs, and generation of acidic byproduct streams, resulting in a global warming potential (GWP) per unit mass of TiO_2 significantly higher than that of conventional cement clinker on an equal mass basis (Baglioni et al., 2012). However, when the mass fraction of TiO_2 in a modified concrete mix is considered — typically 2–5 kg of TiO_2 per tonne of concrete — the incremental GWP per cubic metre of concrete is relatively modest compared with the full-life benefits that accrue from improved durability.

Service life extension is the most impactful environmental benefit of TiO_2-modified concrete from an LCA perspective. If TiO_2 addition extends the service life of a reinforced concrete structure by 20–30 years through improved chloride and carbonation resistance, the avoided maintenance, rehabilitation, and early replacement activities represent substantial avoided embodied carbon over the infrastructure lifecycle (Pade & Guimaraes, 2007). LCA studies of photocatalytic concrete pavements must also credit NOx removal benefits as avoided damage costs in terms of respiratory health outcomes and reduced pharmaceutical treatment needs, employing appropriate damage cost valuation methods to monetize these co-benefits (Ballari & Brouwers, 2013).

9.2 Urban Heat Island Mitigation

The high solar reflectance (albedo) of white TiO_2-modified concrete surfaces contributes to urban heat island mitigation by reducing surface temperature and the associated re-emission of longwave radiation into the urban boundary layer. Reflectance values of TiO_2-modified white cement concrete in the range of 0.65–0.80 have been reported, substantially higher than the 0.25–0.40 typical of grey OPC concrete and 0.04–0.10 for asphalt pavements (Guerrini & Peccati, 2007). Simulation studies have estimated that widespread deployment of high-albedo concrete pavements and facades in dense urban settings could reduce peak summer air temperatures by 1–2°C, with corresponding reductions in cooling energy demand of 5–20% in climate zones where summer cooling dominates energy use (Santamouris, 2013). The photocatalytic self-cleaning function of TiO_2 helps maintain high surface reflectance over time by preventing the accumulation of soiling that would progressively darken conventional white concrete surfaces, enhancing the long-term effectiveness of the urban heat island mitigation strategy.

9.3 Ecotoxicological Considerations

The potential release of TiO_2 nanoparticles from concrete surfaces through weathering, abrasion, and runoff raises ecotoxicological concerns that have received increasing scrutiny as regulatory frameworks for nanomaterials evolve. Laboratory ecotoxicity studies have documented adverse effects of TiO_2 nanoparticles on aquatic organisms including algae,

daphnia, and fish at concentrations in the range of 1–100 mg/L under UV illumination, though effects are significantly reduced in dark conditions owing to the photocatalytic dependence of toxicity mechanisms (Warheit et al., 2007). Field release rates from TiO_2-modified concrete surfaces are estimated to be low (nanograms per square metre per hour under typical weathering conditions), and dilution in stormwater streams would reduce exposure concentrations below ecotoxicological effect thresholds in most scenarios. Nevertheless, the long-term accumulation of TiO_2 nanoparticles in sediments and biofilms warrants continued monitoring, and the development of concrete formulations that combine photocatalytic functionality with minimal nanoparticle release through surface encapsulation strategies is an active research direction.

10. CRITICAL ANALYSIS AND SYNTHESIS OF EXISTING EVIDENCE

A critical reading of the TiO_2 concrete literature reveals several systematic methodological limitations that complicate cross-study comparison and impede confident quantitative generalization. Chief among these is the wide variation in experimental protocols, including differences in cement type and Bogue composition, aggregate grading and source, curing temperature and humidity, age at testing, and specimen geometry, which collectively produce baseline performance variations among control concretes that can exceed the TiO_2-induced incremental improvements being measured. The absence of a standardized protocol for TiO_2 concrete characterization analogous to the ASTM or EN standards that govern conventional concrete testing hampers the development of a coherent quantitative database from which predictive models could be reliably developed.

The dispersion problem deserves particular critical attention. A substantial proportion of published studies have employed simple dry mixing or hand dispersion of TiO_2 powder into dry cementitious ingredients without verification of particle dispersion quality by techniques such as dynamic light scattering (DLS) or electron microscopy of fresh paste, making it likely that agglomeration artifacts contribute to the variability of reported results (Li et al., 2017). Studies that have directly compared dry and ultrasonically dispersed TiO_2 additions have found statistically significant performance differences, suggesting that benchmark studies employing optimized dispersion may overstate the benefits achievable under practical construction conditions where high-energy dispersion equipment is unavailable.

The commercial viability of TiO_2-modified concrete also requires frank assessment. At current market prices of US$5–25/kg for nano-$TiO_2$ depending on purity and polymorph, a 3 wt.% addition to a concrete mix with a binder content of 350 kg/m^3 would add US$52.5–262.5 per cubic metre, representing a 50–250% premium over the material cost of plain concrete. This cost barrier substantially restricts the market for TiO_2 concrete to high-value applications where photocatalytic functionality or extreme durability requirements justify the premium, including landmark architectural structures, airport runways, nuclear waste containment systems, and premium urban paving. The economics improve considerably for applications using micro-scale rather than nano-scale TiO_2, though at the cost of reduced performance per unit mass.

Future research priorities identified from the synthesis of existing evidence include: (1) long-term field performance monitoring of TiO_2-modified concrete elements under real environmental exposure, including UV weathering, thermal cycling, and mechanical wear; (2) development of visible-light-active TiO_2 formulations that extend photocatalytic functionality to indoor applications and overcast climate zones; (3) investigation of TiO_2 interactions with alkali-activated and geopolymer binders as low-carbon alternatives to OPC; (4) standardization of test methods for photocatalytic concrete characterization; and (5) comprehensive lifecycle assessment studies that integrate functional performance data with environmental impact quantification across diverse geographic and climatic contexts.

11. CONCLUSIONS

This review has systematically synthesized experimental evidence from over three decades of research on TiO_2 as a functional additive for concrete, encompassing fresh-state behavior, mechanical performance, durability, microstructural characteristics, photocatalytic properties, and

environmental implications. The following principal conclusions emerge from the critical analysis:

1. TiO_2 addition to Portland cement concrete at dosages of 2–5 wt.% consistently enhances compressive, tensile, and flexural strength by 10–25% through microstructural densification, pore refinement, and ITZ strengthening attributable to the nucleation seeding effect on C–S–H precipitation.
2. Durability properties — including chloride penetration resistance, water absorption, sulfate attack resistance, and carbonation depth — are significantly improved in TiO_2-modified concrete, with RCPT values reduced by 40–60% and chloride diffusion coefficients approximately halved at optimal dosages.
3. Photocatalytic properties of TiO_2-modified concrete enable meaningful NOx removal from urban air (20–70% near-surface efficiency under UV) and organic pollutant degradation through surface hydroxyl radical generation, with practical applications in pavement and façade engineering.
4. The high albedo of TiO_2-modified white concrete contributes to urban heat island mitigation, with surface reflectance values of 0.65–0.80 compared with 0.25–0.40 for conventional grey concrete.
5. Significant methodological heterogeneity in the existing literature, particularly regarding TiO_2 dispersion protocols and the absence of standardized testing procedures, limits the precision of quantitative generalization and underscores the need for more rigorously controlled comparative studies.
6. The economic premium of nano-TiO_2 currently restricts broad deployment to high-value applications, though lifecycle benefits from service life extension and environmental co-benefits from NOx removal may justify the cost in context-appropriate scenarios.

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