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Review

Hydrophobic and Oleophobic Photocatalytic Coatings for Stones and Cementitious Building Substrates: A Bibliometric Perspective (2010–2025)

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Abstract

Hydrophobic and oleophobic photocatalytic coatings are specialised surface treatments that combine either hydrophobicity or oleophobicity and photocatalytic activity. This combination supports applications such as self-cleaning surfaces, anti-fouling, oil–water separation, air purification, and durability enhancement in construction and other industries. These coatings work by creating a surface with carefully engineered surface energy and roughness that resists wetting by both water and oils, while exposing photocatalytic nanoparticles that activate under light to degrade organics. They are often transparent and durable and are now expanding to cementitious building materials, contributing to sustainable, clean, and resilient infrastructure. The motivation for conducting this bibliometric review arises from the fragmented and interdisciplinary nature of the literature on hydrophobic and oleophobic photocatalytic coatings for construction materials, the rapid growth of research in this field, and the absence of a systematic mapping that integrates publication trends, research hotspots, and practical applications. This review delivers a comprehensive quantitative analysis of publication dynamics, encompassing growth trajectories, global research distribution, and thematic evolution, while uncovering dominant and emerging topics. By mapping established innovations and milestones and exposing critical research barriers, it establishes a knowledge framework that will guide future researchers in advancing hydrophobic and oleophobic photocatalytic coatings for construction materials. Another contribution of this review is its ability to capture both past achievements, such as heritage protection and reduced maintenance of existing structures, and ongoing (as well as future) demands, including sustainability, smart city applications, and multifunctional surface technologies, thereby underscoring its relevance across the full spectrum of the built environment.

Keywords: bibliometric review; photocatalytic coatings; hydrophobic surfaces; oleophobic surfaces; research trends; knowledge mapping; thematic structure

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1. Introduction

Construction materials, whether in heritage preservation or modern infrastructure, are highly susceptible to degradation from environmental stressors, including water ingress, oil contamination, and atmospheric pollutants. Water damage, often caused by high humidity, precipitation, or stormwater runoff, can lead to material erosion, loss of cohesion in joints, and increased porosity in stones and mortars, accelerating structural decay over time [1,2]. Oil contamination introduces toxic compounds like polyaromatic hydrocarbons and sulfur-containing chemicals that penetrate porous materials such as stone or brick, causing staining, chemical degradation, and fostering microbial growth that exacerbates deterioration [3]. Atmospheric pollutants, including sulfur dioxide and nitrogen oxides (NOx), contribute to acid rain and dry deposition, which corrode metals, discolor surfaces, and degrade calcareous stones like limestone and marble [4,5]. These pollutants can also cause embrittlement, mass loss, and changes in material porosity. Furthermore, various microorganisms, including bacteria, algae, cyanobacteria, and molds, can damage building materials through direct attack, production of damaging metabolites, and mechanical forces exerted by colony growth [6]. The cumulative impact of these factors not only compromises structural integrity but also necessitates frequent maintenance and restoration efforts to preserve both historical authenticity and modern functionality. Recent progress in surface functionalisation highlights the pivotal roles of fluorinated compounds, silicon derivatives, and photocatalysts, whose unique properties enable transformative applications across diverse sectors. In the construction domain, the integration of hydrophobic, oleophobic, and photocatalytic coatings has gained momentum as a response to the pressing demand for durable, efficient, and sustainable materials. These innovations are driven by the necessity to develop building surfaces capable of withstanding severe environmental stresses, resisting contamination, and lowering maintenance requirements, thereby contributing to the advancement of resilient and sustainable infrastructure.

Photocatalytic coatings are functional surface layers that typically incorporate materials such as titanium dioxide (TiO_2). Upon visible–ultraviolet light irradiation, electron–hole pairs are generated, leading to the formation of reactive radicals (e.g., $\bullet OH$ or $\bullet O_2^-$) that react with environmental pollutants (NO_x and VOCs), degrading them and/or transforming them into harmless by-products such as water, CO_2, or nitrates. When applied to cementitious materials, these coatings offer substantial benefits, including self-cleaning functionality, environmental remediation, and antibacterial activity that suppresses the growth of microorganisms, mold, and algae on building surfaces [7–9]. Despite these advantages, their long-term effectiveness is hindered by challenges of weak and limited durability, particularly under weathering, mechanical abrasion, and environmental stressors [7,10]. Techniques such as spray deposition, dip-coating, and plasma-assisted deposition are employed to achieve uniform coating coverage and enhance interfacial bonding. An effective strategy to address this limitation involves the use of inorganic binders, such as silica shell (SiO_2) coatings, to strengthen the interfacial bond between photocatalysts and the cement matrix. The SiO_2 layer reacts with cement hydration products to form additional hydrated calcium silicates, C–S–H, gel, thereby densifying the surface and enhancing durability and resistance to environmental degradation [11].

Hydrophobic and oleophobic photocatalytic coatings are advanced surface treatments that integrate water- or oil-repellent properties with photocatalytic activity. When applied to building materials, such multifunctional coatings typically extend their performance by enabling air purification, self-cleaning, antimicrobial protection, odour elimination, and enhanced durability, thereby positioning them as highly valuable solutions for sustainable and resilient urban infrastructure. Superhydrophobic coatings replicate the water-repellent behavior of natural surfaces such as lotus leaves, which exhibit contact angles greater than 150° [12]. Essentially, superhydrophobic coatings rely on both chemical and physical effects. Chemically, a surface covered with highly nonpolar compounds (such as waxes, polysiloxanes, or fluorinated polymers) reduces its affinity for water. Physically, a surface that exhibits micro- or nanoscale irregularities (peaks and cavities) and low surface free energy minimizes surface–water interactions, allowing those that do form to break easily. As a result, water droplets do not actually "wet" the surface but instead roll off under the effect of gravity, carrying away contaminants along their path and thus achieving a self-cleaning effect. Typically, nanoparticles like silica or natural zeolites are used to create micro-nano surface roughness, which is then chemically modified with hydrophobic agents such as fluorosilanes or organosilanes to lower surface energy and achieve water contact angles above 150°, resulting in superhydrophobicity. Renowned for their multifunctionality, these coatings offer self-cleaning, oil–water separation, anti-icing, and anti-corrosion properties. By forming highly water-repellent barriers, they inhibit moisture ingress and safeguard structures against damage from leaks, cracking, and structural weakening. Their versatility extends across sectors, including waterproofing in construction, protective textiles, electronic device preservation, agricultural antifouling, energy efficiency improvement, and military equipment maintenance [13,14]. To enable widespread adoption, the development of scalable and cost-effective application techniques such as spray-based deposition remains a critical priority [13]. These technologies, together with a deeper understanding of coating adhesion mechanisms, play a key role in bridging laboratory research and industrial implementation and in improving coating performance and durability. These technological and mechanistic aspects represent relevant and emerging directions within the broader coating research landscape.

Oleophobic coatings, typically formulated with fluoropolymers and nanoparticles, in a manner analogous to that described above for superhydrophobic coatings, impart oil-resistant properties by preventing the adhesion of oil and other hydrocarbon-based contaminants. This functionality is particularly valuable for maintaining the cleanliness and extending the service life of construction materials [15,16]. Photo-fixation of sulphur dioxide on nanocrystalline TiO_2 at high temperature in an oxidising atmosphere forms sulfate species at oxygen vacancies, altering TiO_2's acid–base properties and inducing oleophobicity [17]. On cementitious substrates, these coatings act as protective barriers against aggressive agents such as chloride ions and carbon dioxide, thereby mitigating corrosion and structural degradation. In addition, by lowering water permeability and enhancing resistance to weathering, UV radiation, and other environmental stressors, oleophobic coatings markedly improve the durability of cement-based materials [18,19]. However, their large-scale implementation remains challenged by technical complexities, including the need for consistent performance under diverse environmental conditions and the standardisation of application techniques, factors that are critical for their broader adoption in real-world practice [20].

The need for this bibliometric review arises from the rapid yet fragmented growth of research on superhydrophobic and oleophobic coatings for construction materials. Despite their transformative potential in enhancing durability, reducing maintenance, and contributing to sustainable infrastructure, the existing literature is highly dispersed across disciplines such as materials science, civil engineering, chemistry, and environmental science. This fragmentation, coupled with the absence of systematic knowledge mapping, has limited researchers' ability to identify publication trends, evaluate technological milestones, and connect laboratory innovations with practical applications in the built environment. By quantitatively analysing publication dynamics, including growth trajectories, global research distribution, and thematic evolution, this review not only consolidates knowledge but also highlights dominant and emerging research hotspots, unresolved challenges, and barriers to large-scale adoption. Furthermore, by linking past achievements, such as heritage conservation and maintenance reduction, with present and future needs for sustainability, smart cities, and multifunctional surface technologies, the review establishes a comprehensive knowledge framework. This review establishes a roadmap to guide the development, practical implementation, and broader impact of superhydrophobic and oleophobic coatings in construction materials, reinforcing their relevance across the full breadth of the built environment.

2. Article Identification and Selection Strategy

The Web of Science (WoS) Core Collection was selected as the primary data source for this bibliometric study due to its comprehensive coverage of peer-reviewed scientific publications and its robust citation tracking system. Recognized as one of the most reliable citation databases, WoS indexes more than 21,000 scholarly journals and integrates diverse sources, including the Science Citation Index Expanded (SCIE), Social Sciences Citation Index (SSCI), Arts & Humanities Citation Index (A&HCI), Emerging Sources Citation Index (ESCI), Conference Proceedings Citation Index (CPCI), Book Citation Index (BKCI), as well as Current Chemical Reactions and Index Chemicus [21,22]. Its rigorous editorial selection ensures the inclusion of high-quality, credible, and impactful research, making it an indispensable tool for reliable bibliometric analysis. Although the present study is limited to the Web of Science Core Collection, incorporating additional databases such as Scopus and Google Scholar in future work could enhance the comprehensiveness and robustness of analyses. Adopting a multi-database retrieval strategy would help ensure broader and more inclusive literature coverage.

A carefully designed search strategy was employed to identify documents explicitly relevant to the research topic, using tailored keywords, Boolean operators, and field tags. The scope of building materials was restricted to cementitious substrates, stone, and lime mortars, while the functionality of photocatalytic coatings was confined to hydrophobic and superhydrophobic properties. The central research question guiding this study is: 'What future research pathways can enhance the impact of multifunctional coatings, combining superhydrophobic, oleophobic, and photocatalytic properties, in advancing the resilience and sustainability of the built environment?'

Accordingly, the search string was defined as: ("photocatalytic coating" OR "photocatalytic layer" OR "photocatalytic film") AND ("superhydrophobic" OR "hydrophobic" OR "water-repelling" OR "water repelling") AND ("oleophobic" OR "oil-repelling" OR "oil repelling") AND ("stones" OR "renders" OR "lime mortar" OR "cement mortar" OR "cementitious composite" OR "cementitious material" OR "cementitious construction material" OR "cementitious construction" OR "concrete" OR "cementitious substrate" OR "cement-based material" OR "cementitious system"). The search was limited to English-language publications from 2010 to 2025 and restricted to open-access journals. Data collection was completed on 14 September 2025. The initial search retrieved 367 records, which were subsequently refined through a stringent qualitative screening process to exclude studies falling outside the scope of the research question. The final dataset comprised only those publications addressing coatings that enhance durability, resist contamination, and facilitate surface maintenance in construction applications.

The collected literature was subjected to a rigorous three-stage filtering process, involving systematic screening of titles, abstracts, and keywords to ensure both relevance and completeness. Articles meeting all three screening criteria were systematically categorised into three distinct thematic groups: (1) studies focusing exclusively on photocatalytic activity, (2) those addressing synergistic photocatalytic and superhydrophobic functionalities, and (3) investigations exploring combined photocatalytic and oleophobic properties. The structured search and classification process identified 205 relevant articles centred on photocatalytic processes, reflecting the dominant and sustained research emphasis that has driven progress in this well-established and highly active field. Within this body of work, 23 studies were identified as addressing superhydrophobic–photocatalytic research, a rapidly expanding subfield where surface wettability modulation is increasingly integrated with photocatalytic functionality, reflecting the trend toward multifunctional material design. By contrast, just one article investigated oleophobic–photocatalytic coatings, revealing a nascent yet largely unexplored niche that presents significant opportunities for future research and innovation. The bibliometric analysis was carried out using Biblioshiny, the user-friendly web interface of the R package (version 4.5.1) Bibliometrix (version 5.1.1). This tool facilitated advanced analyses, including co-authorship, co-citation, and thematic mapping, while providing high-quality visualizations that enhanced the robustness and reproducibility of the review.

3. Bibliometric Analysis

3.1. Thematic Landscape and Evolution of Research Fronts

Figure 1 presents a co-occurrence network where nodes represent terms computationally extracted from article abstracts, chosen for their high textual density in capturing thematic structures. Node size reflects the statistical weight of each term, based on frequency or relative importance, while links denote co-occurrence relationships, indicating how often terms appear together within the same abstract. The network reveals three dominant clusters (red, blue, and green), each representing a distinct thematic subdomain. The red cluster centers on photocatalytic activity, with terms such as 'methylene blue,' 'scanning electron microscopy,' 'contact angle,' and 'building materials,' highlighting performance evaluations of stone and cementitious substrates through pollutant degradation tests and surface characterisation. The blue cluster emphasises TiO_2, nitrogen oxides, relative humidity, and air pollution, reflecting research directed toward the environmental applications of TiO_2 photocatalysts in air quality improvement via photocatalytic oxidation. The green cluster is defined by terms such as photocatalytic efficiency, degradation efficiency, visible light, specific surface, and cement mortar, underlining performance optimisation of photocatalytic coatings when integrated into cement-based construction materials. Collectively, the clusters demonstrate a research trajectory that evolves from material property characterisation (red), through environmental functionality (blue), to practical application and efficiency in real-world construction contexts (green).

Figure 2 presents the thematic map, which classifies research themes according to their degree of development (density) and relevance to the field (centrality). The motor themes (top-right quadrant) encompass core topics such as TiO_2 nanoparticles, methylene blue, contact angle, scanning electron microscopy, and water absorption. These represent well-developed, highly central themes that serve as the field's primary drivers.

The basic themes (bottom-right quadrant) comprise two clusters. The first, including terms such as photocatalytic activity, building materials, photocatalytic coatings, degradation efficiency, visible light, cement-based materials, and mechanical properties, reflects applied research on coating performance, material properties, and integration into cementitious substrates. The second, containing terms such as TiO_2, photocatalytic efficiency, photocatalytic degradation, air purification, UV light, and TiO_2 coatings, is similarly central but less developed, pointing to foundational materials research (particularly TiO_2) and its role in pollutant degradation and air purification.

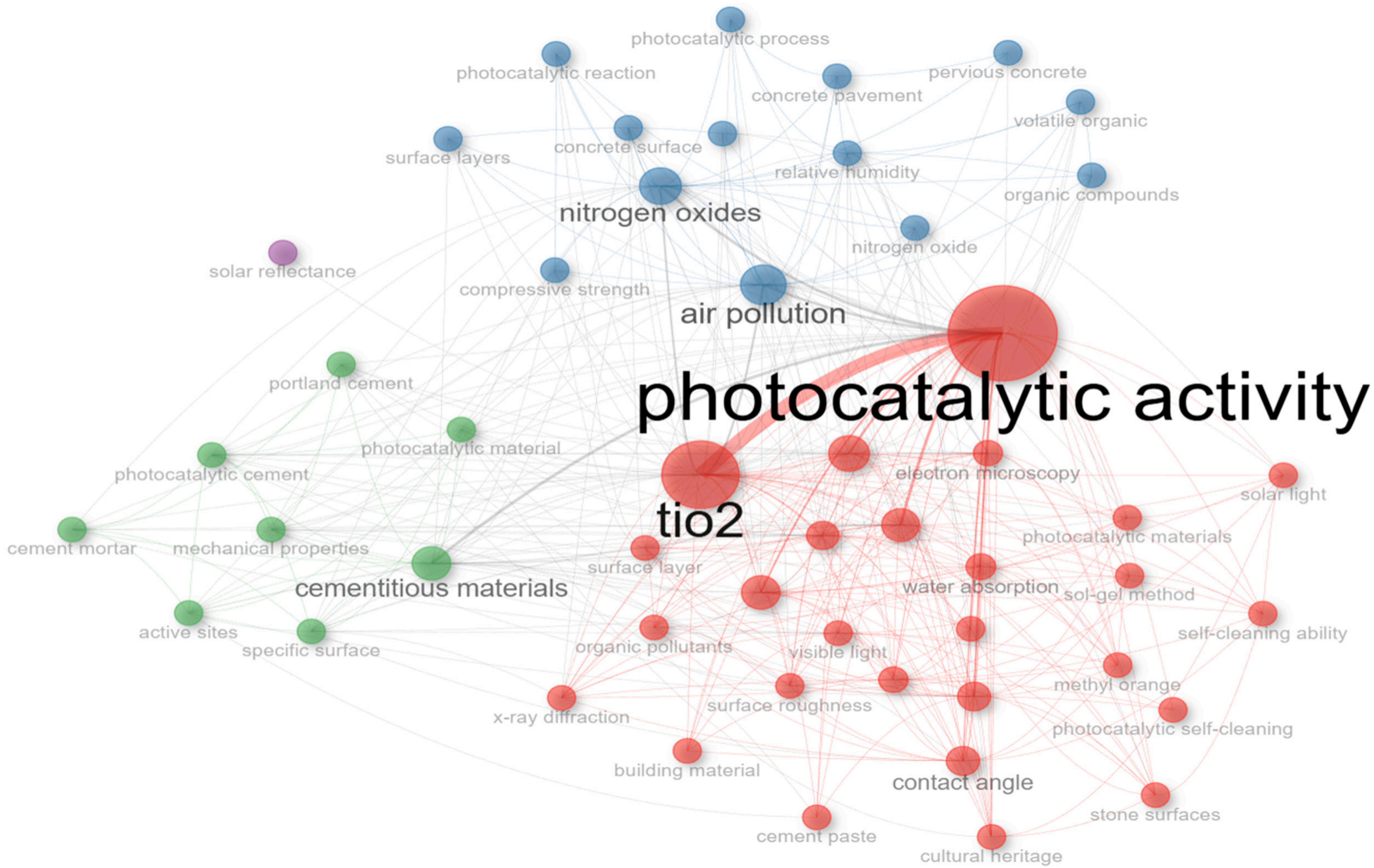


Figure 1. Keyword co-occurrence network based on simultaneous appearances within academic publications.

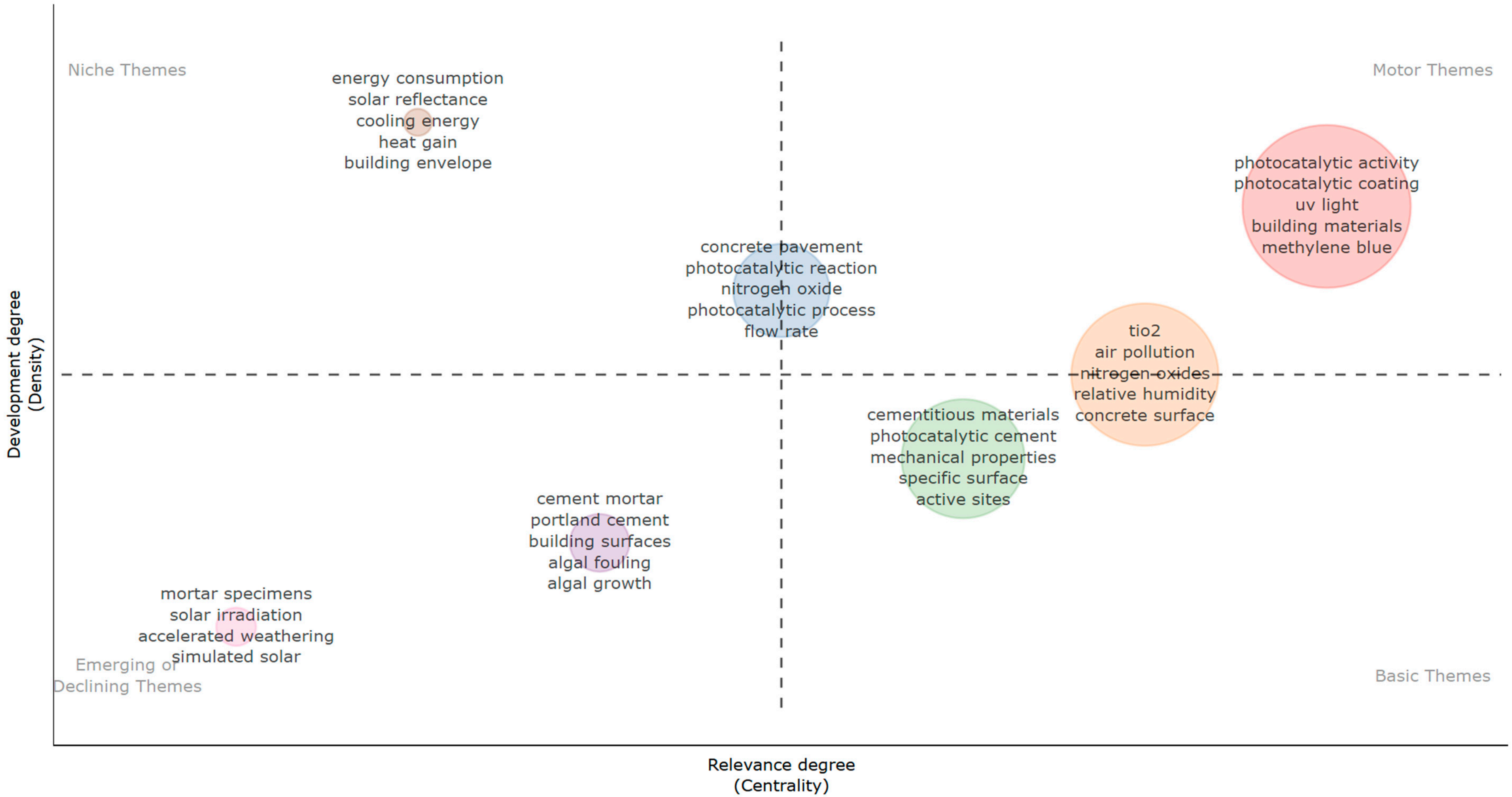


Figure 2. Thematic map within the research field.

The niche themes (top-left quadrant) include an energy-focused cluster, exploring photocatalytic coatings for building energy management, solar heat control, and cooling performance. Although peripheral to mainstream photocatalysis research, this cluster is highly cohesive and represents a mature research niche. Another niche cluster relates to environmental pollution, emphasising nitrogen oxide removal, air purification, concrete surfaces, and the influence of environmental factors such as humidity. While less central, this cluster is also well-developed and thematically self-contained.

The emerging or declining themes (bottom-left quadrant) involve terms associated with substrate durability and weathering, building surfaces, mortar specimens, solar irradiation, accelerated weathering, and simulated solar exposure. These areas remain underdeveloped and less central, suggesting either nascent lines of inquiry or declining research attention.

Overall, the thematic map highlights a well-established foundation in photocatalytic activity and TiO_2-based materials, alongside applied research on coatings for cementitious substrates. Mature but peripheral niches, such as energy efficiency and pollution control, reflect diversification into specialised applications, while underdeveloped themes on durability and weathering point to critical gaps. Together, these insights provide a roadmap for future research, balancing refinement of core themes with exploration of emerging challenges for real-world deployment.

Figure 3 illustrates the thematic evolution of research on photocatalytic coatings for construction materials, capturing shifts in dominant and emerging topics across two periods (2010–2019 and 2020–2025). During 2010–2019, the field concentrated on photocatalytic activity, photocatalytic coatings, TiO_2, nitrogen oxides, and air purification, reflecting foundational investigations into photocatalytic mechanisms, core materials, and environmental applications. As the foundational research on photocatalytic mechanisms and TiO_2-based systems became well understood, researchers began applying this knowledge to specific substrates and engineering contexts. Increasing environmental concerns, particularly related to urban air pollution and sustainable construction, stimulated demand for applied solutions, prompting a shift toward practical materials like concrete and cementitious surfaces. Also, progress in surface modification, nanostructuring, and hybrid material synthesis enabled the design of coatings with enhanced photocatalytic efficiency, durability, and hydrophobicity, supporting a move toward multifunctional applications. Thus, as a consequence by 2020–2025, the thematic emphasis expanded to cementitious materials, concrete surfaces, contact angle, and degradation efficiency, while photocatalytic activity remained central, increasingly examined in relation to applied performance and surface characteristics. The evolutionary links indicate how early research on photocatalytic activity and TiO_2 has converged toward applied studies focused on cement-based substrates, marking a clear transition from fundamental science to material-specific, performance-driven applications.

It can be concluded from the thematic evolution of research that there is a shift from mechanism-focused studies to application-oriented investigations, emphasising the enhancement of photocatalytic efficiency and the engineering of advanced coatings tailored for real-world cementitious and concrete surfaces. However, the durability and long-term performance of these building substrates remain underexplored and warrant increased attention. To drive impactful innovation in sustainable coatings for construction materials, future research must adopt an interdisciplinary framework that integrates fundamental photocatalytic mechanisms, environmental functionality, and practical material applications. These applications aim to enhance building surfaces with beneficial properties like self-cleaning, pollutant degradation (e.g., air purification), antibacterial effects, durability improvement, and resistance to environmental factors.

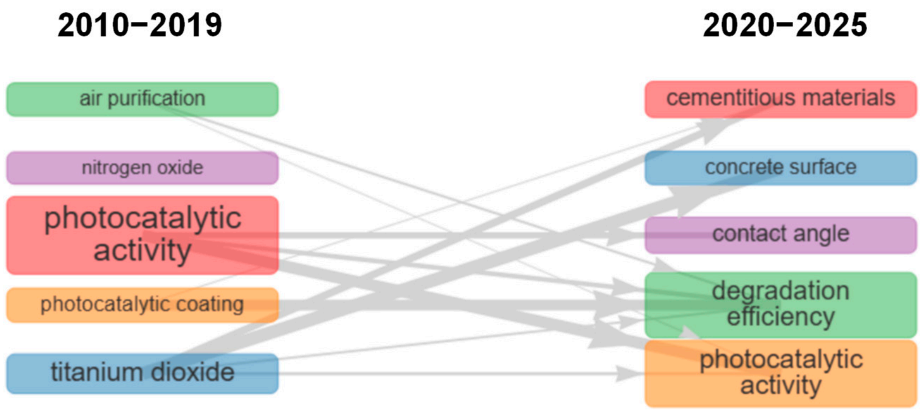


Figure 3. Thematic evolution of key research topics over time.

The thematic evolution of research indicates a clear transition from mechanism-focused studies to application-driven investigations, with growing emphasis on enhancing photocatalytic efficiency and engineering advanced coatings for cementitious and concrete surfaces. Yet, the durability and long-term performance of these substrates remain insufficiently explored, representing a critical research gap. Advancing sustainable coatings for construction materials will require an interdisciplinary approach that bridges fundamental photocatalytic science with environmental functionality and real-world material performance. Such efforts can reveal multifunctional benefits for building surfaces, including self-cleaning, pollutant degradation, antimicrobial protection, durability enhancement, and resilience against environmental pollutants.

Figure 4 presents a historiograph that traces the chronological citation relationships among publications on photocatalytic coatings applied to construction material carriers. It serves as a roadmap of scientific influence, illustrating how earlier contributions have shaped the current research landscape and guiding insights into the future direction of the field. Each red node denotes a first author with publication year (e.g., Hassan et al. [23]; Pinho and Mosquera [24]), with larger nodes reflecting more influential or frequently cited contributions. The connecting lines indicate direct citation links, visualising the flow of knowledge across time. The network progresses from earlier foundational works (2010–2012) at the top toward more recent studies (2018–2022) at the bottom, illustrating how pioneering studies [23,25] provided the conceptual basis for subsequent advances. More recent publications (e.g., Guo et al. [26], Pei et al. [27], Khannyra et al. [28]) highlight the field's ongoing evolution and its expansion into new directions. A summary of the globally highly cited articles, including their keywords, global and local citation scores, and research scope, was compiled to highlight thematic priorities in the field (Table 1). This structured overview serves as a reference point for future researchers, enabling them to identify foundational works, assess their broader and domain-specific impact, and recognise research gaps and opportunities for advancing the study of photocatalytic coatings in construction material. The summary highlights key opportunities in advancing photocatalytic coatings research: developing next-generation photocatalysts (doped TiO_2, heterojunctions, plasmonic and non-TiO_2 systems) for visible-light activity, creating hybrid multifunctional coatings with superhydrophobic/oleophobic properties, establishing standardised long-term field testing under real conditions, and extending applications to heritage preservation of stone materials.

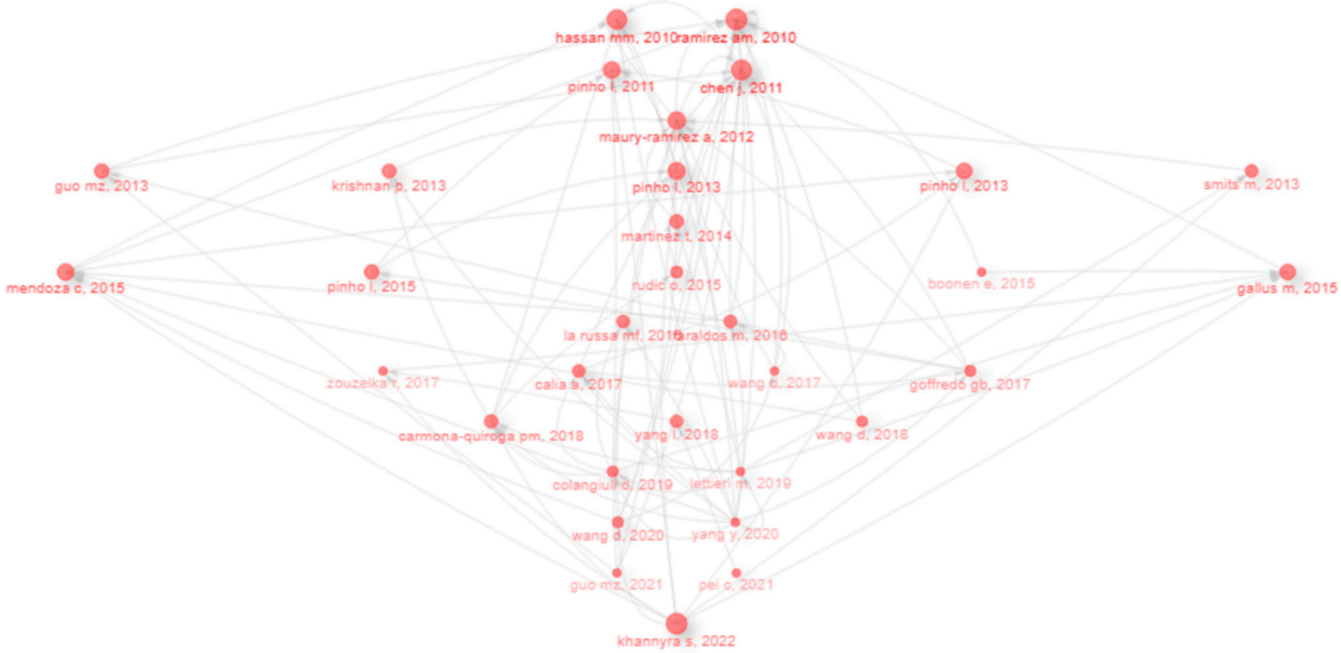


Figure 4. Historiograph within the research field.

Table 1. Top cited studies in photocatalytic coatings: keywords, citation indicators (* GCS: Global citation score; ** LCS: Local citation score), and scope.

Authors, Journal, Reference	Keywords	GCS *	LCS **	Scope
Hassan et al., Constr Build Mater 2010 [23],	Titanium dioxide; sustainable concrete pavement construction; photocatalyst; nitrogen oxides	186	25	Abrasion and wear resistance properties of TiO_2 coatings on concrete pavements, and NO_x removal efficiency of coatings
Ramirez et al., Build Environ 2010 [25]	Heterogeneous photocatalysis; titanium dioxide; cementitious materials; toluene; volatile organic compounds; air purification	163	30	Comparison of air purification potential (toluene removal efficiency) of dip-coated and sol–gel coated TiO_2 enriched concrete samples, and weathering resistance of the TiO_2 coatings loaded on cementitious materials
Pinho and Mosquera, Appl Catal B-Environ 2013 [29],	TiO_2 photocatalyst; mesoporous SiO_2 support; surfactant-synthesized; self-cleaning properties; building materials;	154	13	Synthesis of mesoporous TiO_2-SiO_2 photocatalytic coatings for stones (simple and low-cost process); self-cleaning performance of coatings evaluated
Chen et al., Build Environ, 2011 [30]	Photocatalytic cement-based materials; photocatalytic oxidation; air; pollution mitigation; self-cleaning	153	27	Air pollution mitigation (NO_x and VOC degradation) and self-cleaning (rhodamine B) performance of TiO_2 modified concrete surface layers
Zouzelka and Rathousky, Appl Catal B 2017 [31]	Photocatalysis; TiO_2; NOx; gaseous pollutants; air purification	140	4	Photocatalytic activity of the commercial products (Aeroxide TiO_2 P25 and Protectam FN2) based coatings on concrete blocks and plaster substrate with regard to NO and NO_2 abatement
Pinho and Mosquera, J Phys Chem C 2011 [24]	Crystalline TiO_2 particles; mesoporous silica; methylene-blue; thin-films; nanoparticles; nanomaterials	129	16	Titania-silica nanocomposite-based hydrophobic coatings for stones for self-cleaning action and to improve mechanical resistance

Table 1. *Cont.*

Authors, Journal, Reference	Keywords	GCS *	LCS **	Scope
Pinho et al., Appl Surf Sci 2013 [32]	Stone; non-ionic surfactant; TiO_2-SiO_2 nanocomposite; self-cleaning; agent; consolidant; salt-resistant product	107	17	TiO_2-SiO_2 nanocomposite coatings for self-cleaning action of friable carbonate stones, effect against salt crystallisation also investigated
La Russa et al., Prog Org Coat 2016 [33]	Nano-titanium dioxide; stone coating; built heritage; photodegradation	102	7	Nano-TiO2-based coatings for stone substrates extensively used in built heritage for hydrophobicity, durability and self-cleaning properties
Pinho et al., Appl Catal B-Environ 2015 [34]	Photocatalysis; mesoporous Ag-SiO_2-TiO_2 photocatalyst; Ag nanoparticles; surface plasmon resonance; self-cleaning	94	10	Ag-SiO_2-TiO_2 nanocomposite coatings for stone surfaces. Effect of varying the loading of TiO_2 (1% and 4% (*w*/*v*)) and Ag nanoparticles (1%, 5% and 10% (*w*/*w*) with respect to the TiO_2 content) in the network investigated
Yang et al., Appl Catal B-Environ 2018 [35]	Photocatalytic concrete; NOx; TiO_2 utilization; supported catalysis; cement environment	94	7	Comparison of conventional photocatalyst dispersion in surface mortar coatings versus supported on surface-exposed aggregates; durability of quartz-supported TiO_2 composites

3.2. Keyword Analysis: Frequency, Trends, and Research Dynamics

Table 2 lists the 30 most frequently occurring terms and their counts, extracted from article abstracts within the domain. For systematic interpretation, keywords are categorised into three frequency levels: highly frequent (≥40 occurrences) representing core areas of research, moderately frequent (20–39 occurrences) indicating supporting themes, and less frequent (<20 occurrences) reflecting emerging or specialized areas. The core keywords establish TiO_2 nanoparticles as the dominant photocatalyst, emphasising well-established themes on photocatalytic mechanisms, key materials, applications in building substrates, and performance metrics such as NOx removal and efficiency.

Supporting themes highlight growing attention to context-specific applications (e.g., cementitious materials), characterisation parameters (e.g., contact angle, visible-light activation), and extended performance indicators such as pollutant diversity and degradation efficiency, signifying areas of intensifying research depth.

The less frequent terms capture niche or emerging topics, linked to material durability and multifunctional attributes. While underexplored, these areas represent promising avenues for future innovation and expansion of photocatalytic coating research. Analysis of the less frequent terms reveals emerging and specialised directions within photocatalytic coatings research for cementitious materials. Keywords such as stone surfaces, photocatalytic concrete, concrete pavement, and cultural heritage highlight a growing emphasis on real-world applications in infrastructure and heritage conservation. Terms like mechanical properties, surface roughness, and specific surface indicate an increasing focus on the relationship between surface morphology and functional performance, emphasizing coating durability and optimization.

The appearance of sol–gel method and photocatalytic materials reflects ongoing innovation in synthesis routes and material formulations, aiming for scalable and cost-effective production. Meanwhile, organic pollutants denote a shift toward broader environmental remediation beyond traditional NO_x removal. Overall, these emerging topics suggest the field's evolution from laboratory-scale photocatalytic studies toward multifunctional, durable, and application-oriented coating systems for sustainable construction.

Figure 5 displays the 50 most frequent terms from the abstract in bibliometric data by representing them as slices of the pie-chart sized proportionally to their frequency or importance. The larger slices indicate higher frequency or dominance of a term, and the colours group related or individual items to allow quick visual identification of trends. The percentages represent the relative contribution of each keyword to the total set. For example, "photocatalytic activity" alone accounts for 19% of all keywords in this bibliometric dataset. The pie chart illustrates the proportional distribution of the most frequent terms associated with photocatalytic coatings research. The largest segment corresponds to "Photocatalytic activity" (19%), confirming its role as the core concept in this research area. It is followed by "TiO_2" (13%) and "Nitrogen oxides" (9%), indicating a dominant focus on TiO_2-based photocatalysts and their efficiency in air-pollution mitigation, particularly NO_x degradation. Mid-sized slices such as "Air pollution," "Cementitious materials," and "Photocatalytic coating" (each 4%) highlight the increasing integration of photocatalytic systems within construction materials for environmental remediation. Smaller segments (1%–3%), including terms like "Visible light," "Self-cleaning properties," "Cultural heritage," and "Concrete pavement", represent emerging or specialized research niches. These areas emphasize real-world performance, visible-light activation, and application in heritage conservation and sustainable urban infrastructure. Overall, the pie chart reflects a field strongly centered on TiO_2-based photocatalysis, yet gradually diversifying toward practical, material-integrated, and multifunctional applications in the built environment.

Figure 6 illustrates trends in photocatalysis research from 2010 to 2025, tracking cumulative occurrences of various topics and materials. Photocatalytic activity and TiO_2 dominate the field, showing the steepest and most consistent growth, indicating strong and sustained research interest. Nitrogen oxides and general air pollution show moderate increases, reflecting ongoing environmental and regulatory concerns. Other areas, such as building materials, photocatalytic coatings, and cementitious materials, display slower but steady growth, suggesting a gradual shift toward practical applications. Methylene Blue, used as a model pollutant in laboratory studies, receives minimal attention compared to real-world applications. Overall, the graph highlights a clear trend of increasing attention to photocatalytic research over the past 15 years, with focus expanding from general activity studies toward material-specific and application-oriented studies. Emerging areas like photocatalytic coatings and concrete-related materials indicate growing interest in translating lab research into practical environmental solutions.

Table 2. Top recurring terms in photocatalytic coatings research, their frequency of occurrence, and some illustrative references.

Words	Frequency	References	Words	Frequency	References	Words	Frequency	References
Photocatalytic activity	310	[7,9,26–31,36–39]	Visible light	33	[40–45]	Mechanical properties	17	[37,41,44]
TiO_2	210	[8,17,27–29,32,38,46–53]	Contact angle	32	[36,54–56]	Stone surfaces	17	[41,54,57–60]
Nitrogen oxides	140	[30,46,47,61–65]	Self-cleaning properties	32	[38,40,54,56,62,66–68]	Photocatalytic concrete	15	[43,69–73]
Photocatalytic coating	71	[40,62,66,67]	Surface layer	27	[1,19,46,47,74]	Concrete pavement	14	[23,75–77]
Air pollution	68	[36,38,44,47,77]	Relative humidity	24	[46,76,78]	Organic pollutants	14	[37,42,75,77–79]
Cementitious materials	63	[38,42,49,64,65,80,81]	Cement mortar	23	[37,46,48,70]	Photocatalytic materials	14	[7,9,26–28,46]
Electron microscopy (SEM)	55	[37,46,48,54,61,63]	Water absorption	23	[18,48,49]	Specific surface area	14	[54,61,66,78]
Building materials	48	[40,42,43,45,70,79]	Concrete surface	22	[44,61,66,77]	Surface roughness	14	[37,54,58,67,78]
Methylene blue	43	[36–38,55]	Photocatalytic cement	20	[26,27,30,75]	Cement paste	12	[10,40,75]
UV light	42	[44,46,47,56,64,69]	Cultural heritage	17	[56–59,63,79]	Sol–gel method	12	[54,57,78]

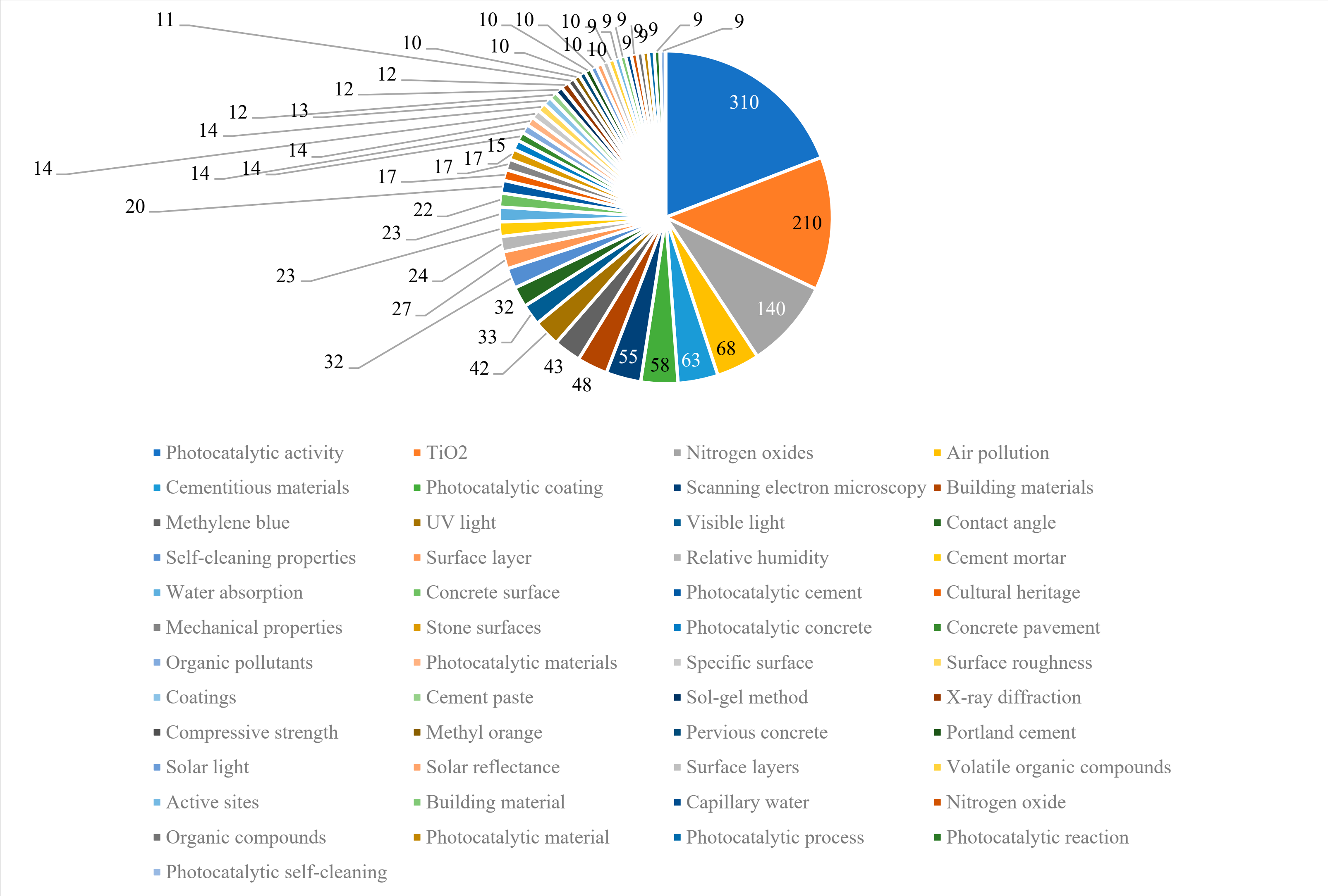


Figure 5. Pie chart showing the prominence of research themes.

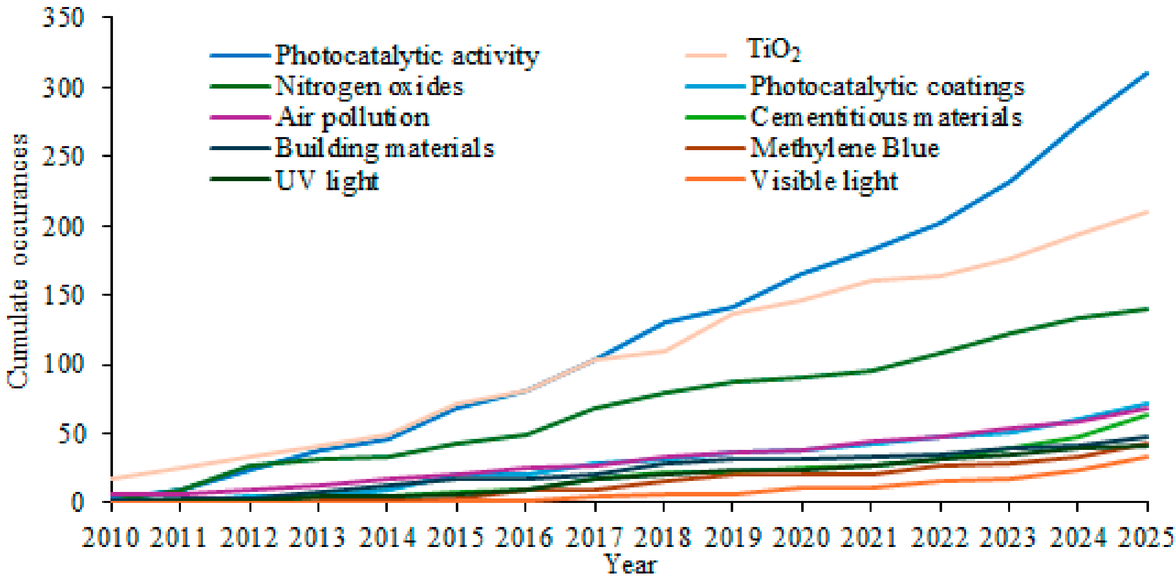


Figure 6. Word frequency over time.

Figure 7 provides a chronological framework that traces the evolution, maturation, and emergence of research themes across the field. In the phase 2012–2016, topics like NOx removal efficiency, photocatalytic asphalt pavements, concrete surface layers, and organic/volatile organic compounds show the initial research push. The research in this phase laid the groundwork for photocatalytic coatings on construction material carriers by demonstrating their feasibility in real-world contexts. Initial studies, largely between 2012 and 2016, focused on NOx abatement, photocatalytic asphalt pavements, and concrete surface layers.

These investigations validated construction substrates such as asphalt pavements as viable carriers for TiO_2-based coatings, while simultaneously establishing performance benchmarks in pollutant removal, surface hydrophilicity, and durability. The phase (2016–2019) represents a pivotal stage in the development of photocatalytic coatings on construction material carriers. During this period, research shifted from demonstrating pollutant degradation in model systems toward systematically applying TiO_2-based coatings onto real substrates such as decorative concrete surface and concrete surface layers. The focus expanded to evaluating coating–substrate interactions through durability and surface property assessments, including capillary water absorption, contact angle measurements, and porosity analyses. Advanced characterisation techniques (e.g., SEM, XRD, EDS) were widely employed to examine coating morphology, adhesion, and stability on construction materials. The recent phase (2020–2024) reveals a decisive shift toward real-world implementation. This evolution is particularly evident in the growing emphasis on photocatalytic cementitious materials, visible-light irradiation, surface wettability (contact angle), and long-term photocatalytic performance. These topics show the field is moving into innovation for practical deployment.

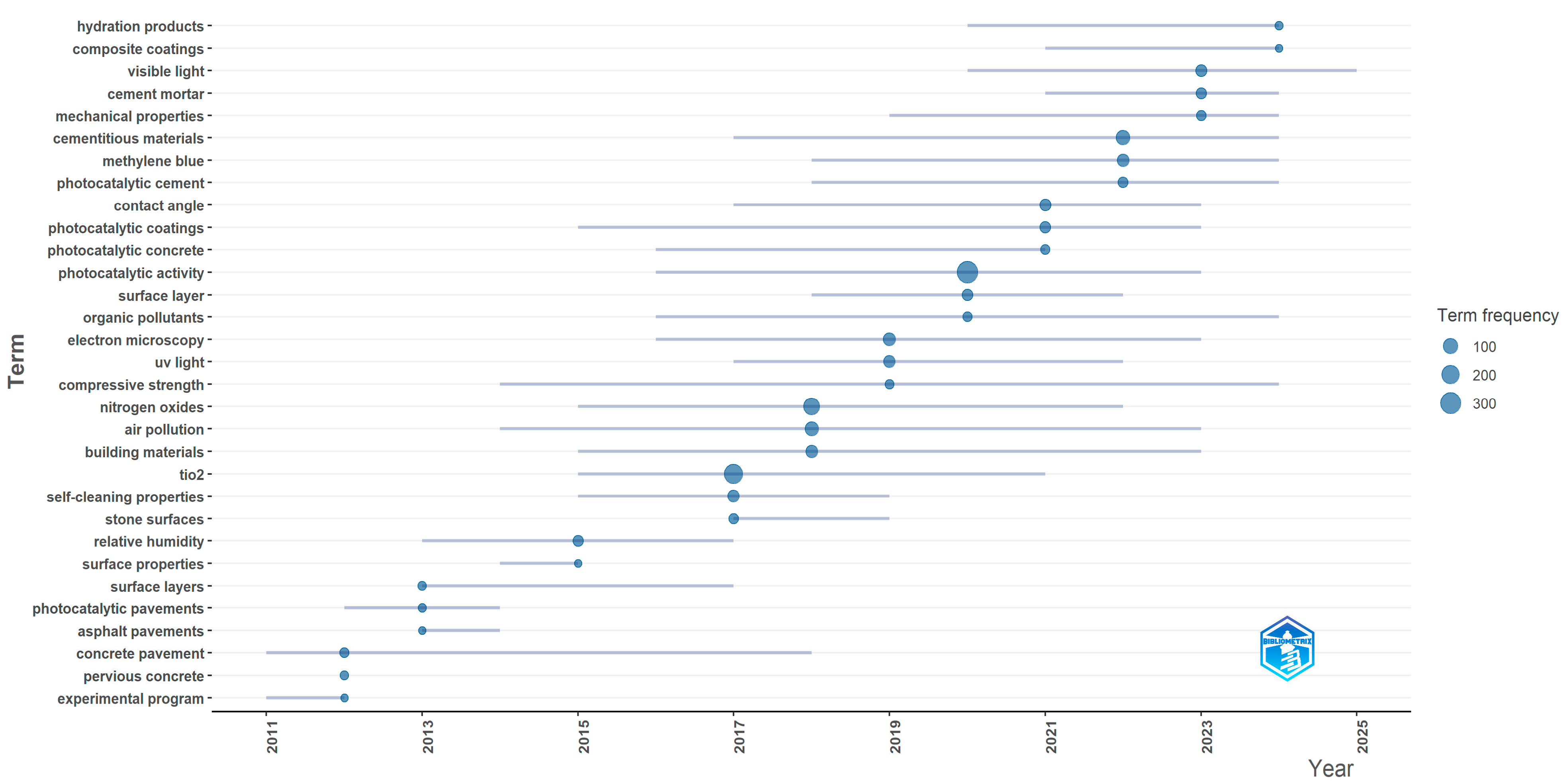
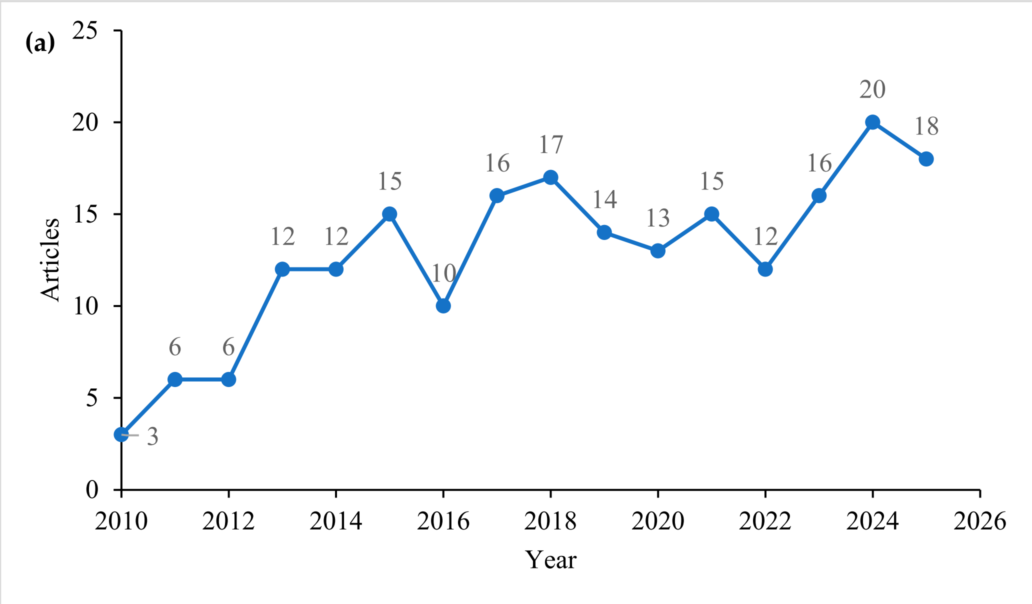


Figure 7. Trending topics—time series analysis.

3.3. Annual Scientific Production and Average Article Citation per Year

The publication trend on photocatalytic coatings (2010–2025) reveals a consistent upward trajectory with intermittent fluctuations (Figure 8a). Early research output was limited, with only a few publications annually until 2012, after which steady growth emerged, indicating increasing scientific interest and technological advancements. Temporary declines around 2016 and again between 2019 and 2022 likely reflect variations in research cycles or external factors; however, the overall progression remained positive. A marked surge in 2024–2025, approaching 20 publications per year, underscores an acceleration of scholarly activity driven by emerging innovations and broadening practical applications.



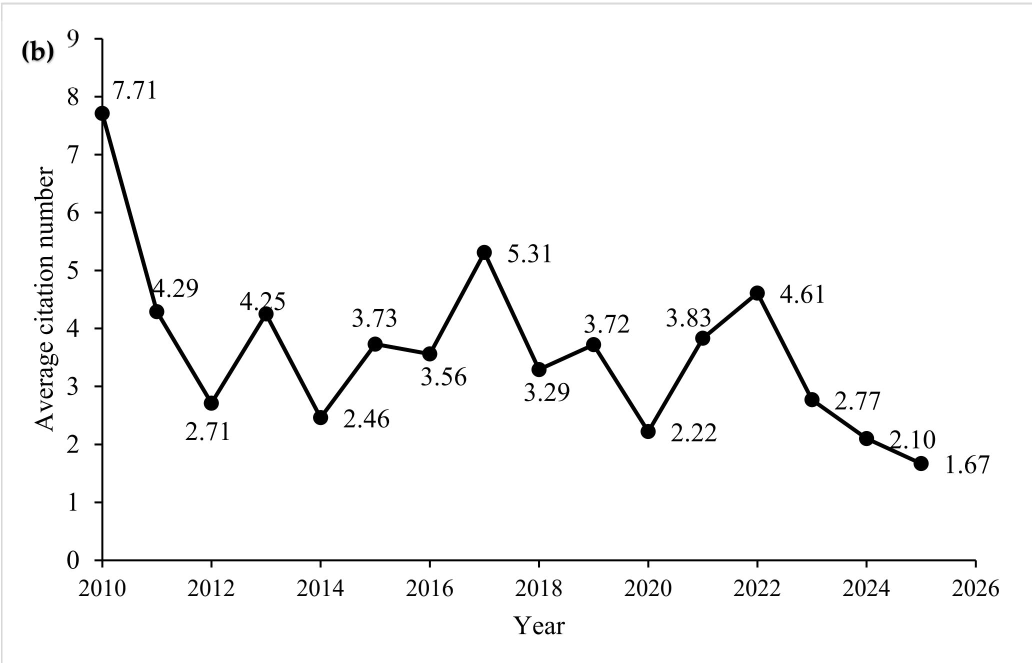


Figure 8. (**a**) Annual scientific production and (**b**) average article citation per year statistics from 2010 till 2025.

Figure 8b illustrates the average annual citations of publications on photocatalytic coatings between 2010 and 2025. The early phase, around 2010, recorded notably high citation rates, suggesting that pioneering studies quickly attracted substantial scholarly attention. Citation activity fluctuated over time, reflecting variations in research impact, publication output, and thematic emphasis, with distinct peaks in 2013, 2017, and 2022 marking periods of heightened influence. The apparent decline after 2022 is attributable to citation lag, as recent publications have had limited time to accrue citations. Collectively, these trends underscore sustained academic interest and dynamic shifts in the research landscape of photocatalytic coatings across the 15-year period.

3.4. Scientific Production by Country: Most Cited Countries

Table 3 presents the contributions of the ten leading countries in scientific output on photocatalytic coatings for construction materials, while Figure 9 illustrates the chronological progression of their research productivity. The dominance of China correlates with the country's push for environmental remediation technologies to address severe urban air pollution. Since 2013, China has enforced robust environmental policies, including air pollution prevention plans, environmental laws, and Paris Agreement commitments, that have spurred advanced research in environmental remediation technologies. The 2013 Air Pollution Prevention and Control Action Plan targeted severe urban pollution, complemented by stringent regulations and tax laws, fostering extensive R&D in photocatalytic materials for reducing nitrogen oxides and particulate matter [36]. These efforts have positioned China as a global leader in photocatalysis research output. European countries like Portugal, Spain, and Italy have focused research on sustainable building materials integrating photocatalysis, balancing environmental goals with construction industry requirements, supported by large-scale projects such as the European Light2CAT initiative focusing on visible-light activated TiO_2 photocatalytic concretes for air purification. Light2CAT aims to create visible-light-activated titanium dioxide concretes that improve air quality across Europe, regardless of local climate. Mexico and India show rising contributions, suggesting growing interest in applying photocatalytic coatings to address urban pollution and sustainability challenges in rapidly developing regions. This distribution suggests that research leadership is concentrated in China and Southern Europe, with strong emerging participation from Asia (South Korea, India) and Latin America (Mexico). Table 3 also reveals the top ten most cited countries. It reveals that while China dominates in total production, European countries and the USA set benchmarks for research influence and citation impact, shaping the scientific discourse around photocatalytic coatings on construction materials.

Table 3. Frequency of publications and total citations.

Countries	Frequency	Total Citations	Average Article Citations
China	213	1253	19.90
Italy	96	736	28.30
Spain	64	1010	56.10
USA	61	638	35.40
Portugal	34	-	-
Belgium	31	447	55.90
Republic of Korea	27	-	-
France	26	-	-
Mexico	21	-	-
India	20	-	-

Table 3. *Cont.*

Countries	Frequency	Total Citations	Average Article Citations
United Kingdom	-	189	47.20
Czech Republic	-	141	47.00
Serbia	-	128	21.30
Germany	-	123	41.00
Iran	-	122	17.40

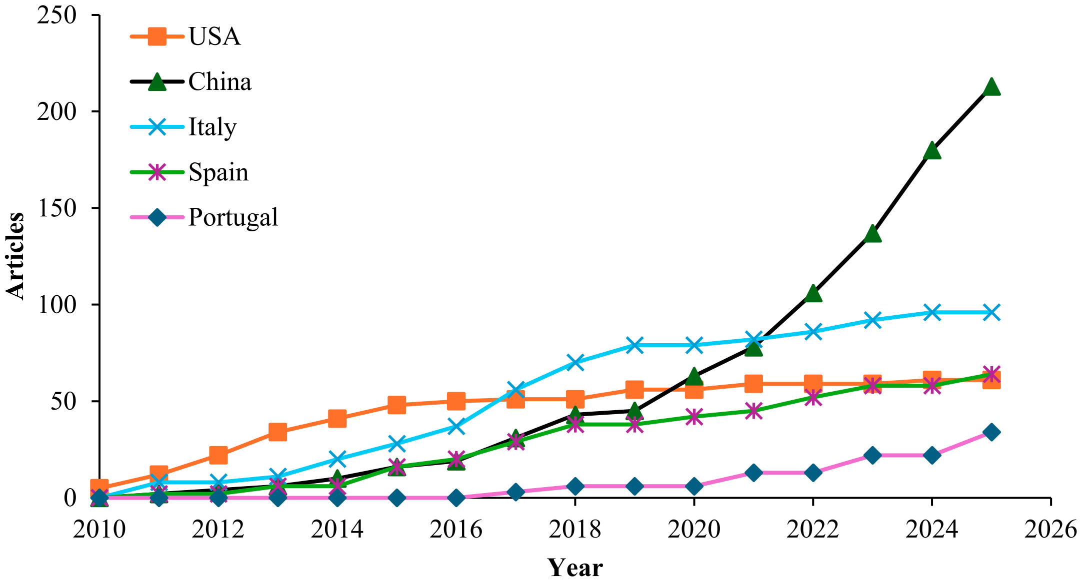


Figure 9. Countries' production over time within the research field.

Figure 10, a three-field plot (Source-Keyword-Country), captures the multidisciplinary and global evolution of research on photocatalytic coatings for construction materials. Leading journals in materials science and nanotechnology (e.g., Applied Surface Science, ACS; Applied Materials & Interfaces; and Ceramics International) anchor the field's foundations, while outlets in civil and construction engineering (e.g., Journal of Building Engineering, Cement & Concrete Composites, and Construction and Building Materials) highlight its transition toward practical applications. Core themes such as TiO_2-based photocatalysis, self-cleaning, NOx removal, durability, and air purification highlight the field's dual focus on material innovation and urban sustainability, with applications extending from modern infrastructure to heritage preservation. Geographically, China, Italy, Spain, and the USA dominate both fundamental and applied research, while European countries like Belgium, Portugal, France, and Germany emphasise specialised, impact-driven themes. Emerging contributors, including Mexico, Iran, India, and Serbia, signal a broadening of participation, often addressing regional sustainability challenges.

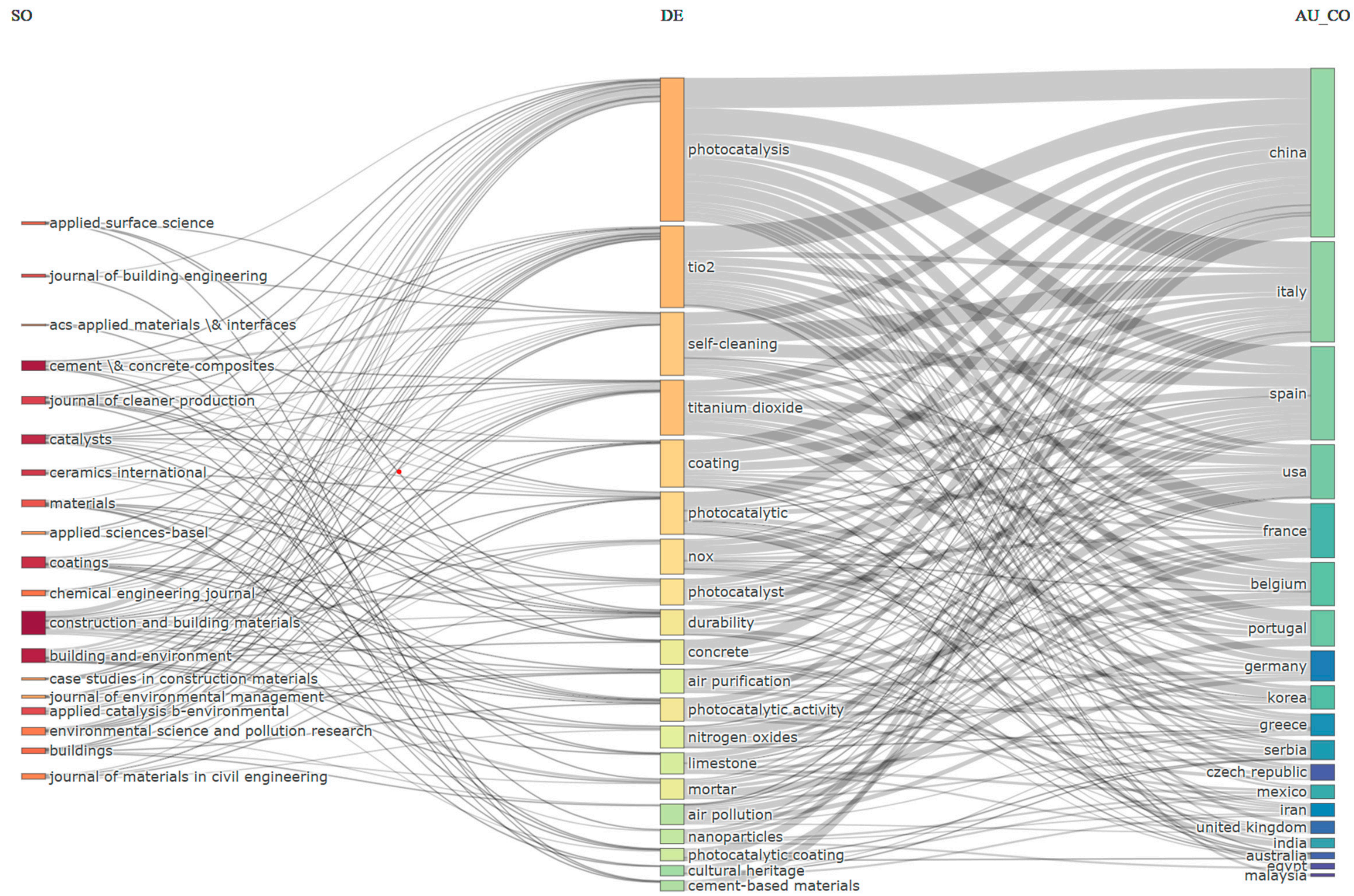


Figure 10. Three fields plot between source field (SO), abstract (DE) and country (AU_CO).

3.5. Social Structure: Collaboration Network and Country Collaboration World Map

Figure 11 presents the international collaboration network among countries engaged in research on photocatalytic coatings for building materials. Each node represents a contributing country, with its size proportional to either publication output or centrality within the network. China and Italy emerge with the largest nodes, reflecting their leading roles and strong influence in advancing this research area. Links between nodes indicate international co-authorships, and link thickness denotes collaboration strength, with a particularly strong partnership visible between China and Australia.

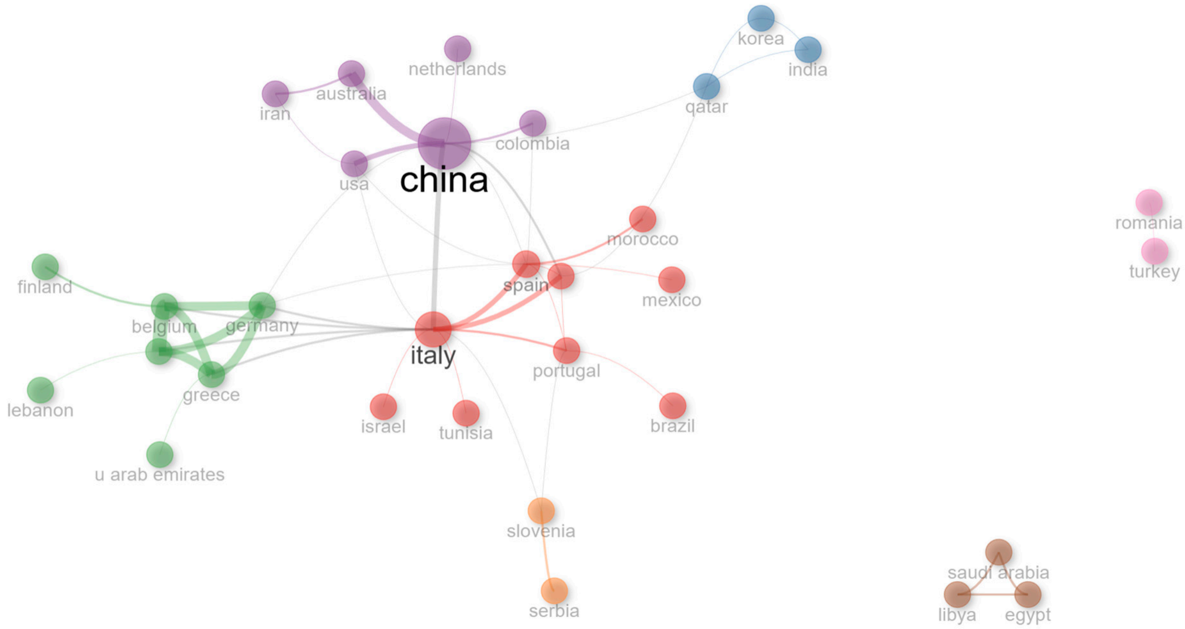


Figure 11. International collaboration network among countries.

The network is organised into six distinct clusters, each representing a sub-community of countries with stronger internal than external collaboration ties. The purple cluster, comprising China, USA, Iran, Australia, Netherlands, and Colombia, forms a major global hub of collaboration. The red cluster, which includes Italy, Spain, Portugal, UK, Israel, Tunisia, Morocco, Mexico, Brazil, Slovenia, and Serbia, reflects a strong European–Mediterranean alliance. The green cluster, encompassing Germany, France, Greece, Belgium, Finland, UAE, and Lebanon, highlights a European–Middle Eastern collaboration axis.

Overall, collaboration network highlights China and Italy act as central hubs of international cooperation in this domain, while the USA, Spain, Germany, and France serve as important bridging countries fostering cross-regional linkages. Although regional clusters (Europe, Asia, Middle East) dominate the structure, certain nations remain relatively peripheral, engaging in limited inter-regional collaborations.

Future studies or new researchers may prioritise building collaborations with leading research hubs such as China and Italy, while simultaneously fostering connections with underrepresented regions. Such efforts would not only enhance individual scientific visibility but also reinforce the global research landscape on photocatalytic coatings for construction materials through new interdisciplinary and geographic linkages.

3.6. Clustering by Coupling

Table 4 outlines the thematic clustering analysis by coupling groups, mapping the research landscape of photocatalytic coatings applied to construction materials based on shared references. It categorises keywords into distinct clusters driven by metrics of frequency, centrality, and scholarly impact. This analysis highlights core applications, fundamental research backbones, niche innovations, and emerging frontiers, offering a roadmap for future exploration in the field. The clustering analysis reveals core applications (Group 1) emphasising self-cleaning, durability, and heritage conservation, establishing well-validated practical uses. The fundamental backbone research (Group 2) centres on TiO_2-based photocatalysis for NOx removal and air purification, representing both the most frequent and influential cluster. The niche innovations (Group 3) explore adhesion mechanisms, aging, and visible-light-active photocatalysts, offering high-impact yet specialised advances. Finally, the emerging frontiers (Groups 4–10) reflect nascent or experimental themes, ranging from novel composites, multifunctional anticorrosion systems, and superhydrophobicity to photocatalytic CO_2 reduction, highlighting directions that may shape future interdisciplinary breakthroughs.

Table 4. Thematic clustering of research on photocatalytic coatings in construction materials based on shared references.

Group	Label (Themes Grouped Under a Cluster)	Frequency	Centrality	Impact	Remarks
1	Self-cleaning, coating, limestone, cultural heritage, durability, biocide	54	0.596	1.92	- High centrality & good impact - Core applications of photocatalytic coatings in construction, especially heritage conservation and durability enhancement. - Researchers should continue exploring practical, real-world uses
2	Titanium dioxide (TiO_2), air purification, NO_x removal, mortar	123	0.512	1.837	- Largest cluster, high frequency and centrality - This is the fundamental backbone of research (TiO_2 for air purification) - Future researchers could focus on improving efficiency, scaling applications, or testing alternative photocatalysts.
3	Adhesion mechanism, visible light photocatalysis, aging, $BiVO_4$, agglomeration control	15	0.247	2.07	- Low centrality but high impact - Opportunities for innovation, especially in mechanistic studies, durability under real conditions, and visible-light-active photocatalysts.
4	Cement-based, piezo-phototronic effect, novel composites (ZnO/BiOCl, Ta-PEI-Ti)	2	0.133	1.2	- Low frequency, low centrality, moderate impact - Very nascent area, but could open new interdisciplinary directions (piezo-phototronic and composite photocatalysts in cement). - Needs more exploration
5	Anticorrosion, multifunctional coatings, nanoparticles, superhydrophobic organic coatings	1	0.099	0	- Isolated theme with no strong impact yet - Emerging experimental direction (anticorrosion + photocatalysis) - Researchers could pioneer this as a new multifunctional application area

Table 4. *Cont.*

Group	Label (Themes Grouped Under a Cluster)	Frequency	Centrality	Impact	Remarks
6	Hydrothermal carbonization, phosphorus, super-hydrophobicity	1	0.192	1.2	- Low frequency, low centrality, exploratory themes - These are frontier or emerging themes, often experimental or interdisciplinary. - They lack integration now but could represent future breakthroughs if developed
7	Prefabricated building, SiO_2 composites	1	0.086	0	
8	Alkali-activated cementitious materials, formaldehyde removal	1	0.095	0	
9	CO_2 reduction, perovskites, formic acid production	1	0.078	0	
10	Black carbon, cooling energy, solar reflectance	1	0.098	0	

3.7. Top Ten Most Cited Research Papers Globally

3.7.1. Publications on Photocatalytic Coatings

Table 5 highlights the scope and key findings of highly influential publications that have shaped the research landscape on photocatalytic coatings for construction materials by their citation impact. This concise yet comprehensive summary provides researchers with a clear overview of the most impactful studies in the field. As outlined in Table 5, earlier research exhibits considerable diversity in photocatalyst formulations, substrate materials, coating application techniques, and evaluation criteria. Ramírez et al. [25], fabricated TiO_2 coatings by immersing cementitious substrates in a sol–gel solution for 5 min, followed by drying (125 °C, 12 h) and calcination (450 °C, 5 h). The authors concluded that sol–gel coatings on cementitious substrates exhibited negligible toluene removal, likely due to reduced active surface area and ionic species that promote charge recombination. However, dip-coated cementitious samples demonstrated markedly higher efficiencies (41%–86%). The porosity of cementitious substrate emerged as a key parameter governing efficient air purification performance, outweighing the influence of surface roughness [25]. On the other hand, Hassan et al. [23], applied a 10 mm-thick surface layer comprising ultrafine TiO_2 in two variations (i.e., 3% and 5% by weight of cement) cement, sand, and water onto cured concrete. In terms of air purification performance, the coating with a higher TiO_2 content (5%) exhibited greater NO removal efficiency (27%) compared to 3% TiO2 coating (18%). The wearing of the samples with 5% TiO2 resulted in a small decrease in the coating NO removal efficiency (26.9% for the original samples vs. 22.4% for the rotary abrasion samples and 23.4% for the loaded-wheel test samples). On the other hand, the wearing of the samples with 3% TiO_2 slightly improved the NO removal efficiency (18.0% for the original samples vs. 21.4% for the rotary abrasion samples and 24.8% for the loaded-wheel test samples). Chen et al. [30], developed self-compacting cementitious mortars incorporating TiO_2 and demonstrated that, while NO removal by TiO_2-modified concrete surfaces was highly effective, toluene conversion was undetectable, emphasising that toluene is an unreliable indicator of photocatalytic performance under typical outdoor conditions. Under UV irradiation, the 5% TiO_2 sample exhibited a significantly higher rhodamine B discoloration rate than the 2% sample within the first 2 h; thereafter, both samples showed nearly constant rates. Conversely, under intense halogen light, discoloration persisted, but increasing TiO_2 content from 2% to 5% had minimal impact, revealing a strong light-source dependency in the photocatalytic response. Ling and Poon [40], investigated NO abatement using a 5 mm-thick TiO_2-intermixed cement mortar surface layer containing 5 wt% TiO_2 (by cementitious material) applied over a concrete substrate. Following 60 min of UV irradiation, TiO_2-based surface layers incorporating 50% and 100% CRT glass achieved 5% and 7% higher NO removal efficiencies, respectively, compared to the control mix. Guo et al. [46], established that TiO_2 spray-coated cementitious surface layers exhibited markedly superior NOx removal efficiency and reaction rates compared to those incorporating 5% TiO_2 by intermixing. Furthermore, the spray-coated samples maintained exceptional durability, preserving significantly higher photocatalytic performance even after 500 abrasion cycles, emphasising their enhanced functional resilience and long-term effectiveness. Zouzelka and Rathouský [31], employed spray-coating of cementitious substrates with a TiO_2-based commercial product, FN2, which is 74% TiO_2 with 26% binder, and demonstrated the photocatalytic performance of the coated samples under diverse testing conditions that simulated real-world conditions in comparison to control (100% TiO_2). They concluded that FN2 coating exhibited enhanced activity in the visible spectrum, owing to binder–TiO_2 interactions that facilitate electron–hole pair generation under longer-wavelength irradiation. Under steady-state conditions with inlet concentrations of 0.1 ppmv NO and NO_2, representative of heavily polluted urban air, the reaction rates reached up to 75 and 50 μmol m^{-2} h^{-1}, respectively. Unlike 100% TiO_2 coatings, which relies on weak electrostatic attachment, the FN2 coating ensures robust adhesion to construction substrates, enhancing strength and durability. It is well established in the literature that the long-term durability of such coatings cannot be guaranteed, as TiO_2 particles deposited on building materials are prone to detachment due to environmental factors and mechanical degradation mechanisms. The commercial titania dispersions in water fail to form adherent coatings on stone, rendering them ineffective for practical applications. Pinho and Mosquera [24], developed titania–silica nanocomposite coatings for stone conservation, demonstrating that formulations incorporating titania–silica–octylamine achieved superior functional performance by generating homogeneous, crack-free films with enhanced mechanical strength, increased hydrophobicity, and improved self-cleaning capability. These n-octylamine-modified coatings mitigate crack-inducing capillary pressures and facilitate silica polymerization within the stone's pore network, thereby enhancing its mechanical strength, and further promote self-cleaning efficiency through the development of a highly porous gel network with enlarged pore structures. Pinho and Mosquera [29], proposed immobilising the photocatalyst within a SiO_2 matrix to prevent its release into the environment. The approach involves a colloidal dispersion of pre-formed titania nanoparticles within a sol of silica oligomers, stabilised by the surfactant n-octylamine, and applied to stone surfaces via an aerosol-assisted process. The authors concluded that while the incorporation of larger, sharper titania particles at 4% (w/v) enhances self-cleaning effectiveness by increasing the availability of surface photoactive sites, further increasing the titania content to 10% (w/v) reduces photocatalytic activity due to a drastic loss of porous volume that limits site accessibility. The titania–silica nanocomposites-based coatings not only impart self-cleaning functionality and enhance the mechanical strength [24,29] but also improves the durability of stone substrates. The impact of environmental factors on the performance and durability of photocatalytic coatings is a critical consideration for their real-world application. Coatings based on TiO_2-SiO_2 nanocomposites have been shown to improve both photocatalytic performance and durability, as silica provides a stabilising matrix that enhances mechanical integrity and particle adhesion. For instance, stones treated with TiO_2-SiO_2 nanocomposites remained virtually unaltered after 30 cycles of Na_2SO_4 crystallisation, whereas untreated stones disintegrated into powder after only three cycles [29].

While TiO_2 remains the predominant photocatalyst in the literature, increasing attention is being directed toward alternative materials for multifunctional coatings. Sierra-Fernandez et al. [37], synthesised Zn-doped MgO nanoparticles and demonstrated their superior performance on stone substrates: after 60 min of UV irradiation, they achieved 87% methylene blue degradation, compared with 58% for ZnO and 38% for MgO, while also markedly suppressing fungal colonization.

The prominence of recent highly cited studies [31,37,46] in Table 5 highlights a growing research shift toward doped and alternative photocatalysts beyond TiO_2, alongside increasing emphasis on spray-coated applications for cementitious substrates and the durability of these functional surfaces.

In short, it can be concluded from the aforementioned studies that the evolution of TiO_2-based coating technologies reveals a clear shift toward optimizing photocatalytic efficiency, durability, and substrate compatibility through advanced material design and deposition strategies. Future research should focus on integrating TiO_2 with multifunctional matrices and hybrid systems—such as silica, alumina, or doped oxide frameworks—to enhance mechanical robustness, adhesion, and long-term environmental stability. While sol–gel and dip-coating methods have demonstrated varying photocatalytic responses depending on substrate porosity and surface chemistry, scalable and uniform deposition routes such as spray-coating and aerosol-assisted processes warrant greater exploration for practical construction applications. The development of nanocomposite coatings, particularly TiO_2-SiO_2 systems modified with organic surfactants or functional dopants, presents a promising avenue for achieving crack-free films with enhanced self-cleaning capability and hydrophobicity, while minimizing photocatalyst leaching. Moreover, deeper investigation into light-source dependency, especially under visible-light or low-UV conditions, is essential to broaden applicability under real-world illumination. The coupling of TiO_2 with plasmonic metals, carbonaceous materials, or narrow-bandgap semiconductors could further extend photocatalytic activity into the visible spectrum. Standardized long-term durability testing under realistic environmental stressors—including abrasion, pollution exposure, and weathering cycles—remains critical to validate coating performance beyond laboratory conditions. Finally, as sustainability and safety become central to material design, future work should explore eco-friendly synthesis routes, low-VOC formulations, and photocatalysts with reduced environmental release potential, while assessing alternative oxide systems (e.g., Zn-doped MgO or ZnO-based composites) for multifunctional air-purifying, antimicrobial, and self-cleaning performance.

Table 5. Top ten globally cited articles on photocatalytic coatings applied to building material substrates.

Authors, Journal, Reference	Total Citation	Scope	Coating Composition and Application Techniques	Concluding Remarks
Hassan et al., Constr. Build. Mater. 2010 [23]	186	- Environmental performance (NO_x removal efficiency) of TiO_2 coating before and after laboratory-simulated abrasion and wearing.	- Composition: Ultrafine TiO_2, cement, fine sand (≤1.18 mm), filler, water-coating prepared at 0.6 water-cement ratio - TiO_2 loading: 3% to 5% by weight of cement - Substrate-Concrete blocks (305 mm × 381 mm × 25.4 mm) in size	- TiO_2 coating offers good photocatalytic durability and wear resistance. - The Ti concentration on worn specimens remained nearly unchanged from the originals. - TiO_2 coating at a 5% content had more NO removal efficiency than that of 3% (i.e., 27% vs. 18.0%). - The wearing of the samples with 3% TiO_2 slightly improved the NO removal efficiency in contrast to 5% TiO_2.
Ramirez et al., Build. Environ. 2010 [25]	163	- Photocatalytic toluene degradation of TiO_2 dip-coated or enriched concrete (sol–gel method) - Weathering resistance of TiO_2 coatings exposed to different abrasive conditions - Comparison of coating techniques (dip-coated and sol-gel coated TiO_2)	- Composition: TiO_2 dip-coating, a suspension of ethanol and TiO_2 (0.05 g/mL), and sol–gel method, a mixture of titanium diisopropoxide bis (acetylonate) (24 mL), isopropanol (171 mL) and water (5 mL) - Types of substrates: Commercial cementitious materials including both concrete and plaster materials-dip coated, and commercial autoclaved white concrete and concrete tiles varying in finishing techniques–coated using both dip-coating and sol–gel methods	- Under UV irradiation, dip-coated concrete achieved toluene removal up to 86% under lab-scale ambient conditions. - Sol-gel coatings on cementitious substrates exhibited negligible toluene removal. - Substrate porosity and roughness are key factors for efficient air purification, with higher porosity giving better results. - In terms of weathering resistance, TiO_2 dip-coated plaster (made of white cement, a polymer, crushed limestone, and an inorganic pigment) proved the most efficient among the tested materials.
Pinho and Mosquera, Appl. Catal. B-Environ. 2013 [29]	154	- Mesostructured titania or TiO_2 incorporated in mesoporous SiO_2 matrix - TiO_2-SiO_2 nanocomposites for long-term self-cleaning and strengthening properties of stone substratum. - Simple and low-cost process to synthesise mesoporous TiO_2-SiO_2 photocatalytic coatings	- Composition: A colloidal system comprising pre-formed titania nanoparticles embedded in a silica oligomer sol, stabilized by the surfactant n-octylamine. - TiO_2 loading in silica matrix: Titania particles (average particle size of 20 µm, 21 nm and 14 nm) used loaded in a silica network in different proportions—1%, 4% and 10% (*w*/*v*) - Substrates: Stone substratum (pure limestone), spray coated	- TiO_2 particle size and shape critically influence the photocatalytic activity of the nanocomposites. - Embedding larger, sharper titania particles (~4% *w*/*v*) in a silica network enhances self-cleaning by increasing surface photoactive sites. - At 10% titania loading, the photocatalytic activity decreases due to reduced pore volume limiting access to photoactive sites, and the coating also adheres less effectively to the stone.

Table 5. *Cont.*

Authors, Journal, Reference	Total Citation	Scope	Coating Composition and Application Techniques	Concluding Remarks
Chen et al., Build. Environ., 2011 [30]	153	- TiO_2 modified cementitious surface layers - Self-cleaning performance, and NO_x and toluene removal potential of TiO_2 modified self-compacting mortars (SCM)	Composition: Mix proportion (0.9:0.1:2.0:0.4) by weight-white cement: metakaolin: aggregate (recycled glass): water; TiO_2 content—0%, 2% and 5% (TiO_2/binder, w/w ratio)—TiO_2 intermixed Substrate: Self-compacting mortars-cylindrical discs Φ75 × 10 mm in size	- Toluene conversion was undetected on the TiO_2-modified concrete surface, while NO was effectively removed: Toluene conversion by photocatalytic cement is not a reliable indicator of performance under outdoor conditions. - In UV light irradiation, discoloration rate of rhodamine B for 5% TiO_2 sample is much higher than that of 2% TiO_2 sample within first 2 h. - Under strong halogen light, discoloration persisted; however, increasing TiO_2 content from 2% to 5% produced no significant change in discoloration behaviour.
Zouzelka and Rathousky, Appl. Catal. B-Environ. 2017 [31]	140	- NO_x abatement by commercial photocatalytic coatings - Photocatalytic performance under laminar and ideally mixed flow, replicating real-world conditions of temperature, humidity, light intensity, and pollutant levels	Composition: Protectam FN2, commercial product: about 74% of TiO_2, the remaining part being an inorganic binder, and water suspension of TiO_2 of 74 wt% Loading: A three-layer coating achieving a total thickness of 10 µm Substrate: Concrete and plaster (each 5 × 10 cm) in size–coating applied by spraying	- Compared to 100% TiO_2 coating, the FN2 coating offers a clear advantage in substrate adhesion. - NO_x reduction at steady state was 1.5–1.8 times higher on plaster coatings than on concrete. - The photocatalytic coating retained high effectiveness on concrete walls beside a busy road even after two years.
Sierra-Fernández et al., ACS Appl. Mater. Interfaces 2017 [37]	136	- Zn doped MgO nanoparticles as antimicrobial agent for dolomitic and calcitic stones - Comparison of Zn doped MgO nanoparticles with ZnO and MgO particles in terms of photocatalytic and antifungal activity.	Composition: Zn-doped MgO nanoparticles were prepared by sol–gel synthesis from Mg and Zn precursors with NaOH precipitation. - Nanoparticles were dispersed in ethanol by vigorous stirring and ultrasonication to obtain a 2.5 g L^{-1} suspension. Substrate: Dolostone and limestone substrates 2 cm × 2 cm × 1 mm in size	- After 60 min UV irradiation, Zn-doped MgO nanoparticles degraded 87% methylene blue, compared to ZnO and MgO, which degraded 58% and 38%, respectively. - Zn-doped MgO treatment markedly reduced fungal colonization, lowering A. niger coverage from ~50% to 8.4% on dolostone and from ~20% to 9.8% on limestone in comparison to untreated substrates, while for P. oxalicum the reduction reached ~79% and ~88%, respectively.
Pinho and Mosquera, J. Phys. Chem. C 2011 [24]	129	- Multifunctional titania-silica composite-based hydrophobic coatings - Self-cleaning evaluation of coatings - Mechanical resistance of coated stones	- Composition: Silica-titania nanocomposites (prepared by mixing silica oligomer, TiO_2 particles and n-octylamine/ phosphoric acid), and aqueous dispersion of TiO_2 particles - Loading: Proportion of TiO_2 to silica varied from 0 to 2% w/v in each - Substrate: Stone (limestone), 5 × 5 × 2 cm in size–sols applied by spraying	- n-octylamine in coatings lower crack-inducing capillary pressure and improved mechanical resistance of substrate. - n-octylamine-based coatings improve self-cleaning properties; the greater self-cleaning effect of coatings is attributed to their higher porosity and the larger pore size of the gel network.

Table 5. *Cont.*

Authors, Journal, Reference	Total Citation	Scope	Coating Composition and Application Techniques	Concluding Remarks
Ling and Poon, J. Clean. Prod. 2014 [40]	126	- Recycled cathode ray tube (CRT) glass as fine aggregate replacement in production of concrete paving blocks - TiO_2 enriched concrete blocks for the removal of nitrogen oxide	- Composition: TiO_2-intermixed cement mortar, i.e., surface layer (5 mm thick) incorporating TiO_2 (5% by wt. of cementitious material) - Substrate: Concrete paving blocks (200 × 100 mm in size)-TiO_2 enriched cementitious layer applied during the mixing process	- Using up to 100% CRT glass as fine aggregate in paving blocks achieved high compressive strength (>45 MPa), low ASR expansion (<0.1%), and enhanced resistance to water absorption and drying shrinkage. - After 60 min of UV exposure, 50% and 100% CRT glass layers showed 5% and 7% higher NO removal than the control. - Potential lead leaching restricts the substitution level of CRT glass to less than 25%.
Pinho et al., Appl. Surf. Sci. 2013 [32]	107	- TiO_2-SiO_2 nanocomposite for self-cleaning action of stones - Comparison of TiO_2-SiO_2 nanocomposites with existing commercial siloxane products	- Composition: a sol comprising silica oligomers, TiO_2 and *n*-octylamine; proportion of *n*-octylamine and TiO_2 to silica oligomers was 0.36% v/v and 2% w/v, respectively. - Substrate: Stone (friable dolostone) friable carbonate stone of 5 × 5 × 2 cm in size-coated by spraying for 25 s	- TiO_2–SiO_2 nanocomposite forms a crack-free adhesive layer and improves mechanical resistance of stone, imparting self-cleaning property. - The nanocomposite significantly enhances protection against damage from salt ($NaSO_4$) crystallisation.
Guo et al., Cem. Concr. Comp. 2017 [46]	107	- Photocatalytic NO_x degradation by concrete surface layers (intermixed and spray-coated with nano-TiO_2) - Abrasion resistance of surface layers	- Composition: Cementitious surface layers with mix ratios (by mass) of 0.75:0.25:3.0:0.3 for cement, fly ash, recycled glass, and water, respectively. - For coated samples: TiO_2 coating, a suspension of ethanol and TiO_2 (30 g L^{-1}), sprayed within 10 min after preparation of surface layers–roughly 0.006 g cm^{-2} of TiO_2 in each sample. - For intermixed samples: TiO_2 added at 5% by weight of cementitious materials to mortar mixture. - Substrate: concrete surface layers (TiO_2 intermixed and spray-coated) 200 × 100 × 5 mm in size	- TiO_2 spray-coated concrete surface layers showed higher NO_x removal efficiency and rate than those with 5% TiO_2-intermixing. - Spray coated samples showed robust resistance to abrasion, retaining higher NO_x removal efficiency than intermixed samples even after 500 abrasion cycles.

Based on summary of Table 5, the collective evidence demonstrates that TiO_2-based superhydrophobic–photocatalytic coatings significantly enhance self-cleaning, pollutant removal (notably NOx and VOCs), and substrate durability under weathering and abrasion. Performance is strongly influenced by particle size, loading, substrate porosity, and application method, with spray-coated and composite systems (e.g., TiO_2-SiO_2, Zn-doped MgO) offering superior stability and efficiency. These findings establish such multifunctional coatings as promising solutions for sustainable construction and heritage conservation, while emphasising the need for optimization toward real-world, long-term performance.

3.7.2. Publications on Photocatalytic and Hydrophobic Coatings

The reviewed studies from Table 6 collectively demonstrate significant advancements in the development of TiO_2-based multifunctional coatings for stone and cementitious materials, aimed at achieving hydrophobicity, self-cleaning, photocatalytic activity, and long-term protection. Early works, such as Pinho and Mosquera [24], and Faraldos et al. [38], explored silica-titania nanocomposites and SiO_2-TiO_2 hybrid coatings, emphasizing hydrophobic behaviour and pollutant degradation on limestone and concrete substrates. Subsequent studies, including Colangiuli et al. [47], and Bai et al. [54], introduced fluoropolymer matrices and core-shell TiO_2@Si-Me systems, which provided durable superhydrophobicity (contact angles up to 147.6°) and enhanced resistance to UV and environmental aging. Similarly, multifunctional coatings incorporating TiO_2-ZnO heterostructures [66], and organic–inorganic hybrid nanocomposites [55], achieved strong water repellency, self-cleaning ability, and weathering resistance, while maintaining substrate breathability and aesthetic integrity. Other formulations, such as benzoic acid-modified TiO_2 [61], and PDMS-SiO_2-TiO_2 composites [56], further improved surface binding and stability across various substrates, enhancing photocatalytic and hydrophobic performance.

It may be noted that environmental exposure (e.g., mechanical abrasion, crystallisation cycles, and weathering) plays a decisive role in coating longevity and performance. Repeated physical wear from wind-blown particles, cleaning, or vehicular movement gradually removes or thins the photocatalytic surface layer. As TiO_2 particles are exposed on the surface, initial photocatalytic efficiency may increase slightly due to higher surface accessibility. However, prolonged abrasion eventually leads to the detachment or depletion of active particles, reducing photocatalytic activity and weakening coating adhesion. In environments where salts are present (e.g., marine or urban atmospheres), crystallization–dissolution cycles cause expansion pressures within the coating and substrate pores. These stresses lead to microcracking, delamination, and loss of cohesion between the photocatalyst and the substrate. Prolonged exposure to sunlight, temperature fluctuations, and moisture accelerates chemical and physical degradation. UV irradiation can induce photocatalyst-induced degradation of organic binders, while thermal expansion and contraction may create microcracks, enabling water ingress and particle detachment. Additionally, pollutants and biofilms can accumulate on weathered surfaces, diminishing photocatalytic efficiency. Overall, these factors collectively reduce coating durability, adhesion strength, and photocatalytic efficiency over time. Studies (e.g., Hassan et al. [23], Azadi et al. [55], and Aldoasri et al. [75]) illustrate the influence of these factors and to highlight strategies for improving coating resilience under real-world conditions. The studies discussed above reveal that combining TiO_2 nanoparticles with siloxane, fluoropolymer, or organic–inorganic hybrid matrices yield durable, multifunctional coatings capable of protecting cultural heritage materials from environmental degradation. However, challenges remain in maintaining photocatalytic efficiency and hydrophobicity under prolonged outdoor exposure. Therefore, future research should prioritise developing hybrid or multifunctional TiO_2-based coatings that integrate silica, alumina, or doped oxide frameworks to improve adhesion, mechanical robustness, and self-regeneration under outdoor conditions. Such developments would provide more accurate and reliable guidance for the application of photocatalytic coatings on various building substrates, ensuring long-term environmental functionality without compromising substrate aesthetics. Integration of green synthesis routes, smart responsive coatings, and long-term field testing will be essential for translating these laboratory-scale solutions into sustainable real-world applications.

Table 6. Ten most cited articles on dual superhydrophobic–photocatalytic coatings for building material substrates.

Reference	Total Citation	Scope	Coating Composition and Application Techniques	Concluding Remarks
Pinho and Mosquera, J. Phys. Chem. C 2011 [24]	129	- Multifunctional titania-silica composite-based coatings - Hydrophobic behaviour of the coatings	- Composition: Silica-titania nanocomposites (prepared by mixing silica oligomer, TiO_2 particles and n-octylamine/phosphoric acid), and aqueous dispersion of TiO_2 particles - Loading: Proportion of TiO_2 to silica varied from 0 to 2% w/v in each - Substrate: Stone (limestone), 5 × 5 × 2 cm in size-sols applied by spraying	- The hydrophobicity in n-octylamine and phosphoric acid gels may arise from residual nonhydrolyzed ethoxy groups, with phosphoric acid-based coatings showing slightly reduced contact angles (92–98°) compared to n-octylamine (88–121°), likely due to surface discontinuities.
Faraldos et al. Catal Today 2016 [38]	72	- Home-made TiO_2 sol - SiO_2-TiO_2 hydrophobic coating for photocatalytic degradation of NO_x and organic pollutants (Methylene Blue dye bleaching)	- Composition: photocatalyst nanoparticles suspended in a siloxane sealant, home-made acidic silica (SiO_2) sol, an acidic TiO_2 sol and commercial sols - Substrate: concrete blocks (10 cm × 10 cm × 30 cm in size) and cement tiles (15 cm × 15 cm × 1 cm) (spraying or dip coated).	- Hydrophobic coatings on cement tiles with loadings above 5% achieved a 90% reduction in diluted NO pollutant concentration. - A threshold of 1% of TiO_2 loading for hydrophilic coatings and 5% for hydrophobic coatings was required to achieve complete NO_x degradation. - Hydrophobic photoactive coatings composed of TiO_2 nanoparticles and a siloxane sealant have shown outstanding efficiency in converting NO gas when applied to concrete surfaces.
Colangiuli et al., Sci. Total Environ. 2019 [47]	47	- TiO_2 nanoparticles/fluoropolymer based multifunctional coatings (TiO_2 nanoparticles embedded in a fluoropolymer host matrix) - Field investigation of hydrophobic and self-cleaning stone coatings incorporating TiO_2 nanoparticles and fluoropolymer.	- Composition: TiO_2 nanoparticles in a water dispersion with a commercial hydrophobic fluoropolymer, and a neat fluoropolymer dispersion in water as control. - Substrate: Stones (limestone)—5 × 5 × 2 cm in size, coated by brush	- Prior to outdoor exposure, both coating mixtures demonstrated high photodegradation efficiency. - After eight months outdoor, the photocatalytic efficiency gradually declined, likely due to the loss of photocatalyst from the coating surface, which may result from polymer alterations caused by aging. - Embedding TiO_2 particles within the polymer reduced the adsorption and buildup of soluble salt ions on the coated surface, potentially lowering the risk of stone damage. - TiO_2/fluoropolymer-based coatings showed a significant reduction in the contact angle values (from 67% to 41% and from 73% to 46%) depending on fluoropolymer/TiO_2 ratio after 4 months of outdoor exposure in comparison to neat coating (56% to 37%). - The coatings effectively protected the surfaces from dirt.

Table 6. *Cont.*

Reference	Total Citation	Scope	Coating Composition and Application Techniques	Concluding Remarks
Bai et al., J. Clean. Prod. 2022 [54]	38	Corrosion resistance and self-cleaning performance of TiO_2-based superhydrophobic coatings for stone surfaces	- Composition: TiO_2@Si–Me core–shell system were dispersed in Paraloid B72 (TiO_2@Si and TiO_2@Si-Me) - Substrate: Granite, sandstone and limestone; size $5 \times 3 \times 1$ cm^3 coating applied by a pipette gun.	- Superhydrophobic TiO_2 was achieved by grafting methyl groups onto the SiO_2 shell. - Superhydrophobic TiO_2 coatings did not change the colour of the stone after UV aging. - TiO_2@Si-Me core-shell system exhibited adsorption and methylene blue degradation rates that were 2.19 and 1.45 times higher, respectively, than those of pure TiO_2 - TiO_2@Si-Me increases the contact angle on marble from 69.87° to 147.6°.
Speziale et al., Int. Journal of Architectural Heritage 2020 [66]	30	- Multifunctional coatings for stones (limestone, granite and sandstone) and lime mortars - Hydrophobicity, photocatalytic activity and self-cleaning as well as water vapour permeability of coated specimens	- Composition: Four dispersions comprising superhydrophobic agent and nano-heterostructures TiO_2-ZnO (weight/weight 50/50 or 10/90), dispersing agents (polycarboxylate ether or melamine sulfonate) - Substrate: Stones and air lime mortars - All coatings were applied by simply depositing the active dispersion onto horizontally placed substrates using a pipette.	- Coatings were synthesised using superhydrophobic agent and nanoparticles of TiO_2-ZnO heterostructures. - Coatings minimises water absorption and imparts a durable hydrophobic barrier to construction surfaces. - Enables effective self-cleaning by reducing the adsorption and promoting removal of soiling contaminants. - Facilitates photocatalytic degradation of surface pollutants, improving material longevity and air quality.
Wang et al. Constr. Build. Mat. 2017 [61]	25	- Surface binding forming for benzoic acid supported on TiO_2 surface - Hydrophobic and photocatalytic properties of cement-based materials coated with TiO_2	Composition: Hydrophobic TiO_2; hydrophobic property achieved by using an organic small molecule, benzoic acid, as a surfactant to prepare the hydrophobic TiO_2. Substrate: Test piece of cement paste prepared at 0.45 water-cement ratio, $4 \times 4 \times 2$ cm in size; suspension of 2 mL sprayed on sample	- TiO_2 synthesised by a solvothermal method - The water contact angle of cement paste coated with TiO_2 reached 90.5°, indicating improved hydrophobicity of the surface. - The colour fading rate of cement paste coated with TiO_2 exceeds 30% within 1 h of exposure, indicating strong photocatalytic activity. - After 15 h of irradiation, TiO_2-coated cement paste showed over 80% colour fading, 3.6 times greater than untreated paste.
Azadi et al. Plastics, Rubber and Composites 2020 [55]	24	- Organic-organic hybrid nanocomposites for stone-made cultural heritage - Thermal resistance, mechanical resistance, weathering resistance, hydrophobicity, and self-cleaning action of coatings	Composition: Acrylate coatings made of methyl methacrylate, 3(trimethoxysilyl) propyl methacrylate, tetraethyl orthosilicate, perfluorooctyl-trichlorosilane, TiO_2 Substrate: Stone samples $2 \times 2 \times 2$ cm^3 in size coated via impregnation.	- A simple synthesis route was developed to produce organic-inorganic hybrid nanocomposite coatings using acrylate components. - Strong covalent Si-O-Si bonds between the coating and the substrate prevent detachment and enhance durability under moisture, UV, and temperature stress. - Highest contact angle about 131° was obtained for TiO_2 based coated stone in comparison to uncoated stone (36°).

Table 6. *Cont.*

Reference	Total Citation	Scope	Coating Composition and Application Techniques	Concluding Remarks
Petronella et al., Coatings 2018 [48]	24	- TiO_2 nanocrystal rods-based coatings for porous limestone (Lecce stone) - Cultural heritage conservation	Composition: TiO_2 nanocrystal rods were synthesised via hydrolysis and polycondensation of titanium tetraisopropoxide - TiO_2 nano crystals were dispersed in n-heptane or in chloroform Substrate: Stone (porous limestone) spray-coated $5 \times 1 \times 5$ cm^3 and $5 \times 1 \times 2$ cm^3 in size	- The spray-coating application of TiO_2 nanorods dispersed in n-heptane shows strong potential for practical use on buildings and monuments. - For coated samples, contact angles ranged from 130° to 136°, indicating a strong decrease in wettability. - SEM and AFM analyses of the coatings demonstrated that n-heptane is the most suitable solvent for dispersing TiO_2 nanorods.
Xu et al., Water Sci Technol 2016 [56]	22	- Photocatalytic efficiency of PDMS-SiO_2-TiO_2 composite based coatings - Stability of photocatalyst	Composition: Mixture of 1TEOS/8H_2O/16ETOH/ 0.04PDMS-OH/2.6H_3PO_4 by mole ratios and SiO_2-TiO_2 sol acted as control Substrate: Pumice stone, medicinal stone, and fiberglass; coating applied by brushing	- The peeling performance test results showed that no material was removed from the surface of the pumice stone when it was treated with the PDMS-SiO_2-TiO_2 composite. - Under identical conditions, coatings demonstrated superior photocatalytic dye degradation when applied to pumice stone compared to medicinal stone or fiberglass. - PDMS-SiO_2-TiO_2 composite treatment enhanced pumice stone hydrophobicity, elevating the static water contact angle to 101°.
Aldoasri et al. Sustainability 2017 [75]	21	- Spray-coated multifunctional TiO_2 nanocoatings for marble stone facades - Self-cleaning and protection treatments on historical and architectural stone surfaces	Composition: TiO_2 nanoparticles dispersed in an aqueous colloidal suspension (2 wt % of TiO_2 content) Substrate: Historic marble stone surfaces by spray-coating; 3 cm × 3 cm × 3 cm in size	- TiO_2 nanocoating enhanced marble surface durability against abrasion and improved its mechanical strength. - The coating prevented dirt build-up on stone surfaces over six months outdoors without altering their original characteristics.

There are practically no studies on the in situ applicability of multifunctional coatings, which is why this should be one of the priority areas of applied research into these materials. To illustrate the relevance and some characteristics of research in case studies, by analogy some work that has been carried out on other coatings can be mentioned to illustrate the practical potential and limitations of such coatings: Fregni et al., 2023 [82] evaluated TiO_2-based self-cleaning treatments on cementitious substrates under aging, showing a gradual decrease in photocatalytic activity and repellency over time. Likewise, Gemelli et al., 2022 [83] conducted a four-year in situ assessment of a TiO_2/SiO_2 antifouling coating applied to historic mortar in a coastal city, demonstrating both the feasibility and durability challenges of photocatalytic systems under real environmental conditions.

3.7.3. Publications on Photocatalytic and Oleophobic Coatings

There are very few studies addressing dual photocatalytic and oleophobic coatings (Table 7). Only two works were identified in the present bibliometric analysis, limiting the possibility of drawing firm conclusions. Nevertheless, this gap highlights a promising research frontier, particularly given its strong relevance for the protection and preservation of historic structures. Tena-Santafé et al. [62,84] published works on the effect of these coatings. Once applied onto different substrates (natural stones and lime and lime-cement mortars), the coatings exhibited hydrophobic–photocatalytic and oleophobic-photocatalytic properties. Active photocatalysts based on nano-Zn_2TiO_4-ZnO and nano-$Bi_{12}ZnO_{20}$-ZnO—incorporated to superhydrophobic and hydro-oleophobic matrices—demonstrated active NO_x removal.

Table 7. Articles on dual oleophobic–photocatalytic coatings for building material substrates.

Reference	Scope	Coating Composition and Application Techniques	Concluding Remarks
Tena-Santafé et al., Catalysts, 2023 [62]	- Bi_2O_3-ZnO based multifunctional coatings for sandstone, limestone, and granite - Hydrophobicity, oleophobicity, and photocatalytic activity	Composition: Bi_2O_3-ZnO (8 wt%/92 wt%) Substrate: Sandstone, limestone, and granite each of size 5 × 5 × 2 cm; coating applied by pipette	- Bi_2O_3-ZnO heterostructure based coatings exhibited higher activity in superhydrophobic medium compared to hydro-oleophobic medium when exposed to UV + visible irradiation - Among different substrates, sandstone yielded highest contact angles, indicating superior hydrophobic nature - Superhydrophobic and oleophobic coatings performed better on limestone due to its alkaline-earth metal oxides and carbonates, which boost NO and NOx adsorption - Long term performance of coatings was assessed; simulation cycles included changes in temperature, UV-VIS radiation exposure, fluctuations in relative humidity, and contact with artificial rainwater - Coatings demonstrated hydrophobic efficiency and self-cleaning capability after the accelerated ageing tests
Tena-Santafé et al., Surf Interfaces 2025 [84]	-Nanoparticles of Zn_2TiO_4 /ZnO and $Bi_{12}ZnO_{20}$/ZnO were used - Hydrophobicity, oleo-phobicity, and photocatalytic activity	Composition: nanostructures of Zn_2TiO_4/ZnO and $Bi_{12}ZnO_{20}$/ZnO Substrate: Lime and lime-cement mortars; coating applied by pipette	- The coatings demonstrated significantly improved oleophobicity, with most samples achieving oil contact angles above 90° - Lime-cement mortars generally exhibited higher contact angles than pure lime mortars, a result linked to their lower porosity and more heterogeneous surface texture - The inclusion of BiZn nanoparticles further enhanced oil repellency across both mortar types

Although the purpose of this study was to develop multifunctional coatings, some details related to construction material applications can be highlighted by focusing exclusively on the oleophobic properties. For example, Mosquera et al. [85] achieved superhydrophobicity and oleophobicity on limestone, granite, concrete, and wood through coatings based on 40 nm silica particles (SiO_2 NPs, Evonik Aerosil OX 50, 40 nm primary size) and Dynasylan F8815 (a water-soluble fluoroalkyl silane containing a fluoroalkyl chain responsible for the hydrophobic/oleophobic character, an amino-alkyl chain, and hydroxyl groups). The coating was prepared using the sol-gel method and applied to the substrates by immersion.

It is important to emphasize that advancing research on photocatalytic coatings requires a strongly interdisciplinary framework that unites materials science, chemistry, and architectural engineering. Integrating insights from these fields can accelerate the development of multifunctional and durable coatings with enhanced environmental adaptability. Future research should therefore promote closer cooperation among materials scientists, chemists, and building engineers to design and optimize photocatalytic coatings tailored to diverse construction materials and real-world performance requirements.

Overall, on the basis of Table 8, the comparative evaluation among different coating types highlights that hybrid and composite coatings, particularly TiO_2-SiO_2 and TiO_2-fluoropolymer systems, offer the best balance between photocatalytic performance, durability, and environmental stability. While pure TiO_2 and sol-gel coatings demonstrate strong initial activity, they often suffer from limited adhesion and long-term degradation under weathering. In contrast, cementitious and hybrid matrices improve wear resistance and scalability, making them well-suited for practical construction applications. Future research should prioritize self-regenerating and multifunctional hybrid coatings capable of sustaining photocatalytic efficiency, hydrophobicity, and aesthetic integrity under real-world environmental factors.

Table 8. Comparative analysis between coatings: types, composition and applicability.

Coating Type/Composition	Advantages	Disadvantages	Applicability
TiO_2–SiO_2 nanocomposites (Pinho & Mosquera [24,29], Pinho et al. [32])	Excellent adhesion, self-cleaning, and mechanical reinforcement; resistant to salt crystallization; high porosity enhances photoactivity	Excess TiO_2 (>4%–5%) reduces pore volume and coating adhesion	Ideal for stone and lime-based substrates; suitable for heritage and restoration applications
TiO_2–fluoropolymer/ TiO_2–siloxane hybrids (Colangiuli et al. [47], Faraldos et al. [38])	Strong hydrophobicity and weathering resistance; effective NOx and dye degradation	Efficiency declines with prolonged outdoor exposure due to polymer aging	Exterior façades and concrete surfaces requiring water repellence and self-cleaning
TiO_2@Si-Me core-shell systems (Bai et al. [54])	Superior superhydrophobicity, UV stability, and color retention; enhanced pollutant degradation	Complex synthesis and higher cost	High-end stone and architectural finishes requiring long-term durability
TiO_2-ZnO/doped oxide heterostructures (Speziale et al. [66], Sierra-Fernández et al. [37])	Multifunctional (antimicrobial, antifungal, photocatalytic); enhances biological resistance	Complex formulation; performance dependent on dopant and substrate type	Cultural heritage protection and humid environments prone to biofouling
TiO_2-modified cementitious coatings (Hassan et al. [23], Chen et al. [30], Guo et al. [46], Ling & Poon [40])	Scalable, cost-effective; strong wear resistance and air purification (NOx removal)	Reduced activity in low UV light; intermixing less effective than surface coating	Pavements, façades, and large-scale infrastructure with high abrasion exposure
Organic-inorganic hybrid (PDMS, acrylate) coatings (Azadi et al. [55], Xu et al. [56])	Excellent UV, moisture, and thermal resistance; durable hydrophobicity; strong adhesion via Si-O-Si bonding	Organic components may limit photocatalytic activity	Decorative or historical stonework requiring minimal visual alteration
Pure TiO_2 nanorod/sol-gel coatings (Petronella et al. [48], Ramirez et al. [25])	Simple application (spray/dip); high initial photoactivity; large surface area	Poor long-term adhesion and durability; particle detachment	Controlled or semi-protected surfaces; need improved binder integration for outdoors

4. Concluding Remarks and Future Trends

This bibliometric assessment from 2010 to 2025 reveals a striking imbalance in research efforts. While 205 studies focus solely on photocatalytic coatings and 23 report dual hydrophobic-photocatalytic functionality, only a single study addresses dual oleophobic–photocatalytic coatings. This indicates that, despite the evident benefits of minimising both water and oil adhesion, oleophobicity remains an almost unexplored dimension in photocatalytic coating research. Given its potential to enhance material protection against a broader spectrum of contaminants, the integration of oleophobicity with photocatalysis represents a promising and underdeveloped frontier for future innovation.

The analysis reveals that research on photocatalytic coatings in construction is heavily dominated by TiO_2-based systems, with core themes centred on pollutant degradation (especially NOx), self-cleaning performance, and laboratory-scale efficiency assessments using standardised test pollutants and characterisation techniques. Supporting themes reflect growing attention to cementitious applications, visible-light activation, and extended performance metrics such as VOC removal, while less frequent keywords highlight niche or emerging directions, such as doped or composite photocatalysts, durability studies under real environmental conditions, and applications in diverse building substrates. Collectively, this indicates a mature research core grounded in TiO_2 photocatalysis, alongside promising frontiers that focus on material innovation, long-term stability, and real-world applicability.

Research over the past decade demonstrates a clear progression from simple TiO_2-based hydrophobic coatings toward increasingly multifunctional nanocomposites (e.g., TiO_2-SiO_2, TiO_2-fluoropolymer, TiO_2-ZnO heterostructures, and hybrid organic–inorganic systems). Innovations such as superhydrophobic modifications (e.g., TiO_2@Si-Me systems) and heritage-compatible formulations (e.g., spray-coated TiO_2 nanorods for limestone and marble) indicate a growing emphasis on real-world durability, substrate compatibility, and preservation of cultural assets. This highlights a transition from laboratory proof-of-concepts toward practical, durable, and scalable coating solutions for both modern and historic constructions.

The bibliometric analysis highlights several underexplored yet promising research avenues. Key priorities include enhancing the visible-light responsiveness of photocatalysts, improving coating adhesion on diverse building substrates, and developing multifunctional systems that combine hydrophobic and oleophobic properties. While antimicrobial photocatalytic coatings were beyond the scope of this review, their potential integration into multifunctional designs remains significant—particularly for healthcare applications and antifungal protection in moisture-prone environments. Advancing these directions will be critical to broadening the functionality, durability, and real-world impact of photocatalytic coatings.

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