

Review

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Keywords: TiO₂; Air purification; Sustainable cities; Photocatalytic buildings



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Review

TiO₂-Based Photocatalytic Building Material for Air Purification in Sustainable and Low-Carbon Cities: A Review

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Abstract: TiO₂-based building materials have air purification, auto-cleaning and sterilization functions, and these innovative green building materials have great potential for energy-saving and emission reduction applications in the future. However, there are still great challenges in improving photocatalytic efficiency and stability from laboratory to practical applications. In recent years, researchers have done a lot of work to improve the efficiency and stability of TiO₂-based building materials. This paper briefly discussed the air purification principle by photocatalytic building, and the preparation techniques of TiO₂-based building materials and the strategies to improve the efficiency of TiO₂. Moreover, this paper has outlined the key factors that affect the photocatalytic building performance in practical applications, and analyzed the limitations and future development trends. Finally, we proposed some suggestions for further research on photocatalytic buildings and its application in practice, aiming to provide an efficient reference for developing highly efficient and stable photocatalytic building materials. The aim of this paper is to provide effective guidance for the application of TiO₂-based photo-catalysts in the field of green buildings, helping to develop more efficient and stable low-carbon buildings for the development of sustainable cities.

Keywords: TiO₂ 1; air purification 2; sustainable cities 3; photocatalytic buildings 4

1. Introduction

In recent years, human activities have caused a significant release of gaseous pollutants into the environment. These pollutants include volatile organic compounds (VOCs), nitrogen oxides (NO_x), sulfur oxide (SO_x) and particulate matter, which have resulted in severe environmental issues [1]. These harmful substances can negatively impact human health, compromising the immune system and leading to conditions such as skin diseases, asthma, chronic respiratory diseases, cardiovascular diseases, and cancer. Shockingly, air pollution has been linked to approximately 26,000 to 48,000 deaths in European countries alone [2]. In addition, these pollutants can also negatively impact plant growth, water and soil quality, and lead to ecosystem collapse, as well as contribute to climate change and global warming issues [3]. Given the gravity of the situation, extensive research and environmental remediation measures are currently underway to address these concerns.

Photocatalytic technology has been widely recognized for its potential to treat air pollutants [4]. This innovative technology works by converting harmful gases into harmless substances, effectively reducing the harmful impacts of air pollution [5]. Unlike conventional treatment methods, photocatalytic technology has low energy consumption and secondary pollution, in addition, photocatalysts are usually renewable and low-toxicity, which provide better environmental sustainability [6]. Additionally, photocatalysis has a wide range of applicability and can be used to

treat a variety of pollutants, including nitrogen dioxide, volatile organic compounds, formaldehyde, benzene, etc. [4].

Based on these advantages, photocatalytic technology has been widely used in various fields, such as construction materials, air purifiers, and wastewater treatment. Especially in the field of building materials, photocatalytic building materials have become a new type of building material, and their potential in mitigating air pollution has received widespread attention [7]. Photocatalytic building materials are capable of converting harmful gases, such as VOCs, NO_x and SO_x, into harmless substances through photocatalytic reactions. Additionally, they can decompose bacteria, viruses, and other microorganisms, improving indoor air quality. In recent years, many countries and regions have started to use photocatalytic building materials to combat air pollution. For example, in Japan, photocatalytic building materials accounted for 60% of the photocatalytic market sales in 2003 [7]. They have developed a range of photocatalytic building materials by adding TiO₂ nanoparticles to glass, ceramics, and mortar to achieve photocatalytic functions of building materials, such as self-cleaning, antibacterial, and air purification [8]. In China, many high-rise buildings and public places, including hospitals, schools, outdoor buildings, and roads, have begun using photocatalytic building materials to purify air and improve the indoor environment.

TiO₂ has received widely attention due to its simple preparation process, high stability, low toxicity and chemical inertness. [9]. TiO₂-based photocatalytic building materials exhibit excellent photocatalytic performance and stability, effectively converting harmful substances in the air into harmless substances under light irradiation. Thus, their applications are of significant importance. Many methods have been studied for preparing TiO₂ nanoparticles, including sol-gel, hydrothermal [10], vapor phase deposition [11], and others [12]. All of these methods can produce nanoscale TiO₂ particles, thereby improving the specific surface area and reaction activity of photocatalysts. In addition, photocatalytic building materials can be prepared by loading TiO₂ onto porous materials, which can improve the stability and mechanical properties of the photocatalytic materials and increase their reactivity [13, 14]. This preparation method is also widely used in the preparation of catalytic materials.

In recent years, TiO₂-based photocatalytic building materials have been widely investigated [14, 15]. However, TiO₂ has a low photocatalytic efficiency due to the fact that only 4% of UV light can be absorbed, additionally, the fast rate of light-induced electron-hole pair complexation leads to the low photocatalytic efficiency of ordinary TiO₂, which greatly limits its practical applications. In order to improve the TiO₂ photocatalytic efficiency, researchers have employed various strategies, such as surface chemical structure modification and loading onto nanomaterials to form composites [16]. Moreover, other factors need to be considered in the preparation of TiO₂-based building materials, including the size of catalyst nanoparticles, structural stability, light-absorbing properties, catalytic activity, and mechanical strength, to ensure their long-term and effective operation. What is more, TiO₂-based building materials in the actual operation are practically optimized and adjusted for specific conditions, such as the angle of installation of the building materials, light conditions, pollutant types, concentrations, rainfall, etc., to achieve the best photocatalytic effect.

This paper reviewed recent advances in TiO₂-based building materials for air purification. We discussed various preparation techniques for producing TiO₂-based building materials, including sol-gel, hydrothermal, spray-drying, anodic oxidation, and microwave-assisted methods. In addition, to solve the problems of aggregation of TiO₂ nanomaterials in suspension, poor adsorption ability, wide band gap, and high recombination rate, we discussed the strategies to improve the catalytic efficiency of TiO₂-based building materials. Finally, based on practical application cases, we discussed the effectiveness of photocatalytic building materials in practical applications, the key factors affecting the catalytic efficiency as well as the limitations and future development trends of photocatalytic building materials. The purpose of this paper is to provide an effective reference for the development of highly efficient and stable photocatalytic building materials, and to improve the public's awareness of green buildings.

2. Working principles and properties of TiO₂-based photocatalytic building materials

TiO₂ photocatalytic materials have received much attention from researchers in recent years as an emerging building material. In the construction field, TiO₂-based building materials are widely used for air purification, deodorisation and sterilisation due to their unique photocatalytic properties. This part will focus on the working principle of photocatalytic building materials for pollution and carbon reduction.

2.1. The basic principle mechanism of photocatalysts

Semiconductor materials are crystals orderly arranged by a large number of atoms or ions, and the dense accumulation of atoms allows the energy-matched adjacent atomic orbits to overlap each other and form different energy bands. The semiconductor material has two energy bands, empty high-energy conduction band (CB) and full-of-low-energy electron valence band (VB), the band gap which is between CB and VB is the forbidden band [17]. As shown in Figure 1 the principle of semiconductor photocatalysis involves the absorption of light by a semiconductor, the VB electron transition to the conduction band of the semiconductor generating photo-generated electron-hole pairs, the photo-generated charge carriers then migrate to the semiconductor surface and transfer to the adsorbed material, which initiates the subsequent oxidation or reduction reactions.

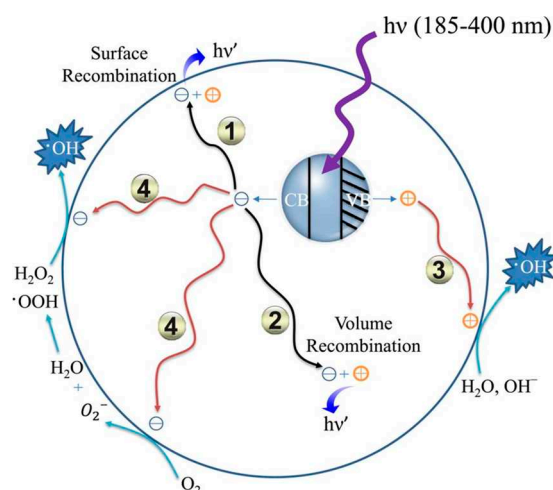


Figure 1. Basic principle of Photocatalytic oxidation for the removal of organic pollutants [18].

The reaction of electron-hole composite reaction is interdependent and competitive with electron-hole reaction with adsorbed material on the catalyst surface throughout the photocatalytic reaction. The total charge efficiency of the interface charge migration is determined by two important competitive processes: (1) the competition of the carrier complex and capture; (2) the competition between the captured carrier composite and interface charge migration. Interface transfer of captured carriers is a rate-determining step in the photocatalytic process that determines the quantum efficiency of TiO₂ photocatalysis.

In the process of electron-hole pair involved in oxidation or reduction reaction, the superoxygen radical ($O_2^{\bullet-}$) was generated by photoelectron reacted with O_2 , while the hydroxyl radical (OH^{\bullet}) was produced by the photohole reacted with H_2O , these reaction oxidation substances (ROS) decomposed various pollutants in atmosphere. The generation of ROS in the photocatalysis process can be depicted as follows:

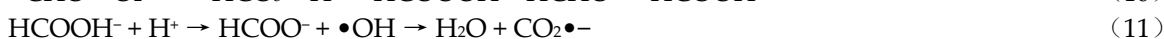
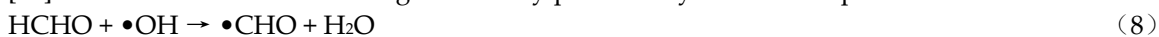


The generation ROS further reacted with the target contaminants, and finally mineralized contaminants into non-toxic substances.

2.2. The mechanism of photocatalysts for air purification and deodorisation

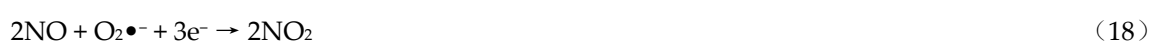
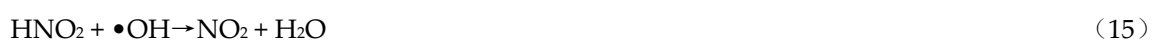
The presence of air pollutants such as VOCs, NO_x and SO_x pose a risk to the environment and human health that cannot be ignored. In the following, we will discuss how TiO₂-based photocatalytic building materials work in degrading some of these gaseous pollutants.

VOCs is the mainly indoor pollutants which is emitted from various sources, such as building and combustion materials, electronic equipment, coal or oil combustion, indoor fuel gas, consumer products and smoking [3]. These pollutants will damage to the sensory system of human beings, and cause various serious acute irritation and chronic disease, especially for the workers who long-term exposure to air pollutants circumstances and the elderly people and young children with low immunity [19]. Photocatalytic oxidation technology is a promising method for VOCs degradation, it could rapidly degrade the organic pollutants in atmosphere through hydroxyl radicals and superoxygen radicals which produced by photogenerated electron-hole pairs reacted with O₂ or H₂O [19]. The mechanism of VOCs degradation by photocatalysis can be depicted as follows:



As can be seen from equation 8 to 13, active substances such as $\bullet\text{OH}$, $\text{O}_2\bullet^-$ and electron holes attack the organic matters and mineralize the organic matters into CO₂ to improving the air quality.

NO_x, which mainly includes NO and NO₂, commonly derived from anthropogenic activities, such as exhaust gases which from traffic and the combustion of fossil fuels in industries, leading to various environmental problems such as photochemical smog, acid rain, haze and so on [20]. According to reports, the greenhouse effect of NO₂ is 200~300 times that of CO₂ which is extremely harmful to the environment [21]. TiO₂-based Photocatalysis is a environmental friendly technology which could remove low concentration NO_x under solar light or UV light irradiation. The photocatalytic degradation of NO_x mainly uses the active substances produced by photocatalysts to convert NO_x to NO₃⁻ to achieve the purpose of reducing NO_x. The reaction process can be depicted as follows:



As shown in equations 14 through 19, $\bullet\text{OH}$ and $\text{O}_2\bullet^-$ convert NO_x to nitrate ions, reducing the concentration of NO_x in the air.

The SO_x is primarily SO₂, which mainly produced by the combustion of sulfur-containing fossil fuels, are extremely harmful for human beings and ecosystems. According to report, SO_x in the air are one of the causes of acid rain formation which could erode building surfaces, accelerate materials aging, grow crops and change the acid and alkaline of the soil [22]. TiO₂-based photocatalysts can

effectively degrade SO_x under solar or UV light excitation. The mechanism of photocatalytic degradation of SO_2 as follows:



As shown in the equation 20 to 21, SO_2 was transform into SO_4^{2-} through free radicals and photogenerated holes.

2.3. The mechanism of photocatalysts for disinfection

Airborne bacteria and viruses are a major source of disease and therefore require effective disinfection and sterilisation measures. In recent years, photocatalytic technology has been widely used in the field of disinfection. It works by producing ROS through photocatalytic materials under light excitation, thus blocking the autosensing signal of colonies and affecting the formation of biofilms to attack bacteria and viruses. As shown in the Figure 2a, ROS attack the bacteria, causing the cell membrane to rupture, ROS enter the cell and attack its intracellular components such as ATPase, SOD, CAT, leading to a reduction in the concentration of the corresponding substances, and ROS also attack DNA, causing it to break. The loss of cytoplasm and the cis-damage of DNA lead to cells that are unable to repair themselves and eventually become fragmented under prolonged light exposure. Similarly, As shown in the Figure 2b, ROS have the same effect on viruses, acting on the RNA of the virus, causing it to break and inactivate the virus.

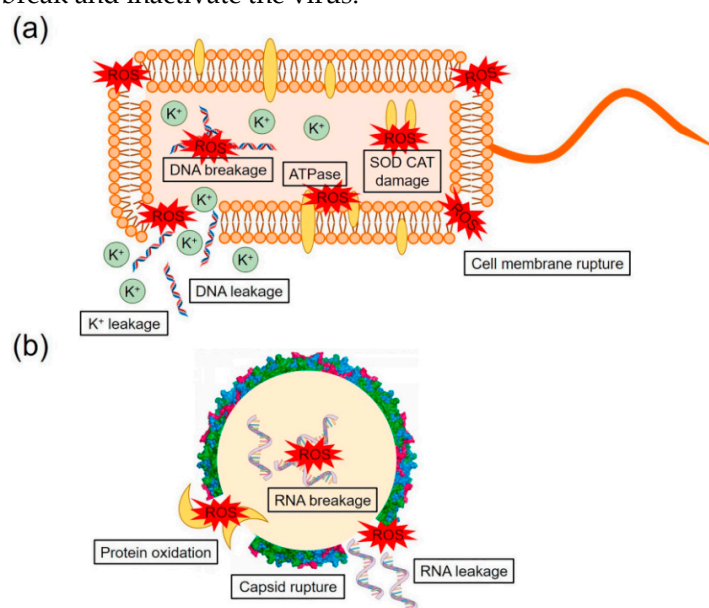


Figure 2. (a) Photocatalytic disinfection mechanism of bacteria and (b) viruses [23].

3. The study status of TiO_2 -based photocatalytic building materials

In recent years, there has been significant progress in the field of TiO_2 photocatalytic construction. TiO_2 has garnered considerable attention as a photocatalyst for organic pollutant degradation because of its chemical stability, low cost, and compatibility with most building materials [24]. In fact, studies have shown that TiO_2 can react with metal oxides in cement to form stable compounds, such as CaTiO_3 , which possesses a band gap energy of 3.5 eV and an isoelectric point pH of 3 [25]. Table 1 shows some of the studies on the addition of TiO_2 -based nanomaterials to building materials to remove airborne pollutants respectively.

Researchers have developed various TiO_2 catalysts with different morphological designs, including nanoparticles, nanotubes, hollow fibers, and mesoporous materials, to improve their

photocatalytic performance [26]. Recent studies have extensively investigated the relationship between TiO₂ crystallinity, crystal phase, crystal size, surface area, pore structure, pore size, and its photocatalytic and adsorption capacities [27]. The use of photocatalysts with building materials began in the early 1990s and since then TiO₂-modified building materials have been used for a variety of purposes such as environmental pollution remediation, self-cleaning and self-disinfection [7]. TiO₂ is a versatile material that can be used both as a photocatalyst and as a structural component. This has led to its widespread use in a variety of building materials, both for exteriors and interiors, including cement mortars, exterior wall tiles, paving blocks, glass, and PVC fabrics. TiO₂-based photocatalytic building materials offer significant advantages and have great potential for a wide range of applications. These materials are compatible with conventional building materials such as cement, without altering any of their original properties. Additionally, they are effective even in ambient atmospheric environments with weak solar radiation [28]. A growing number of research findings proved the viability of the technology in the construction industry. Cárdenas et al. [29] conducted a study demonstrating that TiO₂ nanoparticles are highly efficient photocatalysts in cement paste, and the photocatalytic activity increased proportionally with the percentage of TiO₂ addition. Their findings revealed that cement paste containing 5% TiO₂ exhibited the highest NO_x removal rate. Additionally, Cheung et al. [30] developed photocatalytic building materials by combining TiO₂ with local waste materials, such as cement, crushed glass, and sand, for NO degradation. Intriguingly, they discovered that lower density materials with higher porosity were more effective for NO degradation when mixed with less cement. Furthermore, Demeestere et al. [31] reported that roofing tiles and corrugated sheets containing TiO₂ displayed remarkable photocatalytic activity by effectively removing toluene. They suggested that incorporating TiO₂ into building materials for photocatalytic materials has the potential to significantly contribute to air purification.

In summary, TiO₂ shows great promise for photocatalytic building applications due to its high photocatalytic activity, compatibility with traditional building materials and effectiveness in ambient atmospheric environments under weak solar radiation. However, the efficiency of low-cost TiO₂-based building materials remains unsatisfactory, especially under visible-light or solar-light irradiation due to the wide band gap of TiO₂ (3.2 eV). Consequently, the development of narrow band gap and efficient photocatalysts is essential for practical applications.

Table 1. Selected research literature on air pollutant removal by TiO₂-based building materials.

Building material	Method	Light source	Efficiency	Reference/Year
cement mortar	Mixing with cement mortar	UV	The degradation rate of NO _x can reach 40.0%	[32]2009
cement mortar	Mix with mortar (2 and 5 wt%)	UV	NO (400 ppb) removal rate: 90 μmol/ (m ² ·h) ; Toluene (200ppb) removal: 100%	[33]2011
ceramic tiles	Photocatalyst brushing on the top surface of tiles	UV	Toluene (17-35 ppbv) removal rate up to 512 μg/ (m ² ·h)	[31]2008
cement mortar	Mix with mortar (1-10% wt%)	UV	Formaldehyde (20 ppm) removal rate up to 65%	[34]2011
portland cement	Mix with cement slurry (0.5-5 wt%).	UV	NO _x (1 ppmv) removal amount:120 μmol/m ² , 65 h	[29]2012
Wall paint and plaster	Mixing with 2 wt% TiO ₂	UV	NO _x (400 ppb) conversion range ranges from 80% of 50 days samples to 30% of 1 year samples	[35]2011
cement mortar	Mixed cement (0.5-2.5wt%)	Simulated sunlight	The removal rate of NO (1 ppm) can reach 15%	[36]2014

cement mortar	Mixing with cement mortar Combine photocatalytic materials with building materials using mixing and spraying methods respectively	UV	The degradation efficiency of NO _x (1000 ppb) can reach 60.4%	[37]2015
cement mortar	Mix with cement mortar (0.5~2.5 wt%)	UV Sunlight Visible light	NO (1000 ppb) removal condition: Material for spraying method: 220 μ Mol/(m ² Å h), mixed material: 80 μ mol/ (m ² .h)	[38]2017
cement mortar	Mixing with cement mortar (1-10wt%)	UV	NO (1ppm) removal rate: 72%	[40]2017
Concrete and gypsum	Coating deposited on the . test concrete wall	Sunlight	Efficient removal of NO _x from polluted air.	[41]2017
White cement (WC) and ordinary Portland cement paste	Mixed cement slurry (2-5wt%)	UV	NO (1000ppb) removal condition: OPC is 380 μ Mol/(m ² . h) and WC at 500 μ mol/ (m ² .h)	[42]2018

4. Preparation of TiO₂ Photocatalytic Building Materials

The production of TiO₂ photocatalytic construction materials involves several stages, such as selecting the suitable TiO₂ nanoparticles, fabricating the construction materials, and integrating the nanoparticles into the materials. Several approaches have been documented in literature for the creation of TiO₂ photocatalytic construction materials, which include sol-gel, hydrothermal, and spray-drying methods.

4.1. Sol-gel Method

The sol-gel technique is a widely employed method for creating TiO₂ photocatalytic construction materials. This approach involves the synthesis of TiO₂ nanoparticles by hydrolyzing the titania salt in a solvent and incorporating a stabilizer to prevent the aggregation of the nanoparticles. The ensuing solution is then combined with a construction material such as concrete or gypsum and allowed to dry. This method results in nanoparticles that are uniform in size and shape, thereby increasing the photocatalytic efficiency of the construction material.

The sol-gel technique boasts a significant benefit in its cost-effectiveness, as well as its capacity to maintain precise control over the chemical composition of its products by employing a low reaction temperature. Furthermore, the sol-gel method yields nanoparticles that are uniform in both size and shape, thereby intensifying the photocatalytic activity of the building material. Nonetheless, this method is relatively slow and may produce nanoparticles that lack stability [43].

It is worth noting that the sol-gel method can be used as a forming material in the manufacture of ceramics and can be used as an intermediate between metal oxide films in a variety of applications. Although the sol-gel method is a cost effective way of producing nanoparticles of uniform size and shape that can enhance the photocatalytic activity of building materials, it is a relatively slow process and the resulting nanoparticles can have low stability.

4.2. Hydrothermal Method

The hydrothermal method involves the synthesis of TiO₂ nanoparticles in an aqueous solution under high pressure and temperature. In this method, the precursor solution is placed in a sealed vessel and heated to a high temperature, which promotes the formation of nanoparticles. The resulting nanoparticles are then mixed with the building material and allowed to dry. The advantage of the hydrothermal method is that it produces nanoparticles with a high surface area, which enhances the photocatalytic activity of the building material.

The hydrothermal method is one of the most commonly used methods for the synthesis of TiO₂ nanostructures. It has several advantages over other methods, such as appropriate crystallization temperatures, environmental friendliness, controlled reaction conditions, low energy consumption and low cost. Hydrothermal synthesis is a simple and effective method for the synthesis of TiO₂ nanostructures. It involves the use of alkali solutions such as lithium hydroxide, sodium hydroxide and potassium hydroxide as solvents [44]. The concentration of the base solution used has an effect on the crystallinity, agglomeration ratio, particle size and specific surface area of the resulting TiO₂ phase [44]. NaOH is the most commonly used solvent in material preparation techniques [45]. However, the use of other alkali solutions (e.g. KOH) has been shown to affect the morphology and crystal structure of TiO₂ nanostructures obtained by hydrothermal methods [45]. The use of different TiO₂ precursors as non-homogeneous photocatalysts can also affect the morphology of TiO₂ nanostructures obtained by hydrothermal methods [46]. The photocatalytic performance of the synthesised TiO₂ products at different NaOH concentrations was evaluated by the toxic NO_x gas removal efficiency. The nanostructured TiO₂ samples prepared at higher NaOH concentrations showed higher nitrogen removal efficiency than the TiO₂-P25 precursor [47]. In summary, the hydrothermal method is an effective way to synthesise TiO₂ nanoparticles with high specific surface area, enhancing the photocatalytic activity of the building materials. The use of different alkali solutions and TiO₂ precursor pairs can both affect the morphology and crystal structure of the materials. This affects the efficiency of TiO₂-based building materials in degrading pollutants.

4.3. Spray-Drying Method

The spray-drying method involves the synthesis of TiO₂ nanoparticles by spraying a TiO₂ precursor solution into a hot drying chamber. The hot air evaporates the solvent, leaving behind the nanoparticles, which are then collected and mixed with the building material. This method has several advantages:

1. Production of nanoparticles with a narrow size distribution to enhance the photocatalytic activity of building materials.
2. An efficient and scalable method for producing nanoparticles with a uniform distribution.
3. Allows the phase composition, crystal size and surface area of nanoparticles to be adjusted.

Although spray drying is an efficient and scalable method for the synthesis of TiO₂ nanoparticles, it has a number of limitations. One of the main disadvantages is that the method is highly dependent on the nature of the parent ion solution, such as its viscosity, surface tension and concentration. If the precursor solution is not properly formulated, the resulting nanoparticles may be of poor quality or not form at all [48]. In addition, the method requires a large amount of energy to operate, which can increase production costs.

In conclusion, the preparation of TiO₂ photocatalytic building materials involves the selection of appropriate nanoparticles, the preparation of the building materials, and the incorporation of the nanoparticles into the materials. Various methods have been reported in the literature for the preparation of TiO₂ photocatalytic building materials, including sol-gel, hydrothermal, and spray-drying methods. These methods produce nanoparticles with different properties, which can affect the photocatalytic activity of the building materials. Therefore, the selection of an appropriate method depends on the specific requirements of the application.

4.4. Anodic Oxidation Method

The anodic oxidation technique represents an innovative method to generate photocatalytic building materials with TiO₂. This approach entails electrochemically oxidizing titanium metal or

alloy in an electrolyte solution, which forms a porous TiO₂ layer on the surface. This resulting layer of TiO₂ can serve as a coating for a diverse range of construction materials, including but not limited to steel, aluminum, and glass. As a result of this method, TiO₂ nanoparticles are produced, which possess high porosity and surface area, as well as a morphology and crystallinity that can be adjusted, ultimately enhancing the photocatalytic efficacy of the building material [49].

The anodic oxidation method presents certain advantages over alternative techniques, including a straightforward and eco-friendly process, direct formation of TiO₂ on the substrate without any binder, and a robust adhesion and durability of the coating. Nevertheless, this method is not without challenges, such as the necessity for high-quality titanium metal or alloy as the anode material, the complexity of maintaining uniformity and thickness of the TiO₂ layer, and the potential corrosion of the substrate by the electrolyte solution [50].

4.5. Microwave-Assisted Method

The microwave-assisted method is a modern technique for synthesizing TiO₂ nanoparticles and integrating them into construction materials. This approach employs microwave radiation to heat and activate the titanium precursor and solvent in an enclosed vessel, producing TiO₂ nanoparticles. These particles are subsequently blended with a construction material such as cement or ceramic and cured under suitable conditions. The outcome of this method is TiO₂ nanoparticles with a high level of crystallinity and purity, as well as a narrow size distribution and a spherical shape, ultimately enhancing the photocatalytic efficacy of the construction material [51].

The microwave-assisted method has several benefits over the other methods, such as a rapid and homogeneous heating process, a low energy consumption and environmental impact, and a facile control over the reaction parameters and product properties. However, this method also has some limitations, such as the requirement of special equipment and microwave-absorbing materials, the possible formation of hot spots and thermal gradients in the reaction vessel, and the difficulty in scaling up for industrial applications.

5. Strategies for improve TiO₂ photocatalytic efficiency

TiO₂ which is low-cost and environmentally friendly is a vital and widely used photocatalyst for preparing photocatalytic building materials. Although the great majority of photocatalytic building materials use TiO₂, there are three main problems must be addressed: (1) tendency to rapidly aggregation in a suspension, owing to the diameters of TiO₂ particles is relatively small, considerably decreasing its effective surface area and catalytic efficiency, and the photocatalytic oxidation reaction rate of TiO₂ was restricted owing to its poor adsorptive power; (2) the wide band gap (>3.0 eV) of TiO₂ restricts its utilization of visible light in the solar spectrum; (3) the high recombination rate of the electron-hole pair in TiO₂ restricts its photocatalytic ability.

To broaden the optical response wavelength of TiO₂-based photocatalysts, enhance the photocatalytic efficiency of TiO₂-based photocatalyst. According to present studies about TiO₂-based photocatalysts, this section mainly reviewed the strategies which focus on addressing the problem of TiO₂ aggregation and broadening the light wavelength response and improving the photocatalytic performance of TiO₂ to provide a reliable basis for the future development of TiO₂-based photocatalyst and promote the large-scale industrial application of photocatalytic technology.

5.1. Strategies for reducing aggregation of TiO₂

TiO₂ nanoparticles within smaller particle diameter size have a high specific surface area and more active site could accelerated photocatalytic reaction rate of TiO₂-based photocatalysts [52]. However, for its relatively small diameter size TiO₂ is prone to aggregation in the suspension caused the photocatalytic efficiency was rapidly reduced [53]. Therefore, researchers anchored TiO₂ to various supporting materials, such as activated carbon [54], clay [53] and silicon [12] to reduce TiO₂ aggregation in the reactivation process and improve its adsorption capacity and photocatalytic efficiency. Among these nanoparticles, silica (SiO₂) is a common component in building materials

within high chemical stability and low cost, it is a promising candidate to preparing TiO₂-based nanocomposites [12]. Elena Ghedini et al. [55] synthesized an environmentally friendly and readily-available TiO₂-SiO₂ photocatalyst which with high surface area by using an incipient wetness impregnation method, they found that ethylbenzene could be degraded by TiO₂-SiO₂ photocatalyst under ultraviolet excitation. Their research indicated that multifunctional TiO₂-SiO₂ photocatalyst is expected to combine with building materials to improve air or indoor pollution. Zhou et al. [56] using sol-gel method synthesized TiO₂-SiO₂ based photocatalyst within high specific surface area and high adsorption capacity. They found that TiO₂-SiO₂ based photocatalyst could effectively degrade toluene with UV irradiation indicated that SiO₂ as a carrier combined with TiO₂ porous photocatalyst has high adsorption capacity could promote the subsequent photocatalytic reaction and produce a positive synergistic effect.

As shown in Figure 3, Chen et al. [57] successfully synthesized the FAS12-loaded UV-responsive microcapsules by Pickering emulsion polymerization, which were easily dispersed into waterborne polysiloxane latex. The microcapsule could realize the superhydrophobicity of aluminum plate, sheet, glass, polypropylene, wood and other materials by spraying the microcapsule on the surface of these materials, owing to the microcapsule ruptured under UV irradiation and then released FAS12.

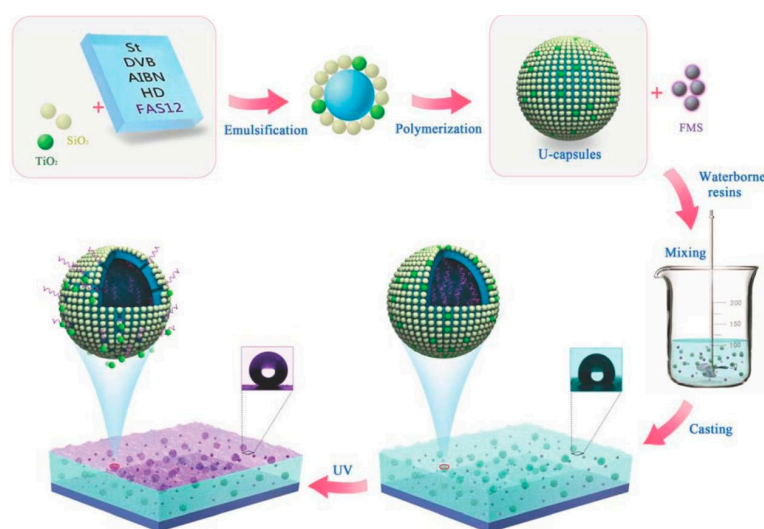


Figure 3. Schematic illustration of the preparation of all-water-based self-repairing superhydrophobic coatings based on U-capsules [57].

In addition to inhibiting TiO₂ agglomeration, SiO₂ can also regulate the crystallization of TiO₂ during high-temperature calcination [58]. It is well known that the crystalline structure of TiO₂ will affect its catalytic properties. According to report [59], anatase has highest photoactivity than other crystalline structure of TiO₂ owing to its admirable specific surface area. Silica can regulate the crystallization of amorphous TiO₂ layer into anatase nanocrystal and limited the growth size of anatase grain during high temperature calcination process [58]. However, mostly TiO₂/SiO₂ nanocomposites can only achieve photocatalytic reaction under UV irradiation, which limited their further applications in building industry. Therefore, the combination of weak visible light induced TiO₂ based photocatalyst with metal elements to effectively use the whole solar light may be a drastically promising way. Zhao et al. [60] successfully synthesized TiO₂/SiO₂/Ag ternary composite aerogel with highly porous structures by a facile sol-gel method combined with a supercritical drying technique. They found that the addition of Ag particles effectively decreased the recombination of photo-electrons and holes and enhanced visible-light photocatalytic activity of TiO₂/SiO₂/Ag ternary composite. Nadeem Raza et al. [61] reported a Ag-doped nanocomposite with low band-gap energy of 2.5 eV, it exhibited an excellent photocatalytic performance for organic dye degradation under

solar-light irradiation. However, the high cost and aggregation of noble-metal materials on the TiO₂ greatly obstacles its industrial application.

In order to obtain a TiO₂-based visible-light photocatalysts which with high adsorption ability and excellent photocatalytic efficiency. Researchers have attempted to combine nanocarbon materials with TiO₂, particularly, carbon nanotubes (CNTs) as a typical one-dimensional nanostructure have been receiving much attention in the preparation of new photocatalytic materials owing to their electrical, chemical properties and mechanical [62]. According to report [63], TiO₂ deposited on the surface of carbon nanotubes can effectively improve the light absorption efficiency of photocatalysts, due to the light shines into the TiO₂ hollow tubes and nanosheets, it will bounce back and forth many times and will eventually be absorbed, thus improving the photon capture efficiency. Nguyen et al [64]. Synthesized nanohybrids TiO₂/CNTs materials though hydrolysis method, and compared with pure TiO₂ or CNTs nanohybrids TiO₂/CNTs materials exhibited better photocatalytic performance for methylene blue degradation. Wang et al. [65] found that the combination of TiO₂ and CNTs could minimize the recombination of photogenerated electrons and holes.

In addition to carbon nanotubes, graphene is also a common carbon-based carrier which make TiO₂ nanoparticles evenly distributed in the liquid and increase the separation and transmission of electron-hole pairs in the TiO₂ [52]. According to report [66], the rGO-based TiO₂ composite improve TiO₂'s photocatalytic capability owing to rGO could retard the electron-hole pair recombination. Similarly, Xue et al. [67] verified that graphene can significantly enhance the photogenic electron-hole pair separation and transport and reduce the reunion. Although those nanocomposites have more potential development than pure TiO₂ for application, the incorporation of TiO₂ in carbon material mesopore volume, drastically reduce the specific surface area of the carbon material result to adsorption inability of pollutants. In addition, carbon materials mostly powder state, no magnetic powder carbon material based-TiO₂ material is not conducive to recycling, thus limiting its application in industry [68]. Presently, there are not many practical applications of carbon-based TiO₂ nanocomposites, and mostly carbon-based TiO₂ nanocomposites are still in the fundamental development stage. Therefore, the development of carbon-based TiO₂ with high photocatalytic efficiency is still highly challenging.

5.2. Strategies for improving the photocatalytic efficiency of TiO₂

Anchoring TiO₂ to silica, carbon nanotubes, graphene and other carriers can reduce TiO₂ agglomeration. However, the specific surface area of carriers were partially covered by TiO₂ cause the photocatalytic efficiencies of carriers decreased [69]. Therefore, in order to obtain nanocomposites with high photocatalytic efficiencies, researchers used metal elements (Fe³⁺, Cu²⁺, Pt⁺, etc.) or non-metallic elements (S/ N/B, etc.) to modify TiO₂ to obtain metal elements/ non-metallic-doped nanocomposites. Previous studies reported that metal atoms doping onto TiO₂ can drastically enhance the efficiency of TiO₂ and broaden its excitation band. Fe as a commonly metal element in the environment with low-cost and environmental friendly is a better potential candidates for modified TiO₂ compared with other metal element dopants [70]. Liu et al. [71] synthesized a visible-light-driven TiO₂ with Fe(III) doped. they found that the visible-light absorption ability of Fe(III)-doped TiO₂ is better than that of pure TiO₂ and the high quantum efficiency of Fe(III)-doped TiO₂ is maintained by the surface-grafted Fe(III) ions.

Liu et al. [72] developed a novel TiO₂ photocatalyst, which can be achieved by visible light, by coupling Ti(IV) and Fe(III) nanoclusters on the surface of TiO₂. The photodegradation mechanism of the novel photocatalyst as shown in Figure 4, they pointed that the holes and electrons were generated under visible light irradiation, Ti(IV) nanoclusters on the surface of TiO₂ would accumulate photogenerated holes and Cu(II) and Fe(III) nanoclusters would accumulate photogenerated electrons, thus, tardily recombination of photogenerated electron-hole pairs improve its solar energy conversion efficiency.

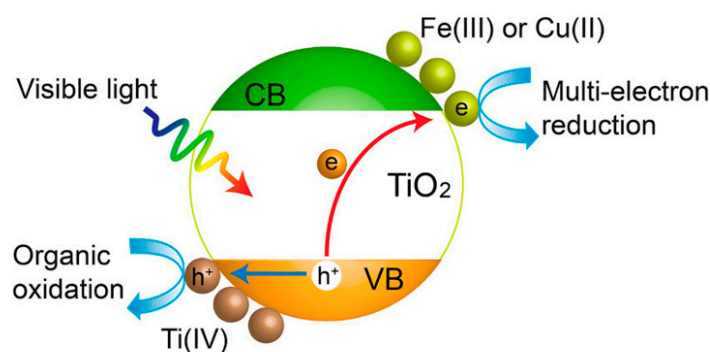


Figure 4. The photodegradation mechanism of the novel photocatalyst. Reprinted with permission from Ref. [72]

Although transitional metal modified TiO₂ can be activated by visible light irradiation, the quantum efficiencies of modified TiO₂ catalysts under visible light irradiation are still unsatisfactory. [72] What is more, transition metal elements modified TiO₂ usually exhibited poor thermal stability and vulnerable to light corrosion. Contrastly, nonmetal decoration can create a narrower band gap in TiO₂ as electron donor or acceptor and improve the visible light absorption capability of the modified TiO₂, which is much more successful than metal decoration. Due to the small ionization energy and stability of nitrogen and comparable atomic size to that of oxygen [73], nitrogen incorporation for improving photocatalytic efficiency of TiO₂ is more appropriate than other nonmetals. Chen et al. [74] synthesized N-doped TiO₂ and immobilized it above the surface of asphalt road to evaluate its photodegradation ability for vehicle emissions. they found that N-doped TiO₂ asphalt road exhibited higher vehicle emissions photodegradation efficiency under visible-light irradiation than that of pure TiO₂ asphalt road demonstrated that the N-doped TiO₂ would provide a valuable channel for the preparation of photocatalytic asphalt road materials with high visible light induced photocatalytic activity. Jun et al. [75] reported N-doped TiO₂ by pyrolysing the coprecipitation of tri-thiocyanuric acid with TiO₂ under 500°C. the results suggested that nitrogen doping into the lattice in TiO₂ can successfully reduce the band gap energy by changing the band structure, enhancing the absorption capacity of the visible light and accelerating the superoxide radical formation. Giacomo Barolo et al. [76] found that N-doped TiO₂ exhibited moderately photocatalytic active under visible light. The synergistic action of the visible light (about 400 nm) and the near-infrared light allows the photocatalytic material to form surface electrons and surface holes to a lower extent.

Although N-doped TiO₂ exhibited visible-light photocatalytic ability, researchers claimed that there are some thorny problems with N-doped TiO₂ limited its practical application: 1. the doping nitrogen concentration is rather low; 2. N doped into the lattice of TiO₂ would generates more oxygen vacancies than that of pure TiO₂, these defects promoting the recombination of photogenerated electron-hole pair; 3. the stability of N-doped TiO₂ is usually unsatisfactory [77]. In order to separate the photogenerated electrons and holes of TiO₂, the method of co-doping of TiO₂ with two different ions to resisting the recombination of photogenerated electron-hole pair has aroused wide concern. Vaiano et al. [78] found that the band gap of Fe and N co-doped TiO₂ become narrow and the modified TiO₂ had a significant photodegradation capability for Acid Orange 7 azo dye under visible-light irradiation. The decolorization and mineralization of Acid Orange 7 azo dye achieve 90 and 83% under LEDs light irradiation with 60 min, respectively. Li et al. [79] reported that Fe and N co-doped TiO₂/GF exhibited better photocatalytic efficiency than that of single doped with Fe-TiO₂/GF and N-TiO₂/GF suggested that N and Fe could synergistically modify the structure of TiO₂ and inhibit the recombination of photogenerated electron-hole pairs.

As shown in Figure 5, Liu et al. [80] synthesized a Fe and N co-doped carbon nanosheets composite by in-situ self-template strategy. They found that Fe-N-CNS composites exhibited excellent ORR activity, high selectivity and admirable stability.

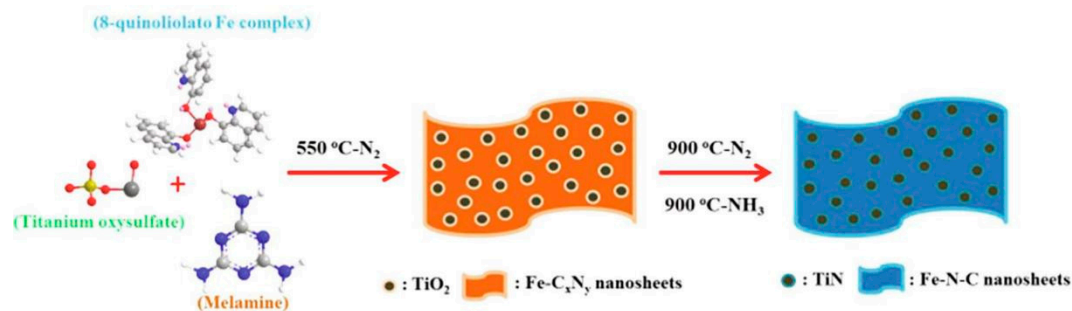


Figure 5. The preparation process of TiN/Fe-N-CNS catalyst [80] .

Hayati et al. [81] successfully deposited N and Fe elements on the surface of the functionalized single-walled carbon nanotubes, the nanocomposites could completely photodegraded sulfathiazole under ultrasonic irradiation at pH: 7.0, and it exhibited an excellent removal rate of real wastewater's COD and TOD indicated that the novel photocatalyst has an excellent photocatalytic efficiency for decontamination of recalcitrant compounds and pharmaceutical wastewater. However, the photocatalytic performance of most photocatalysts is unsatisfactory for industry application. Therefore, it is still a challenging to develop TiO₂-based photocatalysts with high specific surface area, low charge recombination, superior photocatalytic activity and excellent stability.

6. Application status and future prospects of TiO₂-based building materials

Numerous practical applications have demonstrated the feasibility of integrating photocatalytic technology with building materials to achieve pollution and carbon reduction in buildings. In the preceding chapters, we discussed the preparation methods of photocatalytic building materials and the modification strategies of TiO₂ to enhance the photocatalytic performance of TiO₂-based building materials. In this chapter, we discussed some practical examples of photocatalytic building materials to further analyze the effectiveness and critical factors that influence the application of modified functional materials. Lastly, we discuss the limitations and future trends of photocatalytic construction in practice, aiming to deepen understanding of photocatalytic construction materials and provide a reference for the subsequent development of photocatalytic functional building materials.

6.1. Application status and key influencing factors of photocatalytic building materials

After obtaining good results from laboratory-scale tests, the photocatalytic building materials have been used in practical applications, including office buildings, museums and transportation infrastructures. Table 2 lists a number of demonstration projects using photocatalytic building materials. These materials have been employed in different countries such as China, Berlin, and the Netherlands, and have proven to be durable and effective through long-term field testing. For instance, the Toledo Specialist Hospital in Mexico City has employed tiles coated with TiO₂, produced by Elegant Decoration, a construction company based in Berlin. The photocatalytic façade was found to be effective in reducing pollution levels in the surrounding air, as confirmed by long-term field tests. Similarly, the Jubilee Church in Rome, Italy, features a TiO₂ coating on its façade, which has been shown to break down harmful pollutants like NO_x and VOCs into harmless compounds, while retaining the white appearance of the church and preventing the growth of vegetation. In addition, a segment of the north toll station of Nanjing Yangtze River Bridge, China, which spans an area of approximately 6000 m² and is situated in heavily polluted areas, employed loaded nano TiO₂ photocatalytic material. Researchers monitored pollutant levels in buildings within a few months and determined that the removal efficiency of NO_x exceeded 80%.

Despite the encouraging treatment outcomes of these demonstration projects, there are critical issues that must be addressed in the practical application of photocatalytic building materials. The first issue concerns the stability of the building's photocatalytic function. During the use of photocatalytic building materials, the material structure itself is insufficiently stable, leading to the deactivation of building materials. Moreover, during the degradation process of air pollutants, a significant number of intermediate products, such as VOCs by-products or airborne dust, accumulate on the surfaces of photocatalytic building materials, resulting in catalyst contamination and consequently, negatively impacting the building's photocatalytic function. Furthermore, the impact and quantification of production by-products have scarcely been reported. The environmental impact of the intermediate by-products produced during the degradation of pollutants in photocatalytic buildings remains unknown, and further research is needed to gain a deeper understanding of the impact of photocatalytic buildings on the environment.

Table 2. The application of TiO₂ in a building facade or roof.

Building Name	Location	Building Material	Benefits	Difficulties
Palazzo Italia	Milan, Italy	TiO ₂ -based photocatalytic coating on façade	Purifies air, reduces carbon emissions, energy-efficient design, use of renewable energy sources	Cost of installation and maintenance
Jubilee Church	Rome, Italy	TiO ₂ -coated façade	Reduces air pollution, improves air quality by breaking down harmful pollutants	Limited effectiveness in high-traffic areas
Palazzo Lombardia	Milan, Italy	TiO ₂ -coated façade	Purifies air, reduces energy consumption by reflecting sunlight and reducing need for air conditioning	Cost of installation and maintenance
Bullitt Center	Seattle, USA	TiO ₂ -coated roof	Purifies air, reduces air pollution by breaking down harmful pollutants	Limited effectiveness in high-traffic areas
Denby Dale Passivhaus	Yorkshire, UK	TiO ₂ -coated façade	Purifies air, reduces air pollution, reduces energy consumption for heating and cooling	Cost of installation and maintenance
Edificio Malecon	Mexico City, Mexico	TiO ₂ -coated façade	Reduces air pollution, improves air quality, self-cleaning properties, reduces energy consumption	Cost of installation and maintenance
Haze-Free Tower	Beijing, China	TiO ₂ -coated façade	Reduces air pollution, improves air quality, enhances aesthetics, self-cleaning properties	Limited effectiveness in high-traffic areas
Queen's Building	Bristol, UK	TiO ₂ -coated façade	Purifies air, reduces air pollution, self-cleaning properties	Limited effectiveness in shaded areas
Nanjing Green Lighthouse	Nanjing, China	TiO ₂ -coated façade	Purifies air, reduces energy consumption, improves air quality, self-cleaning properties	Cost of installation and maintenance
LaFargeHolcim Headquarters	Switzerland	TiO ₂ -coated façade	Reduces air pollution, self-cleaning properties, improves energy efficiency	Limited effectiveness in high-pollution areas

In practice, photocatalytic building materials need to take into account a variety of factors, such as the catalyst, the installation environment and the building structure, to ensure that the photocatalytic building can operate in a stable and efficient manner. Therefore, photocatalytic building materials need to be selected from catalysts with high activity and stability, and their

structures and morphologies need to be optimised to improve the degradation efficiency and stability of photocatalytic materials. To avoid the accumulation of intermediates and by-products, multifunctional catalysts, such as composites of TiO₂ with other catalysts, can be tried to improve the catalytic activity and selectivity. Secondly, photocatalytic building materials need to be installed in a suitable environment to ensure their effective absorption of light and exposure in air. The location of the installation in the building, such as light openings, vents and walls, can also have a significant impact on the effectiveness of photocatalytic materials. When installing photocatalytic building materials, the reaction rate and light intensity of the material needs to be considered in order to achieve optimum degradation at the time and under the conditions of contact between the pollutant and the light. Finally, it is worth noting that photocatalytic building materials need to be matched to the structure of the building to ensure their effective application. The properties of photocatalytic building materials, such as light transmission, mechanical strength and durability, need to be taken into account during the building design phase. The coating and veneer materials on the building surface also need to be coordinated with the photocatalytic materials to ensure their degradation and aesthetics.

6.2. Future perspective and related problem discussions

In the future, the application of photocatalytic building materials in air pollution prevention is highly promising, as environmental protection awareness increases and technology advances. As urbanization accelerates, urban air pollution poses a significant threat to public health and quality of life. Therefore, using photocatalytic building materials in urban construction and planning can effectively enhance air quality. However, researchers are still exploring more efficient and stable photocatalytic building materials for better application in air pollution prevention and control. Both the government and enterprises should promote and apply photocatalytic building materials widely to maximize their environmental benefits. To better apply photocatalytic building materials in the real environment, the following technical challenges must be overcome:

1. **Stability of photocatalytic materials:** The stability of photocatalytic materials is critical in practical applications. It is important to study the stability of these materials, which undergo prolonged exposure to light and environmental factors, to improve their lifetime. Some factors that may affect the stability of photocatalytic materials include humidity, temperature, pH, pollutants, and microorganisms. Moreover, the photocatalytic materials may also degrade the substrates or binders that they are attached to, resulting in a reduction of mechanical strength and durability [82]. Therefore, developing strategies to enhance the stability of photocatalytic materials and their substrates or binders is necessary for their long-term performance.
2. **Photocatalytic reaction rate:** The photocatalytic reaction rate is a key issue that affects the practical application of photocatalytic building materials. It is necessary to ensure that the reaction rate is fast enough to effectively degrade harmful substances in the air. Therefore, exploring different photocatalytic reaction mechanisms is necessary to increase the reaction rate. Some factors that may influence the reaction rate include light intensity, wavelength, catalyst loading, surface area, morphology, crystallinity, doping, and co-catalysts [4]. Moreover, the reaction rate may also depend on the type and concentration of pollutants, as well as the presence of other substances that may interfere with the photocatalysis [4]. Therefore, optimizing these factors to enhance the reaction rate is essential for achieving high efficiency and selectivity of photocatalysis.
3. **Selectivity of photocatalytic materials:** The selectivity of photocatalytic materials refers to their ability to selectively oxidize or reduce specific pollutants in the presence of other substances [83]. Selectivity is important for achieving high efficiency and avoiding unwanted by-products or secondary pollution. However, most photocatalytic materials have low selectivity and tend to react with various organic and inorganic compounds in the air [84]. This may lead to a decrease in photocatalytic activity and an increase in energy consumption. Therefore, designing and modifying photocatalytic materials with high selectivity for target pollutants is a key challenge for their application in air pollution control.
4. **Economics of photocatalytic materials:** The economics of photocatalytic materials involves the cost-effectiveness and feasibility of their production and application. The cost of photocatalytic materials depends on several factors, such as the type and amount of raw materials, the synthesis

method, the fabrication process, the scale-up potential, and the maintenance cost. The benefits of photocatalytic materials depend on their performance, durability, environmental impact, and social acceptance [58]. Therefore, evaluating and optimizing the economics of photocatalytic materials is essential for their widespread adoption and implementation in air pollution prevention.

7. Conclusions and future perspectives

This paper reviewed recent progress in the photodegradation of atmospheric pollutants through TiO₂-based building materials and discussed the photodegradation mechanism of VOCs, NO_x and SO_x by photocatalyst under light irradiation. Lots of researches confirmed the ability of photocatalytic technology in the decomposition of gaseous pollutants. Particularly, the photodegradation efficiency of low concentrations pollutants is acceptable. Furthermore, we discussed the strategies to improve TiO₂ aggregation and broaden its visible light absorption capability in application, including synthesize composite nanomaterials with silica dioxide, carbon nanotubes, graphene and other materials to reduce TiO₂ agglomeration, and the methods of modifying TiO₂ with metal or non-metallic elements to improve TiO₂ photocatalytic ability and visible light absorption. At present, based on TiO₂ photocatalyst researches have made greatly progress, however, the catalytic efficiency of TiO₂-based building materials under the visible light irradiation in practical application is still fall flat. What is more, the generation path of by-products is unclear, there are no general evaluation criteria, limited simulation tools, the durability of photocatalysts is unknown, and photocatalytic building materials are far from widely commercial applications. To accelerate the commercialization process, there is ample need for conducting more basic research work to overcome the shortcomings of the existing catalysts. We suggested that recent priority research should focus on developing new photocatalysts which have excellent pollutants removal efficiency under solar-light irradiation and without or less low toxicity byproduct, excellent compatibility with building materials and improve its service life. This review provides a reference for optimizing existing methods and exploring new strategies, aiming to design better building materials which with photocatalytic capability to achieve efficient air purification function.

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Design, study conception, and supervision of the whole article is done by Yuanchen Wei and Yongqing Zhang; data collection is done by Xiaoyu Bai, Hong Meng, Que Wu; analysis and interpretation of results by Xiaoyu Bai, Hong Meng and Que Wu;; manuscript preparation and proofreading by Xiaoyu Bai, Hong Meng, Yuanchen Wei and Yongqing Zhang.

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