Applications and Advances in TiO2 Based Photocatalytic Building Materials

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Abstract: TiO2 is currently the most widely used photocatalytic material. Compared with traditional building materials, TiO2-based photocatalytic building materials have unique and significant advantages, which endows them with great potential in application. By summarizing the current application and research status of photocatalytic building materials, the existing problems of photocatalytic building materials and corresponding solutions were pointed out, and current research progress of photocatalytic building materials in terms of carbon emission reduction in buildings was introduced. Finally, some prospects were made on photocatalytic building materials, which would provide a reference for the study on the next generation of photocatalytic building materials.

1. Introduction
Among all the photocatalytic materials, TiO2 is one of the most promising green environmental protection materials [1] and also the most deeply studied photocatalytic material in the field of green building at home and abroad. The potential of TiO2 as a photocatalyst was first discovered by Fujishima and Honda in 1972[2]. Similar to the photosynthesis of plants, the anode made of TiO2 can decompose water into hydrogen and oxygen under light conditions [3], which triggers a series of redox reactions. Using this feature and other physical and chemical properties, a variety of building materials have been developed with TiO2, whose functions mainly involve four aspects: treatment of polluting gases, environmental sterilization, self-cleaning and anti-fogging of building surfaces, and building refrigeration. Most of them exist in the form of photocatalytic coating, self-cleaning glass, functional ceramics, photocatalytic concrete, and other composite building materials[4]. Compared with traditional building materials, photocatalytic materials have special functions such as environment purification and self-cleaning. In addition, photocatalytic materials take natural light as reaction power and hardly need artificial intervention, so they have unique advantages. However, there are some problems in the existing photocatalytic materials. First, the common practice of using photocatalytic materials as admixtures to make composite building materials will cause adverse interactions among different materials [4]. For example, the shading effect of paint or cement on light leads to lower absorption efficiency of the photocatalytic materials; the photocatalyst urges the decomposition of organic molecules in the coating,
so that the coating is easy to fall off. Second, under the existing technical conditions, the photovoltage generated by the light on the photocatalytic materials is usually not enough to drive the high-energy reaction. However, the current photocatalysts used to eliminate pollution only rely on light to complete the reaction. As a result, the types of reactions that can occur are very limited and the work efficiency is relatively low. Third, the current photocatalytic building materials are more sensitive to the surrounding environment and their performance is greatly affected by external dynamic light and application sites. These problems have largely limited the promotion of photocatalytic materials.

In addition to the above applications, the role of photocatalytic materials in the control of the greenhouse effect has gradually attracted the attention of the academic community. Richter et al. [5] used photocatalytic technology to remove non-carbon dioxide greenhouse gases from the centralized exhaust of industrial buildings and achieved good results. However, limited by the level of photocatalysis technology, they did not propose an effective and feasible technical route for living buildings that are more closely related to human activities and the main greenhouse gas carbon dioxide. In recent years, with the in-depth study of industrial catalysis, great progress has been made in photocatalytic carbon sequestration based on TiO2, which makes it possible to control carbon emissions from buildings using photocatalytic materials. In this paper, the application of photocatalytic building materials is reviewed, the existing problems and corresponding solutions are pointed out, and the research progress of photocatalytic building materials is introduced. Finally, the development direction of photocatalytic building materials is prospected, which provides a reference for the research and development of the next generation of photocatalytic building materials.

2. General Application of Photocatalytic Building Materials

2.1. Pollutant Control and Environmental Health

2.1.1. Photocatalytic Mechanism

When the nano-TiO2 material is illuminated with energy greater than the band gap, the electrons in the low-energy valence state are excited to enter the high-energy conduction band and form electron-hole pairs with the positively charged holes on the low-energy valence band, which then separate and migrate to the surface of TiO2 particles under electric field. A part of the excited electrons and holes undergo a series of redox reactions with O2 and H2O adsorbed on the surface of TiO2 to form highly active radicals ·OH and O2-, which can degrade pollutants such as organic compounds in the buildings. The process is shown in Fig.1.

Figure 1 Photocatalytic reaction mechanism of TiO2 particles (modified from Pei et al., 2011 [6])
2.1.2. Pollutant Treatment

In 1976, Carey et al. [7] first reported the technology of separating biphenyl and chlorobiphenyl through TiO₂/UV photocatalytic reaction. Since then, the use of photocatalysis in the treatment of environmental pollutants has gradually received attention. At present, photocatalytic treatment of pollutants is mainly concentrated in two aspects, one is the treatment of indoor pollutants, such as formaldehyde, and the other is the treatment of automobile exhaust, which is mainly used in road engineering.

For the treatment of indoor pollutants, Guarino et al. [8] coated 70 g/m² of TiO₂ on the walls of a 10.95 m × 17.30 m × 2.40 m closed room with a total wall surface of 150 m² to treat the mixed gases NH₃, H₂O, CO₂, and CH₄ under the irradiation of 12 fluorescent lamps (36 W). The results showed that the concentration of the mixed gas decreased greatly under the action of photocatalytic coating. Liu et al. [9] studied the purification function of composite diatomite to formaldehyde in the air in a self-made environmental test chamber. The results showed that the degradation rate of formaldehyde could reach 94.08% under natural light by adding the functional coatings of 40% activated alumina and 10% nano TiO₂. Combined with physical adsorption, the coating could completely eliminate formaldehyde. In addition, Wang [10] studied the effect of paint color additives on the absorption efficiency of formaldehyde. The results showed that the degradation effect of pigment on formaldehyde followed an order of green > yellow > red. The reusability of red paint additives was weaker than that of green and yellow. According to this result, both the color aesthetics and the actual effect should be considered when applying indoor air purification to coatings. In fact, due to its large band gap, TiO₂ usually needs UV light to exhibit photocatalytic activity. Therefore, the effect of photocatalytic treatment of organic compounds such as formaldehyde is not satisfactory when the UV band of indoor illumination is less. The problem can generally be solved by doping silver, cerium, and other elements to TiO₂.

In the field of road engineering, nano-TiO₂ materials can be directly mixed with road mixtures or coated evenly on the road surface, so as to achieve effective treatment of automobile exhaust. TiO₂ sol was sprayed on the asphalt pavement on Maoyuan Road in Fengxian District of Shanghai, which could absorb and purify the exhaust emissions of 500 vehicles every day [6]. Each coating could maintain a continuous effect for 12 months. The research of Guan et al. [13] showed that compared with the concrete pavement without TiO₂ coating, the degradation rate of TiO₂ coated pavement to motor vehicle pollutants was about 6%-12%, and the surface still had a certain catalytic effect after it is polished with a thickness of 2 mm.

Whether it is indoor pollutant treatment or application in road engineering, the application forms of TiO₂ can be divided into coating method and mixing method, both of which, however, have some defects. The main problem of the coating method is that the coating is easy to be aged or fall off under the action of external forces, while the disadvantage of mixing method is that the photocatalyst particles inside the material are difficult to contact with the light, leading to low efficiency. However, the mixing method is simple to operate and can give full play to the structural advantages of concrete and other main materials [14]. Hassan et al. [15] tested the durability of concrete mixed with TiO₂. The results showed that the wear resistance of concrete mixed with photocatalytic materials was not affected and the catalytic efficiency did not decrease significantly. Therefore, the photocatalytic building materials obtained by the mixing method have better durability.

2.1.3. Environmental Sterilization

In 1997, Kikuchi et al. coated a thin layer of nano-TiO₂ on glass and found irradiation for 3 hours could completely kill Escherichia coli [16]. Further experiments showed that nano-TiO₂ had good killing ability to many kinds of bacteria and algae, such as Pseudomonas aeruginosa, Escherichia coli, Staphylococcus aureus, Salmonella, Mycobacterium, Aspergillus, and so on. In traditional inorganic antibacterial agents, metal ions such as silver and copper are usually effective ingredients. Compared with photocatalytic sterilization, traditional inorganic antibacterial agents can inactivate the bacteria without light, but the bacteria will release heat-causing or toxic components such as endotoxin when they die. However, the nano-photocatalyst can completely remove endotoxin and other intermediate products [17]. According to this principle, photocatalysts can be used to kill bacteria and algae in cooling towers [18-19].
2.2. Anti-fogging and Self-cleaning of Building Surfaces

2.2.1. Infiltration Characteristics

Young \cite{20} gave the Young's equation of the static contact angle when a water droplet infiltrated an ideal smooth solid surface (Fig.2(a)). With the introduction of roughness, Wenzel \cite{21} modified the contact angle, introduced the roughness coefficient and proposed the dynamic contact angle. In Wenzel’s model (Fig.2(b)), the liquid infiltrated the valley of the entire solid surface. However, under certain conditions, the liquid would not infiltrate the valley, a state which was called the Cassie Baxter state (Fig.2 (c)). When the contact angle was greater than the threshold, the liquid on the solid surface existed in the form of droplets, which refracted the light and made the field of vision white, resulting in fog effect. Therefore, the key to the anti-fogging of the building surface is to construct a super-hydrophilic surface (fig.2(d)), so that the droplets are in the wet state of the Wenzel state\cite{22}.

![Figure 2](image)

Figure 2 Antifogging mechanism of superhydrophilic surface (modified from Liu et al. \cite{22} and Duran et al. \cite{23})

The methods of constructing superhydrophilic surface include surface physical modification, chemical modification, superhydrophilic coating, and so on. Nano-TiO$_2$ is an inorganic superhydrophilic material, which was first discovered by Fujishima et al. \cite{24} He coated the glass slide with TiO$_2$ and dripped it with water droplets. The initial contact angle was tens of degrees. After being irradiated with UV light, the contact angle dropped sharply to almost zero. After the removal of UV light, the superhydrophilicity disappeared and the contact angle increased, which means the process is reversible. Therefore, TiO$_2$ can be used for anti-fogging of building surfaces. In addition, TiO$_2$ can degrade pollutants through a photocatalytic reaction under UV light, so that the building has a certain degree of self-cleaning. This is the advantage of TiO$_2$ compared to other super-hydrophilic materials.

2.2.2. Progress in Application and Preparation Methods

There are two types of self-cleaning coatings based on TiO$_2$: pure inorganic TiO$_2$ coatings and TiO$_2$ based nanocomposite coatings \cite{25}. Inorganic TiO$_2$ coatings include physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic deposition (ALD), and solution-gel method \cite{26}. Because the preparation of pure inorganic TiO$_2$ coating requires highly of the equipment and vacuum environment, large-area preparation is limited. In addition, the adhesion between TiO$_2$ and organic coating is insufficient. As a result, the preparation of TiO$_2$ based nanocomposite coating is introduced.
The composite coating based on organic polymer carrier can effectively improve the catalytic efficiency. Allen et al. [27] showed that the photocatalytic efficiencies of nanometer- and micrometer-sized anatase and rutile are quite different, with higher efficiency of the former. Allen mixed anatase nano-TiO$_2$ particles of different particle sizes with rutile and then added them into a color paint composed of organic film-forming polymers. In this way, rutile brought alkali stability, while nano anatase provided surface photocatalytic activity. This composite coating could make the surface micronized, and the pollutants attached to the surface could be washed down when being washed by rainwater, so as to achieve a better self-cleaning effect. The micropowder effect was best when the content of nano anatase with particle sizes of 5-10 nm, 20-30 nm and 70 nm was controlled between 10% and 20%. Wang et al. [28] incorporated Fe$^{3+}$ and Ag$^+$ into TiO$_2$-based catalyst and applied the composite nano-TiO$_2$ to fluorocarbon materials after being modified with a silane coupling agent, so that the coating had antibacterial and self-cleaning effects.

The superhydrophilic coating made of TiO$_2$ and inorganic SiO$_2$ can achieve anti-fogging and self-cleaning effects at the same time. The surface of SiO$_2$ is hydrophilic and can be covered by silanol groups (Si-OH), which can form hydrogen bonds with droplets, leading to film condensation and anti-fog function. The reflectivity of SiO$_2$ is low, so its transmittance is higher than that of TiO$_2$ and its light transmission performance is also superior. TiO$_2$ can decompose some pollutants under light, but the wide band gap of TiO$_2$ limits the light absorption to the UV region, which only accounts for 4% of the solar spectrum [31] and does not affect the effect of illumination. Therefore, the combination of SiO$_2$ and TiO$_2$ can achieve the effects of high light transmission and self-cleaning, and get rid of the influence of anti-fog on the illumination effect.

However, the simple layer-by-layer assembly of SiO$_2$ and TiO$_2$ easily leads to the aggregation of the same particles, resulting in a significant decrease in light transmittance. In order to solve this problem, Lee et al. [32] arranged and assembled TiO$_2$ particles at 7 nm and SiO$_2$ particles at 22 nm in layers. The results showed that the coating could not only prevent glass from fogging under non-UV light, but also had the effect of self-cleaning and reducing light reflection. Li et al. [33] developed a raspberry-like SiO$_2$-TiO$_2$ nano-antireflection film. The particle size of SiO$_2$ and TiO$_2$ was modulated by controlling the molar ratio of TEOS/TOPT. After calcination, the amorphous TiO$_2$ was transformed into dispersed anatase nanoparticles on the SiO$_2$ core, resulting in raspberry-like composite particles, as shown in Fig.3. This arrangement leads to high light transmittance of the material while ensuring its super-hydrophilic and photocatalytic properties, so it is suitable for applications in solar panels and architectural glass.

In addition, modern high-rise building glass and coatings put forward higher requirements for durability and strength. Tao et al. [34] used a solution-gel dip coating process to deposit SiO$_2$ particles, hollow SiO$_2$ particles, and TiO$_2$ nanoparticles in order to form a closed-pore structure on the surface of the superhydrophilic film. The light transmittance of this film can reach 96.0%, and it has the characteristics of high temperature resistance and high mechanical strength. It is expected to be used in solar panels and high-rise building glass under severe weather conditions.

At present, the self-cleaning coatings have been applied in some demonstration projects. For example, the roof of the National Centre for the Performing is coated with TiO$_2$ photocatalytic coating to solve the cleaning problem. However, due to the dry climate in Beijing and the lack of precipitation, this application also has certain limitations because its self-cleaning coating relies on rainwater to wash the surface of the building.
2.3. Building refrigeration

The use of TiO₂ in building refrigeration is mainly due to its high reflectivity. Studies have shown that TiO₂ coated on the building roofs can reflect up to about 85% of solar radiation. Although TiO₂ is highly reflective of most visible and near infrared light, it absorbs both violet and UV light, a property that tends to raise the temperature of the coating and is not conducive to keeping the room cool. The research of Mandal et al. [35] showed that using BaSO₄ and polytetrafluoroethylene powder instead of TiO₂ and reducing the concentration of the polymer adhesive with endothermic effect could effectively solve this problem and further improve the reflectivity of the coating. In addition, TiO₂ can also be used for heat transfer enhancement, but this technology is not yet mature and is expected to be used in building air conditioning and refrigeration in the future.

3. Research Progress of Photocatalytic Building Materials

3.1. Photocatalysis and Its Basic Principles

The photovoltage generated by TiO₂ is limited, which limits the types of reactions it can catalyze. For this reason, in recent years, the chemical industry has turned to the research of photoelectrocatalytic technology, that is, the catalytic conversion reaction is carried out with the assistance of external power supply. Take the Cu/Cu₂O-TiO₂ photoelectric catalytic system [36-37] as an example, under the condition of light, the holes generated by the TiO₂ photoanode oxidize H₂O to O₂, the photogenerated electrons conduct to the Cu/Cu₂O dark cathode through an external circuit and reduce CO₂ to CH₃OH in the presence of H⁺. In this process, the photoanode reaction needs to be carried out under the condition of light, while the dark cathode reaction does not need light. The microscopic reaction mechanism involved in the dark cathode is shown in Fig.4.

![Figure 4](image-url) Microscopic reaction mechanism on surface of Cu/Cu₂O (modified from Chang et al. [36])

3.2. Photocatalysis and Building Emission Reduction

The photoelectrocatalytic process described in section 2.1 provides inspiration for artificial carbon fixation and building emission control. Bai et al. [38] from Tianjin University used polymethacrylic acid (2-dimethylamino) ethyl ester hydrogel (PDMAEMA), light absorption agent polyaniline (PANI), silica gel carrier, and photocatalyst TiO₂ to construct a photoelectrocatalytic anode with self-phototropism. On this basis, the concept of reactors on buildings (RB) is proposed. In the RB, the self-phototropic photoelectrocatalytic anode array is assembled on the outer surface of the building, and the Cu/Cu₂O dark cathode array is assembled on the inner surface of the building. The solution system of the two is connected through a pipe passing through the wall with a proton exchange membrane in the middle, forming a Cu/Cu₂O-TiO₂ photoelectrocatalytic system. This system can be simplified to the electrochemical system shown in Fig.5. Under the conditions of sunlight, the RB can reduce the CO₂ enriched by selective membrane to the chemical raw material CH₃OH and release O₂. The total reaction can be expressed as 2 CO₂ + 4 H₂O $\rightarrow$ 2 CH₃OH + 3 O₂. The electrode reaction that occurs at the autotropic photoelectrocatalytic anode array is 2 H₂O – 4 e⁻ $\rightarrow$ O₂ + 4 H⁺, the electrode reaction at the Cu/Cu₂O dark cathode array is CO₂ + 6 H⁺ + 6 e⁻ $\rightarrow$ H₂O + CH₃OH. RB can effectively eliminate CO₂ in the environment, and its application is expected to achieve ultra-low emissions or even "negative emissions" of buildings. This research provides new ideas for the control of building carbon emission and points out the direction for the development of next-generation photocatalytic building materials.
4. Conclusions
At present, the main applications of photocatalytic building materials are pollution gas treatment, environmental sterilization, self-cleaning and anti-fogging of building surfaces, and building refrigeration. In terms of pollutant control and environmental health, the future photocatalytic materials need to focus on solving the problems of working band and using form, that is, developing efficient modification process to make the materials adapt to a wider working band and selecting the appropriate use mode according to the characteristics of coating and mixing methods. In terms of self-cleaning and anti-fogging of building surfaces, photocatalytic materials should move towards stronger light transmission, higher mechanical strength, and less interference from the external environment. For building refrigeration, in the future, photocatalytic materials can be combined with air conditioning in heat transfer enhancement to achieve better refrigeration effect in the future. In addition, the application of photocatalytic technology to carbon emission control in buildings in the form of a dynamic reaction mechanism is also an important direction for the development of photocatalytic materials in the future. For this reason, it is necessary to focus on solving the problems of catalytic efficiency and cost. The above conclusions provide a reference for the improvement and development of photocatalytic materials.

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