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Review

Photocatalytic Cementitious Material for Eco-Efficient Construction—A Systematic Literature Review

Abdul Halim Hamdany [1], Alfrendo Satyanaga [2,*], Dichuan Zhang [2], Yongmin Kim [3] and Jong R. Kim [2]

[1] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore
[2] Department of Civil and Environmental Engineering, Nazarbayev University, Nur-Sultan 010000, Kazakhstan
[3] School of Engineering, University of Glasgow, Singapore 138683, Singapore
* Correspondence: alfrendo.satyanaga@nu.edu.kz

Abstract: Photoinduced processes governed by light activated TiO_2 have been studied in many ways. One of the most active areas is the development of TiO_2 photocatalysis technologies on their application for reducing environmental impacts. The immobilization of TiO_2 on solid support, such as cementitious materials, greatly enhances its use in practical applications. In this review, a wide range of applications for achieving eco-efficient building using cementitious composite materials containing TiO_2 photocatalyst was presented. The basic mechanism of photocatalysis, such as electron excitation, charge transfer process, reactive oxygen species (ROS) generation, and its role to oxidize the pollutant and microorganisms were extensively discussed. Unlike self-cleaning and air purification systems, the study on the antibacterial function of a cement-based surface containing TiO_2 is very limited. In photocatalytic cementitious materials, the key element affecting the photocatalytic performance is the accessible active surface area. However, microstructure of cementitious materials changes with age due to hydration and surface carbonation. Hence, surface area reduction and mass transfer limitation become the main drawbacks of incorporating TiO_2 in cementitious materials. This review, therefore, provides the state of the art in photocatalytic cement-based composite materials and identifies the areas in which future improvement is needed.

Keywords: photocatalysis; cementitious materials; titanium dioxide; composite materials

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1. Introduction

In 2017, the World Health Organization (WHO) reported that environmental risks–for example air pollution, contaminated water, lack of sanitation, and poor hygiene–take the lives of 1.7 million children under the age of five [1]. A polluted environment is a deadly one, and hence, reducing environmental risks could save millions of lives. Technological innovations may address such environmental problems and create an environmentally more sustainable future. Titanium dioxide (TiO_2) has emerged as an excellent photocatalyst for reducing environmental risks. Early works focused on treatment of polluted water using TiO_2 in powder suspension forms [2,3]. This method is efficient due to the large surface area of the catalyst and the absence of mass transfer limitations. However, the widespread application is limited as it has an additional separation problem when used as a suspension: recycling it from the treated water after use, which makes it time-consuming and cost ineffective [4–6].

In order to overcome these problems, many techniques have been proposed for immobilization of TiO_2 on solid support [6,7]. In recent years, there has been increasing interest in using cementitious materials as catalyst supporting media [8–12]. The main strategy is to exploit facades of buildings in urban areas as catalyst supporting media. The cementitious materials used in building facades offer enormous surface area for photocatalytic reactions [13]. This strategy has a good potential in urban pollution control

and at the same time maintaining the aesthetic of the building's appearance [10,14–16]. Furthermore, incorporating TiO_2 photocatalyst into cementitious materials may be able to keep the cement-based surface sterile by inhibiting the growth of microorganisms through photocatalytic degradation [10,17,18]. Thus, utilizing cement-based materials as catalyst supporting media potentially transform ordinary cementitious materials into environmentally friendlier products, such as air-purifying pavement, self-cleaning external wall, and antibacterial concrete, as shown in Figure 1.

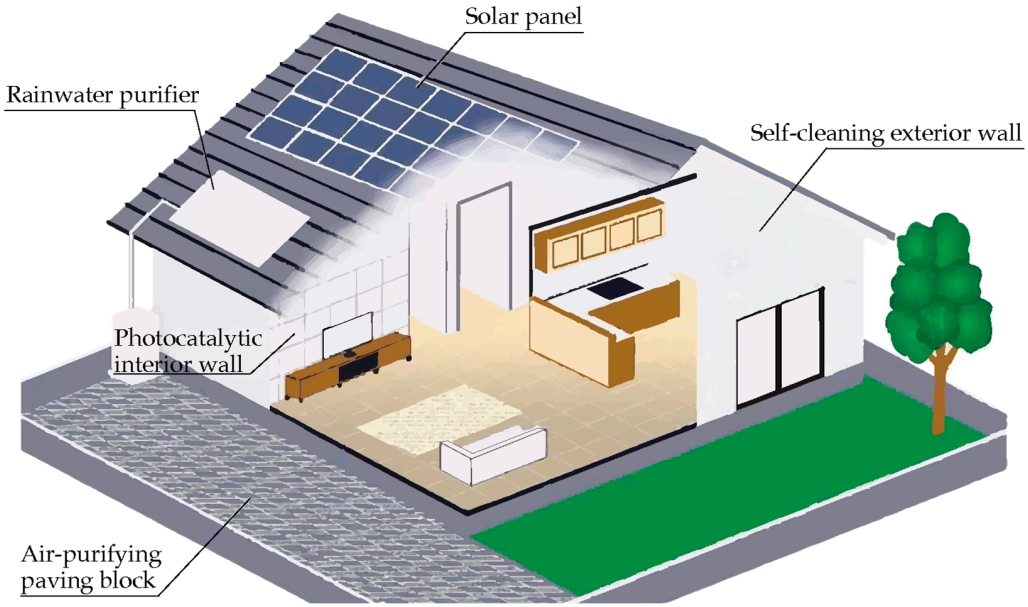

Figure 1. TiO_2-based application for eco-efficient building.

This paper presents a systematic review of the cementitious composite materials containing TiO_2 photocatalyst. The review aims to present the key findings in photocatalytic cement-based composite materials and identify the areas in which future improvement is needed. This review will start with the basic mechanism of photocatalysis, bandgap and energy level position, and improvement of pristine TiO_2 with doping and sensitization, as presented in Figure 2. This will be followed by a discussion on the applications of photocatalytic cementitious materials, such as air purification, self-cleaning, and self-sterilization function. The influence of incorporating photocatalyst into cementitious materials will be summarized and discussed. The efficiency of photocatalytic cementitious materials and the current drawback will also be discussed.

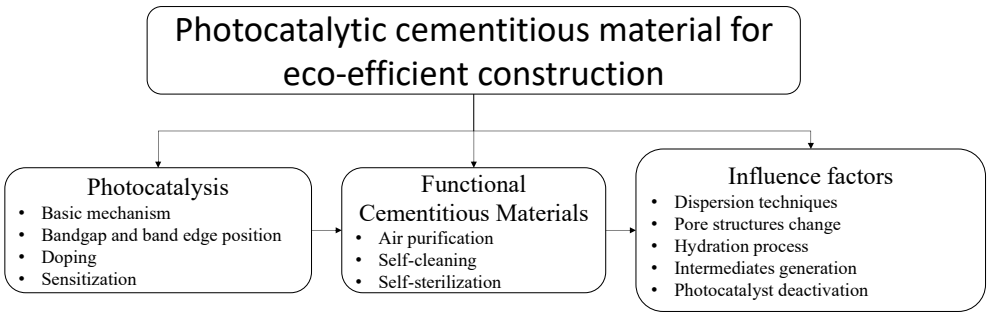

Figure 2. Review frame of photocatalytic cementitious material for eco-efficient construction.

2. Principles of Photocatalysis

Photoinduced electron transfer (PET) is a key process in photocatalysis. Absorption of photon energy greater than the energy barrier of semiconductor materials could activate many chemical reactions [19,20]. Photovoltaic, photocatalysis, and photoinduced super

hydrophilicity are the examples of photoinduced electron transfer. Although these processes could be utilized for many applications, these processes originate from a similar mechanism as shown in Figure 3. Semiconductors can absorb the light with energy greater than their bandgap and generate electron-hole pairs. The generated electron-hole pairs can be utilized for creating electric power (photovoltaic process), promoting chemical reaction (photocatalysis process), or altering its surface properties (super-hydrophilicity) [21]. The use of TiO_2 for facilitating the photocatalytic reaction started decades ago and is becoming more important nowadays as indicated by the large number of publications [13,22–25]. One of the most active areas in the development of photocatalysis technologies is their application for photodegradation of pollutants.

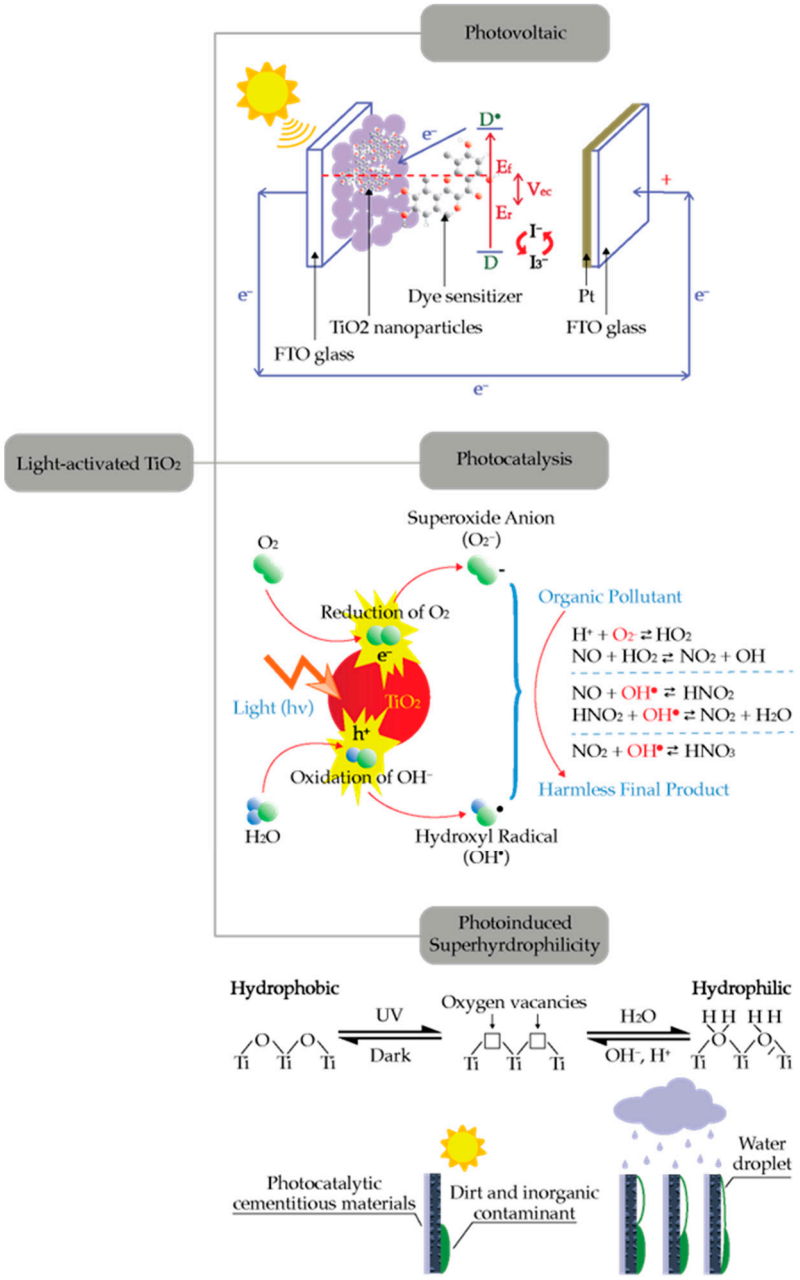

Figure 3. Applications of light-activated TiO_2.

2.1. Semiconductor Photocatalysis

Figure 4 shows the primary steps in the photocatalysis mechanism. Photoinduced charge separation (step 1 in Figure 4a) followed by electron transfer process for redox

reactions (step 3 and 4 in Figure 4b) are the key steps in the photocatalysis process. These steps will generate radicals that have the power to breakdown most of organic pollutant (step 5 in Figure 4b). In the absence of adsorbate, charge separation (step 1 in Figure 4a) will be followed by surface recombination or volume recombination (step 2 in Figure 4b). In this case, the photocatalysis process could not take place and the absorbed photon energy was released as heat.

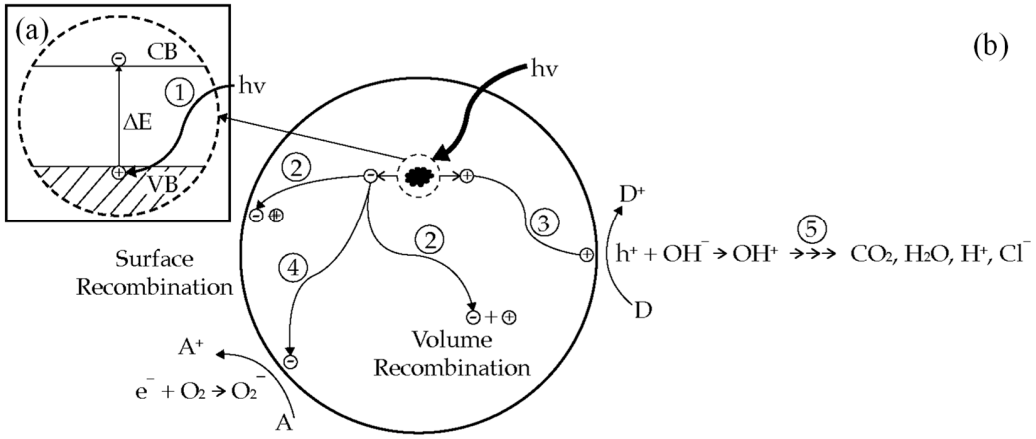

Figure 4. (**a**) Photoexcitation process; (**b**) Primary steps in photocatalytic mechanism.

In semiconductor, the valence band and the conduction band are separated by a bandgap ΔE, a region devoid of energy in a perfect crystal as shown in the enlarged section of Figure 4a. The highest energy band containing electrons is called the valence band (VB); the lowest empty band is called the conduction band (CB) [26]. The energy difference between the highest occupied band (the valence band), and the lowest unoccupied band (the conduction band) is called the bandgap, ΔE. By absorbing a photon energy equal to or greater than the band gap, ΔE, of the semiconductor, an electron is excited from the valence band into the conduction band, leaving behind a hole in the valence band (step 1), as shown in the enlarged section of Figure 4a [27]. The created electron-hole pair has a sufficient lifetime, in the nanosecond regime, to undergo charge transfer to adsorbed species on the semiconductor surface [28]. In the absence of the adsorbate, the excited electrons at the conduction band and holes at the valence band can recombine (step 2) and dissipate the input energy as heat.

If suitable, electron-hole scavengers, or surface defect state, is available to trap the electron or hole, and recombination is prevented and subsequent redox transfer may occur [27]. Photogenerated holes can be utilized to oxidize substrates at the semiconductor surface, as illustrated in step 3 of Figure 4b [29]. The holes trapped at the TiO_2 surface can react with OH^- to generate $OH^\bullet$ radicals. The generated $OH^\bullet$ radicals and holes themselves are a powerful oxidant. This powerful oxidant can degrade most of organic pollutant completely into a harmless final product (e.g., CO_2 and H_2O), as shown in step 5. In addition, the photoexcited electrons can react with electron acceptors adsorbed on the semiconductor surface (step 4). The reduction power of electrons can induce the reduction in molecular oxygen (O_2) to form the superoxide anion (O_2^-). It has been confirmed that the superoxide is almost effective as holes and hydroxyl radicals in the chain reactions for breaking down the organic compounds [8]. Initiating an oxidation and reduction process at semiconductor surface is the principle of photodegradation [29]. Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly [27]. During these processes, semiconductor remains intact and the charge transfer to the adsorbed species is continuous [28]. However, to prevent a build-up of charge, a reducible species should be provided to react with the electrons. In this system, photoinduced molecular transformations or reactions take place at the surface of a catalyst. The relevant photocatalytic processes may occur either at the air–solid interface or at the

liquid–solid interface. Therefore, if the species are pre-adsorbed on the surface, the electron transfer processes could be more efficient.

2.2. Bandgap and Band Edge Position

As the recombination is an obviously destructive process for photocatalytic reaction, the efficiency of photocatalysis greatly relies on the competition between the electron transfer processes and recombination process [2]. The ability of a semiconductor to undergo photoinduced electron transfer to the adsorbed species is governed by the band energy levels of the semiconductor and the redox potential of the adsorbed species [28]. The band energy levels of the semiconductor and redox potential of the adsorbed molecule influence the photocatalytic process by controlling the charge transfer process of such surface photochemical reactions [3,29]. For that reason, knowing the band edge positions of semiconductors and redox potential of the adsorbate is useful for indicating the thermodynamic limitations for the photoreactions that can be carried out with the charge carriers [30].

The band energy positions of several semiconductors is illustrated in Figure 5 [2]. In order to photo-reduce a chemical/adsorbed species, the conduction band position of the semiconductor has to be positioned above the relevant reduction level of the chemical species. In order to photo-oxidize a chemical species, the valence band position of the semiconductor has to be positioned below the relevant oxidation level of the chemical species. As illustrated in Figure 5, the bandgap of several semiconductor materials is in the range of 2.2–3.2 eV, corresponding to wavelength range from 564 to 388 nm. In photocatalysis, visible light photoactivation (>400 nm) is preferred by choosing low bandgap semiconductors. However, scientific investigations showed that the low bandgap semiconductors are subject to photocorrosion (oxidation of semiconductor) that results in loss of activity after a period of time [3]. In contrast, TiO_2 has been found to be chemically stable and resistant to photocorrosion and yet highly photoactive [2,31].

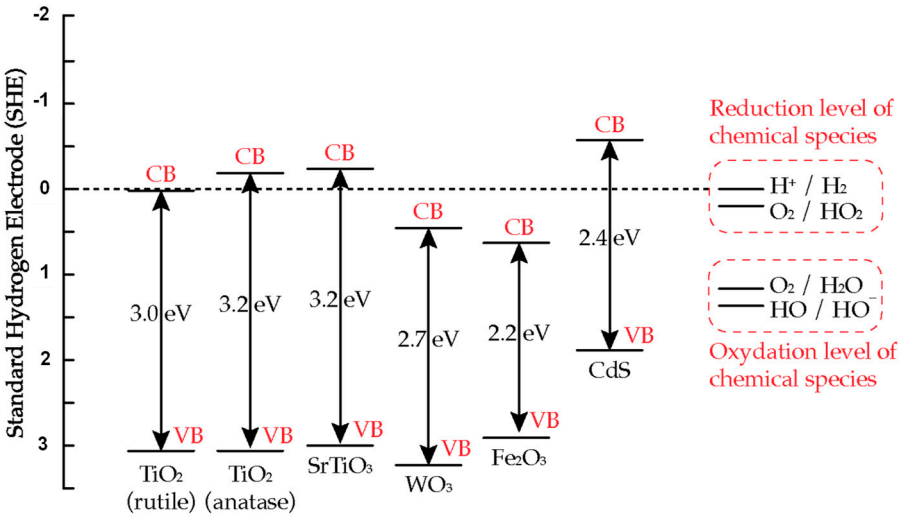

Figure 5. Valence and conductance band positions for various semiconductors and relevant redox couples at pH 0.

2.3. TiO_2 Based Photocatalyst

TiO_2 naturally occurs in three different types of crystal structure: anatase, rutile, and brookite [32]. Two of them, anatase and rutile, are commonly used in photocatalysis. As shown in Figure 5, the bandgap of anatase is 3.2 eV, while the bandgap energy for rutile is 3.0 eV, which is 0.2 eV narrower than anatase. Lower bandgap materials, such as rutile, should be preferred as they could absorb photon with smaller energy for photoactivation. However, in the literature, anatase shows higher photocatalytic activity than rutile under UV light irradiation. This is due to a more negative conduction band position of anatase than that of rutile (Figure 5), resulting in more reactive species formed [21].

The scientific concept of TiO_2 photocatalysis was introduced by Fujishima and Honda [22]. They discovered the photocatalytic water splitting in a photo-electrochemical cell. Using TiO_2 electrodes in a photo-electrochemical cell, water could be dissociated into its constituent parts, hydrogen and oxygen gases, under ultraviolet (UV) illumination. This discovery triggered much research in understanding the fundamental mechanism and in improving the efficiency of TiO_2 photocatalyst. In recent years, one of the most active areas in the development of photocatalysis technologies is their application for environmental cleanup. However, due to wide bandgap of the TiO_2 material, pure TiO_2 photocatalyst can only be activated by UV irradiation [28,33,34]. While it can use natural sunlight-UV irradiation, sunlight only contains a small amount of UV photon that can be used to carry out reactions at the TiO_2 surface. Therefore, one of the main challenges in improving the performance of TiO_2 photocatalyst is to extend their optical response from UV to visible region.

Improving the optical response and photocatalytic performance of TiO_2 in the visible light region can be achieved by doping or sensitization as shown in Figure 6 [35]. Doping is a kind of bulk chemical modification to alter the chemical composition of TiO_2 but maintain the integrity of TiO_2 crystal structure. This technique substitutes the metal (titanium) or the non-metal (oxygen) component in order to alter the optical properties of TiO_2 nanomaterials. Figure 6b shows an example of metal doped, V-doped TiO_2 [36]. V-doped TiO_2 is the metal doping of TiO_2 with vanadium (V) to shift the absorption spectra of TiO_2 to a lower energy region (red shift) with the increase in the concentration of dopant. The red shift is attributed to the charge transfer transition between d-electron (t2g level) of the V dopant and the CB of TiO_2. The bandgap of V-doped TiO_2 is lower than pristine TiO_2. Hence, it can be photoactivated by visible light irradiation.

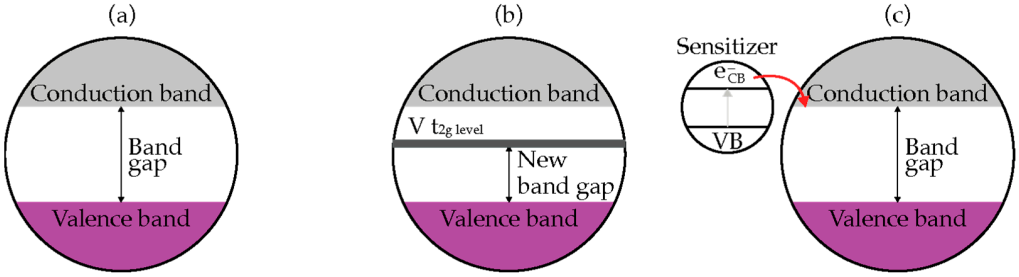

Figure 6. Improving optical response of (**a**) TiO_2, (**b**) V-doped TiO_2, (**c**) sensitization by narrow bad gap semiconductor.

An alternative technique is photosensitization, a photochemical process by which a chemical reaction is induced by energy transfer from the light-absorbing sensitizer [37]. As shown in Figure 6c, charge transfer from the excited sensitizer to conduction band of TiO_2 is a key step in these processes. The match of energy difference between the oxidation potential of the excited sensitizer and conduction band of the TiO_2 acts as the driving force for the charge injection process [38]. The sensitizer for TiO_2 materials can be any materials with lower bandgap, including semiconductors, metals, and organic dyes.

3. Photocatalytic Cementitious Materials

In the building industry, extensive work is underway to develop innovative construction materials containing TiO_2 photocatalyst. Photocatalysis technologies make the production of construction materials with advanced functions, such as self-cleaning, air purifying, and self-sterilizing surfaces, feasible [39]. Applications include self-cleaning building facades, photocatalytic concrete roads for depolluting the air, and antibacterial tiles for hospital building interiors [40]. Moreover, as the applications of photocatalytic construction materials on buildings develop, road facilities and tunneling could be beneficial to alleviate the level of environmental pollution. Finally, it can further contribute to control the urban heat island effect in densely populated cities.

For example, the "smog-eating" facade of Manuel Gea Gonzáles Hospital in Mexico was made from white-cement containing TiO_2 photocatalyst to counteract the pollution from one thousand automobiles per day. In Bergamo Italy, photocatalytic concrete blocks have been used for renovating a street with heavy traffic, claiming almost 40% of NOx abatement [41]. In the case of indoor environment, the treatment of a city tunnel wall in Rome with photocatalytic paint potentially reduces the NOx pollutants up to 20% under artificial UV light illumination [42]. The current commercial technologies, such as TX Active® and TioCem® photocatalytic cement, containing TiO_2 particles can effectively remove various pollutants, including NO_X, SO_X, NH_3, CO, and volatile organic compounds, by exposing the cement to outdoor UV light.

3.1. Air Purifying Cement-Based Materials

The application of photocatalytic cementitious materials for air purification purposes has recently received considerable attention because of its potential for controlling pollutant in the urban areas. Photocatalytic cementitious materials have the capability of destroying airborne pollutants emitted by automobiles, such as nitrogen oxides (NOx) and volatile organic compounds (VOCs). Murata, Tawara [25] have pioneered the development of photocatalytic cementitious materials for air purification. The work demonstrated that the cementitious materials containing TiO_2 particles can be used as a measure for NOx pollution control. In 2013, a German-based company, Elegant Embellishment, developed a customized photocatalytic building facade for Hospital Manuel Gea Gonzáles in Mexico. According to the studies, the facade is capable of decomposing contaminants and neutralizing the pollution of 1000 cars per day.

The basic advantage of using photocatalytic cementitious materials as building facades or concrete pavement is the availability of sunlight and rainwater for photoactivation and regeneration [25]. Furthermore, the systems installed close to an emission source react with the pollutants under higher concentration. As observed by Strini, Cassese [43] and Guo, Ling [44], the photocatalytic activities were linearly dependent on the concentration of air pollutant and irradiance. Therefore, the strategy to immobilize TiO_2 photocatalyst into cementitious materials is attractive for these air-purification systems [45–50].

The mechanism of photocatalytic oxidation of NOx at steady state is illustrated in Figure 7 [51]. The generated $OH^{\bullet}$ radicals are presumed to be the key oxidant in the reactions. At the nitrogen dioxide (NO_2) stage, part of the gas may escape from the photocatalyst surface [34]. Nevertheless, cement matrix possesses an inherent ability to bind NO_2 [45]. Therefore, use of cementitious materials as catalyst supporting media may effectively trap the NO_2 gas.

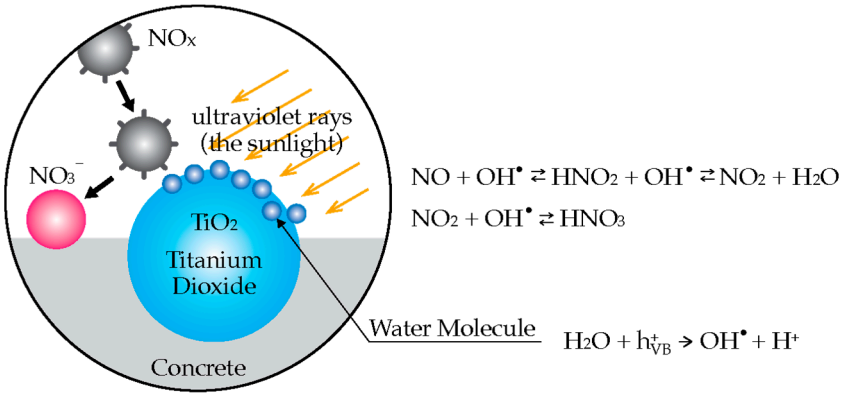

Figure 7. Mechanism of photocatalytic oxidation of NOx at steady state.

To assess the air-purification performance of photocatalytic materials, there are five published ISO methods (ISO 22917 series) nowadays. According to that, removal of nitric oxide (ISO 22197-1:2016), removal of acetaldehyde (ISO 22197-2:2019), removal of toluene (ISO 22197-3:2019), removal of formaldehyde (ISO 22197-4:2021), and removal of methyl

mercaptan (ISO 22197-5:2021) are the five standard test methods based on commonly used model air pollutants. These pollutants are well recognized pollutants found in indoor and outside air [52]. However, the current standard test methods do not consider the surface properties of cementitious materials, such as porosity, heterogeneity, time-dependent variability, and environment-dependent variability [53]. Since the photocatalytic reactions take place at the surface of photocatalyst, the surface properties of cementitious materials are expected to influence their photocatalytic efficiencies.

3.2. Self-Cleaning Cementitious Materials

Prolonged exposure to various atmospheric pollutants also leads to the discoloration of cementitious materials. [24,41]. Due to this discoloration effect, the aesthetic of buildings, monuments, and other infrastructure exposed to outdoor environments is gradually lost with time. In addition to the visible discoloration, the contamination of cement-based surfaces by airborne particles, such as algae and fungi, can have a destructive effect on structural integrity [54,55]. The key role of microorganisms in the deterioration of cementitious materials has been linked to the generation of biogenic acids (i.e., sulfuric acid and nitrifying acid) [56]. These substances cause dissolution of calcium hydroxide ($Ca(OH)_2$) and other calcium containing minerals from concrete matrix. As a result, buildings should be repaired regularly to maintain a good appearance and prevent concrete deterioration.

Biocides treatments are common methods for preventing biodeterioration of cementitious materials. However, it has not been well accepted due to durability issues and its toxicity. Research found that the use of photocatalytic cementitious material was more effective for controlling biodeterioration processes than the conventional biocides [57]. Early development of cementitious materials containing TiO_2 photocatalyst has been carried out primarily to enhance aesthetic durability of cementitious materials, especially those based on white cement [24]. Research has successfully demonstrated that the self-cleaning technique can be applied to various construction materials, such as glass and cement-based materials, i.e., concrete and mortar [13].

Apart from its function to decompose organic contaminants through the photocatalysis process, TiO_2 has another unique photoinduced phenomenon to alter the wettability of its surface. The latter effect is often termed 'super hydrophilicity'. The first phenomenon, photocatalysis process, has been studied extensively for decades while the second one, super hydrophilicity, is more recently discovered. The ability of photocatalyst-based coating to improve the wettability upon illumination highly influences the efficiency of the self-cleaning activity [52]. In this case, after the generation of electron-hole pairs, the photoexcited electrons could react with the Ti^{4+} cations to form the Ti^{3+}, as shown in Figure 8. Meanwhile, the holes could oxidize the $O_2{}^{2-}$ anions to form the molecular oxygen. Then, the oxygen atoms are released, creating oxygen vacancies. The oxygen vacancies could be then occupied by water molecules, forming a layer of chemisorbed OH groups, which tend to make the surface hydrophilic [58]. In the super-hydrophilic surface, the close contact between surface and adsorbed contaminant could be prevented [59]. Hence, even though the number of incident photons may be insufficient to decompose the dirt and other impurities, the clean surface is maintained when water flow is supplied [34].

The efficiencies of the self-cleaning effect lie on the synergy between photocatalysis and photoinduced super hydrophilicity [58]. International standard methods already exist nowadays to determine the efficiency of self-cleaning surfaces and further can be used by manufacturers to ensure the quality and reliability of their products [60]. Measurement of water contact angle (ISO 27448:2009) and organic dye decomposition (ISO 10678:2010) are commonly used test methods to evaluate self-cleaning activity of photocatalytic surfaces. The former method is used to measure the water contact angle under UV illumination. The latter method is used to evaluate the photocatalytic processes by degradation of the dye molecule in aqueous solution under UV illumination.

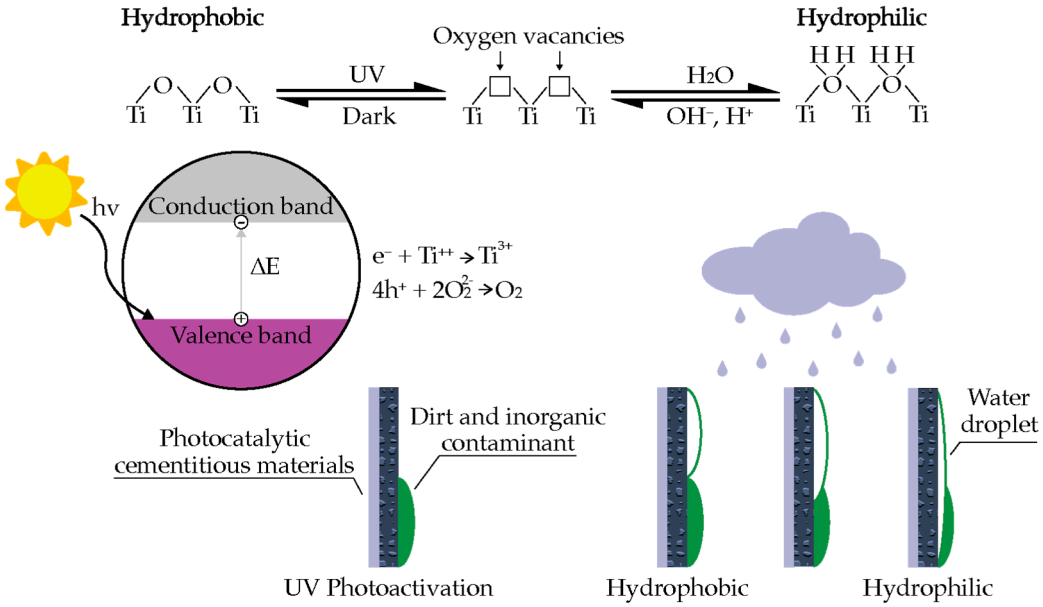

Figure 8. Mechanism of photoinduced hydrophilicity.

TiO_2 photocatalysis produces a more pronounced effect on smooth surfaces, such as glass and ceramic tiles, than on cementitious materials surfaces [41]. The effect on cement-based surfaces is limited due to their relatively high roughness, porosity, and permeability. Nevertheless, through the synergetic effect of photodecomposition and super hydrophilicity, the self-cleaning effect of photocatalytic cementitious materials is still promising. Therefore, the best practice of self-cleaning cementitious materials is for outdoor application due to the availability of sunlight and rainfall to maintain the self-cleaning effect continuously [40,61].

3.3. Self-Sterilizing Cement-Based Coated Surfaces

The researchers have shown that photocatalysis reaction induced by light-activated TiO_2 is significantly effective in destructing the pathogenic microorganisms [23,62–65]. *Escherichia coli*, *Lactobacillus acidophilus*, *Salmonella enteritis*, and *Clostridium perfringens* are ranges of test bacteria that have been investigated [52]. The basic photocatalytic disinfection mechanism is mainly caused by an initial attack on the bacteria cell wall. Carre, Estner [62] revealed dual effects of superoxide anions (O_2^-) on lipid peroxidation that could enhance membrane fluidity and disrupt cell integrity. After eliminating the cell wall protection, the oxidative damage takes place on the plasma membrane of the bacteria, resulting in subsequent rapid death of cell. It was also found that the cell exposed to TiO_2-UV treatment exhibits rapid cell inactivation at the signaling stages, which affects a restricted set of respiratory components [23].

Furthermore, the cells exposed to TiO_2-UV treatment exhibit rapid cell inactivation at the signaling stages, which affects a restricted set of respiratory components [23]. It was possible that superoxide anions (O_2^-) might inhibit the bacterial respiration process. For example, *Shewanella oneidensis* used the cytochromes MtrA, MtrB, MtrC, and OmcA for electron transfer [66–68]. By the cytochromes, the bacteria were able to transfer the electron from an intracellular region to an extracellular space and have the redox reaction in the outer membrane or extracellular space, known as one of the important steps in bacteria [69]. However, the superoxide anions (O_2^-) were highly active, which might further affect the cytochromes stability and/or inhibit the normal redox process in bacterial respiration.

Bacteria were ubiquitous and they formed the biofilms after attaching on the cementitious materials [70]. Previous studies have reported that the bacteria in the biofilm stage were more tolerant in the harsh environment (e.g., temperature fluctuation, antimicrobial agents) compared to the bacteria in the free-swimming stage. The bacteria and the biofilms

might further affect the human body and cause serious infection [71,72]. As a result, the antibacterial and antibiofilm techniques were strongly needed in the cementitious materials. One of the emerging techniques was immobilization of TiO_2 in cementitious materials.

Immobilization of TiO_2 into cementitious materials has led to the development of versatile self-sterilizing cement-based surfaces that are useful for a wide variety of applications. Self-sterilizing surfaces are particularly useful for construction of microbiologically sensitive places, such as healthcare facilities and manufacturing facilities, that produce microbiologically sensitive products. A previous study demonstrated that the photocatalytic cementitious materials could deactivate the *Escherichia coli* under UV irradiation within relatively short time [17,18,54,73,74]. The biocidal capabilities of photocatalytic cement-based surfaces can induce microbial death and maintain the sterile surface. However, compared with air-purification and self-cleaning applications, little research has been carried out to investigate the antimicrobial effect of photocatalytic cementitious materials.

4. Discussion

4.1. Influence of Using Cementitious Materials as Catalyst Supporting Media on Photocatalytic Activity

As discussed earlier, the immobilization of TiO_2 on solid support, such as cementitious materials, greatly enhances its use in practical applications. However, it may reduce the photocatalytic efficiency due to the reduction in active surface and mass-transfer limitations. For TiO_2 immobilized systems, the accessible active surface area is a key element affecting the efficiency of photocatalytic activity. The accessible active surface area depends on the amount of TiO_2 in the hardened cement and the pore structure of cementitious materials. The factors controlling the accessible active surface area should be well understood before developing an efficient photocatalytic process.

4.1.1. TiO_2 Dispersion

The effectiveness of TiO_2 dispersion in cement media has a great influence on the photocatalytic performance of the resulting products. In conventional dispersion methods, the TiO_2 particles were usually mixed with cementitious materials, such as dry powders, by mechanically stirring before adding water. This mixing procedure was inclined to strong aggregation of TiO_2 particles in the cement matrix, resulting in the decrease in the available active surface area in hardened cement [75]. It was found that the hydrodynamic size of TiO_2 nanoparticles dispersed in aqueous solution tends to be larger than the primary particle size. Jiang, Oberdorster [76] shows that probe sonication works very well to significantly decrease the hydrodynamic size. In the next studies, Yousefi, Allahverdi [77] as well as Krishnan, Zhang [14] adopted a wet-mixing procedure in order to suppress the aggregation of TiO_2 particles in cement matrix. In wet-mixing procedure, the TiO_2 particles were first mixed with water using probe ultrasonication before adding other materials. The use of ultra-sonication leads to uniform distribution of the nanoparticles and enhances the photocatalytic performance.

Regardless of the mixing methods, mixing TiO_2 particles with cementitious materials may reduce the active surface area due to the encapsulation of photocatalyst particles by hydration products. Consequently, the photocatalytic activity is seriously limited and sensitive to aging processes [78]. It was observed that dispersion of TiO_2 into coatings can be considered an attractive alternative since the coatings are in direct contact with pollutants and photons and less affected by cement hydration [14,49]. However, the coating method might be susceptible to harsh weathering processes. Hence, the selection of suitable dispersion methods should be adjusted to their intended applications to maximize the active surface area.

4.1.2. Pore Structure

The researchers have shown that there is a direct relationship between photocatalytic performance and microstructures of cementitious materials [50,79]. Microstructure in this

context is defined in terms of pore structure (i.e., pore volume, pore size distribution, interconnectivity). The pore structure of cementitious material is one of the important factors to determine the surface area accessible for the photocatalytic process. Generally, increasing total porosity could enhance the photocatalytic performance due to the increase in accessible active surface area. Additionally, high porosity is advantageous to the TiO_2 particle retention after the weathering process [49].

The structure of porosity also determines the rates of intrusion and the rate of the pollutant accessing the mass of concrete. Insufficient porosity for adsorption of the contaminant may lead to a negligible effect of photocatalytic activity [6]. Hence, high porosity is favorable for pollutant accessing the internal structure of concrete [48]. Hamdany, Ding [10] studied the effect of different lightweight materials on photocatalytic activity. Lightweight ECC using glass bubbles shows the highest photocatalytic activity on decomposition of bacteria. The light-colored glass bubbles are preferable to maintain photocatalytic activity due to the better light transmittance property. At the same time, uniform size of glass bubbles has created better pore structure compared to the use of other lightweight materials, such as air-entraining agent (AEA) or fly ash cenospheres (FAC). However, in some studies, high porosity caused the decrease in photoactivity because the rate of contamination is higher than the rate of decontamination [73,80].

In the long term, the microstructure of cementitious materials changes with age due to surface carbonation. Carbonation of cementitious materials is the irreversible chemical reaction that transforms the hydration product, $Ca(OH)_2$, to calcium carbonate ($CaCO_3$) by the presence of carbon dioxide (CO_2) in the pore water. Since $CaCO_3$ has a different crystal structure and a higher molar volume, carbonation increases the solid volume of cement paste [81]. Thus, it decreases the total porosity and shifts the pore size distribution toward smaller diameters. It was found that carbonation also causes little reduction in the specific surface area [82]. The decrease in porosity and specific surface area could result in the reduction in accessible active surface area. Furthermore, Dias [83] investigated that carbonation alters the sorptivity of concrete to a lower degree, weakening the adsorption of contaminant. Hence, the change in microstructure by surface carbonation may lead to the reduction in photocatalytic performance [14,78,84].

4.2. Effect of Incorporating TiO_2 into Cement-Based Material

Understanding the effect of TiO_2 incorporation on the behavior of cementitious composites is of great importance especially for possible construction applications. In the fresh state of the mix, reduction in workability is the main effect induced by adding TiO_2 materials [85]. Due to their nanometric size, the mix undergoes extensive alteration in the rheological behavior. This change is very pronounced and must be considered to achieve a targeted workability during construction processes. However, several researchers have studied the influence produced by the presence of TiO_2 fine particles on the cement hydration and the concrete strength [47,78,84,86,87]. The addition of TiO_2 fine particles generally increases the strength of concrete, which is attributed to the filling effect. However, there is no general consensus on the effect of TiO_2 fine particles on hydration kinetics. Hence, the impact of TiO_2 on cement hydration kinetics is still a subject of debate.

Early research on this effect found that the presence of fine particles enhances the degree of hydration of the major cement phase [87]. Further studies by Lackhoff, Prieto [78] as well as Bo Yeon and Kurtis [86] confirm that there were specific interactions between the cement matrix and the photocatalysts due to pozzolanic activity of the semiconductors. The addition of TiO_2 particle, which has a high surface area, provides additional nucleation sites for hydration product formation. TiO_2 may react with calcium hydroxide ($Ca(OH)_2$) to form a product similar to calcium silicate hydrates (C-S-H).

In contrast to the research discussed above, Jun and Chi-Sun [84] observed that the incorporation of TiO_2 into cement matrices did not influence the amount of hydration product. Their results indicated that TiO_2 was inert and chemically stable in the cement hydration reaction. Their findings suggest that the TiO_2 particles act only as fillers and did not

influence the amount of hydration product. Recent study by Pérez-Nicolás, Balbuena [47] found that the addition of TiO_2 into iron-rich dark cement gave rise to a heterogeneous matrix, as a result of the TiO_2-ferrite interaction. However, it is suggested that the predominant mechanism of incorporating TiO_2 into iron-lean white cement is physical entrapment, without significant chemical interaction. In this latter case, most TiO_2 in a white-cement matrix remained unaltered and almost fully available for the photocatalytic processes.

4.3. Photocatalyst Deactivation

The photocatalyst lifespan is an obviously important point for economic reasons, as it sets optimum run times between catalyst regeneration and replacement [88]. Performance degradation over time, called photocatalyst deactivation, is among the most severe practical problem. The generation of intermediates is one of the main causes of photocatalytic deactivation. An incomplete process of photocatalytic oxidation produces intermediates that are retained on the surface. Intermediate products can occupy the active sites of the catalyst, leading to a number of problems that include catalyst deactivation. Further catalyst deactivation (and regeneration) studies in photocatalysis are necessary to obtain better understanding on these processes and establish the process economics of this technology.

Research work has successfully demonstrated that using more active photocatalysts could retard the deactivation process [89]. Choosing the correct photocatalyst for each specific application during the manufacturing phase determines the overall durability of the final product in the usage stage. For example, visible light-activated photocatalysts will have a much wider light absorption range and radically improved performances under low light intensity conditions. Improving performance could, at the same time, delay the deactivation processes.

In the usage phase, controlling relative humidity is of great importance for the efficiency of photocatalytic reaction. Water vapor plays a significant role in the formation of active species [90]. Water molecules adsorbed on the photocatalyst will react with the hole and generate some hydroxyl groups, which in turn oxidize pollutants. Figure 9a presents the concentration of air pollutants benzaldehyde and CO_2 with different relative humidity during the photocatalytic reaction process. Ibusuki and Takeuchi [86] found no conversion in the absence of water vapor, and the photocatalytic reaction rate increased linearly with increasing relative humidity over the range 0–60%, as shown in Figure 9a. However, excessive water vapor on the catalyst surface inhibits the photocatalytic reaction because the presence of water vapor competes with contaminants for adsorption sites on the photocatalyst, thus reducing the performance [91]. This is called "competitive adsorption" between water vapor and contaminants.

Although the deactivation mechanism of photocatalyst is not clear, it can be supposed that it is due to the partial saturation of active sites for adsorption, on the photocatalyst surface, with intermediate products. Akhter, Hussain [92] demonstrated that placing the used catalyst in an oven at 30 °C and a relative humidity of approximately 40% for 12 h to evaporate the adsorbed species could recover more than 90% of the catalysts, as shown in Figure 9b. Figure 9b-1 and Figure 9b-2 indicate the image of TNPs after 5 h reaction and after 12 h regeneration in the air, respectively. Figure 9b-3 and Figure 9b-4 indicate the image of Meso. TiO_2 after 5 h reaction and after 12 h regeneration in the air, respectively. The work found that most of the adsorbed species were only adsorbed physically.

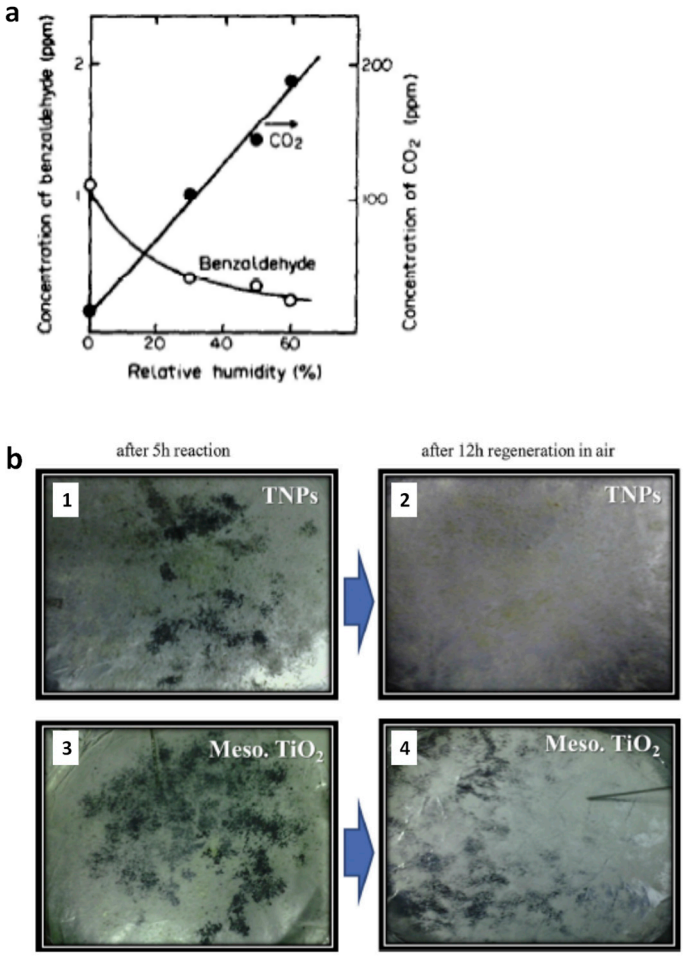

Figure 9. (**a**) Effect of relative humidity Reprinted with permission from Ref. [90] 2022, Elsevier and (**b**) effect of heat treatment Reprinted with permission from Ref. [92] 2022, Elsevier.

Previous studies have shown that environmental temperatures and the water-to-cement ratio significantly affect the leaching kinetics [93–95]. Temperature could increase ionic diffusivity, accelerate diffusion kinetic, and create significant change in cement paste microstructure to create higher porosity. The temperature elevation could result in the vibration of the crystal structure of C–S–H [94,96,97]. Increasing temperature could transform the cement hydrates (C–S–H, ettringite), resulting in an increased porosity and a higher diffusivity of aggressive ions [98–101].

5. Conclusions

In this study, a systematic review of the cementitious composite materials containing TiO_2 photocatalyst was presented. The immobilization of TiO_2 on solid support, such as cementitious materials, greatly enhances its use in practical applications. Photocatalytic cementitious materials with diverse functions, such as air-purifying, self-cleaning, and antibacterial properties, could be achieved. In photocatalytic cementitious materials, the key element affecting the photocatalytic performance is the accessible active surface area. However, microstructure of cementitious materials changes with age due to hydration and surface carbonation. Hence, surface-area reduction and mass transfer limitation become the main drawbacks of incorporating TiO_2 on cementitious materials. Further study on evaluating the antibacterial effect of photocatalytic cementitious materials and using visible light-activated-TiO_2 in cementitious materials is needed as up to this stage little evidence is available on such applications.

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