REVIEW

A systematic review on photocatalytic concrete for pavement applications: an innovative solution to reduce air pollution

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Abstract

Air pollution is one of the major health threats for urban dwellers due to increased concentration of pollutants and vehicular traffic. Approximately 7.0 million premature deaths in the world are associated with air pollution. Although stringent emission standards have been introduced, no significant reduction in air quality index in metro cities has been reported. Alternative solutions such as photocatalytic materials can be utilized as an innovative strategy to reduce the concentration of pollutants. Photocatalytic materials can be used in photocatalytic concrete pavements, which decrease the concentration of NO_x by photocatalytic activity. A systematic review of photocatalytic materials and its application in concrete pavements has been introduced. The laboratory and field investigations of photocatalytic concrete pavements have been discussed. It was found that NO_x reduction up to 60 and 31%, respectively, was observed in laboratory and field conditions. Titanium dioxide (TiO_2) is the mostly commonly used photocatalytic additive in the range of 3–10% by cement weight. The review found that the photocatalytic concrete pavements have not gained significant attention unlike other pavement materials. The demerits of TiO_2 for field application and research lacunae in this domain have been discussed and based on which, future scope of research is proposed. It is envisaged that photocatalytic concrete pavements can play a significant role in reducing air pollutant concentration in urban areas.

Keywords Photocatalysis · Photocatalyst · NO_x · Photocatalytic pavements · Air pollution

Introduction

Air is one of the significant elements for the life to sustain. The quality of air in the atmosphere plays a crucial role in influencing the well-being. However, with the industrialization, the quality of air has significantly worsened over the course of time [1]. In addition to industrialization, one of the other significant factors, which have contributed to lowering the air quality, is vehicle emission from transportation activities, and in particular, on-road vehicles [2]. According to World Health Organization (WHO), 99% of the World's population breathes air, whose quality levels are below the prescribed limits [3]. The air quality is measured using a parameter "*Air quality index (AQI)*", which ranges from 0 to 500, where higher the AQI indicates unhealthier air [4]. The motor vehicle emissions are one of the prime contributors towards higher AQI [5]. The motor vehicles emit gases such as carbon dioxide (CO_2), carbon monoxide (CO), particular matters such as PM2.5 and PM 10, and toxic gases such as nitrous oxide (NO_x) and sulphur oxide (SO_x) [6]. Among these gases, CO_2 contributes to the global warming leading to depletion of ozone but has relatively less impact on respiratory system of urban dwellers. On the contrary, NO_x and SO_x are toxic in nature and are known to cause short- and long-term respiratory disorders along with PM2.5 and PM10. Several studies have shown good association with exposure to the vehicle pollutants and respiratory disorders such as chronic obstructive pulmonary disease, upper respiratory tract infection, asthma, and bronchitis. [7–13]. Further, the extent of air pollution varies spatially depending on the type of settlement, where urban dwellers are more affected from respiratory disorders compared to rural dwellers [14, 15]. The concentration of vehicle pollutants is higher in urban areas due to higher vehicular population and canopy-type built environment. The study by Schneidemesser et al.

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[16] found that the presence of trucks, buses, and mopeds increased the particulate matter concentrations by 40% and this increased with traffic congestions. This clearly indicates that with the increase in number of vehicles, traffic congestions during peak hours, presence of traffic signals at the intersections, etc., are bound to increase the vehicle pollutant concentration further deteriorating the air quality, especially in urban scenario.

In order to reduce the emissions from the vehicles, emission standards are in effect in different countries. In Europe, Euro 6/VI emission standards are adopted and different emissions standards are provided for gasoline and diesel vehicles [17]. The G20 countries, which account for 90%

of global vehicle sales, also adopt a similar emission standards. These emissions standards have been revised and made more stringent to curb the contribution of air pollution from vehicles. The emission standards for Euro 5 and Euro 6 for diesel vehicles are shown in Table 1.

Although emission standards are in force, still the problem of air pollution persists and has been one of the major causes of pollution related deaths. Some cities have adopted traffic congestion mitigation measures, such as car-pooling methods, public transport, but still there is no significant drop in the concentration of pollutants [18].

There is a need to look for solution to curb air pollution problem due to vehicle emissions from different dimension apart from the solutions provided by administrative and economical aspects. One such material technology, which can be considered as a supplement to the existing methods of air pollution mitigation, is photocatalytic concrete [19]. The main objective of this review is to critically assess the performance of photocatalytic concrete in pavement applications as one of the solutions to reduce air pollution from vehicle emissions. The outline of the review is shown in Fig. 1.

Significance of the review

There has been rapid growth in world's population and economic development, which has led to an increase in transportation infrastructure. With the increase in transportation

Table 1 Emission standards for euro 5 and euro 6 [17]

Pollutants	Heavy-duty vehicle in transient mode		Light-duty diesel vehicle in transient mode	
Emission limits (g/km)	Euro 5	Euro 6	Euro 5	Euro 6
CO	4.00	4.00	0.50	0.50
HC	0.55	0.16	–	–
CH4	1.10	0.50	–	–
NO_x	2.00	0.46	0.18	0.08
Particulate matter (pm)	0.03	0.01	0.005	0.005
Particulate number (PN) (#/km)	–	$6*10^{11}$	$6*10^{11}$	$6*10^{11}$
Ammonia (ppm)	–	0.01	–	–
Fuel sulphur limit (ppm)	10.00	10.00	–	–

Fig. 1 Outline of the review
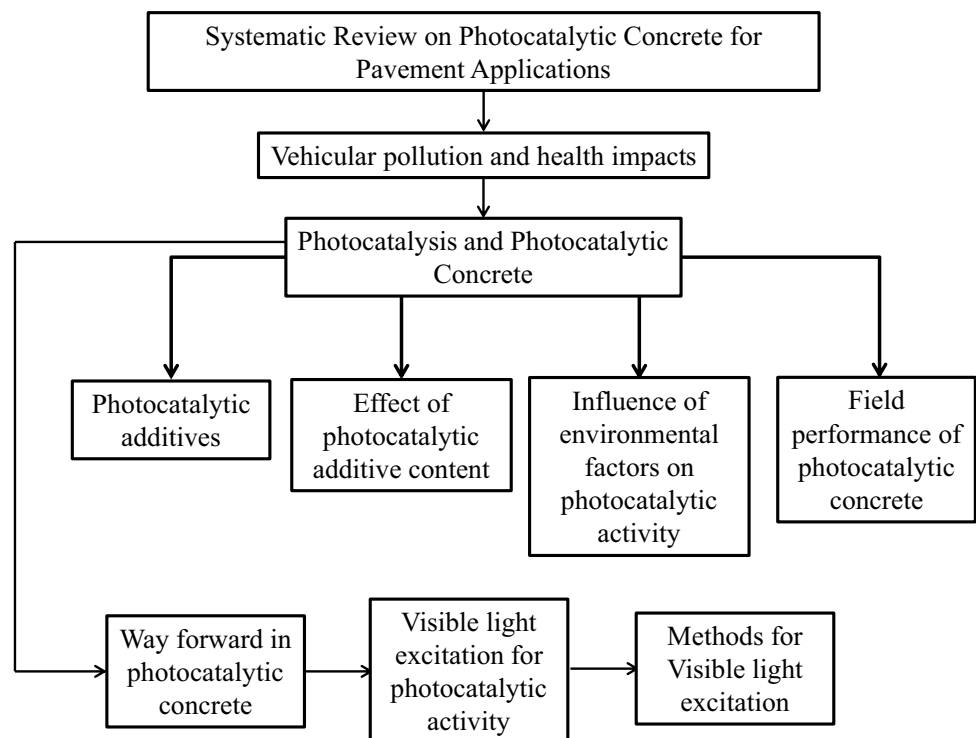
infrastructure, vehicular emission has increased at an alarming rate. Almost 29% of the greenhouse gases (GHGs) are caused due to vehicular emissions [20]. Nearly 10% of work-related diseases are chronic respiratory disease (CRD), majorly caused by air pollution. The increment in the population has increased the demand to travel, which has increased the transportation on the roads. If seen closely, the drivers of buses, autos, and rickshaws are a significant group of people who are continuously exposed to the pollution effect and hence are more prone to get infected with CRDs. Out of all the pollutants, nitrous oxide (NO_x) has the most detrimental impact and has the second-highest societal impact cost after particulate matter (PM) [21]. As far as road infrastructure is considered, it contributes a significant part to the urban sprawl. The total area coverage of roads in the urban areas is nearly 40–60% [22]. With this advantage, several kinds of research have been carried over self-cleaning and air-purifying pavements to reduce air pollution. This review is related to the applicability of photocatalytic concrete in pavements to reduce NO_x pollutant from the atmosphere.

Vehicular pollutants and health impacts

Studies have shown that there has been an average consumption of 100 million tons of fuel every year [23]. The emissions due to the utilization of these fuel include pollutants such as carbon dioxide (CO_2), carbon monoxide (CO), particulate matter (PM) and nitrous oxide (NO_x). One of the major reasons for air pollution is the increasing travel demand of the people, which increases the transportation mobility on the roads. This hiked mobility of the people is converting into a high price in terms of its side effects. The major pollutants are CO_2, CO, PM and NO_x. The primary reasons for the escalation of vehicular pollution are as follows:

- Increased vehicle density in urban areas [24]
- Use of older vehicles [6]
- The dominance of cars and two-wheelers [25]
- Insufficient public transportation system [26]
- Inadequate land use planning [27]
- Improper road conditions [28]

A study conducted by Singh et al. [23] estimated the pollution load from different metro cities in India, which is one of the fastest developing countries and also has highest social cost of carbon [29]. The pollution load estimated for the year 2020 is shown in Table 2. The pollution load corresponds to Euro 4 emission standards, which is equivalent to BS-IV in India. It can be clearly seen the magnitude of the different pollutants being emitted from gasoline and diesel

Table 2 Pollution load from different cities in India [61]

City	Pollution load in metric tons per day			
	CO	NO_x	HC	PM
Delhi	421.84	110.45	184.37	12.77
Mumbai	189.55	46.37	89.93	10.58
Kolkata	137.50	54.09	47.63	10.80
Chennai	177.00	27.30	952.64	7.29
Bangalore	207.04	29.72	117.37	8.11
Hyderabad	163.95	36.89	90.09	8.00
Kanpur	17.93	7.25	11.70	1.91

vehicles in one year. These pollutants will have severe implications on the respiratory health of the urban dwellers [30].

The transportation sector contributes nearly 55% of NO_x production [20], out of which 35% of the NO_x production is from heavy vehicles such as buses and trucks, and the rest is contributed by diesel engine cars. As compared to 2012, the pollution load has drastically increased, and reports suggest that the production of NO_x per day in Delhi is nearly 17,000 kg/sq-km [23]. The damaging effect of these pollutants is more adverse as compared to CO_2. A detailed pollutant-wise health effect is explained in Table 3. It can be seen that NO_x has more negative effects both on the environment and health. Hence, there is a need to reduce the pollutants significantly at the site of production itself.

Photocatalysis

The photocatalysis is a process, where the reaction takes place in the presence of a catalyst activated by the light. The catalyst used in the process of photocatalysis is referred as photocatalyst, as these become active in the presence of light and increase the rate of reaction [31]. The first observation of the photocatalysis was perceived by Fujishima and Honda [32] in electrochemical photolysis of water using semiconductor in the presence of ultraviolet radiations. Most of the semiconductor materials possess photocatalytic property and are used in various engineering applications [33]. Among the various photocatalysts, titanium dioxide (TiO_2) has been studied and applied extensively in the domain of civil engineering in cement concrete applications [34].

Photocatalytic additives

The photocatalytic property in concrete is achieved by the addition of photocatalytic material/additives such as titanium dioxide (TiO_2), zinc oxide (ZnO), zinc sulphide (ZnS), carbon nitride (C_3N_4), and silicon carbide (SiC). Each photocatalytic material is characterized by band gap energy value, which is the energy required for the electron to move

Table 3 Pollutant effects on health and environment

Pollutants	Health effect	Environmental effects
Carbon monoxide (CO) [62]	Headache, dizziness, weakness, nausea, vomiting, and, finally, loss of consciousness	Elevates the soil and water temperature and also responsible to cause extreme weather conditions
Nitrogen oxide (NO_x) [9]	Irritant of the respiratory system as it penetrates deep in the lung, inducing respiratory diseases, coughing, wheezing, dyspnoea, bronchospasm, and even pulmonary oedema when inhaled at high levels	High levels of nitrogen dioxide are deleterious to crops and vegetation, as they have been observed to reduce crop yield and plant growth efficiency
Sulphur dioxide (SO_2) [63]	Respiratory irritation, bronchitis, mucus production, and bronchospasm. Moreover, skin redness, damage to the eyes (lacrimation and corneal opacity) and mucous membranes, and worsening of pre-existing cardiovascular disease have been observed	Environmental adverse effects, such as acidification of soil and acid rain, seem to be associated with sulphur dioxide emissions
Particulate matter [64]	Fine particulate matter may be toxic itself or may carry toxic trace substance and can alter the immune system	Change the nutrient balance in watery ecosystems, damage forests and crops, and acidify water bodies
Hydrocarbon	Potential to cause cancer	Very less impact

Table 4 Band gap energy value for photocatalytic additives

Photocatalytic additive	Band gap energy value*, eV	References
TiO_2	3.20	Coronado et al. [65]
ZnO	3.37	Kamarulzaman et al. [66]
ZnS	3.36	D'Amico et al. [67]
C_3N_4	2.97	Xu and Gao [68]
SiC	3.20	Sahu et al. [69]

Typical values will vary depending on the atomic structure and presence of any dopants

Fig. 2 Electromagnetic spectrum

from valence band to conduction band. The typical band gap energy value for different photocatalytic additives is shown in Table 4. However, among several photocatalytic additives, TiO_2 has gained significant attention owing to its non-toxicity, cost-effective, and stability against photochemical corrosion.

The band gap energy value indicates the minimum energy required for the electron to shift from valence band to conduction band, where this energy is derived from the light source. In the ambient conditions, the solar radiations act as light source providing the required energy for electron to shift from valence band to conduction band corresponding to their band gap energy value. According to the Planck-Einstein relation (Eq. 1), the band gap energy is inversely proportional to wavelength of the light.

$$E = \frac{h * c}{\lambda} \tag{1}$$

where

E = Energy Band Gap, eV; h = Planck's Constant; c = Speed of light, m/s; λ = Wavelength, nm.

Substituting the band gap energy value for TiO_2 in Eq. 1 results in wavelength of 387 nm, which falls in the domain
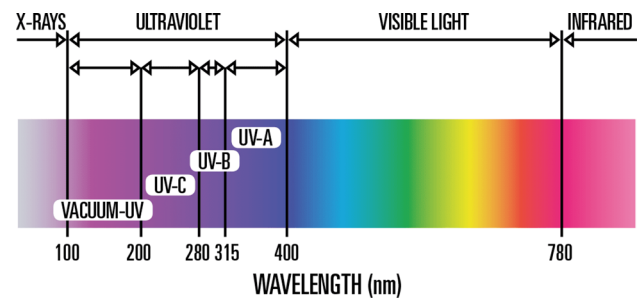
of ultraviolet radiations (UV-A) of electromagnetic spectrum as shown in Fig. 2. In other words, this indicates that photocatalytic activity in TiO_2 can be only activated in the presence of UV-A radiations. The wavelength of light higher than UV-A such as visible light does not result in photocatalytic activity as the energy acquired will not be sufficient to shift electron from valence band to conduction band.
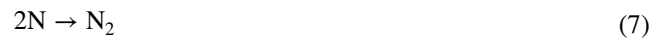
Photocatalytic concrete

Photocatalytic concrete is a special concrete, which possess photocatalytic property that can provide self-cleaning characteristics to the concrete [35]. The photocatalytic concrete has the ability to reduce the concentration of harmful gases such as NO_x and hence has been found applications in the pavements. Road infrastructure constitutes a major part in the urban sprawl. The total area coverage of roads in the urban areas is nearly 40–60% on an average. Several investigations have been carried over self-cleaning [22] and air-purifying pavements in order to reduce the air pollution. The major catalyst used here is TiO_2 and its efficiency to reduce pollutant concentration

especially NO_x in the presence of ultraviolet (UV) radiation will be reviewed in detail in subsequent sections.

The schematic shown in Fig. 3 shows the functioning of photocatalytic concrete in NO_x concentration reduction. The photocatalytic reaction in the concrete is a result of series of reduction–oxidation reactions (redox), which takes place on the surface and also at a certain distance from the surface. When the electron–hole pair is generated in the TiO_2 and no recombination takes place, the first stage of redox reaction takes place with water or oxygen forming free radicals. Further, the electron–hole pair can also initiate redox reactions with pollutants, which is regarded as direct redox reaction. The free radicals, which are formed, tend to detach from the surface forming reactive oxygen species (ROS). ROS are generally in the form of $^\cdot OH, ^\cdot O_2^{-}, HO_2^\cdot, H_2O_2$. ROS decompose the organic and inorganic pollutants thus reducing the adverse effect of the pollutants. Based on this, the photocatalytic reaction process can be classified as direct redox reaction, radical formation and redox reaction, radical-ROS formation and redox reaction [36]. The typical reduction and oxidation reactions, which takes place in the presence of UV light and TiO_2 as photocatalyst, are shown below.

Reduction reactions as shown in Eqs. 2–9 lead to the formation of N_2 by decomposing NO_x as experimentally verified by [37].

$$TiO_2 + hv \rightarrow e^- + h^+ \tag{2}$$

$$NO + e^- \rightarrow N + O \tag{3}$$

$$NO + N \rightarrow N_2O \tag{4}$$

$$NO + O \rightarrow NO_2 \tag{5}$$

$$2O \rightarrow O_2 \tag{6}$$

$$2N \rightarrow N_2 \tag{7}$$

$$2NO \rightarrow N_2 + O_2 \tag{8}$$

$$N_2O \rightarrow N_2 + O \tag{9}$$

where

hv = Incident Photon

e^- = Electron

h^+ = Hole

It should be noted here from Eqs. 2–9 that no free radicals or reactive oxygen species are present in the reactions. In other words, reduction reactions takes place by the formation of electron–hole pair generation and hence increasing the recombination time can improve the reduction reactions as stated in the later sections.

The oxidation reactions leads to the formation of nitric acid (HNO_3), which gets deposited on the surface and can be cleaned easily [38]. Equations 10–18 show the oxidation reactions in the presence of ROS. Equation 10 indicates the generation of charge carrier, while Eqs. 11 and 12 show the formation of ROS. Equations 13–16 show the oxidation reactions. Most of the previous studies have highlighted the formation of HNO_3 due to oxidation on pavement. However, reduction reactions in TiO_2 are seldom due to high electron–hole pair recombination rate.
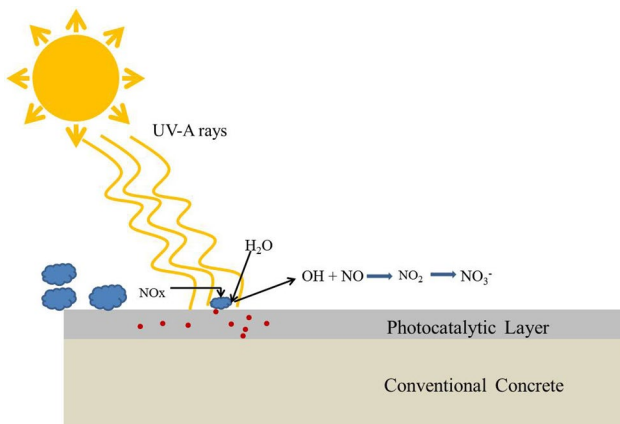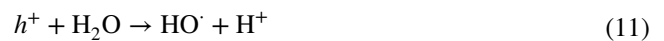
$$TiO_2 + hv \rightarrow e^- + h^+ \tag{10}$$

$$h^+ + H_2O \rightarrow HO^\cdot + H^+ \tag{11}$$

$$e^- + O_2 \rightarrow O_2^{\cdot-} \tag{12}$$

$$NO + HO^\cdot \rightarrow HNO_2 \tag{13}$$

$$HNO_2 + HO^\cdot \rightarrow NO_2 + H_2O \tag{14}$$

$$NO_2 + HO^\cdot \rightarrow HNO_3 \tag{15}$$

$$NO + O_2^{\cdot-} \rightarrow NO_3^{-} \tag{16}$$

Effect of photocatalytic additive content

The efficiency of the photocatalytic concrete highly depends on the quantity of TiO_2 and exposure conditions. The past studies have used photocatalytic concrete as thin layer of concrete on existing pavements as only the concrete surface takes part in photocatalytic action. Poon and Cheung [39] developed

Fig. 3 Schematic of photocatalytic concrete activity

paver blocks of size 200 by 100 mm, where they were provided with 5-mm-thick photocatalytic concrete on the top. The dosage of TiO_2 in the concrete was varied from 0 to 10% per cent in the interval of two per cent. The testing for NO_x degradation was conducted in a close chamber where specimen were tested over 28, 56 and 90 days, respectively. The results showed that the NO_x removal decreased as the age of the specimen increased but it was constant throughout the life after that. The decrease was around 8% and was majorly due to carbonization of cement. The sample with 10% of titanium dioxide showed the best removal efficiency as compared to the lower content. This study indicated that the photocatalytic activity will reduce with time and hence renewal will be required.

Dylla et al. [40] evaluated the efficiency and cost-effectiveness of TiO_2 coating placed over a concrete pavement. The coating consisted of TiO_2, cement, fines, and water. The dosage of TiO_2 varied between 3 and 5% by weight of cement. It was seen that the specimen coating with 5% of TiO_2 with no fines showed the maximum NO_x removal efficiency up to 47% as compared to others dosages. This study indicated that applying a coating of TiO_2-based cement on the existing surface of concrete pavements will function better than adding it into the concrete.

In another interesting study, Asadi et al. [41] utilized TiO_2 in pervious concrete for the first time. The main aim of incorporating TiO_2 in pervious concrete was attributed to the increased surface texture, which increases the reaction sites and also it allows sunlight to penetrate deeper into the concrete increasing the NO_x removal efficiency. Pervious concrete was prepared in two layers, where photocatalytic concrete was provided in top 12.5, 25, 50 and 75 mm to study the effect of thickness on NO_x removal. Similar to Dylla et al. [40], the TiO_2 content was varied from 3 to 5%. The results indicated that highest NO_x removal efficiency was achieved when void ratio was 27% and thickness of photocatalytic concrete was 75 mm. This study clearly indicated that pervious concrete provides added benefit for NO_x reduction due to porous structure and deeper penetration of sunlight.

Janus et al. [42] concentrated on properties of TiO_2 and their influence on performance characteristics of concrete. Two types of TiO_2, calcined at 300 and 600 °C, were used in the range of 1–3%. The results indicated that compressive and flexural strength increased by 10 and 8%, when 3% TiO_2 calcined at 300 °C was added. However, considering the NO_x removal efficiency, 3% TiO_2 calcined at 600 °C was found to be optimal.

Effect of physical parameters on photocatalytic concrete activity

The photocatalysis process is highly affected by both internal and external factors. Internal factors include the properties of the materials, whereas the external factor include physical surrounding characteristic where the reaction is taking place.

Temperature Temperature do not have a significant effect on the process but few of the studies carried out previously reveal that as the temperature increases, the efficiency of reaction decreases [43]. In contrast, some of the research studies concluded that temperature increases the efficiency of photocatalytic activity. Overall temperature can be considered as a neutral parameter.

Relative humidity Relative humidity is considered as one of the important influencing factors for photocatalytic activity. The increased water molecules due to higher RH decreases the reaction sites, thus reducing the efficiency of photocatalysis [Kakinoki et al. 2004]. Due to hydrophilic nature of photocatalyst, they tend to absorb water from atmosphere. This in turn forms layer on the surface of photocatalyst, thereby providing hindrance absorption of pollutant. [44] carried out the experiment at various conditions. The results revealed that the photocatalytic activity was highly significant at humidity level 50%, and beyond it, the photocatalytic activity decreased. [41] found that for TiO_2 photocatalytic pervious concrete, the NO_x removal efficiency decreased from 80 to 10%, when the RH increased from 20 to 80%. Similarly, [45] also found that the NO_x removal efficiency decreases from 55 to 7.5%, when the RH increased from 20 to 80%. Therefore, as the humidity increases, the removal efficiency decreases and vice versa.

The flow rate of the pollutants The flow rate of the pollutants controls the time of exposure for photocatalytic activity. Higher flow rate decreases the availability of pollutants for reaction. [44] found that there was a significant reduction in NO_x removal from 64.29 to 28.88%, when the flow rate of gas increased from 3.0 to 5.0 l/min. [41] varied the flow rate from 3 to 9 l/min for photocatalytic pervious concrete. The increased flow rate resulted in decreased NO_x removal efficiency from 59 to 19%. [45] found that when the flow rate of NO_x was increased from 1.5 to 3.0 l/min, the removal efficiency decreased from 65 to 38%.

Field studies related to photocatalytic concrete

The laboratory studies on photocatalytic concrete depicted the influence of test parameters on the NO_x removal efficiency. However, these tests were conducted on controlled mode under specific conditions. Several studies have implemented photocatalytic concrete in pavements and have quantified the NO_x removal efficiency by various means under realistic conditions. [46] carried out full-scale demonstration of photocatalytic concrete pavement in Hengelo, Netherlands. The pavement consisted of paver blocks of 75 mm thickness, where 70 mm was conventional concrete, while the 5.0 mm was photocatalytic concrete with TiO_2. The field data indicated that under ideal conditions, photocatalytic concrete could reduce the NO_x

concentration by 42% compared to the control pavement. Further, a significant variation was observed in the results due to the influence of several factors. In the year 2010, Hassan et al. [45] applied TiO_2-based water solution in spray form on existing concrete pavement in Louisiana State. The NO_x removal efficiency in field condition was determined using two methods. In the first method, concentration of NO_x was determined before and after application of TiO_2 spray. The NO_x removal efficiency varied on daily basis, where the highest reduction was found from 37 part per billion (ppb) to 7 ppb. In the second method, water was collected from the surface of pavement with and without TiO_2 spray. The chemical test of water indicated that pavement treated with TiO_2 spray had higher content of nitrates indicating NO_x removal. In another study, Dylla et al. [47] applied TiO_2 water-based spray at a rate of 1.5 to 2.0 ml/ft^2. The study evaluated the NO_x removal efficiency under field conditions as a function of wind speed, solar intensity, and relative humidity. Akin the laboratory studies, the field indicated that when RH was high, the removal efficiency was lower and vice versa. The peak reduction in NO_x concentration was found in the mid-day, when the solar intensity was highest. Further, at higher wind speeds (> 2.5 m/s), the NO_x removal efficiency was significantly lower. [48] conducted field evaluation of photocatalytic concrete pavement serving as walkway in the Florianopolis, Brazil. The photocatalytic concrete was laid in three thicknesses of 3, 6 and 10 mm, where the blocks were tested for efficiency in laboratory before installation in the field. After one year of service, few blocks were dismantled and tested again in laboratory. The study found reduction in efficiency of photocatalytic activity with time, and this can be rejuvenated by washing. Further, thinner the photocatalytic concrete, better was the efficiency, which was further enhanced with Anatase variant of TiO_2. The paver blocks were prepared with two variants of TiO_2: Rutile and Anatase. In similar direction, [49, 50] discusses the implementation of photocatalytic concrete pavement in Antwerp, Belgium. [51] determined the efficiency of photocatalytic concrete on pilot test sections in Warsaw. The study indicated that large variability in the NO_x removal efficiency exists under field conditions due to the effect of various factors across the geographic locations. Based on the field measurements, the study found that on an average, 31% reduction in NOx concentration was achieved due to photocatalytic concrete paver blocks.

Developments in the photocatalytic activity of TiO_2 and way forward

The past studies have used TiO_2 as the photocatalytic additive in the concrete. However, TiO_2 depicts photocatalytic activity only due to UV radiations, which constitute 3–5% of electromagnetic spectrum. Under visible light conditions, the efficiency of TiO_2 decreases as the energy will not be sufficient to shift electron from valence band to conductance band (Eq. 1). In order to improve the efficiency in visible light conditions, researchers have adopted the various methods, which can decrease the bandgap energy value of TiO_2.

Visible light excited photocatalytic additives

In order to improve the photocatalytic activity in the visible light conditions, photocatalytic materials, which can be excited in the visible light range, can be used. Visible light photocatalyst can be either developed using TiO_2 as primary material using the method discussed below. On the other hand, non-TiO_2-based visible light photocatalyst has been explored and developed. Some of the non-TiO_2-based photocatalyst include tungsten trioxide (WO_3), silver phosphate (Ag_3PO_4), bismuth vanadate ($BiVO_4$), and graphitic carbon nitride (g-C_3N_4) [52]. The bang gap energy of non-TiO_2 photocatalyst is shown in Table 5. The non-TiO_2-based photocatalysts are currently being investigated for water treatment and hydrogen splitting, while its application for photocatalytic concrete has not been made yet.

Coupling and doping

Coupling is a process of attaching another semi-conducting material to TiO_2 such that the electron remains in the conductance band for longer [53]. Doping is a process, where foreign materials are introduced into the lattice structure of TiO_2, which internally develops different levels of band gap energy [54]. The schematic of TiO_2 coupled with other metals such as zinc oxide and silicon carbide is shown in Fig. 4. It can be seen that the TiO_2 (green circle) is coupled with low energy band gap material. Due to this coupling, the electrons easily shift to conductance band from valence band in the low energy band gap material. Further, instead of shifting to valence band, it remains in the conductance band due to coupling, thus increasing the electron–hole pair recombination duration.

The schematic of doped TiO_2 is shown in Fig. 5. It can be seen that doping includes modifying the lattice structure of TiO_2, which creates additional energy levels increasing the electron–hole pair recombination duration. The doping can be performed using noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) and also non-metals

Table 5 Band gap energy of non-TiO_2 photocatalyst

Non-TiO_2 Photocatalyst	Band gap energy, eV
WO_3	2.69–2.81 [70]
Ag_3PO_4	2.43–2.67 [71]
$BiVO_4$	2.37–2.44 [72]
g-C_3N_4	2.70 [73]

Fig. 4 Schematic of TiO₂ coupling with other semi-conductors
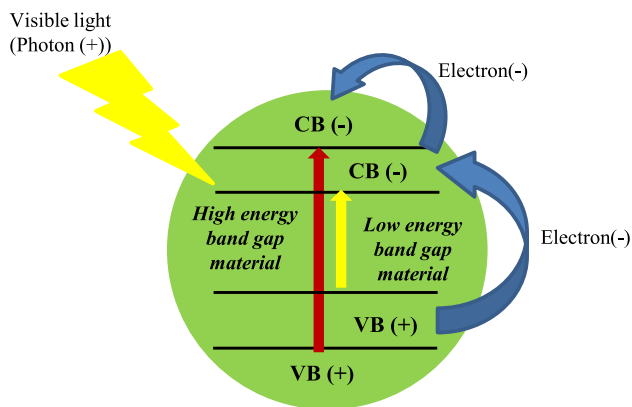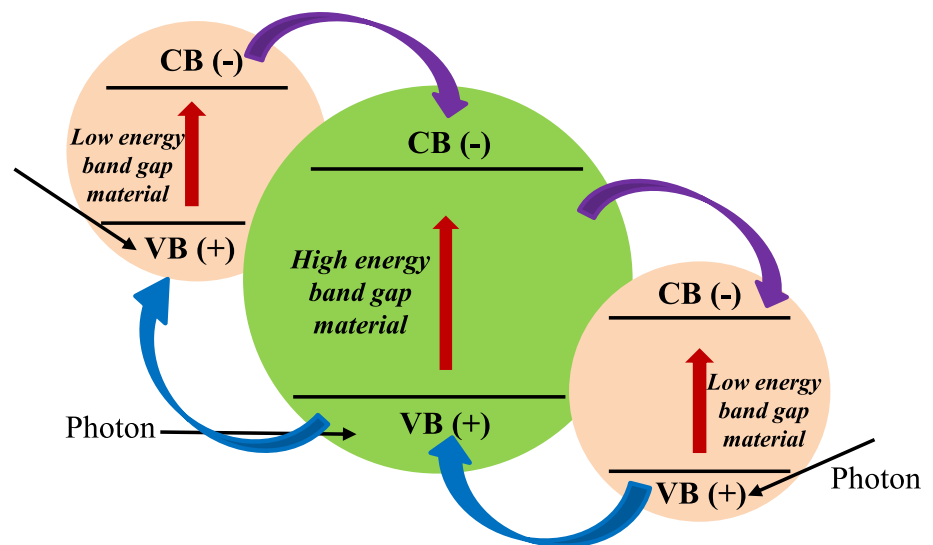
Fig. 5 Schematic of TiO₂ doping with other metals/non-metals

Fig. 6 Schematic of absorbance spectrum of TiO₂ with and without coupling-doping

and metals such as nitrogen (N), carbon (C), silicon (Si), iron (Fe), molybdenum (Mo), respectively. The coupling and doping increase the efficiency of photocatalytic activity as electrons will be excited even in the visible light conditions. A schematic of absorbance spectrum of TiO₂ and coupled-doped TiO₂ is shown in Fig. 6. It can be seen that by coupling-doping TiO₂, the absorbance in the visible light region can be increased leading to photocatalytic activity.

Although there are no studies, where coupled-doped-TiO₂ application in concrete pavement, there are a few studies conducted in concrete for building applications. [55] doped TiO₂ with silver (Ag) and utilized in concrete to understand the self-cleaning nature of the concrete. TiO₂ was modified with silver using the silver nitrate solution via the photo-deposition method. The amount of Ag used was nearly 0.11–0.98% of the total mass present in AgNO₃. Slurry of 1% Ag- TiO₂compound was prepared and sprayed on the concrete, and a dye-degradation test was carried out to check the photocatalytic activity of silver-doped titanium oxide.
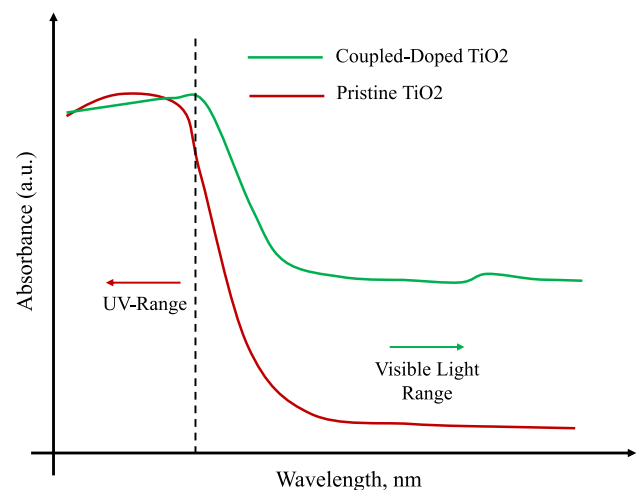
Analysis showed that slurry thus sprayed on the concrete showed an antifungal and self-cleaning effect of the concrete. Though the compound was successful in dye-degradation, it cannot be said that it can also degrade NO$_x$ from the atmosphere. Some additional investigation is required to the NOx decomposition of doped TiO₂ which was not reflected in both pieces of research discussed above. Additionally, visible light decomposition of this doped titanium dioxide was also not discussed in the above research.

Seo and Kim [56] developed concrete walls, which had plastic bars to allow the light to pass through. The aim was to investigate the photocatalysis from the visible light excitation. In order to achieve this, the authors first doped the TiO₂ with Cu, Cr and S by calcination at 1000 °C for 24 h. The calcined product was milled to produce fine powder of doped TiO2. The spectrometer analysis showed that the Cu-doped

TiO$_2$ was very efficient in exciting photocatalytic activity in the visible light environment. A reduction of 15.8% was achieved by Cu-doped TiO$_2$, while Cr- and S-doped TiO$_2$ showed very less degradation rate in the visible light environment. Khannyra et al. [57] investigated the photocatalytic activity in the visible light regime by doping TiO$_2$ with copper. The copper was doped at 2, 5, 10 and 15%, and experiments were conducted under visible light range. In the visible light range of wavelength, TiO$_2$ failed to absorb visible light unlike Cu-doped TiO$_2$ as determined using UV spectrometer. This indicates that by doping copper, one can achieve the photocataysis in the visible light range. The experimental results indicated that the optimum % of copper was 5% even though %NO removed increased with increase in Cu content. The %NOx removed was highest in the case of 5% Cu. Coatings were developed with these materials and were applied for field testing. The results indicated that the region with 5% Cu had very less colour change compared to other coated regions indicating its self-cleaning abilities.

Leaching effect

The past studies have mostly focussed on assessing the pollutant reduction ability of photocatalytic concrete. However, the leaching of photocatalytic materials and nitrates from the photocatalytic pavements are not significantly investigated. Nitrates being the reaction product from photocatalytic activity will enter the groundwater and may increase its concentration in the long run. Studies have shown that higher concentration of nitrates in the drinking water may lead to adverse health issues such as infant methemoglobinemia, colorectal cancer, and thyroid disease [58]. Further, photocatalytic additives may also leach out from the pavement reducing the efficiency of photocatalysis. Relinque et al. [59] investigated the leaching potential in photocatalytic pavement by collecting rainwater runoff for 800 days. The concentration of titanium and nitrates along with pH of water and conductivity was assessed. The results indicated the photocatalytic concrete tiles depicted very low titanium leaching, while photocatalytic cement substrates percolated on asphalt layer showed higher leaching. Further, the nitrate concentration in leachate was in tandem with the photocatalytic reaction. The concentration of both the materials was found to be lower than limits prescribed for drinking water in Madrid city, where the maximum concentration of titanium was found to be only 60 µg/L. Very limited studies are available focussing on the long-term performance of photocatalytic pavements due to loss of photocatalytic materials and eutrophication potential of nitrates released from these pavements. Therefore, in addition to development of novel photocatalytic materials, this domain also provides future scope of research. Based on such studies, decisions can be taken on maintenance of photocatalytic pavements and life cycle analysis aspects.

Summary and conclusion

The main objective of this review article was to critically review the past studies on photocatalytic concrete and propose the way forward for future research as a sustainable application to reduce impact of air pollution. Unlike highways, the air pollutant concentration is found to be higher in urban area and is bound to increase with time due to increase in vehicular numbers. Although strict emission standards are introduced in many countries, still the air pollution problem persists and is known to affect to the health of urban dwellers. One of the innovative solutions to reduce the adverse effect of air pollution due to vehicular emission in urban areas is photocatalytic concrete pavements. The past studies have shown that up to 35–40% of NO$_x$ concentration was reduced in the presence of photocatalytic concrete pavements. Titanium dioxide (TiO$_2$) was found to be the most commonly used photocatalytic material in concrete pavements. Several field studies have applied photocatalytic materials either in the form of spray or a thin layer of photocatalytic mortar as photocatalytic reaction is mainly confined to the surface. Interestingly, increasing the surface porosity, such as, in pervious concrete, can improve the photocatalytic reaction. Although TiO$_2$ is used as a photocatalytic material, its performance is only limited in the presence of UV radiations, which constitutes only 3–5% of electromagnetic spectrum. In this regard, a large scope for research exists in this domain as stated below:

- Development of novel photocatalytic materials, which can be excited in the visible light wavelength range.
- Long-term photocatalytic performance of photocatalytic concrete pavement: the past studies have evaluated the performance over a short term. However, pavements are designed to serve 10–15 y, during which photocatalytic materials may leach out reducing the efficiency. Understanding and modelling the long-term performance will assist in decision-making related to maintenance and rejuvenation of photocatalytic reaction. Past studies have indicated washing with muriatic acid and spray application of the suspended TiO2 particles in water as some of the rejuvenation methods. However, the long-term performance of such rejuvenation methods is yet to be quantified [46, 60]
- Environmental impact assessment: nitrates are deposited on the photocatalytic concrete pavements as product of photocatalytic reaction. The regular maintenance of pavements like washing and rainfall will carry the nitrates into the adjoining soil increasing the nitrates concentra-

tion of groundwater. Investigating the long-term impact of nitrates from such pavements will assist of formulating regulatory measures.

- Life cycle cost analysis (LCCA): photocatalytic materials result in additional material cost increasing the overall cost of project. Further, the regular maintenance associated with photocatalytic concrete pavements such as rejuvenation by spraying photocatalytic materials will also incur additional cost. Therefore, there is a need to perform cost analysis for a given design period including construction and maintenance of photocatalytic concrete pavements. The benefits associated with reduction in NO_x concentration should be converted to monetary values to obtain realistic life cycle cost analysis.

Declarations

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