TiO$_2$-based self-compacting glass mortar: Comparison of photocatalytic nitrogen oxide removal and bacteria inactivation

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Abstract
This paper presents the results of a preliminary study on assessing the photocatalytic activities when nano-TiO$_2$ is intermixed in self-compacting glass mortars (SCGM) in terms of the air pollutant removal and bacteria inactivation. Nitrogen oxide (NO) and E. coli K12 were used as the target air pollutant and bacteria test strain respectively. In addition, the influence of nano-TiO$_2$ dosage (0%, 2% and 5%) and recycled glass colour (light green and transparent) on the fluidity and compressive strength of nano-TiO$_2$-based SCGM was also evaluated. The results showed that more superplasticizer dosage was required to help the dispersion of nano-TiO$_2$ particles to achieve the same fluidity. Meanwhile, with the addition of nano-TiO$_2$ either 2% or 5%, about a 12% compressive strength increment was observed in SCGM. In the case of NO removal, an increasing trend of NO removal was accompanied by an increase in TiO$_2$ content. For a given dosage of TiO$_2$, the SCGM prepared with transparent recycled glass showed a slightly higher NO removal rate than that prepared with light green recycled glass. As for the antibacterial activity, however, all of the TiO$_2$ intermixed SCGMs showed little inactivation ability of E. coli. Taking into account the above obtained results, it can be concluded that compared with NO removal, photocatalytic bacteria inactivation is a more complex process and the results for photocatalytic activity of NO removal cannot always be extrapolated to photocatalytic antibacterial activity.

Keywords: Photocatalysis; Titanium dioxide; Air pollutant removal; Bacteria inactivation; Cementitious materials

1. Introduction
With the rapid economic development, people are becoming more aware of environmental pollution on a global scale. The quality of people’s daily lives is seriously impaired by air pollution arising from vehicle exhausts, such as nitrogen oxides (NO$_x$), and diseases caused by microorganisms. More recently, the outbreak of
lethal diseases caused by aggressive mutant forms of *E. coli* in Europe and Hong Kong has taken a heavy toll on many people’s lives. Traditional technologies have proven to be ineffective in tackling new environmental challenges, like bacterial infection. Therefore, there is an urgent need for new environmentally friendly strategies and approaches to address these pressing problems. In recent years, heterogeneous photocatalytic oxidation (PCO), which involves the generation of highly reactive hydroxyl radicals based on semiconductor sensitized heterogeneous photocatalysis [1], has emerged as a promising and appealing alternative technology to mitigate air pollution. Among many semiconductor candidates for photocatalysts, titanium dioxide (TiO$_2$) finds favour with most researchers due to its favourable and exciting properties, such as low price, non-toxicity, stability, and most importantly, high photocatalytic efficiency.

Ever since 1972, when Fujishima and Honda first discovered the phenomenon of photocatalytic splitting of water in a TiO$_2$ anode photochemical cell under ultraviolet (UV) light [2], there have been enormous efforts devoted to the research of applying TiO$_2$ in environmental protection [3-8]. As a result, the mechanisms underpinning TiO$_2$ sensitized heterogeneous photocatalysis are well understood, which in turn leads to many interesting applications in a wide range of areas. Although TiO$_2$ photocatalysis first drew attention as a method for hydrogen production, the focus quickly shifted to the utilization of the strong photo-produced oxidation power for the destruction of pollutants. In 1977, Frank and Bard reported the decomposition of cyanide in the presence of aqueous TiO$_2$ suspensions for the first time [9]. Subsequently, it was soon discovered that TiO$_2$ mediated PCO has the ability to destruct a wide variety of harmful compounds. Along with the realization that this oxidation power could oxidize most organic compounds came the realization that they could also be applied for disinfecting bacteria. As microorganisms are naturally made up of organic compounds, it is assumed that they are also susceptible to oxidation. The first such reports were those of Matsunaga et al. in 1985 [10], in which they demonstrated that microbial cells, *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *Escherichia coli*, were killed by contact with TiO$_2$/Pt particles under illumination with light. Since then, photocatalytic disinfection has become a fast growing area exemplified by a large volume of work on this topic. However, it should be noted that earlier work on semiconductor photocatalysis was mainly carried out in aqueous solutions and the semiconductor was usually employed in the form of a powdered dispersion. This inconveniently entails the separation of catalyst from liquid at the end of experiments. From the viewpoint of easy handling of photocatalyst and large-scale applications, it is desirable to immobilize TiO$_2$ powders on a solid medium of support. And an important step of development of immobilization techniques was made in the late 1980s by Matthews [11].

More recently, there is growing interest in using cementitious materials as photocatalyst supporting media. The favourable properties of cementitious materials, such as strong binding ability and porous structure, render them ideal supports for the
TiO$_2$ photocatalyst. At the same time, continued breakthroughs have been made in TiO$_2$ nanotechnology in developing TiO$_2$ to have high photocatalytic activity. It has been already demonstrated that the combination of nano-TiO$_2$ particles with cementitious materials results in a synergistic effect in the reduction of pollutants [12-14], setting the stage for fully exploiting other attractive potentials of these materials.

Ruot et al. [15] studied the photocatalytic activities of cement pastes and mortars mixed with different amounts of TiO$_2$ in the anatase form by monitoring the discolouration of rhodamine B. In their studies, for cement paste with 5 wt% of TiO$_2$ added, the initial colouration almost disappeared at the end of the test. Using dip-coating and/or sol-gel methods to enrich a set of concretes and plasters with the TiO$_2$ photocatalyst, Ramirez et al. [16] investigated the toluene removal potential of concrete samples. High removal efficiencies, up to 86%, were observed with the dip-coated samples. But it is important to notice that the dip-coated cementitious materials were prone to loss of the attached TiO$_2$ when subjected to weathering and abrasive conditions. With respect to air purification, a number of groups performed laboratory studies and pilot projects to investigate the photocatalytic activity of TiO$_2$ affixed to paving blocks in terms of NO$_x$ removal. A wide spectrum of NO$_x$ conversion rates was obtained [14, 17-21]. But research studies concerning the photocatalytic antibacterial activity of TiO$_2$ containing cementitious materials is rather scarce. Chen et al. [22] reported that there was an apparent correlation between photocatalytic decomposition of formaldehyde and inactivating *E.coli* because both processes are dependent on the amount of reactive oxygen species produced. Marugan et al. [23] studied the analogies and differences between methylene blue photocatalytic oxidation and *E.coli* inactivation and found that different microbiological aspects made disinfection kinetics more complex than that usually observed for the oxidation of chemical pollutants. This highlights the need for a better understanding of a possible correlation between the two photocatalytic processes (oxidizing NO$_x$ and inactivating bacteria).

The present work aims to compare the photocatalytic activities of nano-TiO$_2$ based (intermixed) self-compacting glass mortars (SCGM) for NO removal and *E. coli* inactivation. In addition, the influence of nano-TiO$_2$ dosage (0%, 2% and 5%) and recycled glass colour (light green and transparent) on the photocatalytic activities is also studied.

2. Experimental
2.1. Materials and sample preparations
In all the experiments, a commercially available nano-TiO$_2$ powder (P25, Degussa) was used as the photocatalyst. The particle size of the TiO$_2$ is 20-50 nm, with a specific BET surface area of 50 ±15 m$^2$ g$^{-1}$. White ordinary Portland cement (WC, TAIHEIYO Cement Corp., Japan) and metakaolin (MK) was used as the cementitious materials. In preparing the nano-TiO$_2$-based architectural cement mortar in this study,
a self-compacting-based approach for decorative application was chosen [24, 25]. Two different colours (light green and transparent/colourless) of crushed recycled glass (RG) derived from post-consumer beverage glass were used as fine aggregates in the SCGM. The post-consumer beverage glass used was sourced from a local eco-construction material company. Prior to the experimental use, all the discarded glass bottles were washed, sorted by colour and then crushed by a mechanical crusher, followed by sieving to a desired particle size. The characteristics of the two types of recycled glass cullets used in the experiment are shown in Table 1.

Table 1: Particle size distributions

<table>
<thead>
<tr>
<th>Sieve size (mm)</th>
<th>Recycled glass (% passing)</th>
<th>Light green glass</th>
<th>White glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td></td>
<td>99.6</td>
<td>97.8</td>
</tr>
<tr>
<td>2.36</td>
<td></td>
<td>86.7</td>
<td>80.8</td>
</tr>
<tr>
<td>1.18</td>
<td></td>
<td>51.9</td>
<td>54.0</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>26.6</td>
<td>32.0</td>
</tr>
<tr>
<td>0.3</td>
<td></td>
<td>12.4</td>
<td>15.5</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td>5.3</td>
<td>6.9</td>
</tr>
</tbody>
</table>

The proportion ratio by weight for the self-compacting glass mortar (SCGM) was 0.8:0.2:2.0:0.4 (WC: MK: RG: water). In order to investigate the effectiveness of TiO$_2$ on photocatalytic activities, two different dosages of nano-TiO$_2$ (2% and 5% by cementitious materials weight) as an addition to the mixture were used. The superplasticizer (SP) used ranged from 1.70% to 2.84% by weight of cementitious materials to obtain the targeted mini-slump flow value of 250±10 mm for self-compacting mortar. The details of the mix proportions are listed in Table 2.

Table 2: Mix proportions of cement mortars (kg/m$^3$)

<table>
<thead>
<tr>
<th>Mix notation</th>
<th>Cementitious</th>
<th>Recycled glass</th>
<th>TiO$_2$</th>
<th>Water</th>
<th>SP* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
<td>MK</td>
<td>Light green</td>
<td>Transparent</td>
<td>Amount (%)</td>
</tr>
<tr>
<td>GG-T0</td>
<td>456</td>
<td>152</td>
<td>1519</td>
<td>-</td>
<td>0 0</td>
</tr>
<tr>
<td>GG-T2</td>
<td>456</td>
<td>152</td>
<td>1519</td>
<td>-</td>
<td>12.16 2</td>
</tr>
<tr>
<td>GG-T5</td>
<td>456</td>
<td>152</td>
<td>1519</td>
<td>-</td>
<td>30.4 5</td>
</tr>
<tr>
<td>WG-T0</td>
<td>456</td>
<td>152</td>
<td>-</td>
<td>1519</td>
<td>0 0</td>
</tr>
<tr>
<td>WG-T2</td>
<td>456</td>
<td>152</td>
<td>-</td>
<td>1519</td>
<td>12.16 2</td>
</tr>
<tr>
<td>WG-T5</td>
<td>456</td>
<td>152</td>
<td>-</td>
<td>1519</td>
<td>30.4 5</td>
</tr>
</tbody>
</table>

*% of SP dosage as cementitious weight.

The procedures for the preparation of the SCGM specimens were as follows. First, all the proportioned materials were mixed uniformly for about 5 min using a mechanical mixer. The fluidity of SCGM was determined using a mini-slump flow
cone with an internal diameter of 100 mm as per EFNARC [26]. The average spread diameter value in two perpendicular directions was measured. Then, the specimens were cast by the self-compacting approach, demoulded and cured in a water tank at a temperature of 27±2 °C for 28 days. For each batch of SCGM, three prisms with dimensions of 40×40×160 mm were used to conduct compressive strength as per ASTM C349 [27] and φ75×150 mm cylinder specimens were cut into 10 mm thickness discs using a mechanical diamond saw to examine the photocatalytic activities.

To prepare the TiO$_2$ dip-coated SCGM, a suspension of methanol and P25 (25 g/L) was prepared. SCGMs prepared with the light green recycled glass were selected as the substrate materials, which were first cleaned by sonication in acetone, ethanol and distilled deionized water (DDW) for 30 min, respectively. Then, the substrate materials were dipped into the suspension for 5 min, followed by oven-drying at 60°C for 120 min.

2.2. Bacterial strains and culture conditions

A UV-resistant *E. coli* K12 was used as the test strain in this study, which is a gram-negative bacterium widely selected as a model microorganism in many photocatalytic bactericidal experiments.

*E. coli* K12 was sub-cultured and maintained on nutrient agar plates. To prepare the bacterial cultures for the experiment, single colonies were isolated from the nutrient broth agar plate cultures and used to inoculate 50 ml of the nutrient broth liquid media (pH 7) in a 250 ml flask. Then the flask was incubated at 37°C for 18 h in an orbital incubator set at 150 rpm. To eliminate broth medium, the cells were harvested by centrifugation at 4000 rpm for 5 min. After that, the treated cells were washed, re-suspended and diluted to the targeted concentration of about $1\times10^5$ colony forming units (CFU)/ml in sterilized 0.9% (w/v) sodium chloride solution. All the equipment and materials were autoclaved at 121°C for 15 min before the experiment to ensure sterility.

2.3. Photocatalytic conversion of NO

2.3.1. Reactor setup

The reactor was made according to the specifications of JIS R1701-1 with slight modifications. The dimension of the reactor was 700 mm in length, 400 mm in width and 130 mm in height. Testing samples were placed on a rack at the centre of the reactor. Two UV-A fluorescent lamps (TL 8W/08 BLB, Philips, Holland) were positioned parallel to each other on the glass cover of the reactor to provide UV radiation. The wavelength of the lamps ranged from 300 to 400 nm with a maximum intensity of 365 nm. The UV between the lamps and the reactor could be adjusted to achieve a required intensity. The UV intensity was measured by a digital radiometer equipped with a DIX-365A UV-A sensor (Spectroline DRC-100X, spectronics corporation, USA). A zero air generator (Thermo Enviromental Inc. Model 111) was
used to supply a constant clean air flow. The testing gas was a mixture of zero air and standard NO (Arkonic Gases, Hong Kong). The humidity in the reactor was controlled by passing the zero air stream through a humidification chamber. The NO concentration was continuously measured using a Chemiluminescence NO analyzer (Thermo Environmental Instruments Inc. Model 42c, USA). A thermometer, a humidity sensor and an adjustable rack supporting the specimens were placed inside the reactor. The reactor was completely sealed with no detectable leakage. A schematic diagram of the experimental setup for this study is shown in Fig. 1.

Fig. 1. Schematic diagram of NO removal experimental set-up

2.3.2. Testing protocol

All experiments were carried out at ambient temperature (25±3°C). The flow of the testing gas (1000 ppb NO) was adjusted by two flow controllers to a rate of 3 L min⁻¹ and the relative humidity (RH) was controlled at 50±5%. The UV intensity was 10 W m⁻² at the centre of the reactor. Prior to all photocatalytic conversion processes, the testing gas stream was introduced to the reactor in the absence of UV radiation for at least half an hour to obtain a desired RH as well as gas-solid adsorption-desorption equilibrium. Then the UV lamps were turned on for the photocatalysis process to begin. For each sample the NO removal test lasted for 1 h and the concentration change of NO and NO₂ at the outlet was recorded. Due to the small amount of NO₂ generation (less than 30 ppb in all tests), the photocatalytic ability of the samples was expressed by NO reduction. Every sample was tested three times and the average value together with the standard deviation was reported. The calculation of the amount of NO removal, following the instructions in JIS R 1701-1, is shown below:

\[
Q_{NO} = \frac{f}{(22.4)} \int_{t_0}^{t_f} (\text{[NO]}_0 - \text{[NO]}) \, dt
\]  

(1)
where:
\( Q_{NO} \): the amount of nitrogen monoxide removed by the test sample (\( \mu \text{mol} \))
\([\text{NO}]_0\): inlet concentration of nitrogen monoxide (ppm)
\([\text{NO}] \): outlet concentration of nitrogen monoxide (ppm)
t: time of removal operation (min)
f: flow rate converted into that at the standard state (0\(^\circ\)C, 1.013 kPa) (L min\(^{-1}\))

The specific NO removal in units of mg h\(^{-1}\) m\(^{-2}\) is calculated by the following formula:

\[
\theta = \frac{Q_{NO} \times MW_{NO} \times 10^3}{\text{Sampling} \times \text{time(h)} \times \text{Surface} \times \text{area(m} \times \text{m})}
\]

where:
\( \theta \): specific photoactivity (mg h\(^{-1}\) m\(^{-2}\))
\( Q_{NO} \): the amount of nitrogen monoxide removed by the test sample (mol)
\( MW_{NO} \): the molecular weight of NO

2.4. Photocatalytic inactivation of bacteria

A total of 1 ml of \( E. \text{coli} \) K12 cell suspension was pipetted onto each mortar sample, which were placed in a sterilized Petri dish to prevent drying (Fig. 2). The Petri dish with the testing sample was subject to illumination by the same UV lamps used in the NO removal experiments. The light intensity striking the surface of testing samples was 10 Wm\(^{-2}\). After irradiation, the cell suspension was collected by washing the sample with 20 ml 0.9% sodium chloride solution at different time intervals of 20, 40, 60, 90 and 120 min, respectively after the irradiation. Then serial dilutions of the collected cells suspension were appropriately performed, and 100 \( \mu \text{L} \) of diluted suspension was spread on the nutrient aga plate and incubated at 37\(^\circ\)C for 18 h. Three replicate plates were used for each incubation. The loss of viability was examined by the viable count of the colony forming units on the plates. In all the experiments, negative control tests in conditions of darkness and positive control ones only for UVA were carried out simultaneously. Each experiment was repeated at least three times to verify the reproducibility of the results.

![Fig. 2. Schematic diagram of bacterial inactivation experimental set up](image-url)
3. Results and discussion

3.1 Fluidity

Self-compacting glass mortar should have sufficient fluidity to flow readily under its own weight. The influence of the nano-TiO$_2$ content on the fluidity of SCGM is illustrated in Table 3. By keeping the same mix proportion, it is evident that there is an increase of superplasticizer dosage used when nano-TiO$_2$ is incorporated into the mixture. For instance, the superplasticizer dosage increased by 16.5-23.0% and 42.0-51.2% with an increase of 2% and 5% nano-TiO$_2$ as compared to the plain mixture without TiO$_2$, respectively. This is understood by the fact that more superplasticizer is required in TiO$_2$-based SCGM to help the dispersion of nano-TiO$_2$ particles to achieve the same fluidity [28].

Table 3: Fluidity and compressive strength of TiO$_2$ based SCGM

<table>
<thead>
<tr>
<th>Mix notation</th>
<th>Average mini-slump value (mm)</th>
<th>Superplasticizer</th>
<th>Compressive strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dosage (kg/m$^3$)</td>
<td>Dosage increase (%)</td>
</tr>
<tr>
<td>GG-T0</td>
<td>245</td>
<td>10.34</td>
<td>-</td>
</tr>
<tr>
<td>GG-T2</td>
<td>253</td>
<td>12.04</td>
<td>16.5</td>
</tr>
<tr>
<td>GG-T5</td>
<td>238</td>
<td>15.63</td>
<td>51.2</td>
</tr>
<tr>
<td>WG-T0</td>
<td>260</td>
<td>12.16</td>
<td>-</td>
</tr>
<tr>
<td>WG-T2</td>
<td>240</td>
<td>14.96</td>
<td>23.0</td>
</tr>
<tr>
<td>WG-T5</td>
<td>242</td>
<td>17.27</td>
<td>42.0</td>
</tr>
</tbody>
</table>

3.2 Compressive strength

The compressive strength of nano-TiO$_2$-based SCGM prepared was tested at 28 days. The results obtained are listed in Table 3 and Fig. 3. It can be noticed that the addition of nano-TiO$_2$ at either 2% or 5% caused about a 12% compressive strength increment. The improved strength is more likely to be related to the filler and pozzolanic effects of nano-TiO$_2$ in the SCGC mixed composition [29].

![Fig. 3. Compressive strength of nano-TiO$_2$ based SCGM](image-url)
3.3 Photocatalytic NO removal of nano-TiO$_2$-based self-compacting glass mortar

Fig. 4 shows the NO removal ability of TiO$_2$ intermixed SCGM with different coloured glass cullets as aggregates after 28 days of water curing. It is clear that there is an increasing trend of NO removal accompanied by an increase in TiO$_2$ content. And it should be noted that compared with the sample incorporating light green recycled glass cullets, the SCGM prepared with transparent recycled glass cullets has a slightly higher NO removal rate.

![Fig. 4. Comparison of NO removal by mortars with different glass cullets.](image)

These phenomena have been previously explained by Chen and Poon [20] who attributed this to the strong correlation between the UV absorption of different coloured glass and photocatalytic activity. In general, different coloured glass has different UV absorption spectra due to the difference in the required activation energy for colouring agents, mainly transition metals [30]. In other words, the lighter the glass colour is, the lower the UV absorbance. Consequently, the samples prepared with clear glass cullets exhibited the highest photocatalytic activity when subjected to the same conditions.

3.4 Photocatalytic bacterial inactivation of nano-TiO$_2$-intermixed self-compacting glass mortar

It has been widely accepted that the photocatalytical chemical oxidation and miroorganism inactivation by TiO$_2$ are based on the generation of reactive oxygen species (ROS) and follow the same physical-chemical phenomena. In addition, the reaction mechanisms are perceived to undergo a similar process, which involves excitation of photocatalyst, generation of electron-hole pairs and ROS, and action of the generated ROS on the target chemical/organisms [22]. The results of bacteria inactivation of TiO$_2$ intermixed SCGM are presented in Fig. 5. The viability of *E. coli* K12 cells was determined by colony counting after 18 h of incubation. In contrast to
NO removal, all samples showed little inactivation of *E. coli* after 120 min of UV irradiation. Neither an increase in TiO$_2$ content nor a change of glass colour in the tested SCGM led to detectable antibacterial activity.

Fig. 5. Photocatalytic inactivation of *E. coli* of different TiO$_2$ intermixed and dip-coated mortars utilizing white glass (a) and light green glass (b) cullets as aggregates.

These findings are contrary to those from a previous study, in which an apparent correlation between photocatalytic decomposing formaldehyde and inactivation *E. coli* was observed using two different dip-coated TiO$_2$ films, and the possibility of using analogy as a potential method to evaluate the antimicrobial effect based on the organic compound degradation effect was established [22]. In contrast, Marugan and
his coworkers studied in depth the analogies and differences between methylene blue photocatalytic oxidation and E. coli inactivation [23], and they pointed out that different microbiological aspects made disinfection kinetics more complex than that usually observed for the oxidation of chemical pollutants. Therefore, the photocatalytic oxidation of organics cannot always be extrapolated to the photocatalytic inactivation of microorganisms. This was further supported by the results of Gladis and Schumann [31], who reported that the high ability of TiO$_2$ coated surfaces to degrade methylene blue did not necessarily correspond to the reduction of aeroterrestrial algal growth. Their results also suggested that chemical activity is not directly comparable to biological activity. It is understandable considering the fact that decolouring the dye only needs relatively minor modifications, and microorganism inactivation is a rather more complex process requiring a certain amount of ROS accumulation and involving much more radicals [32]. Thanks to extensive efforts devoted to elaborating the killing mechanisms of bacteria, it has been generally accepted that the abatement of bacteria may be a complicated process, involving oxidative damage of cell walls, membranes, enzymes, and nucleic acids by the ROS and their stable products [33]. In general, the photocatalytic bactericidal process begins with the accumulation of TiO$_2$ photocatalysis induced ROS on the bacterial cell wall, followed by the initial oxidative damage to the cell wall. After that, the oxidative damage continues to destroy the underlying cytoplasmic membrane, which gives rise to a high permeability. This enables intracellular contents to flow freely and thereby allows ROS to easily penetrate membrane-damaged cells. Subsequently, intracellular components, such as enzymes, amino acids and nucleic acids, are severely damaged. Finally, this process concludes with the death of bacterial cells [34-36].

However, even between different photocatalytic activities in chemical compound oxidation, certain discrepancies were observed. More recently, Chen et al. [37] compared the photocatalytic activity of nitrogen oxides and toluene removal potentials using TiO$_2$ intermixed concrete surface layers. Their results demonstrated that good NO removal but no photocatalytic conversion of toluene was observed. Furthermore, the NO removal ability was not affected by the presence of toluene. A conclusion drawn from these results is that the transport of photons and surface diffusion of reactants are inhibited by the protective cementitious coatings surrounding the photocatalyst particles in the case of the TiO$_2$ intermixed cement mortar samples. Subsequently, the photocatalytic activity is seriously impaired. Therefore, it seems that the key factor determining the photocatalytic efficiency of TiO$_2$ modified cementitious materials is the adsorption of reactants onto the active sites. This explanation was supported by the results of Ramirez et al. [16]. Instead of intermixing TiO$_2$ into the cementitious materials, they prepared photocatalytic concrete samples by dip-coating and sol-gel methods and they found that high toluene degradation efficiencies were obtained.

Based on the results and analysis from the other researchers above, the observed
different performance of photocatalytic NO removal and bacterial inactivation in the present work can be explained. Generally, there are two major reasons contributing to the discrepancy. First, bacterial inactivation is a more complex process, which involves more reactive radicals and requires a certain amount of ROS accumulation. This is ascribed to the complexity of cell walls and the existence of resistant mechanisms in living cells. On the other hand, NO removal seems to be a relatively simple reaction and more sensitive to the attack of photocatalytic generated radicals. Second, intermixing of TiO$_2$ into SCGM unfavourably results in a dramatic decrease in photocatalytic activity. This can be attributed to the fact that the nano-TiO$_2$ particles are surrounded and covered by the hydration products.

3.5 Photocatalytic bacterial inactivation of nano-TiO$_2$-dip-coated self-compacting glass mortar

Another different TiO$_2$ adding method was also employed in this study. Interestingly, by dip-coating nano-TiO$_2$ onto SCGM, a significant increase in photocatalytic activity was achieved. After only 60 min of UV irradiation, a total inactivation of $E$. coli occurred (Fig. 5 (b)). Similarly, this elevated photocatalytic activity has been demonstrated by other researchers, in which Ramirez et al [16] obtained high toluene degradation efficiencies by dip-coating cementitious materials with TiO$_2$, whereas, Chen et al [37] observed no toluene degradation on 5% TiO$_2$ intermixed concrete surface layers. It is obvious that the dip-coating method enables a favourable photocatalytic property in the substrate materials. A relatively extensive exposure of the active sites of the photocatalysts to the reactants can be realized by dip-coating the photocatalyst onto the substrate materials, providing reactants with convenient access to the surface of photocatalysts. It seems that the method, in which TiO$_2$ is added to the substrate materials, plays a vital role in determining the photocatalytic activity attained. Therefore, it is reasonable to assume that the failure to realize the photocatalytic antibacterial activity should mainly be attributed to the TiO$_2$ intermixing method. More details will be provided and further discussed in our next paper to offer clues about the significance of the TiO$_2$ addition method and reveal critical parameters influencing the associated photocatalytic activity.

4. Conclusion

The NO removal and bacteria inactivition of TiO$_2$ intermixed in self-compacting glass mortar (SCGM) were assessed in the present study. The results showed that the presence of nano-TiO$_2$ particles decreased the fluidity of fresh SCGM; however, superplasticizer can be used to disperse the mixture. Meanwhile, with the addition of nano-TiO$_2$ either at 2% or 5%, about a 12% compressive strength increment was observed in SCGM. The results from the photocatalytic activity of TiO$_2$ intermixed SCGM showed that an increase in TiO$_2$ content translated into enhanced photocatalytic NO removal activity. In addition, for a given dosage of TiO$_2$, the SCGM using transparent recycled glass as aggregate showed an insignificantly higher NO removal rate than that prepared with light green recycled glass. In contrast, despite the existence of NO removal, little inactivation ability of $E$. coli was observed
for all of samples under the same UV irradiation.

Overall, it can be concluded that NO removal and bacteria inactivation are two rather different photocatalytic activities, with the latter a more complex process requiring a certain amount of ROS accumulation. Therefore, the photocatalytic activity of NO removal cannot always be extrapolated to the photocatalytic activity of bacteria inactivation. In addition, according to the results and analysis from the present study, it seems that the TiO$_2$ adding method may hold the key to realization of bacterial inactivation through highly improved photocatalytic activity.

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References


