Research Article

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Experimental study on photocatalytic degradation efficiency of mixed crystal nano-TiO_2 concrete

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Abstract: The photocatalytic mixed crystal nano-TiO_2 particles were incorporated with concrete by means of the internal doping method (IDM) and spraying method (SPM) in this paper. To evaluate the photocatalytic degradation efficiency of mixed crystal nano-TiO_2 concrete, the methyl orange (MO) was chosen to simulate pollutants. The physicochemical characteristics and photocatalytic performance of mixed crystal nano-TiO_2 concrete prepared by above two different methods were experimentally investigated under UV irradiation and solar irradiation. Furthermore, the effects of two key influential factors including pollutant concentration and irradiation condition were also analyzed and discussed. Experimental results indicate that the nano-TiO_2 concrete prepared by the spraying method (SPM) exhibits maximum photocatalytic degradation efficiency of 73.82% when the sprayed nano-TiO_2 slurry concentration is 10mg/L. The photocatalytic degradation efficiency of unpolished nano-TiO_2 concrete is much higher than that of polished nano-TiO_2 concrete under the same exposure time of UV irradiation. Moreover, the photocatalytic degradation efficiency of nano-TiO_2 concrete decreases with the increase of pollutant concentration. The irradiation condition has an obvious influence on the photocatalytic degradation efficiency of nano-TiO_2 concrete. In the aspect of applications, the practical recommendations for the nano-TiO_2 concrete with self-cleaning capacity were presented according to the experimental results.

Keywords: mixed crystal; nano-TiO_2 concrete; X-ray diffraction; pollutant concentration; irradiation condition; photocatalytic degradation efficiency

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1 Introduction

With the rapid development of industrialization and urbanization, environmental pollution has become an increasingly serious social problem that can't be neglected indeed. As one of the most significant traditional construction materials (steel and cement), the cement is facing enormous concerns due to its activity has been considered as one of the primary causes of air pollution [1]. To mitigate the environment impact of cement production, varieties of physical, chemical and biological methods such as adsorption, precipitation, and bioremediation have been proposed by scientists [2]. Among the above methods, the photocatalysis technology has been considered as one of the most efficient solutions to address air pollutants owing to its superior photocatalytic activity, low cost, and complete degradation [3].

To seek a superior photocatalyst is one of the most significant problems in photocatalysis technology. Up to now, the nano-TiO_2 has been considered as one of the best choices as a good photocatalyst due to its chemical stability, non-toxicity and high photocatalytic activity. On the other hand, due to the high plasticity, good durability and easy material availability, the concrete has been widely utilized in the field of civil and building engineering. Therefore, it is an innovative idea that a new kind of nano-TiO_2 concrete with self-cleaning capacity is proposed by using the concrete as the carrier.

In recent years, the photocatalytic performance and innovative applications for kinds of novel nano materials have been in-depth investigated and discussed at home and abroad. He *et al.* [4] studied the mechanical and photocatalytic properties of two types of nano-TiO_2 concrete by using X-ray diffraction, scanning electron microscopy, and degradation efficiency tests. It was found that the photocatalytic performance of the modified nano-TiO_2 concrete was much better than that of the original nano-TiO_2 concrete. Elena *et al.* [5] systematically evaluated the photocatalytic activity of the Sol-Gel nano-TiO_2 particles for photocatalytic cement composites by comparing the degradation of Methylene Blue (MB) under UV irradiation. An experimental study on the photocatalytic performance of nano-TiO_2

incorporated self-compacting glass mortar (SCGM) was performed by Guo *et al.* [6]. Experimental results showed that the photocatalytic performance of SCGM proved an obvious decrease of NO with the increase of NO2 under UVA irradiation. Ge *et al.* [7] comprehensively summarized several advances and potential applications of TiO_2 nanotube arrays on the photoelectrocatalytic degradation efficiency of pollutants. Yi *et al.* [8] presented an experimental investigation on the adsorptive degradation performance of hydrophobic/hydrophilic nano-SiO_2 under different organic pollutant solutions. The hydrophobic nano-SiO_2 exhibited superior adsorption capacity on soluble organic compounds. Feng *et al.* [9] prepared photocatalytic TiO_2 composite cement pastes by a smear method and systematically investigated the microstructure, photocatalytic properties and durability. Test results showed that the TiO_2 composite cement pastes possessed better degradation properties after they were immersed in an acid or alkaline solution. A novel active catalyst called as diatom-FeOx composite was experimentally investigated by Krishna *et al.* [10] to study the photocatalytic degradation efficiency. Test results showed that the diatom-FeOx composite exhibited high activity in catalyzing the photodegradation of Rh-6G. Zhang *et al.* [11] evaluated and discussed the effects of nano-SiO_2 on the photocatalytic behavior and durability of cementitious composite incorporated with nano-SiO_2. The results indicated that the nano-SiO_2 could dramatically improve the photocatalytic performance and durability of cementitious composites. Samim *et al.* [12] discussed and compared the visible light photocatalytic activity of the ZnO nanostructures prepared by different modification strategies. The photocatalytic activity of the ZnO nanostructures was significantly correlated with the charge dynamics across the nanostructured interface. The reduced graphene oxide-Bi2WO6 photocatalyst with different RM values were successfully compounded by using hydrothermal method [13]. Experimental results indicated that the photocatalytic activity of oxide-Bi2WO6 for the degradation of Rho-damine-B increased gradually when the RM values were enhanced from 0 to 2%. Huang *et al.* [14] proposed a new type of nano-TiO_2 emulsified asphalt mixture, and investigated four influence factors (nano-TiO_2 particle size, dosage, degradation time and light intensity) on the photocatalytic performance of nano-TiO_2 emulsified asphalt mixture. Shen *et al.* [15] proposed a kind of photocatalytic concrete with ultra-smooth surface manufactured by using the photocatalysis properties of nano-TiO_2 particles. This kind of photocatalytic concrete is considered as a promising self-cleaning finishing material for the urban buildings.

Although many researchers have studied the photocatalytic property of kinds of nano materials, there is still little investigation being performed on the physicochemical characteristics and photocatalytic performance of nano-TiO_2 concrete with self-cleaning capacity. In this research, the mixed crystal nano-TiO_2 particles were incorporated with the concrete by means of the internal doping method (IDM) and spraying method (SPM). The physicochemical characteristics of mixed crystal nano-TiO_2 were identified by X-ray diffraction (XRD). The methyl orange (MO) was adopted to simulate pollutants for the investigation of photocatalytic degradation efficiency of mixed crystal nano-TiO_2 concrete under UV irradiation and solar irradiation. Furthermore, the effects of two key influential factors including pollutant concentration and irradiation condition were also analyzed and discussed. Finally, the practical recommendations for the application of novel nano-TiO_2 concrete with self-cleaning capacity were presented according to the experimental results.

2 Materials and experimental preparation

2.1 Test materials

There were three types of industrial materials used in this experiment, including the cement, nano-TiO_2, and methyl orange. A commercially mixed crystal nano-TiO_2 powder (type P25) was utilized as the photocatalyst for the preparation of nano-TiO_2 concrete. The mixed crystal nano-TiO_2 powder consists of 75 wt% anatase and 25 wt% rutile. The mixed crystal nano-TiO_2 powder was purchased from Degussa, Germany, which has an average particle size of 21 nm, and a specific surface area of 50 m^2/g. Table 1 shows the physical properties of the mixed crystal nano-TiO_2 powder. The Chinese common Portland cement with a strength grade of 42.5 (type P·O 42.5) was utilized to prepare the nano-TiO_2 concrete block samples. The natural medium sand with a maximum size of 4.75 mm is used as fine aggregate, and the crushed stone with the maximum

Table 1: Physical properties of mixed crystal nano-TiO_2 particles

Particle size (nm)	Specific surface area (m^2/g)	Purity (%)	Bulk density (g/l)	pH
21	50	99:5	130	3:5-4:5

(a) Concrete block prepared by IDM

(b) Concrete block prepared by SPM

Figure 1: Nano-TiO_2 concrete block samples

Table 2: Mix proportions of nano-TiO_2 concrete

Nano-TiO_2 concrete strength	Water (kg/m^3)	Cement (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)
C30	183	450	600	1192

size of 30 mm is used as coarse aggregate. The mix proportions of nano-TiO_2 concrete with nominal cube strength of 30 MPa in this study is presented in Table 2. The methyl orange (MO) was used as an organic pollutant to evaluate the photocatalytic degradation efficiency of nano-TiO_2 concrete by measuring its absorbance during the experiment. The methyl orange was purchased from China National Pharmaceutical Corporation.

2.2 Preparation of nano-TiO_2 concrete

The nano-TiO_2 powders are usually incorporated with concrete in two kinds of methods: (1) mix nano-TiO_2 powder with the concrete aggregates directly, which is called as the internal doping method; (2) spray nano-TiO_2 slurry on the surface of concrete blocks, which is called as the spraying method [16–19]. However, these methods generally exhibit a significant difference in the photocatalytic degradation performance of the mixed crystal nano-TiO_2 concrete. Therefore, two kinds of preparation methods including the internal doping method (IDM) and spraying method (SPM) were adopted and then a comparative research was conducted to investigate the photocatalytic degradation efficiency of mixed crystal nano-TiO_2 concrete with self-cleaning capacity.

In this experiment, for the internal doping method, the cement in concrete mix was equivalently substituted by the nano-TiO_2 powders with different contents (2%, 5%, 8%) to prepare the nano-TiO_2 concrete block samples. As for the spraying method, the concrete block samples were firstly prepared, and then the nano-TiO_2 slurry with different concentrations (5mg/L, 10mg/L, 15mg/L, 20mg/L) was sprayed on the surface of the concrete block samples. The sprayed nano-TiO_2 slurry on the surface of the concrete block samples was required to keep uniform and the thickness of spray coating was 1mm. All tested nano-TiO_2 concrete block samples are 8 cm in diameter, 1 cm in thickness and 100 g in weight. The nano-TiO_2 concrete block samples prepared by above methods are shown in Figure 1.

2.3 Nano-TiO_2 characterization

The XRD analysis was conducted by an X-ray diffractometer manufactured by Panalytical Corporation to obtain the physicochemical characteristics of mixed crystal nano-TiO_2 concrete. In this experiment, the tube voltage and current of the measuring instrument were fixed at 45 kV and 40 mA, respectively. Moreover, the UV-Vis spectrophotometer (type LAMBDA 650) was employed to test the material, and UV-Vis diffuse reflectance spectroscopy (DRS) was used to obtain the absorption spectrum, and further analyze the light absorption capacity.

2.4 Photocatalytic performance test

To evaluate the photocatalytic degradation efficiency of mixed crystal nano-TiO_2 concrete, the methyl orange (MO) was utilized to simulate pollutants in this experiment. Moreover, the mercury lamp and xenon lamp with the light power density of 80 W/cm were also utilized to simulate the UV irradiation and solar irradiation condition, respectively, as shown in Figure 2. Especially, for the purpose of mitigating the effect of temperature variation, the temperature of MO solution was sustained at the controlled tem-

(a) UV irradiation test **(b)** Solar irradiation test

Figure 2: Photocatalytic reaction chamber

perature during the tests by placing a cooling jacket on the bottom of the beaker. The experimental process can be described as follows: (1) a volume of 300 ml methyl orange solution with a concentration of 10 mg/L was infused into a flat bottom beaker, and then the nano-TiO_2 concrete brick sample was also put into the beaker. Before illumination, the solution was placed in a photocatalytic reaction chamber and was stirred by a magnetic stirring apparatus for 30 minutes. (2) after the physical adsorption equilibrium of methyl orange solution was reached, a volume of 4 ml solution was extracted, and then centrifuged on a high-speed centrifuge with a speed of 12000 r/min for 1 minute. (3) the supernatant was extracted to measure the solution absorbance (recorded as A_0) by using a UV-Vis spectrophotometer. After the measurement, the initial solution was poured back to the beaker and continued to be degraded. (4) turn on the mercury lamp, and then placed the beaker under a 250W UV irradiation (or solar irradiation) with a distance of 20 cm. (5) after 15 minutes of UV irradiation (or solar irradiation), a volume of 4 ml MO solution was extracted and measured the solution absorbance (recorded as A_{15}) by using a UV-Vis spectrophotometer. After that, the second measured solution was poured back again to the beaker and continued to be degraded. (6) seven times continuous tests were carried out as the previous steps, and the solution absorbance in each time was recorded as At. In this experiment, the photocatalytic degradation efficiency (D) can be calculated by the solution absorbance, which is described by the following equation:

$$D = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Where, D is photocatalytic degradation efficiency. A_0 is the initial absorbance of the MO solution. A_t is the final absorbance of the MO solution after t minute photocatalytic degradation.

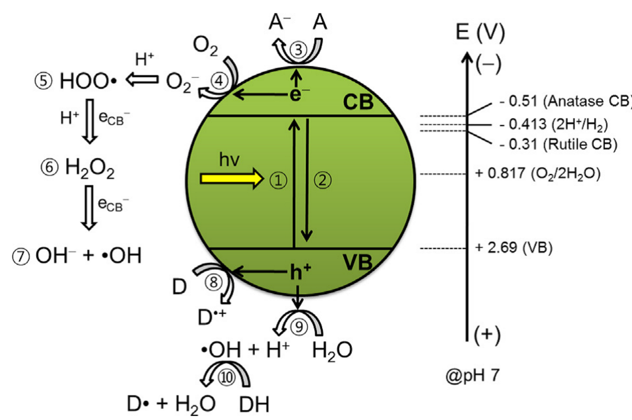


Figure 3: Schematic illustration for photocatalysis mechanism of nano-TiO_2

3 Results and discussions

3.1 Photocatalysis mechanism

Figure 3 demonstrates the primary photocatalysis mechanism of nano-TiO_2 concrete. In this investigation, the nano-TiO_2 is a typical wide bandgap semiconductor material, which possesses a special energy band structure. This energy band structure of nano-TiO_2 consists of a low valence band (VB) filled with electrons and a high empty energy conduction band (CB). When the irradiation energy is larger than the bandgap width of nano-TiO_2, electrons (e^-) in the valence band (VB) can be excited to jump into the

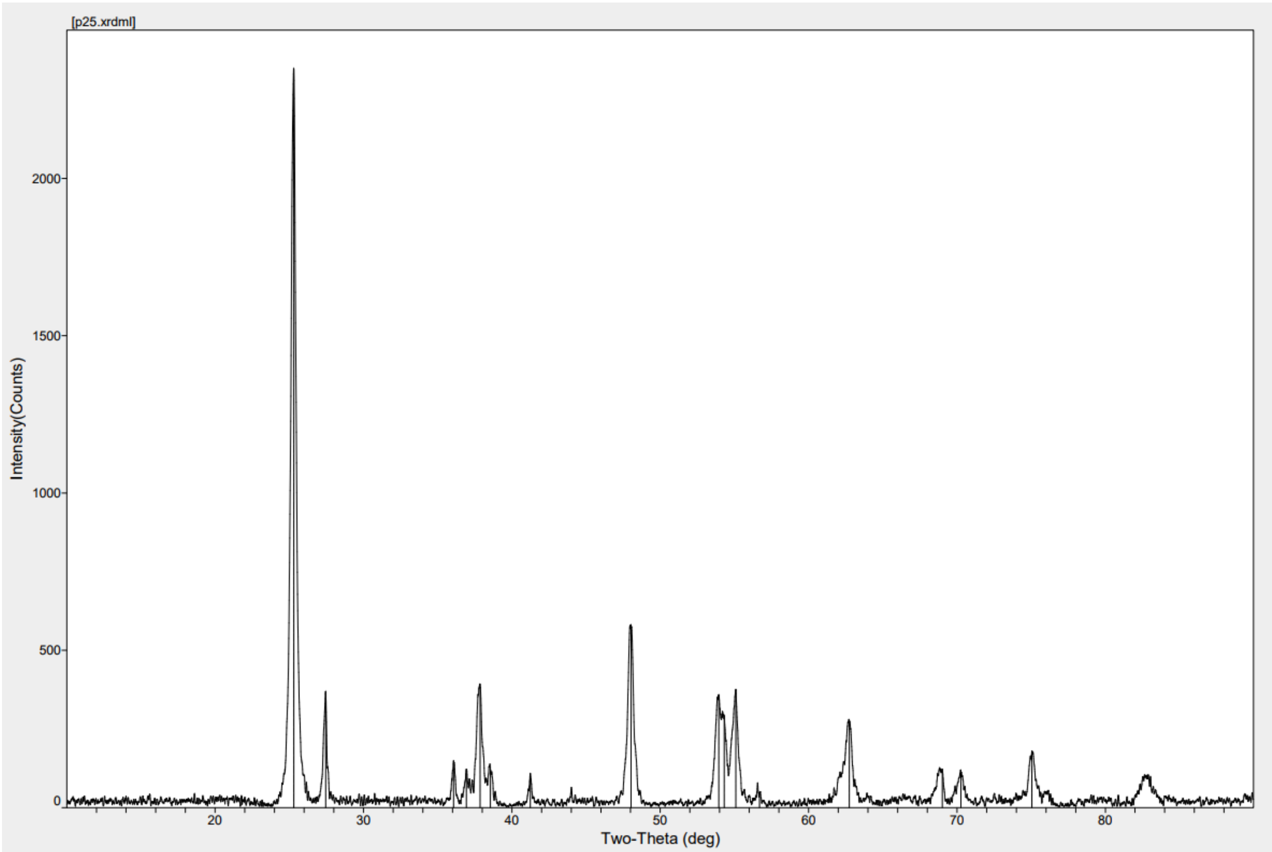


Figure 4: XRD pattern of nano-TiO_2

conduction band (CB), and the corresponding holes (h^+) are generated in the valence band (VB), thus developing an “electron-hole” pair, as shown in equation (2). On the one hand, under the irradiation condition, electrons (e^-) in the conduction band (CB) can further react with the absorbed oxygen (O_2) and produce the superoxide ions ($O_2^{\bullet-}$), as plotted in equation (3). Moreover, these superoxide ions ($O_2^{\bullet-}$) can further react with hydrogen ions (H^+) in water and generate $HO_2^{\bullet}$, as shown in equation (4). Subsequently, $HO_2^{\bullet}$ can react with e^- and H^+ to produce H_2O_2, as demonstrated in equation (5). Finally, H_2O_2 can react with e^- to generate $OH^{\bullet}$ and OH^- [20]. On the other hand, the produced holes (h^+) in the valence band (VB) can capture OH^- in water and then generate $OH^{\bullet}$ [21, 22]. On the whole photocatalytic reaction process, these reactive oxygen species (H_2O_2, $OH^{\bullet}$, $O_2^{\bullet-}$) possess superior redox ability, which can degrade the organism to small green molecules, such as CO2 and H2O. Therefore, the nano-TiO_2 concrete possesses self-cleaning capacity owing to the photocatalytic degradation performance of nano-TiO_2.

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

$$e^- + O_2 \rightarrow O_2^{\bullet-} \tag{3}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \tag{4}$$

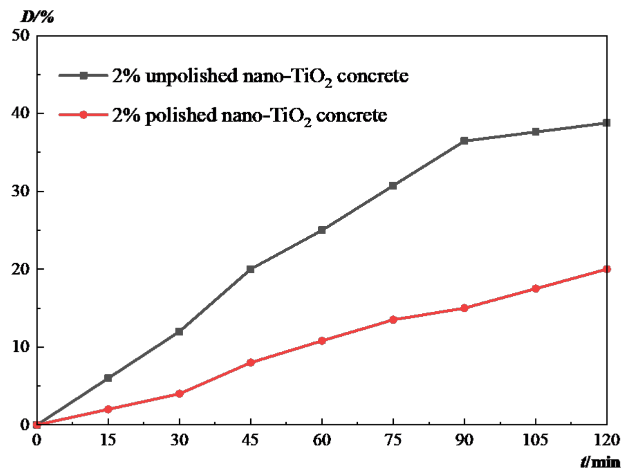
$$HO_2^{\bullet} + e^- + H^+ \rightarrow H_2O_2 \tag{5}$$

$$H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^- \tag{6}$$

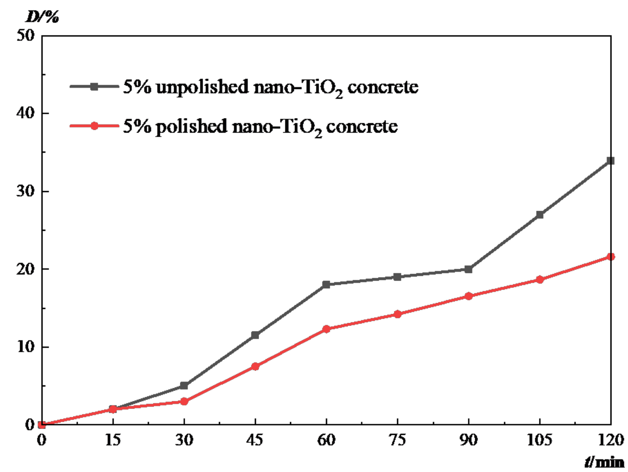
$$h^+ + OH^- \rightarrow OH^{\bullet} \tag{7}$$

3.2 X-ray diffraction (XRD) studies

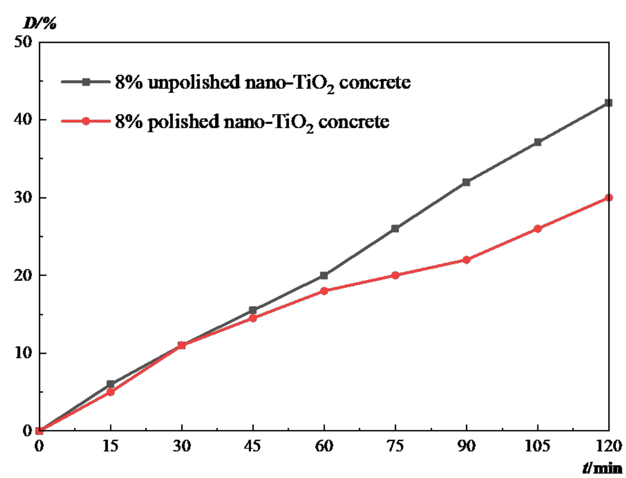
Figure 4 displays the X-ray diffraction (XRD) spectra of nano-TiO_2 particles. As demonstrated in Figure 4, the characteristic diffraction peaks of anatase and rutile forms of TiO_2 can be detected in the spectrum of nano-TiO_2, which indicates that the nano-TiO_2 samples adopted in this paper are comprised of anatase and rutile mixed phase, corresponding to the phase composition of P25.



(a) Concrete mixed with 2% nano-TiO_2



(b) Concrete mixed with 5% nano-TiO_2



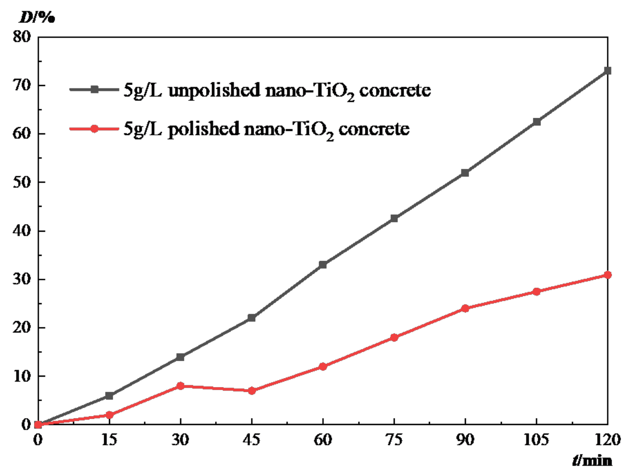
(c) Concrete mixed with 8% nano-TiO_2

Figure 5: Photocatalytic degradation efficiency of concrete with mixed different nano-TiO_2 contents

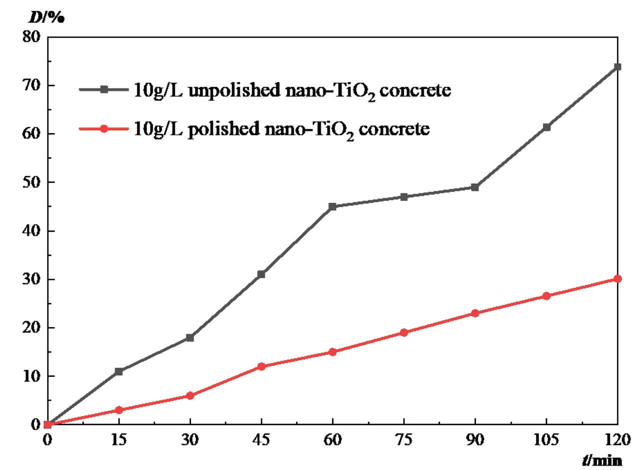
Based on the experimental data, the average crystal size of nano-TiO_2 can be calculated by measuring the broadening of the most intense peak of the phase in a diffraction pattern according to the Debye-Scherrer equation [23]. The calculated crystal size of nano-TiO_2 was about 20.86 nm.

3.3 The effect of internal doping method (IDM)

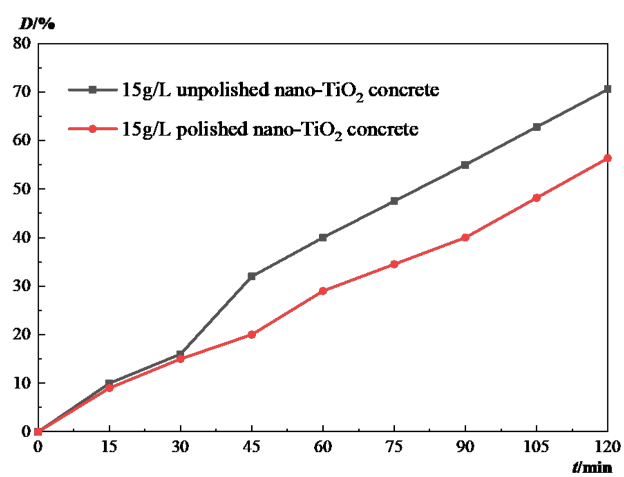
The effect of the internal doping method on the photocatalytic degradation efficiency of nano-TiO_2 concrete is plotted in Figure 5. In these figures, the horizontal coordinate represents the exposure time under UV irradiation (t) and the vertical coordinate represents the photocatalytic degradation efficiency of the nano-TiO_2 concrete (D). It can be obviously seen from Figure 5 that the photocatalytic degradation efficiency of the nano-TiO_2 concrete prepared by the internal doping method is enhanced with the increase of the exposure time of UV irradiation. Moreover, for these nano-TiO_2 concrete after being polished, the photocatalytic efficiency exhibits a linear relationship with the exposure time of UV irradiation. However, for these nano-TiO_2 concrete without being polished, the photocatalytic degradation efficiency versus irradiation time curves are almost nonlinear. As demonstrated in Figure 5(a), when the nano-TiO_2 content is 2%, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 38.78% and 21.81%, respectively, after 120 min of UV irradiation. As demonstrated in Figure 5(b), when the nano-TiO_2 content is 5%, the final



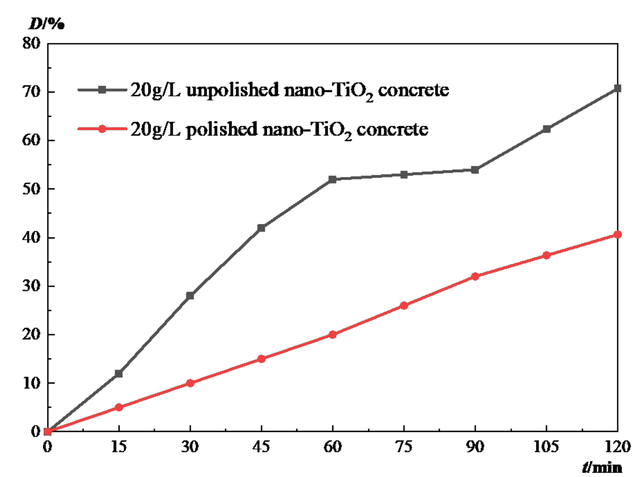
(a) Concrete sprayed with 5mg/L nano-TiO_2



(b) Concrete sprayed with 10mg/L nano-TiO_2



(c) Concrete sprayed with 15mg/L nano-TiO_2



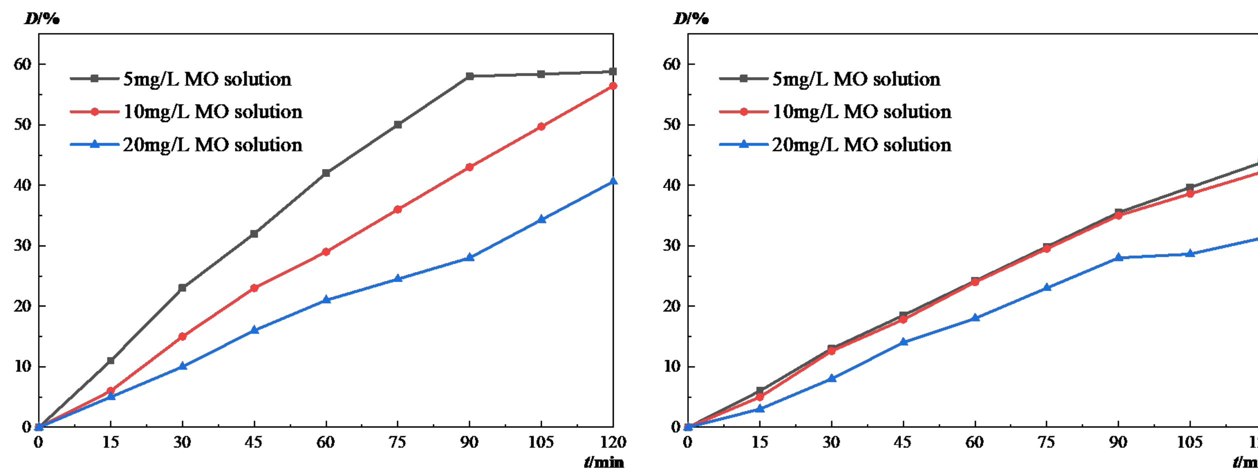
(d) Concrete sprayed with 20mg/L nano-TiO_2

Figure 6: Photocatalytic degradation efficiency of concrete sprayed with different nano-TiO_2 concentrations

photocatalytic degradation efficiency of unpolished concrete and polished concrete is 33.94% and 22.74%, respectively, after 120 min of UV irradiation. As demonstrated in Figure 5(c), when the nano-TiO_2 content is 8%, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 42.19% and 32.48%, respectively, after 120 min of UV irradiation. It can be found from the above analysis that the photocatalytic degradation efficiency of nano-TiO_2 concrete (whether polished or unpolished) increases roughly with the increase of nano-TiO_2 content. The photocatalytic degradation efficiency of unpolished nano-TiO_2 concrete is much higher than that of polished nano-TiO_2 concrete under the same exposure time of UV irradiation, which indicates that the polishing process has a negative influence on the photocatalytic degradation efficiency of nano-TiO_2 concrete. What's more, the nano-TiO_2 concrete still exhibits better photocatalytic performance after being polished, indicating that the nano-TiO_2 concrete possesses excellent surface durability and abrasion resistance compared with the common concrete. Additionally, it can be also observed that the effect of polishing process on the photocatalytic degradation efficiency of nano-TiO_2 concrete becomes smaller with the increase of nano-TiO_2 content.

3.4 The effect of spraying method (SPM)

The effect of the spraying method on the photocatalytic degradation efficiency of nano-TiO_2 concrete is plotted in Figure 6. It can be found from Figure 6 that the photocatalytic degradation efficiency of the nano-TiO_2 concrete pre-



(a) Concrete mixed with 2% nano-TiO_2

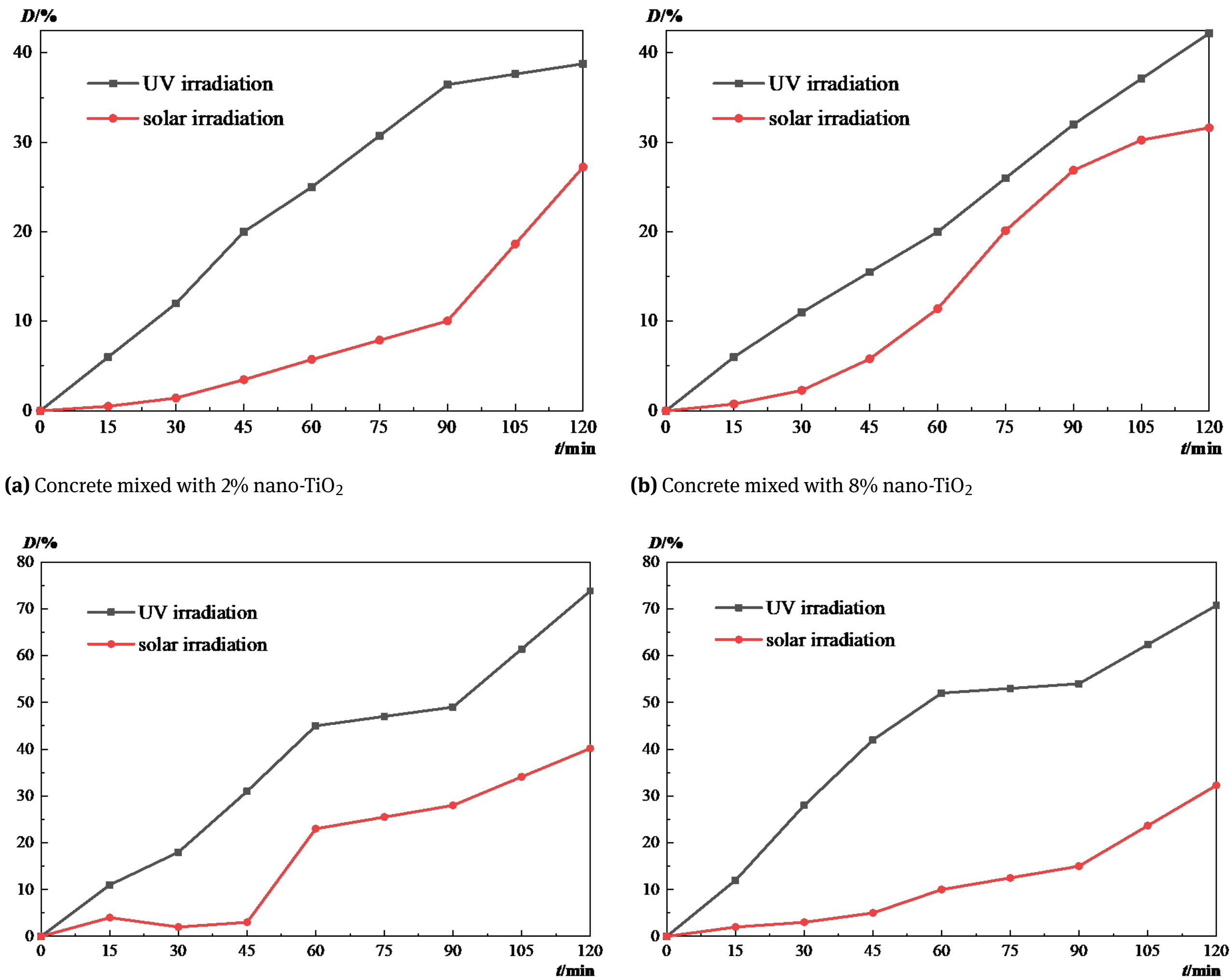
(b) Concrete mixed with 8% nano-TiO_2

Figure 7: Photocatalytic degradation efficiency of nano-TiO_2 concrete under different pollutant concentrations

pared by the spraying method increases with the increase of the exposure time of UV irradiation. The photocatalytic degradation efficiency of nano-TiO_2 concrete prepared by spraying method (SPM) is much higher than that of nano-TiO_2 concrete prepared by the internal doping method (IDM). As shown in Figure 6(a), when the sprayed nano-TiO_2 slurry concentration is 5mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 72.98% and 30.91%, respectively, after 120 min of UV irradiation. As shown in Figure 6(b), when the sprayed nano-TiO_2 slurry concentration is 10mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 73.82% and 30.10%, respectively, after 120 min of UV irradiation. As shown in Figure 6(c), when the sprayed nano-TiO_2 slurry concentration is 15mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 70.55% and 56.36%, respectively, after 120 min of UV irradiation. As shown in Figure 6(d), when the sprayed nano-TiO_2 slurry concentration is 20mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 70.72% and 40.63%, respectively, after 120 min of UV irradiation. It can be found from the above analysis that the photocatalytic degradation efficiency of nano-TiO_2 concrete (whether polished or unpolished) is roughly unchanged with the increase of nano-TiO_2 slurry concentration. This indicates that the increase of nano-TiO_2 slurry concentration can't significantly improve the photocatalytic degradation efficiency when the nano-TiO_2 concrete is prepared by the spraying method (SPM). Furthermore, it can be also concluded that the polishing process has a more obvious influence on the photocatalytic degradation efficiency of nano-TiO_2 concrete prepared by the spraying method than that of nano-TiO_2 concrete prepared by the internal doping method. This is because the polishing process can significantly change the density distributions of nano-TiO_2 particles on the surface of concrete prepared by the spraying method.

3.5 The effect of pollutant concentration

Figure 7 shows the photocatalytic degradation efficiency of nano-TiO_2 concrete under different pollutant (MO solution) concentrations. As shown in Figure 7(a), for the concrete mixed with 2% nano-TiO_2, when the initial concentration of MO solution is 5, 10 and 20 mg/L, the final photocatalytic degradation efficiency of nano-TiO_2 concrete is 58.78%, 56.42%, and 40.60%, respectively. As shown in Figure 7(b), for the concrete mixed with 8% nano-TiO_2, when the initial concentration of MO solution is 5, 10 and 20 mg/L, the final photocatalytic degradation efficiency of nano-TiO_2 concrete is 43.78%, 42.19% and 31.26%, respectively. It can be obviously seen from the above analysis that the photocatalytic degradation efficiency of nano-TiO_2 concrete decreases with the increase of pollutant (MO solution) concentration, signifying that the increase of pollutant concentration has a negative influence on the photocatalytic degradation efficiency of nano-TiO_2 concrete. For the concrete mixed with 2% nano-TiO_2, the photocatalytic degradation efficiency under the concentration of 5 mg/L is much higher than that under the concentration of 10 and 20 mg/L. This indicates that the concrete mixed with 2% nano-TiO_2 presents superior photocatalytic degradation



(a) Concrete mixed with 2% nano-TiO_2

(b) Concrete mixed with 8% nano-TiO_2

(c) Concrete sprayed with 10mg/L nano-TiO_2

(d) Concrete sprayed with 20mg/L nano-TiO_2

Figure 8: Photocatalytic degradation efficiency of nano-TiO_2 concrete under different irradiation condition

efficiency when the pollutant (MO solution) has a low concentration. Moreover, the photocatalytic degradation efficiency of concrete mixed with 2% nano-TiO_2 decreases significantly when the pollutant (MO solution) concentration increases from 5 mg/L to 20 mg/L. However, for the concrete mixed with 8% nano-TiO_2, the photocatalytic degradation efficiency under the pollutant concentration of 5 mg/L is basically the same as that under the pollutant concentration of 10 mg/L. Besides, the photocatalytic degradation efficiency of concrete mixed with 8% nano-TiO_2 only has a slight decrease when the pollutant (MO solution) concentration increases from 5 mg/L to 20 mg/L. It can be concluded from the above comparison that the effect of pollutant concentration on the photocatalytic degradation efficiency of concrete mixed with 2% nano-TiO_2 is more obvious than that of concrete mixed with 8% nano-TiO_2.

3.6 The effect of irradiation condition

Figure 8 shows the photocatalytic degradation efficiency of nano-TiO_2 concrete under different irradiation condition. As plotted in Figure 8(a), for the concrete mixed with 2% nano-TiO_2, the final photocatalytic degradation efficiency of nano-TiO_2 concrete is 38.78% and 27.24%, respectively, when the irradiation condition is UV irradiation and solar irradiation. As plotted in Figure 8(b), for the concrete mixed with 8% nano-TiO_2, the final photocatalytic degradation efficiency of nano-TiO_2 concrete is 42.19% and 31.63%, respectively, when the irradiation condition is UV irradiation and solar irradiation. As plotted in Figure 8(c), for the concrete sprayed with 10mg/L nano-TiO_2 slurry, the final photocatalytic degradation efficiency of nano-TiO_2 concrete is 73.82% and 40.15%, respectively, when the irradiation condition is UV irradiation and solar irradiation. As plotted in Figure 8(d), for the concrete sprayed with 20mg/L nano-TiO_2 slurry, the final photocatalytic degradation efficiency of nano-TiO_2 concrete is 70.72% and 32.27%, respectively, when the irradiation condition is UV irradiation and solar irradiation. It can be found from the above analysis that the irradiation condition has an obvious effect on the photocatalytic degradation efficiency of nano-TiO_2 concrete. The photocatalytic degradation efficiency of nano-TiO_2 concrete under UV irradiation is much higher than that of nano-TiO_2 concrete under solar irradiation. This can be explained by the fact that the photocatalytic activity of nano-TiO_2 concrete is primarily activated and taken effect under the UV irradiation condition. The nano-TiO_2 concrete exhibits low photocatalytic degradation efficiency under solar irradiation owing to the less ultraviolet light in sunlight. In addition, it can be also observed from Figure 8(a), 8(b) that the photocatalytic degradation efficiency of nano-TiO_2 concrete prepared by internal doping method (IDM) can be improved to some extent, when the nano-TiO_2 content increases from 2% to 8%. Nevertheless, the increase of nano-TiO_2 slurry concentration from 10mg/L to 20mg/L fails to enhance the photocatalytic degradation efficiency of nano-TiO_2 concrete prepared by spraying method (SPM), as shown in Figure 8(c), 8(d).

4 Application recommendations

Based on the experimental results and analysis, some practical recommendations about the mixed crystal nano-TiO_2 concrete are put forward. The nano-TiO_2 concrete prepared by the spraying method (SPM) exhibits maximum photocatalytic degradation efficiency of 73.8% when the sprayed nano-TiO_2 slurry concentration is 10mg/L. Therefore, it is highly recommended to incorporate the nano-TiO_2 with the concrete by the spraying method (SPM) in order to obtain superior photocatalytic performance of nano-TiO_2 concrete.

The polished nano-TiO_2 concrete still possesses better photocatalytic performance to some extent, but the photocatalytic degradation efficiency is much lower than that of unpolished nano-TiO_2 concrete. Considering the photocatalytic performance and abrasion resistance, it is recommended to incorporate the nano-TiO_2 with the concrete by the internal doping method (IDM) when the nano-TiO_2 concrete is utilized for pavement materials. However, when the nano-TiO_2 concrete is used for wall building materials, it is suggested to incorporate the nano-TiO_2 with the concrete by the spraying method (SPM) for good photocatalytic performance and convenient construction.

5 Conclusions

In this paper, a novel kind of photocatalytic nano-TiO_2 concrete with self-cleaning capacity was prepared by the internal doping method (IDM) and spraying method (SPM). The photocatalytic degradation efficiency of mixed crystal nano-TiO_2 concrete prepared by above two methods was experimentally investigated. According to the experimental results, the following conclusions can be drawn:

1. The photocatalytic degradation efficiency of nano-TiO_2 concrete (whether polished or unpolished) increases slightly with the increase of nano-TiO_2 content, which denotes that increasing nano-TiO_2 content can enhance the photocatalytic efficiency when the nano-TiO_2 concrete is prepared by internal doping method (IDM).
2. The photocatalytic degradation efficiency of unpolished nano-TiO_2 concrete is much higher than that of polished nano-TiO_2 concrete under the same exposure time of UV irradiation. The polishing process has a negative influence on the photocatalytic degradation efficiency of nano-TiO_2 concrete.
3. The photocatalytic degradation efficiency of nano-TiO_2 concrete (whether polished or unpolished) is nearly unchanged with the increase of nano-TiO_2 slurry concentration. The increase of nano-TiO_2 slurry concentration can't significantly improve the photocatalytic efficiency when the nano-TiO_2 concrete is prepared by the spraying method (SPM).
4. The photocatalytic degradation efficiency of nano-TiO_2 concrete decreases with the increase of pollutant (MO solution) concentration, signifying that the pollutant concentration has a negative effect on the photocatalytic degradation efficiency of nano-TiO_2 concrete.
5. The irradiation condition significantly influences the photocatalytic degradation efficiency of nano-TiO_2 concrete. The photocatalytic degradation efficiency of nano-TiO_2 concrete under UV irradiation is much higher than that of nano-TiO_2 concrete under solar irradiation.

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References

[1] Elena C.P., Sara G.S., Controlled synthesis and microstructural properties of Sol-Gel TiO_2 nanoparticles for photocatalytic cement composites, Nanomaterials, 2019, 9, 1-16.

[2] Singh P., Vishnu M.C., Sharma K.K., Borthakur A., Srivastava P., Pal D., Tiwary D., Mishra P.K., Photocatalytic degradation of acid red dye stuff in the presence of activated carbon-TiO_2 composite and its kinetic enumeration, J. Water Process Eng., 2016, 12, 20-31.

[3] Cirak B.B., Caglar B., Kilinc T., Karadeniz SM, Erdogan Y., Kilic S., Kahveci E., Ekinci AE., Synthesis and characterization of ZnO nanorice decorated TiO_2 nanotubes for enhanced photocatalytic activity, Mater. Res. Bull., 2019, 109, 160-167.

[4] He R., Huang X., Zhang J.S., Geng Y., Guo H.D., Preparation and evaluation of exhaust- purifying cement concrete employing titanium dioxide, Materials, 2019, 12, 2182-2195.

[5] Elena C.P., Sara G.S., Angeles M., Fernando V., Controlled synthesis and microstructural properties of sol-Gel TiO_2 nanoparticles for photocatalytic cement composites, Nanomaterials, 2019, 9, 26-42.

[6] Guo M.Z., Chen J., Xia M., Wang T., C.S. Poon, Pathways of conversion of nitrogen oxides by TiO_2 incorporated in cement-based materials, Build. Environ., 2018, 144, 412-418.

[7] Ge M.Z., Cao C.Y., Huang J.Y., Synthesis, modification, and photo/photoelectrocatalytic degradation applications of TiO_2 nanotube arrays: a review, Nanotechnol. Rev., 2016, 5, 75-112.

[8] Yi Z.G., Tang Q., Jiang T., Cheng Y., Adsorption performance of hydrophobic/hydrophilic silica aerogel for low concentration organic pollutant in aqueous, Nanotechnol. Rev., 2019, 8, 266-274.

[9] Feng S.L., Liu F.H., Fu X., Peng X.Y., Zhu J.L., Zeng Q.L., Photocatalytic performances and durability of TiO_2 cement composites prepared by a smear method for organic wastewater degradation, Ceram. Int., 2019, 45, 23061-23069.

[10] Krishna P.G., Megha T., Sidhartha V., Wei L.P., Dandamudi R.B., Mitra S., Novel diatom-FeOx composite as highly active catalyst in photodegradation of Rhodamine-6G , Nanotechnol. Rev., 2018, 7, 247-255.

[11] Zhang P., Li Q.F., Wang J., Shi Y., Ling Y.F., Effect of PVA fiber on durability of cementitious composite containing nano-SiO_2, Nanotechnol. Rev., 2019, 8: 116-127.

[12] Samim S., Samir K. P., Ultrafast photoinduced carrier dynamics at ZnO nanohybrid interfaces for light-harvesting applications, Nanotechnol. Rev., 2016, 5: 113-134.

[13] Yu H.G., Chu C.L., Chu P. K., Self-assembly and enhanced visible-light-driven photocatalytic activity of reduced graphene oxide-BiWO6 photocatalysts, Nanotechnol. Rev., 2017, 6, 505-516.

[14] Huang M., Wen X.J., Experimental study on the photocatalytic effect of nano-TiO_2 epoxy emulsified asphalt mixture, Appl. Sci., 2019, 9, 2464-2475.

[15] Shen W.G., Zhang C., Li Q., Zhang W.S., Cao L., Ye J.Y., Preparation of titanium dioxide nano particle modified photocatalytic self-cleaning concrete, J. Clean. Prod., 2015, 87, 762-765.

[16] Pacheco-Torgal F., Jalali S., Nanotechnology: advantages and drawbacks in the field of construction and building materials, Constr. Build. Mater., 2011, 25, 582-590.

[17] Fujishima A., Zhang X.T., Tryk D.A., TiO_2 photocatalysis and related surface phenomena, Surf. Sci. Rep., 2008, 63, 515-582.

[18] Jimenez-Relinque E., Llorente I., Castellote M., TiO_2 cement-based materials: understanding optical properties and electronic band structure of complex matrices, Catal. Today, 2017, 287, 203-209.

[19] Jin Q., Saad E.M., Zhang W., Tang Y., Kurtis K.E., Quantification of NOx uptake in plain and TiO_2-doped cementitious materials, Cement Concr. Res., 2019, 122, 251-256.

[20] Li R., Cai M., Xie Z., Zhang Q., Zeng Y., Liu H., Liu G., Lv W., Construction of heterostructured CuFe2O4/g-C3N4 nanocomposite as an efficient visible light photocatalyst with peroxydisulfate for the organic oxidation, Appl. Catal. B Enviro., 2019, 244, 974-982.

[21] Hoffman A.J., Carraway E.R., Hoffman M.R., Photocatalytic production of H2O2 and organic peroxides on quantum-sized semiconductor colloids, Environ. Sci. Technol., 1994, 28, 776-785.

[22] Emilio C.A., Litter M.I., Kunst M., Bouchard M., Colbeau-Justin C., Phenol photodegradation on platinized-TiO_2 photocatalysts related to charge-carrier dynamics, Langmuir, 2006, 22, 3606-3613.

[23] Kibasomba P.M., Dhlamini S., Maaza M., Liu C.P., Rashad M.M., Rayan D.A., Mwakikunga B.W., Strain and grain size of TiO_2 nanoparticles from TEM, Raman spectroscopy and XRD: the revisiting of the Williamson-Hall plot method, 2018, 9, 628-635.