Study on Photo-catalytic Efficiency and Durability of Nano-TiO2 in Permeable Concrete Pavement Structure

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Abstract. In terms of the problems of photo-catalytic degradation of exhaust gas, especially the low efficiency and short durability of NOx, an integrated loading method of fully reclaimed permeable concrete structure from the selection of photo-catalysts, aggregate infiltration and internal incorporation was designed and tested in this study. Through systematic tests, all those methods have fully improved the photo-catalytic oxidation effect, and the NOx degradation efficiency can reach more than 80%. The realization of stereoscopic degradation of exhaust gas and the improvement of photo-catalytic durability provide a technological support for the application of nano-TiO2 in the permeable concrete pavement structure.

1. Introduction
In recent years, environmental problems such as smog and urban heat island in northern China need to be further improved. As citizens' demands for environment and quality of life increased, energy conservation and emission reduction, low-carbon environmental protection, green ecology, and circular economy have become the hot issues for environmental governance and improvement. Pollutant emission remains the main and internal obstacle for improving air quality. There are four main sources of exhaust pollution, namely, industrial pollution, coal pollution, motor vehicles exhaust, and dust, accounting for more than 90% of the source of pollution. And another obstacle is PM2.5, which is composed of nitrates, sulfates, ammonium salts and organic matter, accounting for more than 70%. With the development of China's transportation and automobile industry, the pollution of automobile exhaust has accounted for larger proportion and has greater impact on the environment. In terms of photo-catalytic degradation, Japan was the first country to conduct research and application of photo-catalytic materials, and then launched a wave of theoretical and applied research on photo-catalytic materials in various countries [1]. Attempts to improve photo-catalytic oxidant degradation of automobile exhaust in ordinary concrete pavement, asphalt pavement, road auxiliary facilities and permeable concrete structures have also gained some achievements. For example, in 2005, Professor QianChunxiang of the Institute of Green Building Materials Technology of Southeast University used the pavement material as the carrier and loaded the nanometer titanium dioxide. It was successfully applied in the photo-catalytic pavement of the north toll station of the Yangtze River in Nanjing. It is relatively simple, sharing the advantages of lower cost and higher photo-catalytic efficiency. After nearly one year’s testing, it found that the efficiency of photo-catalytic concrete pavement degradation of nitrogen oxides can reach more than 80% [2]. In 2006, a 120-meter “photo-catalyst ecological pavement” was conducted at the junction of Shanghai Fuxing East Road and South Henan Road. And then Shanghai Environmental Science Research Institute tested it and found that the laminate can absorb nearly 45% of automobile exhaust, which greatly alleviates...
environmental pollution [3]. The nano-titanium dioxide photo-catalyst was implanted on the expressway in Chiba Prefecture, Japan, which can absorb at least 1/4 of the nitrogen oxides of automobile exhaust gas. In the Italian city of Milan, the nano-titanium dioxide was added to the asphalt concrete pavement, and found that the exhaust gas pollution index could reduce by 60%-70% [4]. Although certain applications and pilots have been carried out, the surface-loaded photo catalyst oxidant degradation of exhaust gas still has the disadvantages of large vicious environmental impact and poor durability in its use. Therefore, based on porous reclaimed concrete for waste concrete recycled aggregate and loaded photo-catalyst for photo catalytic pavement application research, this paper aims to offer solutions for resolving the problem of low photo-catalytic efficiency and durability of photo-catalysts with the indoor and outdoor comparative tests.

2. Study design

At present, limited by the complicated, sophisticated, and multiple chemical reactions of loaded-photo catalysts [5], most of the load methods are not suitable for large-scale application. Therefore, this study systematically explored application scope, material selection, load mode, and structural depth to enhance the degradation efficiency to a greater extent, and to improve the photo-catalytic efficiency and durability.

Studies have proved that after spraying photo-catalysts on ordinary asphalt and concrete pavement, the photo-catalyst particles adhered to the surface layer of the road are much easier to fall off, and its photo-catalytic function cannot be maintained for a long time. The photo-catalytic pavement used in Chiba Prefecture, Japan, has many grooves, which reduces the direct contact between the automobile tire and the photo-catalysts, thereby reducing the shedding of the photo-catalysts. Therefore, the ideal photo-catalytic load pavement structure should have a certain structural depth, which is beneficial to the photo-catalysts immobilization. Secondly, the pavement structure should be permeable and light-transitive to improve the durability of the photo-catalytic reaction. This study selected recycled permeable concrete structure with an aggregate structure and interconnected pores not less than about 20% from the surface to the deep structural layer. The photo-catalysts were loaded on the surface and inside the structure to provide more space for the loading of the photo-catalyst particles. In addition, the contact between the catalyst itself and external factors is reduced, which greatly reduces the shedding of the photo-catalyst particles.

3. Aggregate infiltration

As the main component of concrete, coarse and fine aggregates account for about 65-85% of the unit weight. Therefore, we can consider incorporating photo-catalysts into the aggregate to form a permanent carrier. Especially for recycled aggregates, its surface is permeable with many tiny cracks, which can enlarge water absorption rate. These seemingly disadvantageous features provide suitable environment and conditions for supporting photo-catalysts. The recycled aggregate includes recycled coarse and fine aggregate, and both two materials can be supported as a carrier of the photo-catalysts.

3.1 Aggregate infiltration mechanism

The recycled aggregates used in this study have more pores. With the application of nano-titanium dioxide, the recycled aggregates were loaded with nano-titanium dioxide and silica, which fills the pores and cracks of the recycled aggregates. In addition, the specific surface of the nano-titanium dioxide is generally above 500cm³/g with high reactivity. The hydration products are increased by filling the pores and the nucleation effect, which will not only help the aggregate itself to improve load photo-catalysts but also with the filling and nucleation of the nano material will improve the pore structure of the concrete, so that the durability of the concrete such as wear resistance, impermeability and frost resistance can be significantly improved [6].
3.2 Selections of Nano-titanium dioxide and other materials

3.2.1 Nano-titanium dioxide. For mixed crystal TiO2 formed by anatase and rutile, if it is under photo-excitation, the electrons on the anatase TiO2 conduction band will transfer to the lower positive potential rutile phase TiO2 conduction band, so that the anatase TiO2 conducts electrons on the conduction band will be significantly reduced and the photo-catalytic efficiency of TiO2 will be significantly improved [7]. The study results have showed that the catalytic effect of the sample is most significant when the mass ratio of anatase to rutile is 9:1[8]. Therefore, a TiO2 mixed crystal was used for the aggregate loading and the mass ratio of anatase to rutile should be 9:1.

3.2.2 Recycled aggregate. The waste concrete coming from the bridge of Beijing-Shanghai Highway was used for crushing, water washing and drying after R5 type impact crushing equipment. The particle size after impact crushing meets the requirements of single-stage matching with the grain size 4.75mm-9.5mm and 2.36-4.75mm, with its grain shape closing to cube, and the needle-like content less than 5%, which equals Grade I concrete.

3.2.3 Other materials. The nanometer titanium dioxide dispersing agent adopted sodium tripolyphosphate which is sold in the market, and it was analytically purified; the water for mixing used tap water, which meets the drinking water standard;

3.3 Loading process
The 3% dispersion sodium tripolyphosphate was fully dissolved in water, then the nano TiO2 powder was added, and the mixture was stirred at a high speed for 40 min. After that, the mixture was ultrasonically dispersed for 25 min in a water bath to obtain permeable slurry. The prepared titanium dioxide solution was infiltrated into the recycled coarse aggregate and fine aggregate, for soaking not less than 24 hours. Then it was heated in a microwave oven for five minutes, that is, the photo-catalyst loading was completed. Through the application of microwave oven, the drying loading process was completed and the effect of nano titanium dioxide reinforcement was greatly improved in the heated state.

3.4 Test sample production
The regenerated aggregate based on the above method was used to make a panel with 4 cm thickness and its strength and water permeability coefficient satisfying design requirements. The recycled aggregate was blended according to 70%, namely:

Cement: recycled fine aggregate: recycled coarse aggregate: water: water reducing agent = 300:182:1044:90:0.01

In order to compare loading effect, the test samples were divided into groups according to the different amount and types of nano-titanium dioxide (concentration: 0.4%, 0.6%, 0.8%, 1.0%), and they were numbered as J00, J04, J06, J08, J10.

According to the manufacturing process of permeable concrete in CJJ/T135-2009 "Technical Regulations for Permeable Cement Concrete Pavement", when the cement slurry approaches the initial setting, the floating slurry on the surface should be washed away with drinking water, so that the aggregate will be slightly leaked. It is basically consistent with the actual operation state of the road, that is, part of the aggregate is embedded in the road surface. After 7 days of curing, the degradation effect of the recycled aggregate-loaded nana-titanium dioxide can be tested.

3.5 Effect test
This study used the JK90-NOX/SO2 portable muti-functional composite gas analyzer produced by Shenzhen Jishun Technology Company to perform nitrogen oxide degradation detection.

The prepared test sample was placed in the reaction laboratory of the automobile exhaust gas test system to conduct exhaust gas degradation. Two UVA ultraviolet lamps with a power of 15 W were
fixed at the top of reaction laboratory as a photo-catalytic reaction light source. The change in the concentration of the vehicle exhaust gas in the vehicle was measured by an automobile exhaust gas analyzer and a nitrogen dioxide detector connected to the reaction laboratory.

In the laboratory, the degradation test was carried out on the test samples made of the recycled aggregate loaded with nano-titanium dioxide. The specific data was shown in Table 1:

| Durability | J00 | J04 | J06 | J08 | J10 |
|------------|-----|-----|-----|-----|-----|
| 1h         | 0.2 | 1.1 | 3.5 | 5.2 | 5.3 |
| 3h         | 0.4 | 1.6 | 5.7 | 8.9 | 9.8 |
| 7h         | 0.7 | 3.1 | 7.8 | 11.6| 10.7|

Figure 1. Variation diagram of degradation effect of aggregate loaded nano titanium dioxide

The figure has shown:

After the nano-titanium dioxide was loaded on the aggregate, the degradation effect increased with the increase of the surface loading of the aggregate, but the degradation effect and the concentration of 0.8% slowed down when the concentration reached 1.0%. The test showed that the aggregate loaded with nano-titanium dioxide The optimum concentration is 0.8%. The same aggregate loading concentration, with the increase of degradation time (1-3h), the tail gas degradation amount will increase. It can be seen that the recycled aggregate after loading TiO2 can provide photo-catalysts for the deuterium road surface and improve photo-catalytic degradation durability.

4. Cement based photo-catalytic composites
Permeable concrete is mainly composed of aggregate and cement. Besides the method of aggregate infiltration, it is the best choice to incorporate nano titanium dioxide into the cement slurry. At present, as for cement and other admixtures in concrete materials, most of them have experienced high temperature processes and complex physical and chemical changes in such a way to form photo-catalytic properties in cement and admixture minerals. The mineral composition makes the production of photo-catalytic concrete simpler and lower cost. Such materials will be more widely used in construction field. The manufacturing process of the cement-based photo-catalytic composite material in this study is much simpler and more convenient with better effect.

4.1 Material selection

4.1.1 Photo-catalysts. In this study, the commercially available silicon-coated nano titanium dioxide was used. It showed that this material is not only a physical envelope, but also a chemical bond. Si(OH)4 acts as a strong electron acceptor, which will directly be attached to the surface hydroxide Ti-OH group of titanium dioxide, making it active. The Ti-OH group will become a Ti-O-Si bond, broadening the wavelength range of light absorption of nano-TiO2, enhancing the ultraviolet
absorption capacity, and improving excellent degradation effect [9].

4.1.2 Other materials. The cement was made of PO42.5 ordinary Portland cement produced by Shandong Cement Factory Co., Ltd. The fly ash was made of first grade ash, and the dispersion were made of sodium tripolyphosphate which was sold in the market. The water for mixing was tap water, which meets the drinking water standard.

4.2 Production process

The photo-catalytic test sample was prepared by dispersing the surfactant-treated TiO2 in a styrene-acrylic emulsion by ultrasonic vibration, high-speed agitation shearing, and a comprehensive dispersion preparation reagent with a dispersion. In the comprehensive dispersion process, the ultrasonic agitation firstly dispersed the nanoparticles into fine particles, and thus the mechanical agitation can mix the solution in a whole range. At the same time, the appropriate dispersion was added to wrap the nanoparticles, so that the surface of the particles was highly adsorbed. The steric effect of the molecule produces a steric hindrance function, thereby effectively avoiding the agglomeration of the nanoparticles and achieving uniform distribution of the nanoparticles [10].

Under the premise that the reclaimed permeable concrete meets the mechanical performance requirements, the nano-titanium dioxide was blended and the test samples were prepared. The size for test sample was 600mm×600mm×40mm.

4.3 Effect test

In order to test the catalytic performance of cement-based photocatalytic composites, this study used the recycled aggregate without blending with nano-titanium dioxide, and the optimum dosage was determined by the degradation effect. The dosage was calculated according to the mass ratio of cement, which was 4%, 5%, 6%, 7% and 8% respectively. The corresponding test samples were numbered as S4, S5, S6, S7 and S8. After testing, the specific results were as follows in table 2:

|        | 1h  | 24.2 | 36.8 | 42.7 | 48.6 | 50.6 |
|--------|-----|------|------|------|------|------|
| 3h     | 33.7| 52.7 | 64.1 | 66.8 | 64.9 |
| 7h     | 46.6| 63.6 | 82.6 | 86.7 | 85.3 |

Table 2. Degradation effect of cement-based photocatalytic composites (%)

Figure 2. Diagram of degradation effect of cement-based photocatalytic composites

The figure shows:

With the increase of the dosage, the degradation effect of cement-based photo-catalytic composites has been enhanced. The growth rate is faster when the dosage reaches 6% but it will be slower when the dosage remains 7% or 8%. This is mainly because the surface of the test piece has been covered by the catalyzed product, which decreases the degradation effect.

The cement-based photo-catalytic composite has obvious degradation effect on nitrogen oxides,
and it can realize 80.6% degradation when the dosage remains 6%, reaching the expected effect.

5. Wear resistance test
One of the durability of photo-catalysts is wear resistance. The permeable cement concrete pavement has different wears caused by non-motor vehicles and pedestrians. Considering that, this study tested degradation by grinding the road surface by 5 mm. After the testing with the application of JK90-NOX/SO2 portable multi-functional composite gas analyzer, it found that the degradation efficiency can still reach 80.3%.

6. Durability affecting factors and its countermeasures

6.1 Influence of reaction products on durability and its countermeasures
Nano TiO2 as a photo-catalyst, its final reaction product is acidic materials with nitric acid and nitrate, which will directly cover the surface of the photo-catalyst and reduce the photo-catalytic efficiency [11]. Based on this theory, in addition to flushing the road surface by natural precipitation, it also regularly used water to flush, making water directly flowing into the drain pipe through the permeable cement concrete pavement structure, and then entering the road drainage system. Besides, the permeable concrete pavement structure is an alkaline, which can directly neutralize the nitric acid produced by photo-catalytic oxidation, and it can also be mixed with alkaline powder during the preparation of the photo-catalysts. After that, it will be mixed and reconstituted in the recycled aggregate or in a cement slurry thus to improve photo-catalytic durability.

6.2 Light conduction
This study used a regenerated aggregate of 4.75-9.5mm, which has a large aperture and this aperture can bring channels to the input of light. In addition, a certain amount of glass beads were sprayed before the surface layer was completed and the initial setting was performed to improve the light's effective conduction [12]. The reflection and refraction of the sunlight through the glass beads could enter a certain depth of the concrete structure and provide conditions for degradation durability.

7. Conclusion
1) According to the strength and permeability coefficient of permeable concrete, the optimum blending amount of recycled aggregate should not exceed 70% and not less than 30%. If it is less than 30%, the photo-catalyst loading will be too small to realize photo-catalytic effect and the durability cannot be significantly improved.

2) When the recycled aggregate was loaded, the optimum nano titanium dioxide concentration should be 0.8%. If it is possible, the ultrasonic vibration method can also be used to vibrate while infiltrating, and the load effect will be much better.

3) In the preparation of cement-based photo-catalytic composite, the optimum photo-catalyst dosage should be 6% by the methods of ultrasonic vibration, high-speed stirring and comprehensive dispersion preparation.

4) After comprehensive testing and one month of observation, the photo-catalytic efficiency can still reach more than 80%. Based on the above superposition effect, a stereoscopic photo-catalytic effect is obtained, thereby achieving photo-catalytic durability.

5) This technology can mainly be applied to the structures of walkways, non-motor vehicle lanes and parking lots in municipal roads, plazas, parks, residential areas, and permeable concrete pavement.

Acknowledgments
This paper were supported by Shandong Transportation Science and Technology Plan(2018B67), and by Provincial Water Conservancy Science Research and Technology Promotion Projects in 2019 (SDSLKY201909).
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