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Preparation Technique and Properties of Nano-TiO_2 Photocatalytic Coatings for Asphalt Pavement

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Featured Application: Due to having the same color with the asphalt, the prepared nano-TiO_2 photocatalytic coating could be applied directly onto the pavement surfaces, located in densely-populated areas, environmentally-sensitive areas, service areas and parking lots etc., to further play a better role in the degradation of exhaust gas.

Abstract: According to the characteristics of asphalt pavement, a kind of nano-TiO_2 photocatalytic coating was prepared by using the emulsified asphalt as the carrier. All of its properties met the technical requirements. An exhaust gas degradation test device and its test steps were developed. The evaluation indexes, cumulative degradation rate, and degradation efficiency, were put forward. From the two aspects of the nano-TiO_2 content in photocatalytic coatings and the spraying amount of photocatalytic coatings in the surface of slabs (300 mm $\times$ 300 mm), the exhaust gas degradation effects, the performances of skid resistance, and the water permeability of asphalt mixture were analyzed. The test results showed that the cumulative degradation rate of exhaust gas was better when nano-TiO_2 content was increased in the range of 0–8% and the spraying amount was changed in the range of 0–333.3 g/m^2. In practical engineering applications, the anti-skid performance of asphalt pavement can be satisfied when the spraying amount of photocatalytic coating was limited to under 550 g/m^2. The spraying amount of nano-TiO_2 photocatalytic coating had little effect on the water permeability of the asphalt mixture. Therefore, 8% nano-TiO_2 content in the coating and a 400 g/m^2 spraying amount were finally recommended based on the photocatalytic properties, as well as for economic reasons.

Keywords: preparation technique; emulsified asphalt; nano-TiO_2; photocatalytic coating; degradation of exhaust gas

1. Introduction

Vehicles have brought convenience to people but also more and more serious air pollution. A lot of studies on the purification technology of automobile exhaust have been conducted in many countries around the world [1–4]. TiO_2 is generally considered as one of the most effective photoinduced catalysts and is frequently used to oxidize organic and inorganic compounds in the air and water due to its strong oxidative ability and long-term photostability, as well as being a non-expensive and non-toxic material. Therefore, titania-mediated photocatalysis is a very promising approach to the increasing crucial issues associated with environmental pollution [5,6]. Indeed, among the possible solutions, TiO_2-coated materials can significantly decompose a variety of organic (e.g., volatile organic compounds) and inorganic (e.g., NO_x and SO_2) pollutants due to its unique photocatalytic property, which contributes to its ability toward air-purifying and self-cleaning. Nano-TiO_2 has been proved to be a good photocatalytic material, which can degrade harmful substances in waste gas [7,8]. A series of new photocatalytic materials related to TiO_2 have been developed and applied in different situations [6,9–11]. The emissions of harmful air pollutants associated with highway operations often surpass the concentrations from industrial sources, rendering traffic emissions the primary source of urban air pollution [12,13]. Therefore, TiO_2 is widely used in road engineering due to its excellent photocatalytic properties in many countries such as China, Italy, and so on. The air purification effect on both sides of the road area has been improved to a greater extent [14–16].

Currently, there are two ways to apply nano-TiO_2 on the road, which are a blending method (i.e., nano-TiO_2 was directly added to the aggregate and mixed with the asphalt to form a nano-TiO_2 asphalt mixture) and a spraying method (i.e., coatings containing nano-TiO_2 were sprayed on the surface of the pavement or other road-affiliated facilities) [17]. Tan et al. [18] applied nano-TiO_2 to an asphalt pavement using both methods to analyze the photocatalytic degradation of automobile exhaust gas. Test results showed that nano-TiO_2 under the two kinds of applications had a good photocatalytic degradation effect. However, for the blending method, the amount of nano-TiO_2 used was large and the cost was high. Marwa, Hassan, and co-workers [19–21] studied a sustainable photocatalytic asphalt pavement by using TiO_2 as a photocatalytic material to reduce nitrogen oxides and sulfur dioxide. The development of this new sustainable road has the potential to reduce the high pollution level caused by traffic vehicles. The environmental effectiveness of a TiO_2 coating in photodegrading mixed NO_2 and NO gases from the atmosphere was evaluated. David et al. [22] studied the performance of asphalt pavement with a TiO_2 photocatalyst. They developed and tested a new photocatalytic method to quantify the short-term durability of TiO_2 spraying on two kinds of pavements: concrete and asphalt. Clement et al. [23] applied three commercially-available photocatalytic coatings to roadside concrete to elucidate how environmental parameters, exposure, and real roadside conditions impact the degradation of NO_x. The test results for a 20-month period indicated that the efficacy diminished over time. This research shows that the application of photocatalysis technology has a good effect in dealing with automobile exhaust and is rather promising. Under the effect of light, the photocatalyst can react with the automobile exhaust to form water, carbon dioxide, and salt, which prevents secondary pollution to the environment. In spite of these promising findings, the application of this technology to pavements is still in its infancy. Usually photocatalytic compounds used only as a coating are painted on the roadside or crash barrier. Therefore, based on the characteristics of the sprayed asphalt pavement, a photocatalytic coating of nano-TiO_2 and emulsified asphalt as a carrier was prepared in this paper. The effect of the degradation performance of a photocatalytic coating on the exhaust gas was evaluated, and the pavement performance of the asphalt pavement with a photocatalytic coating was analyzed.

2. Materials and Experimental Preparation

2.1. Selection of Nano-TiO_2 Crystals

TiO_2 was divided into three different crystal structures, namely anatase, rutile, and brookite. Table 1 shows the basic properties of the three types of crystal structures. The common ones are anatase and rutile. The internal structures of these crystals composed of TiO_2 are all octahedral and connect with each other. However, they have different material properties and internal electronic structures due to the differences of the degree of deformation of the octahedral and the connection forms. Despite the valence band of the phase, the electron transition produces the same cavitation oxidation performance. However, the band width of anatase is 3.2 eV, while rutile is only 3.0 eV. Therefore, the rutile is more negative, and the reducibility of transitional electrons is stronger. In addition, the electron (e^-)–hole (h^+) pairs produced by the lower-bandwidth rutile electron transition are easier to recover, reducing the redox activity. Therefore, the anatase TiO_2 has better photocatalytic performance than the rutile one. In this study, the anatase TiO_2 was selected. The technical indicators of anatase nano-TiO_2, which were provided by the manufacturer Xuancheng Jingrui New Material Co., Ltd. (Xuancheng, China), are shown in Table 2.

Table 1. The physical properties of nano-TiO_2 crystals.

Crystal Type	Relative Density	Crystal System	The Lattice Constant (nm)		Ti–O Distance (nm)	The Forbidden Band Width (eV)
			a	c		
anatase	3.84	tetragona	5.27	9.37	0.195	3.2
rutile	4.26	tetragona	9.05	5.80	0.199	3.0
brookite	4.17	lorthorhombic	_	_	_	_

Table 2. Technical indicators of anatase nano-TiO_2.

Appearance	Specific Surface Area (m^2/g)	pH	Particle Size (nm)	Loss on Drying (%)	Loss on Ignition (%)	Purity (%)
white powder	80	5	20	0.2	0.25	>99.8

2.2. Materials for TiO_2 Photocatalytic Coating

Besides nano-TiO_2, the materials for the preparation of nano-TiO_2 photocatalytic coatings include:

- Dispersants: Two kinds of dispersants, S-5040 and sodium hexametaphosphate (SHP), were used. The detailed technical indicators, which were provided by the manufacturer Shandong Huali Bio-tech Co., Ltd. (Zibo, China), are shown in Table 3.
- Emulsifiers: Three kinds of representative emulsifiers—rapid-setting cationic emulsifier SY-QCE, medium-setting cationic emulsifier KZW-802, and slow-setting cationic emulsifier SY-CME—were chosen. The technical indicators, which were provided by the manufacturer Jiangsu Xinyue Asphalt Co., Ltd. (Zhenjiang, China), are shown in Table 4.
- Asphalt: A kind of 70# penetration "A" grade asphalt binder was selected (Shell (China) Limited). The main physical properties of the asphalt binder were tested following the Chinese Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTG E20-2011) [24] and met the requirements in the Chinese Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25], as shown in Table 5.
- In addition, $CaCl_2$ (Wuhan Fude Chemical Co., Ltd., Wuhan, China) and hydrochloric acid (Wuhan Fude Chemical Co., Ltd., Wuhan, China) were selected as additives.

Table 3. Technical indicators of dispersants.

Dispersants	Appearance	Solid Content (%)	Viscosity (Pa·s)	Boiling Point (°C)	Solubility
S-5040	Colorless, viscous, and transparent liquid	40	400	110	Extremely easy to dissolve in water
SHP	Transparent glass flake or white powder	—	—	1500	Extremely easy to dissolve in water

Table 4. Technical indicators of emulsifiers.

Emulsifiers	SY-QCE	KZW-802	SY-CME
Appearance (25 °C)	Light yellow liquid	Creamy white paste	Light yellow liquid
Purity of emulsifiers (%)	≥60	≥50	≥75
pH value	9–10	2–4	3–4
Solubility	Easy to dissolve in water	Easy to dissolve in water	Easy to dissolve in water
Type of Emulsifiers	Rapid-setting	Medium-setting	Slow-setting
Adding content of emulsifiers (%)	0.5	0.8	2

Table 5. Basic physical properties of asphalt.

Index	Test Results	Requirements [25]	Methods [24]
25 °C Penetration (0.1 mm)	72	≈60–80	T0604
Penetration index (PI)	0.11	−1.5 to +1.0	T0604
Softening point (°C)	48	≥46	T0606
15 °C Ductility (cm)	>100	>100	T0605
60 °C Viscosity (Pa·s)	213	>180	T0625
Flash point (°C)	288	≥260	T0611
Wax content (%)	1.2	≤2.2	T0615

2.3. Asphalt Mixture for Base Sample

A kind of styrene-butadiene-styrene block copolymer (SBS) modified asphalt binder with 8% high viscosity modified additive by the weight of asphalt was used in this paper. The main technical indexes were tested according to the test methods in the Chinese Standard Test Methods of Bitumen and Bitumen Mixtures for Highway Engineering (JTG E20-2011) [24]. Its basic properties met the Chinese Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25], as shown in Table 6. The aggregate used was taken from a basalt quarry (Qiangyuan Basalt Development Co., Ltd., Zhuzhou, China). It was completely crushed to give larger particles with an angular shape and rough surface texture. The test methods were based on the Chinese Test Methods of Aggregate for Highway Engineering (JTG E42-2005) [26]. Its basic properties met the Chinese Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [24], which are listed in Table 7. In order to make nano-TiO_2 play a better photocatalytic role, open-graded friction course (OGFC) gradation was selected owing to its large air voids and deep structural texture. The design gradation of the aggregate met the requirements of OGFC-10 according to the Chinese Technical Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25], as shown in Figure 1. The designed asphalt aggregate ratio was 4.5%. The results of OGFC design are shown in Table 8.

Table 6. The main technical indexes of high-viscosity modified asphalt.

Index	Test Results	Requirements [25]	Methods [24]
25 °C Penetration (0.1 mm)	42.6	≥40	T0604
Penetration index (PI)	1.21	≥0	T0604
Softening point (°C)	91.0	≥80	T0606
15 °C Ductility (cm)	77.3	≥50	T0605
Toughness (N·m)	38	≥20	T0624
60 °C Viscosity (Pa·s)	73,550	≥20,000	T0625
Flash point (°C)	275.0	≥260	T0611
25 °C Elastic recovery (%)	94.3	≥75	T0662

Table 7. Basic physical properties of the aggregate.

Index	Test Results	Requirements [25]	Methods [26]
Los Angeles abrasion loss (%)	15.6	≤28	T0317
Soundness (%)	0.88	≤12	T0314
Elongated or flat particles (%)	13.3	≤15	T0312
Water absorption (%)	0.52	≤2.0	T0304
Apparent specific gravity	2.774	≥2.6	T0304

Table 8. Results of OCFG-10 design.

Index	Test Results	Requirements [25]	Methods [24]
Volumes of air voids (%)	20.1	18–25	T0705
Draindown (%)	0.25	<0.3	T0732
Cantabro loss (%)	5.9	<20	T0733
Marshall stability (kN)	8.33	≥3.5	T0709

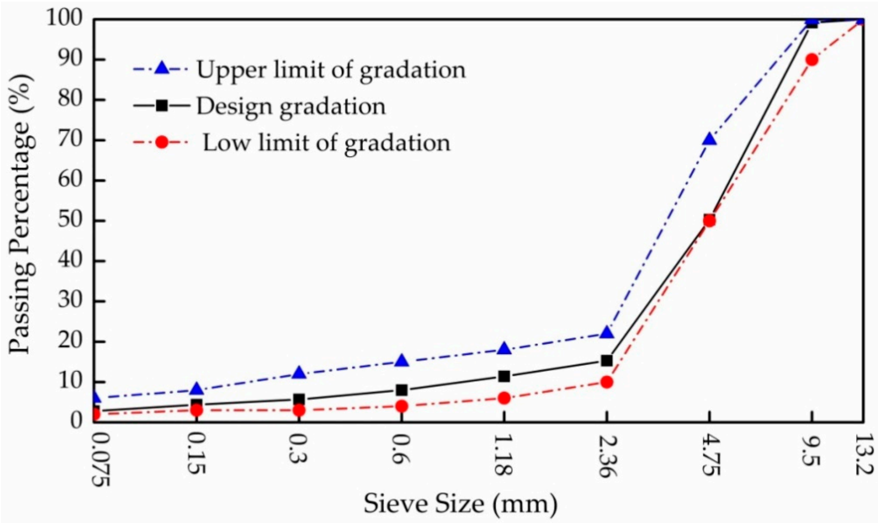


Figure 1. OGFC-10 aggregate gradation curve.

2.4. Exhaust Gas Degradation Test Device and Evaluation Indexes

2.4.1. Exhaust Gas Test Devices and Test Steps

The test devices for measuring the degradation efficiency of exhaust gas were developed, including the exhaust gas analyzer, degradation reaction chamber with build-in two parallel UVA-340 ultraviolet lamps and a small fan, voltage regulator, and a gas cylinder filled with CO, HC, and NO_x. The composition and concentration of the gas mix in the cylinder were similar to automobile exhaust. The test devices are illustrated in Figure 2.

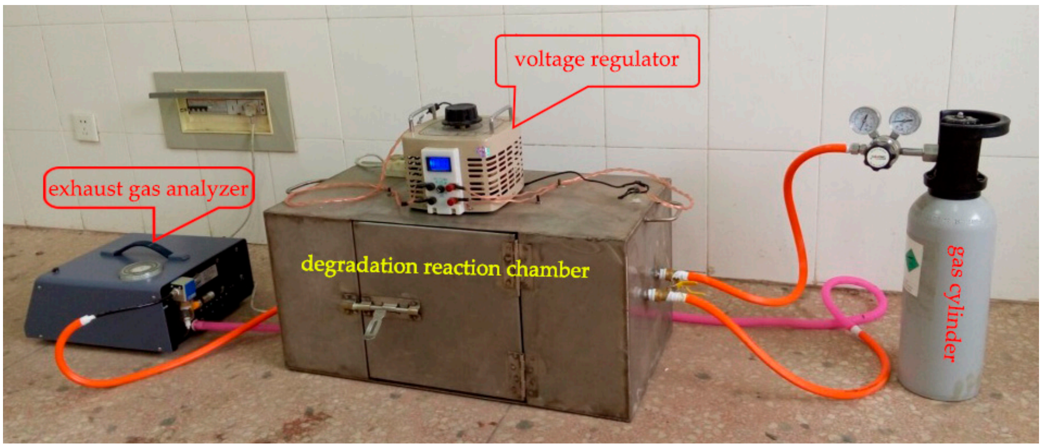


Figure 2. Exhaust gas degradation test device.

Test steps:

- The nano-TiO_2 photocatalytic coating was prepared (the detailed procedures are shown in Section 3.2).
- The coating was then sprayed on the surface of the slab specimen according to the designated amount. The emulsified asphalt coating containing a certain amount of nano-TiO_2 was uniformly painted onto the slab sample with a brush, as shown in Figure 3.
- The coating was put in a dry and ventilated place for more than 24 h to ensure that the coating was completely dry. After that, the slab was put into the degradation reaction chamber. The exhaust gas analyzer was turned on and a certain concentration of exhaust gas was injected into the degradation reaction chamber.
- The UV lamps were turned on, along with a small fan, and the voltage of the UV lamps was adjusted such that the UV irradiance could reach the average outdoor UV irradiance of 26.7 W/m^2.
- The gas concentration in the degradation reaction chamber was recorded every 10 min. The test time was set to 90 min for every specimen. At least three specimens were prepared for each nano-TiO_2 content or spraying amount of photocatalytic coating.

Figure 3. Painting the emulsified asphalt coating on the slab sample.

2.4.2. Evaluation Indexes

1. Cumulative degradation rate

Under a certain initial concentration of the exhaust gas and light intensity, the cumulative degradation rate is defined as a ratio of the decreasing value of the exhaust gas concentration at the time *t* caused by the nano-TiO_2 photocatalytic coating to the initial concentration of the exhaust gas:

$$e = \frac{C_0 - C_t}{C_0} \times 100\%, \tag{1}$$

where e is the cumulative degradation rate, %; C_0 is the initial concentration of exhaust gas, ppm; and C_t is the exhaust gas concentration at the time t, ppm.

2. Degradation efficiency

Degradation efficiency is defined as a ratio of the photocatalytic degradation mass of the exhaust gas caused by the photocatalytic coating with a certain nano-TiO_2 content in the test sample to the maximum photocatalytic degradation mass of the exhaust gas caused by the same mass of no carrier nano-TiO_2 powder that was evenly distributed on the slab within time 0–t:

$$r = \frac{m_t}{m_{\max}} \times 100\%, \tag{2}$$

where r is the degradation efficiency, %; m_t is the degraded mass of exhaust gas under nano-TiO_2 with emulsified asphalt as the carrier during the time t, mg; and m_{max} is the maximum photocatalytic degradation of the exhaust gases under nano-TiO_2 without the carrier during the time t, mg.

3. Preparation of the Nano-TiO_2 Photocatalytic Coating

3.1. Materials Selection

3.1.1. Dispersant

Two dispersants were mixed with nano-TiO_2 in the ratios (dispersant versus nano-TiO_2) of 0, 1:5, 1:10, 1:15, and 1:20. Then, the high purity water was added into the mixture to ensure that the content of nano-TiO_2 in the slurry was 20%. Taking the preparation of the 300 g slurry as an example, the amount of each material in the slurry is shown in Table 9. After that, the conventional mechanical stirring device of DF-101 was used to stir the slurry for 10 min. Then, 50 mL of slurry was poured into the cylinder immediately to observe the stratification states of the slurry at different times. The stratification states of nano-TiO_2 after 72 h are shown in Figure 4.

Table 9. The amount of each material in 300 g slurry.

Ratios	Nano-TiO_2 (g)	Dispersant (g)	High Purity Water (g)
0	60	0	240
1:5	60	12	228
1:10	60	6	234
1:15	60	4	236
1:20	60	3	237

(The ratios from left to right in the figures are 0, 1:5, 1:10, 1:15, and 1:20)

(**a**) (**b**)

Figure 4. The stratification states of nano-TiO_2 after 72 h with (**a**) S-5040, and (**b**) SHP.

As shown in Figure 4, the dispersion effect of S-5040 to nano-TiO_2 is better than that of SHP. When the proportion of S-5040 to nano-TiO_2 was 1:5, the mixed slurry had no obvious stratification and kept better dispersibility and stability after 72 h. All mixtures of SHP and nano-TiO_2 were stratified and separated after 72 h. As a result, S-5040 was chosen to disperse nano-TiO_2, and the ratio was chosen to be 1:5, that is, the amount of dispersant was 20% of the amount of nano-TiO_2.

3.1.2. Emulsifier

Nano-TiO_2 photocatalytic coatings were prepared with three types of emulsifiers for performance comparison. Test conditions: the content of nano-TiO_2 was 8%; the content of dispersant S-5040 was 20% of that of nano-TiO_2; the content of 70# penetration grade asphalt was 50%; the contents of three kinds of emulsifiers (SY-QCE, KZW-802, SY-CME) were 0.5%, 0.8%, and 2%; the temperature of soap solution was 70 °C; the temperature of hot asphalt was 140 °C; the content of the stabilizer ($CaCl_2$) was 0.2%; and a colloid mill (Denimo TECH A/S, Aarslev, Denmark) was adopted as an emulsifying device. The pH value of the SY-QCE solution was adjusted to a range of 3–4 using hydrochloric acid, and the others did not require acid value adjustment. The basic performances are shown in Table 10.

Table 10. Basic performances of nano-TiO_2 photocatalytic emulsion coatings.

Emulsifiers	SY-QCE	KZW-802	SY-CME	Requirements [25]	Methods [24]
Color of emulsion	Brown	Brown	Brown	—	—
Standard viscosity C25,3 (s)	8.32	15.55	15.98	8–20 for SY-QCE and KZW-80210–25 for SY-CME	T0621
1-day storage stability	0.4	1.8	0.5	≤1	T0655

The color of emulsified asphalt was brown, which indicated that asphalt emulsification was in good condition. However, the standard viscosity of SY-QCE emulsified asphalt was only 8 s, approaching the lower limit of the technical requirement of PC-1 (sprinkling cationic rapid-setting emulsified asphalt) in the Chinese Technical Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25]. Therefore, it is improper to spray SY-QCE emulsified asphalt in a practical project.

The standard viscosities of KZW-802 and SY-CME emulsified asphalt met the technical requirements, but the storage stability of KZW-802 was poor. As a result, SY-CME was selected as the carrier of the nano-TiO_2 photocatalytic coating.

3.2. Preparation Process

Taking 1 kg of photocatalytic coating with 8% nano-TiO_2 as an example, the preparation process is given below with the content of each material (by weight) in the coating shown in Table 11. The temperature of the soap solution was 70 °C, the temperature of the hot asphalt was 140 °C, and the colloid mill was adopted as an emulsifying device.

Table 11. The content of each material (by weight) in the photocatalytic coating.

Asphalt	Soap Solution				
	Nano-TiO_2	S-5040	SY-CME	$CaCl_2$	High Purity Water
50%	8%	1.6%	2%	0.2%	38.2%

1. Soap solution

- A total of 2 g $CaCl_2$ was added into 382 g of high purity water. Then, the water was heated and stirred to fully dissolve the $CaCl_2$.
- A total of 20 g of SY-CME was added into the solution and dissolved thoroughly.
- A total of 16 g of dispersant S-5040 was added into the solution and stirred thoroughly, then 80 g of nano-TiO_2 was added and stirred for 15 min. After that, the soap solution was kept at a temperature of 70 °C for later use.

2. Asphalt

The asphalt was heated to the flowing state. Then, 500 g of heated asphalt was weighed and the temperature of the asphalt was kept on standby at 140 °C.

3. Emulsification

The prepared soap solution and heated asphalt were added into the colloid mill successively. After 3 min of emulsification, the emulsified asphalt was cooled. Finally, the emulsified asphalt was placed in a plastic bucket as a reserve.

For the preparation of photocatalytic coatings with different nano-TiO_2 contents, only the amounts of nano-TiO_2 and dispersant needed to be adjusted.

3.3. Performance of the Nano-TiO_2 Photocatalytic Coating

The photocatalytic coatings with different nano-TiO_2 contents were prepared and their basic properties met the Chinese Technical Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25], as shown in Table 12.

1. The color of the photocatalytic coating emulsion with different nano-TiO_2 contents was brown, which indicated that the emulsification effect was better.
2. With the increase of the amount of nano-TiO_2, the standard viscosity of photocatalytic coatings decreased, indicating that the photocatalytic coatings gradually became viscous. The main reason was that nano-TiO_2 had a good adsorption capacity to asphalt because of its small particle size and large specific surface area. Although the coatings became viscous with increasing nano-TiO_2 content, all of the photocatalytic coatings met the technical requirements of the standard viscosity of PC-2 (sprinkling cationic slow-setting emulsified asphalt) in the Chinese Technical Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25].
3. With the increase of the nano-TiO_2 content, the storage stability of the photocatalytic coating became worse. This is mainly due to the increase of the content of nano-TiO_2, which made the nano-TiO_2 particles prone to agglomerate, finally resulting in the reduction of storage stability of the photocatalytic coatings.
4. The abrasion resistance of nano-TiO_2 photocatalytic coating was evaluated using the wet track abrasion loss test. The test results showed that the wet track abrasion loss value of all the asphalt mixture with nano-TiO_2 photocatalytic coating after the specimen being immersed into water for 1 h met the technical requirements of the Chinese Technical Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25] (no more than 540 g/m^2). It showed that the nano-TiO_2 photocatalytic coating had good abrasion resistance.

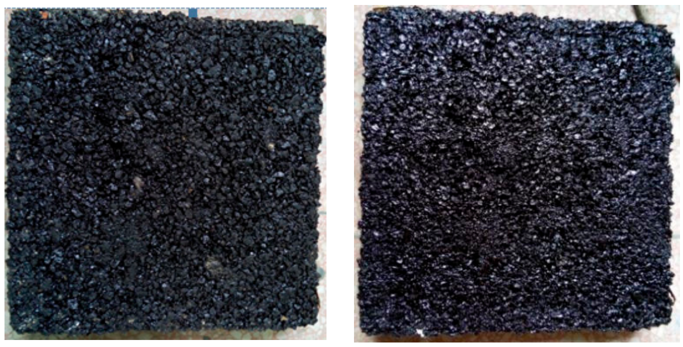
Table 12. Basic properties of photocatalytic coatings with different nano-TiO_2 content.

Nano-TiO_2 Content	3%	5%	8%	10%	15%	Requirements [25]	Methods [24]
Color of emulsion	Brown	Brown	Brown	Brown	Brown	—	—
Standard viscosity C25,3 (s)	16.56	16.12	15.98	15.54	14.65	12–60	T0621
5-day storage stability (%)	3.45	3.76	3.63	3.88	4.13	≤5	T0655
Adhesion, covering area	>2/3	>2/3	>2/3	>2/3	>2/3	>2/3	T0654
1 h wet track abrasion loss (g/m2)	321	356	380	423	463	<540	T0752

4. Evaluation of Exhaust Gas Degradation Effect

4.1. Effects of the Nano-TiO_2 Content on Exhaust Gas Degradation

A total of 30 g of photocatalytic coatings with nano-TiO_2 content of 3%, 5%, 8%, 10%, and 15% were uniformly applied to the surface of the 300 × 300 mm OGFC-10 slab samples to perform photocatalytic degradation of the exhaust gas test. The test specimens are shown in Figure 5. The effect of degradation of exhaust gas by photocatalytic coating with different nano-TiO_2 contents was studied. The test results are shown in Figures 6 and 7.



(**a**) (**b**)

Figure 5. Test specimens: (**a**) without photocatalytic coating, and (**b**) with sprayed photocatalytic coating.

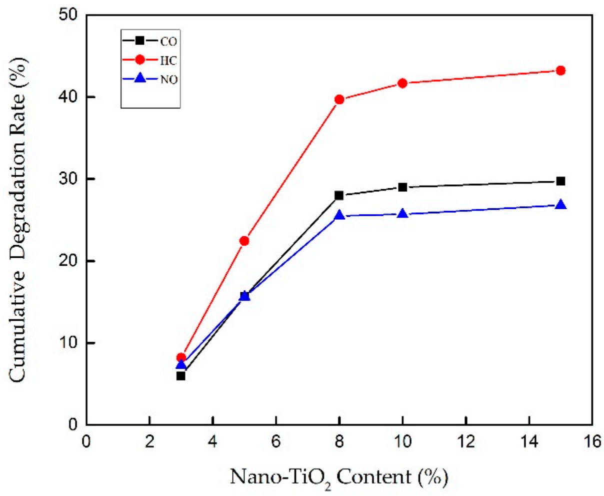


Figure 6. Changes of the cumulative degradation rate of the exhaust gas at different nano-TiO_2 contents.

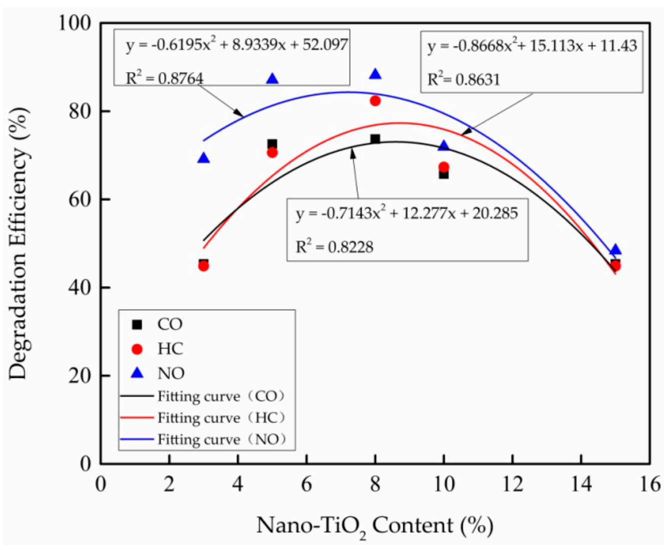


Figure 7. Changes of the degradation efficiency of the exhaust gas at different nano-TiO_2 contents.

As can be seen from Figure 6, with the increase of nano-TiO_2 content, the performance of photocatalytic coatings for degradation of exhaust gas was better. When the content of nano-TiO_2 increased from 0 to 8%, the cumulative degradation rate of CO, HC, and NO increased rapidly. However, the cumulative degradation rate of the CO, HC, and NO grew slowly when the content of nano-TiO_2 was above 8%. Figure 7 illustrates that the nano-TiO_2 content had a good quadratic nonlinear correlation with the degradation efficiency of CO, HC, and NO. With the increase of nano-TiO_2 content, the degradation efficiency of three kinds of exhaust gas increased gradually. However, the degradation efficiency of nano-TiO_2 to three kinds of exhaust gas tended to decrease when the content of nano-TiO_2 was above 8%.

The exhaust gas degradation performance of the coating was related to the size of the effective contact area between the nano-TiO_2 and exhaust gas, and ultraviolet intensity. When the nano-TiO_2 content exceeded 8%, the entire surface of the slab sample was covered by a saturated nano-TiO_2 thin layer. Therefore, there was no substantial increase in the effective number of nano-TiO_2 particles touching with the exhaust gas per unit area with the continuous increase of the content of nano-TiO_2. The degradation performance of the photocatalytic coating was not significantly improved. Furthermore, the degradation efficiency of nano-TiO_2 gradually decreased.

4.2. Effects of the Spraying Amount on Exhaust Gas Degradation

Separately, 10 g, 20 g, 30 g, 40 g, and 55 g of photocatalytic coatings with 8% nano-TiO_2 were uniformly sprayed on the slab samples of OGFC-10 to perform the photocatalytic degradation of exhaust gas test. The performances of nano-TiO_2 photocatalytic coatings with different spraying amounts on the degradation of exhaust gas were studied. The test results are shown at Figures 8 and 9.

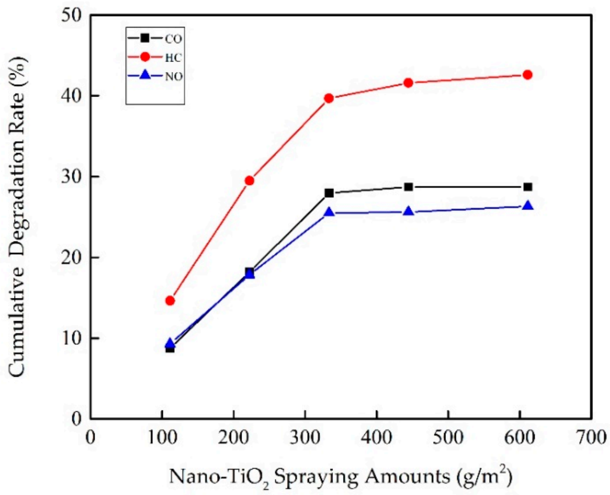


Figure 8. Changes of the cumulative degradation rate of the exhaust gas at different nano-TiO_2 spraying amounts.

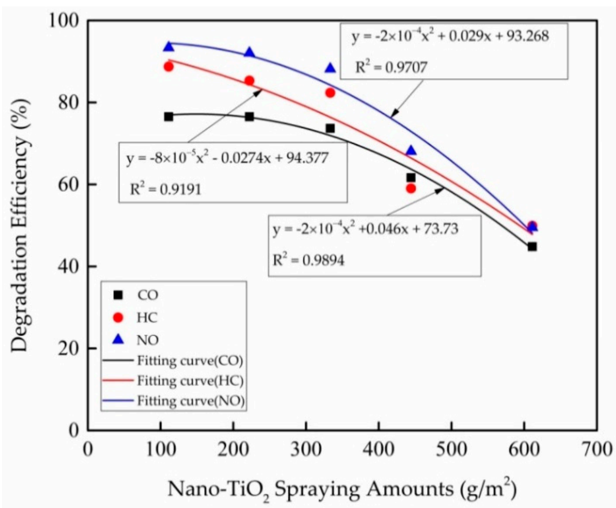


Figure 9. Changes of the degradation efficiency of the exhaust gas at different nano-TiO_2 spraying amounts.

As can be seen from Figure 8. The cumulative degradation rate of CO, HC, and NO increased gradually with the increase of the amount of photocatalytic coating. However, when the spraying amount was over 333.3 g/m^2, the cumulative degradation rate of CO, HC, and NO gas remained unchanged with the continuous increasing of spraying amount. When the spraying amount of nano-TiO_2 photocatalytic coating was less than 333.3 g/m^2, with the increase of spraying amount, the number of nano-TiO_2 particles on the surface of the slab sample and the effective contact area with the exhaust gas and the ultraviolet light gradually increased and the effect of degradation improved. When the nano-TiO_2 photocatalytic coating spraying amount reached 333.3 g/m^2, the effective contact area and quantities of nano-TiO_2 with the car exhaust and ultraviolet also achieved a peak value. After that, the increase of the spray volume only resulted in an even thicker coating that had little effect on improving the effect of degradation on vehicle exhaust gas.

As can be seen from Figure 9, with the continuous increase in the spraying amount of photocatalytic nano-TiO_2, the degradation efficiency of CO, HC, and NO decreased gradually. This was mainly because a small amount of coating being sprayed on the surface of the slab samples can form a very thin film layer. At this time, most of the nano-TiO_2 could act in its photocatalytic role. However, with the increase of the spraying amount, the thickness of the coating film also increased. Those nano-TiO_2 particles at the bottom of film could not effectively contribute to photocatalytic reactions, resulting in the decrease of degradation efficiency.

After comprehensive consideration, when the added content of nano-TiO_2 in the coating reached 8%, the photocatalytic coating had the best performance of degradation of the automobile exhaust gas. When the dosage of nano-TiO_2 increased to more than 8%, the ability of photocatalytic degradation exhaust was no longer a definite improvement with the increase of nano-TiO_2. In addition, the photocatalytic coating containing 8% of nano-TiO_2 was evenly sprayed on the slabs for the photocatalytic degradation of the exhaust gas test. It indicated that with the continuous increase of the spraying amount of coating, the photocatalytic degradation property of exhaust gas was gradually improved. However, the performance of the photocatalytic degradation property of exhaust gas basically kept at the same level after the spraying amount was over 333.3 g/m^2.

5. Pavement Performance Evaluation

5.1. Skid Resistance

The friction coefficient and texture depth were used to evaluate the skid resistance of asphalt pavement at the different spraying amounts of nano-TiO_2 photocatalytic coatings. The friction coefficient of the sprayed nano-TiO_2 asphalt mixture was measured using the pendulum friction meter (Shuyang highway equipment plant, Suqian, China) according to the test method of T0964 in the Chinese Field Test Methods of Subgrade and Pavement for Highway Engineering (JTG E60-2008) [27] and the surface texture depth was determined using the test method of T0731 in the Chinese Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTG E20-2011) [24]. The test results are shown in Figure 10.

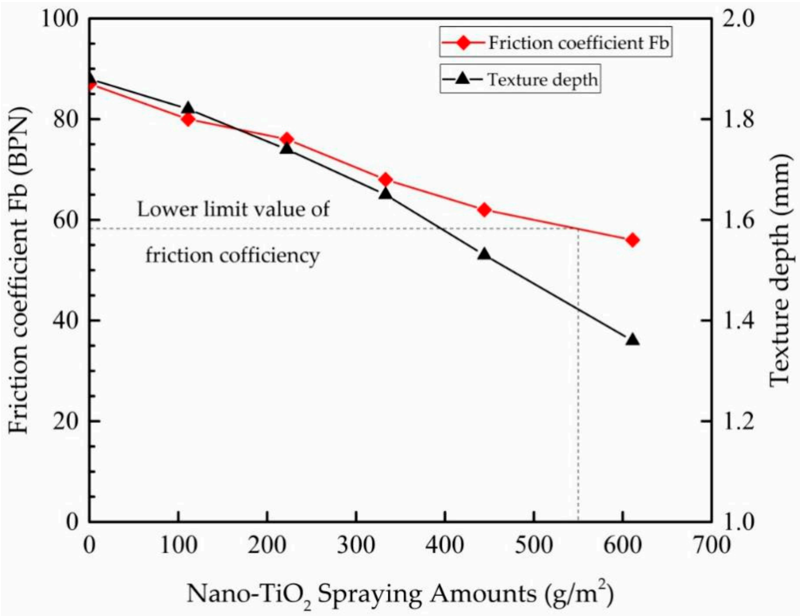


Figure 10. Effect of spraying amount on the skid resistance of asphalt pavement.

It can be seen from Figure 10, both the friction coefficient and the texture depth of the asphalt mixture were reduced with the increase of the spraying amount of photocatalytic coating. It indicated that the skid resistance of the asphalt mixture was decreased due to spraying the nano-TiO_2 photocatalytic coating on the sample surface. When the nano-TiO_2 photocatalytic coating spraying amount was greater than 550 g/m^2, the friction coefficient was close to the critical lower limit value (58BPN) of the technical requirement in the Chinese Specifications for Design of Highway Asphalt Pavement (JTG D50-2006) [28]. Therefore, it is recommended that the spraying amount of nano-TiO_2 photocatalytic coating should not exceed 550 g/m^2 in practical projects.

5.2. Water Permeability

The water permeability of asphalt pavement with different nano-TiO_2 photocatalytic coatings was investigated. The corresponding technical indicator met the requirements of Chinese Technical Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) [25]. The test results are summarized in Table 13.

Table 13. Effect of spraying amount on permeability of asphalt mixture.

Spraying Amount (g/m^2)	0	111.1	222.2	333.3	444.4	611.1	Method [24]
Permeability coefficient C_w (mL/15 s)	>400	>400	>400	>400	>400	>400	T0730

It can be seen from the Table 13 that the water permeability performance of the asphalt mixture was basically not affected by the spraying amount of nano-TiO_2 photocatalytic coating. This was because the amount of photocatalytic coating that was sprayed was so little that it cannot effectively fill the void in the surface of the asphalt mixture. Therefore, the influence of the spraying amount of nano-TiO_2 photocatalytic coating on the water permeability performance of the asphalt pavement can be ignored in practical projects.

6. Conclusions

According to the application characteristics of the spraying method, the emulsified asphalt was selected to act as the carrier, and the materials for preparing nano-TiO_2 photocatalytic coating were determined by comprehensive comparison and selection. The test results indicated that the properties of prepared nano-TiO_2 photocatalytic coating met the Chinese specifications technical requirements. Meanwhile, the color of the coating (seen in Figure 5) was the same as that of the asphalt after setting, having offset the deficiency of different colors between traditional photocatalytic coating and the pavement. Therefore, the coating could be applied directly onto the surface of the pavement using an asphalt distributor, just like fog seal, to play a better role in the degradation of exhaust gas. The coating could be applied to pavement surfaces that are located in densely-populated areas, environmentally-sensitive areas, service areas and parking lots, and so on.

An exhaust gas degradation test device was developed, and its test steps were described in detail. The evaluation indexes, cumulative degradation rate, and degradation efficiency were put forward.

The test results of the performance of exhaust gas degradation of nano-TiO_2 photocatalytic coating showed that, when nano-TiO_2 content was changed in the range from 0–8% and the spraying amount was changed in range from 0–333.3 g/m^2, the performance of the photocatalytic coating on the degrading exhaust gas was significantly improved with the increase of nano-TiO_2 content and photocatalytic coating spraying amount. When over those dosages, the efficacy of photocatalytic coating was not significantly improved regarding exhaust gas degradation.

In practical projects, the amount of spraying should be controlled strictly because the nano-TiO_2 photocatalytic coating can influence the skid resistance of the asphalt pavement to a certain extent. It is recommended that the spraying amount of nano-TiO_2 photocatalytic coating should not exceed 550 g/m^2. The nano-TiO_2 photocatalytic coating had little effect on the water permeability performance of asphalt pavement. As such, excessive dosage cannot effectively degrade exhaust gas but thickens the oil membrane, which leads to an inadequate skid resistance of the pavement, which is unsafe and uneconomical. Therefore, 8% nano-TiO_2 in coating and a 400 g/m^2 spraying amount (considering the loss of construction, etc.) were finally chosen to be the optimum parameters based on the photocatalytic properties as well as economic reasons.

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