Research of new Preventive maintenance materials based on automobile exhaust gas purification and PM2.5 absorption

Zhenxia Li1,2,3, Tengteng Guo1,2,3, Yuanzhao Chen1,2,3,*, Kun Yang1, Xinyu Dong1, Decai Wang1, Jing Wang1 and Lihui Jin1

1 School of Civil Engineering and Communication, North China University of Water Resources and Electric Power, Zhengzhou 450045, Henan, People’s Republic of China
2 Henan Province Engineering Technology Research Center of Environment Friendly and High-performance Pavement Materials, Zhengzhou 450045, Henan, People’s Republic of China
3 Zhengzhou City Key Laboratory of Environmentally Friendly High Performance Road and Bridge Materials, Zhengzhou 450045, Henan, People’s Republic of China
* Authors to whom any correspondence should be addressed.
E-mail: cyz740513@ncwu.edu.cn

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Abstract
In order to reduce the harmful gases and particulate matter in the atmospheric environment, alleviate the pollution of automobile exhaust, this paper studies the preventive maintenance seal based on exhaust gas purification and PM2.5 adsorption. The optimal preparation process at the micrometer is determined by the ratio design at the micro-surfacing. Based on wet wheel wear test and rutting deformation test, the influence of environmental protection material content on wear resistance and high temperature stability of micro-surfacing was studied. A set of automobile exhaust pollutant purification test equipment was developed, and the test method was determined. The exhaust purification performance of environmental protection micro-surfacing and the adsorption effect of PM2.5 and 10 particles was studied. The microstructure of environmental protection materials was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the mechanism of tail gas purification and PM2.5 particle adsorption was revealed. The results show that with the increase of nano TiO2/tourmaline composite content, the viscosity and high temperature stability of SBR modified emulsified asphalt evaporation residue are improved, but the ability to resist deformation at low temperature is slightly reduced. When the content of nano-TiO2/tourmaline is 7%, the wear resistance at the micro-surfacing increases by 4%, and the high temperature stability increases by 14.6%. The purification efficiency of various gas components in automobile exhaust by adding nano-TiO2/tourmaline composite micrometer reached 33.3% of hydrocarbons, 46% of carbon monoxide and 92.8% of nitrogen oxides, respectively. The adsorption effect of particulate component PM2.5 and 10 in automobile exhaust reached 29.9% and 25.2%, respectively. The nano-TiO2 aggregates loaded on the surface of tourmaline particles are uniformly dispersed, and the crystal forms are anatase and rutile. The permanent electric field generated by spontaneous permanent polarization of tourmaline can accelerate the separation of electron-hole pairs and improve the redox ability of nano-TiO2. The permanent electric field of tourmaline and the permanent release of air negative ions can absorb and neutralize the charged suspended particles in the air, so as to achieve the purpose of settlement.

1. Introduction
Automobile exhaust pollution is an important reason for environmental air pollution problems such as photochemical smog and haze. Automobile exhaust pollutants include nitrogen oxides (NOx), carbon monoxide (CO), hydrocarbons (HC) and inhalable particulate matter (PM) [1]. Therefore, it is necessary to
study automobile exhaust purification and PM2.5 adsorption pavement materials to reduce the content of harmful gases and particulate matter in the atmospheric environment, and alleviate photochemical smog, acid rain, haze and urban heat island effect.

By analyzing the exhaust gas purification effect of nano Fe₂O₃ and nano TiO₂ and their influence on asphalt properties, nano TiO₂ is determined as the best catalytic material [2]. Two different ways of adding asphalt concrete have little effect on the photocatalytic performance of TiO₂, and both of them can achieve better degradation effect [3]. When the particle size of TiO₂ powder is 25 nm and the content of TiO₂ is about 10%, the cumulative degradation rate and catalytic efficiency reach the maximum [4]. Moreover, the degradation rate of CO, NOₓ and SO₂ in the environmental cooling micro-surfacing can reach 43%, and the purification effect of PM2.5 and PM10 particulate pollutants can reach 59% [5]. TiO₂ is an excellent photocatalytic material [6]. However, the defects of the material itself limit its photocatalytic activity. The electron-hole pairs are easy to compound, the spectral response range is narrow, and the utilization rate of sunlight is low [7]. According to the characteristics of organic-inorganic materials and metal-nonmetallic materials, scholars in China and abroad have carried out a variety of doping modification of nano-TiO₂. The metal has good conductivity, which can accelerate the transfer of electrons from the material to the surface of the material and promote the separation of electrons and holes. Therefore, metal ions are first used in the study of TiO₂ doping modification [8]. A certain amount of transition metal ions doping can introduce lattice defects in semiconductor crystals to form more photocatalytic activity sites [9]. The doping of metal ions changes the band gap of TiO₂ and affects the photocatalytic performance of TiO₂. The photocatalytic effect is the best when Ag + the band gap is 1.09 eV [10]. The charge transfer between iron ions and TiO₂ enhanced the photocatalytic activity of TiO₂ [11], and the corresponding range of light doped with copper ions TiO₂ extended to visible light. Moreover, the degradation rate of methyl orange is very good, indicating that the doping of copper ions can improve the sensitivity of TiO₂ photocatalytic performance. The photocatalytic effect is the best when Ag + TiO₂. TiO₂ has good conductivity, which can accelerate the transfer of electrons from the surface of TiO₂ to sunlight [12]. The absorption wavelength range of cuprous oxide/titanium dioxide composite is doubled compared with that of pure titanium dioxide [13]. When precious gold precipitates are distributed on semiconductor materials, the photogenerated electron-hole pairs will be redistributed. Electrons are absorbed by the metal from the surface of TiO₂, which promotes a large number of electrons to accumulate on the metal, thus reducing the number of electrons on the surface of TiO₂ [14]. Platinum-doped TiO₂/PEI/RGO composite has significantly improved the activity of the doped materials, and the degradation rate of methylene blue is almost complete [15]. The decomposition rate of formaldehyde in nano-TiO₂/tourmaline composite is close to 90% [16]. Tourmaline has permanent spontaneous electrode properties, surrounded by an electrostatic field. It can not only accelerate the separation of photogenerated electron-hole pairs of nano-TiO₂ to promote photocatalysis [17, 18], but also adsorb charged air molecules and charged particles in the air. The piezoelectric and thermolectric properties of tourmaline release negative ions permanently and neutralize positively charged particles in the nearby environment [19], which can also achieve the purpose of dust removal and PM2.5 [20]. Compared with diatomite, activated carbon, zeolite, montmorillonite and other porous materials for gas and particulate matter absorption efficiency and saturation [21], tourmaline relies on the ability of permanent electric field adsorption and permanent release of electrons has no upper limit on the number of particles settlement absorption, sustainable play effect, so it has good durability.

In summary, nano-TiO₂ is the best catalytic material, but the electron-hole pairs of TiO₂ is easy to compound, and the utilization rate of sunlight is low, which limits its photocatalytic activity. The catalytic activity of TiO₂ can be improved to a certain extent by various doping modification of nano-TiO₂ with organic-inorganic materials and metal-nonmetallic materials.

However the environmental protection function of these modified materials is too single, which can only purify the gas pollutants in the air, but cannot purify a large number of particulate pollutants in the atmosphere, tourmaline can not only promote photocatalysis, adsorb charged air molecules and charged particles in the air, but also achieve the purpose of dust removal and PM2.5. Therefore, nano-TiO₂/tourmaline composite was selected as the research object in this paper. The preparation of environmental protection materials, the purification of automobile exhaust at micrometer and the adsorption of PM2.5, X-ray diffraction test and scanning electron microscopy test were carried out. The influence of the content of environmental protection materials on the road performance of micro-surfacing, the exhaust purification performance of environmental protection micro-surfacing, the adsorption effect of PM2.5 and 10 particles and the microstructure characterization of environmental protection materials were analyzed. The exhaust purification mechanism and the adsorption mechanism of PM2.5 particles were explored to realize the application of functional materials for purifying automobile exhaust and adsorbing PM2.5 in preventive maintenance seals, reduce the content of harmful gases and particles in the atmospheric environment, and alleviate the harm of automobile exhaust pollution.
2. Raw material

2.1. Modified emulsified asphalt
The SBR modified emulsified asphalt provided by Qilu Branch of Sinopec was used in this experiment, and its performance was tested according to the specification requirements [22]. The main technical indexes are shown in table 1.

2.2. Aggregate
2.2.1. Coarse aggregate
The coarse aggregate used in the test was the gravel produced in Xinxiang City, Henan Province, and its performance was tested according to the requirements of the regulations [23]. The performance indexes of each particle size group are shown in table 2.

2.2.2. Fine aggregate
The fine aggregate used in the test was stone chips produced in Xinxiang City, Henan Province, and its performance was tested according to the specification requirements [23]. The performance indexes of each particle size group are shown in table 3.

2.2.3. Mineral powder
The ore powder used in the test was ground limestone powder, and its performance was tested according to the requirements of the regulations [24]. The performance is shown in table 4.

3. Experimental

3.1. Raw materials
3.1.1. Preparation of nano TiO2/tourmaline composite
Experimental materials: tourmaline powder (particle size 1250 mesh, Hebei Shijiazhuang Xuhang Mineral Co., Ltd), the reagents were ammonia solution with analytical purity, TiCl4 solution, hydrochloric acid solution with 36% ~ 38% purity, ammonium sulfate and silver nitrate solid.

(1) In three beakers with 500 ml capacity, 300 ml distilled water and 10 g tourmaline powder were added and stirred in cold water bath (0 °C) for 5 min. In the condition of good ventilation, 0.5 ml TiCl4 reserve solution was absorbed by colloidal dropper, and then slowly dropped into the mixture by scale dropper.

(2) 5 ml of (NH4)2SO4 solution (1.5 mol l⁻¹) and 3 ml of HCl (36% ~ 38% purity) were mixed, and the mixture was slowly dropped into the above reaction system. After full stirring for 15 min, the mixture was heated to 70 °C (magnetic stirrer) for 1 h.

(3) Using a certain volume ratio of dilute ammonia, the PH value of the mixture was adjusted to about 4.4, and the reaction was held for 2 h. The test process was shown in figure 1. The reaction solution was filtered by quantitative filter paper, and the precipitation on the filter paper was repeatedly cleaned by distilled water. When no white precipitate was detected by AgNO3 solution (0.2 mol l⁻¹) in the washing solution, that is, there was no Cl⁻ in the washing solution, anhydrous ethanol was used to clean the precipitate on the filter paper once.

(4) The filter paper, together with the filtered precipitation, was put into the vacuum drying box (D2F-6050 drying box) for 1 h. When the sample was completely evaporated into powder by ethanol, the sample was put into the crucible together with the filter paper and placed in the high temperature resistance furnace.

### Table 1. Main technical indexes of SBR modified emulsified asphalt.

| Test items                                | Unit | Test results | Standard          |
|-------------------------------------------|------|--------------|-------------------|
| Residual amount on screen (1.18 mm screen)| %    | 0.05         | ≤0.1              |
| Standard Viscosity of Asphalt C25,3 S     | S    | 13.6         | 12 ~ 60           |
| Evaporation residue content               | %    | 61.7         | ≥60               |
| Penetration degree (100 g, 25 °C, 5 s)    | 0.1 mm | 59          | 40 ~ 100          |
| Properties of evaporation residue         | °C   | 54.0         | ≥53               |
| Softening point Ductility (5 °C)          | Cm   | 37.4         | ≥20               |
| Solubility (trichloroethylene)            | %    | 99.6         | ≥97.5             |
Table 2. Main technical indexes of 4.75 mm ~ 9.5 mm and 2.36 mm ~ 4.75 mm aggregate.

| Specs       | Crushing value of stone (%) | Losangeles weared value ≤ (%) | Polished drum coating stone value ≥ (BPN) | Ruggedness ≤ (%) | Needle-like content ≤ (%) |
|-------------|-----------------------------|-------------------------------|----------------------------------------|------------------|--------------------------|
| Test results|                             |                               |                                        |                  |                          |
| 4.75 mm ~ 9.5 mm | 22.3                       | 20.9                          | 51                                     | 9.7              | 11.6                     |
| 2.36 mm ~ 4.75 mm | 20.7                       | 18.6                          | 56                                     | 9.2              | 10.8                     |
| Standard    |                             |                               |                                        |                  |                          |
| 4.75 mm ~ 9.5 mm | 26                         | 28                            | 42                                     | 12               | 15                       |
| 2.36 mm ~ 4.75 mm | 26                         | 28                            | 42                                     | 12               | 15                       |
Table 3. Main technical indexes of 1.18 mm ∼ 2.36 mm and 0.6 mm ~ 1.18 mm aggregate.

| Items               | Specs            | Test results | Standard |
|---------------------|------------------|--------------|----------|
| Ruggedness ≤ (%)    | 1.18 mm ∼ 2.36 mm| 8.8          | 12       |
|                     | 0.6 mm ∼ 1.18 mm | 8.6          | 12       |
| Sand equivalent ≥ (%)| 1.18 mm ∼ 2.36 mm| 74           | 65       |
|                     | 0.6 mm ∼ 1.18 mm | 71           | 65       |

Table 4. Main technical indexes of mineral powder.

| Fraction of partial size | Apparent density(t m⁻³) | Moisture content(%) | Facade | Hydrophilic coefficient | Plasticity index(%) |
|--------------------------|-------------------------|---------------------|--------|-------------------------|--------------------|
| Test results             |                         |                     |        |                         |                    |
| 0.3 mm ∼ 0.6 mm          | 2.742                   | 0.2                 | /      | 0.53                    | 2.4                |
| 0.15 mm ∼ 0.3 mm         | 2.765                   | 0.1                 | /      | 0.49                    | 1.8                |
| 0.075 mm ∼ 0.15 mm       | 2.793                   | 0.2                 | /      | 0.71                    | 2.6                |
| <0.075 mm                | 2.722                   | 0.3                 | /      | 0.36                    | 2.2                |
| Technology indexes       |                         |                     |        |                         |                    |
| 0.3 mm ∼ 0.6 mm          | ≥2.50                   | ≤1                  | No agglomerates | <1 | <4 |
(XRIX-4-73 box resistance furnace) to slowly rise to 550 °C. At 550 °C ± 20 °C for 3 h, nano-TiO$_2$/tourmaline composites were obtained by natural cooling, as shown in Figure 2.

3.1.2. Preparation of emulsified asphalt evaporation residues modified by nano TiO$_2$/tourmaline composites

Nano-TiO$_2$/tourmaline composite modified emulsified asphalt is prepared by mechanical method. The specific preparation process is as follows: SBR modified emulsified asphalt with a certain mass is taken in the steel basin, and the steel basin is heated slowly on the electric furnace. The heating setting temperature can be slightly higher than 100 °C but should not cause emulsion spill. During the heating process, the glass rod is used to stir uniformly. SBR modified emulsified asphalt first rises and maintains in boiling state at 100 °C. There are many bubbles on the surface, which generate, swell and break. When the bubble aggregation is to overflow, accelerated stirring or cooling the steel basin can alleviate bubble aggregation. When the surface of modified emulsified asphalt is no longer bubble aggregation, showing a paste, the moisture in the sample has been little but not evaporated, the temperature of the sample began to rise rapidly. When the temperature of the sample exceeds 105 °C, the heating rate of the furnace is adjusted, and the temperature is kept below 140 °C. Continue stirring until the surface of the sample is no longer bubble, and then the temperature rises to 163 °C and stop heating, that is, the evaporation residue of SBR modified emulsified asphalt is obtained. Keeping the temperature unchanged at 163 °C, the high-speed shear head is put into the evaporation residue, and the asphalt is stirred at 2500 r min$^{-1}$. The bottom of the head is about 1 ~ 2 cm from the bottom of the basin, so as to avoid premature aging of asphalt caused by local overheating during heating. After stirring for about 5 min, the nano-TiO$_2$/tourmaline composite with a certain proportion of the evaporation residue of SBR modified emulsified asphalt was slowly added to the asphalt, and the shear speed was increased to 6500 r min$^{-1}$, and the continuous modification was about 30 ~ 50 min. In the process of modification, because the rotor speed inside the rotor head is great, the vacuum area will be formed below the rotor head. The rotor head will absorb the surrounding asphalt and composite materials, and shear modification is carried out by using the relative speed of the rotor and the stator. The nano-TiO$_2$/tourmaline composite can be effectively dispersed in the evaporation residue modified by high-speed shearing, and the expected evaporation residue of emulsified asphalt modified by nano-TiO$_2$/tourmaline composite is obtained.
3.2. Mix proportion design of micro-surfacing

3.2.1. Determination of mineral grading in MS-3 micro-surfacing
In this paper, the intermediate value of each mineral aggregate gradation range of MS-3 specified in the specification is used as the proportion of this gradation range, so as to design the mixture ratio. The upper and lower limits of mineral grading and synthetic grading curve are shown in figure 3.

3.2.2. Mix proportion design of MS-3 micro-surfacing
The dosage of modified emulsified asphalt, water and additive cement was preliminarily selected according to the existing mix design experience, and the range of asphalt-aggregate ratio was preliminarily selected through

| Mineral material/g | Water/g | Cement/g | Amount of modified emulsified asphalt/g | Mix time s⁻¹ | Slurry state | Apparent amount of asphalt |
|--------------------|---------|----------|----------------------------------------|---------------|-------------|---------------------------|
| 100                | 10      | 1.5      | 9.6                                    | 175           | rare         | small                     |
| 100                | 10      | 1.5      | 10.0                                   | 161           | good         | good                      |
| 100                | 10      | 1.5      | 10.5                                   | 150           | better       | good                      |
| 100                | 10      | 1.5      | 11.0                                   | 139           | better       | good                      |
| 100                | 10      | 1.5      | 11.5                                   | 132           | condensed    | big                       |

Figure 3. Mineral grade grading curve of MS-3 micrometer.

Table 5. Mixing test of different SBR modified emulsified asphalt.

Figure 4. Results of cohesion test.
the state of slurry mixture and the crack of specimen in the mixing test and cohesion test. Based on 100 g aggregate, select 5.9%, 6.2%, 6.5%, 6.8%, 7.1% five groups of oil-stone ratio, water use tap water, dosage 9%, cement 325 ordinary Portland cement, dosage 1.5%. The amount of modified emulsified asphalt can be determined by calculating the evaporation residue content of SBR modified emulsified asphalt. The mixing time was recorded in the mixing test, and the slurry state was observed. The test results are shown in table 5.

The mixing test results and phenomenon description show that among the five groups of mixtures with different oil-stone ratios selected in the test, the mixing time of the five groups of test samples meets the requirements of more than 120 s in the specification. However, by observing the slurry state, it is found that the apparent state of asphalt content with oil-stone ratios of 5.9% and 7.1% is not ideal. Five groups of cohesion test samples were prepared according to the five groups of mixture formulations with the oil-stone ratios of 5.9%, 6.2%, 6.5%, 6.8% and 7.1%, and the cohesion values were tested. The test results are shown in figure 4 and table 6.

The initial setting time and open traffic time at the micro-surfacing are related to the cohesion value. Moreover, the forming speed and early strength of the micro-surfacing are both reflected by the value of cohesion within the same time. Therefore, from the test results and phenomenon description of tables 3–4, it can be seen that the cohesion value of the specimen with 5.9% oil-stone ratio is small, which cannot meet the design requirements. The cohesion value of the specimen with the oil-stone ratio of 6.2% is close to the standard design index. The mixture with oil-stone ratio of 6.5% has good molding, and its cohesion value reaches the specification of China, and its test result is the best. The asphalt with the oil-stone ratio of 6.8% and 7.1% completely wrapped the mineral and had good cohesion value, which was primary molding.

3.2.3. Determination of optimum oil-stone ratio

In the design of micro-surfacing mixture ratio, the optimal range of oil-stone ratio is often determined by the wear value of 1 h wet wheel and the amount of adhered sand. The above mixtures with oil-stone ratios of 6.2%, 6.5% and 6.8% were subjected to 1 h wet wheel wear test and load wheel sand adhesion test, respectively. The curve of oil-stone ratio corresponding to 1 h wet wheel wear value and sand adhesion are shown in figure 5.

| Ratio of oil to stone/% | Cohesion value/N·m | 30 min | 60 min | Collapse state |
|------------------------|--------------------|--------|--------|---------------|
| 5.9                    | 0.9                | 1.4    | Unformed |
| 6.2                    | 1.0                | 1.8    | Unformed |
| 6.5                    | 1.4                | 2.4    | Moderate molding |
| 6.8                    | 1.2                | 2.1    | Primary molding |
| 7.1                    | 1.3                | 2.0    | Primary molding |

Figure 5. Determining the asphalt dosage curve at the micrometer.
The optional range of oil-stone ratio can be seen from figures 3–4 of the change curve of 1 h wet wheel wear value and sand adhesion amount. The oil-stone ratio corresponding to the 1 h wet wheel wear value of 540 g m$^{-2}$ is the minimum oil-stone ratio, and the oil-stone ratio corresponding to the sand adhesion amount of 450 g m$^{-2}$ is the maximum oil-stone ratio. The optional range of oil-stone ratio is between 6.4% and 6.7%. When the oil-stone ratio is 6.5%, the mixing time and cohesion value of the micro-surfacing mixture meet the requirements of the specification, and the molding effect of the specimen is the best. The 6 d wet wheel wear index of the mixture is tested with the selected 6.5% oil-stone ratio, and the results are less than 800 g m$^{-2}$, which meets the requirements of the specification. Therefore, the optimum oil-stone ratio is determined to be 6.5%.

### 3.3. Purification of automobile exhaust at micro-surfacing and adsorption of PM2.5

According to the basic concept of air purification test system, relevant instruments were selected, the necessary equipment was processed, and a set of air purification test equipment was produced. The test method of purifying automobile exhaust was determined, and the true use of roads was simulated. The test results of purifying automobile exhaust and adsorbing PM2.5 at the micro-surfacing of nano-TiO$_2$/tourmaline composite were tested.

This test self-made a tail gas purification and PM2.5 adsorption performance test device, schematic figure 6. The detection device includes: 1-reaction chamber, 2-bottom plate, 3-adsorption degradation material, 4-PM2.5 detector, 5-automobile exhaust detector, 6-radiator, 7-inlet, 8-outlet, 9-control valve, 10-guide pipe.

The test method of exhaust gas purification and PM2.5 adsorption test combined with the pavement materials studied in this paper is to connect the inlet and the exhaust port of the vehicle with the guide pipe, open the inlet control valve and the outlet control valve, and launch the vehicle idle running for 1–5 min. Close the inlet control valve and the outlet control valve, record the initial exhaust concentration and PM2.5 content in the reaction chamber. The detection device was placed under the Sunlight or turned on the ultraviolet lamp, and the fan was started. The exhaust gas concentration and PM2.5 content were recorded every half hour, and the final data were recorded after 4 h as the final exhaust gas concentration and PM2.5 content. The purification effect of environmental protection pavement materials is evaluated by the purification efficiency index. The purification efficiency is calculated according to the initial and final exhaust concentration or PM2.5 content. The calculation formula of purification efficiency is as follows:

$$ n = \frac{x - y}{x} $$

In the formula: $n$ is purification efficiency. $x$ and $y$ are the initial and final exhaust concentration or PM2.5 content, respectively.

### 3.4. X-ray diffraction test (XRD)

Phase analysis of X-ray diffraction using X-ray diffraction effect in crystal materials for material structure analysis technology. Each crystalline substance has its specific crystal structure, including lattice type, crystal plane spacing and other parameters. When the sample is irradiated by X-ray with sufficient energy, the substance in the sample is excited, and the secondary fluorescence X-ray is generated. The crystal plane reflection follows the Bragg law. The qualitative analysis of the compound can be carried out by measuring the diffraction angle position (peak position), and the quantitative analysis can be carried out by measuring the integral intensity (peak intensity) of the spectral line. The grain size and shape can be detected by measuring the relationship between the spectral line intensity and the angle.
3.5. Scanning electron microscope

The ZEISS HD 15/Oxford X-Max N scanning electron microscope was used. There are nine small sample platforms on the loading table of scanning electron microscope, and nine samples can be prepared at the same time. The length, width and height of each sample are best within $2\text{cm} \times 2\text{cm} \times 1\text{cm}$. The special double-sided adhesive should be attached to the front bearing table of the sample, and then the sample is bonded to the bearing table and wrapped with the same double-sided adhesive. In the preparation of samples in this experiment, appropriate amount of samples were taken with a medicine spoon and evenly spread on the small bearing platform in the center of the loading platform. Appropriate pressure was applied to make the sample powder uniformly fixed on the double-sided adhesive. The unfixed sample powder was blown off with a suction ear ball to ensure the cleanliness of the loading platform and not affect the next scanning electron microscope. The sample preparation is shown in figure 7 and is located at the central loading table.

![Figure 7. Scanning electron microscope sample.](image)

| Composite material content/% | Penetration degree 25°C/0.1 mm | Softening point/°C | Ductility 5°C.cm⁻¹ |
|-----------------------------|-------------------------------|-------------------|-------------------|
| 0                           | 59                            | 54                | 37.4              |
| 1                           | 57                            | 55.5              | 36.2              |
| 3                           | 55                            | 56.5              | 34.7              |
| 5                           | 52                            | 57                | 33.5              |
| 7                           | 50                            | 58.5              | 31.3              |

4. Test results and analysis

4.1. Effect of nano TiO$_2$/tourmaline composite content on properties of evaporative residues of modified emulsified asphalt

The samples with composite content of 0%, 1%, 3%, 5% and 7% were prepared. The influence of nano-TiO$_2$/tourmaline composite content on the properties of modified emulsified asphalt evaporation residue was studied by three index tests. The properties of modified emulsified asphalt evaporation residue under different dosage are shown in table 7.

It can be seen from table 7 that with the increase in the proportion of nano-TiO$_2$/tourmaline composite, the penetration of evaporation residue of SBR modified emulsified asphalt showed a continuous decrease. When the dosage is 7%, the penetration is reduced to the lowest, the relative 0% dosage is reduced by 0.9 mm, and the
reduction is 15.3%. It can be seen that the addition of nano TiO₂/tourmaline composites increases the viscosity of SBR modified emulsified asphalt evaporation residue; with the increase in the proportion of nano-TiO₂/tourmaline composite, the softening point of evaporation residue of SBR modified emulsified asphalt showed an increasing trend. When the content is 7%, the softening point rises to the highest, the relative 0% content increased by 4.5 °C, increased by 8.3%. It can be seen that the addition of nano-TiO₂/tourmaline composite can improve the heat resistance and temperature stability of SBR modified emulsified asphalt evaporation residue. With the increase in the proportion of nano-TiO₂/tourmaline composite, the ductility of evaporation residue of SBR modified emulsified asphalt showed a decreasing trend. When the content is 7%, the ductility is reduced to the lowest, which is 6.1 cm lower than that of 0%, and the decrease is 16.3%. It can be seen that the addition of nano-TiO₂/tourmaline composite reduces the deformation resistance of evaporation residue of SBR modified emulsified asphalt, but it still meets the specification.

4.2. Performance analysis of nano-TiO₂/tourmaline composite for micro-surfacing pavement

4.2.1. Abrasion performance
Wet wheel wear test was used to test the wear resistance of micro-surfacing. The test results of wet wheel wear at micro-surfacing under different nano-TiO₂/tourmaline composite contents are shown in table 8.

It can be seen from table 8 that with the increase of nano TiO₂/tourmaline content in SBR modified emulsified asphalt, the wet wheel wear value at the micro surface continues to decrease. Therefore, the wet wheel wear value of the doped nano-TiO₂/tourmaline material on the micro surface is decreased by 4% compared with that of the undoped micro surface, that is, the wear resistance of the doped nano-TiO₂/tourmaline material is improved by 4%.

4.2.2. Elevated temperature property
The wheel track deformation test specimens were prepared, and the wheel track width deformation rate and rutting depth rate were tested to evaluate the high temperature stability at the micro-surfacing. Different nano-TiO₂/tourmaline composite content under the micro-surfacing wheel rut deformation test results as shown in table 9.

It can be seen from table 9 that after the addition of nano-TiO₂/tourmaline composite material, the PLD and PVD of the deformation specimen of the mixture wheel track continuously decrease, with the decrease rates of 14.6% and 7.2%. The decrease of PLD and PVD indicates that the rutting resistance of the micro-surfacing mixture is enhanced and the high temperature stability is improved. Therefore, it can be considered that the addition of nano-TiO₂/tourmaline composite can improve the high-temperature stability of the micro-surfacing by 14.6%.

4.3. Purification effect test and analysis of micro-surfacing of composite materials
The mineral aggregate gradation is AC-13 type, and the asphalt is No. 70 A grade asphalt provided by Qilu Branch of Sinopec. The formed volume of rut plate is used as the pavement foundation. The micro-surfacing of 7% nano-TiO₂/tourmaline composite is paved to make the test sample of exhaust gas purification effect. The mineral aggregate gradation at the micro-surfacing is MS-3 type gradation median, and the modified emulsified asphalt is SBR modified emulsified asphalt. The test equipment was placed in the outdoor sunlight, and the exhaust gas purification test sample was placed in the center of the bottom plate. The handheld gas detector (four in one) and high-precision handheld PM2.5 speed tester were opened and placed in the reaction room. The reaction room and the bottom plate were sealed with polyurethane foam sealant. After the sealant curing,

| Table 8. Abrasion value test of different Nano-TiO₂/tourmaline materials |
|-----------------------------|-----|-----|-----|-----|-----|
| Dosage(%)                   | 0   | 1   | 3   | 5   | 7   |
| Wet wheel wearing value(g m⁻²) | 438 | 430 | 427 | 424 | 420 |

| Table 9. Micro-surface rutting resistance of nano TiO₂/tourmaline with different contents. |
|-----------------------------|-----|-----|-----|-----|-----|
| Dosage(%)                   | 0   | 1   | 3   | 5   | 7   |
| Width of the deformation rate PLD/[%] | 4.8 | 4.6 | 4.5 | 4.2 | 4.1 |
| Rutting depth rate PVD/%     | 9.7 | 9.6 | 9.4 | 9.3 | 9.0 |

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connect the automobile exhaust pipe, the automobile idle running 2 ~ 5 min after closing the inlet and outlet control valve, read the value of the two detectors for the initial value, every half an hour to measure a set of data, after 4h to measure the final value, the test site as shown in figure 8, the measured test data are shown in table 10, figure 9.

From table 10, it can be seen that the micrometer of doped nano-TiO$_2$/tourmaline composite has good automobile exhaust purification and PM2.5 adsorption effect. The purification efficiency of the micro-surfacing on automobile exhaust and PM2.5 particles reached 33.3% of hydrocarbons, 46% of carbon monoxide, 92.8% of nitrogen oxides, 29.9% of PM2.5 and 25.2% of PM10, respectively.

4.4. Mechanism analysis of the catalytic performance of of composite materials

4.4.1. Microstructure characterization

Scanning electron microscope photographs of nano-TiO$_2$/tourmaline composites are shown in figure 10.

Figure 10(a) shows that the particle size of tourmaline powder is different, ranging from 10 m to 100 m. The tourmaline powder used in the experiment is single crystal tourmaline, which is produced in Xinjiang. Due to the limitation of processing and preparation process, it cannot obtain uniform particle size products, but does
not affect the experimental study. It can be seen from figure 10(b) that nano-TiO₂ aggregates are loaded on the surface of tourmaline, and the segments are relatively uniform, and the particle size is uniform and large, which is in the micron level. It shows that the nano-TiO₂ loaded on the tourmaline surface still exists in the form of aggregates, but the dispersion is uniform and does not gather together to form larger aggregates. It can be seen from figure 10(c) that the surface of tourmaline powder is relatively flat and smooth without rough surfaces such as grooves or pits, indicating that the strong attachment of nano-TiO₂ aggregates to the surface of tourmaline.

Figure 10. SEM photo of TiO₂/tourmaline.

Figure 11. XRD pattern of tourmaline.
powder may be due to the adsorption force generated by the polarization of tourmaline itself, or the chemical bond between nano-TiO₂ aggregates and tourmaline powder. Figure 10(d) shows that the particle size of nano-TiO₂ aggregates attached to the surface of tourmaline powder is large to 1 μm, small to 0.3 μm, indicating that nano-TiO₂ attached to the surface of tourmaline still exists agglomeration phenomenon. Generally, nano-TiO₂ particles agglomerate together to form large particles of 150–300 nm and adsorb together, while the diameter of nano-TiO₂ aggregates loaded on tourmaline powder surface is about 300 nm and evenly distributed. This indicates that this composite method can reduce the aggregation of nano-TiO₂ aggregates and improve their dispersion, thereby promoting the photocatalytic reaction of nano-TiO₂ materials.

4.4.2. Phase analysis
The tourmaline and nano-TiO₂/tourmaline standard samples were prepared according to the requirements and X-ray diffraction (XRD) was carried out. The diffraction patterns are shown in figures 11 and 12.

It can be seen from figure 11 that obvious diffraction peaks appear in tourmaline samples at 8.8°, 10.5°, 18.6°, 20.9°, 26.7°, 27.2°, 28.0°, 28.5°, 31.8°, 33.0°, 50.1° and 64.6°, among which strong diffraction peaks at 8.8°, 10.5°, 26.7° and 28.5° are characteristic peaks of tourmaline. It can be seen from figure 12 that the TiO₂/tourmaline samples have obvious diffraction peaks at 8.7°, 10.4°, 22.0°, 23.5°, 26.6°, 27.1°, 27.9°, 28.5°, 30.2°, 32.9°, 36.5°, 41.5°, 50.0°, 56.6°, 59.9° and 68.3°, and strong diffraction peaks at 8.7°, 10.4°, 26.6° and 28.5°. In the diffraction pattern, the diffraction peaks at 8.7°, 10.4°, 26.6°, 27.1°, 27.9°, 28.5°, 32.9° and 50.0° are tourmaline characteristic peaks, and the diffraction peaks at 26.6° are significantly enhanced compared with tourmaline characteristic peaks. Compared with the standard comparison cards of anatase and rutile TiO₂, it can be seen that anatase TiO₂ has a characteristic peak at 25.3°, and rutile TiO₂ has a characteristic peak at 27.4°. The enhanced diffraction peak of TiO₂/tourmaline composites appeared at 26.6°. It is speculated that the diffraction peak of anatase TiO₂ at 25.3° and the characteristic peak of rutile TiO₂ at 27.4° superimposed to form the enhanced diffraction peak of TiO₂/tourmaline composites at 26.6°. Moreover, the diffraction peaks of TiO₂/tourmaline composites at 27.9°, 36.5°, 41.5° and 56.6° are close to the characteristic diffraction peaks of rutile TiO₂. Therefore, it can be seen that TiO₂ attached to the surface of tourmaline is not a single crystal, and anatase and rutile are both. The composite prepared by hydrolysis precipitation method did not change the phase of tourmaline. TiO₂ crystal forms attached to the surface of tourmaline were anatase and rutile. Studies have shown that temperature regulation can directly and effectively promote the transformation of anatase TiO₂ to rutile TiO₂, and low-valent anions such as Cl⁻ and F⁻ can also promote the transformation of TiO₂ from anatase to rutile [24]. When the temperature is higher than 600°C, some anatase TiO₂ begins to transform to rutile. Therefore, the TiO₂ crystal forms attached to the tourmaline surface are anatase and rutile, which may be due to the fact that the sample preparation process does not filter and wash clean Cl⁻ or the temperature control is not accurate enough during the high temperature calcination at 550°C, which causes the phase transition of TiO₂ and makes some TiO₂ crystal forms change from anatase to rutile.

Figure 12. XRD pattern of TiO₂/tourmaline.
4.4.3. Mechanism analysis of tail gas purification
After the excitation of nano-TiO₂ by light irradiation, the electron absorption energy transits from the valence band to the conduction band to form an electron-hole pair. Hole can directly oxidize TiO₂ surface materials can also oxidize H₂O and OH⁻ to generate hydroxyl radicals -OH, electrons react with O₂ in air to generate oxygen radicals -O₂⁻ . -OH and -O₂⁻ have very high oxidation ability, which can react with harmful exhaust pollutants in the air to produce harmless CO₂ and H₂O.

The spontaneous permanent polarity of tourmaline makes opposite charges appear at both ends, forming electrostatic field around it, which involves the transfer of photogenerated electron-hole pairs to two opposite directions. The existence of the spontaneous electrode has been proved by experiments, which is explained by the orientation of the silicox tetrahedron SiO₄⁻4. The spontaneous electrode of tourmaline is a spontaneous permanent electrode, which is not affected by external electric field and has nothing to do with temperature change.

The purification efficiency of each component of automobile exhaust at the micro-surfacing of doped nano-TiO₂ tourmaline composite reached 33.3% for hydrocarbons, 46% for carbon monoxide and 92.8% for nitrogen oxides, respectively, which was significantly higher than that of single nano-TiO₂. It shows that the catalytic performance of nano-TiO₂ loaded on the surface of tourmaline has been greatly improved, because tourmaline has its own polarization, forming a permanent electric field around it, which is beneficial to the separation of photogenerated electron-hole pairs and reduces the recombination rate of photogenerated electron-hole pairs, thus improving the photocatalytic performance of TiO₂.

4.4.4. Analysis of PM2.5 adsorption mechanism
Tourmaline is a multi-element natural mineral, the main chemical composition is SiO₂, TiO₂, CaO, K₂O, LiO, Al₂O₃, B₂O₃, MgO, Na₂O, Fe₂O₃, FeO, MnO, P₂O₅, containing magnesium, aluminum, iron, boron and other 10 kinds of beneficial trace elements to the human body. The electrical effect of tourmaline mainly refers to the secondary thermo-electric effect caused by thermal expansion and piezoelectric effect. Its thermoelectricity is a charged, asymmetric and non-harmonic vibration. The thermo-electric coefficient K increases nonlinearly with the increase of temperature. The electric field effect of tourmaline is mainly manifested as: the electrolysis effect of electric field on water; electrostatic field adsorption and neutralization of charged ions, tourmaline also has high mechanical and chemical stability, tourmaline does not have saturation limit.

The purification efficiency of PM2.5 and PM10 particles in automobile exhaust at the micrometer of doped nano-titanium dioxide tourmaline composites reached 29.9% and 25.2%, respectively. This is because natural mineral tourmaline as a special structure of polar crystals, itself can produce long-term ions, and permanently release air negative ions and far infrared. Air negative ions can neutralize positively charged suspended particles in the air, resulting in the settlement of suspended particles. Moreover, tourmaline can form an electric field around itself because of its permanent electrode property, and adsorb charged particles in the air.

5. Conclusion
(1) The addition of nano-TiO₂/tourmaline composites has a certain effect on the properties of evaporation residue of SBR modified emulsified asphalt, which can increase its viscosity by 15.3%, enhance its heat resistance and temperature stability by 8.3%, but reduce its deformation resistance by 16.3%.

(2) Intermediate value of MS-3 mineral aggregate gradation range specified in specification for micro-surfacing. The best oil-stone ratio is 6.5%. The optimum dosage of SBR modified emulsified asphalt is 10.5%. The addition of nano-TiO₂/tourmaline composite can improve the road performance of micro-surfacing to a certain extent, especially the addition of 7% nano-TiO₂/tourmaline composite can improve the wear resistance of 4% and the high temperature stability of 14.6%.

(3) Based on the research direction of this paper and the design idea of relevant design schemes, a detection device for tail gas purification and PM2.5 adsorption effect is independently developed. The test method and evaluation index for the purification and adsorption of tail gas pollutants by preventive maintenance sealing materials were determined.

(4) Doped nano-TiO₂/tourmaline composite has good automobile exhaust purification and PM2.5 adsorption effect. The purification efficiency of automobile exhaust and PM2.5 particles reached 33.3% of hydrocarbons, 46% of carbon monoxide, 92.8% of nitrogen oxides, 29.9% of PM2.5 particles and 25.2% of PM10 particles, respectively.

(5) The composite method of loading nano-TiO₂ on tourmaline surface reduces the aggregation of nano-TiO₂ aggregates, improves the dispersion of nano-TiO₂ materials, and promotes the catalytic reaction of
nano-TiO2 materials. The nano-TiO2 loaded on the tourmaline surface contains anatase and rutile, and the tourmaline phase does not change. The experimental reaction process and the combination of the two substances do not change the structure of the two. The two work together and each can exert the material characteristics.

(6) Tourmaline has its own permanent polarization effect. The generated permanent electric field can accelerate the separation of photogenerated electron-hole pairs of TiO2, improve its redox ability, and also adsorb charged gas molecules and charged particles in the air. The piezoelectricity and thermoelectricity of tourmaline make it permanently release air negative ions, and neutralize the electricity with positive suspended particles in the air, so that the suspended particles settle.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

CRediT authorship contribution statement

Zhenxia Li: Conceptualization, Project administration, Supervision, Writing-Review and Editing. Tengteng Guo: Conceptualization, Formal analysis, Methodology, Visualization. Yuzhan Chen: Supervision, Project administration, Data curation, Formal analysis. Kun Yang: Conceptualization, Writing-Original Draft, Supervision, Investigation. Xinyu Dong: Conceptualization, Supervision, Investigation. Jing Wang: Conceptualization, Supervision, Investigation. Lihui Jin: Funding acquisition, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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ORCID iDs

Yuzhan Chen @ https://orcid.org/0000-0002-6024-5793

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