University of Sunderland

Usage guidelines

1   Photocatalytic oxidation of NO$_x$ under visible light on asphalt pavement surface

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14

15   Abstract:

16   This work examines the potential use of heterogeneous photocatalysis as an innovative oxidation

17   technology. The aim is to demonstrate that this technology cand reduce the damaging effects of

18   vehicle emissions by using nitrogen doped (N-doped) TiO$_2$ as a photocatalyst immobilized above

19   the asphalt road surface. In the study, the photocatalytic effectiveness and durability of N-doped

20   TiO$_2$ photocatalytic asphalt road material were assessed in both the laboratory and the field using

21   direct and indirect measurement. The experimental results show that under visible light irradiation,

22   N-doped TiO$_2$ asphalt road material has a higher activity compared with pure TiO$_2$ asphalt road

23   material. The decontamination rate for NO$_x$ is about 27.6%, 24.6%, 16.3%, and 13.8% under

24   irradiation at light wavelengths of 330–420 nm, 430–530 nm, 470–570 nm and 590–680 nm,

25   respectively. Results of the field test and prediction models suggest that the service life of

26   N-doped TiO_2 asphalt road material is approximately 13 months.

27

28   Key word: Photocatalyst; N-doping; visible light; Photocatalytic asphalt pavement; Nitrogen

29   oxides

30

31   Introduction

32   Urban areas experience high levels of traffic exhaust, which contribute to air pollution, which

33   is a major global concern (Ishihara et al. 2010). Many governments have introduced emission

34   reduction systems in order to decrease emissions. In spite of these efforts,   traffic has continued

35   to increase, adding to concerns about the influence of traffic emissions on health and the

36   environment. Researchers have found that asthma is associated with nitrogen oxide (NO_x), which

37   pedestrians are exposed to due in part to the proximity of roads to walkways. Motor vehicle

38   emissions must be decreased in order to reduce nitrogen oxide emissions, and thus reduce asthma

39   rates (Tarek Mohamed et al. 2009). There are a number of methods that can be used to eliminate

40   NO_x and other pollutants.

41   Recently, heterogeneous photocatalysis has emerged as an ecological technique for

42   controlling air pollutants. In this technique, TiO_2 and pavement materials (such as cement and

43   asphalt) are used together as a photocatalyst; this method has been found to be a promising and

44   valid technology for NO_x control. The de-polluting properties of TiO_2 photocatalytic materials

45   have been assessed by applying this method both in real-world use and in laboratory simulations

46   performed under different experimental conditions. Pone and Cheung (2006) evaluated the NO

47   removal paving blocks produced by waste materials and TiO_2. Their study included an optimum

48   mix design incorporating recycled sand, glass, 10% TiO_2, and cement achieved 4.01 $mgh^{-1}m^{-2}$ NO

49   removal. Husken et al., (2007) performed a comparative analysis of different photocatalytic

50   cementitious products in an optimum laboratory conditions. They found that the efficiency of NO_x

51   degradation varied significantly, with some products achieving 40% degradation while others had

52   no influence. In Bergamo, Italy in 2006 (Guerrini and Peccati. 2007) a 12,000 m^2 area, was

53   developed on the sidewalk and the road using active paving blocks. Environmental monitoring

54   showed an average NO_x abatement of 45% during the daytime (09:00 -- 17:00).

55   In asphalt roads, based on the porous characteristics of asphalt road materials, Meng Chen et

56   al. (2010) used permeability technology to apply asphalt nano-TiO_2 as an environmental

57   protection material. This test showed that this type of photochemical catalysis environmental

58   protection material had a purification function and the ability to protect the environment. Marwa

59   Hassan et al. (2013) used the pray method to make photocatalytic asphalt pavements. Laboratory

60   evaluation showed that the maximum NO_x removal efficiency was reached at an application rate

61   of 0.05 L/m^2. A research team in Italy used a mixed method approach to develop environmental

62   protection materials. TiO_2 was added into asphalt pavements as an apparent layer that is sprayed

63   onto existing pavements. The decrease in efficiency was dependent on the type of TiO_2

64   nanoparticles used, and the NO_x decrease efficiency ranged from 20–57% (Venturini et al. 2009).

65   Photocatalytic asphalt pavements mainly use anatase phase TiO_2. The TiO_2 band gap is 3.2eV,

66   which corresponds to wavelengths less than 388 nm. This limits the photocatalytic practice in the

67   UV light region, which amounts to 4% of the solar spectrum, while the key part (45%) falls under

68   the visible light region (Chun-Hung et al. 2010). Few studies have attempted to use photocatalytic

69   asphalt pavements under visible light irradiation. Therefore, this study focuses on making a

70   photocatalytic asphalt pavement material. As an innovative oxidation technology, it is able to

71   reduce the damaging effects of vehicle emissions by using N-doped TiO_2 as a photocatalyst that is

72   immobilized above the asphalt road's surface under visible light irradiation. The decontamination

73   effect and application durability of the photocatalytic asphalt pavement material are also analyzed

74   in this study.

75

76   Experimental

77   Photocatalysts preparation

78   A non-metal doping approach (N-doped $TiO_{2)}$ was used to extend the utilization of the visible

79   region in the solar spectrum. Titanium powder was prepared using a sol–gel approach that used

80   tetrabutyl titanate (TNBT) and distilled water as the titanium precursor and hydrolyzing agent.

81   First, TNBT was mixed with ethanol and distilled water. Then, the mixed solution was stirred

82   using a machine under an 85℃ temperature bath for 6 hours. The slurry was dried at 80℃ and

83   calcined at 400℃ for one hour. Finally, a white powder was obtained, which was pure TiO_2 (see

84   Figure 1).

85   The pure TiO_2 powder was mixed with urea at molar ratios of 2:1, and then ground in an

86   agate mortar for homogeneity. The mixed powders were heated in a muffle furnace at 500 °C for 3

87   h, resulting in N-doped TiO_2 (Figure 1).

88   Figure 1 shows that the N-doped sample appears yellow in color, compared to the white color

89   of the pure TiO_2. Giacomo Barolo (2012) and Shinri Sato (1986) also observed these differences

90   in color and found that the yellow-colored N-TiO_2 had greater photocatalytic activity.

91   Preparation of asphalt road material through the addition of N-doped TiO_2 nanoparticles

92   We performed a series of penetrating load tests in order to attain a photocatalytic asphalt road

93   material sample. First, based on our preliminary research (Meng and Yan hua. 2010), the penetrant

94   and modified N-doped TiO_2 with silane coupling reagent were prepared. Then, the solution of

95   mixed penetrant and modified N-doped TiO_2 was sprayed onto the bituminous sample's surface. In

96   the load process, every sample was sprayed three times by an atmospheric air compressor. The

97   caliber of the air compressor was 1.5mm and the air pressure was 3.0-3.5MPa. The samples were

98   sprayed at a distance of approximately 20 cm and the speed of the aqueous solution jet was set at

99   8-10g/s.

100   Figure 2 and 3 display the schemes of the asphalt road material sample before and after spraying.

101

102   Analytical methods

103   Material property analytical methods

104   A scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were

105   used in this research in order to analyze the material properties of the N-doped TiO_2 and the

106   photocatalytic asphalt road material. The SEM was a commercial Hitachi S2300 instrument with a

107   tungsten hairpin filament. An accelerating voltage of 25 keV was used on gold samples to

108   eliminate charging. Transmission electron microscopy analyses were performed using a JEM-2010

109   (JEOL) operating at 160 kV. T.

110   Photocatalytic degradation analytical methods

111   Direct and indirect measurement strategies were used in this research to evaluate the

112   pollutant removal efficiency. Direct measurements were used in laboratory tests. In the laboratory

113   test, 500 ppb of NO_x was put into the measurement system. After flowing through the

114   photocatalytic asphalt road material, it was exported via the purification examination photoreactor

115   of the system. Measurement results of the inlet and outlet of photoreactor show that the total NO_x

116   concentration, the NO conversion, NO_2 conversion, and NO_x conversion were:

117
$$NO_x = NO + NO_2 \tag{1}$$

118
$$NO_{conversion} = \left(\frac{C_{NOin} - C_{NOlight}}{C_{NOin}} - \frac{C_{NObin} - C_{NOsb}}{C_{NObin}} \right) \times 100\% \tag{2}$$

119
$$NO_{2conversion} = \left(\frac{C_{NO_2in} - C_{NO_2light}}{C_{NO_2in}} - \frac{C_{NO_2bin} - C_{NO_2sb}}{C_{NO_2bin}} \right) \times 100\% \tag{3}$$

120
$$NO_{Xconversion} = \left(\frac{C_{NO_Xin} - C_{NO_Xlight}}{C_{NO_Xin}} - \frac{C_{NO_Xbin} - C_{NO_Xsb}}{C_{NO_Xbin}} \right) \times 100\% \tag{4}$$

121

122   The parameter meaning of equations 1,2, 3, and 4 are described in table 1.

123   The concentration of nitrates serves as evidence of a photocatalytic decrease of NO_x.

124   Nitrates that accumulate on the pavement surface were measured by dissolving them in deionized

125   water. Using the Japanese industrial standard (JIS TR Z 0018 "Photocatalytic materials--- air

126   purification test procedure"), the nitrogen compound eluted from the test piece was calculated

127   using the following formula (David et al. 2014):

128
$$Q_w = Q_{w1} + Q_{w2} = V_{w1}[(NO_3^-)_{w1} / 62] + [(NO_3^-)_{w2} / 62] \tag{5}$$

129   where Q_w = nitrogen compound eluted from the test piece (μmol); V_w = volume of collected

130   washing (mL); NO_3^- = nitrate ion centration eluent from the test piece (mg/L); and W_1 and W_2 =

131   the first and second DI washes, respectively.

132   Experimental testing: testing system and set-up

133   Experimental testing system

134   Photocatalytic degradation of NO_x was carried out using a continuous flow system that

135   included a gas supply subsystem, photoreactor, and the analytic subsystem. NO_x, N_2, and

136   humidified air were supplied in the gas supply subsystem. Humidified air was prepared by

137   bubbling air through a gas wash bottle containing water. The desired water vapor level can be

138   obtained by varying the flow rate of the humidified air stream. To obtain a stable NO_x

139   concentration, NO_x is mixed with humidified air in a gas mixer. During the experiments, gas flow

140   rates are controlled by calibrated flow meters. The photoreactor in the flow system is made of

141   quartz glass in accordance with the American Material Test Association standard (ASTMD

142   5116-1990) and the Japanese industrial standard (photochemical catalysis material-air purification

143   performance test method (Marwa et al. 2010)). To simulate on-road automobile exhaust, the

144   photoreactor is divided into three parts (1) an inlet, (2) purification region and (3) outlet. The inlet

145   section is nearly a cylinder; a fan controls the stream gas velocity. The purification section is

146   rectangular, which simulates the road surface. Humidity and temperature sensors and a heater

147   were installed in the photoreactor, and the photoreactor was irradiated by a simulation light source.

148   Figure 4 shows the entire photoreactor structure. In the analytic subsystem, NO, NO_2, and NO_x

149   concentration is measured by the analyzer.

150

151   Testing set-up

152   Photocatalytic activity rests: Previous studies on photocatalytic asphalt roads have shown that

153   illumination by a light source is an essential condition for photodegradation of NO_x. Light source

154 illumination can cause the formation of electron–hole pairs on the photocatalytic asphalt road

155 material and the electron–hole pair purified NO_x (Meng and Yan hua. 2010). In this study, we

156 attempt to increase insight into the reduction of NO_x under photocatalytic asphalt road material by

157 looking at the influence of the light source on the process.

158   During the serial experiment, the photocatalytic activity of N-doped TiO_2 photocatalytic

159 asphalt road material was investigated by assessing the NO_x decomposition in the photoreactor.

160 The experiment consisted of three steps.

161 Step 1: the sample was kept in the dark for 40 min, in order to achieve adsorption and desorption

162 equilibrium of NO_x gas in the photoreactor.

163 Step 2: the light source was switched on. The range of the light wavelength is 330–420 nm,

164 430–530 nm (blue LED), 470–570 nm (green LED), and 590–680 nm (red LED).

165 Step 3: Photocatalytic characterizations of samples were shown using different NO_x concentration

166 or decontamination rates. Direct measurement was used throughout the experiment.

167   Tests of application durability: In order to measure long term effects and examine

168 decontamination durability, it is necessary to apply N-doped TiO_2 photocatalytic to asphalt road

169 material to decontaminate exhaust from traffic in an outdoor environment. Vehicular activity and

170 rainwash are major influencing factors in actual outdoor traffic environments.

171   A field and simulation test were adopted in order to predict the durability of the N-doped

172 TiO_2 asphalt road material. In the field test, the test roads were washed once per week. At the same

173 time, traffic volume, temperature, wind direction, wind speed, and humidity were recorded.

174 During the test, the UV−vis spectroscopy (TU-1901) was used to determine absorbency of the

175 gathered sample by N-(1-naphtyl)-cthylcncdiaminc dihydrochloride colori metric (Meng et al.

176   2014). The entire test was executed under nature flow conditions in the daytime and separate

177   specimen exams lasted one hour. The field test location is shown in Figure 5.

178   Two separate simulation tests were conducted. First, in order to study the effect of vehicular

179   activity, the Loaded-Wheel Tester was used to simulate loading and wear on the N-doped TiO_2

180   photocatalytic asphalt road surface (see Figure 6). The photocatalytic activities of samples that

181   were subject to wear were investigated by evaluating the decomposition of NO_x in the

182   photoreactor. The second test studied the rain wash effect. The samples were placed in to **a** traffic

183   environment from June to August in Harbin, China. After this period a wash test was conducted.

184   The samples were washed once a week and direct and indirect measurements were used to

185   evaluate decontamination ability.

186

187   Results and discussion

188   Physical properties

189   TEM was executed to investigate the micrographs and dispersion of N-doped TiO_2 in the penetrant.

190   Fig.6 shows that the micrographs of the N-doped TiO_2 are spherical and there is no significant

191   shape change. The findings show that urea can help to hold or diminish the mean size and increase

192   the homogeneity of the size distribution via the synthesis method, which has been described by

193   other researchers (Hao-Hong et al. 2013). N-doped TiO_2 was also well dispersed in the penetrant

194   as seen in Figure 8. An integrated method was used to ensure the dispersion effect of N-doped

195   TiO_2 in the penetrant. It included three techniques. One technique used a silane coupling agent as

196   a modifier, which should help N-doped TiO_2 to have good compatibility in the penetration process.

197   Another technique involved choosing a magnetic stirrer for stirring the quantitatively modified

198   N-doped TiO_2. In the third tenchnique, an ultrasonoscope was used to disperse the mixing solution

199   in order to reduce spontaneous reunion and flocculation.

200   The comprehensive dispersion method achieved a good dispersion effect for the following

201   reasons: (1) The affinity between the nanoparticles and the solvent increased; meanwhile, it was

202   easier to open the nano-granular equipment, reducing the dispersion time and energy consumption.

203   (2) The strong turbulent motion of the liquid flow caused by the magnetic stirring broke and

204   suspended the nano-particle and the ultrasonic agitation continued to disperse the nanoparticles

205   into small particles, which led to a wide range of the solution region. (3) In the modifier

206   component, one end of the active groups can be adsorbed on the surface of the crashed

207   nanoparticles and the other end of the solvent formed adsorption layer, which produced electric

208   charge repulsion, guaranteeing long dispersed suspension of the nanoparticles in the solvent,

209   avoiding flocculation and ensuring the stability of the system.

210   Photocatalytic activity and purification mechanism

211   Figure. 9 shows the decontamination ability of the pure TiO_2 asphalt road material and

212   N-doped TiO_2 asphalt road material, where the different wavelength lights (330–420 nm, 430–530

213   nm, 470–570 nm, and 590–680 nm) were irradiated to the samples. As seen in Figure 8, there was

214   no loss of photoactivity in 330–420 nm wavelength lights (including in the UV section) on the

215   pure TiO_2 asphalt road material and N-doped TiO_2 asphalt road material. Meanwhile, the N-doped

216   TiO_2 asphalt road material had NO_x decontamination abilities of about 27.6%, 24.6%, 16.3%, and

217   13.8% under the irradiation of light wavelengths 330–420 nm, 430–530 nm, 470–570 nm, and

218   590–680 nm respectively. Further, on the N-doped TiO_2 asphalt road material under light

219   irradiation, the NO decontamination ability was better than the NO_2 decontamination ability.

220   A number of results can be extracted from Figure 9.

221   (1) N-doped TiO$_2$ asphalt road materials have better photocatalytic activity under visible light

222   There are two potential reasons for this. First, it is well known that photocatalysts need light

223   illumination to trigger photocatalytic oxidation. Figure 8 shows that the N-doped TiO$_2$ asphalt

224   road material had better NO$_x$ decontamination ability under a wavelength range of visible light.

225   The N-doped TiO$_2$ asphalt road material absorbed visible light to trigger photocatalytic oxidation.

226   Second, the behavior of the N-doped TiO$_2$ asphalt road material in the NO$_x$ oxidation was also

227   associated with the active species (•OH and O$_2$•−) formed on the photocatalyst's surface

228   (Todorova et al. 2013). Excite electrons were required from the valence band to create electron

229   and hole pairs. Equation 6 (Shu et al. 2004) shows that energy decreases from irradiation for

230   exciting surface electrons and holes with increasing wavelength of the visible light. It indicated

231   that the band gap might be significantly narrowed by mechanical chemistry doping of nitrogen in

232   titanium, for instance 3.08 eV (Gagoa et al. 2012).

233      $$E_g = 1239.8 / \lambda \tag{6}$$

234   where E$_g$ is the band gap (eV) of the sample, λ (nm) is the wavelength of the onset of the

235   spectrum.

236   (2) N-doped TiO$_2$ asphalt road material had different photocatalytic activity under different

237   visible light wavelengths.

238   Figure 9 shows that the activity for the N-doped TiO$_2$ asphalt road material was clearly better

239   than the pure TiO$_2$ asphalt road material activity with increasing wavelengths. The findings were

240   attributed to the introduction of N in the TiO$_2$ lattice and the creation of extra electronic states in

241   the TiO$_2$ band gap (Kumar et al. 2011).

242   The N-doped TiO_2 samples possessed a two-step adsorption spectra. The first step may have

243   been related to the original titanium band structure and the second adsorption step (in the visible

244   light region) may have been related to the formation of additional electronic states during nitrogen

245   doping (Shu et al. 2008).

246   Figure 8 shows that decontamination of the NO_x ability of the N-doped TiO_2 asphalt road

247   material decreased with increasing wavelength of the light in. The rate of electron and hole pair

248   recombination was a key factor affecting the decontamination NO_x ability of N-doped TiO_2

249   asphalt road material (Yao-Hsuan et al.2011). Photoluminescence emission occurs when

250   wavelength photoenergy is absorbed to excite an electron from the valence band and then a longer

251   wavelength luminescence was emitted via recombination of the electron-hole pair (Chun-Hung et

252   al 2012). The greater the luminescence intensity was, the quicker the electron and hole

253   recombined. Therefore, high intensity of luminescence might result in low photocatalytic activity

254   (Yu et al., 2005). Therefore, the N-doped TiO_2 is capable of lowering the luminescence intensity

255   and guiding the higher photocatalytic activity under areas with shorter wavelengths.

256   (3) N-doped TiO_2 asphalt road material had a complicated photocatalytic mechanism.

257   By following the experimental results of the present study, we found that NO_2

258   decontamination ability was lower on the N-doped TiO_2 asphalt road material under light

259   irradiation. It has been shown that NO_2 was created in the photocatalytic purification process to

260   decrease NO_2decontamination ability. This may be explained by a tentative mechanism that is

261   proposed to explain photocatalytic oxidation of NO_x under visible light on the N-doped TiO_2

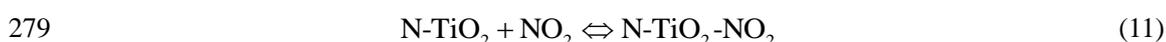262   asphalt road surface, which is shown in Figure. 10.

263   It is widely recognized that photocatalytic oxidation can be divided into 3 core stages: first

264 the transfer of contaminants from bulk to the surface; second the adsorption on the catalyst surface

265 and formation of reactive ions ; finally, degradation by the ions formed on the surface (Chuck et

266 al.2 013). Based on Figure 10, a possible photocatalytic NO_x oxidation mechanism was proposed

267 using equations (7)-(18).

268   N doping can build impurity states below the bottom of the conduction band of TiO_2 asphalt

269 material, causing visible TiO_2 asphalt material to be activated by visible light (Hongqi et al.2011).

270 N-doped TiO_2 asphalt road material was irradiated by appropriate light and energy, creating a hole

271 and electron pair in the N-doped TiO_2 lattice, shown in equation (7).

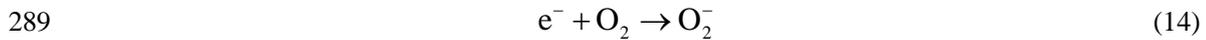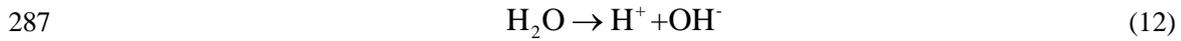272 $$N\text{-}TiO_2 + visible\,light \rightarrow h_{VB}^+ + e_{CB}^- \tag{7}$$

273   During adsorption of the reactants onto the N-doped TiO_2 asphalt road material, the

274 photogenerated hole in the conduction band will absorb water, oxygen, nitric oxide, and

275 nitrogen dioxide in the air as described in equations (8) - (11).

276 $$N\text{-}TiO_2 + H_2O \Leftrightarrow N\text{-}TiO_2\text{-}H_2O \tag{8}$$

277 $$N\text{-}TiO_2 + O_2 \Leftrightarrow N\text{-}TiO_2\text{-}O_2 \tag{9}$$

278 $$N\text{-}TiO_2 + NO \Leftrightarrow N\text{-}TiO_2\text{-}NO \tag{10}$$

279 $$N\text{-}TiO_2 + NO_2 \Leftrightarrow N\text{-}TiO_2\text{-}NO_2 \tag{11}$$

280   In our previous work (Meng et al.2011), we found that adsorbed H_2O on the N-doped TiO_2

281 leads to the formation of a highly hydroxylated surface and also gives off hydrogen ions (H^+) and

282 hydroxide ions (OH^-) by its dissociation. Then, H+ reacts with OH- to generate $\cdot$ OH.

283   Additionally, the photoinduced electron reacts with O_2, forming the superoxide anion (O_2^-)

284 and O_2^- forms $HO_2 \cdot$ radicals with traces of water. Lastly, nitrogen species (NO, NO_2) in the air can

285 be easily photocatalytically oxidized leading to HNO_3 by $HO_2 \cdot$ radicals on the N-doped TiO_2

286   asphalt road surface. The reaction is illustrated in equations (12) to (18).

$$H_2O \rightarrow H^+ + OH^- \qquad (12)$$

$$h^+ + OH^- \rightarrow \bullet OH \qquad (13)$$

$$e^- + O_2 \rightarrow O_2^- \qquad (14)$$

$$HO_2 \bullet + NO \rightarrow NO_2 + \bullet OH \qquad (15)$$

$$NO + \bullet OH \rightarrow HNO_2 \qquad (16)$$

$$HNO_2 + \bullet OH \rightarrow NO_2 + H_2O \qquad (17)$$

$$NO_2 + \bullet OH \rightarrow HNO_3 \qquad (18)$$

294   Durability Analysis

295   Figure. 11 shows the downward trend, over consecutive months, of the NO_x decontamination

296   ability on the N-doped TiO_2 asphalt road. In order to predict the durability of the N-doped TiO_2

297   asphalt road, we hypothesized that the N-doped TiO_2 asphalt road will actively degrade when the

298   NO_x decontamination rate is less 5%. An exponential regression model was used with the

299   observed data that was obtained in the field test (see Figure 11). The model was

300   y=32.01e^(-0.145x), with 95% confidence. Results from the model showed that active degradation

301   of the asphalt pavement lasted for a period of about 13 months. The photocatalytic efficiency

302   defeat was due to the wear from traffic and the rain wash. Wear and wash simulation tests were

303   completed in order to analyze these reasons.

304   In the wear simulation test, as seen in table 2, the data showed s decrease in NO_x

305   decontamination ability after wearing. However, the decrease was small under a certain scope,

306   such as in 8000 cycles where the wheel applied a load of 600 N for every cycle. But when the

307   cycle increased (exceeding 8000 cycles), the degree of decrease in the NO_x decontamination

308   ability increased. This had two possible causes: (1) the samples kept higher NO_x removal

309   efficiencies after wear, and, (2) N-doped TiO_2 was retained on the asphalt road surface and interior

310   after wearing, which may be proven by figure 12. This may be attributed to the research team's

311   use of infiltration liquid with N-doped TiO_2 and the permeability loading method. The infiltration

312   liquid had a special lipophilic penetration ability. When the infiltration liquid is sprayed on the

313   road surface, the nano-material (N-doped TiO_2) can be guaranteed to gradually infiltrate the road

314   surface under the action of the penetrating agent molecular power. Subsequently, with the growth

315   of the concentration of the asphalt pavement surface infiltration liquid and the dual influences of

316   the concentration gradient and porous open graded pavement, N-doped TiO_2 penetrates along the

317   open graded asphalt pavement pore to the core under the action of capillary force and gravity.

318   During the penetration process, when the N-doped TiO_2 molecules are near the asphalt mixture

319   solid surface, N-doped TiO_2 molecules can adsorb on the solid surface in order to achieve the load.

320   This is because of the electric dipole moment and is possible because of the help of the Van Der

321   Waals force. However, when the cycle increases, the loss of weight in the samples also increases.

322   Surface wearing and particle loss may be associated with the loss of N-doped TiO_2 particles,

323   which is shown in figure 13. NO_x decontamination ability decreases as the cycles increase.

324   Table 2 presents the average NO_x decontamination ability for both the original and the

325   washed samples. The table shows that washing the samples results in reduction in the NO_x

326   removal efficiency and this decline was aggravated with time. This indicates time dependency,

327   which will result in a decrease of the NO_x removal efficiency. There are many reasons for this.

328   First, the decrease can be clarified by referencing the NO_x purification mechanisms found in

329   section 3.2 of this paper. HNO_3 should be speedily produced and accumulated on the top of the

330 N-doped TiO_2 asphalt road surface, and this could inhibit the photocatalytic reactions by building

331 a physical fence. Next, regeneration of the purification ability has proven that washing is a better

332 way to keep the NO_x decontamination ability for N-doped TiO_2 asphalt road material. During

333 washing, the HNO_3 was easily removed from the catalyst surface (as indirect measurement results);

334 it can be argued this may contribute to catalyst regeneration. Water can also, through rehydration,

335 replenish the consumed hydroxyl radicals; therefore, it is able to maintain the photocatalyst

336 activity (Meng et al.2011). However, the continuing decrease of the NO_x removal efficiency also

337 indicated that washing did not totally recover the active N-doped TiO_2 asphalt road material. That

338 may be due to the adsorption of indissolvable materials, such as lipids, on the photocatalyst

339 receptor sites of N-doped TiO_2 asphalt road material. Adsorption of NO_x occurred on the N-doped

340 TiO_2 asphalt road.

341 Summary and future work

342   N-doped TiO_2 powders were successfully prepared by sol–gel methods with urea. The

343 modified procedures did not change the crystalline structure or the morphology of the N-doped

344 TiO_2 as compared with initial sol–gel TiO_2. TEM analysis revealed that N-doped TiO_2 powders

345 could be well dispersed in asphalt penetrants. Based on the penetrant, N-doped TiO_2 asphalt road

346 materials were successfully prepared using spray methods.

347   Meanwhile, the N-doped TiO_2 asphalt road materials presented higher activity on NO_x

348 removal than pure TiO_2 asphalt road materials under the irradiation of visible light. The outcome

349 was ascribed to the photocatalytic mechanism. As described by this mechanism, the nitrogen

350 species onto The iO_2 interfaces decreased the absorption band gap energy in the visible light and

351 hindered the electron hole recombination, which helped to improve oxidation of nitrogen oxides.

352   The durability of N-doped TiO_2 asphalt road materials was evaluated through field and

353   simulation testing. Results suggested that the durability of N-doped TiO_2 asphalt road materials

354   spanned a period of approximately 13 months. The results demonstrated that the TiO_2 nitrogen

355   doping approach would provide a worthy channel for photocatalytic asphalt road materials of

356   highly visible light induced photocatalytic activity for the practical decontamination NO_x

357   application in the medium-term.

358   Because the application of N-doped TiO_2 asphalt road materials in demonstrating vehicle

359   emissions is still a relatively new field of study, more research should be conducted prior to field

360   application. Our research team plans to evaluate the potential pollution of nitrates created by the

361   photocatalytic processing in land through plant experiments. We will also attempt to build an

362   evaluation system for N-doped TiO_2 asphalt road materials application for demonstrating vehicle

363   emissions.

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Table 1 parameter nomenclature

Parameter	Meaning
$NO_{conversion}$ (%)	effective purifying rate of NO
$NO_{2conversion}$ (%)	effective purifying rate of NO_2
$NO_{xconversion}$ (%)	effective purifying rate of NO_x
C_{NOin} (mg/m^3)	the initial steady-state NO concentration (before turn on the light source)
C_{NO2in} (mg/m^3)	the initial steady-state NO_2 concentration (before turn on the light source)
C_{NOxin} (mg/m^3)	the initial steady-state NO_x concentration (before turn on the light source)
$C_{NOlight}$ (mg/m^3)	the NO concentration during irradiation phase
$C_{NO2light}$ (mg/m^3)	the NO_2 concentration during irradiation phase
$C_{NOxlight}$ (mg/m^3)	the NO_x concentration during irradiation phase
C_{NObin} (mg/m^3)	the initial steady state NO concentration
C_{NO2bin} (mg/m^3)	the initial steady state NO_2 concentration
C_{NOxbin} (mg/m^3)	the initial steady state NO_x concentration
C_{NOsb} (mg/m^3)	the NO concentration at the end of the blank experiment(without irradiation)
C_{NO2sb} (mg/m^3)	the NO_2 concentration at the end of the blank experiment(without irradiation)
C_{NOxsb} (mg/m^3)	the NO_x concentration at the end of the blank experiment(without irradiation)

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DeNO$_x$ ability	Number of wear (cycle)					Number of wash (time)				
	0	4000	8000	12000	16000	0	2	4	6	8
Direct measurement-purification rate (%)	36.4	34.8	32.1	28.1	22.3	36.4	34.2	32.8	29.3	24.6
Indirect measurement- . nitrate concentrations s in the sample (mg/L)	8.3	8.1	7.2	5.5	3.8	8.3	7.9	7.3	6.1	4.1

Table 2 Degradation effect of wear and wash

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Figure

Fig 1. Pure TiO$_2$ and N-doped TiO$_2$

Fig 2. Asphalt road material sample before spray

Fig 3. N-doped TiO$_2$ asphalt road material sample

Fig 4. Structure of photoreactor

Fig 5. Spot of field test

Fig 6. Simulation test on vehicular activity effect

Fig 7. Micrographs of the N-doped TiO$_2$
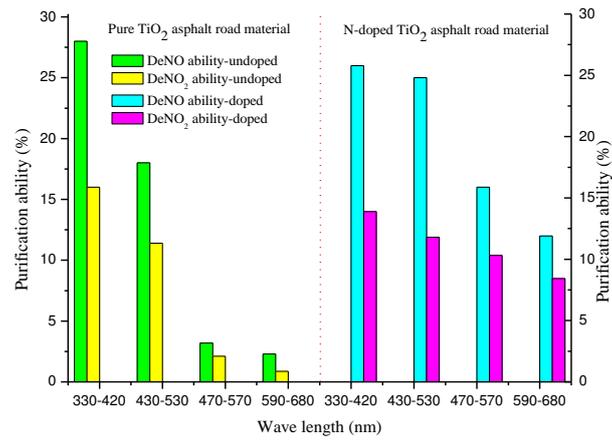
Figure

Fig 8. Dispersion effect of N-doped TiO_2 in penetrant

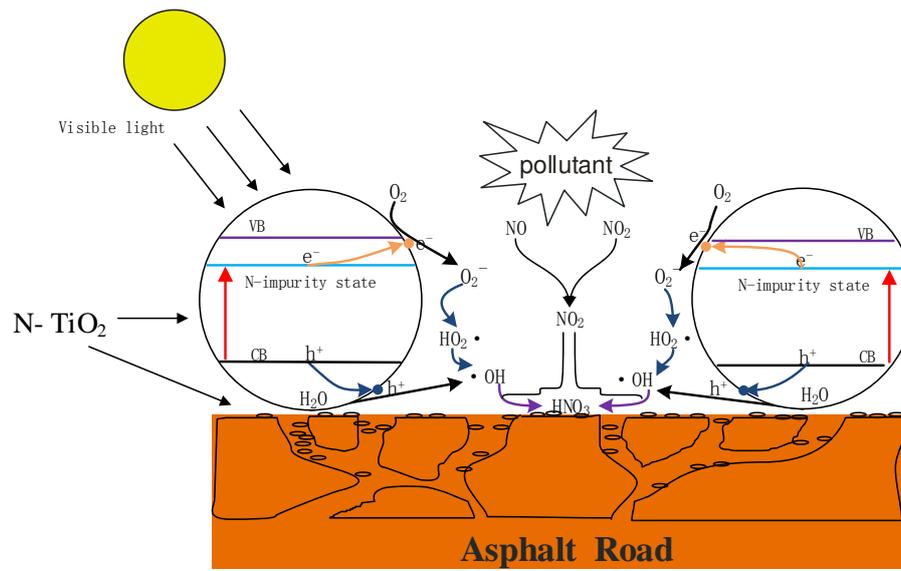Fig 9 Comparison of the photocatalytic activity of undoped, N-doped TiO$_2$ asphalt road material under UV and visible light

Fig 10. Schematic illustration of photocatalytic process on N-doped TiO₂ asphalt road material under visible light
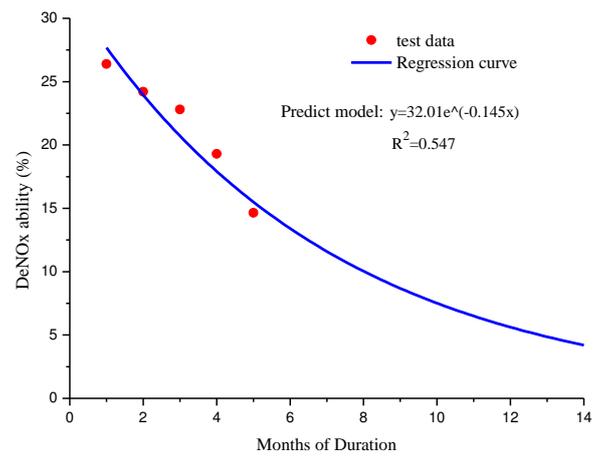
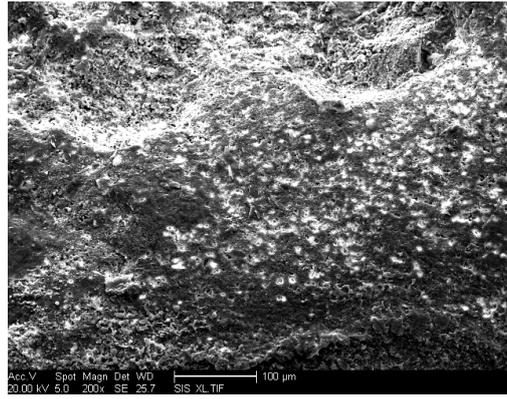Fig 11 Illustration of durability of N-doped TiO_2 asphalt road

Figure

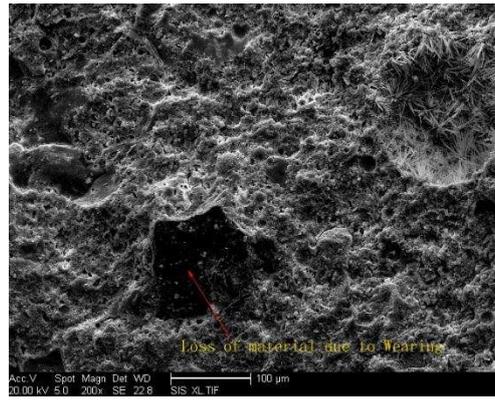Fig 12 SEM image of road surface after wearing

Fig 13 SEM on loss of N-doped TiO$_2$ due to wearing

Figure Caption List

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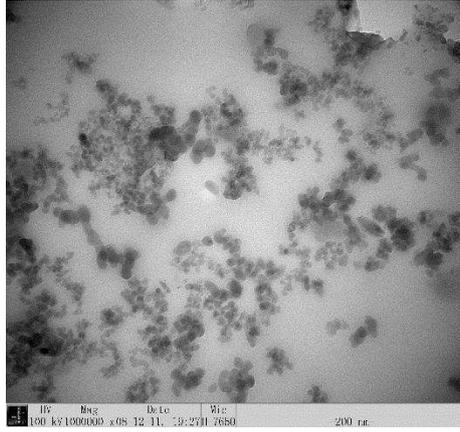
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