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Advanced Solar Photocatalytic Asphalt for Removal of Vehicular NO_x

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Abstract

Conventional use of solar energy is to convert it into a useful form, e.g. heat or electricity. Alternatively, solar radiation can be used to activate photocatalyst for direct functional photocatalytic applications. In the present research, solar photocatalytic asphalt was developed for removal of vehicular nitrogen oxides (NO_x) to mitigate the roadside air pollution problem. Visible-light activated photocatalytic asphalt was fabricated by embedding carbon-modified titanium dioxide (C-TiO₂) onto asphalt surface under proper heat treatment. Material characterizations were conducted to study the surface and light absorption properties. Chamber tests of NO_x removal were conducted under the conditions that simulated the ambient environment under solar irradiation. The experimental results show that NO_x removal by C-TiO₂ photocatalytic asphalt is viable, and is better than the more commonly used P25. The parametric analysis also reveals that the material fabrication process can be optimized for making photocatalytic asphalt that is highly effective, durable and cost-effective. This study demonstrates successful use of solar radiation via photocatalysis for functional application that can solve environmental problem.

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Keywords: Solar Photocatalysis; Carbon Modified TiO₂ Nanomaterial; Road Construction; Air Pollutant; Surface Modification

1. Introduction

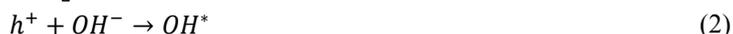
NO_x gases (mainly composed of NO and NO₂) generated from vehicular combustion have raised increasing concerns in recent years. They can cause various environmental and human health problems, including: air poisoning, acid rains, ozone depletion, and lung diseases. These consequences pose great threats to urban area, especially for those with dense population and buildings. Therefore, immediate actions are needed to tackle the vehicular NO_x

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emission problems. Efforts are made in the combustion engine designs and exhaust gas treatments, so that individual vehicular emissions are effectively controlled. However, with the global economy and transportation development, that road traffics are increasing at a very high rate, the vehicular NO_x problem is still becoming more and more serious.

In the past decades, photocatalysis technologies based on novel nanomaterials have experienced rapid development.[1] The porous structure of photocatalyst can adsorb pollutant molecules such as NO_x, and neutralize them through the following reactions[2-5]:



The OH⁻, H⁺, and O₂ are obtained from the air surrounding the photocatalyst. Therefore, after the full process, the harmful NO_x gases can be transformed into water soluble nitrates, and can be washed away by rain or street sprinkling. During the photocatalysis reactions, the TiO₂ remain unchanged, and solar energy is the only energy input. These attractive features have drawn wide research interest for NO_x removal through construction materials.[2-9] Most existing researches used P25 or bare anatase TiO₂ as the photocatalyst, which are only active under UV illumination. Besides, there also lacks a generally agreed optimal incorporating method for loading the photocatalysts onto the base material. Therefore, there's still a long way to go to develop a cost-effective, highly active, and industrially viable photocatalytic material along with a proper loading method.

In this work, we have developed solar photocatalytic asphalt for removal of vehicular nitrogen oxides (NO_x) to mitigate the roadside air pollution problem. Visible-light activated photocatalytic asphalt was fabricated by embedding carbon-modified titanium dioxide (C-TiO₂) onto asphalt surface under proper heat treatment. The C-TiO₂/asphalt composite was characterized. Chamber tests were carried out to evaluate the NO_x removal performance of the photocatalytic asphalt. Comparison between the C-TiO₂ and the traditional photocatalyst P25 were also conducted.

2. Experimental Details

2.1. Material Fabrication

C-TiO₂-asphalt composite samples were fabricated with the following procedures. First, glass-fibre mats were cut into 30 cm x 30 cm squares and were cleaned using detergent and DI water. Emulsified SBS-bitumen was evenly spread onto the mats, and the amount was controlled as 25 mL bitumen per sample. After drying, calculated different amount of photocatalyst powders were suspended in DI water and sprayed onto the bitumen surface using an airbrush. After the DI water totally vaporized, the mats were kept in a preheated 373 K oven for 10 minutes. After cooling down, the samples were characterized or evaluated without any further treatments.

2.2. Characterization

Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the P25 and C-TiO₂ photocatalysts were recorded using a Shimadzu UV 2600 spectrophotometer with BaSO₄ as the reference. The morphology of the photocatalyst loaded asphalt samples was characterized using a EVO-MA10 (ZEISS) scanning electron microscopy (SEM). Before SEM observation, the samples were coated with a layer of gold particles using a Quorum Q150T ES sputter coater.

2.3. Photocatalysis Performance Evaluation

Evaluation of the photocatalysis performance of P25 and C-TiO₂ was carried out in a typical organic dye degradation setup. In a jacketed glass container, 50 mL of 10 ppm methylene orange (MO) aqueous solution was mixed with 0.5 g of photocatalysts. The mixture was stirred under dark conditions for 24 hours to reach the adsorption-

desorption equilibrium. A full-arc xenon lamp equipped with a 420 nm-cut filter was used as the light source, and the power density reaching the reactant was calibrated as 100 mW/cm^2 . During the test experiments, the reactant mixture was exposed to the light with constant stirring, and the reactor was cooled by running tap water. An aliquot of the reactant was taken every half hour, and the suspended photocatalyst powders were separated from the liquid via centrifuge. The concentration of MO solution was analyzed using a Shimadzu UV-2600 UV-vis spectrophotometer.

A testing chamber was manufactured for evaluating the NO_x degradation performance of the photocatalyst loaded asphalt. The schematic diagram of the testing chamber setup is illustrated in Fig. 1. The chamber is made of acrylic boards and sealed with silicon glue. An Osram® Ultra Vitalux 300 W solar spectrum lamp was mounted as the light source. Temperature control and gas mixing were realized through a heat exchanger coupled with a fan. An Alphasense® gas detection sensor was equipped for detecting NO_x concentration, temperature, and relative humidity (RH). All the measurements were conducted in a dark room, and the average irradiance reaching the sample surface was calibrated as 100 mW/cm^2 (1 sun). In a typical measurement, wet air with designated RH was first injected into the chamber, with the lamp, cooling water circulator, and the mixing fan switched on; when the temperature and RH reached a steady state, the NO_x concentration read from the sensor was calibrated as zero; consequently, 400 ppb of NO_x gas was added into the wet air, and after the NO_x level read from the sensor stabilized, which was calibrated as 100% concentration, the gas inlet and outlet were both plugged. Then the NO_x concentration inside the chamber was monitored by the sensor and recorded using a computer.

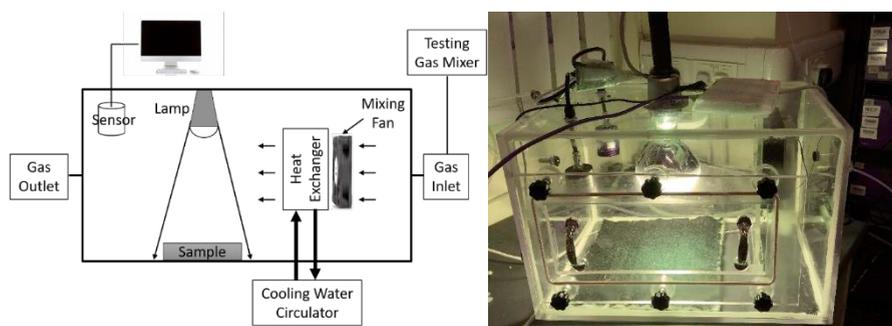


Fig. 1. NO_x degradation testing chamber. Left: schematic diagram; Right: actual photo of the chamber

3. Results and Discussion

By far the most popularly studied photocatalyst is Evonik Aeroxide TiO_2 P25®, which is composed of mixed-phase, namely anatase and rutile TiO_2 . The P25 photocatalyst is favoured for its stability, environmental friendliness, and cost effectiveness. It demonstrates high activity under UV illumination, where highly reactive radicals are generated [Eq. (2) and (3)] and can effectively neutralize the target harmful matters [Eq. (5) and (6)]. However, the relatively large bandgap of P25 ($\sim 3.2 \text{ eV}$) renders its incapability of making use of long wavelength photons ($\lambda > 387.5 \text{ nm}$), which is to say, over 95% of the total solar energy is unutilized, thus the overall performance is limited. To tackle this problem, the catalyst's bandgap needs to be engineered, which can be realized through doping or introduction of co-catalysts.

Recently, Kronos® Inc. developed a novel carbon-modified nano-anatase TiO_2 photocatalyst, KRONOClean 7000® (C- TiO_2). It was claimed that the C- TiO_2 can be activated by visible light and can effectively degrade undesirable compounds in the air, including NO_x , CO, VOCs, *etc.* [10] Tobaldi *et al* conducted quantitative XRD characterization and gas-phase photocatalytic activity testing over the C- TiO_2 photocatalyst.[11] The material was found to be mainly in anatase phase with amorphous phase content between 6.5–8.1 wt%. [11] The particles possess a bimodal nature: mostly $\sim 4 \text{ nm}$ in diameter, but with a small amount of a larger fraction between ~ 12 and 15 nm . [11] An aromatic carbon compound was attached to the surface of these TiO_2 nanoparticles, which was assigned to the origin of the visible light absorption. [11] We have conducted UV-vis DRS tests to compare the light absorption properties of P25 and the C- TiO_2 , and the results are shown in Fig. 2(a). The absorption curve agrees well with that reported in Ref. [11]. Comparing to P25, the C- TiO_2 's absorption onsets from $\sim 700 \text{ nm}$, and shows an obvious discrepancy against the P25 curve at the $400 - 700 \text{ nm}$ region. This indicates the superior visible light absorption ability of C- TiO_2 . The visible

photocatalytic properties were confirmed through the commonly used organic dye degradation experiments. As shown in Fig. 2(b), under visible light illumination ($\lambda > 420$ nm), the C-TiO₂ degraded over 60% of the MO within a half hour, and after 3 hours, the MO has been degraded over 95%. On the other hand, under the same conditions, the P25 didn't show significant degradation. Moreover, the visible light NO_x degradation performance of the C-TiO₂ was also demonstrated in Ref. [11]. Therefore, in this study, the C-TiO₂ was selected as a major photocatalyst candidate.

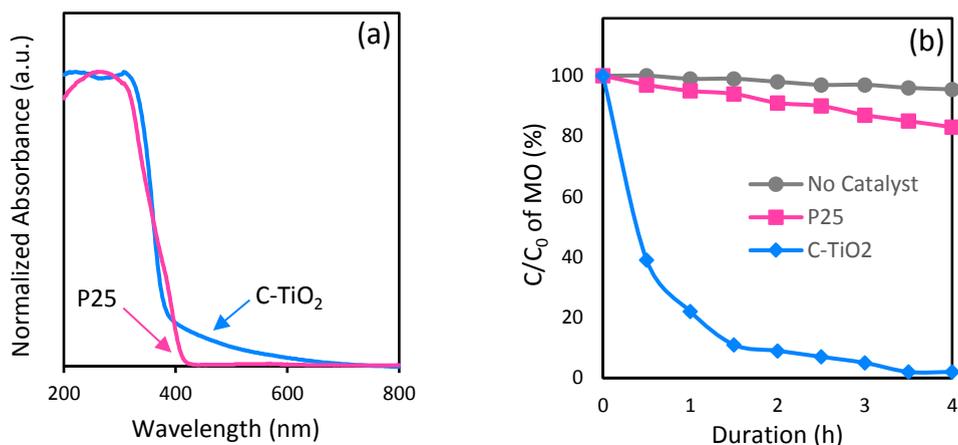


Fig. 2. Comparison of (a) UV-vis DRS spectra and (b) photocatalytic degradation of MO (10 ppm) under visible irradiation (1 kW/m²) between the traditional P25 and the C-TiO₂ photocatalysts

The method for casting the photocatalysts onto the asphalt surface plays a key role in developing the photocatalytic asphalt. Firstly, to make the photocatalytic redox reactions take place, the photocatalysts have to be in contact with the pollutants (NO_x molecules), as well as H₂O and O₂ molecules and incident sunlight; Secondly, asphalt paved road is usually a harsh environment, with heavy traffics and natural weathering, so the attachment between the photocatalyst particles and the asphalt surface is subject to great challenges; Thirdly, for safety reasons, there're strict requirements on the physical properties of asphalt roads, i.e. friction, elasticity, fatigue resistance, anti-cracking properties, and even color, that introduction of photocatalyst shouldn't compromise these properties; Finally, the cost-effectiveness, including raw material, equipment, manpower, *etc.*, is also an important consideration. A feasible casting strategy should satisfy all the above-mentioned considerations.

The existing researches mainly follow three casting strategies: 1) directly blending the photocatalyst with the asphalt/concrete raw material before pavement; [6] 2) casting an additional thin layer of photocatalyst blended material, such as emulsified bitumen and mortar, on the surface of readily compressed asphalt surface; [2, 7] and 3) directly spray a photocatalyst suspension onto the surface of asphalt roads. [6] In our trials, we found that the first two methods suffer from a problem that a large fraction of photocatalysts could be covered by the bitumen, thus compromise the photocatalytic performance. To fully demonstrate the photocatalytic effect of the C-TiO₂, we mainly studied the photocatalyst/asphalt composite obtained via direct spraying. And a post-heat treatment was introduced to enhance the attachments between the photocatalyst particles and the asphalt surface. An SEM image of the C-TiO₂ coated asphalt surface is shown in Fig. 3(a). The C-TiO₂ particles are evenly distributed on the asphalt surface. Most of the particles are partially embedded in the asphalt surface, and the edges can be clearly distinguished. This can be attributed to the post-heat-treatment after the spraying. At ~373 K, the set asphalt's viscosity is reduced and the surface become sticky. The photocatalyst particles sink into the surface and are partially stuck on the surface after cooling down. This structural arrangement is desirable: on one hand, the photocatalysts are well exposed to the surrounding environment, leading to high activity and cost-effectiveness; on the other hand, the partial embedment provides proper structural strength to resist tyre abrasion, rain washing and wind blowing.

The photocatalytic degradation of NO_x performance of the C-TiO₂ coated asphalt is shown in Fig. 3 (b), (c) and (d). From Fig. 3(b), it can be seen that the NO_x inside the chamber can be totally degraded within 1.5 hours by the sample with 7 g C-TiO₂ per sq. meter loading. In this case, the value of the degradation dynamic factor k equals to

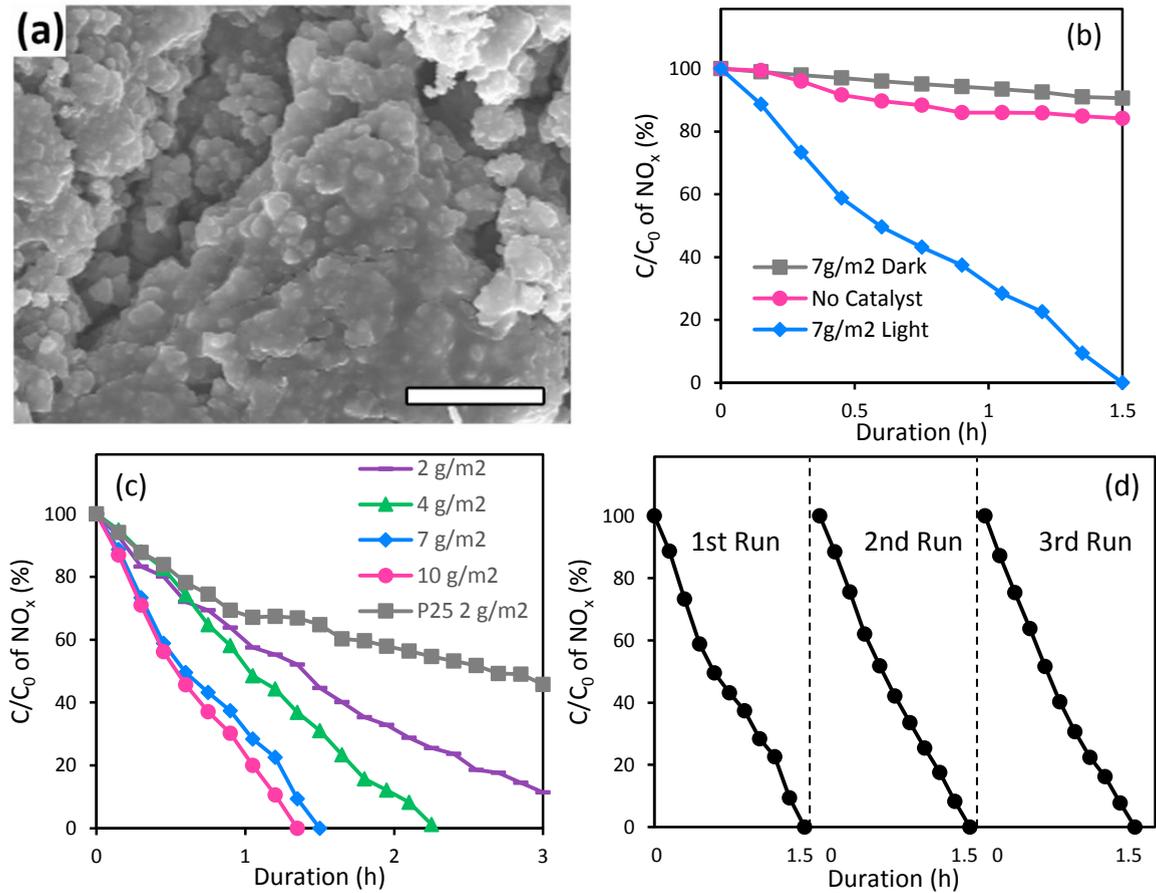


Fig. 3. C-TiO₂ functionalized asphalt: (a) SEM image of the 7 g/m² sample, Scale bar: 10 μm; (b) Verification of the photocatalytic NO_x degradation; (c) Comparison of photocatalytic performance among different C-TiO₂ loadings and P25; (d) Repeatability of the C-TiO₂ photocatalytic asphalt NO_x degradation. Temperature: 30 °C; RH: 38%; Sample Area: 0.09 m²; Original NO_x Concentration: 400 ppb.

286.4 ppb/h. The photocatalytic degradation performance was verified by two control experiments, namely one set of asphalt sample without any photocatalysts (Pink curve in Fig. 3(b)), and the 7 g/m² sample under dark conditions (Grey curve in Fig. 3(b)). These control experiments show negligible NO_x concentration drop over time, and confirm that the NO_x is actually degraded by the photocatalytic effect of the C-TiO₂. In order to find the optimal loading of the C-TiO₂ photocatalyst, asphalt samples with different loadings of photocatalysts were studied. The results are shown in Fig. 3(c). From 2 g/m² to 7 g/m² loadings, the photocatalysis performance increases significantly (118.07 ppb/h to 286.4 ppb/h), which can be explained by the increased density of reaction sites. However, when the photocatalyst loading was increased to 10 g/m², the performance showed only slight improvement (319.9 ppb/h). The improvement in performance could not meet the added cost. Moreover, when the photocatalyst loading is over 10 g/m², the colour of the asphalt surface becomes very bright. This could affect the drivers' judgement of the road signs thus result in safety risks. Therefore, in this case, the optimal loading of the photocatalyst should be around 7 g/m². We have also compared the C-TiO₂ with the traditional P25 photocatalyst. As shown in Fig. 3(c), the 2 g/m² P25 loaded asphalt sample also shows some NO_x degradation activity and degraded over 50% of the NO_x within 3 hours. This activity is due to the UV component of the light source. The same loading C-TiO₂ demonstrates clearly better performance owing to the visible light activity brought about by the carbon modification.

To test the repeatability of the photocatalytic NO_x degradation performance of the C-TiO₂ loaded asphalt, repeated test on the 7 g/m² sample's NO_x degradation was carried out. The results are shown in Fig. 3(d). Three runs of the

experiment were conducted, and the NO_x can be totally degraded within 1.5 hours every time. This clearly shows that a complete reuse cycle is possible for the C-TiO₂, which proved to be very stable all the three consecutive photocatalytic runs for all the three batches used, and suitable for continued reuse.

4. Concluding Remarks and Outlook

In this work, we have presented a novel visible-light-active carbon modified TiO₂ functionalized asphalt for photocatalytic removal of vehicular NO_x. The C-TiO₂ photocatalyst demonstrated superior photocatalytic activities to the conventional P25. The C-TiO₂ photocatalyst was suspended in DI water and sprayed onto asphalt surfaces, followed by a heat treatment, resulting in partial embedment of the photocatalyst particles in the asphalt surface. The C-TiO₂ loaded photocatalytic asphalt demonstrated outstanding NO_x removal performance under simulated sunlight. The optimal sample can degrade 400 ppb of NO_x within 1.5 hours. It was also shown that for the same loading, the C-TiO₂ exhibited better performance than traditional P25. The cost of the spray-coating method for real world applications is estimated as US\$1-3 per square meter. Mass production of the C-TiO₂ might possibly further reduce the cost.

We are now preparing for real-world road tests. A section of asphalt paved road in New Territories, Hong Kong S.A.R. has been reserved for conducting the test. The real-world activities as well as durability of the photocatalytic asphalt can be thus evaluated.

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