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REVIEW

Toward sustainable roads: a critical review on nano-TiO_2 application in asphalt pavement

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Abstract

Among nanomaterials, nano-TiO_2 has shown the potential to improve the rheological properties of asphalt binders, and mechanical and durability properties when used in the mixture phase. These improvements include fatigue resistance, high-temperature performance, aging resistance, and moisture susceptibility. In addition, nano-TiO_2 is known to have remarkable photocatalytic properties, which can lead to pollutant degradation and better air quality. Besides, nano-TiO_2 has the potential to reduce the pavement surface temperature by reflecting the UV rays of the sun and increasing heat dissipation, which may lessen the urban heat island adverse effects on the environment. These interesting features of nano-TiO_2 can be attributed to its remarkable physical and chemical structure and properties. To cast light on these different outcomes of using nano-TiO_2 in asphalt pavements, this article provides a critical review of the rheological, mechanical, durability, and environmental impacts of incorporating nano-TiO_2 into asphalt pavements, and how the chemical properties of nano-TiO_2 are related to these effects. This article also reviews the photocatalytic and pavement cooling performance of nano-TiO_2-modified asphalt pavement to optimize its environmental benefits. Furthermore, the article provides a critical discussion investigating the challenges and potential downsides of using nano-TiO_2 in asphalt pavement, offering helpful discernments for future research and application in the pavement industry.

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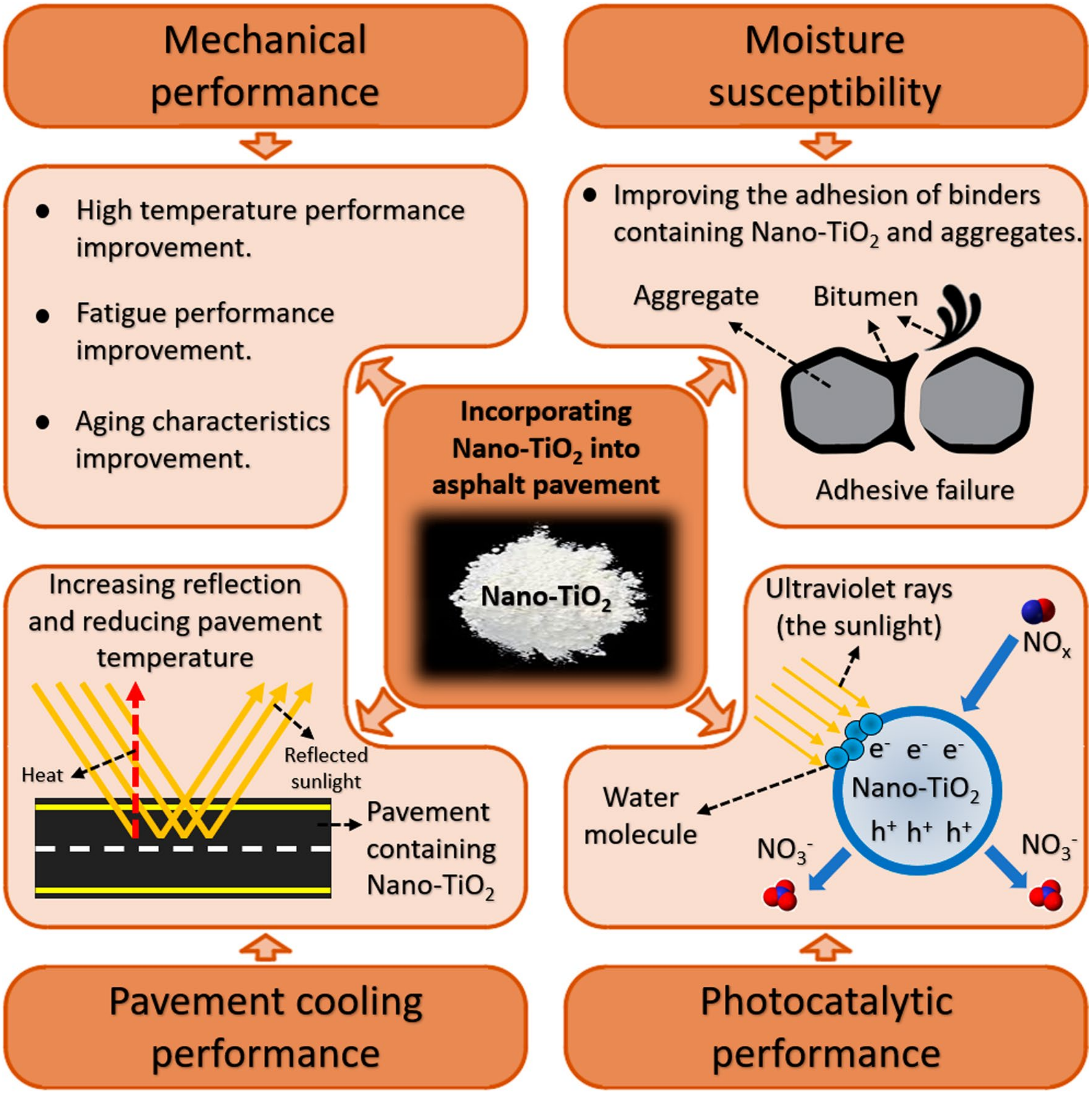
Graphical abstract



Keywords Nano-TiO_2 · Asphalt pavement · Air pollution · Photocatalytic performance · Urban heat island · Cool pavement

Introduction

Growing concerns regarding the climate change effect and other environmental troubles have led the world toward developing sustainable infrastructure [1, 2]. One of the promising development methods is incorporating nanomaterials into road pavement, which enhances durability and reduces the maintenance needs of this infrastructure [3]. Since road pavements are crucial for sustainability implications, researchers are exploring the application of nanomaterials to improve the mechanical performance and other properties of pavement materials like asphalt mixtures [4]. Among these nanomaterials, nanotitanium dioxide (TiO_2) has shown positive outcomes for enhancing the properties and performance of asphalt mixtures, which make it an eligible nanomaterial for asphalt pavement applications and construction [4, 5].

Nano-TiO_2 has also been commonly used in asphalt pavement for degrading vehicle exhaust pollutants [6]. The combustion of fossil fuels in vehicles releases a range of pollutants, which are significant contributors to air pollution and raise serious concerns for global health [7, 8]. Nano-TiO_2 unique photocatalytic properties can efficiently degrade the pollutants onto asphalt pavement and improve air quality [9, 10]. Also, the lighter color of nano-TiO_2 may increase the UV reflection and lower the pavement temperature, resulting in a cooler pavement surface [11]. This lower temperature of asphalt pavement can lead to mitigating urban heat island effects [12]. These environmental outcomes of nano-TiO_2 incorporation into asphalt pavement and its effects on performance enhancement have drawn the attention of the research and construction field [13].

It has been previously discussed in recent related studies that nano-TiO_2 can be obtained through environmentally harmful sulfate or chloride processes, and nano-TiO_2 has a larger surface, smaller diameter, and lower opacity compared to normal TiO_2, making it potentially advantageous for improving the rheological and mechanical performance of modified asphalt binders and mixtures [14–16]. Also, the photocatalytic performance of TiO_2-modified asphalt pavement through different incorporation methods has been discussed in previous studies [17]. However, several gaps exist in this field, including studying the effects of different nano-TiO_2 polymorphs on the properties of the pavement, rheological and mechanical properties of the asphalt binder and mixture, aging resistance, the relationship between chemical modification and asphalt performance after incorporating nano-TiO_2, factors affecting nano-TiO_2-modified asphalt pavement photocatalytic performance, and cool pavements for urban heat island mitigation. Also, the comparison between nano-TiO_2 and typical TiO_2 is missing to justify their applications in pavement construction.

To focus on the mentioned gaps and show a better insight, this study aims to give a critical review of the nano-TiO_2 application in asphalt pavement and its effect on performance and environmental impacts. Accordingly, an introduction to nano-TiO_2 has been given to understand better its chemical characteristics and relationship with the modified asphalt performance. Then, incorporation methods and probable chemical interactions between asphalt binder and nano-TiO_2 are discussed. This section is followed by the rheological and mechanical performance review of nano-TiO_2-modified asphalt binder and mixture. Lastly, the environmental performance of using nano-TiO_2 in asphalt pavement, including photocatalytic performance and urban heat island mitigation, has been evaluated to develop better sustainability. Figure 1 provides a visual overview of the topics presented in this article.

Introduction to TiO_2 and nano-TiO_2

Titanium is a light metal with a white-metallic color. Pure titanium is not soluble in water, but it can be dissolved in concentrated acids [18]. TiO_2 is the most stable oxide of titanium [19]. Moreover, TiO_2 elemental composition is 59.95% titanium and 40.05% oxygen [20]. The distinctive properties of TiO_2 can be directly attributed to its polymorphic form, which, in turn, is mainly dependent on the preparation method and post-fabrication heat treatment [21]. Titanium dioxide naturally exists in four polymorphic forms, including anatase, rutile, brookite, and the most uncommon one, TiO_2 –B [22].

Figure 2 shows the crystal structure of TiO_2 polymorphs and field emission scanning electron microscopy (FE-SEM) image of anatase and brookite. Both rutile and anatase have tetragonal crystal structures, while brookite has an orthorhombic one [23]. Rutile is the most thermally stable phase, and other phases will transform to rutile by heating, while brookite is the least stable polymorph of TiO_2 and is difficult to synthesize [24]. Anatase has a higher surface area compared to rutile due to its more open crystal structure and higher number of exposed surface sites [25]. The FE-SEM images are used to assess the distribution and dispersal of different compounds and changes in the surface morphology of the samples [26]. For nano-TiO_2 samples, they show the presence of nanocrystalline domains in rutile and dense nanocrystalline at the surface of anatase, but the surface of rutile is relatively smoother than that of anatase [27].

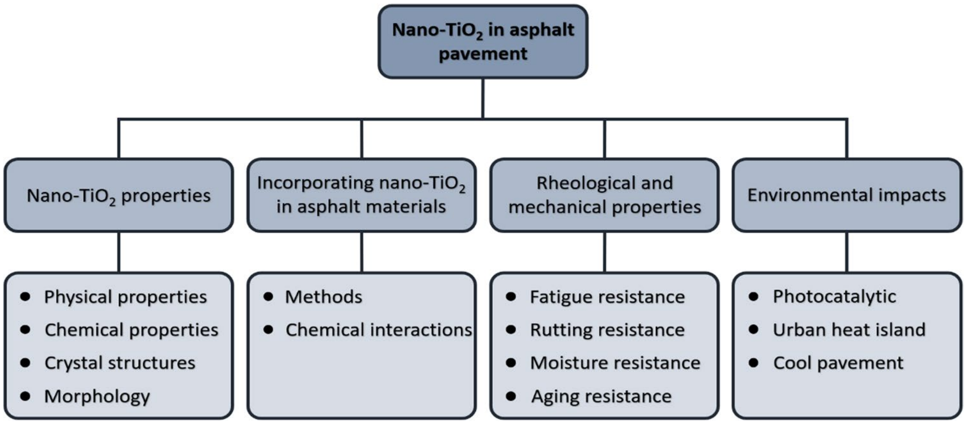


Fig. 1 Schematic view of the subjects reviewed in this study

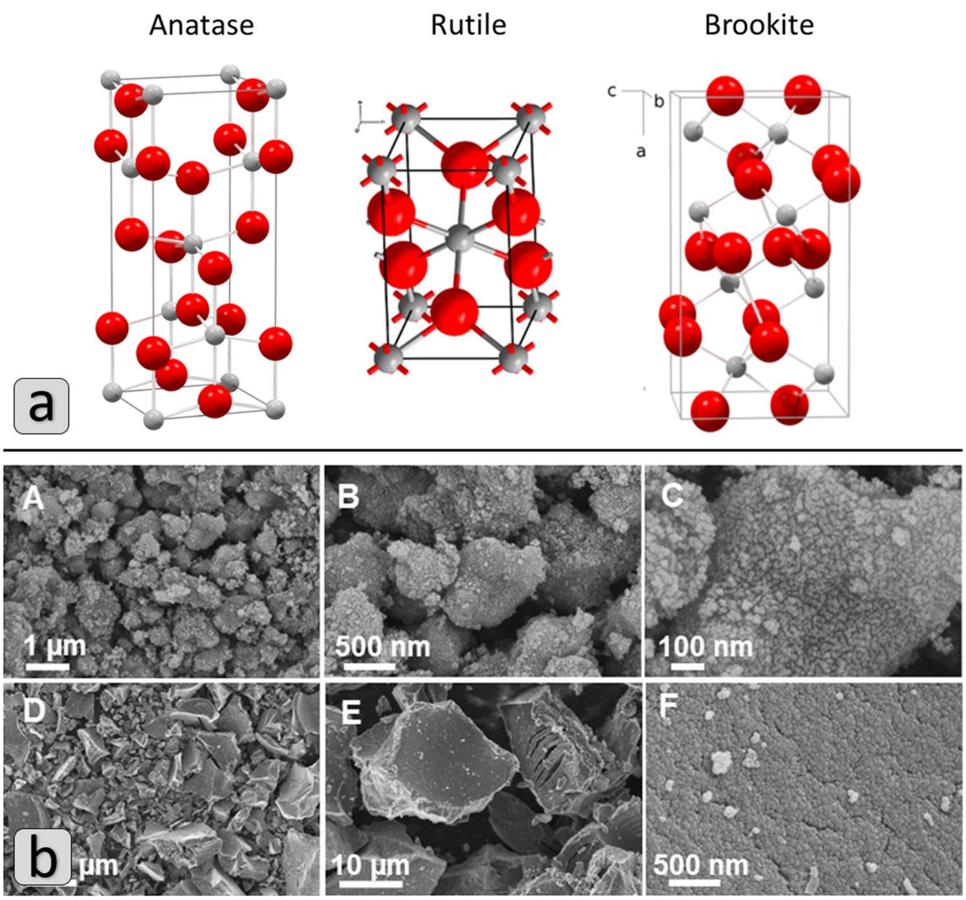


Fig. 2 **a** Crystal structures of TiO_2 polymorphs [25] **b** FE-SEM images of anatase **(A–C)** and rutile TiO_2 **(D–F)** at different magnifications [27]

Thus, it can be predicted from FE-SEM images that anatase can have better photocatalytic performance than rutile. Additionally, due to the higher surface area and reactivity of anatase, which can allow it to form stronger bonds with asphalt molecules, it may be better for improving asphalt rheological and mechanical properties. However, due to the higher thermal and chemical stability of rutile, the optimum proportions of nano-TiO_2 polymorphs for optimum rheological, mechanical, and photocatalytic performance should be evaluated.

Nano-TiO_2 is a form of TiO_2 with nanometer-ranged particle size (typically less than 100 nm) [28]. This size reduction leads to increased surface area and enhanced reactivity [29, 30]. These features result in an improvement in asphalt pavement properties, including mechanical and photocatalytic performance [31, 32]. However, the smaller particles raise concerns about the environmental impacts of utilizing and disposing of this material [33]. The focus of this study is on nano-TiO_2 incorporation in asphalt pavement and its comparison with typical TiO_2.

Incorporating TiO_2 particles into asphalt materials

Application methods

The methods of nano-TiO_2 application in asphalt pavement are critical in determining the effectiveness of the modified pavement [34]. Generally, these incorporation methods can be divided into direct mixing method (i.e., binder modification) and pavement surface applications (coating method and spraying method) [34, 35]. Figure 3 shows the different incorporation methods of TiO_2 and nano-TiO_2 into asphalt pavement in both laboratory and field areas. It should be noted that the figures for field incorporation methods are related to typical TiO_2, and nano-TiO_2 field incorporations need more advanced techniques.

For the surface spraying method, pretreatment of the pavement surface is important for preparing the surface for better spraying efficiency [38, 39]. One of the most

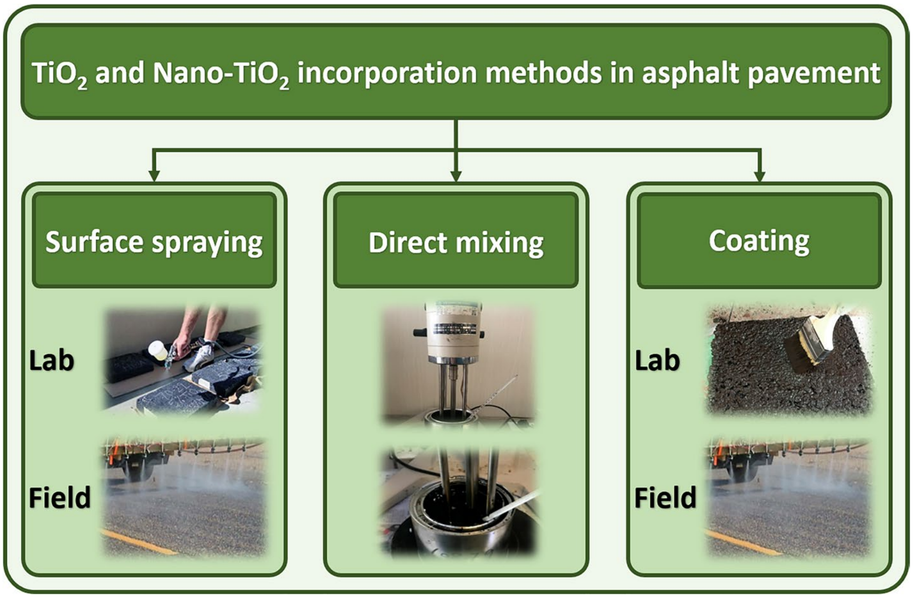


Fig. 3 Methods of incorporating TiO_2 and nano-TiO_2 into asphalt samples and pavement [35–37]

important parts of the spraying method is the solvent of TiO_2, which makes it possible to spray. Liquid solvents can directly solve the TiO_2 particles and be used as spraying emulsions, while solid solvents should be used with water for spraying [40–42]. Post-caring and treatment of the surface is mainly optional and is mostly related to the case.

For the coating method, the procedures are more complicated and require strong solutions to ensure the fluidity and dispersion of nano-TiO_2 coating [43, 44]. It has been previously studied that the coating photocatalytic performance significantly improves with the increase of nano-TiO_2 content and spraying amount up to 8% and 400 g/m^2, respectively, and the recommended maximum spraying amount is 550 g/m^2 to maintain skid resistance because excessive dosage thickens the oil membrane, reduces skid resistance, and is unsafe and uneconomical [35].

However, based on the literature review, the surface spraying and coating methods are not well and clearly distinguished in the studies. Although in this study these two methods are separated, some may find these methods similar, especially in field application. However, the focus of this study is to evaluate the effect of nano-TiO_2 addition to asphalt binder on the chemical, rheological, and mechanical properties, as well as its environmental comparison with surface application of nano-TiO_2 in asphalt pavement.

Chemical or physical interactions of asphalt binder with TiO_2 and nano-TiO_2

The addition of TiO_2 and nano-TiO_2 to asphalt binders as modifiers may change the functional group percentages in the asphalt matrix. Thus, studying the chemical behavior and modification mechanism of incorporating these materials into asphalt pavements is necessary. Fourier transform infrared spectrum (FTIR) is a method to evaluate chemical changes and performance evaluation in materials, especially asphalt binders [45–47]. Also, it can be used to examine the aging phenomenon of asphalt materials, which is due to the chemical changes in the asphalt matrix [48].

By the addition of 1–5% TiO_2 (80% anatase, 20% rutile) and conducting FTIR on modified asphalt samples, it was indicated that increasing TiO_2 content results in increasing absorbance in the wavelengths of below 700 1/cm [49]. Another study, in which FTIR was conducted on the UV-aged samples of the addition of 5% TiO_2 (80% anatase, 20% rutile) to asphalt binder, showed more ester carboxyl functional groups, which showed more progress in aging, and it was shown that there were some significant peaks at below 700 1/cm wavelengths in the spectrum [39]. In another study, FTIR was conducted on the addition of 0.5–10% nano-TiO_2 (80% anatase, 20% rutile) to transparent asphalt samples, and it was shown that the peaks in the spectrum were about 1300 1/cm and below 1000 1/cm wavelength, which shows an increase in aliphatic groups, and no long chains were observed [50].

It should be noted that the peaks beneath 1000 1/cm wavelength can correspond to the polyaromatic groups [47]. Besides, asphaltenes are polyaromatic and heavy compounds in oil reservoirs and asphalt binders [51]. Thus, it can be concluded that the peaks in the spectrums may correspond to more asphaltene content by the addition of TiO_2 to asphalt binder.

Figure 4 shows spectrums of nano-TiO_2-modified binders (binder 50/70) with different nano-TiO_2 content, which indicate no chemical alteration but more absorbance in the wavelengths of between 2800 and 3000, 1200 and 1600, and

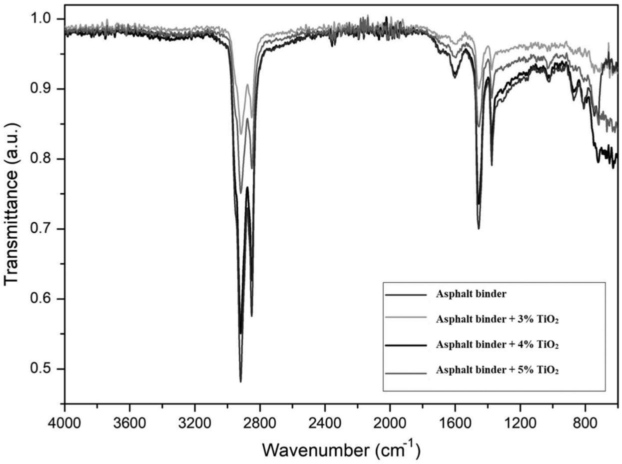


Fig. 4 FTIR spectrum of nano-TiO$_2$-modified asphalt binder [54]

beneath 1000 1/cm. It has been indicated that differences at wavenumbers of 3000–4000 and 700–900 1/cm can be referred to asphaltenes [52]. More asphaltene content leads to more stiffness and elasticity of the asphalt binder and decreases the high-temperature susceptibility [53]. Also, saturate–aromatic–resin–asphaltene (SARA) analysis on the addition of 5% TiO$_2$ to asphalt binder showed an increase in asphaltene and resin and a reduction in aromatic content [39].

Findings may indicate that the TiO$_2$ and nano-TiO$_2$ modification of asphalt binder is related to physical changes, and no new functional groups are created. However, the exact effect of nano-TiO$_2$ on the rheological and mechanical properties of asphalt materials has to be examined.

Mechanical and rheological performance of nano-TiO$_2$-modified asphalt binder and mixture

Fatigue resistance

Repeated vehicular loads contribute to the most common pavement cracking type, fatigue cracking [55]. Nano-TiO$_2$ can form strong interfacial bonding with the asphalt binder molecules, enhancing adhesion between the binder and aggregates [56]. This effect leads to a more durable asphalt pavement capable of withstanding repetitive stress and strain from traffic loading [57]. Table 1 reviews the fatigue resistance of asphalt binders and mixtures after the addition of nano-TiO$_2$. It has been indicated that in almost all cases, the addition of nano-TiO$_2$ can have an enhancing influence on the fatigue lives of conventional binders and mixtures. Also, the addition of other materials like nano-SiO$_2$, multiwalled carbon nanotube (MWCNT), and CaCO$_3$, along with nano-TiO$_2$, can heighten the enhancement of fatigue life caused by this nanomaterial [58–60].

High-temperature performance

Asphalt pavements are constantly exposed to high temperatures, which have recently increased due to the effects of climate change [68, 69]. Thus, it is necessary for binders and mixtures to have great performance against rutting [70]. Incorporated in asphalt pavement, nano-TiO$_2$ can act as a thermal barrier, reflecting a significant amount of solar radiation, reducing the absorption of heat by the pavement surface, and improving rutting resistance [11]. Also, nano-TiO$_2$ high surface area and reactivity lead to increased viscosity and stiffness of the binder at high temperatures, reducing the potential for rutting and permanent deformation [67]. Table 2 reviews the studies related to the high-temperature performance and rutting resistance of nano-TiO$_2$-modified asphalt binders and mixtures. It can be concluded that regardless of binder type, the addition of nano-TiO$_2$ as a modifier leads to improving rutting resistance. These results are compatible with the results taken from the chemical interaction of binder and nano-TiO$_2$, which more stiffness and asphaltene content, signs of better rutting resistance, were concluded after examining chemical experiments.

It should also be noted that using nano-TiO$_2$ along with other materials as binder modifiers may change the performance of the pavement. By incorporating 1–7% nano-TiO$_2$ and 0.4–2.8% nano-SiO$_2$ in a 60/70 binder, it was shown that the incorporation of these nanomaterials results in a higher complex modulus, lower phase angle, and lower permanent deformation [60]. In another study, a combination of 1% organic expanded vermiculite (OEVMT) and organic montmorillonite (OMMT) with 2% nano-TiO$_2$ resulted in better rutting resistance for the binders [71]. Also, using nano-TiO$_2$/CaCO$_3$ resulted in more rutting factor and higher rutting resistance [59]. The incorporation of TiO$_2$ and thermochromic (TC) powder met the maximum rutting depth by conducting Asphalt Pavement Analyzer (APA) rutting test [72]. Also, the addition of 1, 2, and 3% nano-TiO$_2$ along with 2, 4, and 6% thermoplastic polyurethane (TPU) to asphalt binder 80/100 showed better high-temperature performance than the base binder, and TiO$_2$ had a leading effect [73]. The combination of TiO$_2$, ZnO, and basalt fibers as modifiers in asphalt binder led to better resistance to permanent deformation, and nanoparticles also could compensate for the poor cracking resistance of the binder [74].

Low-temperature performance

Low-temperature cracking of asphalt pavement is the main distress of these pavements in cold regions [81]. Table 3 reviews the outcome of nano-TiO$_2$ addition on

Table 1 Fatigue resistance of nano-TiO_2-modified asphalt binders and mixtures

Asphalt type	Nano-TiO_2 dosage	Experiment	Result	References
Binder PG 64-22	5%	Linear Amplitude Sweep (LAS) (at 25 °C)	50% increase in N_f at 2.5% strain	[58]
Binder	3, 9, 15%	LAS (at 20 °C)	8, 19, and 39% increase in N_f, respectively (0% at 7.7% strain)	[61]
Transparent binder Kromatis 50/70	0.5, 3, 6, 10%	LAS	Except for 0.5% dosage, up to 22 and 39% decrease in N_f at 2.5 and 5% strain, respectively	[50]
Binder AC-60/70	2, 4, 6, 8%	LAS (at 25 °C)	61 to 364% increase in N_f at 2.5% strain level. 4 to 47% at 5% strain level	[62]
Binder 60/70	0.3, 0.6, 0.9, 1.2%	LAS	Except for the 1.2% dosage, there is a 15 to 30% increase in N_f at a 2.5% strain level. 17 to 33% at 5% strain level	[63]
Binder 50/70	3, 4, 5%	LAS (at 25 °C)	77 to 122% increase in parameter A, which shows greater resistance to accumulated damage	[54]
Mixture (AC-60/70)	2, 4, 6, 8%	Four-point Beam Fatigue (FPBF)	Increasing the dosage of nanomaterials results in a significant increase in the fatigue life	[62]
Mixture (AC 14 surf 35/50)	3, 6%	FPBF	3% dosage leads to the same fatigue resistance as a base binder, but 6% dosage decreases it	[64]
Mixture (binder 80/100)	2, 4, 6, 8, 10%	Indirect Tensile Fatigue (ITF)	6 to 21% increase in fatigue life by increasing the dosage	[65]
Mixture (binder 85/100)	3, 6%	ITF	Both dosages result in almost the same increase in fatigue life	[66]
Mixture (binder 60/70)	1, 3, 5, 7%	ITF	Increasing the dosage of nanocontent leads to the mitigation of micro-cracks and prevents their propagation	[67]

low-temperature cracking resistance of asphalt binders and mixtures. As it is shown, nano-TiO_2 addition increases asphalt viscosity and decreases its cracking resistance. However, all the samples met the standard requirements for cracking resistance, which shows that this nanomodification can provide acceptable low-temperature performance for asphalt samples.

Aging resistance

Asphalt pavements are exposed to oxidation and environmental impacts like ultraviolet (UV) rays, which result in asphalt aging. Decrease in durability and increasing potential of cracking due to more stiffness and brittleness are the results of asphalt aging [85]. Evaluating the aging resistance and behavior of these nanomodified binders is necessary for improving pavement performance. Table 4 reviews the related studies and shows that incorporating nano-TiO_2 in asphalt binders and mixtures leads to better aging resistance. Studies have shown that the lower aging resistance has an adverse effect on the fatigue cracking of the asphalt mixtures [86]. Thus, better aging resistance to nano-TiO_2-modified mixtures can lead to better fatigue resistance, which is in line with the results in the fatigue performance evaluation section.

It should be mentioned that the increase in the amount of TiO_2 nanoparticles, when used alone, has a better effect on aging resistance than using nanoparticles along with microparticles [87]. Nano-TiO_2 particles have a higher surface area and result in better adhesion and mechanical performance in the mixtures, which leads to better aging resistance [60]. Also, the higher surface area may lead to better and more evenly dispersion of the particles in the binder, but the potential agglomeration probability should also be considered [88]. In addition, using nano-TiO_2 can lead to more efficient photocatalytic and cool pavement performance, which is discussed in the latter sections. However, the chemical mechanism and exact difference of nano-TiO_2 and micro-TiO_2 effects on asphalt aging are areas for further investigation.

Rather than directly mixing with asphalt binder, TiO_2 can be used as a coating agent or surface spraying on the

Table 2 Rutting resistance of nano-TiO_2-modified asphalt binders and mixtures

Asphalt type	Nano-TiO_2 dosage	Experiment	Results	References
Binder	3, 6, 9, 12, 15%	Dynamic shear rheometer (DSR), Multiple stress creep resistance (MSCR)	Increasing nanocontent results in better high-temperature performance	[75]
Binder 60/70	1.5, 3.5, 5.5, 9%	DSR, MSCR	Nano-TiO_2 increases the rutting resistance of asphalt binder	[76]
Binder PG 64-22	5%	MSCR (at 64, 70, 76 °C) DSR (at 58, 64, 70, 76 °C)	Increasing G*/sin (δ) and decreasing J_{nr}	[58]
Binder AH-90	5%	DSR	G*/sin (δ) increases with the addition of nanocontent but decreases with the increase in temperature	[6]
Binder 60/70	0.3, 0.6, 0.9, 1.2%	DSR, MSCR (at 64 °C)	0.9% dosage has the most G*/sin (δ) and lower J_{nr} on the nonaged samples	[63]
Binder 60/70	2, 4, 6, 8%	MSCR (at 52 to 82 °C)	J_{nr} decreases with the increase of nanocontent	[62]
SBS-modified binder	1, 2, 5, 10%	DSR	At over 76 °C, G*/sin (δ) remains the same with increasing the nanocontent	[10]
Binder TZ-70	4, 5, 6%	DSR	5% dosage shows more increase in G*/sin (δ)	[77]
Binder (penetration 103)	0.5, 1, 1.5, 2, 2.5%	DSR (at 58 °C)	G*/sin (δ) increases with the increase of nanodosage	[78]
Mixture (SBS-modified binder)	5%	Rutting test	The modified mixture has a 45% more dynamic stability index	[6]
Mixture (AC-60/70)	2, 4, 6, 8%	Wheel track	Rut depth decreases with the increase of nanocontent	[62]
Mixture (SBS and HEA binder)	2%	Wheel track	Using nanocontent leads to higher dynamic stability due to the high surface volume	[79]
Mixture (SBS-modified binder)	1, 3, 5, 10%	Rutting test	Dynamic stability increases up to 40% by increasing nanocontent to 5%	[80]
Mixture (binder 60/70)	1, 3, 5%	Repeated Load Axial (RLA)	Increasing nanocontent leads to lower deformation, strain, and temperature susceptibility	[67]
Mixture (binder 60/70)	4%	Wheel track	The addition of nano-TiO_2 leads to lower rut depth	[5]

asphalt pavement. By adding 10, 25, and 50% TiO_2 as coating agents, atomic force microscopy (AFM) results showed that the modified binder had a smoother surface and less aging process [89]. Also, using 4 g/L of nano-TiO_2 as surface spraying showed better aging resistance for asphalt samples [87]. It has also been indicated that nano-TiO_2 can fill the microscopic defects in asphalt binders and lead to a more erosion and aging-resistant asphalt pavement surface [90].

Moisture susceptibility

Water penetration into the pavement layers has negative impacts on the pavement performance [96]. As mentioned before, nano-TiO_2 leads to better adhesion between the asphalt binder and aggregate particles [56]. By increasing this adhesion, the asphalt mixture can tolerate more freeze and thaw cycles and shows better moisture susceptibility [97, 98]. Also, due to the higher solubility of nano-TiO_2 in water than in asphalt binder, the moisture susceptibility of nano-TiO_2-modified asphalt mixtures can be ameliorated [99]. It has also been mentioned before that using nano-TiO_2 can reduce the effects of aging factors, which water penetration may be mentioned as one, on the asphalt pavement. It should also be mentioned that although nano-TiO_2 has a hydrophilic nature, it can be modified to hydrophobic, which may be used to enhance the moisture susceptibility of the modified or coated pavement [100, 101].

Table 5 reviews the moisture susceptibility of nano-TiO_2-modified asphalt mixtures. It is shown that by incorporating nano-TiO_2 into asphalt pavement, the Tensile Strength Ratio (TSR) of the mixtures is increased, which shows more durability and better water stability. In another study, it was

Table 3 Low-temperature cracking resistance of nano-TiO_2-modified asphalt binders and mixtures

Asphalt type	Nano-TiO_2 dosage	Experiment	Results	Reference
SBS-modified binder	5%	Bending Beam Rheometer (BBR)	Cracking resistance is reduced but still meets the Superpave specification requirements	[6]
RAP binder	4, 6, 8, 10, 12, 14%	BBR	All the samples met the requirements for creep stiffness and m-value	[82]
Binder PG 52–28 SBS-modified PG 64E-40	3, 5%	Modified BBR	The addition of nanomaterials leads to higher stiffness and lower cracking resistance	[81]
SBS-modified binder	1, 2, 5, 10%	BBR	Nano-TiO_2 has little effect on the low-temperature crack resistance of asphalt	[10]
HEA binder	2%	BBR	Adding nano-TiO_2 powders has no significant influence on low-temperature rheological Properties	[79]
Sasobit/SBS-modified binder	1, 3, 5%	BBR	Nanoparticles do not significantly reduce the low-temperature cracking resistance of binder	[83]
Mixture (SBS-modified binder)	5%	Pavement Performances Analysis	The nano-TiO_2-modified mixture has a better anti-cracking ability at low temperatures due to improving ε_B and S_B	[6]
Mixture (HEA and SBS binder)	2%	Three-point bending beam	The addition of nanomaterial to the HEA mixture leads to better-cracking resistance compared to the SBS mixture	[79]
Mixture	0.9%	Semi-circular bending	The addition of nano-TiO_2 leads to better performance in cracking and fracture mechanics	[84]

shown that the addition of 1, 3, and 5% nano-TiO_2 to semi-warm asphalt mixtures can lead to more viscosity and, therefore, more adhesion, which leads to better moisture susceptibility (about 16% enhancement). It was also found that this modified asphalt mixture shows a minimum of 75% in terms of Resilient Modulus Ratio (RMR) [102].

Optimum dosage

Based on the literature review, the evaluation approach of nano-TiO_2 in asphalt pavement in studies can be divided into two forms: evaluation of modified binder with binder tests and evaluation of mixture made by the modified binder with mixture tests. According to the results of fatigue performance, the suggested optimum dosage of nano-TiO_2 addition is 5% of the weight of binders for binder performance and 3% of the weight of binder for mixture performance, which is congruous with the results of some other studies [66, 67]. It can be seen that the results for binders and mixtures do not match exactly, which shows that the binder tests are not the definitive predictive parameters for asphalt mixture performance. For high-temperature performance, the optimum dosage of nano-TiO_2 is suggested to be 5% for both binder and mixture performance, which is consistent with other studies [77, 80]. For low-temperature performance, aging resistance, and moisture susceptibility, there has not been a clear result for the optimum dosage, but the suggested optimum dosage for other performance criteria (fatigue and high-temperature performance) can meet the minimum and improvement for these parameters, but more research is needed to justify the application. Thus, the literature review shows that the optimum dosage of nano-TiO_2 for binder modification to improve the rheological and mechanical performance of asphalt binder and mixture may be around 5% of the weight of the binder. However, this dosage can be vary in different projects due to the type of binder, aggregates, field conditions, and more importantly, the environmental impacts.

Environmental impacts of incorporating nano-TiO_2 into asphalt pavement

Nano-TiO_2-modified asphalt pavements are credited with many environmental benefits, such as purifying exhaust emission, mitigating the heat island effect, and reducing haze as well as noise [104, 105]. Therefore, the promising environmental benefits of nano-TiO_2, as well as the performance of the asphalt pavement, should be considered to accentuate its application. Photocatalytic performance and mitigating

Table 4 Aging resistance of nano-TiO_2-modified asphalt binders and mixtures

Asphalt type	Nano-TiO_2 dosage	Aging simulation tests	Rheological/mechanical tests	Results	References
Binder SK-70#	4%	Rolling Film-Thin Oven (RTFO)	Atomic Force Microscopy (AFM), FTIR	The samples showed smoother surfaces and a lower aging process	[91]
Bio-modified binder (AH-70)	1%	RTFO	RTFO (mass loss ratio)	Nanomodification results in lower mass loss and better aging resistance	[92]
Binder 60/70	0.3, 0.6, 0.9, 1.2%	RTFO, Pressure Aging Vessel (PAV)	DSR, MSCR, BBR, LAS	The modified binder showed better aging performance	[63]
Binder 50/70	3, 4, 5%	RTFO	FTIR, MSCR, LAS	TiO_2 incorporation resulted in better early aging resistance, lower mass loss, and aging delay	[54]
HEA binder and SMA mixture	2, 3, 4%	The Continuous UV Aging Test (CUAT), RTFO	DSR, BBR, Wheel tracking, Three-point flexible beam	Modification improved UV aging and short-term thermal-oxidation resistance	[79]
Binder A-70	1, 3, 5%	Homemade ultraviolet Radiation environment box	Softening point, Penetration	Nano-TiO_2 can improve the anti-ultraviolet radiation aging properties	[93]
Binder PG 64–16	3, 5, 7%	RTFO, PAV, UV light	DSR, RV, BBR	The modification did not accelerate the aging process	[94]
Mixture (Binder PG 64–22)	3, 5, 7%	Exposing to environmental conditions	FTIR, MSCR	By increasing nano-TiO_2 content, the mixture showed better aging resistance	[95]

Table 5 Moisture susceptibility of nano-TiO_2-modified asphalt mixtures

Asphalt type	Nano-TiO_2 dosage	Experiment	Results	References
Mixture (Binder AH-90)	5%	F-T splitting	TSR value increased from 86.7 to 91.6	[6]
Mixture (Binder 60/70 and limestone steel slag aggregates)	2, 4, 6, 8%	Indirect Tensile Strength (ITS)	With the increase of nano-TiO_2 content, the TSR value increased from 85 to 95 and from 82 to 88 for mixtures containing limestone and steel slag aggregates, respectively	[62]
Mixture (Binder 80/100)	2, 4, 6, 8, 10%	ITS	A mixture with 6% nano-TiO_2 showed the highest TSR value (around 90)	[65]
SMA mixture (Binder 60–70)	0.3, 0.6, 0.9, 1.2%	ITS	The Tensile Strength Ratio (TSR) increases from 77.8 to 82.4 with the nanomodification compared to the base binder value of 76.8	[103]

urban heat island effect, as two important benefits of using TiO_2 and nano-TiO_2 in asphalt pavement, are evaluated in the following sections.

Photocatalytic performance

Asphalt pavements are constantly exposed to vehicle exhaust pollutants. A suitable method to degrade these pollutants, which has become popular recently, is using TiO_2 in asphalt pavements. TiO_2 is a semiconductor material. Accordingly, in terms of solid-state physics, there is a large band gap equal to 3.2 eV for the anatase phase of TiO_2 and 3.02 eV for the rutile phase of TiO_2 between the conduction band (vacant band) and the valence band (filled with electrons). Due to this band gap, electrons in the valence band cannot move to the conduction band; however, in photocatalysts, light is the decisive factor in helping electrons to be excited to the conduction band (photoexcitation). TiO_2 particles applied to surfaces such as roads are highly exposed to UV rays, which contain photons. When TiO_2 absorbs a photon that encompasses the energy greater than or equal to its band gap, 3.2 eV or 3.02 eV, it will result in a process in which electrons from the valence band can be excited to the conduction band (e^-). In other words, this process will bring about electron–hole pairs (h^+) in the valence band [106]. Thereupon, these electrons (e^-) and holes (h^+) react with oxygen (O_2) and water (H_2O), respectively, to produce active superoxide anion (O_2^-) and hydroxyl radical (OH^*); this is because holes and electrons are powerful oxidizing and reducing agents in the process. Furthermore, the superoxide anion will react with $H+$ separated from the water to generate the HO_2^* radical. Finally, hydroxyl radical (OH^*) and HO_2^* react with organic air pollutants such as NO and NO_2, resulting in water-soluble nitric acid (HNO_3), which can be later washed away by rainwater or street sprinkling [42, 107]. Nano-TiO_2 also shows promising photocatalytic performance, which can be used for degrading pollutants in the pavements. Figure 5 shows an illustration of the photocatalytic performance of nano-TiO_2 addition in asphalt pavement.

Also, studies show that the TiO_2 particles can lead to CO_2 reduction photocatalytic performance, as UV light on TiO_2 catalysts produces separated electrons and holes, reacting with water and CO_2 to form oxygen, H radicals, CO, methane, methanol, and hydrogen, which lead to better efficiency when smaller particles are used [108]. Thus, the application of TiO_2 nanoparticles in asphalt pavement can show promising outcomes in reducing air pollution.

Several studies have scrutinized the photocatalytic performance of applying TiO_2 and nano-TiO_2 in asphalt pavements, which leads to pollutant degradation. Accordingly, a brief review of the studies related to photocatalytic pavements regarding the TiO_2 and nano-TiO_2 incorporation method is presented in Tables 6, 7, and 8. It is shown that different incorporation methods have alternative impacts on photocatalytic performance. This may create a challenge that whether binder modification or surface application can meet the optimum performance and environmental criteria. Also, it is shown that using nano-TiO_2 shows better photocatalytic efficiency comparing typical TiO_2. Moreover, materials like carbon, cerium, nitrogen, lanthanum, and Fe^{3+} are used as doping agents and CeO_2, steel slag, montmorillonite, AL_2O_3, rubber, rejuvenators, cationic surfactant, g-C_3N_4, polystyrene, activated carbon, pyrite, specularite, glass beads, polystyrene, Fe_2O_3, CeO_2, and WO_3 are used as additives to enhance photocatalytic performance.

However, the optimum proportion and dosage of nano-TiO_2 for the photocatalytic performance of asphalt pavement needs more research. For micro-surfacing applications, research indicated that the optimum dosage could be 11% of the weight of the binder, showing 40% NO_x absorption, as well as acceptable performance [109].

There are several factors that affect the degradation efficiency of the pavements, which are shown in Table 9. It

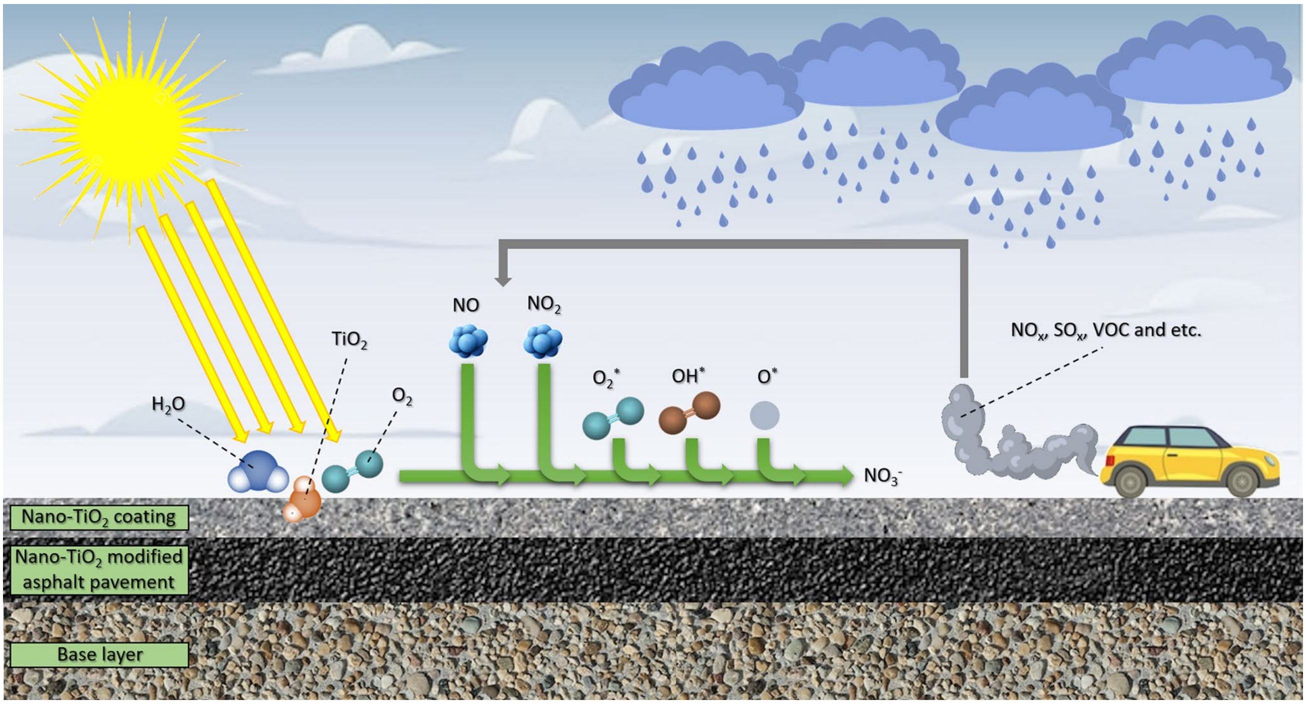


Fig. 5 A schematic view of the photocatalytic performance of incorporating nano-TiO_2 into asphalt pavement

Table 6 Photocatalytic performance of direct mixing incorporation of TiO_2 and nano-TiO_2 into asphalt pavement

Asphalt Materials	Level of Investigation	TiO_2 Type	TiO_2 Phase/Dosage by weight/ Doping Agent or additives	Findings	References
Asphalt mixture	Laboratory experiment	TiO_2	Anatase, (5%)	During 1 h of the experiment, the photocatalytic degradation of TiO_2-modified asphalt was greater than the neat one. The maximum value of the degradation rate of TiO_2-modified asphalt was one ppm/minute for CH and 1.1 ppm/minute for NO_x	[6]
Asphalt binder	Laboratory experiment	Nano-TiO_2	Nano-P25, (3%, 5%, 7%)	The highest capability was achieved with 5% nano-TiO_2 (39% degradation). However, the addition of 7% of nano-TiO_2 was recommended	[95]
Stone mastic asphalt mixture	Laboratory experiment	Nano-TiO_2	(0.6%), CeO_2 and steel slag	The photocatalytic efficiency of TiO_2 increased with adding CeO_2; however, the TiO_2/CeO_2 had a limited short-term photocatalytic activity (first 20 min) According to the Gray Target Decision method, the optimum content of TiO_2 and $CeCO_2$ was 7% and 0.6%, respectively	[110]
Micro-surfacing mixture	Field study in China, laboratory experiment	TiO_2	Rutile, Pyrite, and Specularite	The increase in the value of UV intensity and temperature would improve the purifying effect of pyrite- and specularite-TiO_2-modified micro-surfacing on NOx and COx. Pyrite and specularite are beneficial in improving the photocatalytic performance of TiO_2-modified micro-surfacing mixture	[111]
Asphalt mixtures (AC, PAC, OGFC)	Laboratory experiment	TiO_2	Anatase and rutile	The decomposition efficiency of asphalt mixture with anatase TiO_2 was superior to rutile TiO_2, and the content of 3.5% for TiO_2-anatase resulted in the best decomposition efficiency. Moreover, photocatalytic efficiency has a positive connection with the void volume of asphalt mixture, irradiance, and temperature	[112]
SBS-modified asphalt mixture (OGFC, AC)	Laboratory experiment	TiO_2	Anatase (2.5%)	The relative decomposition of the TiO_2-modified asphalt, which was over 20%, was higher than that of the neat asphalt The more air voids the TiO_2-modified asphalt had, the higher the relative decomposition would be	[113]
Micro-surfacing mixture	Laboratory experiment	TiO_2	Anatase, AL_2O_3 and Rubber	Rubber–titanium–aluminum materials had a higher NO_2 degradation than pure nano-TiO_2 The factors that increased the NO_2 degradation rate: small size of RTA, higher RTA content (4%), proper wavelength, moderate temperature (25C)	[114]
Neat and emulsified asphalt binder	Laboratory experiment	Nano-TiO_2	Anatase, g-C_3N_4	When the proportion of cyanurtriamide (the precursor of g-C3N4) to TiO_2 was 2:1, NOx degradation was at the highest value of 45% Emulsified g-C3N4/TiO_2-modified binder had a photocatalytic efficiency (max 4%) than the neat g-C3N4/TiO2-modified binder (max 0.5%)	[115]

Table 6 (continued)

Asphalt Materials	Level of Investigation	TiO_2 Type	TiO_2 Phase/Dosage by weight/ Doping Agent or additives	Findings	References
Epoxy Emulsified Asphalt Mixture	Laboratory experiment	Nano-TiO_2	Aanatase (10%, 20%, 30%)	Augmentation of TiO_2 content increased the degradation rate of gas exhausts, especially for NO and HC exhausts (maximum rate of 35% and 20%, respectively) The 5-nm particle size of nano-TiO_2 had a better NO and HC degradation performance than the other sizes The extension in the duration of the experiment increased the rate of NO degradation The average illumination of road surface should not be less than 60 lx or 40 lx due to its effect on the degradation performance	[116]
SBS-modified asphalt mixture	Laboratory experiment	Nano-TiO_2	Anatase (5%), Cationic surfactant	At first, NO_2 concentration was increased due to the high temperature. Thereafter, it began to decrease due to the temperature consistency	[10]
Asphalt binder	Laboratory experiment	TiO_2	Anatase, montmorillonite	The UV intensity of 2.6, 5.2, and 10.4 W/m^2 caused a maximum rate of 45%, 50%, and 55% for NO degradation, a maximum rate of 8%,9%, and 11% for CO degradation, and a max rate of 13%, 19%, and 17.5% for HC degradation	[77]
Asphalt mixture (AC, OGFC)	Laboratory experiment	Nano-TiO_2	Anatase, (30 g)	Within 1-h testing, the decomposition rate of OGFC-asphalt was higher than that of AC-asphalt. The highest decomposition rate of OGFC-asphalt was 50% for NO gas The photocatalytic effect of nano-TiO_2 OGFC-asphalt does not diminish after six months due to its stability	[117]
Asphalt binder	Laboratory experiment	TiO_2	Anatase, (3%, 5%, 7%)	The 5% TiO_2-modified binder had a NO removal efficiency of 23.9% with an average NO reduction of 101 ppb; however, the binder without TiO_2 had a NO removal efficiency of 1.6% and an average reduction of 7 ppb	[94]

Table 7 Photocatalytic performance of surface spraying incorporation of TiO_2 and nano-TiO_2 into asphalt pavement

Asphalt Materials	Level of Investigation	TiO_2 Type	TiO_2 Phase /Dosage by weight /Doping Agent or additives	Findings	References
Asphalt mixtures (AC, SMA, OGFC)	Laboratory experiment	TiO_2	Anatase, Nitrogen	The band gap in N-TiO_2 has been reduced, and it also caused a redshift in the absorption band, resulting in a better degradation performance The optimum contents of N-TiO_2 were 6% of emulsified asphalt by mass The N-TiO_2 is more suitable for SMA mixture than OGFC and AC mixtures	[118]
Asphalt binder	Laboratory experiment	Nano-TiO_2	Anatase, (3%, 6%, 9%, 12%, 15%)	The average NOx concentration was 4.26 ppm for the non-TiO_2 binder and 4.11 ppm for the 15% TiO_2-modified binder in the presence of the UV; however, both samples were not efficient in degrading NO_x in the absence of UV	[119]
Asphalt mixture	Laboratory experiment	Nano-TiO_2	Anatase, anatase + rutile (5%), Rejuvenator	The composition of the rutile and anatase phases of TiO_2 caused the proper degrading rates of 26.06 and 43.66% The asphalt treated with TiO_2 and rejuvenator had a lower degradation rate than the asphalt treated with just TiO_2	[39]
Asphalt mixture	Field study in Korea	TiO_2	Anatase, Carbon	According to the results from the field study, the overall NOx concentrations around the C-TiO_2 coated area were lower than the control area	[120]
Stone mastic asphalt mixture	Laboratory experiment	TiO_2	(0.4 g, 0.1 g), glass beads and polystyrene	Considering the no-abrasion condition, the TiO_2-modified asphalt mixture treated with the breath figure process with a higher amount of TiO_2 had the best photocatalytic performance; however, considering the abrasion condition, the glass beads-TiO_2-modified asphalt mixture had the best photocatalytic performance	[121]
SBS-modified asphalt mixture	Laboratory experiment	Nano-TiO_2	Anatase, (3%, 5%, 8%, 10%, 15%)	The cumulative degradation rate of exhaust gas was better when nano-TiO_2 content increased in the 0–8% range, and the spraying amount changed in the range of 0–333.3 g/m2	[35]

Table 7 (continued)

Asphalt Materials	Level of Investigation	TiO_2 Type	TiO_2 Phase /Dosage by weight /Doping Agent or additives	Findings	References
Asphalt mixture	Laboratory experiment	TiO2	Titanium Powder with tetra butyl titanate (TNBT) and distilled water, Nitrogen	The N-doped TiO_2 asphalt mixture had NO-degradation rate of roughly 27.6, 24.6, 16.3, and 13.8% under the irradiation of light wavelengths 330– 420 nm, 430–530 nm, 470–570 nm, and 590 680 nm, respectively, which these values are better than that of pure TiO_2	[122]
SBS-modified binder emulsion	Laboratory experiment	Nano-TiO_2	Nano-P25, Anatase, Carbon	The C-TiO_2 photocatalyst demonstrated superior visible light absorption ability between 400 and 700 (nm) wavelengths than P25 With the increase in the content of C-TiO_2 from 2 g/m^2 to 10 g/m^2, the photocatalysis performance increases significantly from 118.07 to 319.9 ppb/h	[38]
Asphalt mixture	Laboratory experiment	Nano-TiO_2	Anatase, Lanthanum	When the content of Lanthanum was 0.5%, the rate of NO degradation was in the highest value (65.72%) The ultraviolent irradiation had a better NO-degradation performance (max. = 40%) than the visible irradiation (max. = 20%)	[123]
Asphalt mixture	Laboratory experiment	TiO_2	TiO_2, (0.1 g, 0.4 g), polystyrene	The TiO_2-modified asphalt mixture treated with the breath figure process could decrease the NO concentration value from 1200 to 990 ppb. The TiO_2-modified asphalt mixture not treated with the breath figure process could decrease the value of NO concentration from 1200 to 1130 ppb	[42]
Asphalt mixture	Laboratory experiment, Field study in USA	TiO_2	Anatase, (2%)	According to field analysis, the concentration of NO in asphalt pavement with TiO2 increased in the first month of the experiment; however, it decreased after the first month	[124]

Table 7 (continued)

Asphalt Materials	Level of Investigation	TiO_2 Type	TiO_2 Phase /Dosage by weight /Doping Agent or additives	Findings	References
Asphalt mixture	Field study in the USA	Nano-TiO_2	Nanorods-anatase, (2%)	According to artificial intelligence modeling, the increase in wind speed and relative humidity negatively affected the effectiveness of NOx degradation; however, the increase in UV light intensity enhanced NOx removal efficiency	[125]
Asphalt mixture	Field study in USA, Laboratory experiment	TiO_2	Anatase, (2%)	TiO_2 effectively removed NO_x and SO_2 pollutants with 31–55% and 19.8% efficiency rates, respectively. These effects occurred at a coverage rate of 0.05 L/m^2 When the value of UV intensity was at the highest level (2.4 mW/cm^2), the removal efficiency of NO_x reached the highest value of 65%	[126]

should be noted that the reasons for better photocatalytic performance of anatase compared to other TiO_2 polymorphs can be as follows: larger band gap, differences in direct and indirect band gap, and better excitons mobility [134].

Also, studies have shown that the smaller TiO_2 particles can lead to better photocatalytic efficiency. In nano-TiO_2 epoxy emulsified asphalt mixture, the NO-degradation rate is increased from nearly 40% to 70% when particle size is reduced from 10–15 to 5 nm, but the change in CO_2 degradation is not significant [116]. For CO_2 reduction, laboratory studies have shown the optimum nano-TiO_2 particle size can be 14 nm, but using larger or smaller particle sizes than 14 nm can decrease the CO_2 reduction [108]. The controversial results may be due to the difference in nano-TiO_2 samples in the laboratory. It should be noted that although particle size reduction can be effective on photocatalytic performance, other parameters like surface area, voids, band gap energy, and other physical characteristics should also be considered because they can have more influence on photocatalytic efficiency [135]. Thus, the optimum particle size of nano-TiO_2 is an area of further investigation.

All in all, by considering these factors and using an appropriate dosage of materials, the highest efficiency and better photocatalytic performance can be achieved.

Urban heat island mitigation (cool pavement)

There has been a drastic increase in the world population in recent years, resulting in new megacities and existing ones becoming more populated. This has led to the emergence of the urban heat island (UHI) phenomenon, where anthropogenic heat, the blockage effect against urban ventilation, and the implementation of artificial materials result in warmer climatic conditions [139, 140]. Figure 6 shows the schematic view of UHI.

Cool pavements have been introduced for their capability of reducing the pavement surface temperature and mitigating UHI, and they have been categorized into three types: reflective, evaporative, and heat-storage-modified pavements [141, 142]. Reflective technologies such as reflective coating, light-colored pavements, and thermochromic materials are considered suitable strategies to reduce the negative effects of UHI on roads [143, 144]. Also, nanomodifications have been proposed for lowering the pavement temperature and mitigating UHI effects [145, 146]. Accordingly, TiO_2 particles can help reduce the UHI effect in urban areas, as they increase the reflectivity and reduce the temperature of materials, including asphalt coatings [147, 148]. Figure 7 shows the beneficial effects of using nano-TiO_2 in asphalt pavement regarding pavement cooling.

The mechanism behind pavement cooling by nano-TiO_2 particles can be attributed to higher reflectivity and better thermal conductivity. On the one hand, TiO_2 particles

Table 8 Photocatalytic performance of coating incorporation of TiO_2 and nano-TiO_2 into asphalt pavement

Asphalt materials	Level of investigation	TiO_2 type	TiO_2 Phase/Dosage by weight/Doping agent or additives	Findings	References
SBS-modified asphalt mixture	Laboratory experiment	Nano-TiO_2	Nano-TiO_2- Fe_2O_3, CeO_2	The oil degradation rate of nano-Fe_2O_3-TiO_2 and TiO_2-CeO_2 reached about 70% at the highest The nano-Fe_2O_3-TiO_2 photocatalytic coating material had a good application potential and could degrade oil pollution and NO effectively	[43]
Pervious asphalt mixture	Laboratory experiment	Nano-TiO_2	Anatase, (1%, 3%, 5%, 7%, 9%)	When the concentration of nano-TiO_2 composite photocatalyst (TCP) in the asphalt mixture reached 7%, the degradation efficiency would get 73.74%; however, the concentration of TCP reaches 9%, and the degradation efficiency is 74.5%, which shows that 7% concentration of TCP is the optimal value	[127]
Natural asphalt (asphalt Buton)	Laboratory experiment	TiO_2	Anatase	Ashburton TiO_2 composite could effectively adsorb the CO_2, CO, and HC as high as 600, 1500, and 760 ppm, respectively, in an exposure time of only 90 s for each one of the pollutants	[128]
Asphalt mixture	Laboratory experiment	Nano-TiO_2	Anatase, WO_3	The photocatalytic activities of WO_3/TiO_2 hybrid nanoparticles under UV light irradiation were superior to that of pure TiO_2 because WO_3 addition had widened the photocatalytic response range of TiO_2	[129]
Asphalt mixture	Laboratory experiment, Field study in Germany	TiO_2	Anatase (4%)	The asphalt coated with the innovative method could increase the NO-degradation rate (approximately 43%) without applying polish conditions; however, this rate decreased to 13% after applying polishing conditions	[130]
Asphalt mixture	Laboratory experiment, Field study in Germany	TiO_2	Anatase, rutile + anatase, (4%, 7%, 10%)	The anatase phase of TiO_2 with the high content of TiO_2 (99%) had a better NO-degradation rate than the rutile phase and anatase phase with lower content of TiO_2 as well as lower surface area In this innovative coating method, the asphalt modified with 10% of anatase TiO_2 in the illumination value of 46 W/m^2 had the best degradation performance in this experiment (roughly 80%)	[131]

Table 8 (continued)

Asphalt materials	Level of investigation	TiO_2 type	TiO_2 Phase/Dosage by weight/Doping agent or additives	Findings	References
waterborne epoxy resin fog seal	Laboratory experiment	Nano-TiO_2	Nano-P25 (3%, 5%, 7%, 10%, 13%)	The TiO_2 waterborne epoxy resin fog seal was very effective in decomposing NO pollutants from automobile exhaust. When the content of TiO_2 increased from 3 to 13%, the decompose ratio also increased from 80 to 86.6%	[132]
Polymer-modified asphalt mixture	Laboratory experiment	Nano-TiO_2	Nano-P25	The spray method had great advantages due to its high photocatalytic efficiency and its performance on the asphalt structure. This method reduced the application cost as well	[133]
Asphalt mixture	Laboratory experiment, Field study in China	Nano-TiO_2	Anatase	Nano-TiO_2 was capable of purifying vehicle emission pollutants in the actual traffic environments because its degradation rate ranged from 6 to 12% in the actual outdoor road traffic environments	[104]

absorb light at wavelengths of 275–405 nm and reflect light due to their high refractive index ($n = 2.6142$ at wavelength = 587.6 nm), which allows them to be used in sunscreens and photography applications, as well as pavement coatings for cool pavements [149, 150]. On the other hand, TiO_2 particles have, on average, a higher thermal conductivity than the typical asphalt mixtures [151, 152]. This may lead to better thermal conductivity of nano-TiO_2-modified asphalt pavement. However, the majority of studies have focused on the reflective properties, and the thermal conductivity may need further investigation.

A study showed 4–5 °C temperature reduction for asphalt samples and 8–10 °C for binders at the top surface of pigment-modified samples. Also, pigmented mixtures take 25–30% less time to cool down, proving their greater efficiency in heat dissipation. Moreover, red and white pigment-modified asphalt mixtures exhibit decreased rut depth of 35% and 15%, respectively, as compared to typical asphalt mixtures [151].

Furthermore, a study found that the improved thermal behavior of the nanomodified asphalt material could be ascribed to physical modifications that resulted in smoother and lighter-colored surfaces, leading to lower daily surface temperatures and a reduction of the UHI impact of the asphalt [153].

Also, a study found that the green coating with 15% titanium dioxide and 10% floating beads had the best cooling performance, and higher dosages of the coating resulted in better cooling effects [154]. Additionally, by adding 1% TC powder and 3% nano-TiO_2 as the fundaments of the thermochromic asphalt mixture, it was found that this addition leads to a reduction in surface temperature of up to 15 °C [72].

In another study, it was concluded that the use of nano-TiO_2 in asphalt can potentially increase its albedo and reduce pavement temperatures to address the UHI effect. However, micro-TiO_2 may have better reflectance than nano-TiO_2 and nano-ZnO [155]. Also, it was found that using 5–30% TiO_2 quantum dots in asphalt coatings can lead to a 12–17% increase in solar reflectivity compared to 3% for conventional samples [156].

It should be noted that although nano-TiO_2 can be effective in mitigating UHI effects, more research is needed to clarify and justify its application. The effect on TiO_2 particle size and incorporation method in pavement cooling efficiency, the improvement of reflectivity and thermal conductivity of nano-TiO_2-modified asphalt pavement by the addition of other reflective and conductive materials, and the optimum proportions on nano-TiO_2 particles need to be examined to reach better pavement cooling and in result, better sustainability.

Table 9 Factors affecting the photocatalytic performance of asphalt pavements

Factor	Effect	References
TiO_2 phase	Anatase has better photocatalytic performance than rutile	[17, 112, 134]
Size and number of TiO_2 particles	Smaller size and larger number of particles may lead to better degradation performance, but other parameters like surface area, voids, and band gap energy should also be considered	[114, 116]
Doping methods for preparing TiO_2	The doping methods at the level of preparing the nano-TiO_2-modified asphalt can enhance the photocatalytic performance	[122, 136]
Incorporation method	The spraying method has more advantages than the other methods	[41, 133, 137, 138]
Additives	Additives such as steel slag could be helpful in the degradation performance (only in short-term conditions)	[110, 114]
UV light	The increase in UV light intensity improves photocatalytic performance	[111, 125, 126]
Weather conditions	High relative humidity can decrease the photocatalytic performance	[41, 125]
Experiment duration	More duration leads to more degradation	[116, 124]

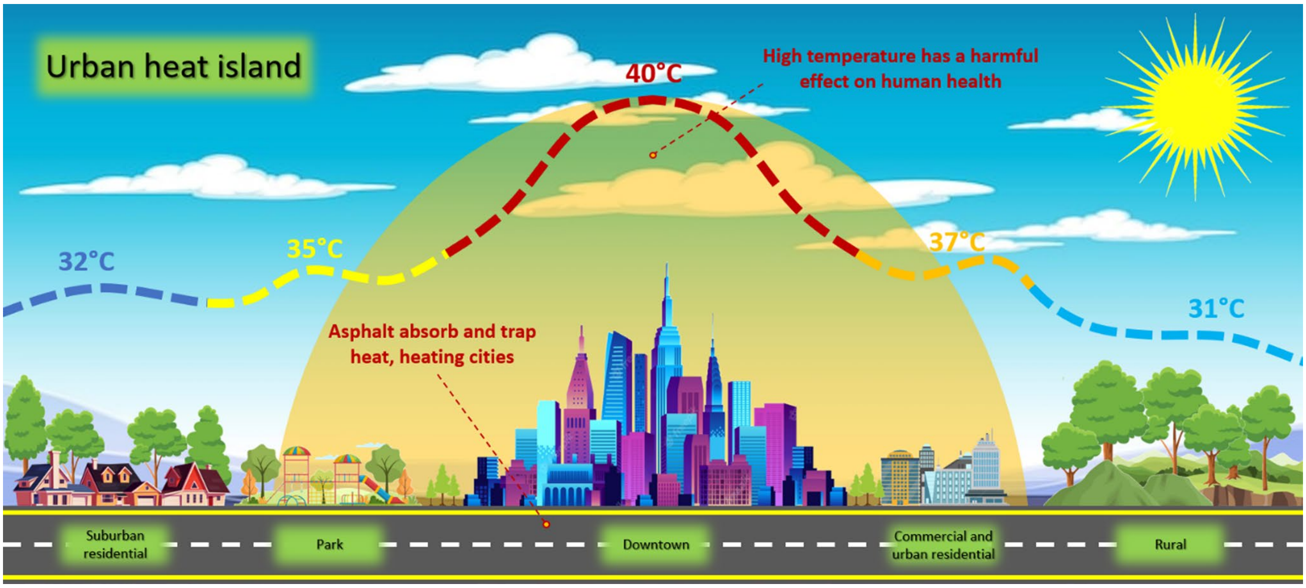


Fig. 6 Urban heat island profile

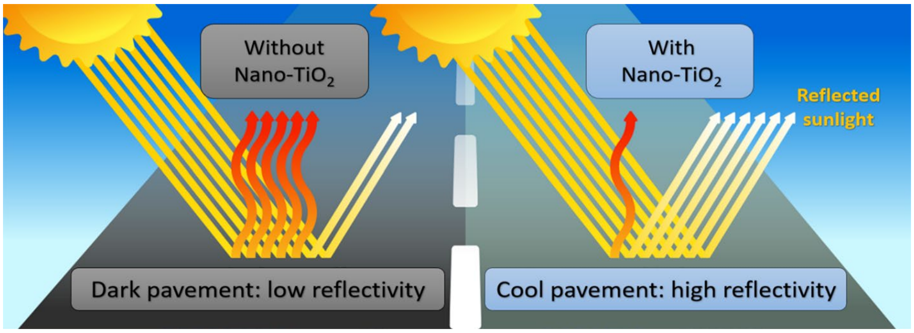


Fig. 7 Using nano-TiO_2 in asphalt pavement for cool pavements

Critical discussion and potential downsides

This literature review has focused on the application of nano-TiO_2 in asphalt pavement and its effects on the pavement performance. Regarding the application methods, direct mixing, surface spraying, and coating can be used to apply the nano-TiO_2 particles in asphalt pavement. The literature review has shown that by using nano-TiO_2 as an asphalt binder modifier, the high-temperature performance, fatigue resistance, aging resistance, and moisture susceptibility of the modified binder and mixture are improved. Also, nano-TiO_2 can lead to pollutant degradation by photocatalytic performance and urban heat island mitigation by cool pavement performance. However, there are challenges that need to be critically examined to investigate the viability and potential downsides of using nano-TiO_2 in asphalt pavement.

Although studies have shown improvements in rheological and mechanical properties of asphalt pavement by using nano-TiO_2, the usage of nano-TiO_2 is expected to also improve the photocatalytic and cool pavement performance in order to reach better sustainability. Thus, the selection of nano-TiO_2 optimum incorporation method (binder modification, surface application, or a combination of both) is a challenge, leading to future investigation. Also, due to the lack of related studies, there need to be research regarding the optimization in mixing (mixing speed, temperature, and time) and spraying (dosage and procedures) and the optimum dosage of nano-TiO_2 for maintaining performance criteria, environmental impacts, and long-term performance of the modified asphalt mixture.

Also, the fracture mechanics of the nano-TiO_2-modified asphalt mixtures should be considered. As mentioned before, nano-TiO_2 can lead to better rutting and fatigue resistance but has a low impact on the low-temperature cracking resistance. Thus, in order to clarify the fracture mechanics of the modified pavement, studying mode I, mode II, and mixed mode I/II is recommended. Related studies have shown that by 0.9% addition of nano-TiO_2, the fracture mechanics of the asphalt mixture in both vertical and angular cracks are improved, and the toughness of the mixture is increased [84].

Additionally, the effect on skid resistance of asphalt pavement after nano-TiO_2 addition is an area of concern. Accordingly, it has been indicated that with the increase of spraying and coating amount of nano-TiO_2, there is a significant reduction in skid resistance (in terms of reduction in the textural depth and friction coefficient), which can lead to lower driving safety and higher accident rate (halving the skid resistance leads to doubling the accident rate) [35, 44, 157]. For controlling the skid resistance, different amounts of nano-TiO_2 have been proposed, from 350 to 550 g/m^2, to control the textural depth from 0.55 to 1.4 mm, respectively [35, 44]. Therefore, there needs to be more research on the skid resistance of asphalt pavements modified with nano-TiO_2, mainly due to the different standards for textural depth and the effect of characteristics of nano-TiO_2 particles and the mixture properties on the skid resistance.

The field applications of nano-TiO_2 in asphalt pavement construction introduce practical challenges. The photocatalytic efficiency and properties of nano-TiO_2 field applications have been discussed before, but some challenges still remain. Using N-doped nano-TiO_2 on a selected field road to evaluate its durability when used as photocatalytic coating has shown that the photocatalytic coating can maintain its performance for approximately 13 months, which is caused by affecting and removal of the coating due to the traffic and rain [122]. In another field study in Germany, the TiO_2 particles were applied on an epoxy resin layer, which was coated on a selected test road, and the sample was cored and extracted from the pavement and then tested, which showed remarkable photocatalytic performance [131].

Although the field results demonstrate appropriate photocatalytic performance, the field conditions, including severe traffic loading repetitions and runoff due to rain, can affect the photocatalytic efficiency and pavement life span. The abrasion caused by traffic loadings can remove the modified layer form; the pavement surface can impair its performance. Also, the rehabilitation and surface treatment of the pavement are affected by the nano-TiO_2 coating, which may be removed from the surface and lose its photocatalytic efficiency due to these proceedings. Another concern regarding nano-TiO_2 particles is their probable aggregation chance due to their smaller size, which can cause larger particles and lower surface area. Achieving uniform dispersion and ensuring the stability of nano-TiO_2 particles throughout the asphalt mixture can be significantly important for better performance. These challenges can affect both the laboratory and field application, especially the field application due to the lower possible controls on the variables.

In addition, due to its smaller particle size, nano-TiO_2 can cause oxidative stress, DNA damage, and genotoxicity in living organisms, ultimately leading to a decrease in growth and reproduction, as well as affecting the microbial communities in soil and water, adversely affecting the overall health of the ecosystem [158]. The recommended exposure limits for fine TiO_2 (including pigmentary TiO_2) are 2.4 mg/m^3 by the US National Institute for Occupational Safety and Health (NIOSH) and 0.3 mg/m^3 for ultrafine TiO_2 (including nano-TiO_2) for up to 10 h per day during a 40-h work week, as a time-weighted average (TWA) concentration [159]. Due to these limits, care should be taken when using nano-TiO_2 in both laboratory and field experiments to avoid its harmful effects, especially when workers use it in asphalt pavement construction.

The reflective properties of nano-TiO_2-modified asphalt pavement are an area of both benefits and challenges. Studies have shown that by doubling the luminance of the pavement, the night to day accidents will decrease by 19% [160]. Although more luminance of asphalt pavement, especially during the night and in the tunnels, can lead to more safety and fewer accidents, the extra luminance and sun glare can result in more crashes [161]. Also, by reducing the texture depth of the asphalt pavement, the accident rate increases [162]. Because nano-TiO_2 addition can affect the micro- and macro-texture as well as the pavement surface color and reflectance, the side effects of the nano-TiO_2 reflective pavement need to be considered.

Contaminants leaching from asphalt pavements are an environmentally important concern [163]. Studies have indicated that nanoparticles can leach out and potentially contaminate water bodies or soil, raising concerns about the long-term environmental impacts [164]. For nano-TiO_2-modified asphalt pavement, there have not been adequate studies regarding the leaching characteristics. These pavements have different and unique leaching characteristics as they have nanomodified asphalt binder and its interactions with water infiltrating (the solubility of nano-TiO_2 in water) and other additives, as well as nanosurface coatings which is affected by runoff water. Therefore, the leaching potential of nano-TiO_2 particles from the asphalt pavement into the environment is an important area for further investigation.

Another important point is that although this study has focused on the application of TiO_2 particles in asphalt pavement, the usage of nanomaterials in concrete pavements has also been regarded. It has been shown that by using different nanomaterials, the performance and properties of the concrete mixture are improved [165, 166]. This can draw attention to the usage of nano-TiO_2-modified composite pavements and lead to further investigations for construction.

Also, for better sustainability approach, the environmental and economical assessment of nano-TiO_2-modified asphalt pavement should be considered. Two main tools for this approach can be defined as life cycle assessment (LCA) and life cycle cost analysis (LCCA). Although nano-TiO_2 has shown photocatalytic performance, which can lead to lower NO_x and CO_2 pollution (lower acidification and global warming potential in LCA), the initial process of nano-TiO_2 production can produce too much pollutants. Thus, the life cycle emission and pollution degradation of these pavements should be considered. For economic analysis, the initial cost of the nanomaterials can affect the life cycle cost of the pavement, which makes it very crucial to be examined. Also, the maintenance of these modified pavements is a challenge in performance, environment, and economic perspectives.

All in all, the application of nano-TiO_2 in asphalt pavement can show improvement in both performance and environmental aspects. But considering both benefits and challenges can lead to a better understanding of the potential advantages and disadvantages of nano-TiO_2-modified asphalt pavement. This approach requires a multicriteria decision making for researchers and pavement constructors. Thus, a comprehensive understanding of these critical aspects is necessary to assess the viability and sustainability of implementing nano-TiO_2 in asphalt pavement construction.

Conclusions and future research directions

This article presents an overview of the research in the field of incorporating nano-TiO_2 in asphalt pavement, emphasizing the chemical, rheological, mechanical, and environmental properties and effects. This article also aims to investigate and determine the possible chemical interactions, optimum dosage for nano-TiO_2, and factors affecting its performance by giving in-depth explanations. Below is a summary of some of the most important conclusions deducted from this review study:

1. Chemical analysis shows that nano-TiO_2 mainly consists of anatase and rutile polymorphs. FE-SEM images show that the rutile surface is smoother than anatase, which, along with differences in band gaps and better excitons mobility, may lead to better photocatalytic performance of anatase. Also, higher surface area and reactivity of anatase, which can lead to stronger bonds with asphalt molecules, may result in better rheological and mechanical properties.
2. FTIR spectrum shows that modification of asphalt binder with nano-TiO_2 may belong to physical reactions, and no chemical alteration is observed. FTIR and SARA analysis may show more stiffness and viscosity of the asphalt binder.
3. Rheological and mechanical assessment of nano-TiO_2-modified asphalt binder and mixture may show higher rutting and fatigue resistance due to more viscosity and stiffness. However, low-temperature cracking resistance may be weakened after modification but still meets the minimum criteria. Also, the long- and short-term aging resistance of nano-TiO_2-modified asphalt can be enhanced. The optimum dosage for nano-TiO_2 in rheological and mechanical performance is variable due to different conditions, but it can be suggested to be 5% of the weight of the binder to improve the characteristics of binders and mixtures.
4. The photocatalytic performance of nano-TiO_2 in asphalt pavement shows improvements, but it depends on many factors, including nano-TiO_2 phase, size and num-

ber of TiO_2 particles, a doping method for preparing nano-TiO_2, incorporation method, additives, UV light, weather conditions, and experiment duration. By optimizing these conditions, better efficiency for pollution degradation can be obtained.

5. Cool pavements have been introduced to mitigate the urban heat island effects on the environment by different mechanisms. Incorporating nano-TiO_2 into asphalt pavement can lead to higher reflectivity, lower surface temperature, and less time to cool down, which could mitigate the urban heat island effects.

Moreover, it is recommended that researchers focus on the points listed below for their future works.

1. Evaluating the different performance and effects of anatase and rutile nano-TiO_2, as well as their particle size, for better rheological, mechanical, and photocatalytic performance of nano-TiO_2-modified pavement.
2. Conducting more chemical tests on the modification of asphalt binder with nano-TiO_2 to acquire a better understanding of the possible reactions and predict the binder and mixture performance and aging resistance, as well as the possible dispersion conditions.
3. Optimum methods, proportions, and dosage of nano-TiO_2 incorporation in asphalt pavement for maintaining both the performance and environmental benefits.
4. Better evaluation of nano-TiO_2-modified asphalt mixture to highlight the possibility and performance of its utilization in future roads and, especially the long-term performance, skid resistance, and abrasion possibility.
5. Exploring the potential for using nano-TiO_2 to enhance the sustainability of asphalt pavement by conducting LCA and LCCA. However, efforts have been made to clarify this part, but no related results were found [167]. Key parameters for LCA may include raw material extraction, manufacturing, application, and disposal, focusing on environmental impacts. For LCCA, parameters encompass initial costs, maintenance, energy use, and long-term performance, evaluating economic aspects. A holistic view of the environmental and economic implications can be obtained by integrating these two methods.
6. Leaching characteristics of nano-TiO_2-modified asphalt pavements for clarifying the potential contaminants and their effects on the environment and human health.

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Data availability All information is sourced from previously published works and is available in the cited references.

Declarations

Conflict of 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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