Nitrogen-Phosphorus Co-Doped Graphene for Enhanced Flame Retardancy and Smoke Suppression in Asphalt

Xiaomin Ren*

Southwest JiaoTong University, Chengdu, Sichuan, 611756, China

*Andy030796264@outlook.com

Abstract

The increasing safety requirements in tunnel engineering have highlighted concerns regarding the flammability and toxic smoke emissions of asphalt materials during tunnel fires. To address these challenges, this study explores the use of graphene-based materials to enhance the flame retardancy and smoke suppression properties of asphalt. Reduced graphene oxide (RGO) was synthesized through an ascorbic acid reduction method and further surface-modified via nitrogen and phosphorus co-doping. The results show that the modified asphalt demonstrates superior flame retardancy and significantly reduces smoke emissions under high-temperature conditions. Compared to conventional flame retardants, the graphene-modified asphalt exhibits exceptional durability and low toxicity, meeting the stringent demands of tunnel and high-temperature environments. Despite these advancements, optimizing the dispersion, high-temperature stability, and durability of graphene in humid and elevated temperature conditions remains a key focus for future research. Further studies will aim to refine graphene production processes, explore the effects of alternative doping elements, and assess the long-term performance of the modified asphalt.

Keywords

Asphalt Modification; Flame Retardant; Smoke Suppression; Nitrogen and Phosphorus Doping.

1. Introduction

With the rapid advancement of highway construction in China, the number and scale of tunneling projects have increased significantly. By the end of 2014, statistics indicated that China had 12,404 road tunnels, with a total length exceeding 10.75 million meters [1]. As infrastructure development progresses, asphalt pavements are becoming more prevalent in tunnel projects because of their superior skid resistance, reduced noise levels, comfort, and ease of maintenance. However, the distinct conditions within tunnel environments pose unique challenges.

Asphalt materials pose a significant fire hazard due to their high flammability, leading to the rapid release of intense heat and the generation of toxic smoke when combusted. This combustion process results in the decomposition of hazardous substances, including sulfur oxides (SOx), volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides (NOx), among others[2]. Exposure to these harmful gases not only causes immediate damage to the respiratory system, skin, and eyes of construction workers, vehicle drivers, and tunnel occupants but also elevates the long-term risk of carcinogenic effects[3]. Furthermore, in the elevated temperatures of tunnel fires, the toxic smoke diminishes oxygen levels, hampers evacuation efforts, and complicates rescue operations.

Existing smoke suppression technologies and materials primarily focus on smoke control during the low-temperature construction phase, aiming to reduce smoke release during construction. However, they do not fully address the issue of toxic smoke generated by asphalt combustion during tunnel fires[4]. Furthermore, conventional compounded flame retardants, with increasingly complex formulations, exhibit poor water resistance and durability in the unique tunnel environment. As a result, they fail to meet the long-term service requirements of hot and humid conditions typical in tunnels[5]. Therefore, it is crucial to develop new asphalt materials with improved durability, reduced toxicity, and enhanced smoke suppression and flame retardancy. These materials should not only reduce smoke generation during tunnel fires but also be adaptable to the hot and humid conditions of tunnels, significantly enhancing tunnel traffic safety and protecting the health of construction and emergency rescue personnel. This research aims to overcome the constraints of existing smoke suppression materials in tunnel settings by integrating innovative graphene-based modifications into asphalt, to boost its flame retardancy and smoke suppression capabilities.

2. Relevant Theoretical Foundations

2.1 Common Types of Flame Retardant

Flame retardants prevent or suppress the combustion of polymers through physical methods (e.g., cooling) or chemical actions (e.g., releasing gaseous flame retardants). Research on fire-retardant asphalts began in the 1950s with halogen and phosphorus compounds, later expanding in the 1970s to include additives like metal hydroxides and intumescent agents for improved combustion resistance. As safety concerns grew, the use of flame retardants in asphalt applications increased. Ideal flame retardants should offer high resistance to flames, low toxicity, good thermal stability, and compatibility with asphalt[6].

2.2 Graphene Flame Retardant

In recent years, graphene has garnered considerable attention in the field of flame retardancy due to its remarkable physicochemical properties. Both graphene and its oxide (GO) exhibit a high aspect ratio, a large specific surface area, and a two-dimensional structure, which allow them to create an effective physical barrier on the material's surface, thereby reducing heat transfer and diffusion of gases. Furthermore, graphene's high thermal stability and chemical resistance make it a promising candidate for enhancing the flame retardancy of polymers and composites. However, the low catalytic charring efficiency of pristine graphene flakes limits their effectiveness in improving the flame retardant performance of composites. Therefore, enhancing the flame retardant efficiency of graphene, reducing the agglomeration of graphene sheets, and improving its compatibility with the matrix material through surface functionalization modification have become key areas of research in this field.

2.3 The Mechanism of Graphene Flame Retardancy

The flame retardant mechanism of graphene primarily depends on the barrier effect of its two-dimensional nanostructure. During combustion, graphene flakes create a physical layer on the material's surface, which restricts the penetration of heat and oxygen, thereby slowing the spread of combustion. Moreover, graphene can promote the formation of carbon layers during combustion, which helps reduce the rate of polymer matrix degradation. However, the thermo-oxidative stability of graphene in air is limited, and it tends to decompose when the temperature exceeds 600 °C [7]. Consequently, enhancing its high-temperature stability has become a key focus for improving its flame retardant effectiveness.

To address the inadequate thermo-oxidative stability of graphene, researchers have explored its modification through doping with flame-retardant elements such as nitrogen, aluminum, phosphorus, silicon and boron[8]. The introduction of these elements enables graphene to release inert free radicals during combustion, which helps disrupt the combustion chain reaction. For example, Baek improved the flame-retardant properties of graphene at high temperatures by doping it with phosphorus or aluminum[9, 10]. During combustion, phosphorus-doped graphene releases free radicals such as PO-, which interact with reactive radicals like H- and OH- in the flame, effectively terminating the combustion reaction. Furthermore, the pyrophosphates generated during phosphorus oxidation can form a protective layer on the surface, which helps to isolate oxygen and heat, thereby greatly improving the flame-retardant efficacy of graphene.

Another approach to enhancing the flame retardant effect of graphene is by compounding it with organic flame retardants. A synergistic flame retardant effect can be achieved by grafting flame retardants containing elements such as nitrogen (N), phosphorus (P), boron (B), and silicon (Si) onto the surface of graphene. For instance, Liao functionalized graphene using a one-step reduction method with DOPO (9,10-dihydro-9-oxa-10-phosphonobenzophenanthrene), which significantly enhanced the flame retardancy of graphene in composites. Similarly, Qian introduced P- and Si-containing compounds onto the surface of reduced graphene oxide (RGO) through the sol-gel technique, which notably increased the carbon residue yield and strength. These modifications improved the dispersion and moisture resistance of graphene, while preventing the issue of flame retardant dissolution in water, making it more suitable for flame retardant applications in hot and humid environments[11].

Research on the flame retardant application of graphene in asphalt materials has also been growing. Graphene oxide (GO) has proven to significantly enhance asphalt properties, including high-temperature resistance, fatigue resistance, and elasticity modulus. When combined with Sasobit, GO further improves the asphalt’s stability at high temperatures and its resistance to cracking at low temperatures, offering a novel approach to enhancing asphalt's flame retardancy under elevated thermal conditions. Graphene-based fire-retardant asphalt materials hold significant potential for applications in tunnels, bridges, and other transport infrastructures with stringent fire safety requirements.

3. Preparation and Surface Modification of Reduced Graphene Oxide Flame Retardants

This study adopted an environmentally friendly method to synthesize reduced graphene oxide (RGO) by using ascorbic acid as a non-toxic reducing stabilizer and agent. Ascorbic acid is a food grade additive with strong reducing properties and low environmental contamination. After the chemical reduction of graphene oxide, the RGO was surface-modified by incorporating varying proportions of urea and polyphosphoric acid. The modified asphalt was then characterized through physical and chemical analyses.

3.1 Preparation of Reduced Graphene Oxide

Currently, the most widely used method for synthesizing graphene is chemical reduction. This involves selecting a suitable reductant to reduce graphene oxide (GO, hereafter referred to as GO) to obtain single-layer or few-layer reduced graphene oxide (RGO). Since graphene obtained by introducing a reducing agent into the GO solution may contain residual heteroatoms, the presence of these heteroatoms can be problematic. Therefore, ascorbic acid was selected as the reducing agent, as it effectively removes oxygen-containing groups while minimizing the introduction of heteroatoms. The principle of GO reduction by the reducing agent is shown in the following figure.

The preparation process was as follows: 1 g of graphene oxide and 1 g of ascorbic acid were added to 1 L of deionized water, and the mixture was sonicated for approximately 2 hours. Raise the temperature of the solution to 60°C and maintain it for 6 hours. After cooling, the solution was filtered and washed with distilled water until the pH reached ≥ 6 to remove any remaining ascorbic acid. Finally, the resulting solid was vacuum-dried at 80°C for 12 hours.

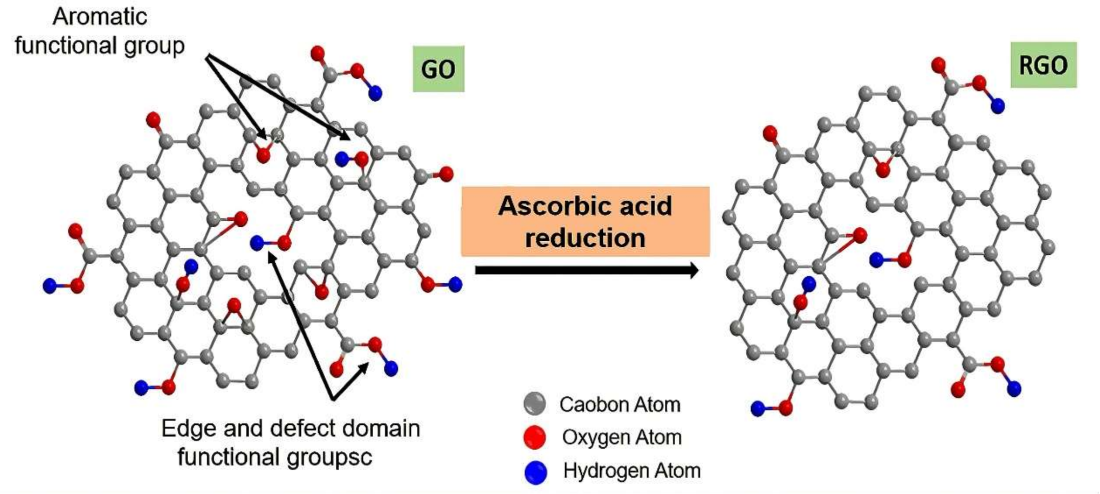

Fig. 1 Reduction principle of GO

3.2 Surface Modification of REDOX Graphene

Flame retardant-modified graphene was obtained through surface modification technology, which combines flame retardant-catalyzed carbonization with the nano and barrier effects of graphene. This modification not only enhances the flame-retardant efficiency of reduced graphene oxide (RGO), but also improves its dispersion and interfacial compatibility in the polymer matrix. This was achieved by grafting an organic molecular layer onto the RGO, using urea and polyphosphoric acid as the nitrogen and phosphorus sources for the modification, respectively[12].

Urea will decompose into NH3 and HNCO under conditions above 150°C. The HNCO produced combines with water to form NH3 and CO2, as represented by the following reaction formula.

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \tag{1}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{2}$$

To accelerate the reduction efficiency of polyphosphoric acid, concentrated phosphoric acid with a concentration of 98% was added as an auxiliary reducing agent during the preparation process, and the principle of reducing graphene oxide by the reducing agent is shown in Fig. 2.

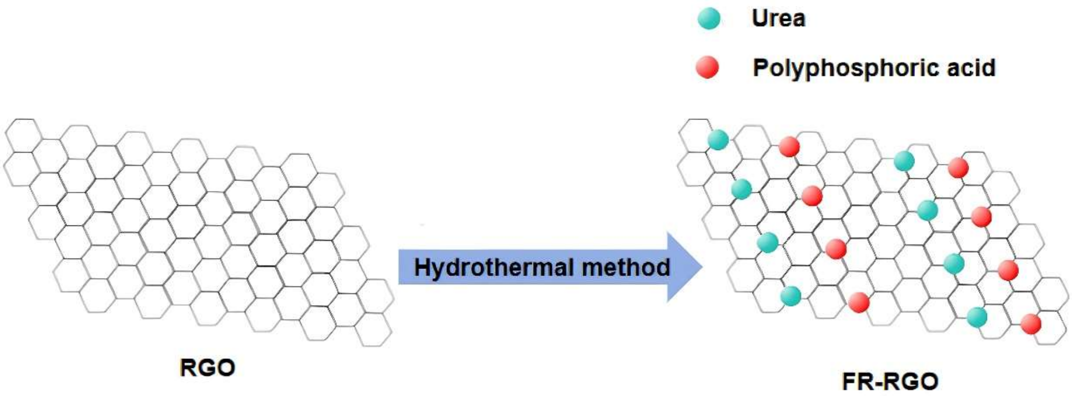

Fig. 2 Principle of surface modification of graphene flame retardants

The research investigates the use of a hydrothermal reactor to elevate the reaction temperature to 180°C in a confined space, enabling the complete reaction of nitrogen and phosphorus sources under hydrothermal conditions(Fig. 3)[13]. To manage the substantial gas production during the reaction and ensure that the solvent addition does not exceed 70% of the inner vessel volume, PN-graphene is synthesized using the hydrothermal method. The synthesis process involves the following steps: Graphene oxide and heteroatom sources (urea, polyphosphoric acid, and concentrated phosphoric acid) are dispersed in deionized water for 1 hour, according to the proportions specified in Table 1.

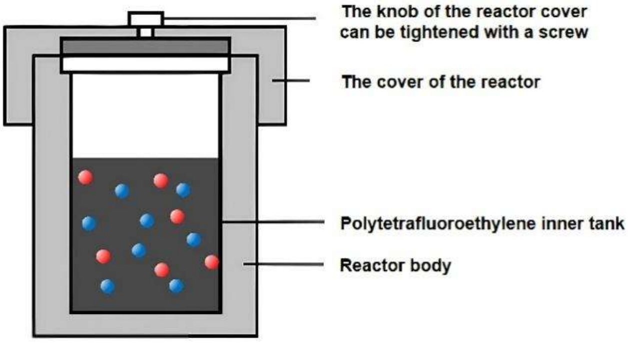

Fig. 3 The surface of hydrothermal reactor was modified with high temperature and high pressure graphite

The mixture is then subjected to a 10-hour hydrothermal reaction in a high-pressure reactor. After cooling completely, the solution is filtered and washed with distilled water until the pH reaches 6~8, to remove any residual heteroatom sources. Finally, the resulting solid is vacuum-dried at 80°C for 12 hours.

Table 1. Raw material ratio of nitrogen and phosphorus doped graphene

Sample	*Graphene (g)*	*Urea (g)*	*Phosphoric acid (g)*	*Polyphosphoric acid (g)*
Graphene	1	-	-	-
***N*-Graphene**	1	10	-	-
***P*- Graphene**	1	-	10	2
***PN*-Graphene**	1	5	5	1

4. GO and RGO Structure Characterization Tests

4.1 X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) is a method to analyze the phase and crystal structures of materials. During XRD analysis, a material is exposed to X-rays, resulting in the generation of a distinct pattern corresponding to its unique structure[14].

This method enables non-destructive examination of crystals and provides detailed crystal information, primarily relying on the intensity and position of diffraction peaks for analysis. The experimental setup for this study involved the characterization of graphene, with instrument parameters set as follows: an instrument voltage of 40 kV, tube current of 200 mA, scanning range from 10 to 70 degrees, and a scanning speed of 4 min-1.

4.2 Scanning Electron Microscope (SEM) Analysis

Morphological observation was conducted using a scanning electron microscope. The principle of this method is to utilize the electrons generated by the excitation of the object in a vacuum environment for imaging. It is one of the most effective and widely used for characterizing material morphological [15]. In this experiment, the morphology of the graphene coating was observed using a HITACHI S-4800 SEM, with a scanning voltage of 15 kV, magnification ranging from 50 to 400,000 times, and a maximum sample loading capacity of 2 kg.

4.3 Fourier-transform Infrared Spectroscopy (FTIR) Analysis

When a specimen is irradiated with infrared light of continuously changing frequencies, the specimen absorbs infrared light to varying degrees across different frequencies. As a result, infrared light passing through the specimen is weakened in some wavenumber ranges and strengthened in others. The absorption curve recorded by the instrument is called the infrared absorption spectrum [16].

In this experiment, a Nicolet 380 FTIR analyzer, manufactured by Thermo Electron Corporation, USA, was used for analysis. A small amount of fully dried sample was mixed with spectroscopically pure KBr in a 1:100 ratio, ground uniformly, and then formed into sample discs of appropriate thickness using a powder tablet press. The samples were then placed in the instrument for testing. The scanning range was 500–3500 cm^{-1}.

5. Results

5.1 The Characterization of Graphene Oxide(GO) and Reduced Graphene Oxide(RGO)

Reduced graphene oxide (RGO), produced by reducing graphene oxide (GO) with ascorbic acid, undergoes a transformation from gray-black particles and from high to low solubility in water.

SEM analysis (Fig. 4) reveals that GO exhibits a mesh-like structure with a large lateral area and some wrinkles. These characteristics arise because they possess functional groups that contain oxygen[17]. In contrast, RGO exhibits a distinct wrinkled morphology, resulting from the removal of most oxygen functional groups during the reduction process. This leads to increased interlayer stacking and the formation of a lamellar flake structure.

Fig. 4 Scanning electron microscope (SEM) images of graphene oxide and reduced graphene oxide

By comparing the XRD analysis results of graphene oxide (GO) and reduced graphene oxide (RGO) (Fig. 5), it is evident that GO exhibits relatively simple diffraction peaks, with the highest peak located near 14°. The characteristic diffraction peaks are sharp and intense. In contrast, the signal peaks corresponding to binding energies are significantly reduced after reduction, indicating that most oxygen-containing functional groups have been removed[18]. The XRD analysis of RGO shows that the insertion of oxygen-containing groups between the carbon atom layers increased the interlayer

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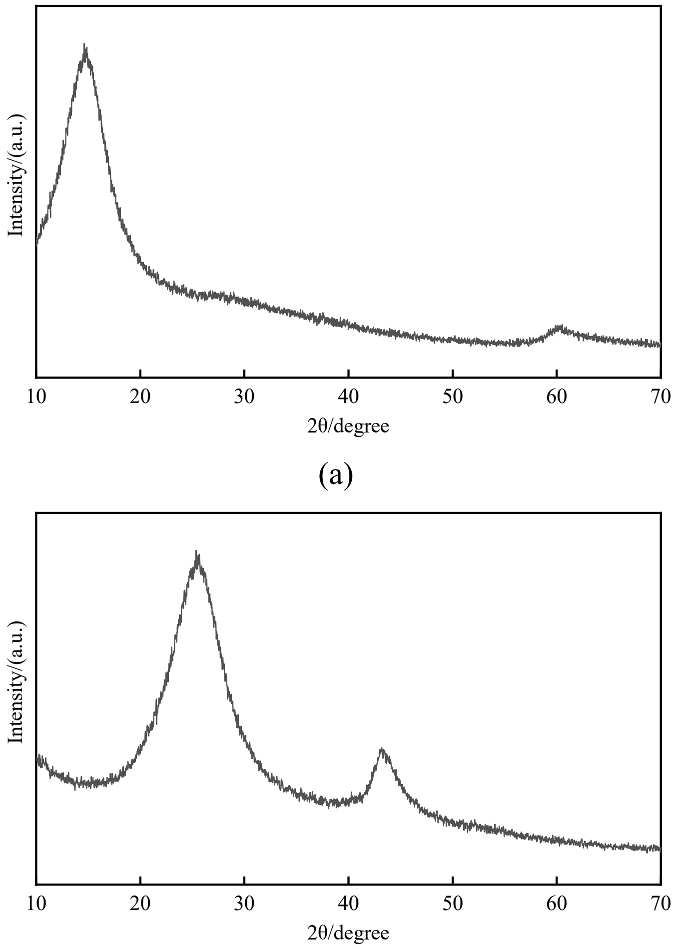
spacing. The sharp peak of GO near 14° disappeared, and a lower, broader diffraction peak appeared near 25°, confirming that graphite had been successfully reduced to RGO.

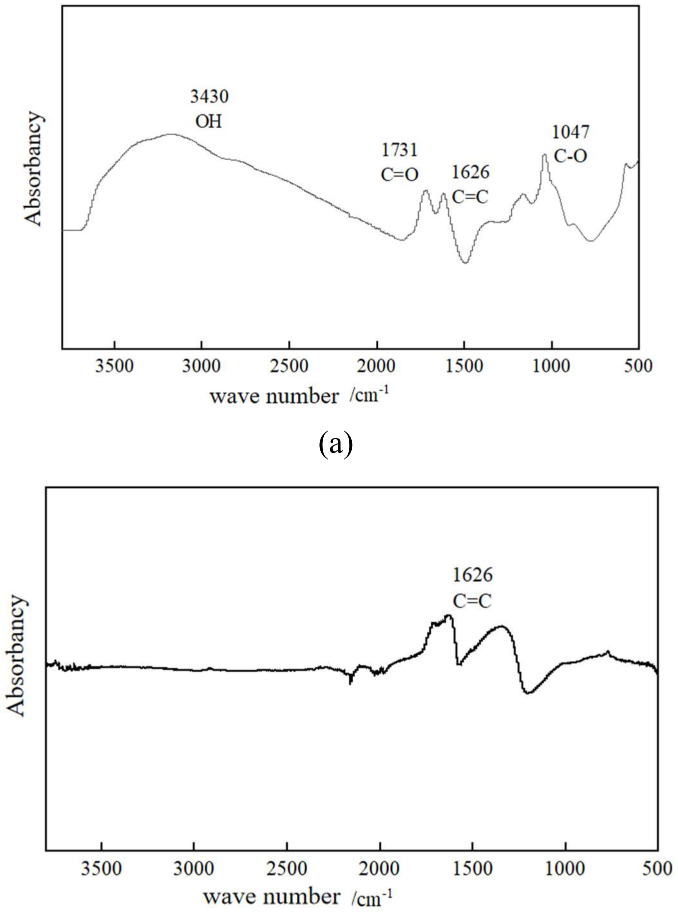


(a)

(b)

Fig. 5 X-ray diffraction (XRD) images of graphene oxide and reduced graphene oxide: graphene oxide; (b) Reduced graphene oxide

The qualitative analysis of graphene oxide (GO) was performed using FTIR, with the results shown in Fig. 6. A strong -OH stretching vibration peak appeared at 3430 cm^{-1}, while the C=O and C=C stretching vibration peaks were observed at 1731 cm^{-1} and 1626 cm^{-1}, respectively. The C-O stretching vibration peak appeared at 1047 cm^{-1}, indicating that the surface of the unreduced graphene oxide contained a significant number of oxygen-rich functional groups, making graphene highly hydrophilic. After hydrothermal reduction, the hydroxyl group peak at 3430 cm^{-1} disappeared, and the intensity of the C=O and C-O peaks decreased significantly, while the intensity of the C=C peak remained largely unchanged. This indicates that the reduction process successfully eliminated most oxygen-containing groups from the graphene surface while preserving the integrity of the carbon skeleton.



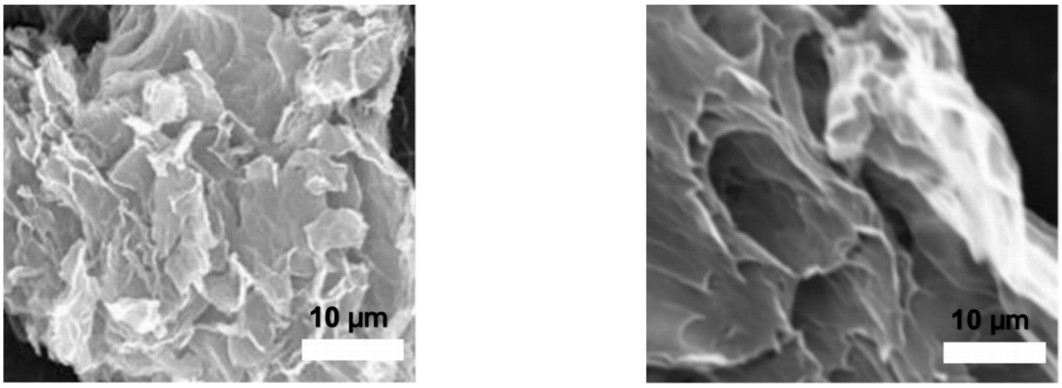
(a)

(b)

Fig. 6 Fourier infrared spectroscopy (FTIR) spectra of GO and RGO: (a) GO; (b) RGO

5.2 Characterization of Surface-modified RGO

To investigate the influence of surface modification on graphene morphology, we compared reduced graphene oxide (RGO), nitrogen-doped graphene (N-RGO), phosphorus-doped graphene (P-RGO), and phosphorus-nitrogen co-doped graphene (PN-RGO) before and after surface modification[19]. As shown in Fig. 7, all RGO variants exhibit similarly smooth surfaces with characteristic wrinkle structures, which arise from the thermodynamic instability of the carbon atom layers.



(a)

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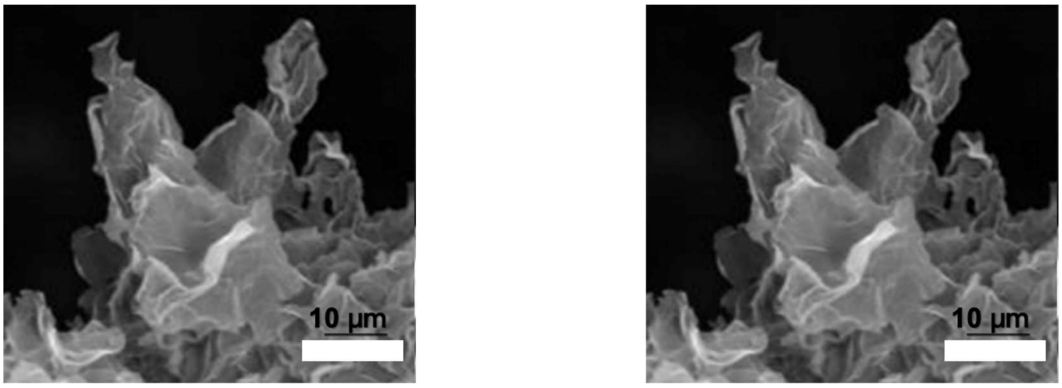


(c) (d)

Fig. 7 Scanning electron microscopy (SEM) images of surface-modified reduced graphene oxide: RGO; (b) N-RGO; (c) P-RGO; (d) PN-RGO

Fig. 8 shows the XRD spectra of RGO, N-RGO, P-RGO, and PN-RGO. As shown in the figure, the reduction process removes most of the oxygen-containing groups, resulting in an increase in the crystal diffraction peaks between 20° and 26.4°. While doping with heteroatoms increases the intensity of the diffraction peaks, the highest intensity was observed for N-RGO, corresponding to a higher degree of reduction. This suggests that nitrogen-phosphorus doping provided the best protection to the internal crystal structure of RGO compared to the individual doping modes.

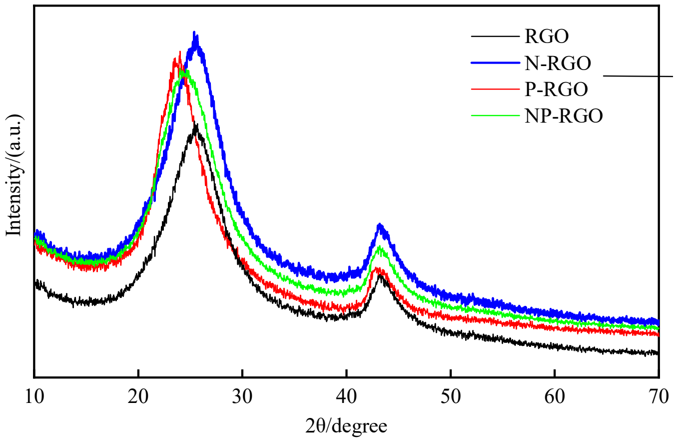
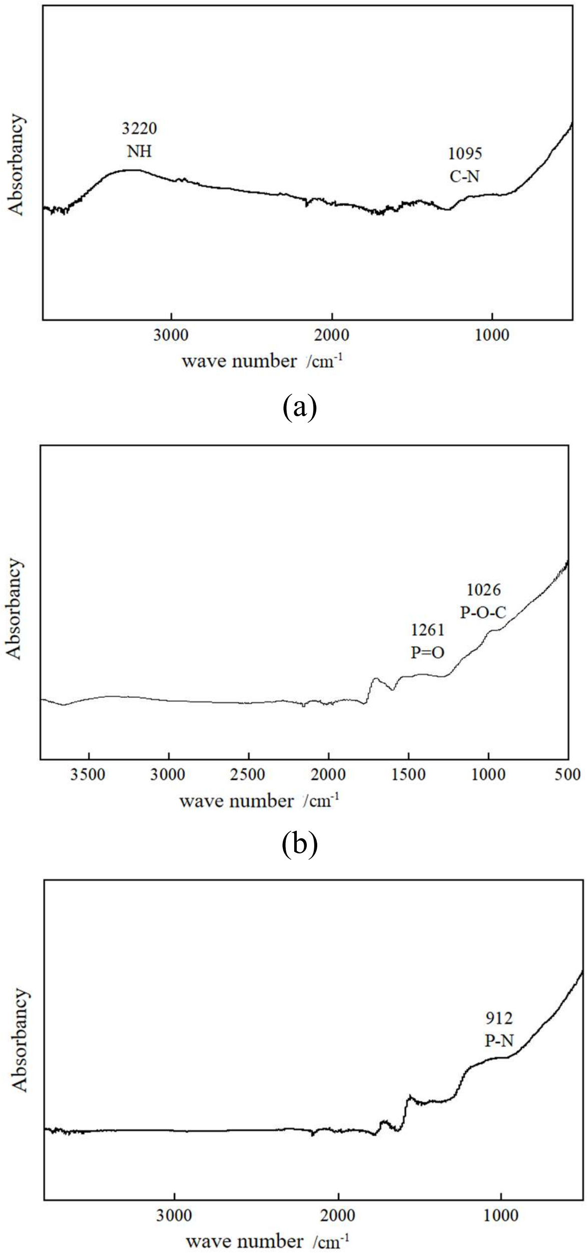


Fig. 8 X-ray diffraction (XRD) images of surface-modified reduced graphene oxide

Fig. 9 shows the infrared spectra of RGO after surface modification. It can be observed that the peaks corresponding to unstable oxygen-containing chemical groups on the surface of hydrothermally treated RGO show substantial reduction or complete absence, including -OH (3430 cm^{-1}), C=O (1731 cm^{-1}), and C-O (1047 cm^{-1}). New absorption peaks appeared on the graphene surface after heteroatom doping, such as -NH- (3220 cm^{-1}) and C-N (1095 cm^{-1}) on the N-RGO surface, and P-O-C (1026 cm^{-1}) and P=O (1261 cm^{-1}) on the P-RGO surface. This indicates that the hydrothermal treatment caused high-temperature chemical bond cleavage, leading to the significant reduction or disappearance of most unstable chemical group peaks on the GO surface. Additionally, a small number of P and N atoms were embedded into the inner structure of the graphite crystals and edges through chemical bonding. Compared to the single-element (P or N) doped RGO, the appearance of P-N (912 cm^{-1}) on the surface of co-doped graphene (PN-RGO) suggests the synergistic effect of the P-N co-doping process.



(a)

(b)

(c)

Fig. 9 Fourier infrared spectroscopy (FTIR) spectra of surface-modified reduced graphene oxide: N-RGO; (b) P-RGO; (c) PN-RGO

6. Conclusion

This study aims to improve the flame-retardant and smoke-suppressing properties of asphalt by incorporating graphene-based materials. Reduced graphene oxide (RGO) was prepared synthesized using the ascorbic acid reduction method, with surface modification achieved by doping with urea and phosphoric acid. The results demonstrate that the PN-RGO co-doped with nitrogen and phosphorus not only exhibits good compatibility with the material interface but also provides a more efficient flame retardant effect by forming dense carbonized layers. This indicates that using ascorbic acid to prepare RGO is highly feasible. This study not only validates the smoke suppression and flame retardancy properties of the modified asphalt in environments such as tunnels but also provides significant experimental and theoretical support for the flame retardant application of RGO and the development of high-performance composite materials.

Despite these promising results, several shortcomings remain. First, although the dispersion of graphene in asphalt has been improved, further enhancement of its uniform dispersion in large-scale production remains a challenge. Second, while nitrogen-phosphorus co-doped graphene demonstrates excellent flame retardancy, its stability under very high-temperature conditions requires further optimization. Additionally, although the modified asphalt shows good high-temperature stability, its durability and performance in hot and humid environments need further verification.

To address these issues, future research should focus on evaluating the long-term durability and adaptability of modified asphalt in tunnels and other extreme environments, particularly under varying climatic conditions. Furthermore, exploring the effects of other doping elements, such as silicon and boron, on the performance of graphene-modified asphalt should be a key area of investigation.

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