Effects of Surface Area and Particle Size of Graphite and Graphene Nanoplatelets on Their Oxidation and Subsequent Use in the Modification of Asphalt Binder

Dineshkumar Sengottuvelu,* Hashem Khaled Almashaqbeh,* Mohammed Majdoub, Avijit Pramanik, Grace Rushing, Jesse Doyle, Sasan Nouranian, Paresh Chandra Ray, Mine G. Ucak-Astarlioglu, Ahmed Al-Ostaz*

ABSTRACT: Graphene oxide (GO) has gained significant attention for its unique physical and chemical properties. GO finds application in a wide range of fields, including biomedicine, electronics, energy, and the environment. It also plays a significant role in the modification of infrastructure materials, such as asphalt and cement, in civil engineering. In this study, we report on the synthesis of GOs from graphite (Gr) powder and graphene nanoplatelets (GNPs) using an improved Hummers' method. We extensively investigated the effects of particle size and specific surface area of the Gr and GNP precursors on their oxidation, which have not been addressed in literature. The results from Fourier-transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses show that the GO made from Gr powder with a large surface area and small size has a higher degree of oxidation with about 9.8% carboxyl functional groups. This provides more opportunities for interactions with different molecules, including asphalt components. In this regard, we investigated the impact of carboxyl-rich GO (higher oxidation percentage) on the high-temperature performance of asphalt binder through rotational viscosity, rheology, multiple stress creep and recovery (MSCR), and anti-aging property measurements. Our experimental results indicate that GO obtained from the Gr powder precursor (designated ox-Gr) can significantly improve the high-temperature performance of asphalt binder. For example, the introduction of only 2 wt.% GO to a performance grade asphalt binder (PG 67-22) can dramatically increase its complex shear modulus (G*), as well as decrease the phase angle (δ), at high temperatures. The MSCR tests showed that the addition of GO to asphalt binder effectively mitigates its permanent deformation and improves its elastic response, as demonstrated by about 39% reduction in the creep compliance (I_{nr}) and an impressive 297% increase in the percent recovery (εR) of the GO-modified binder. Furthermore, the measured viscosity aging index and G* ratio of the GO-modified asphalt binder confirm the significant effect of GO on the improvement of the anti-aging properties of the binder.

KEYWORDS: graphite, graphene nanoplatelets, graphene oxide, Hummers' method, asphalt binder, rheology

1. INTRODUCTION

Graphene and its derivative graphene oxide (GO) offer many potential applications, ranging from catalysis and drug delivery to sensors and energy storage devices.¹⁻⁴ Moreover, GO is increasingly being used as a property modifier for many conventional infrastructure materials, such as cement and asphalt.^{5,6} The most promising method for the large-scale production of graphene involves converting multi-layered graphite (Gr) into GO and reducing it to a nearly single or few-layer substance. GO is a substance composed of ultra-thin graphitic sheets formed through the oxidation of Gr, a cost-effective and easily processable precursor. It can further be chemically or thermally reduced to yield reduced graphene oxide (rGO). The chemical oxidation route for the GO synthesis enables further modification of the physicochemical and mechanical properties of graphene. Gr oxidation is commonly done using Hummers' method,⁷ which introduces functionalities, such as hydroxyl, epoxide, ketone, and carbonyl, to graphene. This is achieved by controlling the quantity and nature of reagents or the physical parameters such as temperature and reaction time.^{8–10} For example, Hummers oxidized flaky Gr powders for half an hour,⁷ while Park et al.¹¹ performed the oxidation in two hours, However, they did not provide any information on the shape, size, and surface area of the Gr flakes used. Wilson et al.¹² oxidized Gr powder for five days. This discrepancy in the reaction conditions coupled with the lack of information on the shape, size, and surface area of the Gr precursors have left an open question of what factors might influence the chemistry of the GO product. To the best of our knowledge, the effects of precursor morphology, particle size, and surface area on graphene oxidation have not been thoroughly investigated in literature.

GO is widely used in many industries, such as carbon-based electronics, gas sensors, polymeric composite materials, and impermeable membranes, thanks to its exceptional structural and functional properties. For example, Yoo et al.¹³ have shown that the layered structure of GO can increase the gas diffusion path length in composite films, resulting in reduced gas flux. GO has also been found to improve the modulus and tensile strength of butadiene-styrene-vinyl pyridine rubber.¹⁴ Paci et al.¹⁵ and Bai et al.¹⁶ have demonstrated that the high modulus, rich surface chemistry, and water solubility of GO makes it suitable for use as reinforcement in various polymers. GO has an extremely large specific surface area. Jin et al.¹⁷ have demonstrated that GO has the potential to enhance the thermal, mechanical, conductive, and rheological properties of poly(methyl methacrylate). GO is also anticipated to yield significant improvements in asphalt binders, enhancing their performance and addressing issues such as rutting,^{18,19} fatigue,^{20,21} and thermal cracking.^{22,23} Additionally, some researchers have proposed that GO could serve as an anti-aging material. For example, Adnan et al.¹⁸ conducted an analysis of the influence of GO on the properties of asphalt binder. They concluded that GO has the potential to enhance the hightemperature properties of the binder and reduce its susceptibility to permanent deformation. In another study, An et al.²⁰ explored the capability of GO in improving the fatigue life of asphalt binders. They found that the inclusion of GO in an asphalt binder effectively extends its fatigue life. Zeng et al.²⁴ and Wu et al.²⁵ utilized GO as an anti-aging modifier in an asphalt binder. Their studies showed that GO enhances the anti-thermo-oxidative aging performance, as well as anti-UV aging performance, of the asphalt binder. Other studies, including those of Pang et al.²⁶ and Apeagyei²⁷, have suggested that the aging of asphalt binder may negatively affect the performance of flexible pavement. In general, GO can enhance the anti-aging performance of the asphalt binder in several ways thanks to its unique molecular structure. One way is by inhibiting the oxygen contact with asphalt, which lowers the reactant concentration during oxidation as part of the aging

process. Second, GO can delay the volatilization of lighter components in asphalt because of its superior barrier property.

Herein, we present a detailed account of the synthesis of GO from two different precursors, i.e., Gr and graphene nanoplatelets (GNPs), with differing particle sizes and surface areas using an improved Hummers' method. Our study aims to explore the impact of Gr and GNP sizes and surface areas on their oxidation to achieve target surface and edge functionalities in the resulting GO product. The physicochemical properties and surface chemistries of the synthesized GOs were extensively analyzed and compared using various spectroscopic techniques. Additionally, we selected an optimal GO with a higher percentage of carboxyl groups, namely ox-Gr based on the product of the oxidation of the Gr powder precursor and added it as a modifier to a performance grade asphalt binder, i.e., PG 67-22, in different weight percentages. We further analyzed the influence of the GO modifier on the high-temperature performance and anti-aging properties of the said asphalt binder. The findings of this work provide insights into the GO synthesis with target functionalities towards applications in infrastructure materials, specifically formulation of asphalt binders with improved high-temperature performance and anti-aging properties.

2. EXPERIMENTAL

2.1. Materials. We used three different GNP grades, i.e., xGnP® M15, M25, and C300, purchased from XG Sciences, Inc., United States, with the mean particle sizes (surface areas) of 14.36 μ m (128.3 m²/g), 24.2 μ m (132.8 m²/g), and 2.63 μ m (295.5 m²/g), respectively. GS-TC-307 nano-graphite powder was purchased from Graphitestore®, United States, with the particle size distribution (surface area) of 0.20-20 μ m (350 m²/g). All other chemicals, i.e., sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂, 30% aqueous solution), and hydrochloric acid (HCl), were procured from Sigma-Aldrich, Inc., United States. The asphalt binder samples were prepared using a performance grade asphalt binder (PG 67-22) procured from Ergon, Inc., United States.

2.2. Synthesis and Purification of GO. The Gr powder and GNP precursors were oxidized using an improved Hummers' method, as described in literature⁹ with slight modifications in this work (Figure 1). In brief, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360 ml/45 ml) was added to the Gr powder (3g) or GNPs (3g) in a 500 ml round-bottom flask and stirred for 10 min. A sixweight equivalent of KMnO₄ (18g) was slowly added to the reaction mixture in ice-cold conditions to prevent the exotherm. Then, the temperature was raised to 60 °C and the reaction mixture was continuously stirred for 12 h in the case of the Gr powder and 3 h in the case of GNPs until the color of the reaction mixture changed from green to brown. The resulting suspension was allowed to cool to room temperature, where after iced H_2O/H_2O_2 (750 ml/9 ml) was added to it while stirring with a glass rod. Once the solution color turned golden yellow, the conclusion of the oxidation reaction was confirmed. The suspension was then washed with 10% HCl, deionized water, and ethanol multiple times by centrifugation at 10,000 rpm until the pH of the supernatant reached neutral. The obtained residue was dried in a vacuum oven at 65 °C for 24 h to yield solid GO. The GOs synthesized from the Gr powder and GNPs are abbreviated as ox-Gr, ox-M15, ox-M25, and ox-C300, respectively.



Figure 1. Schematic illustration of the graphene oxide synthesis using the improved Hummers' method.

2.3. Asphalt Sample Preparation. The asphalt binder was placed in an oven and heated at 160 °C for approximately 2 h. Next, ox-Gr, which was found in this work to have a higher percentage of carboxyl groups, was added to the binder in the amounts of 0.05, 0.1, 0.5, 1, and 2 wt.% and thoroughly mixed in a high-shear mixer at 8000 rpm for 45 min. Subsequently, the mixture was allowed to cool to room temperature. The different asphalt binder formulations are designated PG 67-22 (neat binder), 0.05 wt.% GO (PG 67-22 plus 0.05 wt.% ox-Gr), etc.

2.4. Characterizations. The GO products were first dried in a vacuum oven at 60 °C for 10 h prior to analysis. The Fourier-transform infrared (FTIR) spectra were obtained using a Thermo Fisher Scientific Nicolet iS5 spectrometer with an iD5-ATR (diamond) accessory. The Raman spectra were obtained using a Jobin Yvon HR800 Raman Microscope at 514 nm. The intensity ratio of (ID/IG) was used to characterize the samples. The X-ray diffraction (XRD) patterns were obtained using a Rigaku Smart Lab X-ray Diffractometer, and thermal behavior was studied using a Perkin Elmer Diamond STG-DTA. X-ray photoelectron spectroscopy (XPS) measurements were used to investigate the surface chemistry of the synthesized GOs. The surface morphologies of the samples were analyzed using a JEOL JSM-7200FLV field-emission scanning electron microscope (FESEM), and the shapes and thicknesses of the GOs were determined using a PARK XE-007 atomic force microscope (AFM). Contact angle (CA) measurements were carried out to describe the surface properties of the synthesized GOs. Centrifugation was carried out using an Eppendorf 5810R, and the Heidolph rotavac was used to remove the solvent from the GO suspensions. A probe sonicator (QSonica Q700) was used to produce a pulse with a duration of 10 s, a power output of 500 W, and a frequency of 20 kHz.

The asphalt binder samples were evaluated based on the unaged and short-term aged conditions. The latter was achieved through the rolling thin film oven (RTFO) method, following the AASHTO T-240 standard. An FGB EVO-Series rotational viscometer was used for the rotational viscosity measurements to evaluate the workability of the modified asphalt binders in compliance with the AASHTO T-316 standard. The rotational viscosity was measured at temperatures of 110, 135, 165, and 185 °C. Furthermore, the viscosity aging index (VAI) was employed as a key

indicator to evaluate the influence of ox-Gr on the anti-aging properties of the binders. For the assessment of the rheological properties, a dynamic shear rheometer (DSR) was used, and several tests were performed using a DSR RN 4.3 instrument (Rheotest, Germany). Tests were conducted to determine the complex shear moduli (G*) and phase angles (δ) of both unaged and RTFO-aged binders at temperatures of 64, 70, and 76 °C, following the AASHTO T-315 standard. Finally, the resistance to rutting was evaluated through a series of multiple stress creep and recovery (MSCR) tests, aimed at analyzing the creep and recovery characteristics of both unmodified and modified asphalt binders. This testing protocol was executed on binders that had undergone the RTFO aging process at 64 °C, following the AASHTO T-350 standard. Figure 2 outlines the characterization scheme for the asphalt binder samples. Furthermore, FTIR spectra were used to identify any potential chemical or physical interactions between GO and asphalt binder molecules to better understand the mechanism by which GO improves asphalt binder properties.



Figure 2. Characterization scheme for the asphalt binder samples.

3. RESULTS AND DISCUSSION

3.1. Oxidation of Gr and GNPs. Traditionally, a combination of H_2SO_4 and sodium nitrate (NaNO₃) is used as intercalants in Hummers' method. However, in the improved Hummers' method used in this study, a mixture of H_2SO_4 and H_3PO_4 was employed to investigate the effectiveness of H_3PO_4 in simplifying the purification process and enhancing the properties of the synthesized GOs. Figure S1 in the Supplementary Information section displays various stages of the oxidation of the precursors. The oxidation reaction consisted of three key stages: In Stage 1, Gr salt was formed by adding KMnO₄ and intercalants, leading to a shift in the oxidation state of manganese and a color change from black to green.¹⁰ During Stage 2, the reaction mixture underwent a significant color change, going from light to dark brown, indicating the presence of

the Gr intercalant compounds. In Stage 3 (Figure S1), the reaction was stopped by adding a large volume of water and H₂O₂ to dissolve the manganese salts. The reaction mixture was then allowed to settle through gravity and subsequently separated by centrifugation at 10,000 rpm for 15-30 min at 5 °C. The separated residues were then washed with deionized water, ethanol, and 10% HCl. The resulting oxidized Gr product (ox-Gr) exhibited a wet, thick appearance with a brown color, while ox-M15, ox-M25, and ox-C300 showed a black, gluey appearance. Ox-Gr transformed into a blackish-brown powder upon drying, whereas ox-M15, ox-M25, and ox-C300 formed less dense, black-colored, paper-like sheets. The yield of the hydrophilic oxidized GO was higher for the Grbased than the GNP-based precursor. It is noteworthy to mention that the oxidation process involving lower temperatures and longer reaction times in the absence of NaNO3 is considered a sustainable strategy for producing highly oxidized GOs on a large scale with numerous hydrophilic functional groups, especially -COOH. These functional groups are essential for many applications since they provide sites for favorable intermolecular interactions or further functionalization with other small molecules. The structure of the synthesized GOs comprises numerous hydrophilic functional groups, particularly fused aromatic rings with sp^2 and sp^3 carbon domains (defects due to oxidation), as well as oxygenated species such as -C-O, C=O, -COOH, and -OH on the surface and edges of the graphene sheets.²⁸⁻³⁰ The obtained GOs readily disperse in aqueous due to the presence of the aforementioned hydrophilic functional groups.

As mentioned before, FTIR and XPS were employed to confirm the presence of the functional groups in the synthesized GOs. The FTIR spectra of the GOs are shown in Figure 3a. The successful conversion of Gr and GNPs to GO was confirmed by identifying specific absorption bands associated with various oxygenated functionalities. The vibration modes present in the GOs obtained from both Gr and GNPs were characterized by broad signals centered at 3200 cm⁻¹ (O—H of the phenol, diol, and carboxylic groups), 1730 cm⁻¹ (C—O of the carbonyl and carboxylic groups), 1620 cm⁻¹ (sp²-hybridized C—C, adsorbed water), 1395 cm⁻¹ (C—OH), and 1043 cm⁻¹ (epoxide C—O—C), respectively.³¹ Figure 3a shows the peak intensities of the GOs being significantly different in different regions of 1800–1500 cm⁻¹, 1500–1180 cm⁻¹, and 1180– 870 cm⁻¹. These changes observed in the peak intensities indicate that the use of various particle sizes and surface areas of the precursors, as well as reaction times, resulted in different percentages of the oxygenated functionalities. The bending vibrations of O-H due to water molecules were also observed in the range of 1600–1700 cm⁻¹. To analyze the changes in the peak intensities of the GOs in more detail, we performed a Gaussian fitting to deconvolute the peaks in the 1500-1800 cm⁻¹ range of the FTIR absorption spectra. The results of this analysis are presented in Figure 3b-e. The deconvoluted FTIR absorption spectra revealed the presence of various types of functional groups, including sp^2 -hybridized -C-C-, -C=O (ketonic), and -C=O (carboxyl). In Figure 3b-e, the ox-M25 sample is observed to exhibit a higher percentage of sp^2 -hybridized -C=C, with a value of 57%. On the other hand, the ox-Gr sample shows a lower value of 21.4% for the sp^2 -hybridized —C=C. This information provides insights into the degree of structural disorder and level of oxidation that are present in the synthesized GOs. Compared to the other GOs obtained from the GNP precursors (Figure 3b-d), ox-Gr synthesized from the Gr precursor with a large particle size and surface area with more reaction time (12 h) exhibited a less composition of 21.4% sp^2 -hybridized —C=C— with 78.5% ketonic and carboxyl groups (Figure 3e). This composition provides evidence of high oxidation levels observed in the ox-Gr sample, which are beneficial for further functionalization with small molecules for desired applications.

The UV-visible spectra of GOs were recorded in aqueous solutions and are shown in Figure 3f. The synthesized GOs exhibited absorption bands at 230, 239, 263, and 264 nm for ox-Gr, ox-M15, ox-M25, and ox-C300, respectively, which are attributed to the $\pi \rightarrow \pi^*$ transition of the *sp*²-hybridized —C=C—. The non-bonding orbitals ($n \rightarrow \pi^*$ transition of carbonyl groups), which resulted from the oxidation, are observed in the range of 270 to 300 nm (shoulder).³² Figure 3f indicates a red shift in the absorption maxima of the $\pi \rightarrow \pi^*$ transition from 230 to 264 nm in the GOs, suggesting a more ordered structure in ox-M15, ox-M25, and ox-C300 with a higher retention of the aromatic rings on the basal planes, compared to the highly oxidized ox-Gr. This result shows that ox-Gr has a highly disordered structure on the basal plan than the other GOs due to the higher level of oxidation, which is consistent with the FTIR results discussed previously. Figure 3g shows that the aqueous dispersions of GOs at the same concentration have different colors, indicating the presence of various nanostructures in the GO samples. Ox-Gr appears brown, while ox-M15, ox-M25, and ox-C300 are darker, suggesting an increase in the light absorption. This difference in color could be due to differences in the π -conjugated network extension, flake size, and stacking. The lighter shade shows less conjugation, smaller flake size, and less stacking.



Figure 3. (a) FTIR transmittance spectra and deconvoluted FTIR absorption spectra by a Gaussian fitting of (b) ox-M15, (c) ox-M25, (d) ox-C300 and (e) ox-Gr, showing multiple peaks in the range of 1500-1800 cm⁻¹. (f) UV-Visible spectra of the GOs dispersed in aqueous media. (g) The photographs demonstrate the GO dispersions in the aqueous media (0.1 mg/mL) and the resulting color shifts.

Figure 4a shows the XRD patterns of the synthesized GOs from the Gr and GNP precursors. The (0 0 2) planes at $2\theta = 26.2^{\circ}$ in the XRD pattern of the Gr and GNPs indicate a well-ordered graphene structure. However, the non-appearance of the (0 0 2) plane in ox-Gr confirms the absence of the Gr impurities. The development of (0 0 1) planes at $2\theta = 9.85^{\circ}$ indicates oxidation, which is evidenced by shifts from $2\theta = 26.2^{\circ}$ to 9.85° . The GOs obtained from the GNP precursors show the appearance of a new peak at $2\theta = 11.2^{\circ}$, 11.8° and 9.69° for ox-M15, ox-M25, and ox-

C300, respectively, due to the $(0\ 0\ 1)$ planes. The appearance of $(0\ 0\ 2)$ planes with slight blue shifts indicates the presence of left-over Gr impurities in the oxidized GNPs. The interlayer spacing of the GOs is directly correlated to the degree of oxidation. According to Bragg's equation, the interlayer distance was calculated to be 0.89 nm for ox-Gr and 0.78, 0.74, and 0.91 nm for ox-M15, ox-M25, and ox-C300, respectively. This suggests that ox-Gr has the highest degree of oxidation with non-existent (0 0 2) planes in the graphitic structure among the GOs. The increased interlayer distance indicates the presence of more oxygenated structures between the graphitic layers of ox-Gr, highlighting the role of the reaction time in the oxidation process. The observed interlayer distance of 0.89 nm for the average flake size of 0.20-20 μ m is significant because it falls behind the previously reported maximum interlayer distance of 0.95 nm for a flake size of 150 µm.⁹ This suggests that crystallite size is an important parameter influencing intercalation. XRD investigations indicate that the use of an H₃PO₄/H₂SO₄ mixture coupled with a long reaction time in the GO synthesis process may have facilitated contact and deeper penetration of the oxidant into the Gr layers. This resulted in the highest intercalation and oxidation observed in ox-Gr, followed by ox-C300, ox-M25, and ox-M15. The findings from the FTIR and UV-vis analyses support these observations and confirm a higher degree of oxidation on the basal planes of the ox-Gr samples.

Figure 4b presents the results of Raman spectroscopy, which were used to confirm the density of defects introduced in the GOs synthesized under different reaction conditions and with different precursors. From literature, Gr has a strong G band at 1582 cm⁻¹, corresponding to the first order scattering of the E_{2g} phonon mode of the sp²-bonded carbon atoms and a weak D band at 1354 cm⁻¹, originating from the breathing mode of the A_{1g} symmetry at the K-point.⁸ Upon transformation from Gr to GO (ox-Gr, ox-M15, ox-M25, and ox-C300), both the D and G bands broadened with the D band shifting to a lower wave number by more than 20 cm⁻¹. This shift suggests a reduction in the size of the in-plane sp^2 domains due to oxidation. The ID/IG ratio increased from Gr to GO, reaching its maximum in ox-Gr and ox-C300. This indicates a greater presence of structural defects in the carbon framework. Previous research has established that the ID/IG ratio is a key indicator of structural defects in graphene-based nanomaterials.³³⁻³⁵ Comparing the synthesized GOs to Gr and GNPs, a significant difference in the ID/IG ratio was observed, indicating a higher introduction of defects into the GO structures. The ID/IG ratio for ox-C300 and ox-Gr was found to be 1.54 and 1.35, respectively, while ox-M15 and ox-M25 had values of 1.21 and 1.19, respectively, indicating different degrees of oxidation defects resulting from distinct synthesis procedures. The high density of the lattice defects in GO can be attributed to the presence of various oxygenated functional groups, holes, permanent vacancies, and rearrangements in the carbon framework of the GO. This analysis supports the hypothesis that the basal planes are significantly affected by permanganate oxidation mediated by phosphoric and sulfuric acids. The 2D peak of GO(H) appeared more diffused and broader compared to the peaks of the GOs, making it challenging to determine the stacking pattern of the two peaks.

XPS was employed to analyze the composition and chemical states of various functional groups in the synthesized GOs. The physicochemical parameters of the synthesized GOs are given in Table S1 in the Supplementary Information section. Figure 4c-f presents the C(1s) XPS spectra of ox-M15, ox-M25, ox-C300, and ox-Gr. The peaks were carefully analyzed and fitted using the literature references to identify the chemical states of the functional groups.^{36–39} The analyses revealed five distinct Gaussian peaks at binding energies of 284.5, 285.2, 286.4, 288.1, and 289 eV, representing sp^2 - and sp^3 -bonded C—C/C=C/C—H, —C—O (epoxy)/ —C—OH, —C=O, and —COOH functionalities, respectively. By calculating the percentage composition

8

based on these peaks, it was determined that ox-Gr and ox-C300 (Figure 4e&f) exhibited significantly higher proportions (16.6% and 16.3%) of the sp^3 -bonded C—C/C=C/C—H, whereas ox-M15 and ox-M25 (Figure 4c&d) had lower percentages (less than 10%). This indicates that a higher concentration of defects was introduced during the oxidation process for the latter two GOs. Regarding the percentages of the —C=O and —COOH functional groups, ox-Gr and ox-C300 displayed values of 3.6% and 8.9% for —C=O in ox-C300, and 7.9% and 9.81% for —COOH in ox-Gr, respectively. These values were higher compared to the other two GOs. These findings suggest that the chemicals and reaction times employed during intercalation significantly influenced the degree of oxidation on the basal planes of ox-Gr and ox-C300, as compared to ox-M15 and ox-M25. The presence and types of functional groups determined by XPS align well with the findings from the FTIR analyses presented in Figure 3a. Notably, the higher percentage of 9.81% for the -COOH functional group observed in ox-Gr indicates a higher degree of oxidation, which offers further possibilities for functionalization with various small molecules for select applications. The examination of the GO samples using Raman spectroscopy, XRD, and XPS confirmed the successful transition from Gr to GO, along with the associated degrees of oxidation.



Figure 4. (a) XRD patterns of the GOs, indicating the changes in the interlayer spacing. (b) Raman spectra of GOs synthesized from Gr and GNP precursors. Deconvoluted core level C(1s) XPS spectra of (c) ox-M15, (d) ox-M25, (e) ox-C300, and (f) ox-Gr.

The SEM images of ox-C300 and ox-Gr are shown in Figure 5. The SEM images revealed the presence of rippled, wrinkled, and folded structures, contributing to larger sheet sizes. In Figure 5a&b, images of ox-C300 graphene sheets with a glossy, black appearance and metallic luster are shown. Figure 5d&e display the layered structures and wrinkled morphologies of the GOs. Specifically, in Figure 5d, the SEM image shows a cross-sectional view of the air-dried ox-C300 obtained through centrifugation of an oxidized GNP dispersion in water during the purification stage of the GO synthesis. The SEM images of ox-Gr obtained from the gold sputter-coated samples exhibited a folded and non-uniform morphology due to the overoxidation (Figure 5f&g). Figure 5h-j show the peak profile of ox-Gr and its AFM images. The images illustrate that the ox-Gr nanosheets have a wavy morphology with a lateral size of a few microns and a thickness of a few nanometers, which correspond to multilayer GO nanosheets. The ox-Gr nanosheets possess a significant number of carboxylic functional groups on the basal plan, while the bulk of the graphene sheets remain unmodified. This characteristic feature of ox-Gr allows the occurrence of π - π stacking, which accounts for the formation of multilayer sheets.



Figure 5. (a&b) Photograph of ultra-thin graphene sheets of ox-C300 and (c) ox-Gr powder. (d-g) Crosssectional (d) SEM image of ox-C300 and ox-Gr. (h) AFM height profile and (i&j) tapping mode topographic images of ox-Gr.

The thermal profiles of the Gr and GNP precursors, as well the GOs were elucidated by means of thermogravimetric analysis (TGA) from room temperature up to 700-800 °C with a heating rate of 10 °C min⁻¹ under air. The TGA and difference thermogravimetry ratio (DTG) curves of all samples are depicted in Figure 6, and their thermal parameters are given in Table S2 in the Supplementary Information section. The Gr and GNP precursors primarily exhibited one decomposition stage, corresponding to the -C--C- bond cleavage, occurring at a temperature of around 700 °C. Following chemical oxidation, all samples displayed a completely different thermal behavior, revealing the presence of three distinct decomposition steps. The first decomposition step is observed in the range of 35 to 150 °C, which is assigned to water evaporation. Water is intercalated between the oxidized graphene sheets, confirming their hydrophilic nature. The second decomposition step (170-350 °C) showed different weight losses for different GOs. It was around 40% for ox-Gr, corresponding to the thermal decomposition of the oxygen moieties, including carboxyl, hydroxyl, and epoxy groups.⁴⁰ The final decomposition step was assigned to the total decomposition of the carbonaceous framework by the -C-C- bond cleavage due to the pyrolysis of the labile oxygen-containing functional groups, occurring at a temperature of around 600 °C. It is worth noting that ox-Gr exhibited lower thermal stability than the GNP-based GOs, which can be attributed to the presence of a large number of oxygencontaining functional groups on its surface. Overall, the thermal decomposition of ox-Gr took place at lower temperatures than those of ox-M15, ox-M25, and ox-C300. The significant decrease of the T_{di}-T_{df} range of the second decomposition step (151-248 °C for ox-Gr vs. 132-362 °C, 320-526 °C, and 198-388 °C for ox-M15, ox-M25, and ox-C300, respectively) provide further support to the claim of high oxygen content of ox-Gr compared to the other GNP-based GOs.



Figure 6. (a) TGA and DTG curves of the GOs obtained using the improved Hummers' method with Gr and GNPs as precursors.

3.2. GO-Modified Asphalt. *Rotational viscosity.* Figure 7 shows the effect of GO (ox-Gr) on the rotational viscosities of the unaged and RTFO-aged asphalt binders at different temperatures. For the unaged binders, as the GO content increases, the rotational viscosity of the binders increases too. When the GO content remains below 1.00 wt.%, only a marginal increase in the

rotational viscosity is observed. However, a significant viscosity increase is achieved when the GO content reaches 2.00 wt.%. At 2.00 wt.% GO, the viscosity of the modified asphalt binder increases by approximately 88%, 60%, and 51% at temperatures of 110, 135, and 160 °C, respectively (Figure 7a). Based on the FTIR results, there is no evidence for any chemical interaction between GO and asphalt binder molecules (Figure S2). Thus, this increase in the viscosity may be attributed to the ability of the functional groups of the GO to interact physically (π — π interaction) with asphalt binder molecules leading to densification.¹⁹ Similar trends are observed with the RTFO-aged binders, but the increase in the binder viscosity is smaller (Figure 7b). This observation may provide insights into the role of GO in improving the aging resistance of the asphalt binder, as aging typically leads to an increase in viscosity. To gain a better understanding of the impact of GO on the aging resistance of the asphalt binder, VAI is employed at a temperature of 135 °C. The VAI is computed using the following equation:

$$VAI(\%) = \frac{\eta_{RTFO-aged} - \eta_{unaged}}{\eta_{unaged}} x \ 100\%$$
(1)

where η is the rotational viscosity of the binder. Figure 7c presents the VAI at 135 °C for the GOmodified asphalt binders. A lower VAI value means better resistance to aging. Based on the VAI data, the GO content below 2.00 wt.% is observed to have a negligible effect on the aging resistance of the binder. In contrast, a GO content of 2.00 wt.% leads to a remarkable reduction in the VAI at 135 °C, going from 51.1 to 24.3%, which indicates an impressive 52% decrease. This observation supports the fact that the presence of GO plays an important role in improving the aging resistance of the asphalt binder.^{25,41} It is noteworthy to mention that the AASHTO standards dictate that the asphalt binder viscosity at 135 °C should be below 3 Pa s to ensure suitable workability during mixing with aggregates and subsequent compaction. All GO-modified asphalt binders in this study are observed to meet this standard, suggesting that adding GO to the asphalt binder does not hinder the mixing or compacting process.



Figure 7. Rotational viscosities of the GO-modified asphalt binders. (a) Rotational viscosities of the unaged binders, (b) rotational viscosities of the RTFO-aged binders, (c) viscosity aging index (VAI) @ 135 °C.

Rheological properties. Figure 8 shows the relationship between the complex shear moduli (G^{*}) and phase angles (δ) of the unaged and RTFO-aged asphalt binders at different testing temperatures. Figure 8a&b demonstrate a significant enhancement in the G* and a decrease in the δ when 2.00 wt.% GO is used to modify the asphalt binder. This improvement in stiffness and elastic characteristics of the binder contribute to an increased resistance against deformation and improved stability at elevated temperatures. The significance of these observations becomes clearer when the rutting parameter ($G^*/\sin(\delta)$) is examined, following the AASHTO standards, as shown in Figure 9a&b. For all GO contents and testing temperatures, increasing the amount of GO leads to a noticeable increase in the rutting parameter with the maximum impact observed when GO content reaches 2.00 wt.%. For example, in the case of the unaged binders, adding 2.00 wt.% GO improves the rutting parameter by 120, 119, and 95% at temperatures of 64, 70, and 76 °C, respectively. These observations are in a good agreement with the literature data.^{21,42} This improvement in the rutting parameter can be attributed to the ability of the GO to create a more compact crosslinking framework between the GO and asphalt, resulting in decreased molecular mobility of the binder. In Figure 9c, the failure temperature (T_f) values for both unaged and RTFOaged binders are presented. These values were obtained in reference to the AASHTO M320 binder specification. The unaged control PG 67-22 binder displays a failure temperature (Tf) of 70 °C. All GO-modified binders have increased T_f values that are greater than 70 °C. This observation remains consistent with the other results, where the addition of 2.00 wt.% GO exhibits the

maximum increase in T_f (76.5 °C). When combining the results of the unaged and short-term aged binders, it becomes apparent that GO-modified samples exhibit significantly improved resistance to rutting.



Figure 8. Complex shear modulus (G*) as a function of phase angle (δ) of the GO-modified asphalt binders at different testing temperatures. (a) G* (Pa) as a function of δ (°) of the unaged binders, (b) G* (Pa) as a function of δ (°) of the RTFO-aged binders.



Figure 9. Impact of GO on the rutting parameter (G*/sin(δ)) of the asphalt binders at different testing temperatures. (a) Unaged asphalt binders, (b) RTFO-aged asphalt binders, (c) Failure temperature (T_f) of the asphalt binder modified with different GO content.

In evaluating the anti-aging properties of the asphalt binders, the G* ratio (G* RTFO/G* unaged) was utilized as an indicator. Specifically, a lower G* ratio indicates superior resistance to aging.⁴³ Figure 10 illustrates the G* ratios of the GO-modified samples at 64 °C. Overall, the inclusion of GO in the asphalt binder is found to enhance its aging resistance with the most remarkable anti-aging performance achieved when incorporating 2.00 wt.% GO.^{41,44} These results are in strong agreement with the VAI indicator, confirming that the presence of GO can significantly enhance the resistance of the asphalt binder to aging. This can be attributed to potential interactions between the GO and asphalt, leading to a reduction in the volatility of the asphalt components. Another potential reason can be the ability of GO to work as a physical barrier that hinders the penetration of oxygen into the asphalt and, hence, the oxidative degradation of asphalt.

MSCR tests. The MSCR tests were conducted on the RTFO-aged binders at a temperature of 64 °C, following the AASHTO T-350 standard, to assess the influence of GO on the rutting performance of the asphalt binder. The results are presented in terms of two key parameters, i.e., unrecoverable creep compliance (J_{nr}) and percent recovery (εR) , where J_{nr} represents permanent deformation and εR reflects the elastic response of the binder. J_{nr} and εR values at 64 °C, tested at 1 and 3.2 kPa, are shown for the GO-modified asphalt binders in Figure 11. Adding even a small amount of GO is observed to significantly reduce J_{nr} and increase εR , indicating enhanced rutting resistance, reduced permanent deformation, and improved elastic behavior of the asphalt binder. For example, at 3.2 kPa, the addition of 0.05, 0.10, 0.50, 1.00, and 2.00 wt.% GO to the binder can reduce J_{nr} by about 20.1, 23.1, 23, 34.6, and 39.1%, respectively. This reduction in J_{nr} can be attributed to the ability of GO to enhance the stiffness of the binder, leading to a substantial decrease in its permanent deformation. Furthermore, at the same loading, GO increases εR by 8.6, 27.9, 31.7, 100, and 297.1% for the GO contents of 0.05, 0.10, 0.50, 1.00, and 2.00 wt.%, respectively. This significant enhancement in εR points to a much more elastic RTFO-aged binder.^{21,24} One potential explanation for this improvement is the ability of the GO to enhance the aging resistance of the binder and improve its anti-aging properties, leading to a more elastic RTFO-aged binder.



Figure 10. G* ratios of the GO-modified asphalt binders.



Figure 11. MSCR results of the GO-modified asphalt binder at a temperature of 64 °C. (a) J_{nr} @ 1.0 and 3.2 kPa, (b) εR @ 1.0 and 3.2 kPa.

4. CONCLUSION

In this work, we used the improved Hummers' method to synthesize different GOs from graphite (Gr) and graphene nanoplatelet (GNP) precursors with different particle sizes and surface areas. Our study examined how the average particle sizes and surface areas of the Gr and GNP precursors affect the oxidation process. We extensively analyzed and compared the physicochemical properties and surface chemistries of the GOs using various spectroscopic techniques. Our synthetic strategy is practical for industrial use because it does not require sodium nitrate, uses a low reaction temperature, and provides an easy purification with an acid/co-acid intercalant mixture. We found that Gr powder with a large surface area and small size achieves a greater degree of oxidation (the GO product designated as ox-Gr), resulting in a 9.81% higher percentage of the carboxyl functional group. This creates more opportunities for functionalization with small molecules for desired applications. On the other hand, our experimental results demonstrate that the incorporation of ox-Gr into a performance grade asphalt binder (PG 67-22) significantly

improves its high-temperature performance and anti-aging properties. This improvement may be attributed to the establishment of a more compact crosslinking framework and a reduction in the molecular mobility within the matrix. Adding 2.00 wt.% GO to the asphalt binder improves the rutting parameter by 120, 119, and 95% at temperatures of 64 °C, 70 °C, and 76 °C, respectively. Furthermore, the multiple stress creep and recovery test results indicated that even small amounts of GO can reduce the permanent deformation and increase the elastic behavior of the binders.

■AUTHOR INFORMATION

Corresponding Authors

- Hashem Khaled Almashaqbeh Center for Graphene Research and Innovation, University of Mississippi, University, MS 38677, United States; Email: <u>hkalmash@olemiss.edu</u>; <u>https://orcid.org/0000-0002-5153-1739</u>
- Ahmed Al-Ostaz Department of Civil Engineering, University of Mississippi, University, MS 38677, United States; Center for Graphene Research and Innovation, University of Mississippi, University, MS 38677, United States; Email: <u>alostaz@olemiss.edu</u>;
 <u>https://orcid.org/0000-0003-3101-5996</u>

Authors

- **Mohammed Majdoub** Center for Graphene Research and Innovation, University of Mississippi, University, MS 38677, United State; D <u>https://orcid.org/0000-0002-5674-0089</u>
- Avijit Pramanik Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi 39217, United States
- Grace Rushing Department of Civil Engineering, University of Mississippi, University, MS 38677, United States; Center for Graphene Research and Innovation, University of Mississippi, University, MS 38677, United States
- Jesse Doyle Geotechnical and Structures Laboratory, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 39180-6199, United States
- Sasan Nouranian Department of Chemical Engineering, University of Mississippi, University, MS 38677, United States; Center for Graphene Research and Innovation, University of Mississippi, University, MS 38677, United States; D <u>https://orcid.org/0000-0002-8319-2786;</u>
- **Paresh Chandra Ray** Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi 39217, United States
- Mine G. Ucak-Astarlioglu Geotechnical and Structures Laboratory, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 39180-6199, United States

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work described in this document was conducted in the Center for Graphene Research and Innovation at the University of Mississippi. The authors acknowledge the support provided by the U.S. Army Engineer Research and Development Center (ERDC) and the Military Engineering Research and Development Area under contract W912HZ21C0040. Permission to publish was granted by the ERDC Geotechnical and Structures Laboratory.

FUNDING

The research described and the resulting data presented herein, unless otherwise noted, were funded under CA BO340 497014 Project, "Graphene Applications for Military Engineering," under Contract W912HZ21C0040, and managed by the U.S. Army Engineer Research and Development Center (ERDC).

SUPPORTING INFORMATION

Digital images of the reaction mixture at different stages of preparation of graphene oxide from graphite. Particle size, surface area and surface functional group data of graphite and GOs. Thermal decomposition data of the synthesized GOs.

REFERENCES

- Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* 2004, *306* (5696), 666–669. https://doi.org/10.1126/science.1102896.
- (2) Urade, A. R.; Lahiri, I.; Suresh, K. S. Graphene Properties, Synthesis and Applications: A Review. *JOM* **2023**, *75* (3), 614–630. https://doi.org/10.1007/s11837-022-05505-8.
- (3) Liu, Z.; Robinson, J. T.; Sun, X.; Dai, H. PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs. J. Am. Chem. Soc. 2008, 130 (33), 10876–10877. https://doi.org/10.1021/ja803688x.
- (4) Avouris, P.; Dimitrakopoulos, C. Graphene: Synthesis and Applications. *Mater. Today* **2012**, *15* (3), 86–97. https://doi.org/10.1016/S1369-7021(12)70044-5.
- (5) He, J.; Hu, W.; Xiao, R.; Wang, Y.; Polaczyk, P.; Huang, B. A Review on Graphene/GNPs/GO Modified Asphalt. *Constr. Build. Mater.* **2022**, *330*, 127222. https://doi.org/10.1016/j.conbuildmat.2022.127222.
- (6) Zhao, L.; Guo, X.; Song, L.; Song, Y.; Dai, G.; Liu, J. An Intensive Review on the Role of Graphene Oxide in Cement-Based Materials. *Constr. Build. Mater.* **2020**, *241*, 117939. https://doi.org/10.1016/j.conbuildmat.2019.117939.
- (7) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. J. Am. Chem. Soc. 1958, 80 (6), 1339. https://doi.org/10.1021/ja01539a017.
- (8) Yadav, N.; Lochab, B. A Comparative Study of Graphene Oxide: Hummers, Intermediate and Improved Method. *FlatChem* 2019, 13 (January), 40–49. https://doi.org/10.1016/j.flatc.2019.02.001.
- (9) Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. ACS Nano 2010, 4 (8), 4806–4814. https://doi.org/10.1021/nn1006368.
- (10) Yu, H.; Zhang, B.; Bulin, C.; Li, R.; Xing, R. High-Efficient Synthesis of Graphene Oxide Based on Improved Hummers Method. *Sci. Rep.* **2016**, *6*. https://doi.org/10.1038/srep36143.
- (11) Park, S.; An, J.; Piner, R. D.; Jung, I.; Yang, D.; Velamakanni, A.; Nguyen, S. T.; Ruoff, R. S. Aqueous Suspension and Characterization of Chemically Modified Graphene Sheets. *Chem. Mater.* 2008, 20 (21), 6592–6594. https://doi.org/10.1021/cm801932u.

- (12) Wilson, N. R.; Pandey, P. A.; Beanland, R.; Young, R. J.; Kinloch, I. A.; Gong, L.; Liu, Z.; Suenaga, K.; Rourke, J. P.; York, S. J.; Sloan, J. Graphene Oxide: Structural Analysis and Application as a Highly Transparent Support for Electron Microscopy. *ACS Nano* 2009, *3* (9), 2547–2556. https://doi.org/10.1021/nn900694t.
- (13) Yoo, B. M.; Shin, H. J.; Yoon, H. W.; Park, H. B. Graphene and Graphene Oxide and Their Uses in Barrier Polymers. J. Appl. Polym. Sci. 2014, 131 (1), 1–23. https://doi.org/10.1002/app.39628.
- (14) Tang, Z.; Wu, X.; Guo, B.; Zhang, L.; Jia, D. Preparation of Butadiene–Styrene–Vinyl Pyridine Rubber–Graphene Oxide Hybrids through Co-Coagulation Process and in Situ Interface Tailoring. *J. Mater. Chem.* 2012, 22 (15), 7492–7501. https://doi.org/10.1039/C2JM00084A.
- (15) Paci, J. T.; Belytschko, T.; Schatz, G. C. Computational Studies of the Structure, Behavior upon Heating, and Mechanical Properties of Graphite Oxide. J. Phys. Chem. C 2007, 111 (49), 18099–18111. https://doi.org/10.1021/jp075799g.
- (16) Functional Composite Materials Based on Chemically Converted Graphene Bai 2011 -Advanced Materials - Wiley Online Library. https://onlinelibrary.wiley.com/doi/10.1002/adma.201003753 (accessed 2023-11-13).
- (17) Jang, J. Y.; Kim, M. S.; Jeong, H. M.; Shin, C. M. Graphite Oxide/Poly(Methyl Methacrylate) Nanocomposites Prepared by a Novel Method Utilizing Macroazoinitiator. *Compos. Sci. Technol.* 2009, 69 (2), 186–191. https://doi.org/10.1016/j.compscitech.2008.09.039.
- (18) Adnan, A. M.; Luo, X.; Lü, C.; Wang, J.; Huang, Z. Physical Properties of Graphene-Oxide Modified Asphalt and Performance Analysis of Its Mixtures Using Response Surface Methodology. *Int. J. Pavement Eng.* 2022, 23 (5), 1378–1392. https://doi.org/10.1080/10298436.2020.1804061.
- (19) Singh, D.; Kuity, A.; Girimath, S.; Suchismita, A.; Showkat, B. Investigation of Chemical, Microstructural, and Rheological Perspective of Asphalt Binder Modified with Graphene Oxide. J. Mater. Civ. Eng. 2020, 32 (11), 04020323. https://doi.org/10.1061/(ASCE)MT.1943-5533.0003385.
- (20) An, X.; Wang, R.; Kang, X.; Yue, J. A More Accurate Fatigue Characterization of GO-Modified Asphalt Binder Considering Non-Linear Viscoelastic Behaviour and UV Exposure Effects. *Int. J. Fatigue* 2023, *168*, 107396. https://doi.org/10.1016/j.ijfatigue.2022.107396.
- (21) Liu, K.; Zhang, K.; Wu, J.; Muhunthan, B.; Shi, X. Evaluation of Mechanical Performance and Modification Mechanism of Asphalt Modified with Graphene Oxide and Warm Mix Additives. J. Clean. Prod. 2018, 193, 87–96. https://doi.org/10.1016/j.jclepro.2018.05.040.
- (22) Li, S.; Xu, W.; Zhang, F.; Wu, H.; Zhao, P. Effect of Graphene Oxide on the Low-Temperature Crack Resistance of Polyurethane–SBS-Modified Asphalt and Asphalt Mixtures. *Polymers* **2022**, *14* (3), 453. https://doi.org/10.3390/polym14030453.
- (23) Liu, K.; Zhang, K.; Shi, X. Performance Evaluation and Modification Mechanism Analysis of Asphalt Binders Modified by Graphene Oxide. *Constr. Build. Mater.* **2018**, *163*, 880–889. https://doi.org/10.1016/j.conbuildmat.2017.12.171.
- (24) Zeng, W.; Wu, S.; Pang, L.; Sun, Y.; Chen, Z. The Utilization of Graphene Oxide in Traditional Construction Materials: Asphalt. *Materials* 2017, 10 (1), 48. https://doi.org/10.3390/ma10010048.
- (25) Wu, S.; Zhao, Z.; Li, Y.; Pang, L.; Amirkhanian, S.; Riara, M. Evaluation of Aging Resistance of Graphene Oxide Modified Asphalt. *Appl. Sci. Switz.* **2017**, 7 (7). https://doi.org/10.3390/app7070702.

- (26) Pang, L.; Liu, K.; Wu, S.; Lei, M.; Chen, Z. Effect of LDHs on the Aging Resistance of Crumb Rubber Modified Asphalt. *Constr. Build. Mater.* 2014, 67 (PART B), 239–243. https://doi.org/10.1016/j.conbuildmat.2013.10.040.
- (27) Apeagyei, A. K. Laboratory Evaluation of Antioxidants for Asphalt Binders. *Constr. Build. Mater.* **2011**, *25* (1), 47–53. https://doi.org/10.1016/j.conbuildmat.2010.06.058.
- (28) Ranjan, P.; Agrawal, S.; Sinha, A.; Rao, T. R.; Balakrishnan, J.; Thakur, A. D. A Low-Cost Non-Explosive Synthesis of Graphene Oxide for Scalable Applications. *Sci. Rep.* 2018, 8 (1). https://doi.org/10.1038/s41598-018-30613-4.
- (29) Skákalová, V.; Kotrusz, P.; Jergel, M.; Susi, T.; Mittelberger, A.; Vretenár, V.; Šiffalovič, P.; Kotakoski, J.; Meyer, J. C.; Hulman, M. Chemical Oxidation of Graphite: Evolution of the Structure and Properties. *J. Phys. Chem. C* 2018, *122* (1), 929–935. https://doi.org/10.1021/acs.jpcc.7b10912.
- (30) Majdoub, M.; Essamlali, Y.; Amadine, O.; Ganetri, I.; Zahouily, M. Organophilic Graphene Nanosheets as a Promising Nanofiller for Bio-Based Polyurethane Nanocomposites: Investigation of the Thermal, Barrier and Mechanical Properties. *New J. Chem.* 2019, 43 (39), 15659–15672. https://doi.org/10.1039/c9nj03300a.
- (31) Sengottuvelu, D.; Shaik, A. K.; Mishra, S.; Ahmad, H.; Abbaszadeh, M.; Hammer, N.; Kundu, S. Multicolor Nitrogen-Doped Carbon Quantum Dots for Environment-Dependent Emission Tuning. ACS Omega 7 (31), 27742–27754. https://doi.org/10.1021/acsomega.2c03912.
- (32) Saxena, S.; Tyson, T. A.; Shukla, S.; Negusse, E.; Chen, H.; Bai, J. Investigation of Structural and Electronic Properties of Graphene Oxide. *Appl. Phys. Lett.* **2011**, *99* (1), 013104. https://doi.org/10.1063/1.3607305.
- (33) Lucchese, M. M.; Stavale, F.; Ferreira, E. H. M.; Vilani, C.; Moutinho, M. V. O.; Capaz, R. B.; Achete, C. A.; Jorio, A. Quantifying Ion-Induced Defects and Raman Relaxation Length in Graphene. *Carbon* 2010, *48* (5), 1592–1597. https://doi.org/10.1016/j.carbon.2009.12.057.
- (34) Ferrari, A. C. Raman Spectroscopy of Graphene and Graphite: Disorder, Electron–Phonon Coupling, Doping and Nonadiabatic Effects. *Solid State Commun.* **2007**, *143* (1), 47–57. https://doi.org/10.1016/j.ssc.2007.03.052.
- (35) Cançado, L. G.; Jorio, A.; Ferreira, E. H. M.; Stavale, F.; Achete, C. A.; Capaz, R. B.; Moutinho, M. V. O.; Lombardo, A.; Kulmala, T. S.; Ferrari, A. C. Quantifying Defects in Graphene via Raman Spectroscopy at Different Excitation Energies. *Nano Lett.* 2011, *11* (8), 3190–3196. https://doi.org/10.1021/nl201432g.
- (36) Stankovich, S.; D. Piner, R.; Chen, X.; Wu, N.; T. Nguyen, S.; S. Ruoff, R. Stable Aqueous Dispersions of Graphitic Nanoplatelets via the Reduction of Exfoliated Graphite Oxide in the Presence of Poly(Sodium 4-Styrenesulfonate). J. Mater. Chem. 2006, 16 (2), 155–158. https://doi.org/10.1039/B512799H.
- (37) Shulga, Y. M.; Baskakov, S. A.; Baskakova, Y. V.; Volfkovich, Y. M.; Shulga, N. Y.; Skryleva, E. A.; Parkhomenko, Y. N.; Belay, K. G.; Gutsev, G. L.; Rychagov, A. Y.; Sosenkin, V. E.; Kovalev, I. D. Supercapacitors with Graphene Oxide Separators and Reduced Graphite Oxide Electrodes. *J. Power Sources* **2015**, *279*, 722–730. https://doi.org/10.1016/j.jpowsour.2015.01.032.
- (38) Lomeda, J. R.; Doyle, C. D.; Kosynkin, D. V.; Hwang, W.-F.; Tour, J. M. Diazonium Functionalization of Surfactant-Wrapped Chemically Converted Graphene Sheets. J. Am. Chem. Soc. 2008, 130 (48), 16201–16206. https://doi.org/10.1021/ja806499w.

- (39) Chen, J.; Yao, B.; Li, C.; Shi, G. An Improved Hummers Method for Eco-Friendly Synthesis of Graphene Oxide. *Carbon* **2013**, *64*, 225–229. https://doi.org/10.1016/j.carbon.2013.07.055.
- (40) Pan, S.; Aksay, I. A. Factors Controlling the Size of Graphene Oxide Sheets Produced via the Graphite Oxide Route. *ACS Nano* **2011**, *5* (5), 4073–4083. https://doi.org/10.1021/nn200666r.
- (41) Wang, R.; Qi, Z.; Li, R.; Yue, J. Investigation of the Effect of Aging on the Thermodynamic Parameters and the Intrinsic Healing Capability of Graphene Oxide Modified Asphalt Binders. *Constr. Build. Mater.* 2020, 230, 116984. https://doi.org/10.1016/j.conbuildmat.2019.116984.
- (42) Li, Y.; Wu, S.; Amirkhanian, S. Investigation of the Graphene Oxide and Asphalt Interaction and Its Effect on Asphalt Pavement Performance. *Constr. Build. Mater.* **2018**, *165*, 572–584. https://doi.org/10.1016/j.conbuildmat.2018.01.068.
- (43) Effects of the Geometric Characteristics of Graphene Nanoplatelets on the Physico-Rheological Properties of Asphalt Binder. https://doi.org/10.21203/rs.3.rs-3297081/v1.
- (44) Liu, W.; Yan, K.; Ge, D.; Chen, M. Effect of APAO on the Aging Properties of Waste Tire Rubber Modified Asphalt Binder. *Constr. Build. Mater.* 2018, 175, 333–341. https://doi.org/10.1016/j.conbuildmat.2018.04.098.