A dual-criterion optimization for sulfonated asphalt-assisted aqueous phase exfoliation to prepare graphene suitable for protective coating of aluminium

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Abstract

In this work, we aimed to prepare graphene with high concentration (C_G) or quality (indicated by \( I_D/I_G \)) by sonication-assisted exfoliation in aqueous sulfonated asphalt (SAS) solution. The highest C_G can reach 0.181 mg ml\(^{-1}\), while the smallest \( I_D/I_G \) is only 0.331 in the investigated range. Meanwhile, we observed that C_G and \( I_D/I_G \) changed in the opposite trend with the increase of SAS concentration, and reached their extreme values simultaneously. This was attributed to SAS’s agglomeration-induced redistribution of total energy absorbed by graphite between exfoliation and crushing. The graphene size was mainly within 100–400 nm and most of layer number was <5. The stabilization of graphene dispersion comes from the electrostatic repulsion between negatively charged SAS groups adsorbed on the graphene sheets. As the protective coating of aluminium, the graphene with relative small (for \( H_2SO_4 \) solution) or large (for NaCl solution) size, relative high defect content and annealing at proper temperature can improve the anticorrosion performance of graphene.

1. Introduction

All the time, graphene (G) has attracted extensive attention since its birth due to its unique hexagonal honeycomb structure and the resultant excellent physical and chemical properties [1–3]. After more than ten years of development, with the application of graphene in more and more fields, the demand for graphene is increasing day by day. However, up to date, the price of high-quality graphene is still expensive, and the preparation process is accompanied by the problems of pollution and safety [4]. As a result, the preparation technology of high-quality graphene with cost saving, scalability, and non-pollution increasingly becomes a research focus [1, 5]. So far, the preparation methods of graphene mainly includes micromechanical cleavage [6], liquid phase exfoliation (LPE) [7], chemical vapor deposition [8], reduction of graphene oxide [9, 10], etc. Among these methods, LPE is thought to be a promising method for industrialization due to its simple equipment, scalability, low cost, and high quality of obtained graphene [5, 11, 12]. In the LPE, graphite (Gi) is exfoliated into graphene in liquid media under ultrasound, microwave, or shear force, etc [5] As far as we know, three liquid media have been used for exfoliation, namely water, organic solvents, and ionic liquids [5, 13]. Obviously, water is more advantageous in large-scale preparation because of its environment-friendly and cost-effective features. However, due to super hydrophobicity of graphene, the addition of dispersants/stabilizers into water is indispensable in the exfoliation process. Many substances have been used as dispersants, including graphene oxide [14], carbon dots [15], alkaline lignin [12], fulvic acid [5], various surfactants [16], and some biomolecules such as nucleotides, DNA, RNA, proteins/peptides, polysaccharides, plant extracts, and bile salts [17]. However, relatively low graphene concentrations [5, 12, 16], high cost or/toxic stabilizers [14–17]
hinder the industrialization of the method. Thus, it is valuable to explore new dispersants to assist the exfoliation of graphite into graphene in aqueous solution.

Asphalt is a black-brown complex mixture, mainly classified as coal tar asphalt, petroleum asphalt, and natural asphalt depending on their source [18, 19]. Asphalt is mainly composed of alkane, cycloalkane, aromatic hydrocarbon, polycyclic aromatic hydrocarbon, and heterocyclic hydrocarbons containing sulfur/nitrogen [19]. The aromatic groups in asphalt make it possible to form π–π interactions with graphene. Unfortunately, asphalt is insoluble in water and cannot be used as dispersants. Yet sulfonated asphalt (SAS) prepared from asphalt is soluble in water and is suitable for the exfoliation of graphite. In industry, SAS, mainly as a component of drilling fluid, has been produced on a large scale [20], which makes SAS economically competitive as dispersants.

For the large-scale production of graphene by LPE method, high graphene concentration \( C_G \) is beneficial to improve the economy of process, and the defect content (indicated by \( I_D/I_G \), where \( I_D \) and \( I_G \) are peak intensities of D and G peaks in Raman spectrum) affects greatly its performance in application. Therefore, it is desire to prepare graphene with the highest possible concentration and defect contents suitable for specific applications. Therefore, based on \( C_G \) and \( I_D/I_G \) to obtain optimized operation parameters (called as double-criterion optimization), the production of graphene, which is beneficial economically and suitable for specific applications, can be realized.

In this work, graphene was prepared by SAS-assisted aqueous-phase exfoliation of graphite under sonication. First, the operation parameters, i.e., subfraction of SAS, power \( P \), concentration of SAS \( C_{\text{SAS}} \), and sonication time \( t_s \), were optimized based on \( C_G \) or \( I_D/I_G \). Meanwhile, the mechanism of the effect of \( C_{\text{SAS}} \) on \( C_G \) and \( I_D/I_G \) (figure 1) was explored to guide graphene production. Then the quality of as-exfoliated graphene was evaluated, and the stability mechanism of graphene dispersion was elucidated. Finally, the as-exfoliated graphene was used as anticorrosion coating of aluminium, and the effects of graphene size, defects and annealing on anticorrosion performance were investigated in \( \text{H}_2\text{SO}_4 \) or \( \text{NaCl} \) solutions.

2. Experimental

2.1. Materials and chemicals

Graphite (325 mesh, CAS: 7782-42-5) was purchased from Aladdin Industrial Co., China, SAS (CAS: 68201-32-1) was provided by Xinxiang Dongfang Oilfield Auxiliaries Co., Ltd, Henan, China, \( \text{H}_2\text{SO}_4 \) (AR, 95–98 wt%) was purchased from Chengdu Cologne Chemicals Co., Ltd, China, and \( \text{NaCl} \) (AR, 99.5 wt%) was purchased from Nanjing Chemical Reagent Co., Ltd, China. All samples except SAS were used directly without further purification.

2.2. Subfraction preparation of SAS with different molecular weight

SAS with different molecular weight has different interaction with graphene. Therefore, SAS was separated into several subfractions with different molecular weights by centrifugation. In a typical procedure, 200 ml of aqueous SAS solution with a concentration of 10 mg ml\(^{-1}\) was sonicated in water bath for 2 h. After a two-step centrifugation, the obtained precipitate was dried for the next research.

2.3. Preparation of graphene dispersion and powder

Before preparation, graphite is first pre-treated to remove possible impurities and very small graphite sheets by 30 min water-bath sonication, 600 rpm centrifugation (Relative centrifugal force (RCF): 5013) for 30 min, the
resultant precipitate washed with deionized water for three times, and dried in turn for use below. The preparation procedure of graphene dispersion and powder is similar to those described in our previous work [5]. In a typical operation, a certain amount of graphite and SAS were added into 200 ml deionized water in a 250 ml beaker, then an ultrasonic cell disruptor (Model: ULD43-1200, 1 cm² Ti horn, Ningbo Sincere Ultrasonic Equipment Technology Co., Ltd, China) was used to disperse the mixture at 20 kHz and a certain amplitude with 1200 W and impulse 2 s on and 2 s off for a certain period of time, and the treated mixture was laid aside for 12 h. Then, the liquid mixture was centrifuged at 2 and 5 krpm (the corresponding RCF is 557 g and 3481 g for the used centrifuge) for 1 h, respectively. The obtained sediment was re-dispersed in deionized water and re-centrifuged at 5 krpm to wash out residual SAS triple. The final sediment was freeze-dried to obtain black graphene powder.

2.4. Determination of graphene concentration in dispersion
Graphene concentration in dispersion can be determined through the Lambert-Beer law: \[ A = \alpha \times C_G \times l \]
where \( A \) is absorbance, \( \alpha \) is absorption coefficient, \( C_G \) is graphene concentration, and \( l \) is the optical path length (0.01 m, here) [21]. The value of \( \alpha \) was determined from the slope of linear relation of \( A \) and \( C_G \) (figure S1 is available online at stacks.iop.org/MRX/6/1250j2/mmedia), from which the absorption coefficient was 2396 l g\(^{-1}\) m\(^{-1}\). It should be pointed out that the content of residual SAS in graphene need to be deducted from the mass of graphene powder due to the unavoidable residue of SAS in the graphene powder. The content of residual SAS in the graphene powder can be determined by an annealing method (see below) proposed in our previous work [5].

2.5. Preparation of corrosion samples
The as-exfoliated graphene was used as an anticorrosion coating of aluminium. The preparation of corrosion samples is similar to our previous work [5] and described simply as follows. First, a square aluminium foil with a side length of 1.5 cm was polished with 500, 1500, and 2000 mesh sandpapers, respectively, then sonicated in ethanol and water in turn for 10 min to remove debris from the surface, and dried. Next, 0.1 mg ml\(^{-1}\) graphene dispersion was prepared by bath sonication for 15 min 10 ml of the dispersion was coated uniformly on both sides of the aluminium foil by a spin-coating apparatus (Model: KW-4A, Institute of Microelectronics, Chinese Academy of Sciences, China). The spin coating was done at 500 rpm for 10 s and subsequently at 1000 rpm for 30 s. The spin-coated samples were dried in vacuum at 80 °C for 12 h to remove residual water. Some coated samples were annealed at 200, 400, 600 °C, respectively, for 2 h. All the graphene-coated aluminium foils were used for electrochemical measurements to test their anticorrosion performance. Each experiment was done in parallel three times, and their average values were recorded.

2.6. Electrochemical measurements
An open three-electrode system was used to test the corrosion performance of the graphene-coated aluminium foils. A calomel electrode, a platinum wire, and a graphene-coated Al foil were used as the reference, counter, and work electrode, respectively. 0.5 M H\(_2\)SO\(_4\) or 0.6 M NaCl was used as the electrolytic solution. An electrochemical analyzer (model: CH1660d, CH Instruments, Inc., USA) was used to measure potentiostatic polarization curves at room temperature. The open-circuit potential was first measured, and when the open-circuit potential was no longer changed with time, the polarization curves of dynamic potentials were measured. Three parallel measurements for each electrode were done and their average values were recorded.

2.7. Characterization
Ultraviolet visible absorption spectra were recorded in a spectrometer (Model: TU-1900, Beijing Persee General Instrument Co., Ltd, China). The incident light is set at 660 nm. Graphene dispersion was diluted by 5–10 times to avoid exceeding the instrument range. The size and Zeta potential of SAS aqueous dispersion were measured by the dynamic light scattering (DLS) method with an instrument (Model: Zetasizer Nano ZS, Malvern Instruments Co. Ltd, UK).

TEM and SEM images were obtained by a transmission electron microscope (Model: JEM-2100, Electronic Co., Ltd, Japan) and a field emission scanning electron microscope (Model: SU8010, Hitachi Hi-Tech Co., Ltd Japan), respectively. AFM images were obtained by an atomic force microscope (Model: MultiMode 8, Bruker Daltonics Inc., USA).

X-ray photoelectron spectroscopy (XPS) measurements were conducted with a spectrometer (Model: ESCFAAB250Xi, Thermo Fisher Scientific Co., Ltd, USA). Raman spectra were obtained by a Raman confocal spectrometer (Model: HORIBA XploRA ONE, with 532 nm excitation wavelength, HORIBA Jobin Yvon, France). The preparation of graphene films for Raman spectra were similar to that described in the reference [22]. The 100-fold diluted graphene dispersion was first filtered through a mixed cellulose membrane (pore
spectra were obtained by an infrared spectrometer (Model: Model: ST2253, Suzhou Jingge Electronic Co., Ltd, China) and then the membrane removed by dissolving in acetone. It should be noted that the thickness of graphene films should be limited to a maximum of 20 nm to avoid large aggregation [23]. Fluorescence emission spectra were obtained by a fluorescence spectrometer (model: Perkin Elmer LS-55, American PerkinElmer Ltd, USA) with an excitation wavelength of 660 nm. Fourier transform infrared (FTIR) spectra were obtained by an infrared spectrometer (Model: Nexus 670, Thermo Nicolet Co. Ltd, USA).

The sample for the measurement of conductivity were prepared by compressing freeze-dried graphene powder into a wafer, and its conductivity was measured by the linear four-probe method with an instrument (Model: ST2253, Suzhou Jingge Electronic Co., Ltd, China). Resistivity was determined directly by this instrument and the conductivity is calculated by the following equation: $\sigma = 1/R_{sq}d$, where $R_{sq}$ is the sheet resistance ($\Omega$ sq$^{-1}$) and $d$ is the wafer thickness (m).

### 3. Results and discussion

#### 3.1. Optimization of exfoliation process

In the optimization, the absorbance of the supernatants obtained after 2 or 5 krpm centrifugation were measured, respectively. Therefore, the graphene concentration ($C_G$) can be calculated based on Lambert-Beer law with the difference of two absorbance values above. Furthermore, the $I_D/I_G$ of graphene was determined by Raman spectra.

Here, based on $C_G$ and $I_D/I_G$, four parameters, i.e., subfractions of SASx ($x = 1, 2, 3, 4$ and $5$) obtained by two-step centrifugation (table 1), sonication power ($P$), SAS concentration ($C_{SAS}$), and sonication time ($t_s$) were optimized. Incidentally, for the subfraction SAS1-5, their molecular weight arranges in a descending order. It should be pointed out that the subfractions with molecular weight higher than SAS1 and smaller than SAS5 were discarded and not studied due to the very small amount.

| Subfraction | Low speed centrifugation | High speed centrifugation |
|-------------|--------------------------|---------------------------|
|             | Revolution (krpm) | RCF (g) | Revolution (krpm) | RCF (g) |
| SAS1        | 5                        | 3481    | 6                  | 5013    |
| SAS2        | 6                        | 5013    | 7                  | 6823    |
| SAS3        | 7                        | 6823    | 8                  | 8911    |
| SAS4        | 8                        | 8911    | 9                  | 11278   |
| SAS5        | 9                        | 11278   | 10                 | 13924   |

The effect of above four parameters on $C_G$ and $I_D/I_G$ are shown sequentially in figures 2(a)–(d). Obviously, from figure 2(a), $C_G$ reaches the highest value with SAS1 as the dispersant. This can be attributed to the highest molecular weight of SAS1 leading to the strongest interaction of SAS1 with graphene. Interestingly, the lowest values of $I_D/I_G$, meaning the lowest defect content, were also obtained with SAS1 as the dispersant. This may be the reason of the best protection against aggregation during sonication process due to the strongest interaction of SAS1 with graphene. It has been noted that the errors of $I_D/I_G$ are relatively large, but it does not affect the conclusion. In the follow optimization, SAS1 is used as the dispersant for further research and is still marked as SAS for the sake of convenience.

From figure 2(b), when the $P$ exceeds 480 W, the increase of $C_G$ becomes slow, but the $I_D/I_G$ values increase sharply. Therefore, the optimal $P$ was fixed at 480 W for subsequent study.

From figure 2(c), when $C_{SAS} \approx 0.3$ mg ml$^{-1}$, $C_G$ reaches the highest value. The similar results were also found in the case of other dispersants [5, 12]. At the same time, the $I_D/I_G$ reaches the minimum at the same $C_{SAS}$. Therefore, an interesting phenomenon can be observed that $C_G$ and $I_D/I_G$ values change in opposite trend with $C_{SAS}$, with a maximum for $C_G$ and a minimum for $I_D/I_G$ at the same time.

The observed phenomenon can be explicated as follows. Firstly, we assume that the total energy absorbed by graphite is a constant under a fixed $P$ and $t_s$ in exfoliation processes. When $C_{SAS}$ was very low ($<0.3$ mg ml$^{-1}$), the amount of SAS available for exfoliation (namely forming complex with graphene, see below) was very small, resulting in a low concentration of graphene. In another word, in the total energy absorbed by the graphite, only a small proportion was used for exfoliation and a large proportion was used for making defects (leading to high $I_D/I_G$). With the increase of $C_{SAS}$, more SAS would take part in the exfoliation, and therefore the energy used for exfoliation increased and the energy used for making defects decreased accordingly (decreased $I_D/I_G$). When
values increased faster when graphene obtained under the optimization conditions was used for exfoliation and the lowest proportion of energy was used for making defects, leading to the lowest efficiency as the dispersant particles were used for production of graphene, respectively. Therefore, this should be a general law in liquid phase exfoliation by sonication. This mechanism of the effect of \( C_{\text{SAS}} \) on \( C_G \) and \( I_D/I_G \) in sonication-induced exfoliation is illustrated in figure 1. Finally, the effect of \( t_s \) on exfoliation is shown in figure 2(d). With the increase of \( t_s \), both \( C_G \) and \( I_D/I_G \) increased. The highest \( C_G \) reached 0.181 ± 0.004 mg ml\(^{-1}\) at \( t_s = 5 \) h. It should be pointed out that sonication time of exceeding 5 h was not suitable for large-scale preparation due to reduced efficiency [24]. Further, the \( I_D/I_G \) values increased faster when \( t_s > 2 \) h. This may be attributed to the fact that when \( t_s < 2 \) h and \( t_s > 2 \) h, different types of graphene defects have been produced. When \( t_s < 2 \) h, edge defects are dominant, and when \( t_s > 2 \) h, bulk defects are dominant [25]. Therefore, if the graphene with less defect contents \( (I_D/I_G = 0.331 ± 0.021) \) was required, the sonication time \( t_s = 2 \) h should be a better choice.

It should be noted that each experiment of exfoliation was conducted triple and the average values were reported with the maximum relative errors less than 10% for \( C_G \) and \( I_D/I_G \).

As a result, under \( P = 480 \) W, \( C_{\text{SAS}} = 0.3 \) mg ml\(^{-1}\), \( C_G = 15 \) mg ml\(^{-1}\), the \( I_D/I_G \) value is as low as 0.331 ± 0.021 \( (C_G = 0.103 \) mg ml\(^{-1}\)) with \( t_s = 2 \) h, and the \( C_G \) value can reach 0.181 ± 0.004 mg ml\(^{-1}\) \( (I_D/I_G = 0.410) \) with \( t_s = 5 \) h. Therefore, \( t_s \) at 2 or 5 h are more suitable for low-defect or high-concentration production of graphene, respectively.

In addition, the \( C_G \) of the supernatant after 2 krpm centrifugation was 0.138 mg mL\(^{-1}\) \( (t_c = 2.0 \) h) or 0.235 mg mL\(^{-1}\) \( (t_c = 5.0 \) h), respectively. Therefore, our graphene accounted to 74.6% \( (t_c = 2.0 \) h) and 77.0% \( (t_c = 5.0 \) h) of full-size graphene, respectively. Incidentally, due to less sonication time used in our work, the concentration of our graphene is slightly lower than some literature values [5, 26]. In the following study, the graphene obtained under the optimization conditions \( (P = 480 \) W, \( C_{\text{SAS}} = 0.3 \) mg ml\(^{-1}\), and \( t_c = 2 \) h) was used unless otherwise stated.

It should be noted that the yield of our graphene is low \( (0.68% \) with \( t_c = 2 \) h). Recycling of sediment graphite for exfoliation is an effective method to raise the yield to 3.6% with five-time cycles (see Supplementary Material: 2. Re-cycling of sediment graphite).

**Figure 2.** Concentration (left coordinate) and \( I_D/I_G \) (right coordinate) of graphene at different subfraction \( (SAS, x = 1,2,3,4,5) \) \( (t_s = 2 \) h, \( P = 480 \) W, \( C_{\text{SAS}} = 0.3 \) mg ml\(^{-1}\), \( C_G = 15 \) mg ml\(^{-1}\)) (a), power \( (t_s = 2 \) h, \( C_{\text{SAS}} = 0.3 \) mg ml\(^{-1}\), \( C_G = 15 \) mg ml\(^{-1}\)) (b), concentration of SAS \( (C_{\text{SAS}}) \) \( (t_s = 2 \) h, \( P = 480 \) W, \( C_G = 15 \) mg ml\(^{-1}\)) (c), and sonication time \( (t_s) \) \( (P = 480 \) W, \( C_{\text{SAS}} = 0.3 \) mg ml\(^{-1}\), \( C_G = 15 \) mg ml\(^{-1}\)) (d).
3.2. Characterization of graphene

As is known to all, the size, layer number, and defect content of graphene would affect its performance in applications. Thus, the estimation of the size, layer number, and defect content of graphene is essential. The size of graphene can be determined by SEM, TEM, and AFM; the layer number can be estimated by AFM, TEM, and Raman spectra; and the defect content can be evaluated by the ratio $I_D/I_G$ in Raman spectra. Furthermore, the content of residual dispersant in graphene is an important index to affect graphene quality because it affects performance of the graphene in use [5, 12].

Figures 3(a)–(c) shows typical SEM, TEM, and AFM images of the graphene, respectively. From these images, we can observe that the thickness of the graphene is very thin, and the size is within a few hundred nanometers, which is much smaller than that of its precursor graphite (44 μm). The greatly size reduction of graphene may be attributed to the effect of sonication-induced crushing [27]. SEAD pattern of TEM (inset of figure 3(b)) shows the characteristic of circular regular hexagon pattern with uniform distribution and the same bright diffraction spots at the innermost layer and the second inner layer, indicating a typical characteristic of monolayer graphene sheet with good crystal [7, 12].

In the AFM images with their height profiles shown in figure 3(c) and figure S5, the graphene thickness of (0.7–1.4) nm, (1.5–1.8) nm, (2.4–2.9) nm, (3.2–3.8) nm, and (4.0–4.2) nm marked with (1)-(3) may be regarded as a monolayer to 5 layers, respectively [5, 21]. This existence of monolayer is consistent with the result of TEM. To determine the size and layer number distribution of the graphene, we randomly selected 238 graphene sheets...
obtained under \( t_s = 2 \) and 5 h in the AFM images as the statistical samples. The resultant normalized histograms of the length, width, and layer number distribution are shown in figure S6. From these histograms, the length and width was mainly in the range of 100–400 nm, and the proportion of the graphene with 1–4 layers reached 98% for \( t_s = 2 \) or 5 h.

Raman spectroscopy is a versatile tool for studying the properties of graphene [28, 29]. It can provide information about not only the defect content but also the number of layers per flake [28]. Raman spectra of graphene are characterized by a D-band (~1350 cm\(^{-1}\)), a G-band (~1582 cm\(^{-1}\)) and a 2D-band (~2700 cm\(^{-1}\)) [21]. In Raman spectra, the intensity ratio of D-band and G-band \((I_D/I_G)\) can be used to characterize the defect content of graphene, as illustrated in Subsection 3.1; and the position and shape of 2D peak can be used to evaluate the layers number of graphene [14]. Raman spectra of the graphene obtained in optimization condition \((t_s = 2 \) or 5 h) are shown in figure 4(a). Spectra of graphene oxide (GO), reduced GO (RGO), and raw Gi are also provided in figure 4(a) for comparison. In the spectra of our graphene, the existence of 2D peak indicates that the quality of our graphene was much better than that of the GO and RGO (for GO and RGO, no 2D peak was observed) [30]. The 2D-band of less than 2700 cm\(^{-1}\) (532 nm laser excitation) with the symmetrical shape indicates that the graphene obtained was few-layer (<5 layers) [14], consistent with the results of AFM. The ratio of \(I_D/I_G\) for graphite, graphene obtained for \( t_s = 2 \) and 5 h, GO, and RGO was 0.083, 0.331, 0.410, 0.94, and 1.10, respectively. The much lower \(I_D/I_G\) values of the graphene for 2 and 5 h than those of GO and RGO indicates that the defect content of our graphene was much lower than that of the graphene obtained by chemical method (such as Hummers method and its various improved methods) [5, 12]. Furthermore, the lower \(I_D/I_G\) value of the graphene obtained for \( t_s = 2 \) h than that for \( t_s = 5 \) h shows that a longer \( t_s \) would produce more defects [26]. It should be pointed out that the \(I_D/I_G\) value was an average of ten parallel measurements of freeze-dried samples, with a relative deviation of less than 10%.

Besides the layer number, size, and defect content of graphene, the determination for the content of residual dispersants in graphene is also an important aspect of characterization. The residual dispersant in graphene is difficult to be removed, and its content depends on the type of dispersants and the separation procedure of graphite, sulfonate asphalt, and graphene from dispersions [7, 17, 21]. Figure 4(b) shows the C1s XPS spectra of graphite, sulfonate asphalt, and graphene, revealing the existence of several types of carbon: C=O, C=S/N/O, and C-H in the prepared graphene [12, 30, 32–34]. Compared with the C1s spectra of graphite and SAS, the graphene sample had several types of carbon derived from SAS. This proves the existence of SAS in the graphene sample. Here, the content of residual SAS in graphene samples was determined by the annealing method proposed in our previous work [5]. According to the weight change of SAS, graphene, and graphite before and after the annealing at 600 °C for 2 h, the content of residual SAS in the graphene can be calculated to be 11.4 wt%, which is similar to that of other dispersant residues in the graphene obtained by the filtration method [5, 7, 21, 35, 36].

Conductivity is also an important property of reflecting the quality of graphene. The conductivity of our graphene is 10134 S m\(^{-1}\), which is one of the highest conductivities for the graphene prepared by the LPE method [5, 13]. The conductivity of the graphene by annealing at 600 °C for 2 h under N\(_2\) atmosphere can increase to 23781 S m\(^{-1}\), which is among the highest values [13]. The graphitization of SAS molecules absorbed on the surface of graphene at 600 °C, through the pyrolysis of oxygen/sulfur-containing groups (as indicated in figure S7), may be a reason for the great increase of conductivity.
3.3. Exfoliation and stabilization mechanism

The weak alkalinity ($\text{pH} = 8.2$) and negative zeta potential ($\zeta = -43.3 \text{ mV}$ for 0.3 mg ml$^{-1}$ SAS solution) of aqueous solution of SAS indicated that SAS was dissociated into large negatively charged ions and counter medium ions in water. The large negatively charged ions of SAS play an important role in the stabilization of graphene dispersion.

The exfoliation process of graphite in aqueous SAS solution can be described as follows: First of all, sonication leads to a cavitation of water, i.e. a large number of small bubbles occur, grow up or suddenly burst. The resulting strong impact force on graphite would enlarge the spacing in graphite layer instantaneously. In the meantime, some negatively charged SAS ions enter the interlayers and are adsorbed on the surface of the graphene sheets due to their strong interactions, thus isolating the graphite layers on both sides. Therefore, the graphite layers cannot restore even if the ultrasound stops. Furthermore, the distance of graphite layers further increases due to the electrostatic repulsion between the negatively charged SAS ions adsorbed on the graphite layers, resulting in the complete exfoliation of adjacent graphite layers. Finally, the negatively charged graphene sheets continually attract cations in aqueous solution to form the stable electric double layer. The exfoliation and stability mechanism of graphite into graphene in aqueous SAS solution are also supported by the results reported in the literature [5, 12, 21].

Whether the above mechanism works or not depends on the formation of the complex of SAS with graphene (G-SAS). Only when SAS and graphene form a complex, there be energy transfer between them, leading to the graphene negatively charged. The formation of the G-SAS complex can be confirmed by their fluorescence and infrared spectra in figure 5. Figure 5(a) shows that compared with pure SAS, the fluorescence of the SAS adsorbed on the surface of graphene (G-SAS) was quenched. This proves that there is an energy or electron transfer between graphene and SAS, which is a strong evidence for the formation of G-SAS complex [12, 37]. The red shift of characteristic absorption peaks of SAS adsorbed on the surface of graphene (see figure 5(b)) also provides an evidence for the formation of the complex. For SAS, there are four absorption peaks at 536.1, 626.8, 1051.0, and 1130.0 cm$^{-1}$ derived from sulfonic acid group [38]. Yet for the residual SAS absorbed on the surface of graphene, there are similar peaks at near the four locations (503.3, 624.8, 1041.0, and 1028.0 cm$^{-1}$), but all of them have a red shift, thus also confirming the formation of G-SAS complex.

In addition, the stability of the G-SAS complex was indicated by its high zeta potential ($\zeta = -38 \text{ mV}$) in the dispersion, whose absolute value exceeds the accepted stable value ($|\zeta| = 25 \text{ mV}$). After a month, the zeta potential was kept to $\zeta = -36 \text{ mV}$, further also confirming the good long-term stability of the graphene dispersion.

3.4. Effect of graphene quality on the anticorrosion of aluminium

Aluminium is one of the most widely used metals, but it is also one of the metals with the lowest electrode potential, which makes it easier to be corroded in applications [39]. Therefore, the study of aluminium anticorrosion is interesting in practical application.

One of the most widely used anticorrosion methods of aluminium is to coat its surface with a layer of material to isolate it from the environment. As far as we know, many materials have been used to coat Al surface for anticorrosion, such as metals (Au, Pt, Ni, Ti, and their alloy) [40, 41], polymers and their mixtures with carbon materials (e.g. carbon nano-tube and graphene) [42, 43], and stearic acid-modified ZnO nanoplates [44]. Among all these materials, graphene is a good candidate due to ultrathin coating, excellent thermal stability, good chemical inertia, high mechanical strength, etc [45] Graphene oxide (GO) [45], polyvinyl alcohol-reduced

![Figure 5.](image)

Figure 5. (a) Fluorescence spectra of the aqueous dispersion of sulfonated asphalt (SAS) and graphene-sulfonated asphalt (G-SAS) complex. (b) Infrared absorption spectra of SAS, G, and annealed G (a-G) at 200, 400 and 800 °C, respectively.
GO (PVA-rGO) complex [46], and monolayer graphene prepared by the CVD method [6] have also been successfully used as anticorrosion coating to protect aluminium effectively.

In our previous work, we used the graphene obtained by the fulvic acid-assisted exfoliation as an anticorrosion coating of Al [5]. In this work, with the prepared graphene as an anticorrosion coating of Al, we studied systematically the effect of the size, defect content of graphene and the annealing on the anticorrosion of Al. Herein, the electrochemical measurements were done in 0.5 M H₂SO₄ and 0.6 M NaCl aqueous solutions, simulating the electrolytes in lead-acid battery and seawater, respectively. It should be noted that each experiment of anticorrosion was performed triple and the average values were recorded.

It should be noted that, when Al foils contact with water saturated with oxygen, hydroxyl groups are formed [46]. When the graphene was spin-coated onto the Al surface, the oxygen-containing functional groups of residual SAS would form covalent bonds with hydroxyl groups. Therefore, the existence of the residual SAS in the graphene is beneficial for improving anticorrosion.

Before studying the effect of graphene quality and the annealing on aluminium anticorrosion, the graphene materials and corrosive samples were named for the convenience of the discussion below. In the markers of G−t−(l + h) or a-G(Tₐ)−t−(l + h), G and a-G(Tₐ) refer to graphene and annealed graphene at Tₐ(°C), and (l + h) refers to the low and high centrifugation speed (krpm) in two-step centrifugation (see subsection 2.3 above). The markers of Al/G−t−(l + h) or Al/a-G(Tₐ)−t−(l + h) refer to the corresponding graphene-coated Al foil samples.

For the surface of Al/G−2−(2 + 5) sample, the representative SEM and AFM 3D images with scanning areas of 2 × 2 μm² and 10 × 10 μm² were shown in figures S8(a)–(c). From figure S8(a), the whole surface has been covered completely, indicating the effectiveness of the spin-coated method. From the figures S8(b)–(c), the average roughness (Rₐ) and root-mean-square roughness (Rₛ) of the scanning areas 2 × 2 μm² or 10 × 10 μm² were 5.14 and 3.86 nm, or 50.7 and 36.1 nm, respectively. Compared with the SEM image, the 3D images of AFM were more intuitive to show the corresponding morphology. It should be pointed out that the great fluctuation of the surface was attributed to the grooves caused by polishing.

First, two graphene materials of G−2−(2 + 3.5) and G−2−(3.5 + 5) were used to study the effect of the graphene size on Al anticorrosion. Tafel curves of Al/G−2−(2 + 3.5) and Al/G−2−(3.5 + 5) or Al/G−5

Figure 6. Tafel curves of Al foils coated by graphene with different size in 0.5 M H₂SO₄ (a) and in 0.6 M NaCl (b), and different defect content in 0.5 M H₂SO₄ (c) and 0.6 M NaCl (d), respectively.
Table 2. Corrosion potentials (E_{corr}) and corrosion current densities (j_{corr}) in 0.5 M H_{2}SO_{4} and 0.6 M NaCl.

| Samples                                      | 0.5 M H_{2}SO_{4}  | 0.6 M NaCl     |
|----------------------------------------------|-------------------|----------------|
| Al samples coated with different size graphene |                   |                |
| Al/G–2−(2 + 3.5)                            | 535               | –1196          |
| Al/G–2−(3.5 + 5)                            | 519               | –1006          |
| Al/G–5−(2 + 3.5)                            | 527               | –952           |
| Al/G–5−(3.5 + 5)                            | 522               | –1080          |
| Al samples coated with different defect content graphene |                   |                |
| Al/G–2−(2 + 5)                              | 518               | –116            |
| Al/G–5−(2 + 5)                              | 517               | 7.20 x 10^{-5}  |
| Al samples coated with different annealing temperature graphene |                   |                |
| Al/a−G200−2−(2 + 5)                         | 501               | –1158          |
| Al/a−G400−2−(2 + 5)                         | 534               | –914           |
| Al/a−G600−2−(2 + 5)                         | 319               | –823           |
| Al/a−G200−5−(2 + 5)                         | 484               | –1080          |
| Al/a−G400−5−(2 + 5)                         | 498               | 7.30 x 10^{-7}  |
| Al/a−G600−5−(2 + 5)                         | 494               | –928           |

Notes: Al/G−t_{a}−(l−h) or Al/a−G(T_{a}−t_{a}−(l+h) refer to the unannealed or annealed graphene-coated Al foils samples, respectively, in which T_{a}, t_{a} and h refer to annealing temperature, sonication time, low and high centrifugal speeds (unit: k rpm) in the preparation of graphene, respectively. Based on three parallel experiments, the maximum relative errors of corrosion potential and corrosion current are less than 10%.

–(2 + 3.5) and Al/G–5−(3.5 + 5) samples, along with polished Al for comparison, are shown in figures 6(a)–(b). And the corresponding corrosion potential (E_{corr}/(mV versus SCE)) and corrosion current density (j_{corr}/(A cm^{-2})) were listed in table 2. From table 2, in 0.5 M H_{2}SO_{4}, a smaller j_{corr} for Al/G–2−(3.5 + 5) or Al/G–5−(3.5 + 5) than that for Al/G–2−(2 + 3.5) or Al/G–5−(2 + 3.5) meant that the graphene with a smaller size was more effective to protect Al foils from corrosion. This may be attributed to the more perfect coating produced with the smaller size graphene than the larger size graphene. On the contrary, figure 6(b) shows a smaller E_{corr} for Al/G–2−(2 + 3.5) or Al/G–5−(2 + 3.5) than that for Al/G–2−(3.5 + 5) or Al/G–5−(3.5 + 5), meaning that the graphene with larger size was more effective to protect Al foils in 0.6 M NaCl. This can be interpreted by less corrosion sites for the larger size graphene coating (G–2−(2 + 3.5) or G–5−(2 + 3.5)) on the surface of Al foils.

For H_{2}SO_{4} and NaCl solutions, the reverse effect of size on j_{corr} may result from stronger permeability of chloride ion (Cl^{-}) than sulfate ion (SO_{4}^{2-}) [47, 48]. The coating formed by the graphene with smaller size would provide more ion channels and thus is more likely to be pierced by smaller Cl^{-} instead of larger SO_{4}^{2-}.

As indicated at subsection 3.1, the defect content of G–2−(2 + 5) is smaller than that of G–5−(2 + 5) (their I_{D}/I_{G} is 0.086 and 0.123, respectively). Here, the graphene samples of G–2−(2 + 5) or G–5−(2 + 5) were used as the corrosion inhibitor to investigate the effect of the defect content on the anticorrosion of Al. Figures 6(c)–(d) show Tafel curves of Al/G–2−(2 + 5) and Al/G–5−(2 + 5), and their E_{corr} and j_{corr} are also listed in table 2. The j_{corr} value for Al/G–2−(2 + 5) is larger than that for Al/G–5−(2 + 5), indicating better anticorrosion performance of Al/G–5−(2 + 5). The higher defect content of G–5h−(2 + 5) provided more opportunity for SAS to bond with the graphene [25, 49]. This may be why the corrosion resistance of Al foils coated by the higher defect content graphene was improved.

It should be pointed out that the effect of size and defect content of graphene on the corrosion resistance of coated aluminum cannot be arbitrarily extended to a wider range of size and defect content. If the size and defect content are far beyond those of our graphene, the conclusion needs to be re-validated.

Next, the effect of the annealing temperature on the corrosion resistance was investigated. Here, G–2−(2 + 5) or G–5−(2 + 5) were used as the coating to investigate the effect of the annealing on the corrosion resistance of Al. Tafel curves of the graphene-coated Al foils annealed at 200, 400, and 600 °C for 2 h are shown in figure 7, and the relative corrosion parameters are also listed in table 2. With the increase of annealing temperature, the j_{corr} for the used two materials increased in 0.5 M H_{2}SO_{4} solution, and the j_{corr} for the used two materials decreased at first and then increased, with a minimum at 200 °C in 0.6 M NaCl solution. The effect of the annealing on the corrosion current density can be explained as follows.

First of all, we noted that the high temperature of annealing led to SAS decomposition, while the graphene didn’t. The graphene (i.e. G-SAS complex) attached to the surface of Al goes through two changes with the increase of annealing temperature. At low temperature range (< 230 °C, see TG curve of SAS in figure S7), the trace bound water and/or absorbed small gas molecules in the G-SAS complex would evaporate to remove. The
evaporation would not cause desorption of the graphene from the Al surface, rather, would cause the graphene to be adhered more closely to the Al surface due to the remove of trace water and gas molecules. This is beneficial to improve the corrosion resistance (Factor I). As the temperature continues to increase (>230 °C), SAS would be pyrolyzed (figure S7), resulting in the escape of a large number of small gas molecules from the gap between the graphene and Al, which were produced due to these reactions of the cyclization, aromatization, and/or polycondensation of SAS pyrolysis products [50]. Unlike the case in low temperature, in high temperature the escape of a large number of small gas molecules would disrupt the adhesion of the graphene to Al surface, which is disadvantageous to the improvement of corrosion resistance (Factor II). But these reactions of cyclization, aromatization and/or condensation of pyrolysis products increase the graphitization degree of SAS, and thus result in an enhancement of the \( \pi - \pi \) interaction between graphene and SAS, which can be confirmed by IR spectra of the aromatic ring (1400–1600 cm\(^{-1}\) wavenumber) of annealed SAS at 200, 400, and 600 °C, respectively (see figure 5(b)). The graphitization is beneficial to improve the corrosion resistance of the samples (Factor III). Therefore, the corrosion resistance of the samples after annealed at high temperature depends comprehensively on the three factors above. In 0.5 M H\(_2\)SO\(_4\), the \( j_{corr} \) increases with the annealing temperature, indicating that Factor II is dominant. Further, the higher the temperature (>230 °C), the greater the contribution from Factor II. This is because higher temperature causes more gas molecules to escape, and thus makes greater disturbance to the graphene absorbed on the surface of Al foils. In 0.6 M NaCl, for the annealing temperature of less than 200 °C, the corrosion current density decreases with the increase of annealed temperature until 200 °C. Therefore, in the temperature range (<200 °C), the corrosion current density is dominated by Factor I instead of Factor III, which can be confirmed by a slightly reduced weight at 200 °C in TG curve of SAS shown in figure S7. When the temperature is in the temperature range (>200 °C), Factor II dominates, which is supported by the significantly decreased weight under > 200 °C (see figure S7). In addition, in H\(_2\)SO\(_4\) and NaCl solutions, the annealing temperature has different effect on anticorrosion of Al foils, which may be due to different penetration abilities of SO\(_4^{2-}\) and Cl\(^-\) ions.

Of all the tested samples of our graphene as the anticorrosion coating, Al/G−5−(2 + 5) and Al/a−G200−5−(2 + 5) shows the best corrosion resistance in 0.5 M H\(_2\)SO\(_4\) \( (j_{corr} = 7.20 \times 10^{-7} \text{ A cm}^{-2}) \) and in 0.6 M NaCl
(\(J_{\text{corr}} = 7.30 \times 10^{-7} \text{ A cm}^{-2}\)) solution, respectively, which both are superior to the U.S. DOE target (\(J_{\text{corr}} < 10^{-6} \text{ A cm}^{-2}\)) [41]. Furthermore, they indicated high anticorrosion efficiencies (87.6% in 0.5 M \(\text{H}_2\text{SO}_4\) and 99.4% in 0.6 M \(\text{NaCl}\), respectively). In addition, not only the anticorrosion efficiencies of the graphene prepared in this work are higher than those reported in our previous work [5], but also the operation is much simpler due to only a single coating required.

4. Conclusions

In summary, a new dispersant (SAS) was used successfully to exfoliate graphite into graphene in aqueous solution under sonication. A called double-criterion optimization method was proposed, i.e. the \(C_G\) and \(I_D/I_G\) of as-exfoliated graphene, which are both used as two optimization criterions simultaneously. Under the optimized conditions, the highest \(C_G\) can reach 0.181 mg ml\(^{-1}\), and the lowest defect content was 0.331. The as-exfoliated graphene sheets were \(<5\) layers and mainly within 100–400 nm. The stabilization of the graphene dispersion comes mainly from the electrostatic repulsion between negatively charged graphene flakes. When the graphene was used as the protective coating of aluminium, relatively small size in \(\text{H}_2\text{SO}_4\) solution or large size in \(\text{NaCl}\) solution, relatively high defect content and proper annealing temperature were beneficial to the improvement of anticorrosion performance. The new dispersant (SAS) and the proposed two-criterion optimization would promote the development of the large-scale liquid-phase exfoliation of graphite into the graphene for the applications where specific defects are required.

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