Performance of graphene dispersion by using mixed surfactants

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Abstract

In this work the ability of pure surfactant Sodium Dodecyl Sulfate (SDS), Cetyltrimethyl Ammonium Bromide (CTAB) and their mixed surfactants for graphene dispersion in aqueous solution was investigated. The uniform and stable dispersion solution was obtained for graphene with the mixtures of SDS and CTAB at lower concentration as compared to the pure one. The SDS-based surfactants exhibited better dispersion as compared to CTAB-based surfactants due to smaller-sized graphene as was investigated via Zeta potential measurements. Zeta potential was utilized to characterize the colloidal stability of surface charges within the mixtures. The mixed surfactants utilized in the present study showed a better ability to disperse graphene and its derivatives and hence are well suited for practical applications.

1. Introduction

The unique structure of graphene makes it excellent in performance, due to its strong mechanical properties, good thermal and electrical conductivity, and high specific surface area and light transmittance. Graphene has various potential applications in many fields, such as composite materials, transparent flexible electronics, semiconductor and energy storage equipment [1–3]. The large van der Waals forces between graphene monolayer sheets make it compact and clustered, hence can hinder its applications due to poor solubility and dispersion in water and other organic media [4, 5]. The currently available graphene synthesis techniques such as chemical vapor deposition, solution-phase exfoliation method and chemical-reduction method usually fail to produce single-layer graphene [6, 7]. Even after obtaining a single layer of graphene, agglomeration and stacking mechanism is always inevitable, affecting the dispersion and stability of the material. Furthermore, uniform and stable graphene dispersion is necessary to obtain graphene reinforced matrix composites by utilizing solution blending method [8–11]. In order to solve this problem, two methods are currently used for the dispersion of graphene. One is physical dispersion and the other is chemical modification. Physical dispersion includes mechanical dispersion, ultrasonic dispersion and microwave radiation, involving the breakdown of van der Waals forces between the graphene layers by utilizing the external force [12]. However such strong forces can disrupt the inherent sp2 hybridized structure and morphology, which contributes towards the exceptional behavior of graphene [13]. In contrast, chemical modification involves the non-covalent and covalent functionalization by dispersing the graphene into aqueous, organic and alkaline solution containing a modifier [14–18]. Covalent functionalization refers to the bonding of different chemical functional groups on the surface of graphene. The non-covalent functionalization is considered to be more favorable because it does not change the structure of π-electron, consequently preserving the electrical properties of graphene [19]. The surface of graphene is embedded with the modifier’s molecule, and the van der Waals forces between the graphene layers are dominated by electrostatic or intermolecular forces, providing a stability to graphene dispersion. In order to achieve best effects in applications, usually both the methods can be used at the same time.

Several researchers have used the pure graphite, graphene, its derivatives, and carbon nanotube as precursor obtained via various surfactants for stable aqueous suspensions. The stability of the dispersion can be attributed...
towards the type of material, concentration of surfactants, percentage of dispersed materials, centrifugation rate and sonication time [20–22]. The thermodynamic enthalpy and electron transport between graphite carbon layer and solvent molecules can clearly elaborate how graphene is stably dispersed in organic solvents with appropriate surface energy or in aqueous solutions of any surfactants. Coleman et al [23] proposed an approximate expression that solvents with similar surface energy (about 40 ~ 50 mN m⁻¹) to graphene are considered as favorable dispersion media. The surface energy of water is too high to match graphene unless it is used with some surfactants.

The surfactant is usually adsorbed on both sides of graphene sheet, and the electrostatic repulsion or intermolecular force is used to stabilize the distribution of graphene in the solution. In addition, surfactants are intercalation agents, widening the distance between the graphite layers. The optimal surfactant concentration is close to the critical micelle concentration (CMC) [20, 24]. The concentration of the surfactant is critical in the dispersion process, which is not only significant for dispersing specific surfactant, but also is of economic value. We concluded that it is necessary to utilize appropriate amount of surfactant to obtain better dispersion and uniformity. Phase separation occurs when the number of surfactant molecules is high [25]. Considering the ability of dispersion efficiency, the high cost of surfactant dispersed graphene and its adverse environmental impact, it is vital to explore a new formula containing smaller amounts of surfactants, with the dispersion ability improved.

Mixed surfactants can be used in almost all the applications because groups interact by changing the surface charge on dispersed substance and modifying the attractive or repulsive force even at a very low concentration [26, 27]. Although there has been a lot of research about pure surfactant, more exploration is needed. Han et al [28] modified rGO with polystyrene sodium sulfonate (PSS), which did not accumulate or precipitate in aqueous solution in several weeks. The hydrophilicity of graphene was greatly improved, because the benzene rings on PSS produced large steric resistance between graphene sheets and finally a stable dispersion was obtained. B Sohrabi et al [29] studied two pure surfactants (sodium dodecyl sulfate) SDS and CTAB (Cetyltrimethyl ammonium bromide) and various mixtures of different ratios of SDS/CTAB. The best dispersion and strong adsorption onto CNTs surface was found with the mixtures ratio of CTAB: SDS: 90:10.

In this study, we investigated the dispersion of graphene by mixing SDS and CTAB at different ratios. This study provided the details about the better performance of mixed surfactant to disperse graphene.

2. Experimental procedure

2.1. Sample preparation

Graphene oxide with length of 0.8–2.1 nm diameter of 500 nm-5 um, and a monolayer rate of 99% by the Hummer’s method was purchased from Nanjing XFNANO Materials Tech Co., Ltd. It was prepared by Hummer and freeze drying method. The surfactants such as sodium dodecyl sulfate (SDS, >99%) and Cetyltrimethyl ammonium bromide (CTAB, >99%) were provided by Beijing Chemical Works. The chemical structures of surfactant used in this study are shown in figure 1. All the experiment were carried out with deionized water. In order to obtain a surfactant-stabilized GO dispersion, the experimental steps followed were: (1) 1 mg graphene oxide powder were sonicated for 30 min with 10 ml deionized water. After sonication, 30 ml aqueous solutions of SDS, and CTAB with different proportions such as SDS/CTAB ((1:9), (2:8), (3:7), and (4:6)) and SDS/CTAB ((9:1), (8:2), (7:3), and (6:4)) were added to the prepared solution. All these samples were sonicated at room temperature for 30 min with a tip ultrasonic processor Brutsch Ruegger TPC-15 in order to get the surfactant-coated graphene oxide. (2) Ammonia water was used to adjust the pH at a value of 9 ~ 10. Hydrazine hydrate was added as the reducing agent, and then the solution was kept for 1 h in water bath at 80 °C. (3) To obtain a uniform and stable graphene dispersion, the prepared dispersion was dialyzed to neutral with deionized water and were afterwards investigated further. The critical micelle concentration (CMC) of SDS and CTAB are 6 and 0.8 mM, respectively. Therefore, for pure SDS and CTAB system, three series of aqueous solutions of any surfactants. Coleman et al [23] proposed an approximate expression that solvents with similar surface energy (about 40 ~ 50 mN m⁻¹) to graphene are

Figure 1. Chemical structures of the SDS and CTAB surfactants.
2.2. Characterization techniques

In order to investigate the effect of surfactant upon the graphene dispersion, all the samples were tested Bruker Optics VERTEX70 spectrophotometer at a wavelength range of 200–800 nm. The temperature of the scattering cell was controlled at 298 K. Zeta potential measurements were performed at 298 K by utilizing Nano-ZS90 (MALVERN) in order to determine the stability of the graphene dispersion. The reduction effect of GO flakes in graphene dispersion solution, deposited on silicon substrate was determined by using Raman spectroscopy (Raman microscope renishaw) at a laser wavelength of 532 nm.

3. Results and discussion

3.1. Comparison between dispersion ability of pure and mixed surfactants

In view of the fact that there was a linear relationship between the absorbance and concentration of graphene, as shown in figure 2, the dispersion of rGO in aqueous media was in excellent agreement with Lambert–Beer Law. Similar to carbon nanotubes [20–32], monolayer graphene exhibited better activity in UV–vis region, attributing towards the additional absorption peaks in one-dimensional Van’t Hoff singularities. However, multilayer graphene was found less active in the wavelength of 200–800 nm. The amount of graphene dispersion was determined by the absorbance intensity of the solution at 200–800 nm. The optimal concentration for aqueous graphene dispersions with various SDS and CTAB concentrations and ratios was ensured by UV–vis spectra as depicted in figure 2.

In any case, the absorption intensity of the graphene dispersion will start to increase with the increase of the surfactant concentration until it drops near the optimal dispersion concentration point, as shown in figures 2 and 3. As the surfactant concentration increased, more surfactant molecules adsorbed onto the graphene surface, resulting in an increase in the dispersed graphene concentration. As the surfactant concentration increases further, the absorbance of the dispersed graphene begins to decrease. At this point, surfactants tend to gather together to form micelles rather than disperse and stabilize the graphene. The adsorption intensity of SDS dispersed graphene was recorded greater as compared to that of CTAB at any concentration tested, indicating the better dispersion effect of SDS under the optimal concentration. Because the alkyl chains of SDS surfactant are shorter, and the repulsive interactions are reduced, which facilitates the packing and improves the absorbance. Similar absorbing behavior was previously observed on CNTs when the concentration of SDS and CTAB is 8 and 0.6 mM, respectively [33]. Thus, these values were considered as optimal concentration for SDS and CTAB. The absorbance intensity of all the samples was increased initially with the increase in surfactants concentration still the optimal values, and then started to decrease. A large number of surfactant monomers in the suspensions were absorbed onto the surface of graphene, increasing the concentration of graphene dispersion. Furthermore, when the concentrations of SDS and CTAB exceed their optimal value, useless and undesirable results occur. Because beyond the optimal concentration limit the surfactants tend to cluster
together instead of providing the stability to graphene. Similar results have been reported by Mahdiyeh with the optimal concentrations, slightly lower than that of CMC surfactants [33].

The higher absorbance for SDS/CTAB (9:1) revealed the increased number of independent dispersed graphene as shown in figure 3(a), whereas the effect of imparity trend was observed for the SDS/CTAB (1:9) as shown in figure 3(b). The dispersion abilities of surfactants at both the concentration SDS/CTAB (9:1) and SDS/CTAB (1:9), were found greater as compared to that of the pure SDS or CTAB. Moreover, the dispersion efficiency for SDS/CTAB (9:1) was relatively better than that of SDS/CTAB (1:9). Furthermore, the CMC value of mixed surfactants and the amount of dispersed graphene were generally lower than those pure surfactant, and mixed surfactants are less costly and more beneficial to the environmental protection in table1.

Based on different effects of dispersions dominated by either cationic or anionic species, the graphene dispersions at different concentrations of SDS and CTAB was investigated as shown in figure 4(a). The dispersion abilities of various concentration ratios of SDS/CTAB followed the sequence as follows;

SDS/CTAB(9: 1) > SDS/CTAB(8: 2) > SDS/CTAB(7: 3) > SDS/CTAB(6: 4)

As the proportion of CTAB in the mixed dispersant increased, the adsorption of CTAB on graphene surface became more effective. SDS and CTAB are anionic and cationic surfactants respectively, with opposite charges, and when two surfactants with opposite charges meet in an aqueous solution or adsorb on the graphene surface at the same time, they are neutralized and the effect of individual surfactant becomes weak. The same tendency was found in CTAB-based cationic mixed dispersion system, as can be seen in figure 4(b). Hence, the dispersion effect of mixed surfactants on graphene is much higher. The better dispersive ability was observed for two surfactants whose molar fractions differ greatly. And irrespective of the proportion of SDS and CTAB in mixed surfactants, the dispersion effect on graphene was far better as compared to that of pure surfactant.

3.2. Comparison of the surface charge between pure graphene and mixed surfactants

The Zeta potential is the strength index for repulsion or attraction between particles, indicating the stability of colloidal dispersion. The greater absolute value of Zeta potential represents the better stability of the system. The
The standard value for Zeta potential is 30 mV, and the electrostatic repulsion interaction with a Zeta potential value less than \(-30\) mV or higher than \(+30\) mV is considered as a stable system. Within the dispersed graphene, the cationic or anionic surfactants were adsorbed and charges were transferred onto these flakes. Electrostatic repulsions between graphene flakes coated with ionic-surfactants stabilized the dispersion against re-aggregation. The concentration of graphene dispersion is related to electrostatic repulsion potential barrier between the sheets. The electrostatic potential barrier can be reflected by Zeta potential, so the concentration of the dispersion can be determined by the potential change \([34]\).

The dispersion effect of each surfactant and each concentration was found better and stable, as the Zeta potential of graphene dispersion for SDS and SDS/CTAB \((9:1)\) was lower than \(-30\) mV, whereas, for CTAB and SDS/CTAB \((1:9)\) was higher than \(30\) mV, as shown in table 2. Also, the Zeta potential value for SDS and SDS-based anionic mixed dispersion was found higher as compared to CTAB and CTAB-based cationic mixed dispersion system. This fact can be explained as the alkyl chain of SDS is shorter as compared to CTAB, so it is easier for SDS to be adsorbed easily into graphene sheets. White et al \([34]\) systematically studied the Zeta potential distribution for surfactant-coated single-walled carbon nanotubes (SWNTs) in water. The negative potential for the solution at the mixture ratio of SDS: CTAB: 1:2, carbon nanotubes were more favorable to bond with SDS. They proposed that when increasing the concentration of SDS and reducing the alkyl chain length of anionic surfactants, the Zeta potential of the solution was increased. The shorter alkyl chain caused more adsorption on the carbon nanotube due to steric packing.

### 3.3. Raman analysis

The quality of graphene was determined via Raman spectrum analysis of structural defect peak (D peak at \(1343\) cm\(^{-1}\)), in-plane vibration peak of sp\(^2\) carbon atom \((G\) peak at \(1586\) cm\(^{-1}\)) and 2D peak of graphene layer number, as shown in figure 5. The Raman spectra for rGO dispersions was analyzed by films coated with SDS, CTAB, SDS/CTAB \((1:9)\), SDS/CTAB \((9:1)\), SDS/CTAB \((4:6)\) and SDS/CTAB \((6:4)\) on a silicon wafer substrate. The content of defect was expressed in terms of the intensity of D peak relative to G peak, such as \(I_D/I_G\) as summarized in table 3. The \(I_D/I_G\) values of rGO were recorded larger as compared to GO, indicating the existence of more defects within the synthesized graphene. Moreover, \(I_D/I_G\) values of the other samples were roughly the same attributing towards the same ultrasonic power and time.
In this study, investigations were carried out to analyze the effects of surfactant mixture on the dispersion properties of graphene, and the structure and the stability of surfactant assemblies. The performance of SDS, CTAB and SDS/CTAB mixtures for graphene dispersion were systematically evaluated. Mixtures of SDS and CTAB surfactants with different concentration and ratios were studied in order to determine the optimum parameters. The pure SDS and CTAB, as compared to SDS/CTAB (9:1) and SDS/CTAB (1:9) were found more favorable for the dispersion of graphene even at lower concentration. The higher surface charges due to electrostatic attraction between the surfactants were considered responsible for the better dispersive power of graphene. To disperse graphene with mixed surfactants would be of greater practicality in terms of reducing the cost and the environmental impact.

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Conflicts

None

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