Study on Nano Graphene Oxide Used to Enhance the Stability of Emulsion

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Abstract. Graphene oxide is prepared by carbonization, and then the graphene oxide is grafted with dodecylamine by one step to adjust the wettability. XRD and optical pattern tests of graphene oxide showed that the process of grafting dodecylamine modification can expand the layer spacing of graphene oxide by 0.044nm and enhance the intensity of fluorescence. The grafting dodecylamine modification can significantly change the solubility and wettability of graphene oxide in water, and the contact angle of the modified graphene oxide with water is 165°. Modified graphene oxide can effectively enhance the stability of emulsions stabilized by SDBS surfactants.

Keywords: emulsion, graphene oxide, surfactant.

1. Introduction
Emulsions have been widely explored and used in industrial processes and in daily consumables, including the petroleum, food, pharmaceutical, and cosmetic industries. [1-4] The stability of the emulsion plays a decisive role in its application. [5] There are four main reasons for the instability of the emulsion, including the stratification of the emulsion caused by the floating or sinking of the emulsion droplets; emulsion demulsification due to the flocculation and the aggregation of the emulsion droplets caused Oil-water separation, and the reverse rotation of the emulsion. [6-10] In order to enhance the stability of emulsions, people usually developed emulsion stabilizers with better properties, such as gemini-surfactants. On the other hand, the research had achieved the same goal by compounding solid particles and surfactants. [11-12]

In this paper, nano-graphene oxide was used as the auxiliary stabilizer. Experiments were conducted to explore the synergistic effect of nano-graphene oxide and SDBS in stabilizing the emulsion together.

2. Experimental Section

2.1. Materials
Citric acid monohydrate, Dodecylamine, 4-dimethylaminopyridine, DDC, Tetrahydrofuran solvent, SDBS (The above items are provided by Chengdu Kelong Company), Xylene. Deionized water was used in all of the experiments.
2.2. Preparation of the Emulsions
Solutions of the modified graphene oxide (m-GO) were prepared by dissolving m-GO (5mg) in xylene (5g) and SDBS (5.75mg) in 5mL of deionized (DI) water and subsequently subjecting them to ultrasonication for 10 min. Then, 5mL of SDBS solution was added to the equal volume of the m-GO solutions. The solutions were emulsified using a homogenizer for 1 min at 12000rpm.

2.3. Observation of the Emulsions
The microscope images of the manipulating process on droplets were obtained through observing the emulsions in the middle of two pieces of glass slides separated by a distance of 1mm. A Nikon Eclipse Ni light microscope was used to image the emulsions. The stability of the emulsions has been evaluated by monitoring the size variation of at least 200 droplets against aging in a bulk sample (1mL of emulsion).

3. Results and discussion

![Figure 1. XRD patterns of CA, GO, m-GO](image)

We used the method of carbonizing citric acid monohydrate to prepare graphene oxide, and then modified it by grafting dodecylamine. [13-14] Citric acid monohydrate is a crystalline configuration compound. In the XRD pattern, it can be found that the citric acid monohydrate had a regular crystal structure with outstanding crystal peaks. It was known from the strength of the peak that the crystallinity is high. The XRD pattern of graphene oxide had a single broad peak at around 18°, indicating that the crystallinity of the product was relatively poor and the internal small molecules are irregularly arranged. The XRD pattern of the modified graphene oxide also showed a single peak at 20°, but the peak became narrower and the intensity increased. It can be seen from the XRD pattern that the process of preparing nanometer graphene oxide from carbonized citric acid is a process of converting small crystal molecules of citric acid into amorphous materials. According to Bragg equation: \( 2d \sin \theta = n \lambda \) (\( d \) is the interlayer distance; \( \theta \) is the incident angle; \( n \) is the rank of diffraction; \( \lambda \) is the x-ray wavelength of irradiation). The one-step graft modification with octylamine extended the layer spacing of GO by 0.044nm. [15-16] This transformation process reveals the structural change of nanometer graphene oxide during carbonization and grafting. The modification has a little effect on the crystal form and structure of the nanometer graphene oxide.
Figure 2. (a) UV-vis spectra of the solutions of nano-GO and m-GO. (b) PL spectra of the solution of nano-GO and m-GO at 370nm excitation wavelengths.

Figure 3. (a) Photograph images describe the solubilities of the nano-GO, m-GO. (b) Photograph showing the dispersibility of m-GO in water, Xylene and N-heptane. (c) Photographs of the Contact angle of m-GO with water (d) Contact angle of m-GO with water.

The effect of modification on the absorption and emission spectra of GO and m-GO was shown in Figure 2. UV–vis spectra of nano-graphene oxide and modified nano-graphene oxide both showed peaks at 210nm due to π–π* transition of C=C moieties and the shoulder peak at 280nm of modified nano-graphene oxide was due to n–π* transition of C=O moieties (Figure 2a), owing to modification of dodecylamine and electron enriching, respectively. In addition, in the low energy absorption range>400nm, the optical absorption of GO was negligible. [17-18] But the absorbance increased in the range of 350 to 550 nm upon modification. Interestingly, the absorption intensity of the n–π* transition of nano-GO increased due to modified by the dodecylamine, possibly revealing that the
modification enhanced the radiative recombination of e–h pairs generated within localized states. Optical properties of GO and m-GO were measured to reveal effect of modification on PL behaviors (Figure 2b). The initial nano-GOs show a peak at 480 nm (blue emission) when excited under 370 nm wavelength (Figure 2b). For m-GO under 370 nm excitation, the emission wavelength was changed from 480 nm to 450 nm. Furthermore, the modification enhanced the photoluminescence intensity.

To investigate the effect of the modification on the solubility of the GO and m-GO, 3 mg of GO or m-GO were separately dissolved in 14 mL of a water/xylene (1:1 v/v) mixture (Figure 3a). Whereas GO was only soluble in the water phase. In contrast, m-GO was soluble only in the organic phase. Thus, the surface properties of the modified GO were controlled systematically, converting from hydrophilic to hydrophobic surfaces. Furthermore, to demonstrate the solubility of the m-GO was dispersed in other hydrophobic solvents, such as water, xylene, N-heptane. As shown in Figure 5b, the m-GO was clearly dispersed in xylene without any aggregation. However, the m-GO was only partially dispersed in N-heptane due to relatively strong hydrophilic property. Figure 3c and d showed the wettability of m-GO to prepare the emulsions. It is observed that m-GO makes contact angles of 165.4° with water as indicated in Figure 3c, d.

Proper adjustment of the wettability of graphene oxide will be more conducive to its aggregation at the oil-water interface. The nano-GO increased the hydrophobic character by the modified of dodecylamine. In addition, the concentration of the m-GO is an important factor in the formation of emulsions, and it was markable influence on the emulsion stability and on the average droplet size[20]. We explored the effect of modified GO as a co-stabilizer in enhancing the stability of emulsions stabilized by SDBS surfactants.

![Figure 4](image)

**Figure 4.** (a) Change in the volume fraction of the residual emulsion as a function of time for emulsions stabilized by different concentrations of m-GO. (Inset: Photographs of the volume fraction of the residual emulsion) (b) Average droplet diameter as a function of time.

As shown in Figure 4a, the volume fraction of the emulsion without modified graphene oxide decreased rapidly. After being emulsified for 30 min, the emulsion was layered and stabilized, and the volume fraction of the emulsion was 50%. Then, 0.2 mL oil was precipitated in the upper part of the emulsion in the next 4h. For m-GO concentrations was 0.1%, the emulsion stratification time was delayed, the volume fraction of the emulsion was larger than the blank group at the same time, and no oil was precipitated in the upper part of the emulsion at the later time. The volume fraction of the residual emulsion was 58%. For m-GO concentrations was 1%, the emulsion did not precipitate water and oil, and the emulsion appeared stratification in about 30 minutes, and the lower layer emulsion had better light transmittance than the upper layer emulsion.

By observing the morphology and droplet size of the prepared emulsion by optical microscopy, as expected, the average droplet size decreased as the m-GO concentration increased. For the blank group, the average droplet size of the emulsion increased from the initial 7.71 μm to the maximum value (15.54 μm) and then slowly decreases to 11.97 μm. For 0.1% GO concentrations, the average droplet
size of the emulsion increased from the initial 6.5μm to 12.12μm. Then the value of the average droplet size decreases little. For 1%GO concentrations, the concentration has increased from the initial 5.75 μm to 7.61 μm (Figure 4b). Microscopically, the size of the emulsion droplets shows a process of decreasing from small to large, which is consistent with the emulsion is delaminated and demulsified within one-hour, macroscopically. As the concentration of modified nano-graphene oxide increases, the delamination and demulsification time of the emulsion are postponed and the particle size of the emulsion is also reduced. The surface energy of the system reduced with migration of GO from the dispersion onto the oil−water interface, and an increase in the surface area of GO causes a reduction in the free energy and makes the system more stable. [21] An increase of GO concentration within a certain range results in an increase of the total surface area of GO assembling at the liquid−liquid interface, which facilitates the formation of Pickering emulsions with greater stabilities.

4. Conclusions
One-step grafting of dodecylamine can expand the interlayer distance of graphene oxide by 0.044nm. In addition, the modification can greatly enhance the fluorescence emission ability of graphene oxide. The modified graphene oxide can effectively enhance the stability of SDBS emulsion due to the transformation of its own wettability. Macroscopically, the modified graphene oxide with a mass concentration of 1% can make the SDBS emulsion with a molar concentration of 0.1% not precipitate oil and water within 30 minutes, while the emulsion volume fraction of the emulsion without graphene oxide under the same conditions is 50%. The microscopic measurement of the particle size of the emulsion particles is consistent with the macroscopic change of the volume fraction of the emulsion.

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