Improved stability of Graphene Oxide in Salt Water modified by Situ Polymerization

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Abstract. A modified Graphene Oxide (GO) with excellent water dispersion, high salt tolerance and good temperature resistance was prepared by grafting short chain water-soluble polymer onto small particle size (200.5nm) GO as the matrix by in-situ radical polymerization. The functional groups, particle size, thermal stability, water dispersion stability and salt tolerance of m-GO (m-GO) were studied by FTIR, DLS, TG and stability analysis, respectively. FTIR analysis shows the significant characteristic peaks of water-soluble polymer chains. In addition, the average particle size increases from 200.5nm to 360.5nm and Zeta potential changes from -27.5mV to -4mV for GO and m-GO, indicating the successfully modification of polymer chain into GO. From TG analysis, thermal stability of m-GO is also greatly improved, as the initial thermal decomposition temperature increases from 88℃ (mass loss of 5%) to 197℃. The stability analysis reveals that m-GO has well dispersibility in water solution under room temperature for 180d and excellent salt tolerance under several high temperatures for more than 90d.

1. Introduction
The application of nanotechnology to enhance oil recovery is one of the frontier trends in petroleum industry[1]. GO nano-particles[2], silicon dioxide nano-particles (SiNPs)[3-4] and others are thought to have the ability to increase oil production while being environmentally friendly. However, with the addition of inorganic salts, the double-layer balance between nano-particles is destroyed, resulting in poor salt tolerance stability, which limits its application[5].

The salt tolerance stability of nano-particles is related to main surface charge and steric resistance[6]. Because of the charge on the surface of nano-particles, the anti-sign ions are attracted around them, forming the diffusion double layer. The Zeta potential is the potential difference between the double layers. The stability of aqueous dispersion of nano-particles is related to Zeta potential. The higher the absolute value of Zeta potential is, the more stable the water dispersion system is. The salt-tolerant stability of nano-particles is also related to Zeta potential. The higher the absolute value of Zeta potential, the dispersion is more likely to be negatively affected by strong ionic solutions (such as oilfield brine), that is, the lower the absolute value of Zeta potential, the better its salt tolerance. There is a paradox between the water dispersion stability and salt tolerance of nano-particles with Zeta potential. How to control the potential of nano-particles while ensuring their water dispersibility and salt tolerance is a difficult problem.

The salt tolerance stability of nano-particles can be improved by increasing the steric resistance between nano-particles[7]. In order to change the Zeta potential of nano-particles and the steric resistance between nano-particles, the surface modification of nano-particles was mainly carried out.
The results showed that the salt tolerance stability of nano-particles could be realized with increasing steric hindrance modified by polymer[8]. The long chain steric resistance of polymer can be used to increase the repulsion to achieve the stability of the particles. Modification of nano-particles through water-soluble polymer can also increase its salt tolerance ability by a shell formed on the colloid particles. For instance, Christopher Griffith[9] modified the biochar surface by adding 24wt% PVA (Mw= 100,000) which could be stabilized in seawater for 30 days. Lan Ma[10] modified MWNTs by PSS (Mw= 70,000) through radical polymerization which was able to stabilize over 30 days in saline (15wt% NaCl).

In this paper, GO with small particle size was selected as matrix and situ radical polymerization with monomer was used to reduce the surface charge of GO, improving its salt tolerance stability, so as to prepare the m-GO with excellent water dispersion and salt tolerance. The successful modification was proved by Fourier infrared spectroscopy and Zeta potential granulometer. The thermal stability and its stability in water or salt water of m-GO were analyzed by TG and stability analyzer, respectively.

2. Experimental section

2.1. Materials
Graphene Oxide paste (GO) was obtained from the Sixth Element (ChangZhou) Materials Technology Co., Ltd. Modified monomer (MA) was purchased from XinYong Bio-chemical (ZheJiang) Co., LTD. Potassium persulfate (K₂S₂O₈) was got from Shanghai Aladdin Bio-Chem Technology Co., LTD. Deionized water was self-made.

2.2. Fabrication of m-GO
GO paste was mixed into a water dispersion with a certain concentration water according to the content requirements. Then ultrasonic device was turned on for ultrasonic dispersion, so that the particle size of GO was controlled at around 200nm. Situ radical polymerization was adopted to modify GO and the mechanism was showed in Figure 1. Small size GO and the monomer (MA) were added to deionized water at a certain ratio and treated with nitrogen (N₂) for 30min. After deoxygenation, the mixed solution was heated with the set temperature of the oil bath at 55℃. Then K₂S₂O₈ was added, and the reaction stopped after 3h at 80℃. The reaction products was put into the material barrel for reserve.

Figure 1. Preparation principle of m-GO

2.3. Characterization and performance
The functional group changes of m-GO were observed by Fourier infrared spectroscopy (SEM, S4800, Hitachi Ltd). The particle size and potential changes were assessed with Zeta potential granulometer (ZEN3700, Marvin). Thermogravimetric (TG, NETZSCH, Netzsch Technology Co., Ltd) tests were conducted to study the thermal stability changes before and after modification. The m-GO water dispersion was diluted to 50 ppm and placed at room temperature for 30d, 90d and 180d, to testify its water dispersion ability observed by naked eye and stability analyzer, respectively. Salt resistance was tested by adding different salinity brine (1w, 10w, 20w, formation water of sinopec BN oilfield with 2.5w salinity, formation water of cnooc S oilfield with 1w salinity, formation water of cnooc J oilfield with 2000 salinity, formation water of cnooc B oilfield with 7000 salinity) into the m-GO water dispersion diluted to 50 ppm, and placed in different temperature (25℃,55℃, 85℃) for 0d, 30d, 60d and 90d respectively to observe its stability.
3. Results and discussions

3.1. Analysis of infrared spectra and Zeta particle size analyzer

The infrared spectrum of m-GO is showed in figure 2. There are three obvious absorption peaks of GO at 3185cm$^{-1}$, 1614cm$^{-1}$ and 1027cm$^{-1}$, which correspond to the stretching vibration of hydroxyl group, carboxyl group and epoxy group on GO. The infrared spectra of m-GO shows significant characteristic peaks of the modified monomer, among which the position at 3334cm$^{-1}$ and 3185cm$^{-1}$ are typical absorption peaks of amide. 2934cm$^{-1}$ is the characteristic absorption peak of methylene antisymmetric stretching vibration. The characteristic absorption peak of carbonyl group is at 1644cm$^{-1}$. The characteristic absorption peak of amide (N-H bending vibration) is at 1601cm$^{-1}$. These results preliminary indicate that the small chain water-soluble polymer has been grafted onto GO.

![Figure 2. IR spectra of GO before and after modification](image)

![Figure 3. The size distribution of GO before and after modification](image)
In order to further prove the success of GO modification, the particle size and potential before and after modification of GO were compared, as shown in Figure 3, 4 and 5. It is found that after modification, the average particle size increases from 200.5nm to 360.5nm, and the absolute value of potential decreases from 27.5mv to 4mv, indicating that the polymer chain has been grafted to the GO surface, increasing its hydration radius.

3.2. Thermogravimetric analysis

The TG diagram of m-GO is showed in figure 6. Before the modification of GO, the initial thermal decomposition temperature is 88°C (mass loss of 5%). After modification, the initial thermal decomposition temperature increases to 197°C, and the thermal stability is significantly improved.
3.3. Water dispersion stability analysis

Figure 7. m-GO water dispersion with 50ppm at room temperature for (a) 30 days, (b) 90 days, (c) 180 days

As shown in Figure 7(a,b,c), the m-GO water dispersion at 50ppm was placed at room temperature for 30d, 90d and 180d. No color changes were observed and no visible deposits were generated. The time-dependent curves of the transmission and backscattering spectra of m-GO water dispersion (50ppm) after placed at room temperature for 180d are showed in Figure 8 tested by a stability analyzer. It can be seen from the figure, the transmitted light and backscattering intensity are basically unchanged, which indicates the particle size of the m-GO water dispersion has also not changed, also proving the good water dispersion stability of the m-GO.

Figure 8. Transmission and backscattering patterns of m-GO water dispersion with 50ppm at room temperature for 180 days

3.4. Salt tolerance stability analysis

The stability of m-GO water solution under different salinity brine are showed in Table 1. It can be seen from the table that the m-GO water dispersion has excellent salt tolerance more than 90d. This is mainly because the surface charge of GO is shielded after modification, and its absolute value potential decreases from 27.5mV to about 4mV, as shown in figure 4. The lower the absolute value of Zeta potential of m-GO water dispersion, the better its salt tolerance is. At the same time, the surface of m-GO contains a large number of carboxyl groups and amide groups, which also ensure the good water dispersion stability of m-GO.
Table 1. Stability of m-GO water solution (50ppm) with different salinity

| Number | Sample                        | Salinity        | Stability at normal temperature/d | Stability at 55-85°C/d |
|--------|-------------------------------|-----------------|-----------------------------------|------------------------|
| 1      | m-GO                          | 1w              | >90                               | >90                    |
| 2      | m-GO                          | 10w             | >90                               | >90                    |
| 3      | m-GO                          | 20w             | >90                               | >90                    |
| 4      | m-GO, formation water of sinopec BN oilfield with 2.5w salinity | >90 | >90 |
| 5      | m-GO, formation water of cnooc S oilfield with 1w salinity  | >90 | >90 |
| 6      | m-GO, formation water of cnooc J oilfield with 2000 salinity | >90 | >90 |
| 7      | m-GO, formation water of cnooc B oilfield with 7000 salinity | >90 | >90 |

In order to further explain the salt-tolerant stability of m-GO, its water dispersion at 50ppm with 20w salinity were placed at different temperatures (55°C, 85°C) for different times (0d, 30d, 60d, 90d) and then a stability analyzer was used to test the TSI index, as shown in table 2. The TSI stability index is an evaluation of the stability of the whole dispersed system. It can be seen from the table that TSI index of the m-GO water dispersion (20w salinity) has not changed at different temperatures for different times, indicating that the m-GO water dispersion has excellent stability under the conditions of high-price salt and medium-high temperature.

4. Conclusions

A m-GO with excellent water dispersion and salt tolerance was prepared by using ultrasonic treated small particle size GO as matrix and grafting of water-soluble small molecule polymer by in-situ radical polymerization. Fourier transform infrared spectroscopy indicates that the group of water-soluble small molecule polymer has been successfully introduced into GO. While, the particle size increases from 200.5nm to 360.5nm and the potential increases from -27.5mV to -4mv after modification of GO further proved that GO was successfully modified. Thermogravimetric analysis shows that the thermal stability of m-GO is greatly improved with initial thermal decomposition temperature increasing from 88°C (mass loss of 5%) to 197°C. The structure of the stability analyzer indicates that the m-GO water dispersion has good water dispersion stability up to 180d and excellent salt tolerance (20w salinity) at different temperatures (55~85°C) up to 90d.

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