

POSITIVELY CHARGED GRAPHENE OXIDE MODIFIED WITH TWO SILANE MOLECULES FOR MULTIPLE APPLICATIONS

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ABSTRACT

Graphene oxide (GO) is water soluble which is benefit from the ionizable edge -COOH groups. Due to the largely hydrophobic basal plane, GO is also a colloidal surfactant. However, the application of a single negatively charged GO in the aqueous phase is limited by the type of the surface charge. In this paper, positively charged graphene oxide (PGO) was prepared by silanization with two silane molecules. The resulting PGO nanosheets were characterized by FTIR and XPS. It was evident that the silane molecules were grafted on GO surface by covalent bondings. PGO can be well dispersed in different ionic types of polymer solution while GO can only be dispersed in anionic polymer solution. Compared with GO, PGO has a better emulsifying property and in a wide range of pH values, PGO is still a available emulsion stabilizer. PGO was used to expand the application of traditional graphene oxide in this study.

1 INTRODUCTION

Graphene oxide (GO) has acquired significant attention in science and technology as a functional derivative of graphene. Like graphene, GO exhibits high mechanical strength [1–3] and high aspect ratio [4, 5]. In addition to advantageous properties inherited from graphene, GO is also water soluble which is benefit from the ionizable edge -COOH groups [6] and it is easy to be chemically modified due to multiple oxygen functional groups on GO. However, sometimes the application of negatively charged GO in the aqueous phase has been limited by the type or the strength of the charge. For example, when GO is mixed with a positively charged colloidal particles, the agglomeration of GO was observed and its dispersion stability was destroyed due to electrostatic attraction. GO can also be used as a colloidal surfactant with a largely hydrophobic basal plane and hydrophilic edges [7, 8]. But the amphiphilicity of GO is especially dependent on pH value and this phenomenon restricts the applicable conditions of GO in the field of surfactants. For example, the effect of GO as a surfactant to stabilize oil/water emulsions (also known as Pickering emulsions) was greatly influenced by pH [9].

Positively charged graphene oxide (PGO) has also been studied in the literature. Cai et al. [10] employed ethylenediamine to modify GO through an acyl chlorination and amidation process that allows a net positive surface charge at pH < 8.1. The PGO improve removal efficacy for a wide range of anionic organic contaminants. Tu et al. [11] prepared several chemically modified GOs to control neurite outgrowth and branching and they found PGO is most beneficial to neurite.

Here, we used two kinds of silane molecules to functionalize GO surface. (3-glycidyloxypropyl)trimethoxysilane (GPTMS) and (3-aminopropyl)triethoxysilane (APTES) were reacted with GO sequentially. The amino groups were introduced into the GO surface that PGO can be positively charged in the solution at some pH range. The introduction of silanol groups makes the GO still hydrophilic near the isoelectric point of PGO. During the modification process, the organic solvent is avoided and compared to polymers, silane are highly reactive. Under certain circumstances (for example, in the absence of water), tunable condensation may occur between silane molecules on GO surface.

In this paper, we fabricated positively charged graphene oxide and explored its multiple applications. Dispersion stability in different ionic types of polymer solution is researched. By characterizing the prepared Pickering emulsion, we also studied the scope of application of PGO as a emulsion stabilizer.

2 EXPERIMENTS

2.1 Fabrication of single silane functionalized GO

Graphene oxide (GO) was purchased from Angstrom Materials (Xiamen, China). 3.5 mL of GPTMS were mixed with 0.7 mL H₂O and 0.25 mL acetic acid while stirring at room temperature for 24 h to allow hydrolysis of GPTMS. 5 mL of GO (2 mg mL⁻¹) was added to the mixture. The mixture was treated by a microwave reactor at 110°C for 30 min while stirring, followed by highspeed centrifuge at 25,000 rpm for 10 min and washing with deionized (DI) water repeatedly to eliminate the unreacted GPTMS. The resulting silanized GO (GPTMS-SGO) was then dispersed in DI at a concentration of 2 mg mL⁻¹.

2.2 Preparation of positively charged GO

0.196 mL of Acetic acid and 0.588 mL APTES were added to 3 mL of GPTMS-SGO aqueous dispersion and stirred for 5 days. After the reaction, the excess silane molecules was removed by centrifuged at 25,000 rpm repeatedly and the obtained positively charged graphene oxide (PGO) was dispersed in DI at a concentration of 2 mg mL⁻¹.

2.3 Fabrication of graphene microcapsules in Pickering emulsions

An aqueous solution of GO or PGO (2 mg mL⁻¹, 4 mL) was mixed with 2 mL toluene by ultrasonic dispersion for around 2 min to prepare Pickering emulsions. The pH values of GO and PGO solution were modified by adding HCl (1 M) or NaOH (1 M) solution.

2.4 Characterization

The surface chemistry of GO and silanized GO was characterized using fourier transfer infrared spectrometry (FTIR, Spectrum 100 Perkin Elmer) and X-ray photoelectron spectrometer (XPS, PHI5300 ESCA). FTIR spectra were collected in reflection mode for the wavenumber range 4000–600 cm⁻¹ at a resolution of 4 cm⁻¹. XPS was equipped with a monochromatic Al K α at 14 kV. The surface charges of different kinds of the graphene oxide in water (1 mg mL⁻¹) were analyzed by ζ potential measurements using a Zetasizer Nano ZS (Malvern Instruments, U.K.). A polarized light optical microscopy (POM, Zeiss Axio Imager A2m) was employed to characterize the Pickering emulsions.

3 RESULTS AND DISCUSSION

3.1 Silanized GO

The FTIR spectra of GO, GPTMS-SGO and PGO were presented in Fig. 1. The peaks at 2926 cm⁻¹ and 2865 cm⁻¹ were attributed to C-H stretching vibrations [12]. The two peaks were most likely from alkoxy of uncompletely hydrolyzed silane molecules or the organic chains on the silane. The GPTMS-SGO and PGO samples showed peaks at 1080 cm⁻¹ and 960 cm⁻¹, corresponding to the vibration of Si-O groups [13]. The peaks at 1199 cm⁻¹ and 861 cm⁻¹, corresponding to ester group and epoxy group respectively. It was suggested that GO had been silanized by GPTMS. PGO exhibited peaks at 876 cm⁻¹, 844 cm⁻¹ and 733 cm⁻¹, corresponding to the amino groups from APTES. Given that the modified GO samples have been washed thoroughly to eliminate the unreacted silane, the FTIR results evidenced that the GO had been successfully silanized.

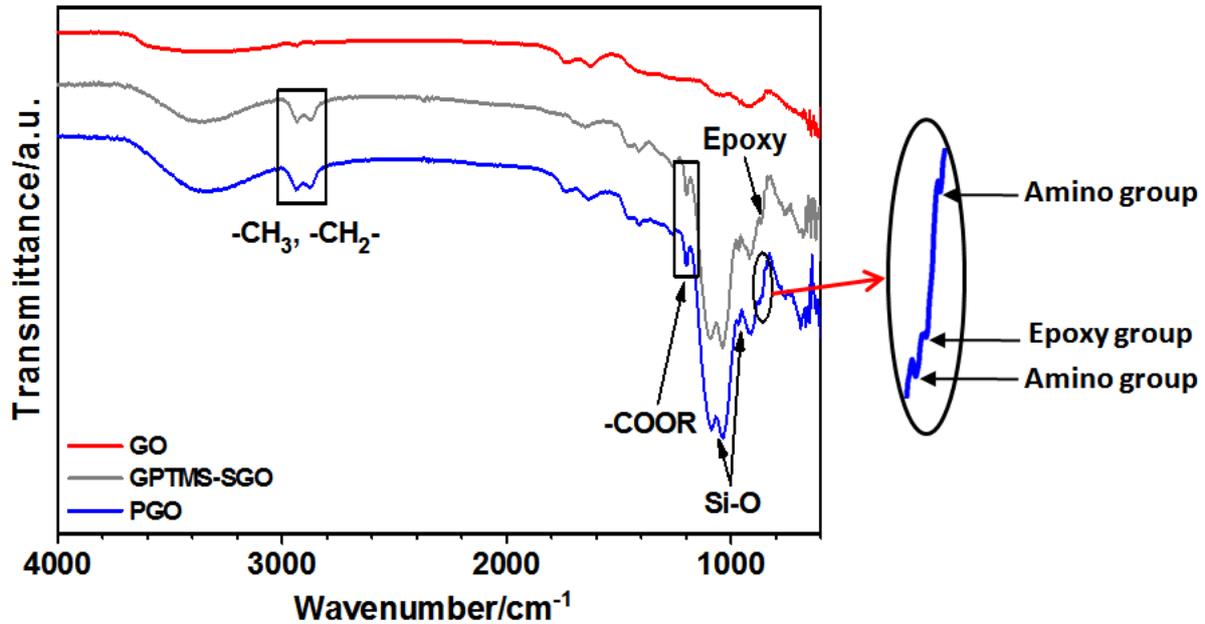


Fig. 1 FTIR spectra of GO, GPTMS-SGO and PGO.

The carbon, oxygen, silicon and nitrogen elements were detected with XPS scan and the corresponding atomic concentration was listed in Table 1. The atomic content of Silicon reached 9.86% for GPTMS-SGO indicating that a considerable amount of GPTMS reacted with GO. The reduced C/O ratio of GPTMS-SGO is also due to the introduction of GPTMS (C/O is only 1). After further modification by APTES, Si content of PGO continued to rise to 11.49% and the N element was detected with the introduction of amine silane. At the same time we can also found that the C/O ratio increased. This may be due to the condensation between silanol groups of GPTMS-SGO and APTES.

Table 1 Atomic composition of C, O, Si and N for different GOs.

Samples	C/O	Concentrations of various elements (%)			
		C1s	O1s	Si2p	N1s
GO	2.32	69.88	30.12	-	-
GPTMS-SGO	1.65	56.11	34.03	9.86	-
PGO	1.78	55.91	31.39	11.49	1.21

Fig. 2 illustrated the reaction between GO and silane molecules. Firstly, the carboxyl groups on GO reacted with the epoxy groups from GPTMS at heating condition and produced ester bonds. Then APTES was used to further modify GPTMS-SGO to make the graphene surface positively charged. The condensation reaction of silanol groups between GPTMS-SGO and APTES may occur and the amino groups from APTES will offer the positive charge of PGO. ζ potential analysis further verified the successful synthesis of PGO. The ζ potential of GO was -29 mV at pH 4. However, after functionalization with APTES, PGO was positively charged with a zeta potential of +24.6 mV at pH 4. ζ potential of PGO as a function of pH value was measured in Fig. 3a. It can be found that the ζ potential value increased with the decrease of pH and in acidic condition (pH below 7), PGO particles are positively charged in water.

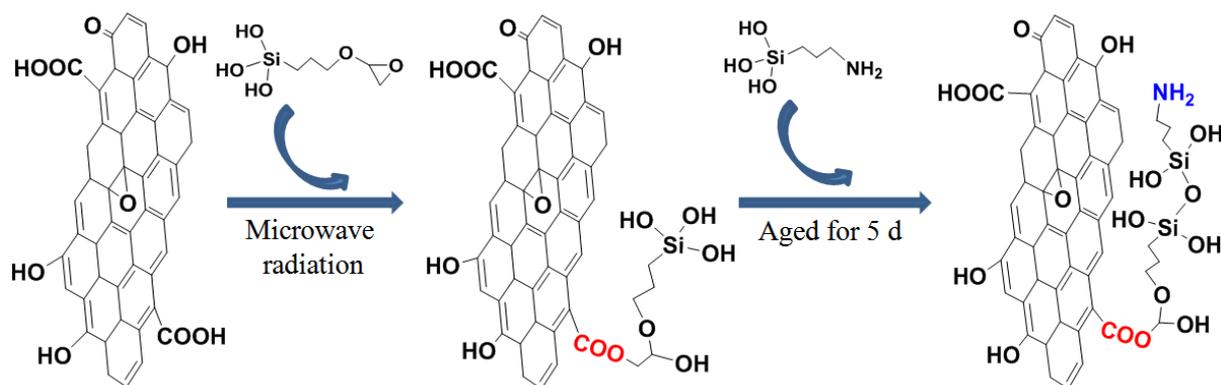


Fig. 2 Reaction scheme for the silanization by GPTMS and changing the surface charge by APTES. After washing, a final sonication step in water produces well dispersed PGO.

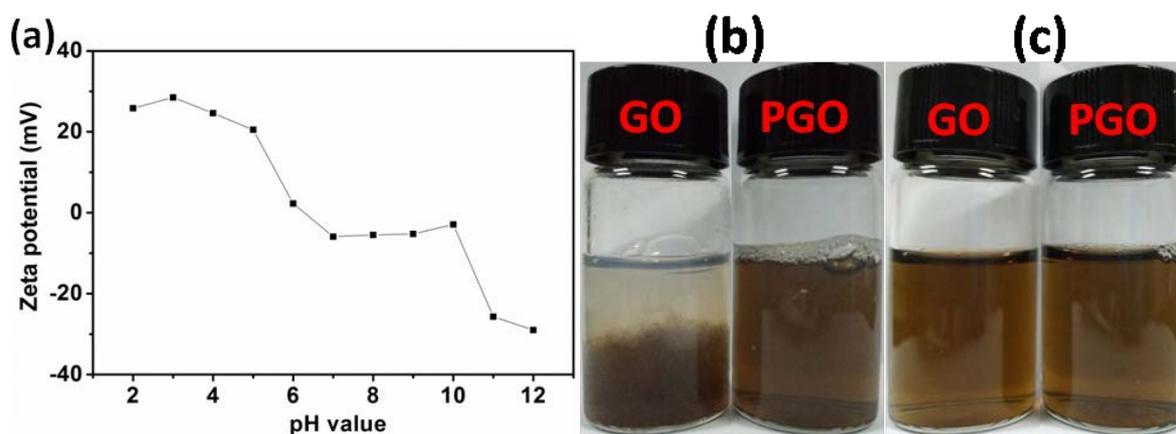


Fig. 3 (a) ζ potentials of PGO in the aqueous solution at different pH values. Dispersion stability of GO and PGO in (b) cationic polymer solution (pH 4) and (c) anionic polymer solution (pH 11) standing for 10 h and 1 h, respectively.

3.2 The compatibility of PGO with polymer solution

Fig. 3 (b, c) showed the suspension stability of GO and PGO in different ionic types of polymer solution. GO and PGO was added to cationic and anionic polymer solution respectively. In Fig. 3b, precipitation can be clearly observed in the first bottle after only 1 h of standing, which due to the electrostatic attraction between negatively charged GO and cationic polymer. But PGO has a very good dispersion status because cationic polymers are often dispersed in acidic environments to ensure good dispersion in water and in this environment (pH 4), the PGO surface is positively charged. In alkaline environments, GO and PGO are both negatively charged so that they can be well dispersed in anionic polymer solution (pH 11) after 10 h of standing, as shown in Fig. 3c. This phenomenon benefit from the electrostatic repulsion between the same charged colloidal particles.

3.3 The stability of the Pickering emulsion at different pH values

Varying the pH changes the amphiphilicity of the particles that possess ionizable surface groups. Therefore, the emulsion stabilized by graphene oxide is greatly affected by the pH. The influence of the pH on the stability and morphology of the emulsions were also extensively investigated [8, 9, 14]. A stable Pickering emulsion generally require the pH to be limited to a certain interval. Based on this situation, we prepared PGO that can stabilize the Pickering emulsion in a wide range of pH.

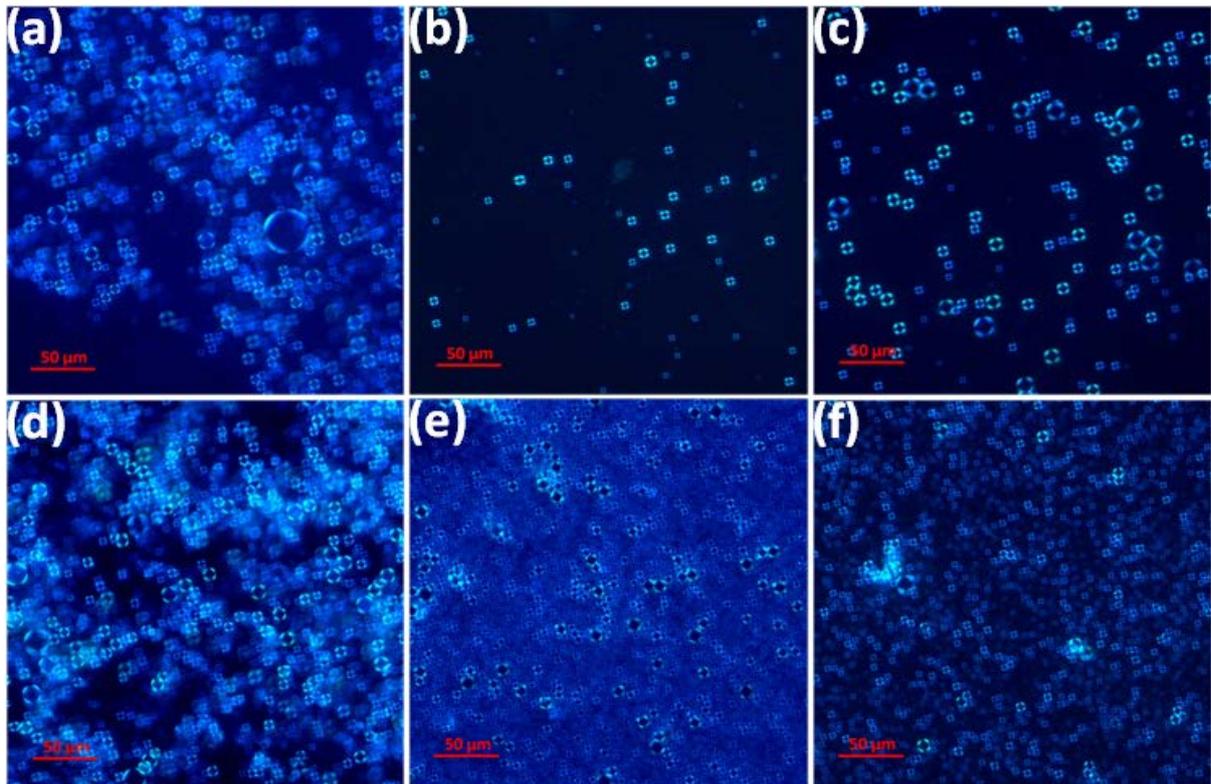


Fig. 4 POM images of GO microcapsules in Pickering emulsions preparation at different pH values: (a) pH = 2, (b) pH = 8, (c) pH = 12. POM images of PGO microcapsules in Pickering emulsions preparation at different pH values: (a) pH = 2, (b) pH = 8, (c) pH = 12. GO concentration: 1 mg mL⁻¹. Toluene/water ratio: 1:2.

Fig. 4 (a-c) showed the POM images of GO microcapsules in Pickering emulsions preparation at different pH values. In acidic condition (at pH 2), a larger number of GO microcapsules were observed. But the size of microcapsules varied significantly (Fig. 4a) and a phase separation appeared in the emulsion as shown in Fig. 5a (pH 2). The bottom layer was transparent because the more hydrophobic GO was extracted from water and entered non-polar toluene phase. As the increasing of the pH value, GO sheets changed from amphiphilic to hydrophilic, so that they escaped from the toluene/ emulsion phase and dissolved in the water which exhibited darker colour. The size of the bright rings in POM images was decreased and become uniform at first. Then the bright rings showed increased size with increasing the pH value and the size distribution became larger simultaneously. No matter in a relatively neutral (at pH 8) or alkaline (at pH 12) environments, the volume fraction of the emulsion decreased as shown in Fig. 5a. The results signify a less efficient emulsification under these pH conditions.

The POM images of PGO microcapsules in Pickering emulsions preparation at different pH values were showed in Fig. 4 (d-f). Microcapsules with narrow size distributions were obviously found in a wide range of pH. PGO participating Pickering emulsions were more stable than that contain GO as shown in Fig. 5b. The solution were all full emulsion state and no phase separation was observed. But in Fig. 4e, we found the each microcapsule cling to each other instead of separating from each other in other emulsions. Fig. 5c shows the higher magnification for the POM images of PGO microcapsules in Pickering emulsions at pH 8. PGO microcapsules have a particle size of about 3 to 7 nanometers. The contact between the capsules leads to the diversity of their shapes instead of uniform sphere (the adding light blue circles only represented the approximate profile of capsules to make it look more clearly). This phenomenon is due to the charge reduction on the surface of the capsules. At pH 8, the ζ potentials of PGO is -5.5 mV so that there is not enough electrostatic repulsion between the PGO-wrapped microcapsules. The touched capsules are also observed in other literature when the emulsion stabilizer is non-ionic [15] or with only a small amount of charge [16]. Similarly, the introduced silane

molecules which contain hydrophilic silanol groups makes the PGO still amphiphilic. Therefore, PGO that exhibits almost non-ionic properties at a specific pH can also be an emulsion stabilizer.

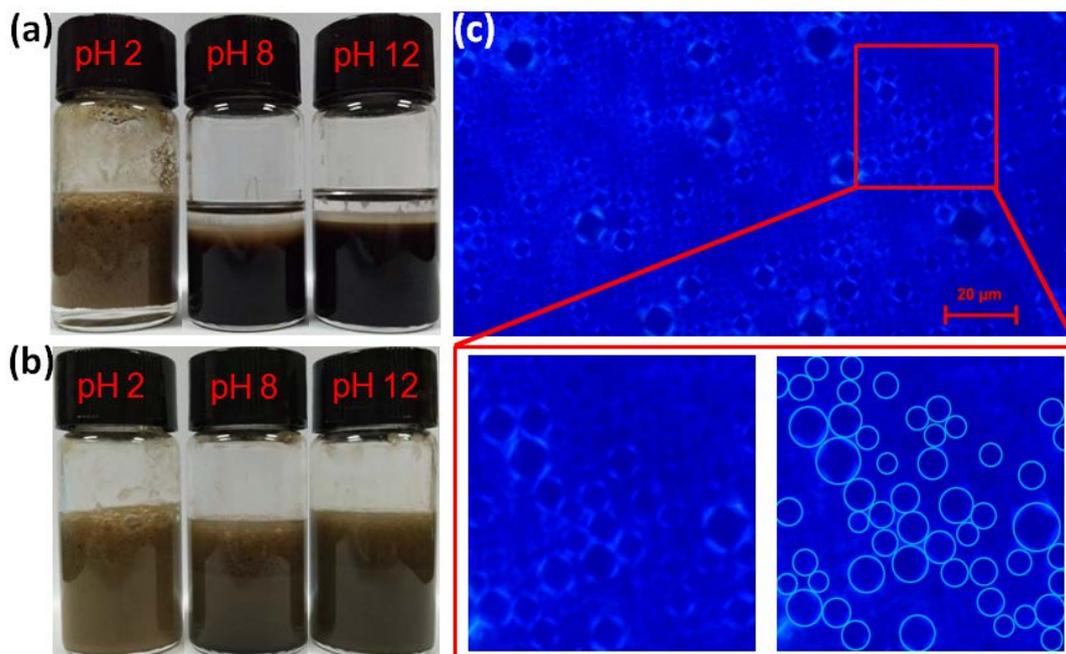


Fig. 5 Photographs of Pickering emulsions stabilized by (a) GO and (b) PGO at different pH values. (c) POM images of PGO microcapsules in Pickering emulsions at pH 8. The adding light blue circles only represented the approximate profile of capsules and does not show the actual shape of the capsules.

4 CONCLUSIONS

PGO was prepared by chemical reaction between GO and two kinds of silane through a two-step process. After silanization, GO is positively charged at a certain pH range. The resulting PGO can be well dispersed in different ionic types of polymer solution. As a colloidal surfactant, PGO has a better emulsifying property than GO. More importantly, PGO is an improved emulsion stabilizer that can be used in a wide range of pH values. PGO in this paper expands the use of general graphene oxide.

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