Nanoscale silica-coated graphene oxide and its demulsifying performance in water-in-oil and oil-in-water emulsions

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Abstract
In current work, GO@SiO 2 nanocomposite was prepared by coating nanoscale silica onto graphene oxide (GO). GO@SiO 2 was characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (IF-IR). Additionally, the demulsifying performance of GO@SiO 2 was investigated by bottle test. The results showed that GO@SiO 2 had a good demulsifying performance in both oil-in-water (O/W) and water-in-oil (W/O) emulsions. When the concentration of GO@SiO 2 was 200 ppm in the O/W emulsion, the optimal light transmittance of aqueous phase (LTA) and corresponding oil removal rate (ORR) at room temperature could reach 86.9% and 99.48%, respectively. Also, GO@SiO 2 had an excellent salt tolerance under acidic condition. Furthermore, GO@SiO 2 also could demulsify the W/O emulsion, and the efficiency at 70 °C could reach 80.5% when the concentration was 400 ppm.

Keywords Nanocomposite · Oil-water emulsion · Demulsification · Mechanism

Introduction

The development of oil extraction technologies usually accompanies with the formation water, which causes the ultimate production to exist in the form of emulsion. In addition, the development of petroleum industry generates a large amount of oily wastewater (Fang et al. 2016, Peng et al. 2019, Sun et al. 2020, Teng et al. 2019). The oil-water emulsion can cause pipeline blockage, equipment corrosion, and serious water environmental pollution (Yuan et al. 2020, Zhang et al. 2011, Zhao et al. 2020). Therefore, the demulsification of oil-water emulsion is of great necessity.

Typically, an oil-water emulsion is fairly stable. It is stabilized by natural surface active substances (asphaltenes, waxes, and resins) and inorganic solids through the vigorous π-π interaction (Zhang et al. 2020b). Furthermore, steric effect and electrostatic force can also affect the stability of oil-water emulsion (Ma et al. 2020). In recent decades, chemical and physical methods have been two main demulsifying approaches. Typical physical treatment techniques include centrifugation, electric field, membrane separation, and microwave radiation (Chen et al. 2019a, Ghanbari & Esmaeilzadeh 2018, Hue et al. 2021, Ichikawa et al. 2004, Liue et al. 2011, Peng et al. 2018, Tan et al. 2007, Xiong et al. 2018, Yi et al. 2019). However, they have many disadvantages such as high energy, low processing efficiency, and needing complex equipment. The chemical method is used to demulsify the emulsion by adding the demulsifier. It has the advantages of low energy consumption, fast processing speed, and low cost. Therefore, it is being widely used at present.

Chen et al. (Chen et al. 2019b) synthesized a magnetically responsive demulsifier called Fe 3O 4@hyperbranched polyanidoamine-graphene oxide (MKh-GO) to treat an O/W emulsion, and the oil removal rate (ORR) reached 96.0% when the dosage was 20 mg/L at 40 °C. Furthermore, MKh-GO could be recycled seven times without obvious reduction of efficiency. Kuang et al. (Kuang et al. 2020) prepared a hyperbranched demulsifier (PTC) with trimethyl citrate as centronucleus. Light transmittance of aqueous phase (LTA) could reach 91.5% with 50 mg/L of PTC at ambient temperature.
The surface of carbon-based materials has a huge \( \pi \)-conjugate system. The oil-water interfacial film in crude oil emulsion is easily destroyed with the aid of \( \pi-\pi \) or \( p-\pi \) interaction between carbon-based materials and asphaltenes/resin (Cote et al. 2010). As a result, the droplets can gather at the interface and achieve the oil-water separation. Liu et al. (Liu et al., 2015a, b, Wang et al. 2016) reported some carbon-based demulsifiers such as functionalized multiwalled carbon nanotubes, graphene oxide, and reduced graphene oxide, which could initiate and achieve the oil-water separation in O/W emulsion. Moreover, the carbon-based materials are environmentally friendly and readily available. Recently, Chen et al. (Chen et al. 2015) used a two-step coating process to prepare a demulsifier. In their work, amorphous SiO\(_2\)-coated Fe\(_3\)O\(_4\) particles were further functionalized by KH-1231. It showed an excellent demulsifying performance. Furthermore, the demulsifier can be recycled and reused. Wang et al. (Wang et al. 2011) prepared a demulsifier by grafting nano-SiO\(_2\) onto TA1031 to demulsify an O/W emulsion, and the demulsifying efficiency could be improved by 20% and reached 97%. In our previous work, some carbon-based demulsifiers such as SiO\(_2\)@CS, Ox-CB@SiO\(_2\) and MCNT@\( \beta \)-CD were used to demulsify the oil-water emulsions Ye et al., 2019, 2020b, Yuan et al. 2020). Although all of them had an excellent demulsifying performance, there were still some disadvantages such as overdose, high operating temperature, or low applicability which only applies to one type of emulsion (O/W or W/O emulsion).

For the purpose of improving the demulsifying performance and broadening the application scope, nano-SiO\(_2\)-coated graphene oxide (GO@SiO\(_2\)) was prepared by the sol-gel method in current work. GO@SiO\(_2\) is environmentally friendly, non-toxic, and efficient. Especially, it can treat both W/O and O/W emulsions. It is expected to be applied to break the oil-water emulsion in petroleum and chemistry industry.

**Materials and methods**

**Materials**

Sodium chloride (NaCl) and flake graphite (700 meshes, \( \geq 99.9\% \)) were supplied by Shanghai Macklin Biochemical Co., Ltd. Concentrated sulfuric acid (H\(_2\)SO\(_4\), \( \geq 95\% \)), hydrochloric acid (HCl, 37%), potassium permanganate (KMnO\(_4\), 99.5%), hydrogen peroxide (H\(_2\)O\(_2\), 35%), and sodium nitrate (NaNO\(_3\), 99%) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. Ethanol and tetraethyl orthosilicate (TEOS, 97%) were purchased from Aladdin Chemistry (Shanghai, China). Diesel oil was supplied by Fushan Oilfield (Hainan, China, density at 20 °C: 0.8362 g/cm\(^3\), viscosity at 25 °C: 200.4 mPa·s, asphaltenes: 16.5%, resin: 9.3%, wax: 16.8%, water: 1.5%). Diesel was provided by local gas station. All chemical reagents were analytical grade and directly used without further purification.

**Preparation of graphene oxide**

GO was prepared by a modified Hummers method (Venugopal et al. 2012). First, 2.5 g of NaNO\(_3\) and 2.0 g of graphene powder were dispersed into 180 mL of H\(_2\)SO\(_4\), and the mixture was ultra-sonicated for 30 min in an ice bath. Then, 15 g of KMnO\(_4\) was slowly added to the mixture and constantly stirred for 24 h at room temperature. Next, 180 mL of distilled water was poured into the mixture. The temperature was increased to 98 °C and hold for 1 h. Afterward, 120 mL of H\(_2\)O\(_2\) was added under stirring condition when the temperature of the mixture naturally deceased to 70 °C. The mixture was continuously cooled to the ambient temperature and stirred for 1 h. Finally, the as-prepared sample (GO) was washed with 5 wt% HCl solution and distilled water several times and dried by vacuum freezing.

**Preparation of nanoscale silica-coated graphene oxide**

GO@SiO\(_2\) was prepared by the sol-gel method. Briefly, 10 g of GO sol was dispersed into a mixed solution containing 30 mL of ethanol and 75 mL of distilled water by ultra-sonicating for 30 min. The pH value of the mixture was adjusted to 5 by adding a few drops of HCl. Next, 20 mL of absolute ethanol containing 5 mL of TEOS was slowly dripped into the mixture and sonicated for 30 min. Subsequently, the reaction mixture was transferred to a thermostat water bath and stirred for 10 h at 30 °C. Finally, the as-prepared sample was washed with NaOH solution (4 wt%) and distilled water several times until the pH value reached about 7. The resulting product was dried by vacuum freezing and named as GO@SiO\(_2\) I. In addition, for the purpose of exploring the impact of NaCl on the demulsifying performance, some products were washed several times with a large amount of distilled water to remove NaCl and called as GO@SiO\(_2\) II. The synthesis schematic of GO@SiO\(_2\) is illustrated in Fig. 1.

**Preparation of oil-water emulsion**

Oil-water emulsion was prepared by mixing crude oil and distilled water. Briefly, a certain amount of crude oil was directly added into the distilled water to prepare the O/W emulsion (1 wt% crude oil) or W/O emulsion (22 wt% crude oil). The mixtures were then stirred at 11,000 rpm for 30 min using a homogenizer (FJ-200, Shanghai). The two emulsions kept stable for at least 24 h at room temperature. The pH value of the emulsions was adjusted by adding HCl or NaOH aqueous solution. Figure 2 shows the micrographs of the oil-water emulsions that were observed under a polarizing microscope.
equipped with a digital camera (Caikang, DM2500P). It is obvious that Fig. 2a and b show typical O/W emulsion and W/O emulsion, respectively. The diameter of oil droplets and water droplets is about 1 to 5 μm and 3 to 7 μm, respectively.

**Demulsification test**

The demulsifying experiments were carried out by bottle test. Typically, the suspensions containing different concentrations of GO@SiO₂ were added into 20 mL of O/W emulsion at room temperature or 20 mL of W/O emulsion at 70 °C. Subsequently, each bottle was violently shaken by hand for 2 min to assure that the demulsifier was entirely dispersed into the emulsions. Then, the O/W emulsion was stood at ambient temperature and the W/O emulsion was settled in water bath at 70 °C to explore the demulsifying performance. The demulsifying performance of O/W emulsion was estimated by the measurement of LTA and ORR. The demulsifying efficiency (DE %) of W/O emulsion was defined as DE(%) = V/V₀ × 100%, where V₀ is the volume of water in initial emulsion, and V is the volume of separated water.

**Characterization**

FT-IR (Nicolet 6700, USA) was used to detect the groups on the samples with a resolution of 4 cm⁻¹. FE-SEM (MIRA3, TESCAN Co., Czech) was used to observe the morphology of the samples. The acceleration voltage of EDS was 15 kV. X-ray diffraction spectrum was obtained with Cu radiation X-ray diffractometer (Bruker, Germany) within a 2θ range of 5–80° at a rate of 0.05/min. Dynamic interfacial tension (IFT, mN/m) and wettability were measured with a DSA 30 Process Tensiometer (Kruss, Germany) at 25 °C. The tensiometer was calibrated before each measurement. LTA was measured with an UV-vis spectrophotometer (UV-2600, Shimadzu, Japan) at a wavelength of 569 nm.

**Results and discussion**

**FT-IR spectra**

The FT-IR spectra of GO, SiO₂, and GO@SiO₂ II are shown in Fig. 3. The peak at 3422 cm⁻¹ is attributed to the stretching vibration of the -OH groups from H₂O in air (Javadian & Sadrpoor 2020). The peak at 3135 cm⁻¹ is ascribed to the stretching vibration of O-H. The peaks at 2925 cm⁻¹ and 2854 cm⁻¹ are attributable to the sp² and sp³ C-H stretching bonds generated at the defect sites of graphene network. The peak at 1731 cm⁻¹ is assigned to the C=O stretching of the carboxyl groups on GO (Ye et al. 2020a). The peaks at 1625 cm⁻¹ and 1629 cm⁻¹ are ascribed to the stretching of the C=C bond and O-H groups attached to the SiO₂ surface, respectively. The peak at 1400 cm⁻¹ is attributed to the bending vibration of the O-H bond. The absorption band of symmetrical stretching vibration of Si-O-Si and Si-O-C is appeared at 1090 cm⁻¹. The peaks at 790 cm⁻¹ and 460 cm⁻¹ are attributed to the symmetrical stretching vibration and bending vibration of Si-O-Si, respectively. The peak of the wagging vibration of Si-OH is at 950 cm⁻¹. Therefore, it is believed that SiO₂ is successfully coated onto GO.
FE-SEM observation

The surface morphology of GO and GO@SiO₂ II was observed by FE-SEM and it is shown in Fig. 4. As shown in Fig. 4a, the surface of GO is visibly curly and corrugated, it has a commonly ribbon structure of graphene oxide. In addition, it also can be found from Fig. 4b that a number of SiO₂ microspheres attach to the surface of GO, and their diameter are about 100 nm. In order to further explore GO@SiO₂ II, the elemental composition and distribution was observed using an energy dispersive X-ray spectrometer (EDS). The EDS spectrum shows that the expected elements (C, O, and Si) can be observed in the sample. Besides, the EDS mapping shows that Si (yellow) is evenly distributed onto the surface of GO in Fig. 4c. The C element completely comes from GO, and the Si element completely come from SiO₂. The O element mainly comes from silicon dioxide, and the rest comes from GO. Moreover, it can be seen from Table 1 that the atom ratio of C and Si is about 5.45 by the EDS analysis. The result also indicates that SiO₂ was coated onto the surface of GO.

XRD patterns

In XRD patterns, the crystal structure shows a strong narrow diffraction peak, while the amorphous structure shows a wide diffraction peak. The XRD patterns of GO, SiO₂, and GO@SiO₂ are displayed in Fig. 5. It shows that the peak at 10.29° is corresponding to the (006) plane of graphite (Mousavi et al. 2020). The characteristic diffraction peaks of GO located at 26.6° and 42.43° are ascribed to the (002) and (100) planes of hexagonal lattices in graphite, respectively (Zhong et al. 2020). The reflection of (002) plane is clearly, it may be because the samples are abundantly ordered along the stacking direction and consist of graphene sheets (Gong...
et al. 2012). The reflection of (100) plane is related to the in-plane length of C-C in the network structure. The broad peak at 23.55° is attributed to amorphous SiO$_2$. As shown in Fig. 5b, the broad peak of SiO$_2$ is still obvious in GO@SiO$_2$ I and GO@SiO$_2$ II. Some sharp peaks located at 27.36°, 31.7°, 45.45°, 53.85°, 56.45°, 66.20°, 73.04°, and 75.26° are corresponding to the (111), (200), (220), (311), (222), (400), (331), and (420) planes of NaCl (JCPDS: No.77-2064). NaCl comes from the addition of HCl and NaOH in the adjustment process of pH value. Although the peak of GO is particularly low due to the influence of highly crystallized NaCl, it can still be identified in GO@SiO$_2$ I. It also can be found that the characteristic diffraction peaks of NaCl in GO@SiO$_2$ II disappear in Fig. 5b. As mentioned above, it confirms that the targeted composite is GO@SiO$_2$.

### Interfacial activity of GO@SiO$_2$

The interfacial activity is a significant factor affecting the migration of materials to the oil-water interface (Kaushal et al. 2020, Zhang et al. 2020a). GO is amphiphilic which has hydrophobic carbon substrate and hydrophilic -COOH and -OH groups on its surface, while SiO$_2$ is completely hydrophilic. However, the hydrophilicity of SiO$_2$ decreases due to the reaction of GO and SiO$_2$ in the preparation process of GO@SiO$_2$. Therefore, the as-prepared GO@SiO$_2$ maybe has a good interfacial activity. The interfacial activity of different samples was investigated in experimental bottles by observing their distribution in the oil-water interface. Each bottle contains 10 mL of water and 10 mL of diesel. The bottles were violently shaken by hand for 200 times and settled for 10 min or 3 days.

It can be seen from Fig. 6a that oil and water are insoluble, and the diesel-water interface is clear when the bottles were settled without shaking. A number of GO (Fig. 6a2) are dispersed to the bottom of the bottle and the water is brown, it may be because it is strongly hydrophilic and some fine GOs are evenly dispersed in water. Meanwhile, GO@SiO$_2$ (Fig. 6a3) stays at the diesel-water interface and the water phase is very clear. It means that GO@SiO$_2$ and GO have completely different hydrophilic properties. After shaking for 200 times and settling for 10 min or 3 days, the oil-water interface is still clear in blank sample. However, a portion of GO still stay at the bottom of the bottle, while most of them disperse into the oil phase and become anomalous spherical bubbles (Fig. 6b2 and c2). Moreover, these spherical bubbles remain unchanged after 3 days, and the water phase always keeps pale yellow. It is believed that GO forms the Pickering emulsion because it has the characteristic of colloidal particles (Cote et al. 2010, Lee et al. 2010). It also can be found that the volume of the diesel has increased slightly; it may be because the oil droplets are enveloped by the membranous structure of GO. GO@SiO$_2$ (Fig. 6b3, c3) promptly transfers to the oil-water interface and stays there. It shows that an emulsion layer appears at the oil-water interface after standing for 10 min, and its thickness is about 2 mm. It is because that GO@SiO$_2$ can act as an emulsifier due to its amphiphilic structure. After 3 days, the emulsion layer for GO@SiO$_2$ disappears in Fig. 6c3. However, GO@SiO$_2$ II still stays at the oil-water interface without further sinking or diffusing into the water phase. It demonstrates that GO@SiO$_2$ possess a high interfacial activity.

### IFT of GO@SiO$_2$

IFT can reflect the penetration ability of demulsifier molecules to the interfacial film, so it is a significant factor affecting the demulsifying performance. The IFT of GO, SiO$_2$, and GO@SiO$_2$ in the diesel-water interface is shown in Fig. 7a. The concentration of all samples is 200 mg/L. It shows that the blank sample has a higher IFT (38.92 mN/M) than the other

| Materials       | C (%)  | O (%)  | Si (%) |
|-----------------|--------|--------|--------|
| GO@SiO$_2$ II   | 72.31  | 14.41  | 13.28  |
samples. It also can be noticed that IFT of GO (36.94 mN/M) is higher than that of GO@SiO₂ (33.04 mN/M), which means that GO@SiO₂ has a larger reduction of IFT than GO. Nevertheless, IFT of SiO₂ is 25.64 mN/M, which is lower than all other samples. It is reported that IFT is closely related to the demulsifying performance, and a lower IFT has a better demulsifying performance (Razi et al. 2011). In our previous work, it was found that IFT was not a decisive factor in demulsifying process. The demulsifying performance is affected by interfacial tension and interfacial activity, which are determined by the structure of a demulsifier (Ye et al. 2020a). An excellent demulsifying performance needs not only high interfacial activity but also lower IFT. Higher interfacial activity can promote the rapid migration of demulsifier to the oil-water interface, while lower interfacial tension will endow the demulsifier a stronger ability to replace interfacial active substances (He et al. 2019).

Figure 7b shows the IFT of GO@SiO₂ with different dosages. IFT decreases from 36.21 to 33.04 mN/M with the increase of dosage from 50 to 200 mg/L. However, IFT increases from 33.04 to 34.24 mN/M when the dosage of GO@SiO₂ increases from 200 to 300 mg/L. In other words, IFT reaches the lowest value when the dosage is 200 mg/L. In demulsifying process, GO@SiO₂ can quickly migrate to the interface and displace the intrinsic surfactants due to its high interfacial activity and low IFT. However, too much GO@SiO₂ can form a stronger interface film and even initiate a new emulsification (Javadian & Sadrpoor 2020).

Wettability

The wettability of the demulsifier is also an important factor which can affect the demulsifying performance. Three-phase contact angles (θ) can reflect the hydrophilicity and lipophilicity of the samples. The θ value of different samples was detected by a powder tablet-pressing method. As shown in Fig. 8, the θ value of GO is 83.62° ± 0.40°, which indicates that GO has slightly hydrophilic character. It may be because there are hydrophilic groups such as -COOH and -OH groups on the surface of GO (Kim et al. 2010). It is also found that the contact angle of SiO₂ is 42.52° ± 0.11°. It demonstrates that SiO₂ has strong hydrophilic character due to a large number of hydrophilic groups on its surface. However, the θ value of GO@SiO₂ is 88.75° ± 0.34°, which indicates that GO@SiO₂ has an excellent amphiphilicity. It may be because hydroxyl groups of SiO₂ react with hydroxyl groups and carboxyl groups of GO, which causes a part of hydrophilic groups to disappear. When the θ value is close to 90°, it shows that the materials can stay at the oil-water interface well. The hydrophilic ends orientate to the water phase, while the lipophilic ends orientate to the oil phase. In addition, it is reported that the demulsifier has the optimal demulsifying effect when the θ value is between 85 and 95° (Lan et al. 2007, Ye et al. 2020a). Therefore, it is concluded that the θ value of GO@SiO₂ is more beneficial to the demulsification.
Demulsifying performance

Demulsifying performance of different samples

Demulsifying performance of the samples in the O/W emulsion was evaluated by bottle test at ambient temperature and acidic condition (pH = 6). The dosage of all samples is 300 mg/L. The LTA after standing for 30 min is displayed in Fig. 9. It is noticed that the blank is very stable and there is no obvious change. Although GO and SiO₂ can initiate the oil-water separation, the water phases remain brown and light yellow, respectively. The LTAs of GO and SiO₂ are 4% and 47.1%, and the corresponding ORRs are 96.1% and 97.9%, respectively. However, GO@SiO₂ I and GO@SiO₂ II exhibit an excellent demulsifying performance. LTA is 78.4% and 81.6%, and the corresponding ORR is 99.14% and 99.27%, respectively. It demonstrates that SiO₂-modified GO greatly improves the demulsifying performance. Furthermore, GO@SiO₂ II has a higher LTA than GO@SiO₂ I. Therefore, GO@SiO₂ II was used to demulsify the O/W emulsion in the following experiments.

Effect of GO@SiO₂ dosage on the demulsifying performance

The demulsifier dosage significantly affects the demulsifying efficiency. In the current experiments, the demulsifying performance of GO@SiO₂ II with the dosage from 0 to 300 mg/L is investigated at room temperature and acidic condition (pH = 6). The result is shown in Fig. 10. It is obvious that the blank remains stable and has no obvious oil-water separation. LTA increases from 33 to 86.9% with the increase of dosage from 50 to 200 mg/L, which indicates that the demulsifying performance increases with increasing dosage. It may be because more demulsifiers move to the oil-water interface to replace or destroy the interfacial film with the increase of the GO@SiO₂ dosage. However, LTA decreases with further increasing dosage. On the one hand, the demulsifiers cannot exert their action on the interface film after they have reached a saturation state. On the other hand, too much demulsifiers may lead to further emulsification of oil droplets due to its amphiphilic structure (Grenoble & Trabelsi 2018). Therefore, the optimal dosage is 200 mg/L, and the corresponding LTA and ORR are 86.9% and 99.48%, respectively. It can be seen from Fig. 10 inset, although there is a small amount of GO@SiO₂ attached to the bottle wall, the separated water is very clear.

Effect of pH value on the demulsifying performance

The effect of pH value on the demulsifying performance was also explored with 200 mg/L of GO@SiO₂ II at ambient temperature. As shown in Fig. 11, there is no obvious oil-water separation in all samples under neutral and alkaline conditions. It may be based on the reason that the electrostatic interactions between the charged oil droplets and GO@SiO₂ II are not strong enough to stabilize the emulsion.
repulsion between demulsifier and oil droplets is enhanced because the protons of hydroxyl or carboxyl groups on GO@SiO₂ are neutralized under the alkaline condition, which results in a low demulsifying efficiency. However, the demulsifying efficiency increases with the decrease of pH value at acidic condition. The LTA is 86.3%, 88.9%, and 90.3%, and the corresponding ORR is 99.45%, 99.56%, and 99.61% when the pH value is 6, 4, and 2, respectively. It is because hydroxyl groups or carboxyl groups on GO@SiO₂ can exert their hydrophilia, which promotes the electrostatic attractive force between GO@SiO₂ and oil droplets, thus improving the demulsifying efficiency.

Effect of salinity on the demulsifying performance

The salinity has a significant influence on the properties of an emulsion. For the purpose of assessing the effect of salinity on the demulsifying performance, a series of emulsions with various salinities (different NaCl concentrations) were prepared and 200 mg/L of GO@SiO₂ II was added to the emulsions. The results are shown in Fig. 12, the LTA slightly decreases from 86.6 to 78.8% and corresponding ORR also decreases from 99.46 to 99.15% with the increase of salinity from 0 to 10,000 mg/L. This is also consistent with the lower LTA of GO@SiO₂ I (containing NaCl) in Fig. 9. It may be because an appropriate salinity affects the interfacial properties by changing the stability and viscosity of the emulsion. However, LTA and ORR are reduced by only 7.8% and 0.31%, respectively. It indicates that GO@SiO₂ has an excellent salt tolerance.

The demulsifying performance of GO@SiO₂ in the W/O emulsion

For the purpose of investigating the demulsifying performance of GO@SiO₂ in the W/O emulsion, GO@SiO₂ I with different dosages from 0 to 500 mg/L were added to the W/O emulsion at 70 °C for 180 min. In current experiments, it is found that GO@SiO₂ I has a higher demulsifying efficiency than GO@SiO₂ II in the W/O emulsion. Therefore, GO@SiO₂ I was used to demulsify the W/O emulsion. As shown in Fig. 13, the blank control is fairly stable at a temperature of 70 °C. The demulsifying efficiency increases from 25.34 to 88.48% with increasing dosage from 100 to 700 mg/L. Moreover, the demulsifying efficiency of 80.5% can be obtained when the dosage of GO@SiO₂ I is 400 mg/L. Although higher demulsifying efficiency may be obtained when more demulsifier was added, it indicates that the increase of the efficiency is not obvious. It also can be seen
from Fig. 13 inset that the water phase is very limpid, and the oil-water interface is clear. As mentioned above, it is believed that the demulsifier also has a good demulsifying performance in the W/O emulsion.

**Possible demulsifying mechanism**

The possible demulsifying mechanism of GO@SiO₂ is described in Fig. 14. Typically, the stability of an emulsion is mainly attributed to the protective film composed of asphaltenes and resin at the oil-water interface. Therefore, the decisive factor of demulsification is that the demulsifier can quickly move to the oil-water interface and destroy the interfacial film (Huang et al. 2020). As shown in Fig. 1, the matrix of GO@SiO₂ is hydrophobic, while its edge is hydrophilic due to the modification of hydrophilic groups (-COOH and SiO₂). Once it is added to the emulsion, GO@SiO₂ can quickly migrate to the oil-water interface. As shown in Fig. 14e, the demulsifiers can be stabilized at oil-water interface by standing with the hydrophilic edge facing to the water phase in the O/W emulsion. In the W/O emulsion, the sheets of GO@SiO₂ can be stayed at the oil-water interface with more hydrophobic areas facing to the oil phase (Fig. 14k) (Ma et al. 2016). When the demulsifier migrates to the oil-water interface, it will destroy the protective film by strong adsorption with asphaltenes and resin through π-π or n-π interaction (Liu et al. 2015b). Subsequently, small droplets can flocculate and coalesce to form the large droplets, and the oil and water can eventually be quickly separated under the gravity field (Teng et al. 2019).

**Conclusion**

In this work, a new GO@SiO₂ demulsifier was prepared by coating SiO₂ onto GO using a simple sol-gel method. Compared with traditional chemical demulsifiers, GO@SiO₂ is environmentally friendly, non-toxic, and efficient. Besides, it can quickly demulsify the O/W and W/O emulsions. In the O/W emulsion, LTA and ORR of GO@SiO₂ II could reach 86.9% and 99.48%, respectively, with the dosage of 200 mg/L under optimal conditions. Furthermore, it had a high salt tolerance and excellent acid resistance. In the W/O emulsion, GO@SiO₂ I had an efficiency of 80.5% when the dosage was 400 mg/L at 70 °C. In addition, the possible demulsifying mechanism was also explored. The current work shows that GO@SiO₂ has a good application prospect in petroleum and chemical industry.

**Author contribution** Conceptualization, data curation, investigation, methodology, software, and visualization: Liwei Shen and Yuanzhu Mi; funding acquisition, supervision, and project administration: Yuanzhu Mi; writing - original draft and writing - review and editing: Liwei Shen; investigation, validation, and visualization: Wenxiang Hu, Ying Yang, and Xuening Feng; formal analysis, validation, and resources: Zhiyun Lei, Jianguo Peng, Enxiong Zhu, Xuanwei Zhang, and Ming Yang.

**Data availability** All data generated or analyzed during this study are included in this published article (and its supplementary information files).

**Declarations**

**Ethics approval and consent to participate** Not applicable.
Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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