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# Physicochemical properties and potential applications of silica-based amphiphilic Janus nanosheets for enhanced oil recovery

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ABSTRACT

Nanofluid flooding has recently garnered significant attention as a novel enhanced oil recovery (EOR) technology; however, there are limitations to the current simple nanofluid flooding. Compared with the commonly used homogeneous spherical nanoparticles, amphiphilic Janus nanosheets have a higher interfacial activity and greater application potential for EOR. In this paper, a carboxyl/alkyl composite silica-based amphiphilic Janus nanosheets (CSAJN) were prepared by a bottom-up synthesis strategy, and the physicochemical properties and EOR potential were systematically investigated. The results showed that the CSAJN displayed a distinct ultrathin flake-like morphology and a lateral size in the range of hundreds of nanometres. More specifically, the CSAJN had two different sides, one side containing a carboxyl group that was hydrophilic, and the other side containing an alkyl group that was hydrophobic. Because of the amphiphilic and Janus nature, the CSAJN could be dispersed in different polar solvents, reduce the oil-water interfacial tension and enhance the oil-water interfacial film strength. Core displacement experiments showed that the CSAJN nanofluid could significantly increase the efficiency of oil recovery to ~18.31% even at an ultralow concentration of 0.005 wt% and cause minimal impairment to the permeability. By observing and analysing the interfacial behaviour of CSAJN in a toluene/brine system, it was found that the formation of a climbing film and high-strength elastic oil-water interfacial film by CSAJN may play an important role in EOR mechanism. This work reveals the physicochemical properties of silica-based amphiphilic Janus nanosheets and provides a novel efficient nanofluid system for EOR.

## 1. Introduction

Conventional chemical flooding (such as with surfactant, polymer, alkali, alkali/surfactant/polymer, etc.) is increasingly restricted due to the high cost of chemicals, harsh reservoir conditions, serious environmental pollution and potential formation damage [1,2]. In recent years, nanofluid flooding has attracted increasing attention as a novel, low-cost and environmentally friendly enhanced oil recovery (EOR) technology [3–5]. $SiO_2$ and metal oxides ($TiO_2$, $Al_2O_3$, $ZrO_2$, ZnO and so on) are common nanoparticles used for nanofluid flooding [6–10]. In particular, the study of nanosilica for EOR has been widely reported [11,12]. However, many study results indicated that the effect of a simple nanofluid was not satisfactory [13–15]. To improve the efficiency of nanofluid flooding, surfactants and polymers are generally introduced to nanofluid systems [16–18]. The displacement efficiency and stability of the nanofluid are improved by the co-operation of polymers and surfactants with the nanoparticles [19]. However, this technique still belongs to the conventional chemical flooding regime and does not resolve the downsides of conventional chemical flooding, such as serious environmental pollution. Therefore, the development of high-efficiency nanoparticles is one of the main research directions of nanofluid flooding. Surface modification of the nanoparticles has been proven to be an effective method to increase the nanofluid flooding efficiency [20,21]. Dai et al. [22] prepared a new silica nanoparticle through surface modification with vinyltriethoxysilane and 2-mercaptobenzimidazole as modified agents, and spontaneous imbibition tests indicated that the modified silica nanofluid can evidently improve oil recovery.

To further improve the EOR efficiency, nanoparticles with higher interfacial activity are demanded. Amphiphilic Janus nanosheets have two sides: one hydrophilic, and the other hydrophobic. Thus, they have certain features in common with surfactants [23]. The amphiphilic Janus nanosheets have higher interfacial activity and interfacial stability when compared with homogeneous nanoparticles [24,25]. In addition, the Janus nanosheets can form a strong elasticity interfacial film at the oil-water interface, which can be attributed to the fact that the

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rotation of Janus nanosheets at the interface is greatly restricted [26]. Recently, a nanofluid of graphene-based amphiphilic Janus nanosheets for enhanced oil recovery has been reported, and the core flooding test indicates that the oil recovery factor reaches 15.2% at the concentrations of 0.01 wt% [27]. However, there is still a lack of research on nanofluids based on amphiphilic Janus nanosheets for EOR.

Original attempts to fabricate amphiphilic Janus nanosheets relied on top-down approaches, in which the unprotected side was directly modified from sheet materials [28]. For example, Wu et al. [29] showed a general facial strategy to produce amphiphilic Janus graphene oxide nanosheets via a Pickering emulsion template. In this strategy, a wax-in-water Pickering emulsion stabilized by graphene oxide was prepared under high-temperature conditions. The wax microspheres covered with a monolayer of graphene oxide were obtained after cooling to room temperature. The amphiphilic Janus graphene oxide nanosheets were obtained by grafting hydrophobic chemicals on the outer side and dissolving the wax template. The top-down approaches are the universal and most direct methods and can control the Janus structure accurately. The premise of this strategy is that there are nanosheet materials that can be functionalized. Unfortunately, natural modifiable nanosheet materials are rare. Clay is widespread in nature, but its surface cannot be grafted by chemicals due to the absence of reactive chemical groups [30,31] In addition, the efficient large-scale preparation processes of graphene oxide are still quite lacking and require a large investment [32–35]. Considering the high costs of crude oil extraction at present, the graphene-based amphiphilic Janus nanosheets may not be suitable for the petroleum industry.

The bottom-up approaches are proven to be reliable and successful strategies to fabricate complex molecular assemblies, based on the rational design of novel systems and materials at the nanoscale [36]. In particular, polymer-based or silica-based amphiphilic Janus nanosheets can be synthesized based on the self-assembly of block copolymers or molecular interfacial self-organized sol-gel process [37–39]. Liang et al. [40] reported a bottom-up approach for the large-scale production of amphiphilic Janus nanosheets in which silica Janus hollow spheres were first synthesized by a self-assembled sol-gel process at an emulsion interface to form a shell, and then amphiphilic Janus nanosheets were obtained by crushing the hollow spheres. Compared to the top-down synthesis approaches, the bottom-up approaches have wider sources of raw material, lower cost, larger-scale production, and more particle size choices. Moreover, amphiphilic Janus nanosheets can be given various levels of stimulus responsiveness by adjusting the compositions of the reactant [41]. Another notable problem is that polymer-based materials are prone to degradation in harsh environments, especially under reservoir conditions [42]. In summary, silica-based amphiphilic Janus nanosheets synthesized by the bottom-up method are more suitable for the petroleum industry than other nanomaterials.

More importantly, we found that researchers pay more attention to the synthesis of different types of amphiphilic Janus nanosheets, but there are few studies on their physical properties and applications. At present, it is generally believed that amphiphilic Janus nanosheets can reduce the interfacial tension and act as solid surfactants to stabilize the emulsion [43,44]. In all past work, the effect of Janus nanosheets on the interfacial visco-elasticity of the oil-water interface has been neglected. However, recent studies have demonstrated that the interfacial shear viscosity of oil-water has a great influence on oil recovery [45]. Therefore, it is necessary to clarify the physical properties (especially the interfacial properties) of amphiphilic Janus nanosheets and expand their applications.

In this work, we demonstrated the physicochemical properties and displacement efficiencies of a novel nanofluid based on silica-based amphiphilic Janus nanosheets. The carboxyl/alkyl composite silica-based amphiphilic Janus nanosheets (CSAJN) were preferentially synthesized using bottom-up approaches, and the morphology and chemical composition were characterized. Subsequently, the CSAJN were dispersed in deionized water to form a nanofluid for EOR through adequate ultrasonication. Contact angle, dispersibility, zeta potential, interfacial tension and interfacial shear viscosity measurements were performed to investigate the physical properties of the CSAJN. Core flooding experiments were conducted to test the effect of the CSAJN nanofluid when used for enhanced oil recovery. Moreover, the potential EOR mechanisms of the CSAJN nanofluid were studied and explained through an interfacial behavioural observations experiment.

## 2. Experimental section

### 2.1. Materials

Maleic anhydride (MAH), 3-mercaptopropyltrimethoxysilane (MPTS), octadecyltrichlorosilane (OTS) and azodiisobutyronitrile (AIBN) were purchased from Shanghai Macklin Biochemical Co. Ltd. Calcium carbonate ($CaCO_3$), toluene ($C_7H_8$, > 99.9%), absolute alcohol ($C_2H_5OH$, > 99.9%), aqueous ammonia ($NH_3{\cdot}H_2O$, 40%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), sodium chloride (NaCl) and calcium chloride ($CaCl_2$) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. The crude oil was obtained from an oilfield in China, which had a viscosity of 31.6 mPa·s at 25 °C. The synthetic brine (4.0 wt% NaCl + 1.0 wt% $CaCl_2$ solution) was prepared by dissolving NaCl and $CaCl_2$ in deionized water as reservoir brine. Three Berea sandstone cores were used for the oil displacement experiments, and the key parameters are shown in Table 1.

### 2.2. Synthesis of CSAJN

The CSAJN were synthesized by a surface sol-gel process of the self-assembled monolayer of an amphiphilic silane onto the template particle [46]. First, the amphiphilic silane was synthesized by stirring the mixture of MAH (0.49 g), MPTS (1.01 g) and AIBN (0.1 g) in a nitrogen atmosphere at 65 °C for 4 hr. The amphiphilic silane was confirmed by Fourier transform infrared spectrometer (FT-IR) analysis (Fig. S1). Then, the amphiphilic silane (0.2 g) was added to the dispersion of $CaCO_3$ particles (1.0 g) in toluene (30 mL). The mixture was stirred at room temperature with a speed of 400 rpm for 24 hr and then centrifuged, washed with toluene and dried in a vacuum, resulting in amphiphilic silane covered $CaCO_3$ ($CaCO_3$@AS) particles. Afterward, the $CaCO_3$@AS particles (1.0g) were dispersed in absolute alcohol (30 mL), and aqueous ammonia (10 µL) was added. The mixture was stirred at room temperature at 400 rpm for 24 hr and then centrifuged, washed with alcohol and dried in a vacuum, resulting in silica Janus shell coated $CaCO_3$ ($CaCO_3$@$SiO_2$) particles (Fig. S2). Following that, a mixture of the $CaCO_3$@$SiO_2$ particles (1.0g), OTS (0.1g), and toluene (30 mL) was refluxed at 80 °C for 8 hr. After that, the mixture was cooled to room temperature and then centrifuged, washed with toluene and dried in a vacuum, resulting in carboxyl/alkyl composite silica Janus shell coated $CaCO_3$ ($CaCO_3$@$SiO_2$-$C_{18}$) particles. Finally, the $CaCO_3$@$SiO_2$-$C_{18}$ particles (1.0g) were etched with HCl (2.0 M, 10 mL) at 50 °C under ultrasonication. After cooling to room temperature, the CSAJN were derived by centrifugation, washed with deionized water and dried in a vacuum. Non-amphiphilic silica-based Janus nanosheets (SJN) that were not grafted with alkyl groups were prepared by etching the $CaCO_3$@$SiO_2$ particles with HCl.

**Table 1**
Key parameters of Berea sandstone cores.

| Core number | Length (cm) | Diameter (cm) | Porosity (%) | Permeability ($10^{-3}$ µm$^2$) | Pore volume (cm$^3$) |
|---|---|---|---|---|---|
| Ber-1 | 9.91 | 2.55 | 20.48 | 63.71 | 10.55 |
| Ber-2 | 9.81 | 2.55 | 20.41 | 43.25 | 10.23 |
| Ber-3 | 9.92 | 2.55 | 21.46 | 68.74 | 10.88 |