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Microgel evolution at three-phase contact region and associated wettability alteration

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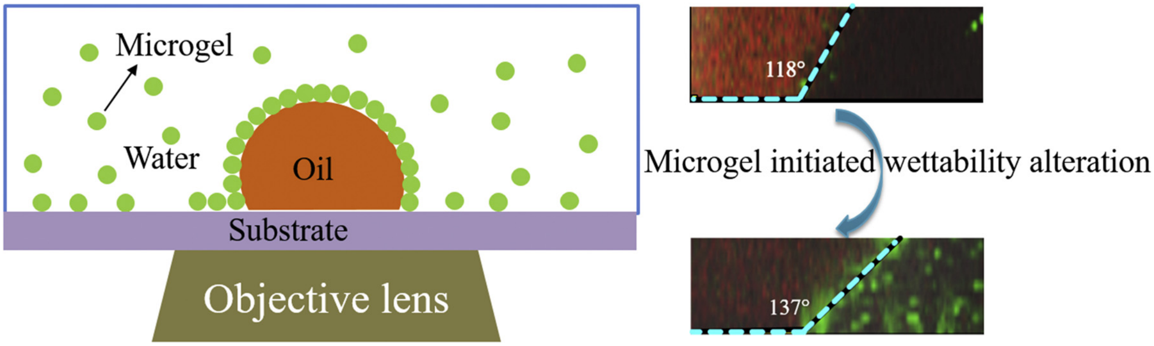
GRAPHICAL ABSTRACT



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ABSTRACT

Wettability alteration induced by nanoparticle and polymer have a broad application range in the industry and attracts a growing attention. Microgel as a special material with polymer/colloid duality is a potential candidate to initiate wettability alteration though seldom addressed in the field. This work provides direct observation on microgel-induced contact angle change of the sessile oil droplets in a microscopic view. The distribution of fluoresced microgels in the vicinity of the oil/water/solid three-phase contact line (TPCL) has been quantitatively investigated using confocal laser scanning microscopy (CLSM). Slow wettability alteration of the glass substrates towards oil-phobic direction induced by microgels has been demonstrated. The mechanism of microgel induced wettability alteration has been proposed based on the interaction between microgel and TPCL. The findings pave the way for microgel-induced wettability alteration towards enhanced oil recovery (EOR).

Abbreviations: TPCL, three-phase contact line; CLSM, confocal laser scanning microscope; EOR, enhanced oil recovery; IFT, interfacial tension; PPG, preformed particle gels; TFMA, 2,2,2-trifluoroethyl methacrylate; NIPAM, N-isopropylacrylamide; MBA, *N,N'*-methylenebis(acrylamide); AAc, acrylic acid; APS, ammonium persulfate; C7, coumarin 7; NR, nile red; *CI*, concentration of microgel at the water/solid interface; *CFI*, concentration of microgel at the far-interface (water/solid interface); *RI/FI*, ratio between *CI* and *CFI*

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1. Introduction

The wettability of materials determines their performances in a wide range of applications such as self-cleaning [1,2], anti-icing [3], and super-hydrophobic [4,5] or super-hydrophilic [6] materials. Changing the wetting state of surfaces has attracted much attention in a variety of fields covering both engineering and science. In oil reservoirs, wettability alteration usually refers to the process of changing the original reservoir rock wettability, which is presumed to be water wet or oil-phobic [7] for enhanced oil recovery (EOR) purpose. Typical wettability alteration reagents are interface active materials such as surfactants, polymers, nanoparticles, and their combination [7–10]. Oil/water interfacial tension could be decreased after the adsorption of these interface active materials [11,12], leading to the tangential force imbalance at the TPCL and ultimately altering the wettability [13]. Other than that, nanoparticles induced disjoining pressure at the oil/water/solid three-phase contact region significantly contributes to the wettability alteration [13–15]. The nanoparticles form a wedge film, leading to a higher structural disjoining pressure near the oil/water/solid three-phase contact line (TPCL) than in the bulk meniscus, responsible for the TPCL moving forward with a progressive cleavage of the oil-solid contact and eventually detaching the oil droplet [13,15]. The spreading of nanoparticles at TPCL driven by the structural disjoining pressure has been studied both experimentally and analytically [16–18]. The effects of size, hydrophobicity and chemical composition of nanoparticles on the wettability alteration have been investigated [19–21].

Nowadays, EOR technology development reaches a bottleneck, and new materials are excepted to bring synergetic effects and new prospective to the current system of EOR reagents. Microgels are crosslinked polymer particles that can swell in solvent. Poly N-Isopropylacrylamide (PNIPAM) based microgels share many common features with the abovementioned wettability alteration reagents. First, microgel (refers to PNIPAM based one) has a core-corona structure [22], and the heavily crosslinked core brings particle-like property while the slightly crosslinked shell endows polymer-like behavior. As a result, microgel possesses polymer/colloid duality [23]. Moreover, microgel is strongly active at an interface, similar to surfactants [24,25]. Ngai et al. found that diffusion and deformation of microgels were two dominating mechanisms controlling oi/water interfacial tension drop using pendant drop tensiometry [26]. Microgels have been investigated as emulsion stabilizers, which can respond to environmental stimulations [27,28]. Microgels have also been studied for conformation control towards EOR application [29–31]. Microgels combine characteristic properties of the colloids, polymers, and surfactants [32], thus sharing many common features with other wettability reagents [33]. However, the effects of microgels on the wettability alteration and the behavior of microgels at oil/water/solid three-phase system haven't been reported to the best of our knowledge. This paper for the first time demonstrates that the core-shell structured microgels can also initiate wettability alteration of solid substrate. The fluorescent core is embedded for the direct observation of microgel distribution around TPCL by confocal laser scanning microscopy (CLSM). Our previous work has shown that the core has a very limited effect on the interfacial behavior of the microgels [34]. The evolution of microgel accumulation at TPCL region and the profile of oil droplet are monitored and analyzed. The results give a comprehensive and visual perception on the fundamental mechanism governing microgel induced wettability alteration. It guides the application of microgel suspension in the field associated with wettability alteration.

2. Experimental section

2.1. Materials

2,2,2-Trifluoroethyl methacrylate (TFMA), N-Isopropylacrylamide (NIPAM), N,N'-methylenebis(acrylamide) (MBA), Acrylic acid (AAc), ammonium persulfate (APS), Coumarin 7 (C7), Nile Red (NR) were purchased from Sigma-Aldrich. Limonene (purity of 96%) was purchased from Fisher Scientific. All reagents were used as received. Millipore water with a resistivity of 15 MΩ cm was used as ultrapure water.

2.2. Characterization of microgels in oil/water/solid system

The microgel synthesis followed the protocol described previously [35]. Briefly, PTFMA cores with embedded fluorescent C7 were synthesized and served as seeds for the following polymerization of P(NIPAM-co-AAc) shell. The morphologies of as-formed core-shell structured microgels and PTFMA cores are shown in Fig. S1 in Supporting information. Zeta-potential and hydrodynamic diameter of microgels at pH 10 were −30.83 ± 0.91 mV and 380.8 ± 3.6 nm measured by using Malvern Zetasizer Nano ZS.

Limonene was chosen as the oil phase in this study due to its nonpolarity [36]. 30 μL of limonene dyed with fluorescent NR was placed on a glass bottom microwell dish (MatTek 35 mm petri dish, 10 mm microwell), which was cleaned in an ultrasound bath with ethanol and Millipore water sequentially for 3 times prior use. Then 3 ml of microgel suspension (pH was adjusted to 10) with investigated concentration 0.4, 1.0 and 2.0 mg/ml was added into the limonene contained microwell dish to create a three-phase system. The limonene separated into several microscale sessile oil droplets at the bottom of the container due to the addition of the microgel suspension. The microwell dish was fixed on the sample stage of CLSM (Zeiss LSM510 META MP) and the sessile oil droplets were observed using oil objective lens (63×). NR in the oil phase (limonene) was excited using 543 nm laser and the emission was detected from 565 to 615 nm. The dye C7 embedded in the core of microgel was excited by a 488 nm argon ion laser and the emission was detected from 500 to 550 nm. 3D image of the three-phase system was recorded by scanning the *xy* plane slides by a constant increment (0.38 μm) along the z direction.

2.3. Contact angle measurement

Contact angle of sessile oil droplet was determined based on the 3D CLSM image of TPCL region (as shown in Fig. 1). Since the contact angle hysteresis existed, the contact angle evolution with time was always measured at the same point on TPCL in this study. First, the interested point on TPCL was selected, and then the plane determined by the curvature radius of that point at $z = 0$ was selected. The oil profile of the droplet in the plane was captured and loaded into ImageJ. The angle between the tangent line of the curvature at that point and the oil/solid interface was read by the ImageJ, used as the contact angle of the oil droplet.

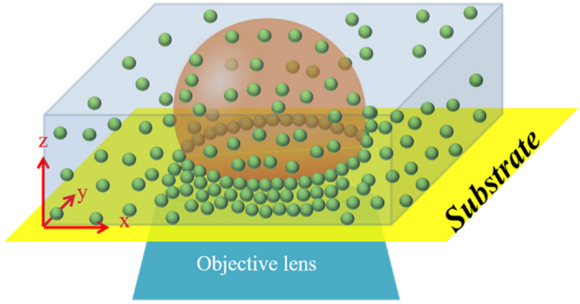

Fig. 1. Schematic setup of CLSM measurement. The grey box, red droplet and green dots represent water, oil and microgels, respectively. The CLSM images of *xy* plane are collected along z direction during the measurement. The coordinate system in the figure applies to the following sections of this paper (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).