

Stabilization of pickering emulsions by generating complex colloidal layers at liquid–liquid interfaces



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ABSTRACT

Typical Pickering emulsions accumulate particles to form a robust colloidal layer at an immiscible liquid–liquid interface. However, if the particles are smaller than tens of nanometers, they have a tendency toward coming off from the interface, thereby destabilizing emulsion drops. To solve this problem, a technique that can make the adsorbed nanoparticles stay at the interface should be developed. This study introduces a practical method that allows us to obtain a mechanically stable Pickering emulsions; n-decane was emulsified to form an oil-in-water emulsion of which interface was stabilized with a complex colloidal layer consisting of 12 nm-sized silica nanoparticles, a poly(vinyl alcohol) binder, and an alkyl-chained silane coupling agent. We have found that in the conditions of high salinity, the emulsion drops attract each other and form an emulsion gel phase. However, even in such harsh conditions, the complex silica layer maintains its original structure at the interface, thus stabilizing the emulsion drop against coalescence.

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1. Introduction

Solid particles are able to assemble between two immiscible liquids, typically oil and water, thus generating mechanically stable emulsions. The interface stabilized by solid particles prevents breaking-up or coalescence of emulsion drops. This particles-stabilized emulsion is referred to as the Pickering or Ramsden emulsion [1,2]. A feature of this emulsion system is that the solid particles generate a flexible but robust colloidal layer at the liquid–liquid interface. Also, manipulation of the particle properties facilitates control over phase inversion from oil-in-water to water-in-oil emulsion system and *vice versa*. Many different types of colloidal materials, including inorganic particles [3–5], polymer particles [6], clay particles [7], or graphene sheets [8–10], have been used for fabrication of Pickering emulsions. In principle, once the particles well pack to form a layer at the interface, those colloidal materials can afford to structure the interface. Thus, to obtain a structurally stable Pickering emulsion, the particle size [11], shape [12], and surface anisotropy [13,14], as well as the wettability to the liquids consisting of the interface [15].

One of key parameters that determine the stability of Pickering emulsions is to balance the hydrophilicity and lipophilicity of the solid particles. This can be estimated in terms of the contact angle, θ , made by a particle adsorbed at the oil–water interface. Reading

the contact angle, we are able to determine the adhesion energy of the particle. The adhesion energy can be expressed as $E = \pi\alpha^2\gamma(1 \pm \cos \theta)^2$, where α is the radius of the particle and γ is the surface tension [16,17]. Hydrophilic particles always show the contact angle lower than 90° and prefer to generate an oil-in-water emulsion. By contrast, if the contact angle is higher than 90° , the particles are hydrophobic and readily wet by an oil phase. This results in a water-in-oil emulsion. Particle size is also critical to changing the adhesion energy. As the adhesion energy increases in proportion to the square of particle size, the larger particles provide the better emulsion stability. Despite this advantage, the large particles of which size ranges in micrometer length scales require application of a strong stress in order to effectively adsorb them at the interface. This is because their thermal motion is weak. In comparison with the large particles, small nanoparticles adsorb to the interface more favorably. However, if the particle size is too small, they may come off from the interface due to the low adhesion energy, thereby destabilizing the Pickering emulsion [18].

The goal of this study is to introduce a methodology to produce a structurally stable Pickering emulsion with particles whose size is in nanometer length scales. The essence of our approach is to fix nanoparticles at the fluid interface by using both chemical reaction and physical attractions. This approach is indeed advantageous in that the complex colloidal layer provides the emulsion with a mechanically robust barrier, which is quite comparable to conventional Pickering emulsions solely made of particles. The complex colloidal layer was made of silica nanoparticles, a poly

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(vinyl alcohol) binder, and a hydrophobic silane coupling agent. Microscopic analysis was carried out to characterize the morphological feature for the Pickering emulsion produced in this study. The improved emulsion stability was experimentally confirmed by examining the creaming kinetics and emulsion rheology at high salinity conditions.

2. Experimental

2.1. Materials

A hydrophilic fumed silica (Aerosil 200, a specific surface area $\sim 200 \text{ m}^2/\text{g}$) and a silane coupling agent (hexadecyl tri-methoxy silane, HTS) were purchased from Evonic (Germany). The oil was *n*-decane (>99%, Sigma, USA). Poly(vinyl alcohol) (PVA, 1.3×10^4 – $2.3 \times 10^4 \text{ g mol}^{-1}$, saponification value 87–89%) was purchased from Sigma and used with a 5 wt% solution. To detect the location of silica and PVA in the emulsion, they were dyed with fluorescein 5(6)-isothiocyanate (FITC, Sigma). NaCl (>99%), NaOH, and dimethyl sulfoxide (DMSO) were purchased from Sigma and used without further purification. Deionized distilled (DI) water was used for all experiments.

2.2. Preparation of Pickering emulsions

The oil part was prepared by dissolving 1.8 mL of HTS in 22.2 mL *n*-decane (7.5 vol%). This concentration was determined after observing the effectiveness of HTS for improving the emulsion stability. The water part was an aqueous solution consisting of 1.8 wt% Aerosil 200 in 35.4 mL DI water. To make sure fine dispersion of Aerosil 200, sonication was applied to the mixture for 10 min before emulsification (Powersonic 510, Hwa Shin, Korea). Then, 0.0348 ml of NaOH aqueous solution (1 N) was added in order to adjust pH of the aqueous solution to 7. The primary emulsion was prepared by mildly homogenizing the water part with a speed of 1000 rpm, while slowly pouring the oil part. To produce micron-sized emulsion drops, the primary emulsion was strongly homogenized again at $1.6 \times 10^4 \text{ rpm}$ for 2 min. In the meantime of emulsification, 0.6 ml of PVA solution (5 wt%) was poured in the emulsion. The homogenizer used in this study was Ultra Turrax T25 (a 25 mm head size) from IKA (Germany). Emulsification was carried out at room temperature. The procedure for production of Pickering emulsions is schematically illustrated in Fig. 1.

2.3. Characterization of Pickering emulsions

The emulsion produced was observed with a bright field microscope (NSB-80T, Samwon, Korea). The emulsion drop diameter was measured by analyzing the microscope image. More than 100

individual drop diameters were measured from a digital image and the average was taken. In the case of showing the coupling reaction of HTS with hydroxyl groups of Aerosil 200 and PVA, the dried emulsion was analyzed with a FT-IR spectrometer (FTS 1000, Varian, USA). The IR sample was prepared first completely drying the *n*-decane and water from the emulsion in a vacuum oven at 50 °C for 48 h. Then, some remaining HTS was repeatedly rinsed with a mixture of ethanol/water (5/5, v/v). To directly visualize the colloidal layer, free hydroxyl groups from silica and PVA were labeled with FITC. For this, approximately 0.001 wt% FITC was dissolved in DMSO and then, 0.05 ml taken from the FITC solution was added into the emulsion (5 ml). After the reaction was carried out at room temperature for 2 h, the continuous aqueous phase was repeatedly replaced with DI water to remove excess FITC remaining in the continuous phase. The fluorescence in the FITC-labeled emulsion was detected with a confocal laser scanning microscope (CLSM, TCS SL, Leica, Germany).

2.4. Observation of emulsion phase separation

As the oil drops are lighter than the continuous aqueous phase, they float to top, which is well-known as creaming event. Taking advantage of this event, the emulsion stability was evaluated in the presence of a salt, NaCl. For this, the emulsions with a different amount of NaCl were prepared and placed in glass tubes. Each tube contains 20 ml emulsion. The dimension of a tube was 1 cm inner diameter and 15 cm height. The interface generated by the creaming was imaged with the time interval at room temperature. Snapshot was taken at every 30 s with a digital camera (STC-GEC83A, Sentech, Japan). By comparing the initial height of emulsion (H_0), which was 12 cm, with the separated emulsion height (H), the creaming kinetics was evaluated.

2.5. Measurement of emulsion rheology

The elasticity of the emulsion was investigated in the presence of NaCl by measuring the storage modulus changes in response to oscillatory shear stress. This measurement was made using an AR 2000 rheometer (TA Instruments, US) in a controlled rate mode with a truncated cone. The dimension was 1° cone angle, 20 mm cone diameter, and 30 μm gap distance. Before the measurement, the emulsion was shaken to make sure mixing of any floating emulsion drops. Continuously, 0.3 ml of emulsion sample was carefully dispensed on a rheometer plate. For an oscillatory measurement, after preconditioning, the amplitude stress of the oscillation was scanned between a lower and an upper limit in a series of logarithmic steps at a constant frequency (typically 0.1 Hz). All the measurements were carried out at room temperature.

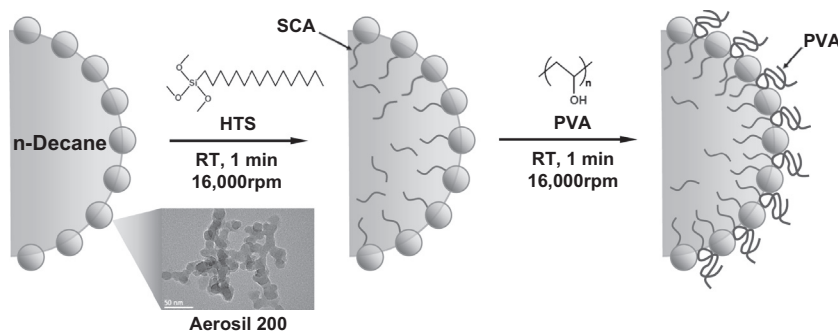


Fig. 1. A schematic for formation of a complex colloidal layer at an interface of *n*-decane and water. The inset is a transmission electron microscope image for Aerosil 200 used in this study.

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