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New pickering emulsions stabilized by silica nanowires

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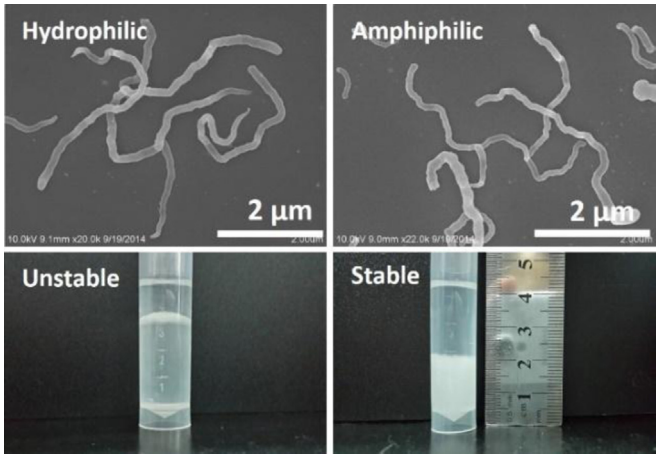
HIGHLIGHTS

- Both hydrophilic and amphiphilic silica nanowires were synthesized via a wet-chemical process.
- Pickering emulsions were prepared by use of the two types of silica nanowires.
- Emulsions stabilized by amphiphilic nanowires show exceptional stability for over 4 months.

GRAPHICAL ABSTRACT

Pickering emulsions stabilized by hydrophilic and amphiphilic silica nanowires separately were prepared. The effect of length and concentration of the nanowires, and oil/water volume ratio on the stability of the emulsion were investigated.



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ABSTRACT

In this work, oil-in-water and water-in-oil emulsions stabilized by hydrophilic and amphiphilic silica nanowires separately were investigated by scanning electron microscopy (SEM), optical microscopy and visual observation. The effects of length, concentration and wettability of the nanowires on the stabilization of the emulsion were investigated. The hydrophilic silica nanowires of 10 μm length can be used to prepare stable oil-in-water emulsions, with a network forming on the surface of the emulsion droplet is believed to be beneficial for the emulsion stability; whereas, the amphiphilic silica nanowires of all three lengths (1.5, 2.5 and 5 μm) can produce water-in-oil emulsions stable for at least 4 months, and it was found that increasing either the length or concentration of silica nanowires resulted in the enhancement of the stabilization of emulsions by nanowires. Phase inversion from oil-in-water to water-in-oil can be easily achieved by increasing the oil volume fraction in the amphiphilic silica nanowire stabilized emulsions.

1. Introduction

Pickering-Ramsden (Pickering) emulsions [1,2] refer to the emulsions formed by solid particles serving as stabilizing agent,

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such as polymer latex [3], Laponite clay [4], montmorillonite [5], calcium carbonate [6] and carbon graphite [7]. Because of their quite ease of formulation, Pickering emulsions have attracted constant attention over the past 10 years, especially in health and cosmetic fields where surfactants are undesirable [8]. Moreover, such emulsions offer good stability and mechanical properties over surfactant stabilized emulsions and can be used to create new materials, including colloidosomes [9] and yeastosomes [10]. Factors such as particle concentration [11], shape [12], size [13] and wettability [14] that influence the stability of the emulsions have been systematically investigated in the last few decades.

It is proved that the crucial factor determining whether solid particles could stabilize at the interface is particle wettability [15], which is directed by the hydrophilic or hydrophobic properties of particle surface. Particles with hydrophilic surface, e.g., iron oxide, will result in formation of oil-in-water emulsions. On the contrary, the hydrophobic ones, e.g., polystyrene latex, will result in water-in-oil emulsions [14]. However, no emulsions would form if the particles were completely wetted by water or oil, and the particles would remain in either of the phase. In Pickering emulsions, the interaction driving particles to stay at the oil/water interface differs from spherical to non-spherical particles. The interaction between spherical particles is governed mainly by electrostatic and/or van-der-Waals forces, while for non-spherical particles, the interface mediated capillary forces become dominant [16,17]. For example, for ellipsoidal particles the capillary interactions are attractive and overrule the electrostatic repulsion, which could lead to the self-assembly of ellipsoidal particles forming a two dimensional network [12]. Using the anisotropic particles brings out specific advantages to the emulsion systems. On the one hand, it can help to decrease the percolation threshold [18], which is believed to be a crucial factor to the mechanical rigidity of the interface [19]; on the other hand, the maximum packing density can be increased, and leads to stronger materials [20]. Therefore, there is a clear need to study the behavior of anisotropic particles at the interface and their stabilized Pickering emulsions.

Among the anisotropic particles used in Pickering emulsions formulation, ellipsoidal or rodlike particles are of the most interest. Emulsions stabilized by cellulose nanocrystals [11], polystyrene ellipsoids [12], gold nanowires [21], and cadmium selenide (CdSe) nanorod [22] were successfully prepared and showed better stability compared to spherical particle stabilized ones when they were of the same size and surface property. Silica nanowires, being the relatively new silica nanomaterials, have drawn great attention because of the unique physical and chemical stability. A variety of methods for synthesizing silica nanowires have been developed, including chemical vapor deposition [23], electrochemical sol–gel nanodeposition [24] and wet chemical process [25,26]. The application of silica nanowires concentrates in making biological and environmental sensing devices, due to their high loading capacity and ease of surface modification [27]. The use of silica nanowires to stabilize Pickering emulsions would bring unique properties to the system, thus help to extend the application of silica nanowires and the resulting Pickering emulsions at the same time.

In the present study, both hydrophilic and amphiphilic silica nanowires of various lengths were synthesized through a facile process. Oil-in-water emulsions stabilized by hydrophilic silica nanowires and water-in-oil emulsions stabilized by amphiphilic silica nanowires were successfully prepared. For the emulsions stabilized by hydrophilic silica nanowires, length of the nanowires played a key role in stabilizing the emulsions. In the amphiphilic silica nanowire stabilized emulsions, the effect of nanowire length and concentration, and the oil/water volume ratio were investigated. And it is found that a catastrophic phase inversion from oil-in-water to water-in-oil occurred while increasing the oil volume fraction.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP, average molecular weight 40 k, Sigma–Aldrich), *n*-pentanol (Acros), ethanol (Sinopharm), sodium citrate (Sinopharm), ammonium hydroxide solution (28.0–30.0 wt%, Alfa), tetraethoxysilane (TEOS, Alfa), hexadecyltrimethoxysilane (HDTMOS, Adamas), *n*-hexadecane (Sinopharm), and paraffin (Sinopharm) were all used without further purification. High-purity deionized water (18.2 MΩ cm) was used.

2.2. Silica nanowire preparation

Silica nanowires of various lengths were synthesized using a wet-chemical method described in details elsewhere [25]. A typical synthetic procedure for hydrophilic silica nanowires with a length of 7 μm and a diameter of 240 nm is as follows. In a 250 mL round-bottom flask, PVP (15 g) was dissolved in *n*-pentanol (150 mL) under sonication for 4 h. Upon dissolved, deionized water (5.1 mL), ethanol (15 mL) and sodium citrate aqueous solution (1 mL, 0.18 M) were added to the above pentanol solution. The flask was shaken by hand for 5 min to mix all the components. Then, ammonium hydroxide solution (1.15 mL) was added, and the flask was shaken by hand for another 3 min. TEOS (2 mL) was added to the mixture, followed by gently shaking the flask for 30 s before left to rest at ambient temperature overnight to proceed the hydrolysis of TEOS. The synthesis of 10 μm silica nanowires was conducted in a Teflon-lined autoclave at 150 °C for 12 h.

For the synthesis of amphiphilic silica nanowires, HDTMOS (400 μL) was added to the above product mixture, and the flask was gently shaken for 30 s again [26]. After 12 h hydrolysis of HDTMOS, the reaction mixture was washed five times by ethanol under centrifugation at 6000 rpm for 15 min. In the end, all the silica nanowires were collected in a crucible and dried in an oven at 60 °C for the preparation of Pickering emulsions.

2.3. Pickering emulsion preparation

To prepare oil-in-water (the volume ratio of o:w = 3:7) emulsions, hydrophilic silica nanowires (7 mg, 2 g/L) of various lengths were dispersed in deionized water (3.5 mL) in a plastic vial under sonication (180 W) at room temperature for about 30 min. Then hexadecane (1.5 mL) was added to the solution. Emulsification was carried out by vigorously stirring the mixture using an Ultra-Turrax (IKA T10) at 11,500 rpm for 1 min. The preparation of the water-in-oil (the volume ratio of o:w = 7:3) emulsions using the amphiphilic silica nanowires followed the same procedure. Specifically, deionized water (1.5 mL) was added to the hexadecane dispersion (3.5 mL) containing hydrophilic silica nanowires (7 mg), emulsification process was the same as mentioned above. All the emulsions prepared were kept undisturbed under ambient temperature for stabilization test. The stabilization of the Pickering emulsions was assessed by comparing the emulsion volume and droplet size before and after a certain period of time. Unless otherwise specified, the oil to water volume ratio was fixed at 3:7 for oil-in-water emulsions, and 7:3 for water-in-oil emulsions, and the concentration of hydrophilic and amphiphilic silica nanowires in dispersed phase was fixed at 2 g/L.

2.4. Characterization

Scanning electron microscopy (SEM). Average length of the prepared silica nanowires and distribution of nanowires on the emulsion droplet surface were examined using SEM (S-4800,