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Roles of methyl orange in preparation of emulsions stabilized by layered double hydroxide particles

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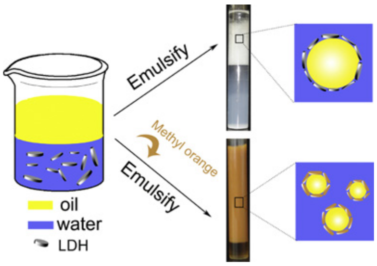
HIGHLIGHTS

- Methyl orange acts as a fluorescent amphiphile in Pickering emulsions.
- Methyl orange enhances particle hydrophobicity and improve the emulsion stability.
- In situ microscopic imaging reveals particle adsorption onto the emulsion droplets.
- Hollow colloidosomes have been fabricated with obtained emulsions as templates.

GRAPHICAL ABSTRACT

Methyl orange molecules act as fluorescent amphiphiles in emulsions stabilized by layered double hydroxide (LDH) particles.



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ABSTRACT

The roles of a fluorescent dye, methyl orange (MO) in the emulsions stabilized by layered double hydroxide (LDH) particles have been investigated in detail. The hydrophilic LDH particles are rendered partially hydrophobic by the in situ surface modification with MO, leading to the enhanced stability of emulsions. The variation of contact angle, zeta potential and emulsion stability demonstrates the amphiphile-like behaviors of MO. Exploiting the fluorescence of MO, we have shown in situ microscopic images of MO-modified particle adsorption onto droplet surface using confocal fluorescence microscopy. Furthermore, the adsorption of MO-modified LDH on liquid droplet surface has also been exploited to produce hollow colloidosomes, the morphology of which has been observed with SEM.

1. Introduction

It is well-known that colloidal particles of suitable wettability can adsorb at liquid–liquid interfaces and thus behave as emulsion stabilizers [1,2]. Investigations of emulsions stabilized by particles, commonly named Pickering emulsions, reveal that the wettability of particles at the oil–water interface is a crucial factor dominating the type and stability of emulsions [2–4]. Stable emulsions are prepared with particles of intermediate wettability (contact angle approaches 90°). To meet the need of appropriate wettability, the particles are usually modified through prior chemical surface treatment [3,5] or the adsorption of amphiphilic molecules [6–14].

These methods have been successfully used to tailor the wettability of particles in liquids and thus prepare stable emulsions. Binks et al. have investigated the stability of emulsions containing silica particles by changing the extent of chemisorbed silane on their surfaces [5] or adding a variety of surfactants such as nonionic surfactants of the CnEm (alkyl poly(oxyethylene)) type [6], anionic SDS (sodium dodecylsulfate) [7] and cationic CTAB (cetyltrimethylammonium bromide) [8]. Haase et al. investigated emulsions stabilized with weak polyelectrolytes coated alumina or silica particles [15]. Ultrastable o/w emulsions have been prepared

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using nanoparticles modified with short amphiphiles [12]. The presence of these surface-active materials could adjust the wettability of particles in liquids and thus improves the stability of Pickering emulsions.

In addition to emulsion stabilization, the adsorption of colloidal particles on liquid droplets in Pickering emulsions has also been exploited to produce colloidosomes and macroporous materials [16]. Emulsions stabilized by the functional particles could result in the materials with expected function [17,18]. However, all the approaches referred to above just aid to tailor the wettability of particles in liquids. Very few studies focused on the particle hydrophobization through the adsorption of functional amphiphiles, although it could offer a facile way to fabricate functional materials. Herein, we introduce methyl orange (MO), a common dye to adjust the wettability of layered double hydroxide (LDH) particles in liquids and functionalize the particles in a single-step process. Fluorescent dyes have been used to synthesize fluorescent hybrid materials [19,20]. Furthermore, Thijssen et al. have confirmed that fluorescent dyes can significantly affect the polymeric particles at liquid interface [21]. Therefore, it is anticipated that MO molecules could act as fluorescent amphiphiles in Pickering emulsions.

In this study, the roles of MO in the emulsions stabilized by LDH particles have been investigated in detail. Liquid paraffin-in-water emulsions have been prepared by mixing oil with LDH dispersions after in situ modification of the particles with MO. MO can tailor the wettability of particles in liquids, confirmed by the increased contact angles and enhanced emulsion stability. Then the fluorescence of MO was exploited to offer the in situ microscopic images of particle adsorption onto droplet surface using confocal fluorescence microscopy. Finally, with the obtained emulsion as a soft template, hollow colloidosomes composed of MO-modified LDH with fluorescence were fabricated and observed with SEM.

Owing to the fluorescence and amphiphilic property of MO, the LDH particles are rendered fluorescent and partially hydrophobic in a single-step process, leading to the self-assembly of fluorescent particles at oil/water interfaces. This could open further opportunities for the development of a facile way to fabricate fluorescent materials. Moreover, due to the fact that some dye molecules may affect the particles at liquid interfaces, we also offer a valuable warning for future investigations that fluorescent dyes should not be blindly employed as probes in Pickering emulsions.

2. Experimental

2.1. Materials

Deionized water, purified by ion exchange, was used in all the experiments. The oil material used in this work was paraffin oil (Sinopharm Chemical Reagent Co., China) with purity greater than 99% ($d_4^{20} = 0.835 - 0.855$). The viscosity of liquid paraffin is 20.8 mPa s at 25 °C. The composition of liquid paraffin is mainly isoalkane and the main carbon number distribution measured with Agilent 6820 GC (Agilent Co., USA) is between 16 and 26. Methyl orange, sodium 4-(dimethylamino) azobenzene-4-sulfonate, was provided by Alfa Aesar and used without further purification. The molecular structure of methyl orange is shown in Fig. 1.

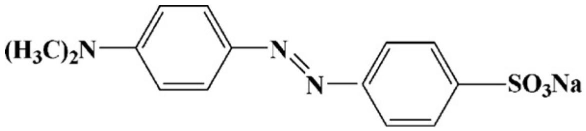

Fig. 1. The molecular structure of methyl orange (MO).

Layered double hydroxide (LDH) particles used here were $Mg_2Al\text{-}NO_3$ LDH prepared according to the literature [22–24]. The final product was an aqueous dispersion with a concentration around 10 wt%. The stock dispersion of LDH was diluted with distilled water to maintain the particle concentration at 2.0 wt%.

2.2. Methods

2.2.1. Preparation, stability and characterization of LDH/MO dispersions

The LDH/MO dispersions were prepared by diluting the stock LDH dispersions with MO solutions. The pH was adjusted to 10 with NaOH or HCl. The prepared dispersions were stirred for 24 h to attain adsorption equilibrium at 25 °C. The prepared dispersions were transferred into a stoppered glass tube with internal diameter 1.6 cm and length 15 cm to observe the stability of the dispersions 24 h after preparation. The zeta potentials of the particles were measured with a JS94H microelectrophoresis instrument (Shanghai Zhongchen Digital Technic Apparatus Co., China).

After equilibration, the prepared dispersions were centrifuged for 20 min at 12,000 rpm in order to separate the LDH particles from the supernatant. MO in the supernatant was analyzed by TOC-5000A (Shimadzu, Japan). The adsorbed amounts were calculated from the difference between initial and equilibrium concentrations of MO and divided by the weight of the LDH particles in the dispersions. The particles in sediment were washed with deionized water three times to remove the free MO. Then the obtained sediment was dried in a vacuum at 25 °C for 24 h and crushed into powders for X-ray diffraction (XRD) characterization. The XRD patterns of the particles were obtained on a D/max-γB model diffractometer with a Cu target at 40 kV and 120 mA, at a speed of 2°/min and a step of 0.06° (2θ). Data were collected over the 2θ range from 2° to 40°.

The contact angle of particles was measured by the compressed disk method described previously [25,26]. The powders of particles were compressed to a pressure of 10 mPa into circular disks with a pellet press. The thickness of all disks was about 1 mm. The disk was placed at the bottom of an open, transparent glass vessel filled with paraffin oil. Then a drop of water was placed on the surface of the particle disk using a syringe, and the shape of the water droplet was photographed (Tracker, I.T.Concept, France). The data of contact angles were obtained using the image analysis software.

2.2.2. Preparation, stability, and characterization of emulsions

All the emulsions were prepared by adding the oil phase in the LDH/MO dispersions and then emulsifying the mixed liquids using a homogenizer (Shanghai Forerunner M&E Co., China) operated at 6000 rpm for 2 min. Immediately after homogenization, emulsion conductivities were determined using a DDS-370 digital conductivity meter (Leici Co., China). The emulsions were transferred into the glass vessels mentioned in section 2.2.1 for observation of emulsion stability at 25 °C. The stability of the emulsions to creaming and coalescence was assessed 24 h after emulsification by monitoring the positions of the water–emulsion and emulsion–oil interfaces respectively. The morphology of emulsion droplets was observed with an Axioskop 40 optical microscope (ZEISS, Germany). The average size of emulsion droplets was obtained by processing the image using the microscopic image analysis software. The adsorption of LDH particles on the droplet surfaces was observed under a laser-induced confocal microscope (Olympus Fluoview 500, Japan).

2.2.3. Preparation and characterization of colloidosomes

Colloidosomes composed of particles were prepared from the emulsion obtained in section 2.2.2 using previously reported procedures (Supporting Information) [27]. The powders composed of colloidosomes were transferred onto a clean glass plate and coated