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Short communication

Photocatalysis: A novel approach to efficient demulsification

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ABSTRACT

Using the theories of photocatalysis and emulsification, photocatalytic demulsification was introduced and studied for developing a direct method for destabilization and separation of oil-in-water emulsion. This was systematically investigated by photocatalysis and quiescent gravitational settling. The results demonstrated that the high demulsification efficiency directly correlated with photocatalysis. The photocatalytic effect and demulsifying enhancement have theoretically and experimentally been displayed and attributed to photocharge generation, redistribution of the self-oriented nano-TiO_2, and photocatalytic oxidation of emulsifiers inside oil–water interface film under illumination. The extension of the classical photocatalysis is presented and effectively shifted to a novel process for practical demulsification.

1. Introduction

In order to reduce oil losses and water discharges, oil content has to be minimized in the aqueous phase by breaking up surfactant-stabilized emulsions. Demulsification is an important topic because of its effects on the environment and economy. Considerable effort has been made to develop effective treatment techniques, such as electrochemical demulsification [1,2], chemical demulsification [3,4], magnetic demulsification [5–7], and biological demulsification [8,9]. Although these methods have been proven to be effective, processes involved in them, for example, heating and electrical methods, are expensive and energy intensive [10,11]. Thus, it is necessary to develop an alternative method with properties including high oil removal rate and fast oil–water separation.

Photocatalysis has been extensively studied for many years [12–15]. High-efficiency photooxidation has been reported in the literature for application in many fields [16,17]. Our earlier work discovered that nanometer-sized TiO_2 particles can be self-adsorbed and oriented onto oil–water interface of emulsions [18]. Although the nano-TiO_2 particles on the interface can be charged by UV treatment, reactive photoholes generated by photocatalysis primarily oxidize the oriented organic substances and damage the film between oil and water. At the same time, the surface-charged TiO_2 particles alter the electrical balance of emulsions. Therefore, we report on a novel approach in this study that can achieve effective demulsification by efficient photocatalysis. The experimental results demonstrated that the high demulsifying capacity is correlated with photocatalysis of a model system emulsified by a typical molecule of sodium oleic acid. Because of its high efficiency and easy recovery of the photocatalyst, photocatalytic demulsification can be effectively used in many industrial areas with high performance.

2. Experimental

The photocatalyst used in this experiment was nano-TiO_2 powder (P25, Degussa). X-ray diffraction (XRD) patterns estimated the diameter of the TiO_2 particles as 12 nm in their major part of the anatase form. The photocatalysis measurements (Fig. 1) were carried out with a suspension and standstill system. A 125-W Hg lamp was used in the perpendicular direction for illuminating a quartz-graduated tube filled with emulsions.

Deionized water and paraffin oil (technical grade) were used to prepare the emulsions at room temperature. A known amount of organic emulsifier (sodium oleic acid, AR grade) was first dissolved in deionized water to make a solution of 1.5% (W/W). This solution (17 ml) and nano-TiO_2 powder – sometimes without the powder – were added to paraffin oil (8 ml) in a 25-ml measuring cylinder made of quartz. The emulsion was obtained by even mixing with a wrist-action shake of the cylinder at a constant speed. The pH of the deionized water was initially adjusted using HCl or NaOH.

The ability and degree of demulsification were measured by a quiescent gravitational settling technique at room temperature [19]. The prepared emulsions were allowed to cream several minutes for stability. The height of emulsion was recorded as the initial value. Then, they were settled in a still stand with or without illumination, such that the aqueous phase, oleic phase, and emulsion with TiO_2 particles were creamed by gravitational settling. The volume of the emulsion layer (denoted by emulsion in Fig. 2) was recorded by measuring phase separation of quiescent settling at intervals. The type of emulsion was identified by combining dilution method and filter paper wetting

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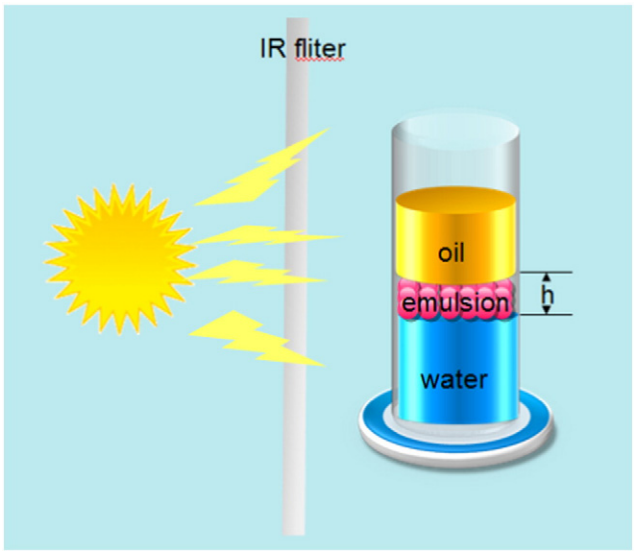

Fig. 1. Schematic diagram of photocatalysis measurements.

method [20]. Microscopic images were obtained from a computerized microscope (Olympus Corporation) for studying the microstructure of the emulsion. The emulsion sample was placed under a microscope to record the microstructural image, which was then recorded by a computer.

3. Results and discussion

On the basis of the theory of interface chemistry, the following three major mechanisms are possible for the stability of emulsions against phase separation: (1) steric stabilization due to the orderly arranged interfacial film between water and oil; (2) depletion stabilization due to the surface-charged film; and (3) structural stabilization due to the shape and viscosity of interfacial substances. In general, the interfacial film, which resists droplet coalescence, is a key factor that affects emulsion stability. Thus, a key to demulsification is to destroy the structure of the interfacial film between water and oil. The film consists of orderly arranged emulsifiers (e.g., surfactants, sometimes fine particles). A change or removal of the emulsifiers is an important route to demulsification.

In this experiment, water, paraffin oil, and sodium oleic acid were used to prepare the emulsion system From microscopic measurements and filter paper wetting methods, the emulsions were found to be stable, and to be of even diameter (40–70 μm) and oil-in-water (O/W) type (for anatase, the water contact angle is 72° [13]). Figs. 2 and 3 depict microscopic images of the emulsion.

It is evident from Fig. 2 that the external and internal phases are water and oil, respectively. The droplets are well distributed, existing stably for a long time. Microscopic image in Fig. 3 clearly shows the existence of the even and stable film with orderly arranged particles on the oil–water interface. Oil is trapped in the droplet by water. In other words, a film with an oriented arrangement was formed by adsorbing TiO_2 particles and organic emulsifier molecules on the oil–water interface. Thus, the contact and interaction of TiO_2 particles with organic emulsifiers favor a transition to photocatalysis.

Photocatalysis originates from photogenerated holes following the generation of electron–hole pairs on illumination of a semiconductor surface. This insolation means that (1) the photocatalyst particles are photocharged on the surface depending on the semiconductor type for the charge polarity and (2) strongly oxidizing species for oxidation exist nearby in organic compounds. These two actions favor the demulsification of emulsions. Fig. 4(A) shows photocatalytic demulsification in a model system of emulsions. Initially, the photo-demulsification yields a higher efficiency with illumination than without illumination. Thus, this effect correlates with the photocatalysis. The emulsion under illumination disappeared within 3 h, which was stable for 27 h without illumination only by a gravitational settling. Then, the increase of emulsion stability for 1% TiO_2 indicates that the nanoparticles entered the interfacial films and stabilized the emulsions.

The effect of nano-TiO_2 concentrations on photo-demulsification is shown in Fig. 4(B). The demulsification efficiency significantly depends on the volume of photocatalyst used. The high efficiency of degradation occurred monotonically in the concentrated photocatalyst. The contribution of the photocatalytic effect is evident. As shown in Fig. 4(C), the efficiency of photo-demulsification increases with a decrease of pH in the aqueous phase. This implies that the TiO_2 particles are charged differently at different values of pH. The phenomenon is explained in the following section.

According to the experimental results demonstrated above, a schematic diagram was proposed for illustrating the emulsion microstructure and photocatalytic mechanism (Fig. 5).

The microstructure of emulsions consists of droplets dispersed in the continuous phase with oil and water as internal external phases, respectively (Figs. 2 and 3). The emulsifier molecules are ordered and situated

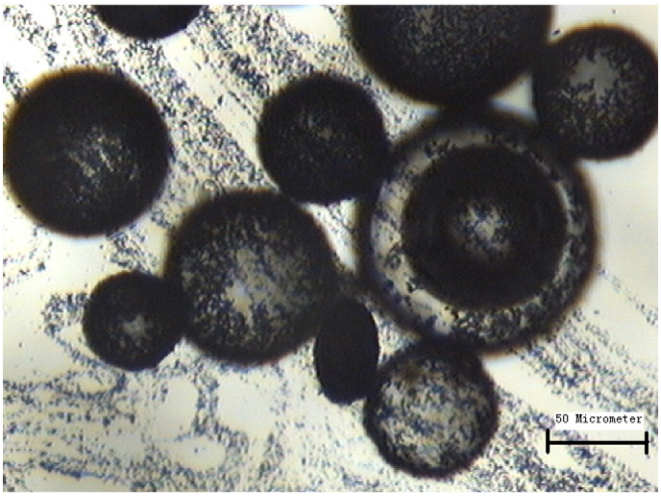

Fig. 2. Microscopic image of microstructure of emulsions (O/W emulsions by 1% TiO_2 + 1.5% emulsifier without illumination).

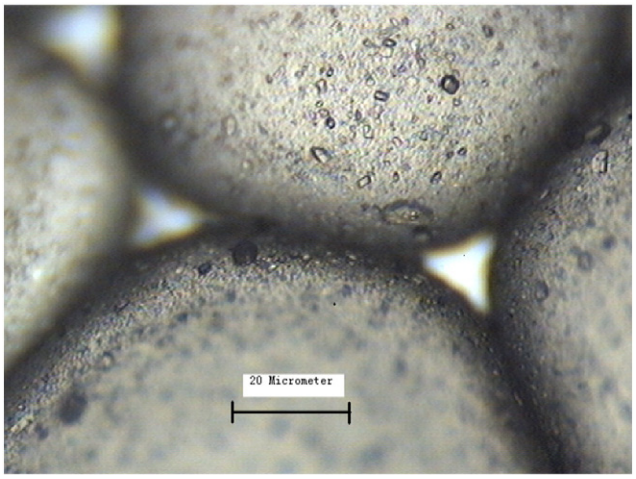

Fig. 3. Microscopic image of microstructure of emulsions (O/W emulsions by 1% TiO_2 + 1.5% emulsifier without illumination and an aggregation of TiO_2 clusters, leading to the large particles in the figure).