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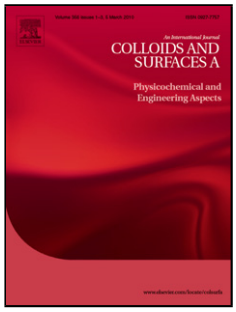


Fine tuning of surface properties of SiO_2 nanoparticles for the regulation of Pickering emulsions

Yan Meng, Wenxing Sun, Hao Yang, Wei Wang, Nan Jin, Yuchao Zhao, Xunli Zhang, Hongying L*ü*

PII: S0927-7757(20)30196-5

DOI: https://doi.org/10.1016/j.colsurfa.2020.124603

Reference: COLSUA 124603

To appear in: *Colloids and Surfaces A: Physicochemical and Engineering Aspects*

Received Date: 3 January 2020

Revised Date: 13 February 2020

Accepted Date: 14 February 2020

Please cite this article as: Meng Y, Sun W, Yang H, Wang W, Jin N, Zhao Y, Zhang X, L*ü* H, Fine tuning of surface properties of SiO_2 nanoparticles for the regulation of Pickering emulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2020), doi: https://doi.org/10.1016/j.colsurfa.2020.124603

Fine tuning of surface properties of SiO_2 nanoparticles for the regulation of Pickering emulsions

Yan Meng[1], Wenxing Sun[1], Hao Yang[1], Wei Wang[1], Nan Jin[1], Yuchao Zhao[1,*], Xunli Zhang[2,*], Hongying Lü[1]

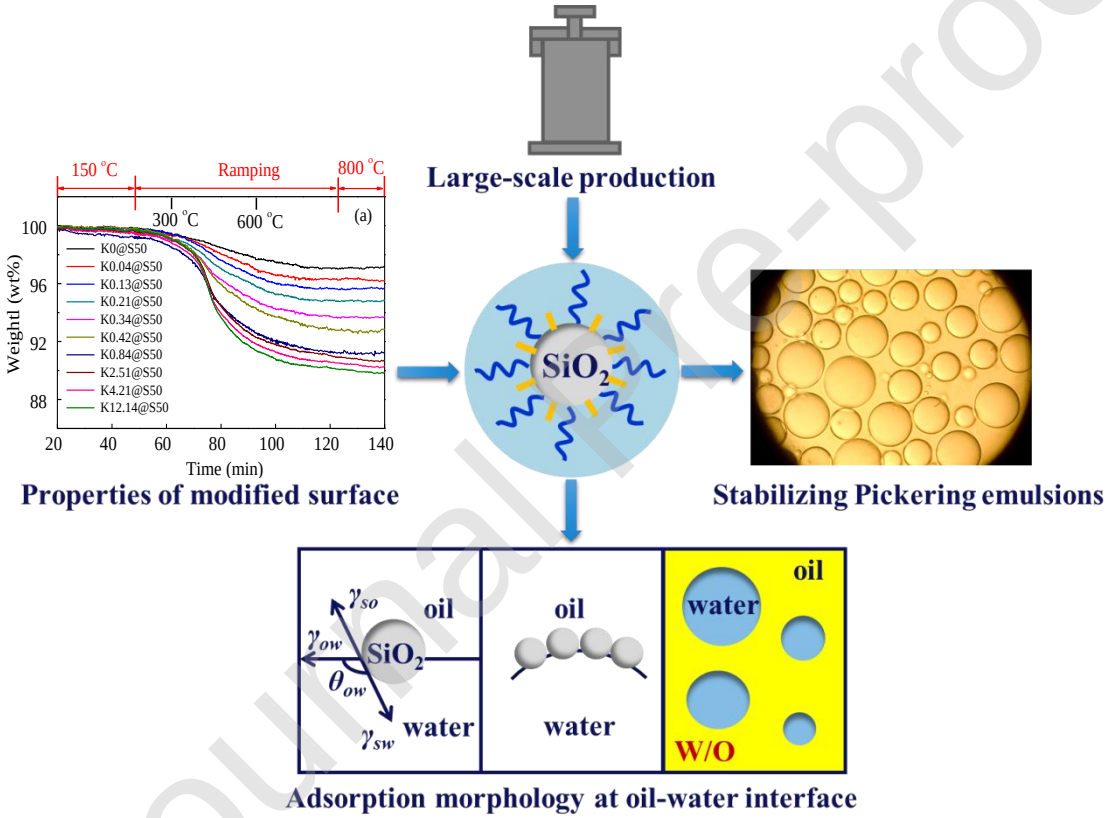
[1] Shandong Collaborative Innovation Center of Light hydrocarbon transformation and utilization, College of Chemistry & Chemical Engineering, Yantai University, Yantai 264005, China

[2] School of Engineering & Institute for Life Sciences, University of Southampton, Southampton SO17 1BJ, UK

[*] Corresponding Authors.

E-mail addresses: yczhao@ytu.edu.cn (Yuchao Zhao); XL.Zhang@soton.ac.uk (Xunli Zhang).

Graphical Abstract



HIGHLIGHTS

- Surface modification of SiO_2 nanoparticles was finely tuned by a novel large-scale production method
- Phase inversion of Pickering emulsions was regulated by the amount of KH-570 grafted

on the nanoparticles surface

- Geometry and stability of emulsions were affected by the coverage area of dispersed droplets provided by the stabilizing particles
- Solid-oil intermolecular energy provided an indicator to predict the type of Pickering emulsions

Abstract

Pickering emulsions hold great potential in solving the mass transfer limitation in gas-liquid-solid and/or liquid-liquid-solid multiphase systems. In the present study, the surface properties of SiO_2 nanoparticles were finely tuned by a novel large-scale production method, which determined the final geometry of the dispersed droplets and their stability. By controlling the amount of KH-570 grafted on the nanoparticles surface the phase inversion of Pickering emulsions was regulated. The addition of stabilizing nanoparticles, the particle size, and the amount of dispersed phase all significantly affected the geometry and stability of the dispersed droplets, mainly attributed to the varying coverage area of dispersed droplets provided by the stabilizing particles at varying grafting degrees. Mechanistic investigation suggested that estimating the value of the solid-oil intermolecular energy provided an indicator measure to predict the type of Pickering emulsions, while the estimate of interfacial tension values gave an additional measure to determine the amount of solid particles needed for forming stable Pickering emulsions.

Keywords: Pickering, emulsion, SiO_2 particles, surface modification, KH-570, stability

1. Introduction

Gas-liquid-solid and/or liquid-liquid-solid multiphase systems are commonly involved in chemical processes, such as hydrogenation [1-4], oxidation [5], and enzymatic reactions [6-12]. However, the overall performance of these processes is largely limited by the inefficient mass transfer step within the complex multiphase system, which is inherently attributed to the poor dispersion of one phase in another, and relatively small interfacial area [13-15]. To address these issues, emulsions containing aqueous-organic biphasic systems have been widely used, which are adopted as an effective approach for intensifying multiphase mass

transfer [16]. Despite the enhancement in reaction efficiency, the conventional emulsions mostly stabilized with organic surfactants are still confronted with great difficulties in product separation and purification [17-19]. In this regard, the use of solid particles to stabilize the emulsion, namely, Pickering emulsions has provided a promising route, where the solid particles have superiorities in functionalities and recyclable abilities [20-23]. Pickering emulsions, found by Pickering et al. in the early 1900s [24], consisting of immiscible liquids are stabilized by solid phase particles, which have great potential in a wide range of industrial applications [25,26].

Fundamentally, of central importance in Pickering emulsions is the hydrophilicity or hydrophobicity (also known as wettability) of the particles by two liquid phases, which is commonly quantified by the contact angle (ϑ) of the particles adopted at the interface [26]. If the wettability of particles is sufficiently strong or more hydrophilic where $\vartheta < 90^o$, oil-in-water (O/W) emulsions are formed. Conversely, more hydrophobic particles generate water-in-oil (W/O) emulsions where $\vartheta > 90^o$. Therefore, by selecting the wettability of the stabilizing particles, it provides a useful approach to control the type of Pickering emulsions, to be O/W or W/O emulsions [27]. In addition, the controllable process provides a powerful platform for gaining a deeper insight into the significance of the role the solid particles play in such solid-stabilized systems, which still remains challenging at present to be fully understood. Silica (SiO_2), one of the most commonly used Pickering emulsifiers [28], have a large number of active hydroxyl groups which can be linked or replaced with hydrophobic organic groups e.g. silane coupling agents to modify the surface wettability of the SiO_2 nanoparticles [29].

Yang et al [20]. modified SiO_2 particles with hydrophilicity/hydrophobicity switchable surface triggered by varying pH, while the separation and recycle of the solid particles were realized. Binks and Clint [30] established a mechanism model for predicting the types of Pickering emulsions based on the components of the surface energy by incorporating an important parameter, namely three-phase contact angle. However, this contact angle has been found difficult practically to measure though much effort has been made, e.g. by Weston et al [29]. investigating a range of methods for characterizing the water-air contact angle of silica nanoparticles. That further demonstrated the challenges faced in predicting and ultimately controlling the wettability of the stabilizing SiO_2 particles in Pickering emulsions,

largely due to the lack of mechanistic understanding of the thermodynamically unstable system.

At the same time there remain technical challenges for producing SiO_2 particles with modified surface having different levels of wettability. Currently, the widely used method for particle surface modification involves the reflux of suspension in a glass flask heated with oil bath [31,32]. One technical issue frequently faced with this process is the attachment and/or adhesion of SiO_2 nanoparticles to the inner glass wall due to their strong hydrophilicity, resulting in non-uniform surface modification. In addition, for achieving uniformity in each batch a relatively small quantity of samples is processed that, however, leads to possible inconsistency for quality control over batches, limiting the large-scale production for industrial application.

The present study was aimed to investigate the significant role that the surface modified SiO_2 nanoparticles played in stabilizing Pickering emulsions. The nanoparticles were first modified with a rotating reactor system with silane coupling agents. That was followed by characterization of the surface property of the produced SiO_2 particles with the contact angle measurement, FT-IR spectroscopy and thermogravimetric analysis (TGA). The performance of the surface-modified SiO_2 particles for stabilizing Pickering emulsions was then examined by quantifying the effect on droplet geometry and stability. Finally, a mechanistic investigation was carried out for gaining a deeper understanding of the role of surface-modified SiO_2 particles in stabilizing Pickering emulsions, by analyzing theoretical models in the processes of phase inversion and self-assembly of SiO_2 particles on oil-water interface.

2. Experimental

2.1. Materials

Four sizes of SiO_2 particles (with an average diameter of 50 nm, 100 nm, 200 nm, and 500 nm, respectively, > 99.8 wt%) were purchased from Beijing Shenghe Haoyuan Technology Co. Ltd. *γ*-Methacryloxypropyl trimethoxy silane (KH-570, 99.5 wt%, Aladdin) was chosen as the silane coupling agent. Ethyl acetate, toluene and *n*-octane (> 99.5 wt%, Sinopharm Chemical Reagent Co., Ltd) were used as the oil phase to prepare emulsions.

2.2. Modification and characterization of SiO_2 particles

Fig. 1 schematically shows the reactor system developed in-house for modifying particles with KH-570, having six reaction vessels in the unit. The inner wall of the vessel made of stainless steel (with an inner diameter 52.22 mm, height 132.85 mm, and working volume 100 mL) was Teflon-lined to form a smooth hydrophobic surface in order to prevent SiO_2 nanoparticles from "sticking" to the wall surface.

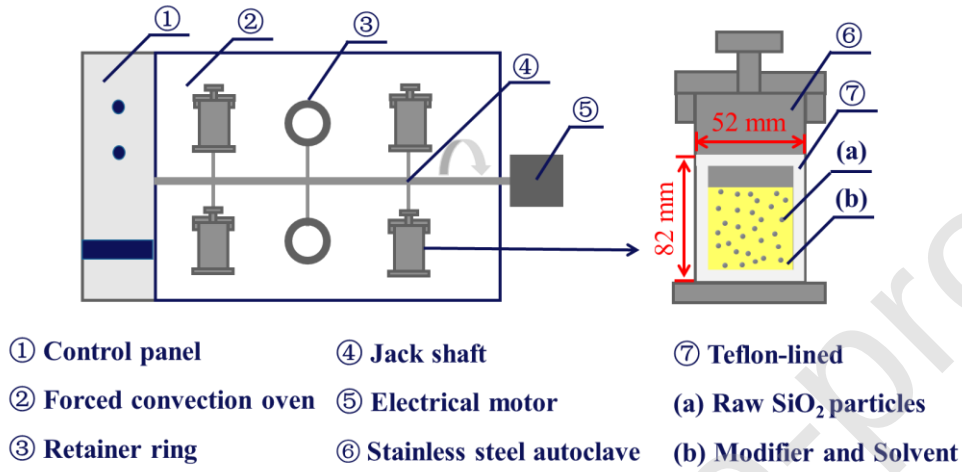


Fig. 1. Experimental set-up for the surface modification of SiO_2 particles

In a typical process of surface modification of SiO_2 particles, raw SiO_2 particles (1.0 g), KH-570 (with selected amount) and toluene (30 mL) were successively added into the reactor vessel (100 mL). The six vessels in the unit contained either the same mixture for increasing production, or different ones for examining multiple parameters. The rotating unit, placed in a forced convection oven (KLJX-8a, Yantai Branch Chemical Equipment Co., Ltd) set at 130 ^{o}C, operated at an optimized rotating rate of 10 Hz for 12 h. The product was collected from the under-toluene phase after separation by centrifugation at 10,000 rpm for 5 min, that was followed by washing with methanol for 5 times, and drying at 50 ^{o}C for 24 h in a vacuum drying oven, ready for further characterization and application.

The contact angle was measured through the water phase with an optical tensiometer (JC2000, Shanghai Zhongchen Digital Technology Equipment Co., Ltd) to quantify the hydrophobicity or hydrophilicity of the modified particles surface. After dispersing the particles in methanol, the dispersion was dripped on a square glass groove to form a film after the methanol evaporation. A water droplet was then placed on the surface of the film where

the water contact angle was measured. To keep the square glass groove clean, it was washed with deionized water and methanol for 3 times, and then dried at 60 ^{o}C. The uniformity of methanol dispersion was achieved by applying ultrasound treatment.

The FT-IR spectra of the SiO_2 particles surface were recorded using a PerkinElmer FT-IR spectrometer (Frontier). Thermogravimetric analysis, or TGA (STA409PC, NETZSCH-Gerätebau GmbH) was conducted in N_2 atmosphere by programmatically heating from 25 °C to 150 °C and remaining there for 30 min, which was following by ramping up to 800 °C at a heating rate of 10 °C/min, and then remaining constant at the high temperature level for 30 min.

2.3. Preparation and characterization of Pickering emulsions

To prepare Pickering emulsions, a certain amount of SiO_2 particles was firstly dispersed in the continuous phase assisted by ultrasonic (SB-3200D, Ningbo Xinzhi Biotechnology Co., Ltd) at 20 kHz for 5 min. The dispersed phase was then added into the particle-containing continuous phase under mixing with a Vortex apparatus (Vortex-2, IKA) operating at 13500 rpm for 4 min. The morphology and microstructure of such formed Pickering emulsions droplets were analyzed by an inverted microscope (IX73, Olympus) with the magnification of 20X together with software ImageJ and Matlab.

3. Results and Discussion

3.1. Preparation of surface-modified SiO_2 particles

Table 1 SiO_2 particles with surface modified by KH-570

Amount of KH-570 used for modification, mmol/g_{silica}	Average diameter of SiO_2 particles, D_p/ nm	Denoted by
0	50	K0@S50
0.04	50	K0.04@S50
0.13	50	K0.13@S50
0.21	50	K0.21@S50
0.34	50	K0.34@S50
0.42	50	K0.42@S50
0.84	50	K0.84@S50

2.51	50	K2.51@S50
4.21	50	K4.21@S50
12.14	50	K12.14@S50
4.21	100	K4.21@S100
4.21	200	K4.21@S200
4.21	500	K4.21@S500

To address the challenges commonly encountered in the process of nanoparticle surface modification, the rotating reactor was designed with two key features (Fig. 1). Firstly, the Teflon lining (or coating) facilitated the reactor with a smooth hydrophobic inner surface eliminating the potential attachment and/or deposition of nanoparticles to the reactor wall. Secondly, the accommodation of multiple reactor vessels in a single operation unit enabled a higher throughput process for large-scale production. There were six vessels in the unit developed in the present study, however, the number of vessels can be increased potentially. By setting the optimized operational conditions, it provided controllable approach for large quantity production with consistent quality. Using this system, a range of SiO_2 particles (Table 1) were produced for further characterization and application.

3.2. Properties of the modified surface of SiO_2 particles

The hydrophobicity of the particle surface was characterized by measuring the contact angle of water droplets on the film of SiO_2 particles. Fig. 2 compares the water droplet contact angles on the film of SiO_2 particles before and after surface modification. After modification of the particle surface with KH-570, the water contact angle increased from 13^o to 155^o, remarkably enhancing the hydrophobicity of the particle surface. As can been seen, Fig. 2 just examples the enhanced hydrophobicity of SiO_2 surface as a result of modification, indicating the availability of KH-570 on the SiO_2 surface. To establish a quantitative correlation between the contact angle and the amounts of KH-570, a systematic investigation is required by employing a range of coupling agents at different concentration.

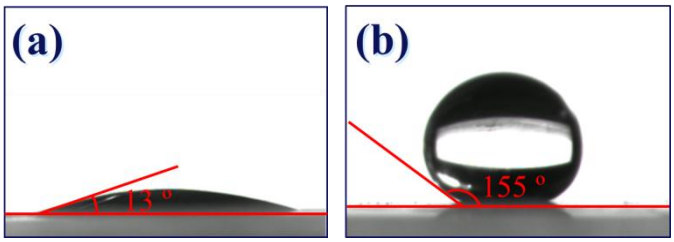


Fig. 2. Water contact angles of raw and modified SiO_2 particles. (a) K0@S50, (b) K4.21@S50

These unmodified and modified particle surfaces were further examined by FT-IR in order to characterize the grafting chemically. Fig. 3 depicts the spectra of unmodified (K0@S50) and modified (K4.21@S50) surface of SiO_2 particles. As can be seen, with the modified surface (K4.21@S50) there exhibit new characteristic absorption peaks at 2957 cm^{-1} and 1408 cm^{-1} that can be reasonably attributed to aliphatic C-H stretching and CH_2 symmetrical scissoring in Si-CH_2, respectively, confirming the grafting on K4.21@S50 surface with hydrophobic organic groups originated from KH-570. Although the peaks of 2957 cm^{-1} and 1408 cm^{-1} (as marked in the figure) are relatively weak, they are convincingly indicative of the existence of the characteristic absorption groups. The broad band located around 3432 cm^{-1} is assigned to the Si-OH stretching, while the strong peaks at 1114 cm^{-1} and 797 cm^{-1} are due to Si-O-Si stretching vibration of silica. These peaks are observed in both spectra, suggesting the existence of some unmodified hydroxyl groups on the particle surface.

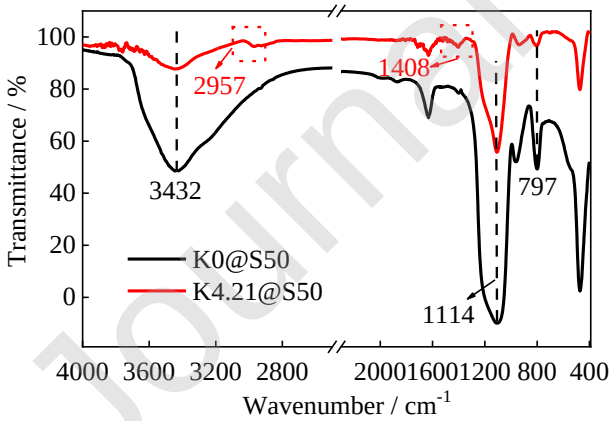


Fig. 3. FT-IR spectra of unmodified (K0@S50) and modified (K4.21@S50) SiO_2 particles

In view of applications at different temperatures, the thermal stability of the modified surface was investigated by TGA between 150 °C and 800 °C with all samples prepared. The particles with unmodified surface were also measured for comparison. The results are

illustrated in Fig. 4. In Fig. 4(a) the abscissa of the TGA profile is set to time in order to represent the constant temperature levels kept at the first stage of 150 ºC (for 30 min) and the final stage of 800 ºC (for 15 min), where the temperature scale is also shown at the top of the plot. The TGA profiles (Fig. 4(a)) for all samples display a similar trend passing through three stages. At the first stage the temperature was set at 150 °C for 30 min in order to remove any moisture showing a slight weight loss. That was followed by a sharp weight loss stage in the temperature range of 300-600 °C, contributing to about 80% of the total weight loss. This can be attributed to the decomposition of the grafted organic groups and the dehydration of the unmodified hydroxyl groups. The last stage at 800 ºC exhibited approximately a constant weight for all samples including unmodified SiO_2 particles though at different levels.

As expected, SiO_2 particles modified with a higher concentration of modifying agent (KH-570) experienced a bigger weight loss where more grafting was believed to occur on the particle surface. The mass of the unmodified SiO_2 particles remained 97.13 wt% at the stable stage (800 °C), being the highest among all samples. That was expected as no grafting attached to the particle surface which, however, provided a reference to determine the grafting extent on the particle surface, i.e. the weight ratio of the grafting organic groups to substrate particles, termed as Grafting Ratio (GR), equal to the difference between the weight losses (wt%) of modified and unmodified SiO_2 particles at the final stage (800 °C).

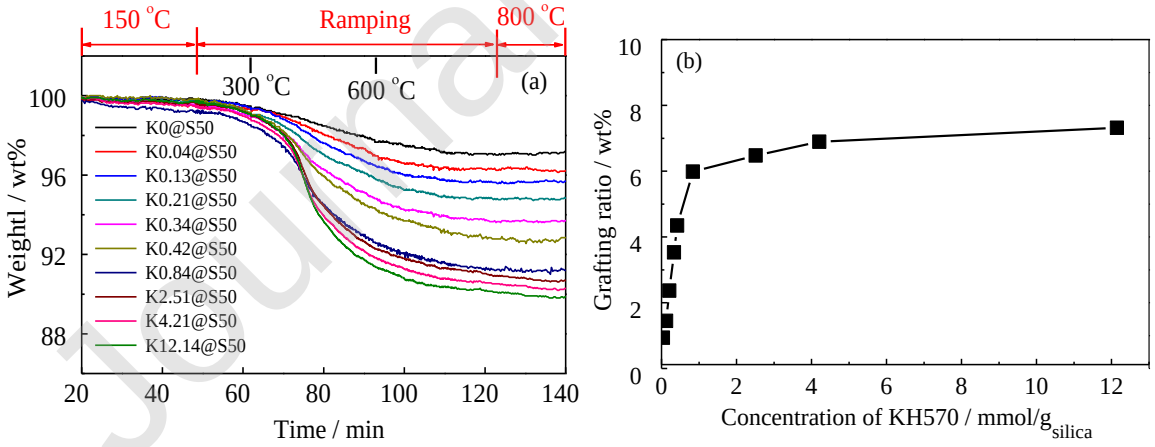


Fig. 4. (a) TGA curves and (b) the grafting ratio of unmodified and modified SiO_2 particles

Fig. 4(b) plots GR as a function of grafting agent concentration for all samples examined. The GR increased approximately linearly from 0 to 6 wt% with increasing concentration of KH-570 in the lower range (up to 0.84 mmol/g_{silica}). With further rising KH-570 concentration,

increase in GR was still observed but on an incrementally smaller scale, between 6 and 8 wt%, until reaching a plateau. Following the plateau, no further increase in GR was demonstrable.

It has been generally understood that the surface modification involves two competing process. One is the alcoholysis reaction occurring between KH-570 and the hydroxyl groups on surface of SiO_2 particles, while the other is the self-condensation among the modifying agent itself.[33] At the lower concentrations of KH-570 (< 0.84 mmol/g_{silica}), the former was believed to dominate, resulting in increase in GR. In the higher range of KH-570 concentration (> 0.84 mmol/g_{silica}), the self-condensation process probably became dominant, giving a slower rise of GR [34,35]. In this regard, it was likely that most of the active sites of hydroxyl groups on the SiO_2 particle surface were modified when the KH-570 concentration increased to 0.84 mmol/g_{silica}. This suggested that the GR can be regulated by controlling the concentration of KH-570 in the range of 0-0.84 mmol/g_{silica}.

3.3. Performance of surface-modified SiO_2 particles for stabilizing Pickering emulsions

3.3.1. Effects of stabilizing SiO_2 particles on droplet geometry of Pickering emulsions

It is well-known that the thermodynamic stability of Pickering emulsions is strongly dependent on the size of the dispersed droplets. This is largely due to the fact that the addition of stabilizing SiO_2 particles between on the dispersed and continuous phases reduces the oil-water interface energy. The effects of surface-modified SiO_2 particles on droplet size and size distribution were investigated by varying the addition of SiO_2 particles, the size of SiO_2 particles, and the volumes of both dispersed and continuous phases. The results are depicted in Fig. 5. The micrographs of the emulsions formed and their size measurements are also detailed in Figs. S1-S4 (in Supporting Information).

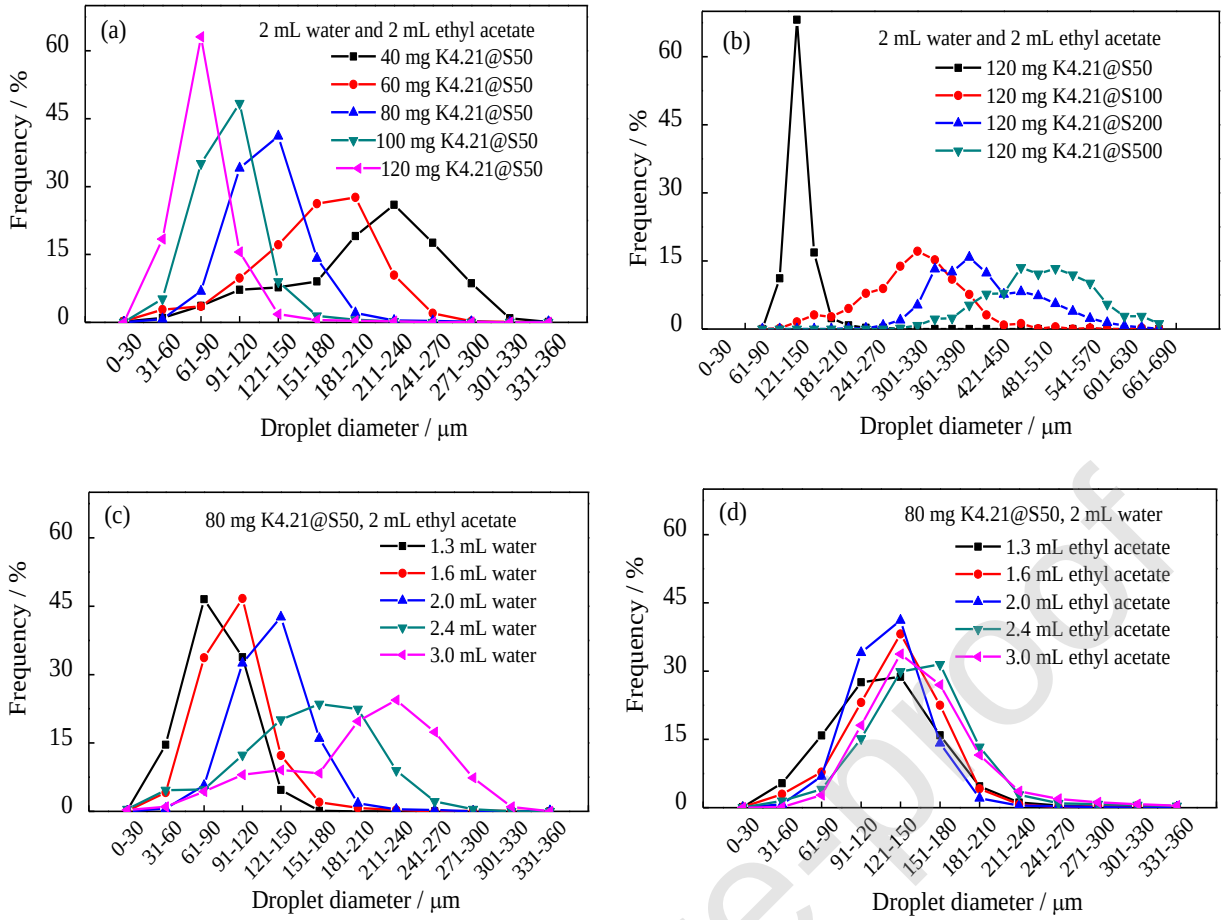


Fig. 5 Effects on Pickering emulsion droplet size by varying (a) mass of SiO_2 particles, (b) size of SiO_2 particles, (c) volume of dispersed phase, and (d) volume of continuous phase

In the ethyl acetate-water system, as can be seen in Fig. 5(a), by adding more SiO_2 particles (40-120 mg) the droplet size of Pickering emulsions decreased accordingly from around 200 μm down to 50 μm. This was mainly due to the increased amount of SiO_2 particles having larger coverage area of dispersed droplets, hence smaller and more droplets. It was also observed that the smaller droplets had a narrower size distribution, i.e. a sharper peak. This was most likely associated with the formation process of droplets involving breakup and coalescence (to be analyzed further later).

By using different size of SiO_2 particles (50, 100, 200 and 500 nm) with a given amount (80 mg) of SiO_2 particles added (Fig. 5(b)), it was found that SiO_2 particles with smaller diameter created smaller dispersed droplets. When the diameter of SiO_2 particles increased from 50 nm to 500 nm, the droplet size decreased from around 500 μm to 100 μm. This was similarly due to the increase in both number and coverage area of smaller SiO_2 particles added with a

given mass.

Varying the volumetric ratio of the dispersed and continuous phases revealed that more dispersed phase added in the oil-water system resulted in larger dispersed droplets (Fig. 5(c)). When the volumetric ratio of water: oil changed from 1.3:2.0 to 3.0:2.0, the size of the dispersed droplets increased from 50 μm to 210 μm. This was attributed to the lack of stabilizing particles, with a given amount of SiO_2 particles and volume of the continuous phase, thus forming larger size of dispersed droplets through coalescence of small ones. In contrast, varying the amount of the continuous phase in the oil-water system had insignificant effect on the size of the dispersed droplets (Fig. 5(d)), since covering capacity of SiO_2 particles and the oil-water interfacial area were largely associated with the dispersed phase.

Overall, the diameter of the Pickering emulsion droplets prepared in this work was relatively larger than the diameters of droplets reported in other studies. This was designed in this work to facilitate the measurement for mechanistic investigating into particle-particle interactions. Nonetheless, stable Pickering emulsions with smaller droplets are still achievable by applying greater force strength or long vibration time, based on the understanding that, for the same composition of Pickering emulsions, the initial oil-water interface area is determined by the external forces.

3.3.2. Quantitative analysis of the effects of SiO_2 particles on droplets' geometry and stability

It is generally understood that the stabilized droplets in Pickering emulsions are formed through coalescence and breakup processes, as schematically illustrated in Fig. 6. When the amount of stabilizing SiO_2 particles is insufficient to fully cover the oil-water interface, small dispersed droplets tend to merge into larger ones by coalescence. Conversely, if free SiO_2 particles remain in the continuous phase, large dispersed droplets split into smaller ones through breakup. It is the 'solid' layer of SiO_2 particles with modified surface surrounding the dispersed droplet that plays a crucial role in stabilizing the Pickering emulsions.

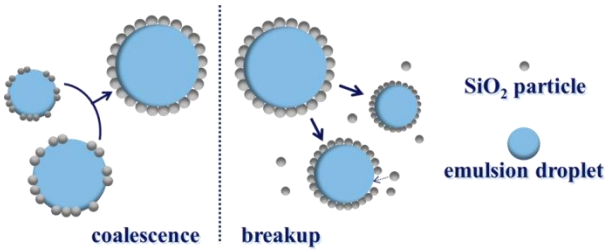


Fig. 6. Coalescence and breakup of Pickering emulsion droplets

The stability of Pickering emulsions can be determined by the coverage degree (τ) of the oil-water interface area covered by the stabilizing particles.

$$\tau = \frac{S_{\mathrm{p}}}{S_{\mathrm{d}}} \tag{1}$$

where τ is the coverage degree measuring the stability of Pickering emulsions measured; S_{d} and S_{p} are the total area of the oil-water interface, and the oil-water interface area covered by SiO_2 particles, μm^2, respectively.

$$S_d = N_d \pi D_d^2 = \frac{6V_d}{D_d} \tag{2}$$

$$S_p = N_p \frac{\pi D_d^2 \sin^2 \theta_{ow}}{4} = \frac{3m_p \sin^2 \theta_{ow}}{2\rho_p D_p} \tag{3}$$

where N_{d} and N_{p} are the total number of droplets and SiO_2 particles, respectively; D_{d} and D_{p} are the average diameter of droplets and SiO_2 particles, respectively; V_{d} is the dispersed phase volume; m_{p} and ρ_{p} are the total mass and density of SiO_2 particles, respectively; ϑ_{ow} is the oil-water contact angle. Thus, the coverage degree can be expressed as

$$\tau = \frac{\mathrm{m}_p D_{\mathrm{d}} \sin^2 \theta_{ow}}{4\rho_p D_P V_{\mathrm{d}}} \tag{4}$$

When $\tau < 1$, the Pickering emulsion droplets are unstable and tend to coalesce into bigger ones. When $\tau = 1$, the oil-water interface is just covered by the stabilizing SiO_2 particles where Pickering emulsions are at a critical point of being thermodynamically stable. If $\tau > 1$, free SiO_2 particles begin to appear in the continuous phase where large Pickering emulsion droplets tend to split into smaller ones.

For a given Pickering emulsion system at a stable stage, the τ value is expected to remain constant which can be obtained by using Eq. 4 through experimental measurement. Table 2

summarizes the calculated τ values for a set of representative Pickering emulsions by measuring the relevant physical parameters.

Table 2 Calculated τ values using Eq. 4 through measurements

m_p/mg	D_p/nm	V_d/mL	D_d/μm	τ
40	50	2.0	203	9.23
60	50	2.0	163	11.11
80	50	2.0	126	11.45
100	50	2.0	95	10.80
120	50	2.0	77	10.50
120	100	2.0	279	19.02
120	200	2.0	405	13.81
120	500	2.0	504	6.87
80	50	1.3	84	11.75
80	50	1.6	98	11.14
80	50	2.4	155	11.74
80	50	3.0	199	12.06

As can be seen from Table 2, the τ values largely fall into the range of 9.23 to13.91, except for two measurements of 6.87 and 19.02. The exception may be related to the largest amount of particles (120 mg) added, especially with the biggest size (500 nm), bringing in more uncertainty, though the detailed cause remains unclear. Nevertheless, if an average value of τ taken from the measurements, i.e. 11.62, is used in Eq. 4, it can provide an approach to predict the average diameter of the stable droplets in this Pickering emulsion system by Eq. 5.

$$D_d = 11.62 \times \frac{4\rho_p D_p V_d}{m_p} \tag{5}$$

Using this model (Eq. 5), the average diameter of the stable droplets was estimated with a range of parameters varied in the Pickering emulsion system. The predicated droplet diameters (Eq. 5) were then compared with the experimental measurements (Fig. 7).

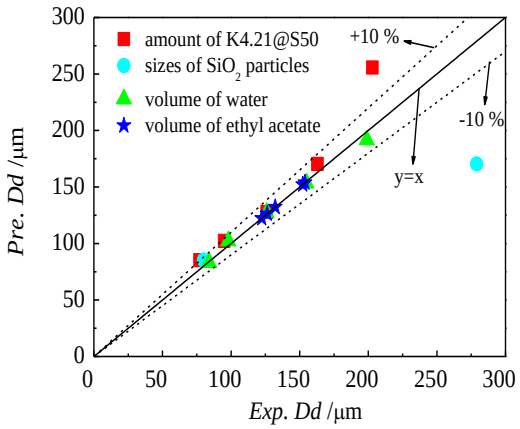


Fig. 7. Comparison of experiment (*Exp.*) D_d with predicted (*Pre.*) D_d

The deviations were mostly within the range of ±10%, showing a reasonably good prediction with the model. It should be noted that, when Pickering emulsions were prepared with unmodified raw SiO_2 particles (in three sizes of 100 nm, 200 nm and 500 nm), the relative errors were -38.9%, -15.8% and 69.1%, respectively. The significant deviation with the unmodified raw SiO_2 particles was likely associated with the assumption of the average oil-water contact angle (ϑ_{ow}) being 90°. That assumption was reasonable for droplets stabilized by surface-modified SiO_2 particles, however, may not be fully applicable with the unmodified raw SiO_2 particles where the interfacial energy can be significantly different. To fully understand this observation, further investigation is required.

To verify the universality of the theoretical calculation formula, further experiments were conducted. For example, Pickering emulsions were prepared with SiO2 modified by methyltrimethoxysilane using the identical procedure. By measuring the relevant physical parameters (Eq. 4), the average value of τ was calculated to be 10.55 (instead of 11.62 with KH-570). The predicated droplet diameters (Eq. 5) were compared with the experimental measurements, displaying deviations mostly within the range of ±10%. As a systematic study on this specific topic, more results are to be reported separately.

3.3.3. Kinetics during the transition period towards forming stable Pickering emulsions

As discussed above (Fig. 6), a stable state of Pickering emulsions is reached through coalescence and/or breakup of the initially formed fresh dispersed droplets, mainly due to the lack or excess of stabilizing SiO_2 particles. Therefore, the kinetics of the coalescence or

breakup process plays a crucial role in determining the final size and size distribution of the stable droplets dispersed, as demonstrated in Fig. 2 and Table 2. In addition, during this transition process, different amounts of continuous phase can separate out that can simultaneously alter the amount of the final stable Pickering emulsions. Thus, the measurement of both volumes of separated continuous phase and final stable Pickering emulsions can be used for quantitatively characterizing the kinetics of this transition process. Fig. 8 shows the measurement results of the volume of the separated continuous phase as a percentage (V_c, vol%) of the initial Pickering emulsion volume as a function of time, under different conditions. Fig. 9 demonstrates the corresponding final volume of the resulting stable Pickering emulsions (V_e, mL). Images of the stable emulsions after separation are also shown in Fig. S5 (in Supporting Information).

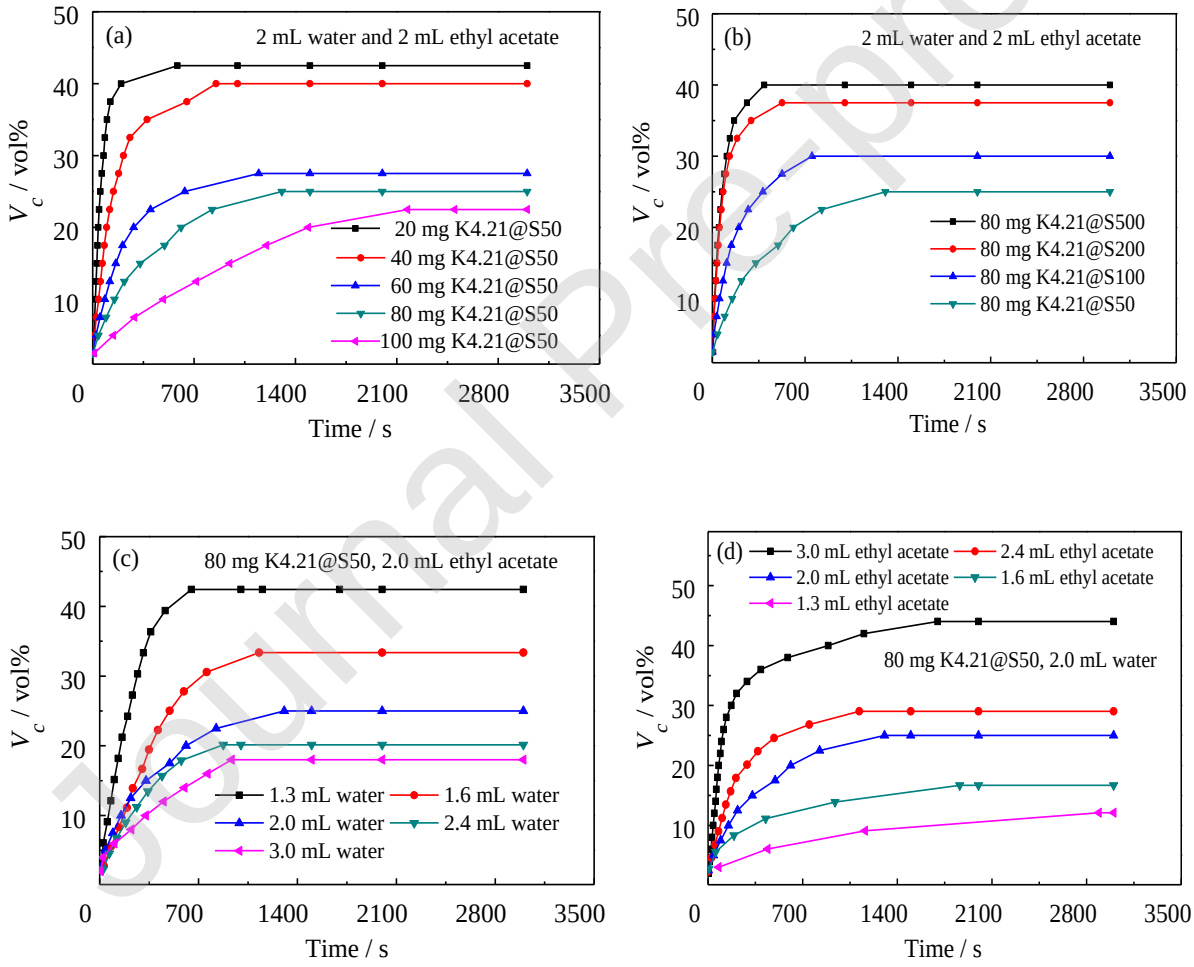


Fig. 8 The separated volume of the continuous phase as a function of time by varying (a) SiO_2 particles mass, (b) SiO_2 particles size, (c) dispersed phase volume, and (d) continuous phase

volume

Fig. 8(a) shows that the separated volume increased approximately linearly with time at the first stage before reaching a plateau. This trend was observed for all different amounts of SiO_2 particles added, however, rising initially at different slopes, and then reaching different levels of plateaus. Increasing the amount of SiO_2 particles reduced the separation rate (i.e. a smaller positive slope on the V_c-t curve), thus took a longer transition period to reach the stable stage which was, however at a lower level. With 20 mg SiO_2 particles added, it took about 6 min to become stable resulting in a final V_c level of about 42 vol%. When 100 mg SiO_2 particles was added, the transition period took about 35 min, however reaching a much lower V_c level (23 vol%).

As shown in Fig. 5(a), adding more SiO_2 particles produced smaller droplets in Pickering emulsions mainly through breakup. In that case, a larger number of droplets in smaller size were involved and formed probably requiring more time to settle down before reaching a stable stage. At the same time, the free or excess SiO_2 particles dispersed in the continuous phase tend to form some three-dimensional (3D) network structures in the vicinity of the disperse droplets [36,37]. Such 3D network structures can increase the apparent viscosity of the continuous phase that, in turn, slow down the separation of the continuous phase, i.e. having a longer transition period. In addition, the 3D network structure, together with the larger number of droplets formed in smaller size all contributed to forming more and stable Pickering emulsions volume, while keeping the separation at a lower level.

In a similar way, smaller SiO_2 particles reduced the separation rate (i.e. giving a smaller positive slope on the V_c-t curve, Fig. 8(b)), while resulting in a lower level. With 50 nm SiO_2 particles added, it took about 22 min to reach the stable state with a final V_c level of about 25 vol%. When 500 nm SiO_2 particles was used, the transition period reduced to about 6 min, however reaching a much higher V_c level of 40 vol%. With a given mass (80 mg) of SiO_2 particles, practices with a larger dimeter provided a smaller number of particles, relatively smaller interfacial surface, all of which were unfavorable for retaining the continuous phase in the emulsion, i.e. tending to separate out.

By varying the amount of water added, a similar pattern was observed with the V_c-t profiles

(Fig. 8(c)). Overall, adding more water reduced the rate for the continuous phase to be separated out, also resulted in a smaller amount of separation. This was largely due to the addition of more dispersed phase decreased the distance between the dispersed droplets. In addition, the reduced space further enhanced the supporting effect of the 3D network structures formed between adjacent droplets. This was also reflected in the effect of adding more ethyl acetate which provided a longer distance between the dispersed droplets and weakened the 3D network support (Fig. 8(d)), thus an opposite effect compared to adding more water (Fig. 8(c)).

Correspondingly, the resulting final volumes of Pickering emulsions (V_e) were measured during the above examination on the four key variables. The results are depicted in Fig. 9. As expected, a lower level of continuous phase separation (lower V_c) gave a larger amount of stable Pickering emulsions (higher V_e), and vice versa.

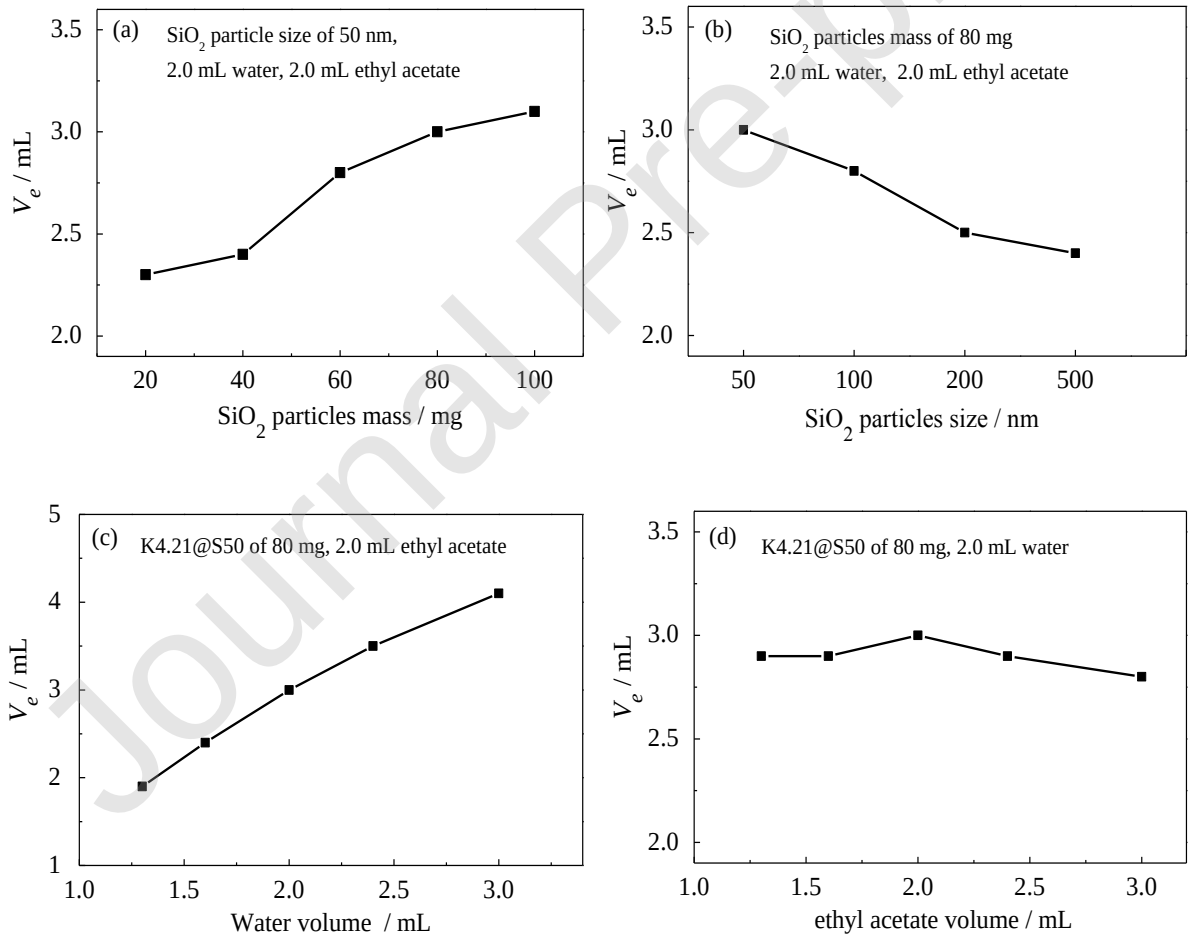


Fig. 9 The final volumes of Pickering emulsions (V_e) measured by varying (a) SiO_2 particles

mass, (b) SiO_2 particles size, (c) dispersed phase volume, and (d) continuous phase volume

3.4. The role of surface-modified SiO_2 particles in stabilizing Pickering emulsions

3.4.1. Effect of modified surface of SiO_2 particles on Pickering emulsion phase inversion

The surface property, in particular the hydrophobicity and hydrophilicity of the solid particles plays an important role in the formation and stabilization of different types of Pickering emulsions. In the present study, the wettability of the modified surface of SiO_2 particles was controlled by the dosage of KH-570 loaded on the particle surface. By tuning the surface wettability, it provided a controllable approach for Pickering emulsion phase inversion, i.e. from oil-in-water (O/W) to water-in-oil (W/O), and vice versa. Fig. 10 shows schematically the phase inversion occurring at a KH-570 concentration of 0.56 mmol/g_{silica} for the ethyl acetate/water Pickering emulsions. However, for similar systems of toluene/water and *n*-octane/water, the phase inversion took place at 0.80 mmol/g_{silica}. This indicated that in the ethyl acetate/water system, which was the main focus of the present study, the Pickering emulsions phase inversion required fewer solid particles to change from O/W to W/O.

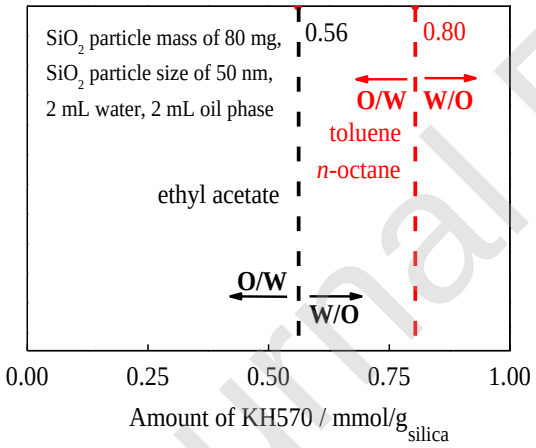


Fig.. 10 Phase inversion of Pickering emulsions for different systems

In order to quantitatively characterize the inversion process, a three-phase contact angle ϑ_{ow} (angle at the three-phase boundary of solid particles, continuous phase and dispersed phase) is commonly employed to measure the possibility of the solid particles to be wetted at the oil-water interface. If one liquid wets solid particles more than the other, the better wetting liquid becomes the continuous phase and the other becomes the dispersed phase [28,38]. As illustrated in Fig. 11, when $\vartheta_{ow} < 90^o$ O/W emulsions are formed (left panel), while

ϑ_{ow} being greater than 90° generates W/O Pickering emulsions.

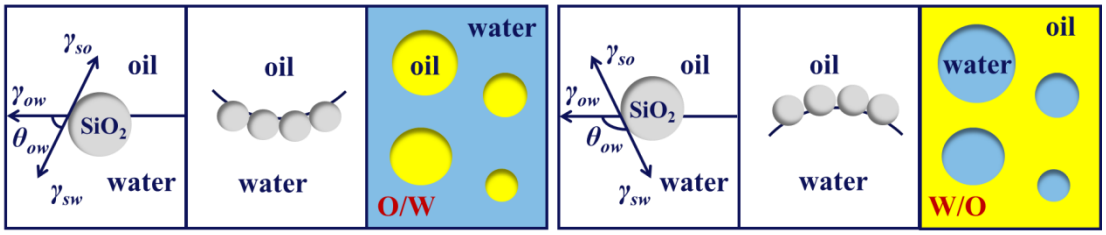


Fig. 11. Schematic representation of phase inversion of Adsorption morphology of oil-water Pickering emulsions stabilized by SiO_2 particles with different wettability

However, the three-phase contact angle ϑ_{ow} around single particles is impractical to obtain through experiment, mainly due to the nanoscale size of the particles and the diversity of the oil-water-solid interfaces. In this regard, the Young equation (Eq. 6) provides a route to determine contact angle ϑ_{ow}.

$$\cos\theta_{ow} = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} \tag{6}$$

where γ is the interfacial tension, N/m. The subscripts *so*, *sw* and *ow* refer to solid-oil, solid-water and oil-water interfaces, respectively.

If the three interfacial tensions could be estimated it would be possible to use Eq. 6 to obtain the contact angle ϑ_{ow}. However, there at present are no direct methods available to measure γ_{so} and γ_{sw} though the oil-water interfacial tension (γ_{ow}) can be measured experimentally [30]. In this regard, an attempt was made in the present study by using the density functional theory (DFT) to theoretically calculate the intermolecular energy E^{int} (kJ/mol) first, which was then used to determine (γ_{so} - γ_{sw}) with Eq. 7, based on the model schematically shown in Fig. 12.

$$\gamma_{so} - \gamma_{sw} = n_{org} E_{so}^{int} / A_{so} - n_{OH} E_{sw}^{int} / A_{sw} \tag{7}$$

where n_{org} and n_{OH} refer to the amount of the organic and hydroxyl groups, respectively, mol; A_{so} and A_{sw} are the area of a single solid particle immersed in oil and aqueous phase, respectively, m^2.

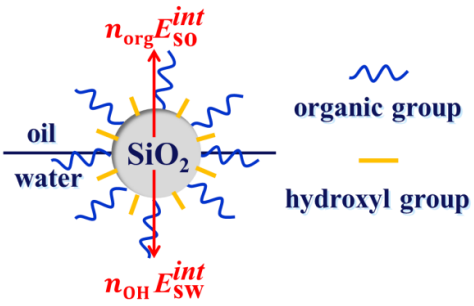


Fig. 12. Intermolecular energies around a single solid particle at the oil-water interface

In principle, the solid particle is adsorbed at the oil-water interface due to the intermolecular energy between solid and liquid (Fig. 12). There are four types of intermolecular energies involved to balance for reaching a stable state. They are the intermolecular energies of; (i) the organic groups between modified SiO_2 particles surface and oil molecules (E_{so}^{int}), (ii) the hydroxyl groups between modified SiO_2 particles surface and water molecules, $E_{sw}^{\text{int}} = 27.13$, (obtained by DFT calculation using Gaussan 09 at B3LYP/6-31g* level), (iii) the hydroxyl groups between modified SiO_2 particles surface and oil molecules, and (iv) the organic groups between modified SiO_2 particles surface and water molecules. Compared to the first two energies, the other two intermolecular energies may be neglected, due to the weak interaction of hydroxyl groups-oil molecules, and organic groups-water molecules.

Although the DFT calculated results were in accordance with our current experimental data, a large amount of experimental data is needed in order to establish a quantitative relationship between the intermolecular energy and the types of Pickering emulsions. This would form part of our future work in this direction.

As analyzed above (Fig. 11), at the critical point for phase inversion e.g. from O/W to W/O, ϑ_{ow} = 90°, when the immersed area of a single solid particle in oil is equal to that in aqueous phase. By combining Eqs. 6 & 7, it gives Eq. 8.

$$E_{so}^{\text{int}} = n_{OH} E_{sw}^{\text{int}} / n_{org} \tag{8}$$

It can be seen from Eq. 8 that, for a given modified SiO_2 particle, the larger the value of E_{so}^{int} is, the larger the ratio of n_{OH}/n_{org}, i.e. the less organic groups are required to be grafted on the

surface of SiO_2 particles. Therefore, the value of E_{so}^{int} provides a measure to predict the type of Pickering emulsions for different oil-water systems. For example, from DFT calculation the values of E_{so}^{int} for the three oil-water systems involving ethyl acetate, toluene and *n*-octane (Fig. 10) were found to be 12.21, 2.68 and 1.10 kJ/mol, respectively. This was in accordance with the amount of SiO_2 particles needed at the critical phase inversion point (Fig. 10).

3.4.2. Self-assembly of SiO_2 particles on oil-water interface

In a simplified model, the formation of Pickering emulsions involves the self-assembly of solid particles accumulating on the oil-water interface. Thus, the amount of the solid particles adsorbed at the oil-water interface together with the kinetics of the adsorption process all plays an important role to form stable Pickering emulsions [39]. By using surface-modified SiO_2 particles (K4.21@S50) to form W/O Pickering emulsions with the three oil-water systems involving ethyl acetate, toluene and *n*-octane, the critical masses needed were found to be 10, 80 and 110 mg, respectively (Fig. 13), indicating that Pickering emulsions are easier to be obtained with ethyl acetate as the continuous phase.

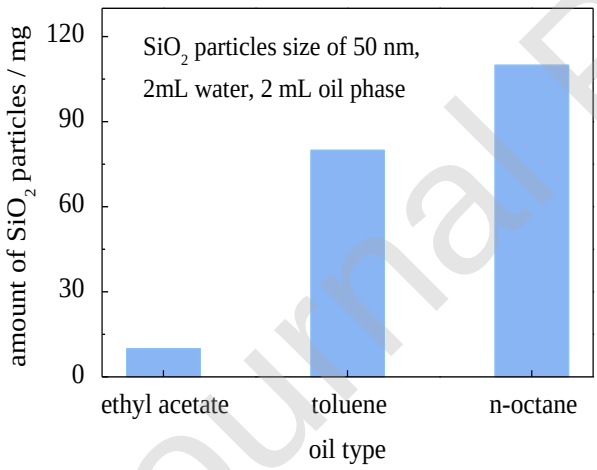


Fig. 13. Critical mass of SiO_2 particles for preparing different oil-water Pickering emulsions

During the preparation of Pickering emulsions, the modified SiO_2 particles are first completely wetted by the oil phase, and then contact with the aqueous phase while self-assemble at the oil-water interface. The driving force of the wetting process can be quantified by estimating the work of adhesion, W_a (kJ/m^2), expressed by Dupré's equation [39].

$$W_a = \gamma_{so} + \gamma_{ow} - \gamma_{sw} \quad (9)$$

where W_a represents the reversible work required to replace the unit area of oil-solid and oil-water so as to form the unit area of solid-water. Combined with Eq. 6, it results in a simplified expression of W_a.

$$W_a = \gamma_{ow}(1+\cos\theta_{ow}) \quad (10)$$

This indicates that the work needed to form a stable oil-water interface facilitated by solid particles is proportional to the oil-water interfacial tension γ_{ow}. In the three oil-water systems examined above involving ethyl acetate, toluene and *n*-octane (Fig. 10), their interfacial tension γ_{ow} were measured to be 7.23, 35.48 and 49.32 /kJ, respectively, where the ethyl acetate-water system was found to require the least amount of SiO_2 particles for stabilization (Fig. 13). Therefore, the γ_{ow} value provides an additional measure to gauge the amount of solid particles for forming stable Pickering emulsions; the higher the interfacial tension of oil-water is, the more difficult the adsorption of the solid particles on the interface is, requiring more solid particles to stabilize Pickering emulsions.

4. Conclusions

In this work, the surface of SiO_2 nanoparticles was modified with silane coupling agents with a rotating reactor developed in-house. The modification provided the particle surface with hydrophobicity, having a contact angle between 13º and 155º, that was attributed to the grafting of hydrophobic organic groups originated from KH-570. Thermogravimetric analysis (TGA) further quantified the amount of organic groups grafted on the particle surface, in terms of Grafting Ratio, ranging from 0 to 6 wt%, by comparing the weight loss of particles with and without modification subject to thermal decomposition at temperature up to 800 ^oC.

In Pickering emulsions stabilized by the surface-modified SiO_2 nanoparticles, the size (i.e. diameter) of the dispersed droplets varied in response to different conditions. By adding more SiO_2 particles, or using smaller SiO_2 particles it resulted in smaller but more droplets that was mainly due to the relatively larger coverage area of dispersed droplets provide by the

stabilizing particles. Varying the volumetric ratio of the dispersed and continuous phases revealed that more dispersed phase added in the oil-water system resulted in larger dispersed droplets likely through coalescence of small ones due to the lack of stabilizing particles. In contrast, varying the amount of the continuous phase in the oil-water system had insignificant effect on the size of the dispersed droplets. By theoretical analysis also with measuring the emulsion stability the droplet size was predicted showing a reasonably good agreement with the experimental results. Kinetic studies of the transition period towards forming stable Pickering emulsions further demonstrated the role of the stabilizing SiO_2 particles in determining the final geometry of the stable droplets dispersed through coalescence or breakup.

Finally, a mechanistic investigation of the processes of phase inversion and self-assembly of SiO_2 particles on oil-water interface suggested that by estimating the value of the solid-oil intermolecular energy (e.g. through DFT) it provided an indicator to predict the type of Pickering emulsions, while the estimate of interfacial tension values provided an additional measure to determine the amount of solid particles required for forming stable Pickering emulsions.

Author statement

Manuscript title: Fine tuning of surface properties of SiO2 nanoparticles for the regulation of Pickering emulsions

I have made substantial contributions to the conception or design of the work; or the acquisition,

analysis, or interpretation of data for the work; AND

I have drafted the work or revised it critically for important intellectual content; AND I have approved the final version to be published; AND

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Yuchao Zhao

13 February 2020

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We gratefully acknowledge the financial supports from National Natural Science Foundation of China (Nos. 21978250, 21808194), Natural Science Foundation of Shandong Province (ZR2017BB058) and Key Technology Research and Development Program of Shandong (2019JZZY010410).

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