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# Light-switched reversible emulsification and demulsification of oil-in-water Pickering emulsions

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**Abstract:** Pickering emulsions have been shown to be an excellent platform for interfacial catalysis. However, developing simple and efficient strategies to achieve the goal of product separation and catalyst and emulsifier recovery is still a challenge. Herein, we report for the first time the switchable transition between emulsification and demulsification triggered by UV and visible light in a novel class of light-responsive Pickering emulsions fabricated from Pd supported silica nanoparticles, azobenzene ionic liquid surfactant, *n*-octane and water. It is shown that light-switchable emulsification and demulsification of the Pickering emulsions is attributed to the adsorption of azobenzene ionic liquid surfactant on the surface of the nanoparticles and the light switched surface activity of the ionic liquid surfactant. This feature enables the Pickering emulsion to be used as an easily controlled micro-reactor with the functions of catalytic reaction, product separation as well as emulsifier and catalyst recycling. As an example, highly efficient catalytic hydrogenation of some unsaturated hydrocarbons at room temperature and atmospheric pressure has been performed in this system, with product separation and emulsifier and catalyst re-use achievable in a simple way.

Pickering emulsions stabilized by colloid particles of suitable wettability<sup>[1]</sup> have been known for more than a century<sup>[2]</sup>. Compared with conventional emulsions stabilized by surfactant or polymer, Pickering emulsions possess many advantages such as better stability against coalescence, biological compatibility and environmental friendliness, and have proven to be useful alternatives to conventional emulsions in food, pharmaceuticals, emulsion polymerization, drug delivery and cosmetics<sup>[3]</sup>. Due to the unique interfacial properties, Pickering emulsions have also been successfully applied in various interfacial catalytic reactions in recent years.<sup>[4]</sup>

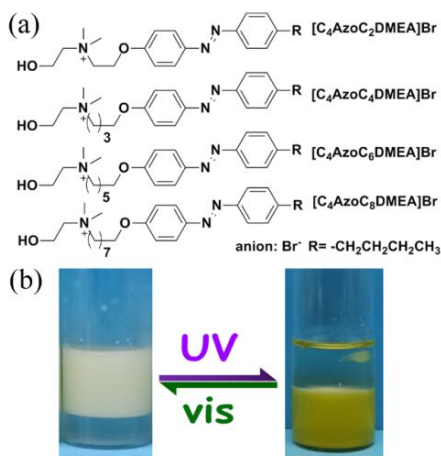
Frequently, Pickering emulsions are ultra-stable as their oil-water interfaces contain a dense layer of particles,<sup>[5]</sup> which is critical for their stability. However, this feature is not conducive to their demulsification for catalyst recovery and product separation after the reaction, and this obstacle has not been solved satisfactorily so far.<sup>[6]</sup> In general, centrifugation and filtration are common methods to destroy a stable Pickering emulsion in a continuous reaction process.<sup>[7]</sup> Although these methods have been widely used in the separation of catalysts from reaction systems, they are challenging when the catalyst particle size is sub-micrometer. Catalyst loss, filter blocking, long time and high energy consumption are inevitable, and there is a risk of oxidation in catalyst transport.<sup>[8]</sup> Moreover, product separation and emulsion recycling are still a problem. Thus, these methods cannot meet the principles of green chemistry and a sustainable process. To solve these problems, it is necessary to develop new strategies which can be used to integrate chemical reaction, product separation, catalyst recovery and emulsion recycling into a sustainable process.

In recent years, much effort has been made to develop stimuli-responsive Pickering emulsions and great progress has been achieved in this area. Generally, temperature<sup>[9]</sup>, CO<sub>2</sub> bubbling<sup>[10]</sup>, pH<sup>[10b, 11]</sup>, magnetic field<sup>[12]</sup>, redox<sup>[13]</sup>, ionic strength<sup>[14]</sup>, light irradiation<sup>[15]</sup> or their combinations<sup>[16]</sup> can be used to tune and control the microstructure and stability of Pickering emulsions. Therefore, stimuli-responsive Pickering emulsions

are capable of on-demand demulsification or phase inversion (change in emulsion type)<sup>[17]</sup>, which facilitates catalyst recovery. However, if product separation, catalyst recovery and emulsion recycling are simultaneously required, the stimulus response must be reversible so as to switch between emulsification and demulsification or between oil-in-water (O/W) and water-in-oil (W/O) emulsion types.

Of the triggers mentioned above, light has clean and non-invasive characteristics and can be delivered remotely and precisely in time and space<sup>[18]</sup>. Some valuable work has been reported on light-responsive Pickering emulsions in recent years. In this context, a light-responsive Pickering emulsion stabilized by titania nanoparticles with tailored wettability was reported by Bai *et al.*<sup>[15a]</sup> Demulsification was observed under UV light irradiation but the light response was not reversible. Chen *et al.*<sup>[15b]</sup> used Stenhouse adduct-functionalized silica to prepare photo-responsive Pickering emulsions capable of phase inversion upon visible light irradiation. By tuning the hydrophobicity of the functionalised silica particles with visible light, phase inversion was easily achieved from W/O to O/W. However, an irreversible transition was also observed in this system<sup>[15b]</sup>. Chen *et al.*<sup>[15c]</sup> designed and prepared functional nanoparticles grafted with photochromic spiropyran, and used them to achieve reversible phase inversion of a light-triggered Pickering emulsion for biphasic enantioselective biocatalysis. Interestingly, based on the reversible phase inversion of the Pickering emulsion, product separation and catalyst and emulsifier recycling was simultaneously realized. This is a significant progress in the sustainable chemical process mentioned above. However, no light switched reversible emulsification and demulsification of Pickering emulsions has been reported so far.

Herein, for the first time, we report on the switchable transition between emulsification and demulsification triggered by UV and visible light in a novel class of light-responsive Pickering emulsions stabilized by silica microspheres (SM) functionalized with surface-loaded metal Pd (Pd@SM) and water-soluble azobenzene-based ionic liquid surfactant (ILS) [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br, [C<sub>4</sub>AzoC<sub>4</sub>DMEA]Br, [C<sub>4</sub>AzoC<sub>6</sub>DMEA]Br or [C<sub>4</sub>AzoC<sub>8</sub>DMEA]Br (see chemical structures in Figure 1a). It was found that stable Pickering emulsions were destabilized resulting in complete phase separation of water and oil upon UV irradiation with stirring, but could be restored by subsequent irradiation with visible light after homogenisation. Thus the system could be reversibly switched between emulsified and demulsified by alternate irradiation with UV and visible light (Figure 1b). We show that the light-switchable emulsification and demulsification is attributed to the light switched surface activity of the ILS. As an example of applications, highly efficient catalytic hydrogenation of several unsaturated hydrocarbons was carried out in the Pickering emulsion at ambient conditions coupled with product separation and emulsifier and catalyst recycling.

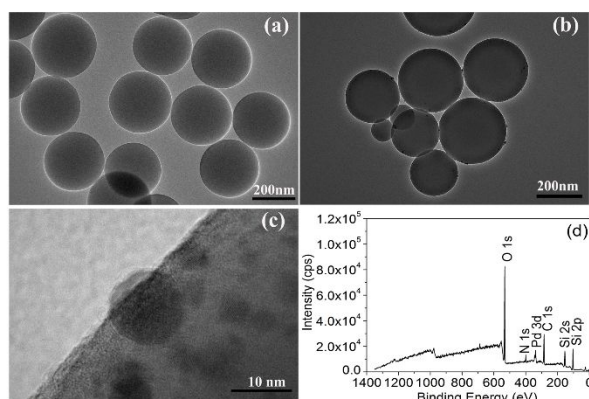


**Figure 1.** (a) Chemical structure of azobenzene-based ILS; (b) photo of the reversible, light-induced transition between complete phase separation and emulsification of a Pickering emulsion containing ILS.

The synthesis and  $^1\text{H}$  NMR characterization of the azobenzene-based ILS are described in the Supporting Information. Dibromoalkanes were used in the synthesis of the ILS to shorten the reaction time and enhance the yield of the product. The palladium-containing silica microspheres, Pd@SM, were prepared according to the Stöber method<sup>[19]</sup>. For metal Pd support, the silica surface was first modified by *N*-(2-aminoethyl)-3-aminopropyltriethoxysilane to obtain amino-functionalized silica (SM-NH<sub>2</sub>), and the detailed procedures are provided in the Supporting Information. The structure and morphology of the as-prepared Pd@SM were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), and the results are shown in Figure 2 and Figures S1-S4. TEM results showed that the SM and Pd@SM particles were spherical with diameters of about 200 nm (Figure 2a and 2b), and Pd was coated on the surface of the silica to a thickness of 3-5 nm (Figure 2c). The XPS spectrum (Figure 2d) confirmed that the Pd content was 1.21 wt.%. XRD results (Figure S1) indicated that after Pd loading, a new diffraction peak appeared near 40° which is characteristic of the (111) crystal plane of Pd(0)<sup>[20]</sup>.

It was found experimentally that Pd@SM alone could not emulsify a mixture of *n*-octane and water (oil:water ratio of 1:1) to form a stable Pickering emulsion within the investigated concentration range (Pd@SM 0.0001-0.5 wt.%, Figure S5). The air-water contact angle on Pd@SM was determined to be 16°, indicating a very hydrophilic material. It is this strong hydrophilic property that prevents Pd@SM from emulsifying *n*-octane and water. However, addition of aqueous [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br into *n*-octane in the presence of Pd@SM results in a more or less stable O/W Pickering emulsion depending on the concentration of [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br. According to orthogonal experiments, the effects of the concentration of both [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br and Pd@SM on Pickering emulsion stability were studied, and the results are shown in Table S1. It is noted that when the concentration of [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br was 1×10<sup>-3</sup> mol/kg, the required minimum content of Pd@SM for the formation of a stable Pickering emulsion was 0.5 wt.%. However, as the concentration of [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br increased to 3×10<sup>-3</sup> mol/kg, as little as 10<sup>-4</sup> wt.% of Pd@SM was enough to form a stable Pickering emulsion. [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br alone forms a stable O/W emulsion with *n*-octane and water without particles, which means that it is also surface-active. Thus [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br and Pd@SM exhibit a synergistic effect in Pickering emulsion stabilisation. The droplet test<sup>[15b, 21]</sup> was used to determine the type of emulsion formed. For this purpose, a drop of emulsion in the system [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br/Pd@SM/*n*-octane/water was added separately to water and *n*-octane, and the results are

shown in Figure S6. An O/W emulsion was clearly confirmed, backed up by fluorescence microscopy images with sodium fluorescein dyeing (Figure S7). Moreover, the optical microscope image in Figure 3a indicates that the droplets are polydisperse with diameters between 5 and 30 μm.

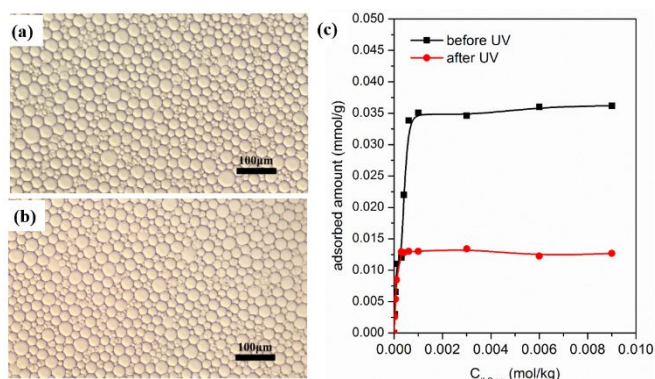


**Figure 2.** (a) TEM image of SM; (b) TEM image of Pd@SM; (c) Magnified TEM image of Pd@SM; (d) XPS spectrum of Pd@SM; (e) elemental distribution on SM and Pd@SM.

| material | C     | Si    | O     | N    | Pd   |
|----------|-------|-------|-------|------|------|
| SM       | 10.03 | 31.63 | 58.33 |      |      |
| Pd@SM    | 32.88 | 20.40 | 39.79 | 5.72 | 1.21 |

**Figure 2.** (a) TEM image of SM; (b) TEM image of Pd@SM; (c) Magnified TEM image of Pd@SM; (d) XPS spectrum of Pd@SM; (e) elemental distribution on SM and Pd@SM.

To evaluate the influence of the chemical structure of the ILS on the formation of Pickering emulsions, [C<sub>4</sub>AzoC<sub>4</sub>DMEA]Br, [C<sub>4</sub>AzoC<sub>6</sub>DMEA]Br and [C<sub>4</sub>AzoC<sub>8</sub>DMEA]Br, where the hydrophilicity of them decreases with increasing chain length but all remain water soluble and octane-insoluble, were used separately with Pd@SM for emulsification and the results are given in Tables S2-S4. Similarly, they could emulsify *n*-octane and water in the presence of Pd@SM to fabricate O/W emulsions, but in a much wider concentration range. A photograph of representative stable Pickering emulsions is shown in Figure S8, and the minimum content of ILS and Pd@SM for the formation of a stable Pickering emulsion in the different systems is listed in Table S5, together with the critical aggregate concentration (CAC) of the ILS determined in water. It can be seen that for a given amount of Pd@SM, the concentration of ILS in water required to form a stable Pickering emulsion is gradually reduced in the order: [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br > [C<sub>4</sub>AzoC<sub>4</sub>DMEA]Br > [C<sub>4</sub>AzoC<sub>6</sub>DMEA]Br > [C<sub>4</sub>AzoC<sub>8</sub>DMEA]Br. For example, when the content of Pd@SM was 0.5 wt.%, the minimum concentration of [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br, [C<sub>4</sub>AzoC<sub>4</sub>DMEA]Br, [C<sub>4</sub>AzoC<sub>6</sub>DMEA]Br and [C<sub>4</sub>AzoC<sub>8</sub>DMEA]Br is 1×10<sup>-3</sup>, 3×10<sup>-4</sup>, 1×10<sup>-4</sup> and 3×10<sup>-5</sup> mol/kg, respectively. This result shows that increasing the alkyl spacer length between the azobenzene group and the cationic head group significantly reduced the concentration of ILS required for the formation of a stable Pickering O/W emulsion. Actually, this concentration is lower than the CACs of the ILS in water. This implies that in the presence of Pd@SM, only a small fraction of the ILS is sufficient to emulsify *n*-octane and water.



**Figure 3.** Optical micrographs of  $[C_4AzoC_2DMEA]Br/Pd@SM$  *n*-octane-in-water emulsion droplets (a) before light irradiation and (b) after the fifth cycle of UV and visible light irradiation; (c) adsorbed amount of  $[C_4AzoC_2DMEA]Br$  on the surface of  $Pd@SM$  vs equilibrium concentration of  $[C_4AzoC_2DMEA]Br$  before and after UV irradiation at 25 °C.

Interestingly, a stable Pickering emulsion could be demulsified resulting in complete phase separation of oil and water upon UV irradiation for 30 min at 25 °C with stirring. Subsequently, using visible light to irradiate the system for 60 min at the same temperature with stirring, a stable Pickering emulsion was re-formed after homogenisation. Therefore, we could achieve reversible switching between a stable Pickering emulsion and complete demulsification by alternate exposure to UV and visible light with stirring. Moreover, this demulsification and re-emulsification process did not have any significant effect on the microstructure and morphology of the emulsion after 5 cycles (Figure 3b). Similar switchable transitions between stable and unstable Pickering emulsions fabricated by  $[C_4AzoC_4DMEA]Br$ ,  $[C_4AzoC_6DMEA]Br$  or  $[C_4AzoC_8DMEA]Br$  was also observed. It should be noted that turbidity of the Pickering emulsion can prevent the transmission of light and reduce the speed of demulsification and re-emulsification. Thus, stirring was used to mitigate the effect of turbidity on demulsification and re-emulsification. Moreover, reducing the thickness of the sample and increasing the light intensity and irradiation area could all speed up the demulsification and re-emulsification. For example, as shown in Table S6, decreasing the thickness of the emulsion from 2.70 cm to 0.75 cm caused the demulsification time to decrease from 30 min to 10 min. Increasing the irradiated area of the system from 0.28 cm<sup>2</sup> to 0.84 cm<sup>2</sup> caused the demulsification time to be reduced to 5 min, while the re-emulsification time was shortened from 60 min to 8 min by decreasing the thickness of the emulsion and simultaneously increasing the irradiated area and light intensity.

To understand the reversible transition of the Pickering emulsion, the zeta potentials of  $Pd@SM$  in water, the adsorption isotherm of  $[C_4AzoC_2DMEA]Br$  onto these particles and the air-water surface tension of  $[C_4AzoC_2DMEA]Br$  solutions were determined. The zeta potentials of SM, SM-NH<sub>2</sub> and  $Pd@SM$  (0.5 wt.%) in pure water were -34.0, +9.1 and +28.9 mV respectively, indicating that modification of SM with amine and then Pd led to an increase in the zeta potential. On the other hand, the zeta potential of  $Pd@SM$  increases with an increase in the concentration of  $[C_4AzoC_2DMEA]Br$  in water. It reached +46.8 mV at a concentration of  $1 \times 10^{-3}$  mol/kg (Table S7), and the dispersion of  $Pd@SM$  in aqueous  $[C_4AzoC_2DMEA]Br$  became more stable.<sup>[22]</sup> This result suggests that  $[C_4AzoC_2DMEA]Br$  was adsorbed onto the surface of  $Pd@SM$ . In order to understand how  $[C_4AzoC_2DMEA]Br$  adsorbs onto the surface of  $Pd@SM$ , 4-((4-butylphenyl)diazenyl)phenol ( $C_4AzoOH$ ) which is an important structural segment in cations of our ILS, was used as an adsorption dye on the surface of SM, SM-NH<sub>2</sub> and  $Pd@SM$ . It is shown that  $Pd@SM$  has significant absorption of  $C_4AzoOH$  (see Figure S9), but SM and SM-NH<sub>2</sub> do not. This provides evidence that the coordination interaction of Pd on the surface of  $Pd@SM$  with -OH groups and delocalized  $\pi$  electrons of the

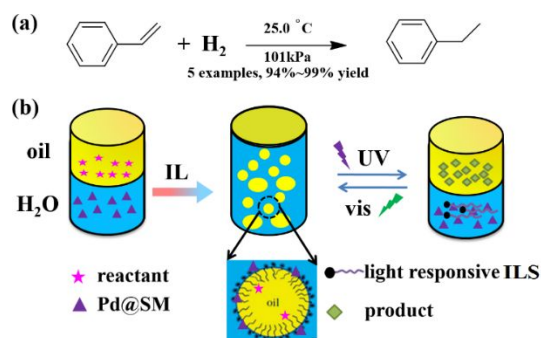
azobenzene functional group may be the main driving force for the adsorption of ILS onto particles.

The adsorption isotherm of  $[C_4AzoC_2DMEA]Br$  onto  $Pd@SM$  was also determined. It can be seen from Figure 3c that the adsorbed amount initially increased rapidly with  $[C_4AzoC_2DMEA]Br$  concentration and then reached a plateau of 0.036 mmol/g at  $1 \times 10^{-3}$  mol/kg, corresponding to a molecular area of 0.34 nm<sup>2</sup>/molecule. For comparison, we also determined the surface tension of aqueous  $[C_4AzoC_2DMEA]Br$  solutions as a function of concentration. The minimum area per molecule ( $A_{min} = 0.51$  nm<sup>2</sup>/molecule) at the air-water interface was estimated using the Gibbs adsorption isotherm.<sup>[10b]</sup> Clearly, the molecular area of  $[C_4AzoC_2DMEA]Br$  adsorbed on  $Pd@SM$  is less than that at the air-water interface. This adsorption of  $[C_4AzoC_2DMEA]Br$  on the surface of nanoparticles enhanced the surface activity of  $Pd@SM$  at the oil-water interface.<sup>[5a]</sup>

Moreover, it is noted from Table S7 that after UV irradiation, there was no obvious change in the zeta potential of  $Pd@SM$  in the presence of  $1 \times 10^{-3}$  mol/kg  $[C_4AzoC_2DMEA]Br$  in water, implying that light irradiation has no effect on the particle charge at the studied concentration. However, the adsorbed amount of  $[C_4AzoC_2DMEA]Br$  on the surface of  $Pd@SM$  significantly decreased after UV irradiation (Figure 3c). This decrease weakens the emulsifying ability of the nanoparticles, resulting in demulsification of the Pickering emulsion.

It is known that the configuration of the azobenzene-based compound cation can be changed from *trans*- to *cis*- isomer under UV irradiation in water (Figure S10), leading to a significant enhancement of the hydrophilicity of the ILS,<sup>[23]</sup> increase of the surface tension of an aqueous solution and reduction of its surface activity. For example, after UV irradiation, the surface tension of  $1 \times 10^{-3}$  mol/kg  $[C_4AzoC_2DMEA]Br$  in water increased from 49.6 mN/m to 56.3 mN/m, and its CAC increased from  $2.3 \times 10^{-3}$  to  $1.3 \times 10^{-2}$  mol/kg (Figure S11). The decrease in surface activity of  $[C_4AzoC_2DMEA]Br$  is not beneficial for the formation of a Pickering emulsion. On the other hand, by further irradiation with visible light, the reverse isomerization of  $[C_4AzoC_2DMEA]Br$  cation from *cis*- to *trans*- isomer was observed. Therefore, the reversible switching between demulsification and emulsification of the Pickering emulsion originates from the change in the amphiphilic character of the azobenzene-based ILS after isomerisation of the azobenzene groups.<sup>[18b]</sup>

The above reversibly switched Pickering emulsions may be of great importance for the design of efficient and recyclable reaction systems. As a proof of concept, our light-switchable Pickering emulsions were used as a micro-reactor for the highly efficient catalytic hydrogenation of several unsaturated hydrocarbons at 25 °C and atmospheric pressure (see Figure 4a), where H<sub>2</sub> was bubbled into the emulsion and  $Pd@SM$  was used as catalyst in the reaction. In addition to its own scientific significance, catalytic hydrogenation of unsaturated hydrocarbons in gasoline is also an important method to produce high quality gasoline and to resolve the environmental problems caused by incomplete combustion of gasoline and discharge of particulate pollutants into the atmosphere. Since the emulsion is O/W, unsaturated hydrocarbons such as styrene could diffuse into the center of the oil dispersed phase with stirring to take part in the reaction. After the reaction was complete, the system was irradiated by UV light and the stable Pickering emulsion was destroyed to give complete phase separation of *n*-octane and water (residual *n*-octane in water was ~ 5 ppm). After separation of the product, the two-phase system could reform into a stable Pickering emulsion using visible light irradiation and homogenisation again. In this way, the ILS and catalyst could be recycled simply.



**Figure 4.** (a) Catalytic hydrogenation of styrene in O/W Pickering emulsion at 25 °C and atmospheric pressure; (b) schematic illustration of the light-switchable emulsification and complete phase separation of a Pickering emulsion for catalytic hydrogenation, product separation and recycling of the ILS and catalyst.

above first arrow, change IL to ILS

Based on the above strategy, the catalytic hydrogenation of styrene, phenylpropene,  $\alpha$ -methylstyrene, phenylacetylene and methyl acrylate in [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br/Pd@SM *n*-octane-in-water Pickering emulsions was investigated, and the results are shown in Table 1. It is clearly noted that except for phenylpropene, the other four reactants achieved quantitative conversion within 90 min, indicating the excellent reaction efficiency in the Pickering emulsion. As an example, the catalytic hydrogenation of styrene was used to evaluate the cycling performance of the light-responsive Pickering emulsion, and the results are shown in Figure S12. As can be seen, there was no clear decrease in catalytic activity after 6 cycles of emulsification and phase separation, indicating that the Pickering emulsion reported here has good recyclable performance for efficient catalytic hydrogenation, and [C<sub>4</sub>AzoC<sub>2</sub>DMEA]Br is stable in this process (confirmed by UV-vis spectra, Figure S13). In addition, highly efficient catalytic hydrogenation was performed at room temperature and atmospheric pressure which reduces the risk caused by high pressure and temperature in the hydrogenation reaction. Therefore, the Pickering emulsions designed in this work are an efficient, safe and recyclable catalytic hydrogenation vehicle. By using these novel Pickering emulsions, the limitations caused by conventional Pickering emulsions can be overcome.

In addition, Knoevenagel reactions of aromatic aldehyde and malononitrile were performed in the light-switchable Pickering emulsion, and the results are shown in Table S8. It is shown that these reactions are highly efficient and the yields are always not above 98% at 40 °C.

**Table 1.** Conversion of catalytic hydrogenation in an O/W Pickering emulsion at 25 °C and 101 kPa.

| Substrate | Product | Reaction time (min) | Conversion (%) |
|-----------|---------|---------------------|----------------|
|           |         | 40                  | >99            |
|           |         | 90                  | 94             |
|           |         | 80                  | >99            |
|           |         | 80                  | >99            |
|           |         | 30                  | >99            |

C<sub>ILS</sub> = 9x10<sup>-3</sup> mol/kg, C<sub>Pd@SM</sub> = 1 wt.%, 1.5 mL *n*-octane and 1.5 mL water were used to form the Pickering emulsion. The conversion of the reaction were determined by <sup>1</sup>H NMR.

In conclusion, we designed and prepared a novel class of light-responsive Pickering emulsion. It was found that water and *n*-octane could be emulsified using a mixture of Pd@SM and azobenzene-based ILS as stabiliser, and the Pickering emulsions could be reversibly switched between stable and unstable by alternate irradiation with UV and visible light. Adsorption of the azobenzene-based ILS cation on the surface of Pd@SM is the main reason why synergism is observed. UV irradiation results in a decrease in the surface activity of the azobenzene-based ILS and leads to demulsification/complete phase separation of the Pickering emulsions. However, visible light irradiation enables re-emulsification to a stable Pickering emulsion again with stirring. Considering the fact that light is a non-invasive, clean and remotely controlled stimulus, these light-switchable Pickering emulsions are clean and easily controllable micro-reactors for chemical reaction, separation and recycling. As a result, these light-switchable Pickering emulsions were used for the highly efficient catalytic hydrogenation of several unsaturated hydrocarbons at room temperature and atmospheric pressure. It was found that the conversion was above 94%. In the light-switchable process within a Pickering emulsion, the hydrogenation reaction, product separation and emulsifier and catalyst recycling were well integrated in a simple way. The strategy developed in this work opens a new pathway for the development of sustainable chemical processes.

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**Keywords:** Pickering emulsion ·light switchable ·ionic liquid

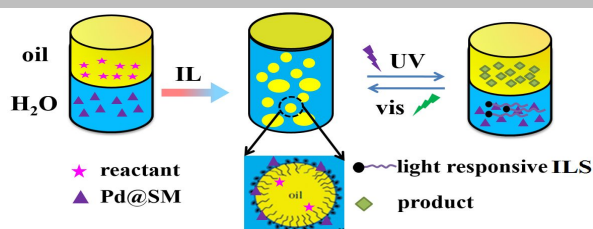
surfactant ·reversible emulsification/demulsification ·catalytic hydrogenation

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## Entry for the Table of Contents

### COMMUNICATION



A novel class of light-switchable Pickering emulsion was designed and prepared, which could be reversibly switched between stable and unstable by alternately using UV and visible light. By utilizing this novel phase behavior of the Pickering emulsion, highly efficient catalytic hydrogenation, product separation and emulsifier and catalyst recycling was achieved.

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**Page No.1 – Page No. 5**

Light-switched reversible  
emulsification and demulsification of  
oil-in-water Pickering emulsions

above first arrow, change IL to ILS