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ARTICLE

Biphasic Biocatalysis using a CO_2-Switchable Pickering Emulsion

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Biphasic biocatalysis such as the hydrolysis of olive oil and the esterification of octanol with oleic acid were performed in a CO_2/N_2-switchable Pickering oil-in-water emulsion stabilized by silica nanoparticles hydrophobized *in-situ* by a CO_2/N_2-switchable surfactant (*N*,*N*-dimethyldodecylamine). Compared with biphasic systems, the enzyme in the Pickering emulsions displays a higher reaction efficiency, demulsification and recycling of the enzyme can be simply realized by bubbling with N_2/CO_2. Moreover, the recycled enzyme still possesses significant catalytic activity.

Introduction

Enzymes as powerful biocatalysts have attracted a great deal of attention in environmentally friendly and sustainable industrial chemistry owing to their overall high chemo-, regio- and stereo-selectivity under mild conditions.[1-3] However, widespread applications of enzymes are still limited by the fact that substrates of interest are usually of low solubility in water, whereas the enzymes are typically active in water. Thus enzymatic reactions are often carried out in organic-aqueous biphasic reaction systems. Unfortunately, conventional biphasic systems often suffer from low reaction efficiency, due to a low organic-aqueous interfacial area.[4,5] Furthermore, long-term exposure of enzymes to the organic solvents used would lead to their inactivation.[6-8]

Recently, Pickering emulsions stabilized by nano- or micro-sized colloidal particles offer a promising platform for conducting interfacial reactions between immiscible reagents.[9-32] Appropriate functionalization of the surface of the particles with catalytic centers can accelerate interfacial reactions (*i.e*. Pickering interfacial catalysis (PIC)).[9] A variety of nanoparticle catalysts in PIC has been successfully applied in various organic reactions. For example, Jiang *et al*. have recently reported enzymatic catalysis in a Pickering emulsion with hydrophobic silica nanoparticles.[31] It is noticed however that to date the PIC catalysts are mostly prepared *ex situ* by surface grafting with hydrophobic chains. The wettability of the particle surfaces depends on the grafting ratio and is fixed once grafting is finished, which has limited their applications in large-scale processes. Beside the *ex situ* coating method, particles can also be made surface-active by *in situ* hydrophobization[33-35] so as to be able to stabilize Pickering emulsions. The latter method, based on the adsorption of ionic surfactants on oppositely charged particle surfaces, has advantages that the wettability/surface activity of the particles can be controlled by selection of the concentration and structure of the amphiphiles.[33] However, PIC catalysts using *in situ* hydrophobized particles are rarely reported.

Unlike traditional emulsions stabilized by surfactant or polymer, Pickering emulsions have a dense layer of particles at the oil-water interface, which leads to ultra-stable droplets.[33-35] This, however, provides an obstacle to liquid/liquid separation for catalyst recovery or recycle, which has not been sufficiently addressed yet.[12,14] Appropriate shear forces could induce coalescence of the Pickering emulsions.[36] Centrifugation was used to separate the Pickering emulsions drops from the continuous phase containing the product,[3,17,18] which is not practical for continuous reaction processes.[30] Recently, membrane ultrafiltration was reported to separate the Pickering emulsion in continuous biocatalysis. [30]

On the other hand, stimuli-responsive Pickering emulsions developed recently have attracted considerable attention owing to their long-term stability and smart tunability. [34,35, 37-46] In these smart systems, the wettability of the particle surfaces can be easily regulated by external stimuli. Thus, demulsification or phase inversion of stimuli-responsive Pickering emulsions, which facilitates the separation of products and the recycling of enzymes, can be achieved in a simple way. For example, some stimuli-responsive Pickering emulsions are designed for enzymatic reactions using *ex situ* surface-grafted particles responsive to triggers such as light,[1]

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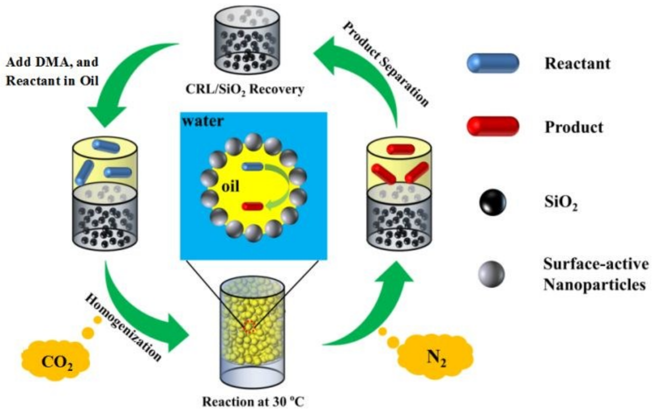
temperature,[43] pH[44] and electric potential.[46] A different but simple protocol to prepare Pickering emulsions is to use commercially available inorganic nanoparticles, such as silica, hydrophobized *in situ*[34] by physisorption of trace amounts of oppositely charged responsive or switchable surfactant.[47] Fortunately these Pickering emulsions can also be made responsive to environmental stimuli, such as pH, temperature, CO_2, specific ion concentration and light irradiation.[35] Among these triggers, the CO_2/N_2 trigger is particularly attractive because both CO_2 and N_2 are inexpensive and environmentally benign.[48] Moreover, CO_2 and N_2 show little damage towards enzymes since they are non-toxic, non-corrosive and can also be easily removed from the system on demand.

Herein, we report a simple yet powerful strategy for biphasic biocatalysis in a CO_2/N_2-switchable Pickering emulsion system. The emulsions are stabilized by bare silica nanoparticles in combination with a trace amount of *N*,*N*-dimethyldodecylamine (referred to as DMA), which all are cheap and commercially available. As shown in Scheme 1, by loading a lipase (CRL) from *Candida rugosa* in the aqueous phase, an enzymatic reaction is performed in the oil-in-water Pickering emulsion stabilized by silica nanoparticles hydrophobized *in situ* by DMA-CO_2 (ammonium bicarbonate, cationic). At the end of reaction, the Pickering emulsions are subjected to demulsification by bubbling N_2 at room temperature, which turns DMA-CO_2 to DMA (neutral). As a result, the oil phase containing the products can be easily separated, and the enzyme and silica nanoparticles in the water phase can be recycled.



Scheme 1. Schematic illustration of the CO_2/N_2 stimulus-responsive Pickering emulsion for recyclable enzymatic reactions.

Results and discussion

Figure S1 shows the transformation of DMA (insoluble in water) to positively charged ammonium bicarbonate surfactant (DMA-CO_2, active form, cmc ≈ 0.6 mM) by exposure to CO_2 in water. Reversibly, the bicarbonate can be re-converted to the amine (inactive form) by bubbling N_2 or air at room temperature. The inter-conversion between the inactive and active forms of DMA can be monitored by conductivity measurement and ^{1}H-NMR (Figures S2 and S3 and Table S1).

With pure isooctane as oil phase and an oil:water volume ratio of 1:1, the bare silica nanoparticles (primary diameter ≈ 20 nm) which are negatively charged at neutral pH (Figure S4) are too hydrophilic to stabilize emulsions alone. No stable emulsion was formed by DMA-CO_2 alone either at concentrations below 5 mM (Figure S5(a),(b)). However, Pickering emulsions stable to coalescence were formed when the particles (0.5 wt.%) were in combination with DMA-CO_2 at concentrations well below 5 mM (Figure S5(c), (d)).

In this mixture, silica nanoparticles are hydrophobized *in situ* by the cationic surfactant (DMA-CO_2) *via* the electrostatic attraction between the surfactant head-group and the negatively charged silica particle surface.[33-35] The zeta potential of particles progressively reduces in magnitude upon increasing the surfactant concentration becoming zero around 5 mM (Figure S4). The type of emulsion can usually be identified by employing staining and dilution.[33] As shown in Figure S6, here Nile red was used to stain the oil phase and green emission was observed in the droplets which clearly confirmed an oil-in-water morphology.

The amount of DMA-CO_2 adsorbed onto silica surfaces was quantified by measuring the surface tension of an aqueous dispersion (with silica nanoparticles (0.1 wt.%)) and comparing with the surface tension of pure DMA-CO_2 solution as calibration. As shown in Figure S7(a), the surface tension of the dispersion was higher than that of the surfactant solution alone due to loss of surfactant on particle surfaces. The calculated adsorbed amount of DMA-CO_2 on silica increased upon increasing the initial concentration of surfactant (Figure S7(b)). Silica particle surfaces become partially hydrophobic as a result of the formation of a surfactant monolayer on their surfaces exposing hydrophobic chains to water.[28,29] The surface-modified particles can then adsorb to the oil-water interface and stabilize oil drops in water. This *in situ* hydrophobization of DMA-CO_2 on silica nanoparticles can be further monitored by evaluating the change in the wettability of a negatively charged glass slide (mimic of bare silica particle surface) immersed in solutions of DMA-CO_2. Using the captured oil droplet method, the contact angle through the aqueous phase of an oil drop under aqueous surfactant solution is seen to increase gradually with increasing DMA-CO_2 concentration between 0.01 and 0.6 mM (Figure S8). As with silica nanoparticle surfaces, DMA-CO_2 adsorbed at the negatively charged glass slide-water interface *via* electrostatic interactions forming a hydrophobic monolayer.

The switchable performance of the Pickering emulsions stabilized by a mixture of silica nanoparticles and DMA-CO_2 was examined, as shown in Figure 1. The emulsion containing silica (0.5 wt.%) and DMA-CO_2 (0.6 mM) demulsified completely after bubbling N_2 at a steady rate of 100 mL min^{-1} at 25 °C for 40 min. The bicarbonate surfactant (DMA-CO_2) was deprotonated to the neutral state and desorbed from particle surfaces, rendering silica nanoparticles hydrophilic again resulting in demulsification. However, a stable emulsion was re-formed by bubbling CO_2 through the oil-water mixture at 25 °C for 10 min followed by re-homogenization for 2 min, where the neutral tertiary amine was protonated again enabling adsorption onto silica particle surfaces rendering them surface-active. It was noticed that the average droplet diameter (60 µm) of the re-stabilized emulsion is similar to that of the original emulsion (Figure 1(a), (c)).

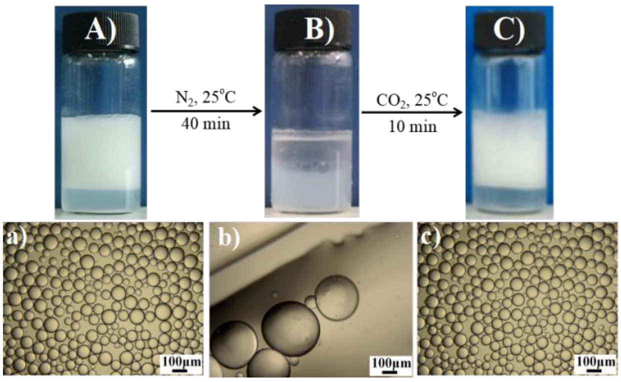


Figure 1. Photographs (A-C) and corresponding micrographs (a-c) of isooctane-in-water Pickering emulsions stabilized by silica nanoparticles (0.5 wt.%) in combination with DMA-CO_2 (0.6 mM) . (A, a) Original emulsion, (B, b) after bubbling N_2 at 25 °C for 40 min, (C, c) after bubbling CO_2 through the oil-water mixture at 25 °C for 10 min followed by re-homogenization for 2 min, one week later.

To verify the performance of the above Pickering emulsions as an enzymatic reaction medium, a catalytically active lipase enzyme from *Candida rugosa* (CRL) was added to catalyze the hydrolysis of olive oil. Typically, isooctane (4 mL) containing dissolved olive oil (5 vol.%) and an equal volume of aqueous phase containing CRL (1 mg/L), silica (0.5 wt.%), and DMA-CO_2 of different concentrations were homogenized to form Pickering emulsions. The Pickering emulsions containing CRL still exhibit remarkable stability against coalescence, and no further creaming was observed after 24 h (Figure S10). The mean droplet diameter of the emulsions in the presence of CRL was approx. 70 µm (Figure S11), and was less dependent on the surfactant concentration compared with those in the absence of CRL (Figure S9).

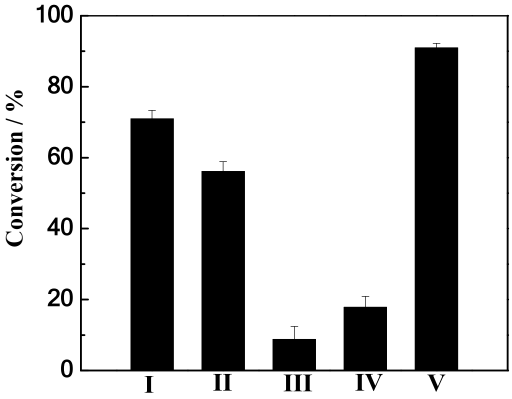


Figure 2. Hydrolysis conversion of olive oil (5 vol.%) dissolved in 4 mL isooctane in contact with 4 mL water with 1 mg/mL CRL in different systems at 30 °C for 30 min. Average of three measurements. (I) Stirring at 600 rpm with nothing else; (II) stirring and with DMA-CO_2 (0.6 mM); (III) stirring and with silica nanoparticles (0.5 wt.%); (IV) stirring and with DMA-CO_2 (0.6 mM) and silica (0.5 wt%); (V) in Pickering emulsion containing DMA-CO_2 (0.6 mM) and silica (0.5 wt.%).

A comparison of different systems containing CRL (1 mg/mL) for the hydrolysis of olive oil was performed at 30 °C for 30 min. As shown in Figure 2, the hydrolysis conversion of the olive oil in the biphasic system (I) without particles or surfactant was 71%. However, the conversion decreased to 56 % after DMA-CO_2 was added as a phase transfer catalyst (II), which further decreased to 10% when silica particles (0.5 wt.%) were added into the biphasic system (III). It is likely that certain interactions between CRL and surfactant or silica nanoparticles lead to denaturation of the enzyme[49-52] and reduction of its catalytic activity. In the biphasic system (IV) containing surfactant and particles the conversion was also low (17%), but impressively the conversion reached as high as 91% once the combined system was homogenized to form a Pickering emulsion (V). Although the average drop size of Pickering emulsion is larger than that of the traditional emulsions or micelles, the negative effects of the surfactants have been significantly inhibited in the Pickering emulsion. The reason is that the amount of surfactant needed to stabilize the emulsion decreases significantly in the presence of silica (<< cmc), and the positively charged surfactants prefer to adsorb on silica particles surface *via* electrostatic interaction. As shown in Figure S4, the zeta potential of the silica particles in the aqueous phase changes with the concentration of DMA-CO_2 due to neutralization of the negative charges on particles by adsorbed surfactant. The concentration of free ionic surfactant in the solution is therefore very low and the electrostatic interactions between surfactant and enzyme are significantly reduced, which is beneficial for reducing the damage of the surfactant to the enzyme. Interestingly, when the oil phase was replaced by either hexane or ethyl acetate, the hydrolysis conversion (30 min) of the olive oil reach as high as 90% and 87%, respectively. Therefore, the Pickering emulsion provides a more suitable microenvironment for protecting the enzyme from denaturation.

In Pickering emulsions, the location of CRL is critical to its performance, as CRL is only soluble in the aqueous phase.[53] To confirm the location of CRL in the Pickering emulsions, the enzyme was labeled with fluorescein isothiocyanate (FITC). As shown in Figure 3, the green emission, the obvious fluorescent signal, was concentrated at the surface of the oil drops (without olive oil dissolved in) although a weak fluorescent signal was also observed in the aqueous phase, indicating that most of the enzyme molecules were transferred to the oil-water interface by emulsification. A similar image was observed for the emulsion with olive oil dissolved in the oil phase (Figure S12). It has been shown in many examples that lipases can adsorb on hydrophobic supports.[53] Therefore, CRL may adsorb on the surface of the hydrophobized silica particles with the enzyme active center opened, which permits the attainment of a high reaction rate in a Pickering emulsion. Compare with the free dispersion of enzyme in aqueous phase of the biphasic system (Figure 2, exp. I), the particle layer

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coated with adsorbed enzyme at Pickering interfaces maximizes the extent of the liquid-catalyst-liquid interfacial areas and facilitates mass transfer between the two phases.[17]

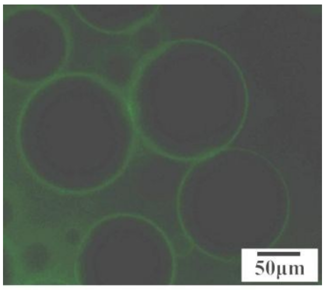

Figure 3. Fluorescence microscopy image of the Pickering emulsion (without olive oil in the oil phase) stabilized by a mixture of 0.5 wt.% silica, 0.6 mM DMA-CO_2 and 1 mg/mL CRL labelled with FITC.

The effects of various parameters on the hydrolysis conversion were investigated and are illustrated in Figure 4. Figure 4(a) shows the difference in dynamic conversion between the Pickering emulsion (V) and the biphasic system (I). Although at long time the conversion in the former is only slightly higher than in the latter, the difference between the two is high at short times. For example, in 5 min. the conversion in the emulsion reached 62% *cf.* 24% in the biphasic system. The high initial catalytic efficiency of CRL in a Pickering emulsion is a result of the rapidly increased oil-water interfacial area and accumulation of the enzyme at the interface which enhances the contact of its active center with the substrate.[1-5, 9-13]

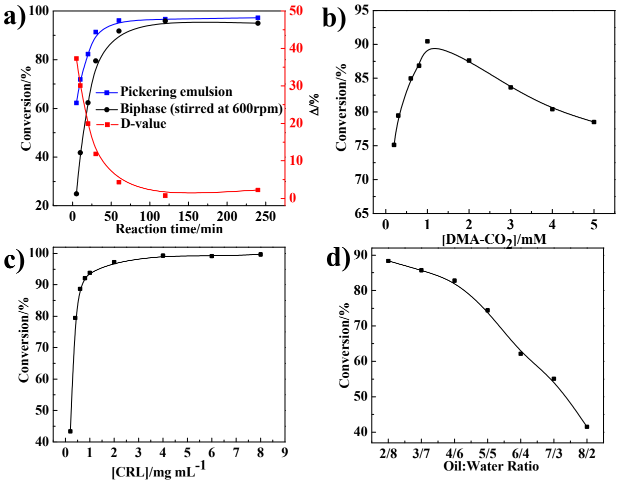

Figure 4. Effect of various factors on the hydrolysis conversion of olive oil (5 vol.%) at 30 °C. (a) Effect of reaction time in biphasic system (I) and in a Pickering emulsion (V), (b) effect of surfactant concentration in Pickering emulsion with 0.5 wt.% silica and 1 mg/mL CRL 30 min, (c) effect of enzyme concentration in Pickering emulsion with 0.5 wt.% silica and 0.6 mM DMA-CO_2 for 30 min, d) effect of oil:water ratio in Pickering emulsion with 0.5 wt.% silica, 0.6 mM DMA-CO_2 and 1 mg/mL CRL for 30 min.

The effect of surfactant concentration on the catalytic efficiency of CRL is shown in Figure 4(b). The hydrolysis conversion of olive oil increased initially from 75% to 91% upon increasing [DMA-CO_2] from 0.2 mM to 1 mM. This may be due to the slight decrease in the oil droplet size (Figure S11). However, the conversion decreased gradually for concentrations beyond 1 mM. The denaturation of the enzyme may account for this effect, caused by the surfactant inducing unfolding of the enzyme.[51,52]

The effect of enzyme concentration is shown in Figure 4(c), where the hydrolysis conversion increased dramatically between 0.2 mg/mL and 1 mg/mL and much less above 1 mg/mL. The effect of varying oil:water ratio on the catalytic efficiency was also investigated (Figure 4(d)). The emulsion type (oil-in-water) did not change in this range, though the properties of the Pickering emulsions may be affected. A higher efficiency of the enzymatic reaction was achieved upon decreasing the volume fraction of oil in the emulsion due to a reduction in droplet size (Figure S13) and therefore an increase in oil-water interfacial area.

As a commercial and widely applicable lipase, CRL can also catalyze esterification reactions. As an example, the esterification of octanol with oleic acid (both dissolved in isooctane) catalyzed by CRL in a Pickering emulsion was investigated with the results shown in Figure 5. The esterification yield reached 64 % in 1 h (Figure 5(a)), much higher than that in the biphasic system (17%). The yield further increased to 90% by 2 h with esterification almost complete by 4 h (Figure 5(b). In contrast, the yield reached only 70% after 4 h in the biphasic esterification system. It is seen therefore that CRL exhibits a much higher catalytic esterification performance in a Pickering emulsion compared with that in a biphasic system.

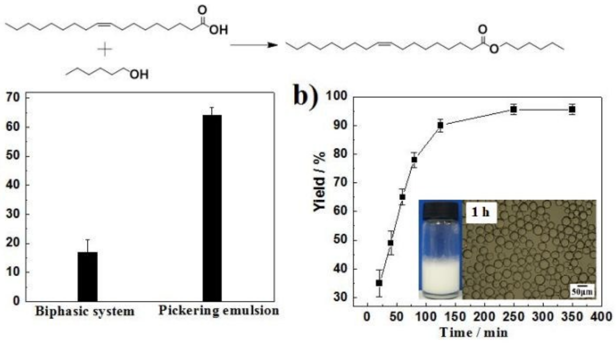

Figure 5. Esterification yield of octanol with oleic acid (total 5 vol.% in isooctane) catalyzed by CRL (1 mg/mL) in biphasic or Pickering emulsion systems with an equal volume of isooctane and water at 30 °C. (a) Yield in two different systems for 1 h, (b) yield in the Pickering emulsion (0.6 mM DMA-CO_2, 0.5 wt.% silica) as a function of reaction time; inset shows the appearance and microscopy image of the emulsion.

We further assessed the separation and recyclability of the Pickering emulsion for the enzymatic reaction of the hydrolysis of olive oil. As shown in Figure 6(a), the Pickering emulsions were demulsified by bubbling N_2 for 40 min at the end of the reaction (Figure S14) at room temperature. The cationic bicarbonate surfactant (DMA-CO_2) was then turned to its neutral state (DMA), which can no longer adsorb at particle surfaces rendering silica nanoparticles hydrophilic or surface-inactive. The silica particles thus desorb from the oil-water interface and enter the aqueous phase resulting in demulsification. The conversion of the DMA-CO_2 to DMA has been proven by conductivity (Figure S2) and ^{1}H-NMR (Figure S3) measurements. The zeta potential of the silica nanoparticles (Figure S4) is also the evidence of desorption of the surfactant from the particles by bubbling with N_2. In the absence of CO_2, the zeta potential of the particles remained almost unchanged with increasing DMA concentration. This indicates that the surface charge of the silica nanoparticles was changed by adsorption of the cationic ammonium surfactant, but not the neutral DMA.

After demulsification, both the enzyme and particles were retained in the aqueous phase whereas a trace of inactive DMA together with the product dissolved in the upper oil phase. Isooctane was then collected by evaporation of the oil phase. The inactive "surfactant" DMA was separated and collected by rinsing the crude product (such as fatty acid) with carbonated water for three times. The aqueous phase containing enzyme and particles was directly utilized for the next reaction cycle (Figure S14(c)). As shown in Scheme 1, isooctane and DMA were added into the recycled aqueous phase. The Pickering emulsion was reformed by bubbling CO_2 through the oil-water mixture (Figure 6(b)) at 25 °C for 10 min followed by re-homogenization for 2 min (Figure 6(c)), and the enzymatic reaction was carried out as before. It was observed that the hydrolysis conversion decreased by about 5% after each cycle. Nevertheless the conversion in the 6th cycle was still as high as 65% (Figure S16). Therefore, the enzyme in the recycled Pickering emulsion maintained significant catalytic activity. The decrease in conversion during the recycling process might be attributed to deactivation of CRL by silica and surfactant.[49-52]

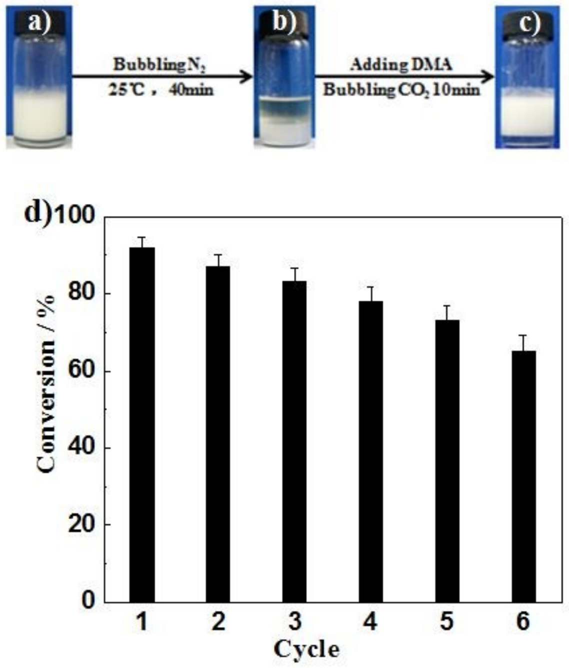

Figure 6. (a) Digital photograph of CO_2-switchable Pickering emulsion (for olive oil hydrolysis) after reaction for I h, (b) after bubbling N_2 for 40 min at 25 °C, (c) after adding fresh oil and DMA, bubbling CO_2 for 10 min and homogenization for 2 min, (d) hydrolysis conversion of olive oil in 6 cycles.

Compared with other separation methods for Pickering emulsions such as centrifugation or ultrafiltration,[30] the strategy of using N_2/CO_2 enables facile addition for large-scale operation in industrial production, which does not need special or expensive equipment. Demulsification and recycle of the enzyme and particles can be achieved by bubbling N_2 at ambient temperature. Furthermore, both the surfactants separated from oil phase and the CO_2-switchable Pickering Emulsion reaction system can be effectively reformed via CO_2 trigger.

Conclusions

In summary, enzymatic hydrolysis and esterification reactions have been successfully performed in a CO_2/N_2-stimulus-responsive Pickering emulsion. The catalytic performance of the enzyme lipase is remarkably promoted in the Pickering emulsion stabilized by silica nanoparticles hydrophobized *in situ* by the switchable surfactant *N*,*N*-dimethyldodecylamine. Demulsification and the recycling of aqueous solution of the enzyme and particles can be easily achieved via N_2trigger. The CO_2-switchable Pickering emulsion reaction system can be effectively reformed by bubbling CO_2, which still maintains significant catalytic activity yielding higher reaction efficiency than that of biphasic system. It is anticipated that this novel protocol to immobilize an enzyme in a Pickering emulsion without complicated surface grafting of particles may provide an important industrial route to conduct enzyme reactions of high efficiency and multi-recyclability. Of course, further studies on CO_2/N_2-switchable Pickering emulsions in the case of more vulnerable enzymes are important and are underway in our labs.

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