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Decorateable hybrid film patches stabilized Pickering emulsions and their catalytic applications

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The CNTs/Fe$_3$O$_4$/ODTS/PDDA hybrid film patches were fabricated and used to stabilize Pickering emulsions (PEs). Their hydrophilic sides were modified with Pd nanoparticles taking the advantage of rupture-reform property of PEs. Pd nanoparticles modified hybrid film patch stabilized PEs exhibited great performance on hydrogenation of acetone.

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ABSTRACT

We demonstrated a method to fabricate functional hybrid film patches, which were used for Pickering emulsion (PE) formation. The hybrid patches were made of carbon nanotubes, Fe3O4 nanoparticles, octadecyltrimethoxysilane (ODTS), and poly(diallyldimethylammonium chloride) (PDDA). The aqueous phase of hybrid patch stabilized PEs can be easily separated by applying magnetic fields. The hybrid film patches stabilized PEs are so stable as to survive for 8 months at room temperature. The patches stabilized PEs are easily ruptured by adding ethanol, and regenerated by vortexing the patches in aqueous/oil mixtures, which enables the inner hydrophilic side of the patches easily to be modified with metal nanoparticles. As an example, the palladium nanoparticles were embedded into the surface of the hybrid patches using in situ reduction method. The Pd functionalized patches formed PEs showed an excellent catalytic performance of hydrogenation of acetone with a yield of 99.5%. The same batch of Pd functionalized patches was recycled 13 times without losing their catalytic activities. The hybrid patches formed PEs have a great potential in catalytic field.
etherification of an aldehyde[4]. Zhou et al. exploited the Au-carbonaceous spheres formed Pickering emulsion to reduce p-nitroanisole by sulphide to p-anisidine with the conversion yield up to 96% within 5 h [15]. Other examples of the PE interfacial catalysis includes using Ru/CNT-TiO2 complex to catalyze benzaldehyde[16], and Ag3PO4–MWNT complex to photocatalyze H2O to O2 [17].

Adsorption of solid particles at the oil–water interface requires the partial wetting of the particles by water and oil [18]. Many types of particles, such as titania [19, 20], silica [21, 22], clay [13, 23], Fe3O4 [13, 24], CNTs [4, 14], and organic materials [25, 26], fulfill the partial wetting condition for most common oils. Pickering emulsions can also be stabilized by bio based material such as bacteria [27], botanical spore [28]. Compared with spherical particles, the PEs made of hybrid film patches are more stable, since the rotation of hybrid patches at the PE interface is greatly restricted. Hybrid film patches as building blocks are easier to modify and recycle due to their larger surface area. These advantages make them suitable for catalysis application. So far there are few reports on forming Pickering emulsion using large scale film patches as building blocks [29].

Herein, we combined polymerization and electrostatic methods to obtain stable CNTs/Fe3O4/ODTS/PDDA hybrid film stabilized Pickering emulsions. Interestingly we found that those emulsions could rupture and form hybrid film patches upon addition of ethanol, and reform emulsions after adding water and hexane mixture by vortexing. This property allows us to flexibly modify the inner side of the hybrid film and change the aqueous contents of the Pickering emulsions. In order to demonstrate it, we decorated the inner side of the film with Pd NPs, which showed excellent catalytic activity towards hydrogenation of acetone. Therefore they can find great potential in catalysis field.

2 Experimental

2.1 Materials

n-hexane, toluene, and chloroform were provided by Xilong Chemicals (China). PdCl2 was purchased from Shanghai Boka Company (China). Ethylene glycol, sodium hydroxide and sodium acetate were purchased from Sinopharm Chemicals (China). Octadecyltrimethoxysilane (ODTS), FeCl3·6H2O and poly(diallyldimethylammonium chloride) (PDDA) were purchased from Sigma-Aldrich (China). Ultrapure water (18.2 MΩ·cm, Millipore Co., USA) was used in all experiments. Carbon nanotubes (CNTs) were purchased from Chengdu Organic Chemicals (China).

2.2 Synthesis of iron oxide nanoparticles

Iron oxide nanoparticles were synthesized through the solvothermal reaction according to the previous reports [30,31]. Typically, 1.5 g of FeCl3·6H2O and 4.5 g of sodium acetate were dissolved in 30 mL of ethylene glycol under magnetic stirring. After vigorously stirred for 30 min, the obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave. After 8 h at 200 °C, the autoclave was cooled to room temperature naturally. The obtained black magnetite particles were isolated by magnetic decantation, washed with ethanol, and then dried in vacuum at 60 °C for 12 h.

2.3 Surface functionalization of CNTs

Chemical oxidation of CNTs was carried out using 3.0 M nitric acid in order to functionalize CNTs with hydroxyl groups, which is required for further silanization. 0.2 g of the agglomerated CNTS was mixed with 50 mL 3.0 M acid solutions under sonication at 60 °C for 15 min [32]. Then the slurry was filtered and thoroughly washed with distilled water, followed by drying in a convection oven at 150 °C for 4 h.

2.4 Preparation of Pickering emulsions

The hydrophilic CNTs and Fe3O4 NPs were transferred into hexane phase by silanizing them into ODTS-capped CNTs and ODTS-capped Fe3O4 NPs,
i.e. 0.9 mg CNTs and 0.1 mg Fe$_3$O$_4$ were added into 1.0 mL hexane containing 10 μL ODTS, followed by 15 minute sonication.[33]. The silanization of CNTs renders CNTs more hydrophobic, which is good for hybrid film formation. The resulting oil phase contains ODTS-capped CNTs, ODTS-capped Fe$_3$O$_4$ NPs, and unreacted ODTS. It was then mixed with certain volume of PDDA aqueous solution (4 μL/mL) by vortexing for 1 min. Consequently CNTs/Fe$_3$O$_4$/PDDA/ODTS hybrid film protected water in oil emulsions were formed.

2.5 Hybrid film patches formation and their modification with Pd nanoparticles

After removing the hexane by magnetic separation, the CNTs/Fe$_3$O$_4$ NPs/ODTS/PDDA film stabilized droplets kept stable in the air. Upon addition of ethanol the droplets can rupture into small patches. Replacing the ethanol / water solution with 300 μL of 0.012 M H$_2$PdCl$_4$ and as water phase and 1 mL hexane as oil phase, the emulsion was reformed by vortexing for 1 min, which were kept at room temperature overnight for PdCl$_4^{2-}$ adsorption on the inner surface (aqueous side) of the film. After that, inner aqueous solution was replaced by ascorbic acid (0.06 M) by “rupture – reform” process as mentioned above. The Pd NPs were formed on the hydrophilic side of the film after 12 hours at room temperature (25 °C).

2.6 Catalyzing test of the functionalized emulsions

The hydrogenation of acetone was done using Pd NPs modified hybrid film patches stabilized emulsions. Pd NPs modified patches (2 mg) were mixed with 0.5 mL of NaBH$_4$ aqueous solution (0.1 mM) and 3 mL of hexane to reform the emulsion by vortex for 1 min. Acetone (10 μL) was added into the emulsion solution under gently shaking at room temperature. The catalyzing reaction was monitored using Cary 5000 Scan UV-Vis-NIR spectrophotometer (Varian, USA). To confirm the formation of isopropanol by hydrogenation of acetone, we carried out a gas chromatography analysis using an Agilent 7890A GC instrument equipped with flame ionization detector (FID). Analytes were separated by a HP-INNOWax fused silica capillary column (30 m × 0.25 μm i.d., 1.0 μm film thickness). Nitrogen (purity 99.999%) was used as the carrier gas at the flow rate of 6.0 mL min$^{-1}$. The instrument was operated under constant temperature of 55 °C. The yield of isopropanol was then obtained from the change of acetone concentration calculated using the relation,

$$\frac{C_i - C_f}{C_i} \times 100\%$$

where $C_i$ and $C_f$ were the initial and final concentrations of acetone, respectively.

2.7 Characterizations

Fourier transform infrared spectra (FTIR) were acquired from a Thermo Scientific 50 Nicolet iS10 spectrophotometer. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were obtained using a Nova NanoSEM600 (FEI, The Netherlands) instrument. For SEM imaging, the thin films were deposited onto Si substrates. X-ray diffractograms (XRD) were recorded using a Rigaku Smart Lab diffractometer equipped with parallel beam optics and Cu-Kα radiation (40 kV, 100 mA) was incident at a grazing angle of 0.3°. A Cary 5000 Scan UV-Vis-NIR spectrophotometer (Varian, USA) was used for UV-Vis spectra measurements. Optical images of emulsion droplets were taken by a Nikon 80i fluorescence microscope. The average size of emulsion droplets was obtained by processing the image using the image J analysis software (Version 1.44p, USA).

3 Results and discussion

The Pickering emulsions (W/O) were stabilized by a hybrid film containing CNTs, Fe$_3$O$_4$ NPs, ODTS and PDDA. Small amount of Fe$_3$O$_4$ NPs (wt_CNTs : wt_NPs = 9 : 1) were introduced into the interface to enable the magnetic property of the emulsions. The microscopic images of these emulsions are shown in Fig. 1a. After applying the magnetic field, the aqueous droplets were collected at the magnet side, as shown in Fig. 1b. The more detailed information on emulsion droplets moving in the magnetic field was shown in Fig. S1 and a video in supporting
information. The insets in Figure 1a and b are the sample photos before and after applying magnetic field respectively. The homogeneously dispersed emulsion droplets accumulated towards the inner side wall of the vial when the external magnetic field was applied. The morphology of the CNTs/Fe₃O₄/PDDA/ODTS hybrid film was characterized using SEM. From Fig. 1c, it is noted that the Fe₃O₄ NPs are embedded in the carbon nanotube networks. In order to further confirm the spheres to be Fe₃O₄ NPs, the same region was observed using a backscattered electron detector as shown in Fig. 1d. Since heavy elements backscatter electrons more strongly than light elements, the bright dots in Fig. 1d are Fe₃O₄ NPs. The thickness of hybrid film patch was measured to be approximate 400 nm, as shown in Fig. 1e.

The chemical composition of the hybrid film was investigated by IR spectroscopy. Fig. 1f shows the infrared spectra of CNTs/Fe₃O₄/ODTS/PDDA film (black curve) and CNTs/Fe₃O₄ film (red curve) respectively. The wave number region between 4000 and 400 cm⁻¹ covers the frequencies of the entire IR characteristic vibrations of the films. Compared with the red curve, the absorption bands at 1636 cm⁻¹ (C=C) and 1466 cm⁻¹ (C=C) in the black curve correspond to the characteristic bands of PDDA, while 1191 cm⁻¹ (Si–O–C), 1089 cm⁻¹ (Si–O–Si), 815 cm⁻¹ (Si–C), 721 cm⁻¹ (Si–C), 660 cm⁻¹ (Si–C) are attributed to the presence of ODTS.

The Pickering emulsions (w/o volume ratio, 0.3 mL: 1 mL) were initially stabilized only by CNTs and Fe₃O₄ (weight ratio of 9:1). But they were not stable when additional water (1 mL) was introduced to emulsion, as shown in Fig. 2a. The droplets broke and merged into aqueous phase. The similar situations happened when using only CNTs or Fe₃O₄ to stabilize PEs, as shown in Fig. S2. When 1% ODTS and PDDA (0.4 v%) was introduced into hexane and water phase initially respectively, the Pickering emulsion (w/o volume ratio, 0.3 mL: 1 mL) became very stable, as shown in Fig. 2b. The emulsion droplets sit on the bottom of the hexane phase without any damage. The control experiments with only PDDA (Fig. 2c) or ODTS (Fig. 2d) indicated that the emulsions were not stable. The functions of ODTS are twofold. One is the silanization of CNTs and Fe₃O₄ make them more hydrophobic, which is good for PE stability. Due to the presence of hydroxyl groups on CNTs and Fe₃O₄ NPs, they are easily modified with ODTS[33]. The other is ODTS molecules hydrolyze at the oil/water interface and then forming polymers. The positively charged PDDA in the aqueous phase binds to the negatively charged ODTS polymers, which further strengthen the emulsion stability. The concentration of PDDA was optimized as shown in Fig. S3. The PEs became stable at PDDA concentration over 4 μL/mL.
Figure 2  The stability of the CNTs/Fe3O4 stabilized Pickering emulsions at the interface between water and hexane with a) no PDDA and ODTS, b) PDDA and ODTS, c) PDDA but no ODTS, d) ODTS but no PDDA. Water to oil ratio (0.3 mL: 1 mL) and the amount of the stabilizing particles (0.9 mg CNTs and 0.1 mg Fe3O4) were kept same for all conditions.

The size of Pickering emulsion droplet depends on oil to water ratio. Figure 3a-c show microscopy images of emulsions prepared by the water / oil ratio of 0.1, 0.4 and 1.2, respectively, while keeping the amount of CNTs and Fe3O4 to be 2 mg. It is noted that the size of emulsion droplet increases with increasing water volume fraction. Fig. 3d summarizes the size distributions at each water / oil ratio, and the size dependency on the water/oil volume ratios. The size increases gradually from 45.48 ± 17.67 to 373.95 ± 178.94 μm with the increase of water / oil ratio from 0.025 to 1.4. The size distribution at each ratio was statistically obtained by measuring large number of emulsion droplets. When the ratio is over 1.4, the droplet is too large to be stable.

Figure 3  Microscopic images of hybrid film stabilized Pickering emulsions with different water/oil ratios: a) 0.1, b) 0.4, and c) 1.2. d) PE size distributions as a function of water/oil ratio. Scale bars are 100 μm.

Interestingly, we found that Pickering emulsion droplets could rupture into small patches upon addition of ethanol, and could re-form emulsions by adding water/hexane solution, as shown in step 1 and 2 in Fig. 4a. Fig. 4b shows the optical image of the CNTs/Fe3O4/ODTS/PDDA hybrid film patches. The rupture-regeneration property of the emulsions gives a lot of opportunities on their applications. The inner aqueous phase can be easily changed. The patches can be easily modified with other particles to enable the emulsion to possess new functions. The patches can be easily recycled after reactions due to the magnetic property.

In order to demonstrate the replacement of inner phase, we chose 0.1 wt% rhodamine B as aqueous phase during the reformation. Fig. 4c and d are the bright field and fluorescent microscopy images of reformed Pickering emulsions, respectively. Figure 4d confirmed the rhodamine B solution was wrapped inside the emulsions. From Fig. 4b and c, the average patch area is about 0.018 mm² obtained by area measurement function of ImageJ software, and average PE droplet area is about 0.092 mm². Therefore simple calculations indicate that fewer patches can cover the same interfacial area than particles, meaning that the hybrid film patches are more efficient to stabilize emulsions. Hybrid film patches stabilized PE remains stable for at least 8 months at room temperature, as demonstrated in Figure S4.

The rupture mechanism of PEs upon ethanol addition is probably due to the deduction of surface tension of hybrid film at the oil/water interface.[34] The patch is presumed to be hydrophilic on one side and hydrophobic on the other. By adding water / hexane phase, they stabilize water droplets in hexane phase after shaking.
Figure 4  a) Schematic illustration of PE rupture (step 1), regeneration (step 2). b) The microscopy image of hybrid film patches in ethanol solution. The bright field c) and fluorescence d) microscopy images of the patches formed PEs with inner solution of 5 μg mL⁻¹ rhodamine B solution.

Pickering emulsions are good medium for catalysis reactions[4]. In order to do this, we need to modify the emulsion with catalyst at the interface. The rupture-regeneration property of the emulsion makes this modification very easy. The inner sides (PDDA side) of hybrid patches were modified with Pd NPs using in situ reduction method. In circled area of Fig. 5a the small bright dots on the CNT matrix are Pd NPs. The SEM image of the same area (Fig. 5b) using a backscattered electron detector shows the Pd NPs more clearly. Energy-dispersive spectroscopy (EDS) shows Pd element and gives its content of 2.58 wt%, as shown in Fig. 5c. The existence of Pd NPs on the patch is also confirmed by X-ray diffraction analysis as shown in Fig. 5d and Fig.5S. The peaks in the spectrum at the 2θ of 38.4°, 45.2° and 68.0° agree well with JCPDS card No. 05-0681 for the powder diffraction file (PDF) of face-centered-cubic -phase Pd crystal, where peaks at 2θ = 40.0, 46.5 and 68.0 are associated with the (111), (200) and (220) planes, respectively. According to the Scherrer equation, the average size of the Pd NPs is also evaluated to be 11 nm using the diffraction peak of (111) lattice plane. Two peaks at 2θ of 25.9° and 44.5° correspond to the CNTs in hybrid patches. The characteristic diffraction peaks, located at 30.0°, 35.4°, 43.1°, 51.5°, 56.9° and 62.5°, implies that the Fe₃O₄ NPs possess typical inverse spinel structure [9].

Figure 5 SEM images of Pd NPs modified hybrid film patches a) using a secondary electron detector, and b) using a backscattered electron detector. c) and d) are EDS spectrum and XRD spectrum of Pd NPs modified hybrid film patches. The content of Pd element is 2.58%. The symbols of ◆, ♣, and ♥ indicate the peaks for CNTs, Fe₃O₄ NPs and Pd NPs, respectively.

The hydrogenation of acetone in the oil/water biphasic system was chosen to demonstrate the catalysis activity of Pd NPs modified hybrid patch reformed Pickering emulsion. NaBH₄ acted as a hydrogen resource. 0.015 g, 0.025 g and 0.035 g Pd NPs modified CNTs/Fe₃O₄/ODTS/PDDA patches were used to reform the Pickering emulsions, which show different reaction yields as shown in Fig. 6a. The data in Fig. 6 were obtained from 4 repeats. The production of isopropanol was confirmed using chromatogram technique as shown in Fig. S6. The maximum isopropanol yields obtained from 0.015 g, 0.025 g and 0.035 g reformed Pickering emulsions are 77.1%, 83.1%, and 99.5%, respectively. According to the leveling off point in Fig. 6a, the reaction finished within 20 minutes. As a control, the yield is only 54.6% when those hybrid patches sitting on the water/oil interface without forming PEs. This demonstrates the advantages of Pickering emulsion on converting acetone to isopropanol. This is also an example of obtaining high conversion yield using catalyst loaded PEs.[15,16] The reason for that is due to the larger surface area after reforming the Pickering emulsions. The
catalyst can be recycled and reused 13 times without losing its catalytic activity, as shown in Fig. 6b.

Figure 6  
(a) Time-dependent yield of isopropanol in PE catalytic system formed with 0.015 g, 0.025 g and 0.035 g Pd functionalized patches;  
(b) The recycling results of Pd functionalized patches formed PEs on catalyzing hydrogenation of acetone.

4 Conclusions

In conclusion, the CNTs/Fe3O4/ODTS/PDDA hybrid film patches were fabricated by ethanol triggered rupture of corresponding Pickering emulsions. The patches were modified with Pd nanoparticles using in situ reduction method, which could be extended to other noble metal nanoparticle modification. As an example, the Pd functionalized patches formed PEs was applied to catalyze the hydrogenation of acetone to isopropanol. This system effectively converted the acetone to isopropanol with a yield as high as 99.5% for only within 20 min without producing any other by-product, which reflects the high selectivity of the system. The Pd functionalized patches were recycled 13 times for the same reaction with negligible catalyst loss. It confirmed the potential of hybrid film patches formed PEs in catalytic field.

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References


Electronic Supplementary Material

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Figure S1 Microscopy images of the CNTs/Fe$_3$O$_4$/PDDA/ODTS hybrid film stabilized Pickering emulsions before (a), after (b, c) applying magnetic field. Image b and c were taken at different time.

Figure S2 The stability of only CNTs (a, 0.9 mg) or Fe$_3$O$_4$ (b, 0.1 mg) stabilized Pickering emulsions after introducing 1 ml water. Water to oil ratio is 0.3 mL: 1 mL.
Figure S3. Photographs of 1 mL hybrid film stabilized water-in-oil emulsions prepared with various PDDA concentrations in aqueous phase mixed with 1 mL water. Oil to water volume ratio is 1 mL: 0.3 mL.

Figure S4. The microscopy images of hybrid film stabilized PEs just after the preparation (a) and 8 month after the preparation. Scale bar is 100 µm.

Figure S5. XRD spectra of Pd NPs modified hybrid film patches (a), Fe₃O₄ NPs (b), and CNTs(c). The symbols of ◆, ♣, and ♥ indicate the peaks for CNTs, Fe₃O₄ NPs and Pd NPs, respectively.
Figure S6 Representative chromatogram of acetone (a) and isopropanol (b) in a ultrapure water at optimized conditions by gas chromatography. (c) The products during the hydrogenation of acetone catalyzed by Pd NPs modified hybrid film stabilized PE. The experimental conditions are explained in the “Experimental section”.