

Multiple Pickering emulsions stabilized by surface-segregated micelles with adaptive wettability

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Experimental Section

Materials

2-(dimethylamino) ethyl methacrylate (DMAEMA, Aladdin, 99%) and benzyl methacrylate (BzMA, Aladdin, 98%) were first vacuum distilled from CaH₂ and then stored under a nitrogen atmosphere at -20 °C. Ethylene glycol dimethacrylate (EGDMA, Aladdin, 98%) was purified by passing through a neutral alumina column to remove inhibitors. Dichloromethane (DCM, 99%) was dried over CaH₂ and distilled prior to use. AIBN (Aldrich) was purified by recrystallization twice from ethanol. Tetrahydrofuran (THF, 99.5%) was distilled under nitrogen atmosphere from Na/benzophenone immediately prior to use. The 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized as reported.¹ All the following materials were

used as received without further purification: Monocarbinol-terminated poly(dimethylsiloxane) (PDMS-OH, DP = 60, Sigma-Aldrich), *N, N'*-dicyclohexylcarbodiimide (DCC, Sigma-Aldrich, 99%), *p*-nitroanisole (Aladdin, 98%), Nile red (Aladdin, 95%). Anhydrous isopropanol (99.5%), 4-(dimethylamino) pyridine (DMAP, 99%), methyl iodide (99.5%) and PdCl₂ (99%) were purchased from Energy Chemical. Toluene (99.5%) was purchased from Guangzhou Chemical Reagent Factory. Methanol (99.5%) was purchased from Shanghai Runjie Chemical Reagent Co., Ltd (Shanghai, China). NaBH₄ were obtained from Chengdu Kelon Chemical Reagent Factory.

Methods

Synthesis of SSMs micelles

SSMs consisting of PDMAEMA, PDMS and PBzMA were synthesized by polymerization induced self-assembly (PISA) as shown in Scheme 1. Dispersion polymerization of benzyl methacrylate in isopropanol was performed at 65 °C with the weight percent of feed monomer with two macro-CTAs at 11%. In a typical polymerization, [BzMA]₀: [D₆₀-CTA+E₄₆-CTA]₀: [AIBN]₀=400: 2: 0.4, in which [D₆₀-CTA]₀: [E₄₆-CTA]₀ = 1: 4. D₆₀-CTA (0.124 g, 0.025 mmol), E₄₆-CTA (0.760 g, 0.100 mmol), BzMA (4.400 g, 0.025 mol), AIBN (4.0 mg, 0.025 mmol) and 1, 3, 5-trioxane (internal standard, 158.4 mg, 1.76 mmol) all dissolved in isopropanol (54.5 mL) were added into a 250 mL round bottle flask with a magnetic bar. The flask content was vigorously stirred for 5 min and degassed with nitrogen for 30 min, and then the polymerization was initiated by immersing the flask into a preheated oil bath at 65 °C for 30 h. An aliquot of the reaction solution was extracted for GPC and ¹H NMR. EGDMA was

introduced into the flask under nitrogen using a syringe. Crosslinking was allowed to occur for another 4 h. The reaction was stopped by cooling to room temperature and exposing to air. In order to examine the obtained self-assembled nano-objects, the samples were diluted by isopropanol, and then subjected to DLS and TEM analysis.

Preparation of Pd-coated [D₆₀/(E₄₆)₄]-B₁₉₅ hybrid nanoparticles

The nanoparticles loaded palladium were *in situ* prepared by the reduction of the inorganic salt precursor with NaBH₄ as reductant. The detail of loading the Pd nanoclusters was given as following: The pre-prepared 1.50 g of [D₆₀/(E₄₆)₄]-B₁₉₅ nanoparticles isopropanol dispersion was first diluted with 75.0 mL of isopropanol under continuous stirring. And then, 8.6 mg of PdCl₂ (4.8×10^{-5} mol Pd) in 12.5 mL of methanol solution was added dropwise, and the mixture was further stirred for 1 h at room temperature. Subsequently, 37.5 mL of freshly prepared cold NaBH₄ (1.9×10^{-3} mol) aqueous solution was added dropwise into the above dispersion. After 10 h of stirring, the solid was isolated by centrifugation and thoroughly washed by turns with water and methanol until the supernatant was clear. After being dried under vacuum, the solid catalyst was achieved, which was denoted as Pd/[D₆₀/(E₄₆)₄]-B₁₉₅.

Emulsion Preparation.

Emulsion samples were prepared using equal volume of toluene and deionized water at [D₆₀/(E₄₆)₄]-B₁₉₅ or Pd/[D₆₀/(E₄₆)₄]-B₁₉₅ nanoparticles concentration of 0.15 wt% of the total mass of oil and water. Nanoparticles toluene solutions were first prepared. 0.1 M HCl and 0.1 M NaOH solutions were used to prepare aqueous solutions at different pH values. A polymer-containing oil (2.0 mL) and an aqueous solution (2.0 mL) were placed in contact at room temperature overnight before emulsification. The total emulsion volume was kept at 4 mL for

all samples. All of the pH values reported in this work were measured after overnight contact between both phases. Emulsions were then obtained by mixing both phases using an Ultra Turrax T25 homogenizer (10 mm head) operating at 15,000 rpm for 120 s. However, it was unknown whether the $[D_{60}/(E_{46})_4]$ -B₁₉₅ emulsifier was present in form of assemblies or individual copolymer chains, since the polymeric nanoparticles were uncrosslinked. Therefore, the following experiments were carried out to verify. When pH = 2, the sizes of the emulsions were measured by changing the concentration of the emulsifier particles (0.15 to 1.00 wt% of the total mass of oil and water).

Interfacial Catalytic Reduction of *p*-nitroanisole by NaBH₄.

Toluene (2 mL) containing *p*-nitroanisole (30 mM) and Pd/ $[D_{60}/(E_{46})_4]$ -B₁₉₅ and aqueous (2 mL) with different pH were charged into 10 mL of a clean glass vial at room temperature. The content of Pd/ $[D_{60}/(E_{46})_4]$ -B₁₉₅ was 0.15 wt % versus the total weight of both oil and water for the formation of Pickering emulsion. The pH of aqueous solutions was adjusted to the required value with 0.1 M HCl and 0.1 M NaOH solutions. Pickering emulsion was generated by homogenization making use of an Ultra Turrax T25 homogenizer (10 mm head) operating at 15,000 rpm for 2 min. Then, excess NaBH₄ (0.36 M) aqueous solution was added into Pickering emulsion accompanying gentle stirring. After 6 hours of reaction and complete phase separation by centrifugation, the Pd/ $[D_{60}/(E_{46})_4]$ -B₁₉₅ nanoparticles gathered at the biphasic interface between toluene containing *p*-nitroanisole/*p*-anisidine and aqueous solution. The upper oil phase was carefully collected, purged with nitrogen and dried in vacuum. Yields were determined by ¹H NMR.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance400 spectrometer at ambient temperature. Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm).

Gel Permeation Chromatograph (GPC), a Waters 1515 gel permeation chromatograph equipped with a RI 2414 detector to determine the number average molecular weight (M_n) and polydispersity index (M_w/M_n). Monodispersed polystyrene standards were used in the calibration and 95% v/v THF, 3% v/v trimethylamine and 2% v/v hexafluoroisopropanol was used as an eluent at a flow rate of 1.0 mL/min. Samples were dissolved in THF and passed through 0.25 μm filters before each measurement.

Dynamic light-scattering (DLS) measurements using a Malvern Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) at 25 °C and a scattering angle of 90° was used to determine the size characterization of the samples. The particle size in isopropanol was measured by directly diluting the dispersion to 0.1 wt%. After dialyzing isopropanol dispersion with water, the aqueous dispersion was obtained and diluted to 0.05 wt%. The hydrodynamic diameter of nanoparticles in water was measured at different pH. It was unstable to disperse the particles directly in water, while stable aqueous dispersion can be maintained by dialysis.

Zeta potential measurement was used a Malvern Zetasizer Nano ZS (Malvern Instruments, Malvern, UK). The zeta potentials were measured in the capillary electrophoresis cell. Stable aqueous dispersions at different pH were obtained by the same way as above.

Transmission electron microscopy (TEM) images were obtained using JEM-1400 Plus

instrument at 100 kV equipped with a Gatan 1 k CCD camera. The TEM specimen was prepared as follows: one drop of dilute dispersion solution was cast on a copper mesh covered with a thin collodion film coated with carbon, and then drying in air. To discern the PDMAEMA domain, the specimen was stained with CH_3I vapor in a closed bottle for 4 h at room temperature.

Energy-dispersive spectrum (EDS) was taken on JEM-2100F (Joel, Japan) transmission electron microscopy.

Confocal laser scanning microscope images (CLSM) were taken on a Leica TCE SPE DM5500 CSQ VIS confocal system (Leica Microsystems, Germany). Emulsion type was directly observed using Confocal Laser Scanning Microscopy using Nile Red in toluene as a hydrophobic fluorophore and the oil phase appears in red in the pictures. The samples were excited by using a 488 nm He/Ne laser. A droplet of suspension was placed on a glass surface, and visualized directly.

Optical microscopy images were recorded on a Leica DC 300 digital camera connected to a Leica DMLAM microscope with an N PLAN 4 \times /0.40 BD objective. Emulsion droplets were placed directly onto a glass slide and captured under 40 \times magnification.

Contact angles (CA) were measured by using a POWEREACH JC2000D1 contact angle measuring instrument (China). The three-phase contact angle, θ_{ow} , of the $[\text{D}_{60}/(\text{E}_{46})_4]$ -B₁₉₅ nanoparticles was measured using the classic drop shape method.^{2, 3} $[\text{D}_{60}/(\text{E}_{46})_4]$ -B₁₉₅ was carefully ground to fine powder. Then the powder (0.1 g) were pressed into a circular disk using a tablet device (Tianjin Tianguang Optical Instrument Co., Ltd., Tianjin, China) at a pressure of 40 MPa to a thickness of about 1-2 mm. The disk was then placed at the bottom of an open

transparent glass vessel. The contact angle was measured as follows: a certain mass of toluene was carefully poured onto the particle layer. Then, a drop of water of known pH (about 5 μ L) was then slowly placed at the interface of the oil and particle layer with a syringe. Photographs of the drop were successively taken after equilibrium and the contact angle was obtained from the shape treated with appropriate software. The contact angles were determined on three different spots. The values of the contact angle are expressed as mean (\pm standard error).

Interfacial tension (IFT) was measured using contact angle measurement equipment (model JC2000D1, Powereach, China). The aqueous phase at working pH was loaded into a syringe and injected from a syringe to form a droplet at the tip into an optical glass cuvette containing toluene phase. The nanoparticles are dispersed in toluene. Image capture software was used to take an image of the droplet when it equilibrated over timescales of 1 min at room temperature. The digitized images were analyzed and the surface tensions were obtained by fitting the experimental drop profile according to instruction of JC2000D1 software (Powereach, China).

Additional Results

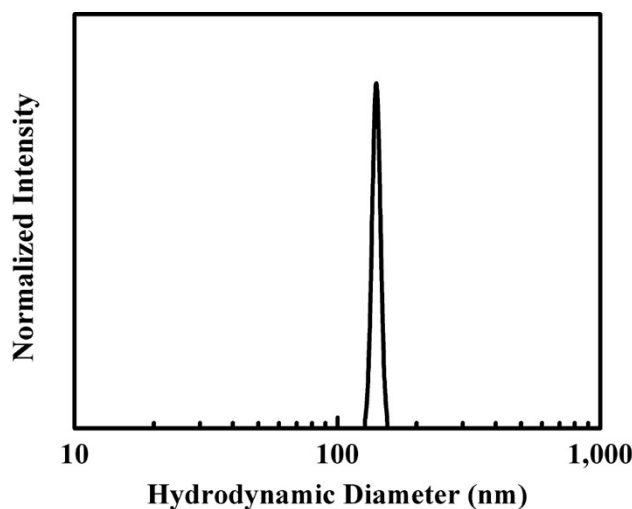


Figure S1. DLS size distribution of $[D_{60}/(E_{46})_4]-B_{195}$ nanoparticles in isopropanol.

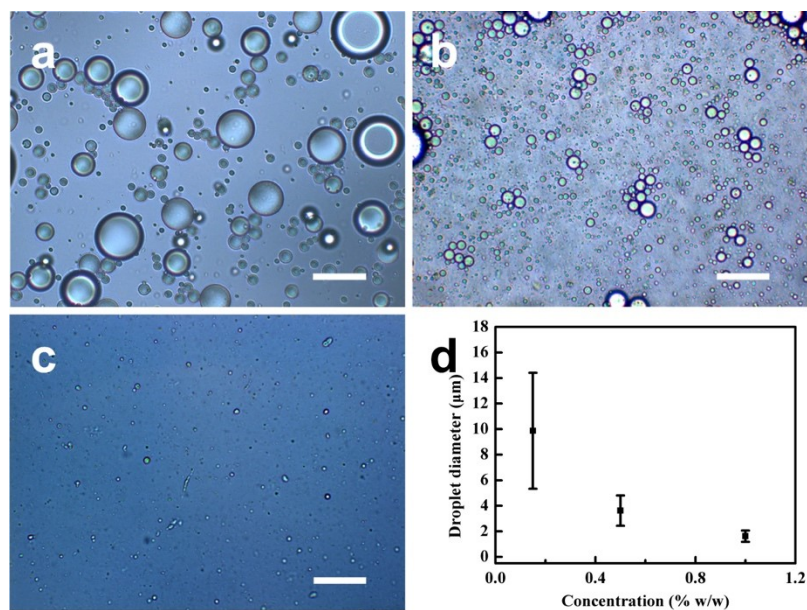


Figure S2. Optical microscopy images for O/W Pickering emulsion stabilized by $[\text{D}_{60}/(\text{E}_{46})_4]\text{-B}_{195}$ nanoparticles with concentrations from 0.15 to 1.00 wt% of the total mass of oil and water (pH = 2), (a) 0.15 wt%, (b) 0.50 wt%, (c) 1.00 wt%. (d) The effect of concentration of micellar aggregates on the droplet size of Pickering emulsions. The scale bars in a, b and c are $30 \mu\text{m}$.

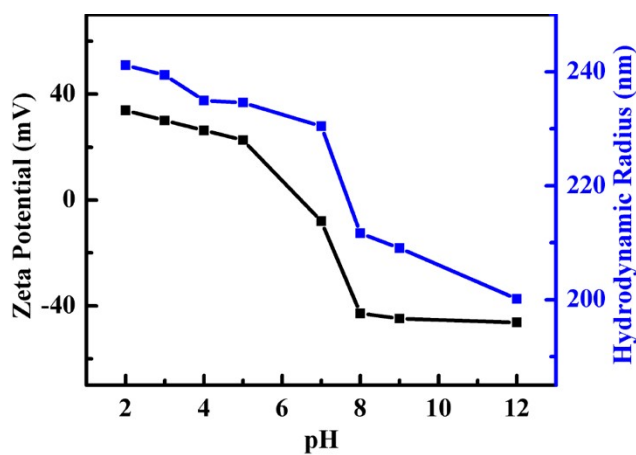


Figure S3. The variation of zeta potential (black line) and hydrodynamic radius (R_h) (blue line) of the $[\text{D}_{60}/(\text{E}_{46})_4]\text{-B}_{195}$ copolymer mixture at different pH values from 2 to 12.

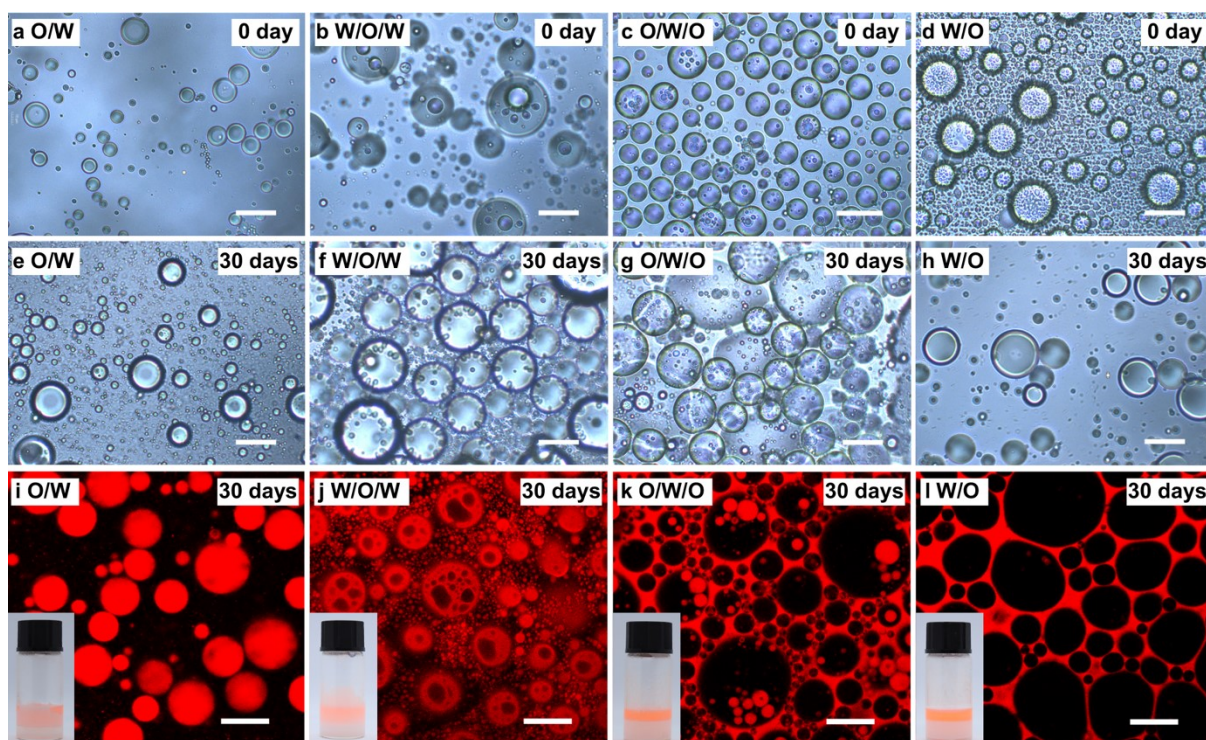


Figure S4. Optical microscopy images recorded for the (a-d) fresh (0 day) and (e-h) aged 30 days of Pickering emulsions stabilized by $[D_{60}/(E_{46})_4]$ - B_{195} nanoparticles. Digital photographs and CLSM images recorded for the (i-l) aged 30 days of Pickering emulsions stabilized by $[D_{60}/(E_{46})_4]$ - B_{195} nanoparticles. Scale bar: $30 \mu\text{m}$.

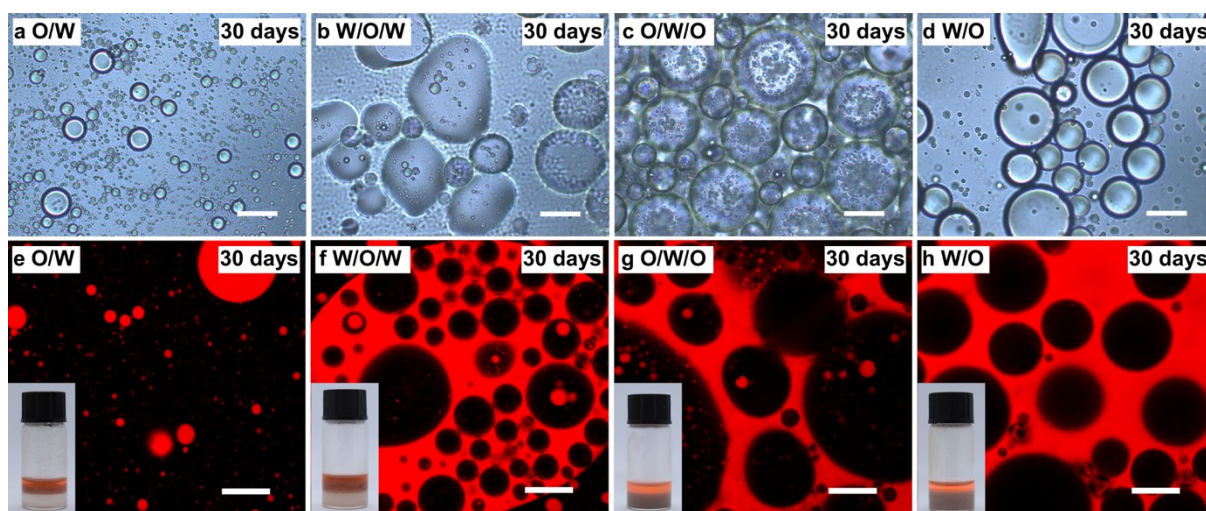


Figure S5. (a-d) Optical microscopy and (e-h) digital photographs and CLSM images recorded for aged 30 days of Pickering emulsions stabilized by $\text{Pd}/[D_{60}/(E_{46})_4]$ - B_{195} nanoparticles. Scale bar: $30 \mu\text{m}$.

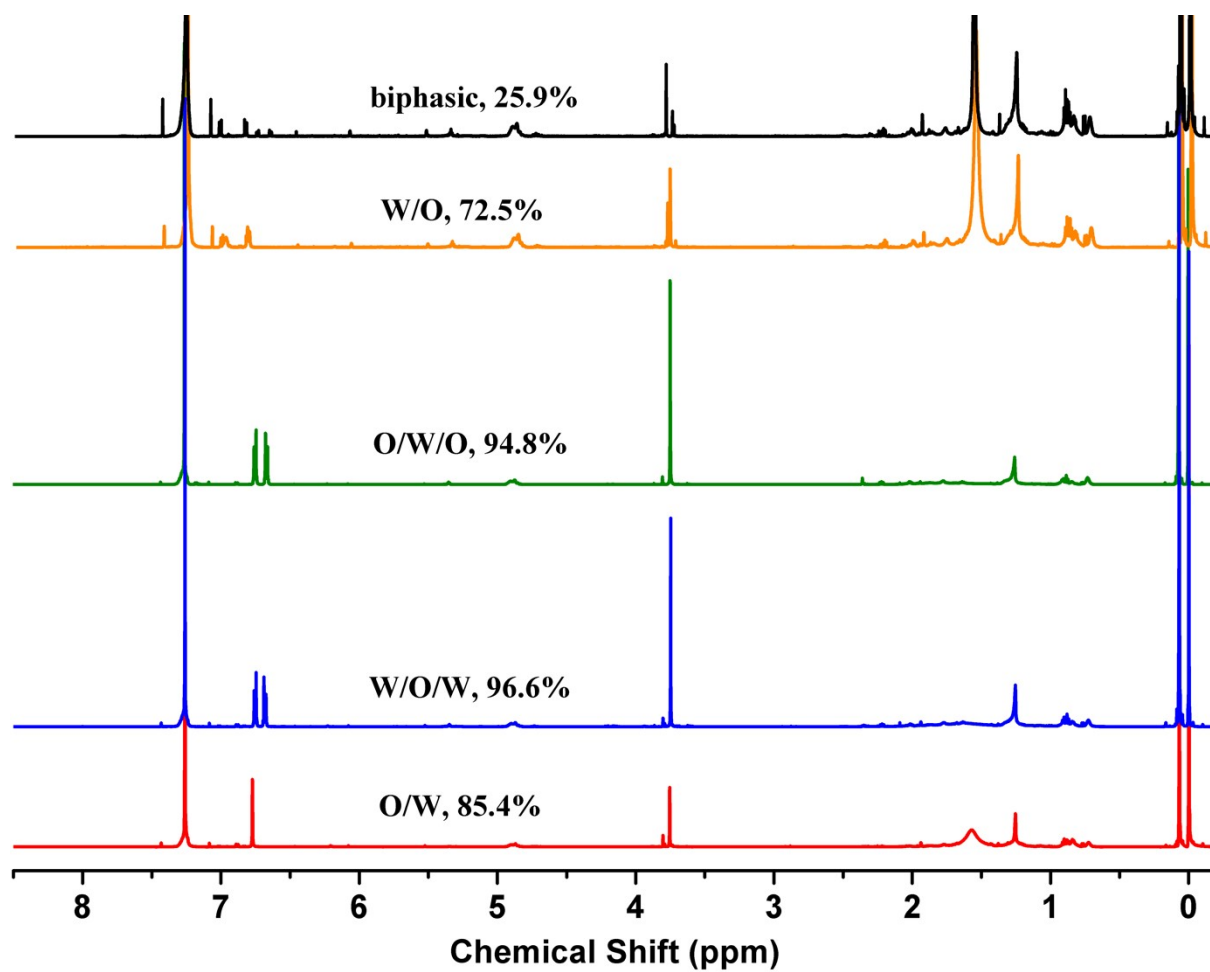


Figure S6. ¹H NMR spectra of *p*-nitroanisole dissolved in toluene in contact with water with at different pH value at 25 °C for 360 min (in CDCl₃). The yields of *p*-nitroanisole were determined from the ratio of peak area of methyl groups, δ3.80 (CH3O-C6H4-NO2), δ 3.75 (CH3O-C6H4-NH2) of ¹H NMR spectra.

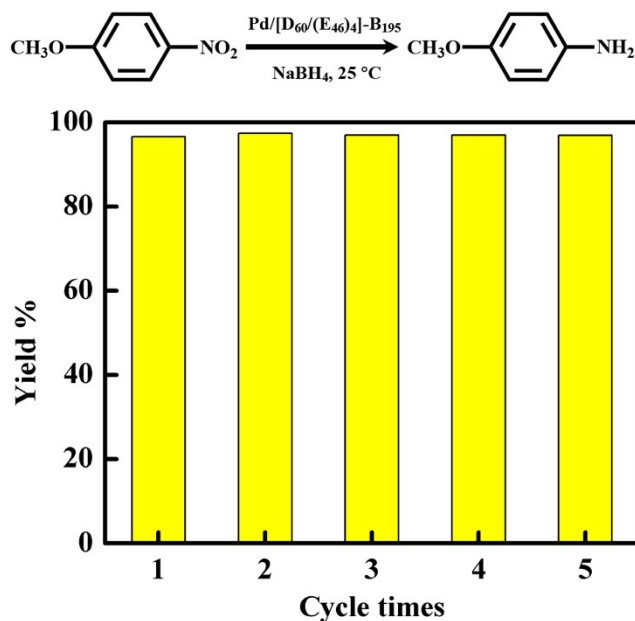


Figure S7. Recycling results for the catalytic hydrogenation of *p*-nitroanisole by interfacial Pd/[D₆₀/(E₄₆)₄]-B₁₉₅ nanoparticles in the W/O/W (water/toluene/water) system at pH=7. Reaction conditions: *p*-nitroanisole (30 mM), NaBH₄ (0.36 M), Pd/[D₆₀/(E₄₆)₄]-B₁₉₅ (5.61 mg), toluene (2 mL), water (2 mL), 25 °C, 360 min. Yields were determined by means of ¹H NMR.

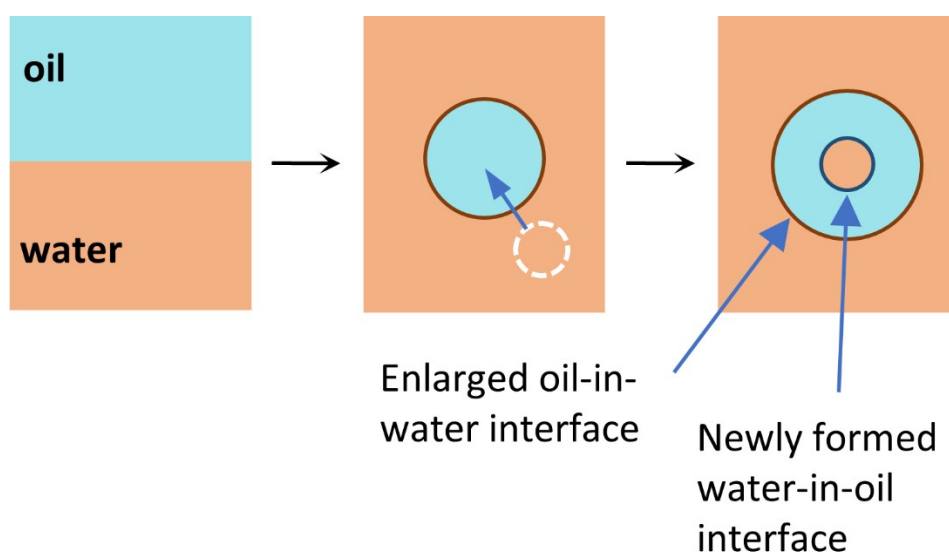


Figure S8. Schematic diagram of changes in interfacial area of O/W and W/O/W emulsions.

Calculation of interfacial areas of prepared emulsions.

The interfacial area (S) of simple emulsions can be calculated by the following equations:

$$S = \frac{6V}{D}$$

where V is the total volume of the dispersion phase, D is the average volume-surface diameter of the emulsion droplets.^{4, 5} For W/O/W multiple emulsions, the interfacial area can be estimated by the following equations:

$$S = \frac{6V_o(D_m^2 + D_i^2 \times n_i)}{(D_m^3 - D_i^3 \times n_i)}$$

Where V_o is the volume of oil, D_m is the average volume-surface diameter of the droplets of multiple emulsions, D_i is the volume-surface diameter of the internal droplets, n_i the average of internal droplets in each multiple emulsion droplet. From Figure 2e and Figure 2f, the interfacial areas of O/W and W/O/W multiple emulsions are 0.95×10^4 and 1.15×10^4 cm², respectively.

Reference

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