Electronic Supplementary Information

Hydrophobized Nanocomposite Hydrogel Microspheres as Particulate Stabilizers for Water-in-Oil Emulsions

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Experimental Procedures

Materials. *N*-Isopropylacrylamide (NIPAm, purity 98%), *N*,*N'*-methylenebis(acrylamide) (BIS, 97%), styrene (99%), potassium peroxodisulfate (KPS, 95%), fumaric acid (FAc, 98%), cyclohexane (98%), 1-butanol, 1-pentanol, 1-octanol, and methyl methacrylate (MMA) were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Decane and hexadecane were used as received from Tokyo Chemical Industry Co., Ltd. Nile Red (97.5%) was purchased from J&K Scientific Ltd. and also used as received. Fluorescein sodium salt was purchased from Sigma-Aldrich and used as purchased. For all experiments, water was distilled and then ion-exchanged (EYELA, SA-2100E1) before use.

Synthesis of Core Microgels.

The parent microgels were synthesized by conventional precipitation polymerization.[1] Initially, 440 mL of water, NIPAm (6.8747 g, 90 mol%), BIS (0.5204 g, 5 mol%), and FAc (0.3918 g, 5 mol%) were poured in a three-neck round bottom flask (1 L) equipped with a mechanical stirrer and a condenser. Next, the monomer solution was heated to 70 °C in a temperature-controlled oil bath and sparged with nitrogen for 30 min to purge the oxygen dissolved. Then, the KPS initiator (0.2433 g, 2 mM) dissolved in 10 mL of water was added to the monomer solution to start the polymerization. Subsequently, after 4 h, the monomer solution was cooled to room temperature and purified twice by centrifugation/redispersion with pure water. In this study, the microgels are denoted as **NF**, where **N** refers to pNIPAm and **F** to fumaric acid.

Synthesis of Nanocomposite Microgels.

Hydrophobized nanocomposite microgels were synthesized by surfactant-free seeded emulsion polymerization (SEP) in the presence of **NF** microgels. Initially, a suitable amount of water (total volume: 200 mL) was poured in a three-neck round bottom flask (300 mL) equipped with a mechanical stirrer and a condenser. Next, the water was heated to 70 °C in a temperature-controlled oil bath and sparged with nitrogen for 30 min to purge the oxygen dissolved. Then, a solution of NaOH (1 M) was added to maintain the pH value of the system under basic conditions (pH ≈ 10), before the purified **NF** microgel dispersion (final concentration: 0.17 wt%) and the KPS initiator (0.0540 g, 1 mM) were added dissolved in 5 mL of water. Finally, styrene (2.1028 g or 6.3084 g) or methyl methacrylate (4.0048 g) were injected to start the polymerization. The reaction was allowed to proceed for 24 h, and the resulting microgel dispersions were cooled to room temperature in an ice bath. The composite microgels were purified twice by centrifugation/redispersion with water. In all polymerization processes, secondary nanoparticles were not observed by FE-SEM imaging.

Synthesis of Polystyrene Microspheres (PS).

Polystyrene microspheres (henceforth: **PS**) were prepared by soap-free emulsion polymerization. Initially, water (490 mL) was poured in a three-neck round bottom flask (1 L) equipped with a mechanical stirrer and a condenser. Next, the monomer solution was heated to 70 °C in a temperature-controlled oil bath and sparged with nitrogen for 30 min to purge the oxygen dissolved. Then, styrene (52.5700g, 1 M) and the KPS initiator (0.1622 g, 2 mM) dissolved in 10 mL water were added to start the polymerization. The polymerization was allowed to proceed for 24 h under a nitrogen atmosphere, and the resulting microgel dispersion was cooled to room temperature in an ice bath. The composite microgels were purified twice by centrifugation/redispersion with water.

Synthesis of Core–Shell Microgels.

Core/hard–shell/gel microgels were synthesized by seeded precipitation polymerization [2] in the presence of polystyrene-based microspheres. At first, the core microspheres were prepared by soap-free emulsion polymerization: water (290 mL), NIPAm (3.3948 g, 10 mol%), and styrene (28.3978 g, 90 mol%) were poured in a three-neck round bottom flask (300 mL) equipped with a mechanical stirrer and a condenser. Next, the monomer solution was heated to 70 °C in a temperature-controlled oil bath and sparged with nitrogen for 30 min to purge the oxygen dissolved. After that, the KPS initiator (0.1622g, 2 mM) dissolved in 10 mL water was added to start the polymerization. The polymerization was allowed to proceed for 24 h, and the resulting microgel dispersion was cooled to room temperature in an ice bath. The polystyrene-based microspheres were purified twice by centrifugation/redispersion with water. In this manuscript, the polystyrene-based microspheres are denoted as **PSN**, where **S** refers to polystyrene and **N** to polyNIPAm.

Subsequently, the core–shell microgels were prepared by seeded precipitation polymerization. Initially, water (total volume: 30 mL) was poured in a three-neck round bottom flask equipped with a mechanical stirrer and a condenser. Next, a suitable amount of water was heated to 70 °C in a temperature-controlled oil bath and sparged with nitrogen for 30 min to purge the oxygen dissolved. After the addition of the concentrated **PSN** microsphere dispersion (final concentration: 1 wt%), the KPS initiator solution (1 mM, 0.0162 g) was injected. Finally, the monomer solution (5 mL) was injected to start the polymerization. The reaction was allowed to proceed for 4 h, and the resulting microgel dispersion was cooled to room temperature. The composite microgels were purified twice by centrifugation/redispersion with water. In this manuscript, the composite microgels are denoted as **PSN-N(*X*)**, where **PSN** indicates the core microspheres, **N** refers to polyNIPAm, and ***X*** indicates the monomer concentration during the seeded precipitation polymerization.

Preparation of Particle-stabilized Emulsions.

Particle-stabilized emulsions were prepared by mixing 1 mL of the particle dispersion at a suitable particle concentration (2–6 wt%) and 1 mL oil in an Ultra-Turrax T25 homogenizer. If not further specified, all emulsions were prepared with a T25 homogenizer operating at 5000 rpm for 60 s. The emulsions were first prepared without addition of a fluorescent dye. However, for optical microscopy imaging, the oil and water phases were stained with Nile red (~0.1 mM) and fluorescein sodium (~0.1 mM), respectively. In the present study, the pH value of the microgel dispersion was adjusted with NaOH (1 M).

Characterization Methods.

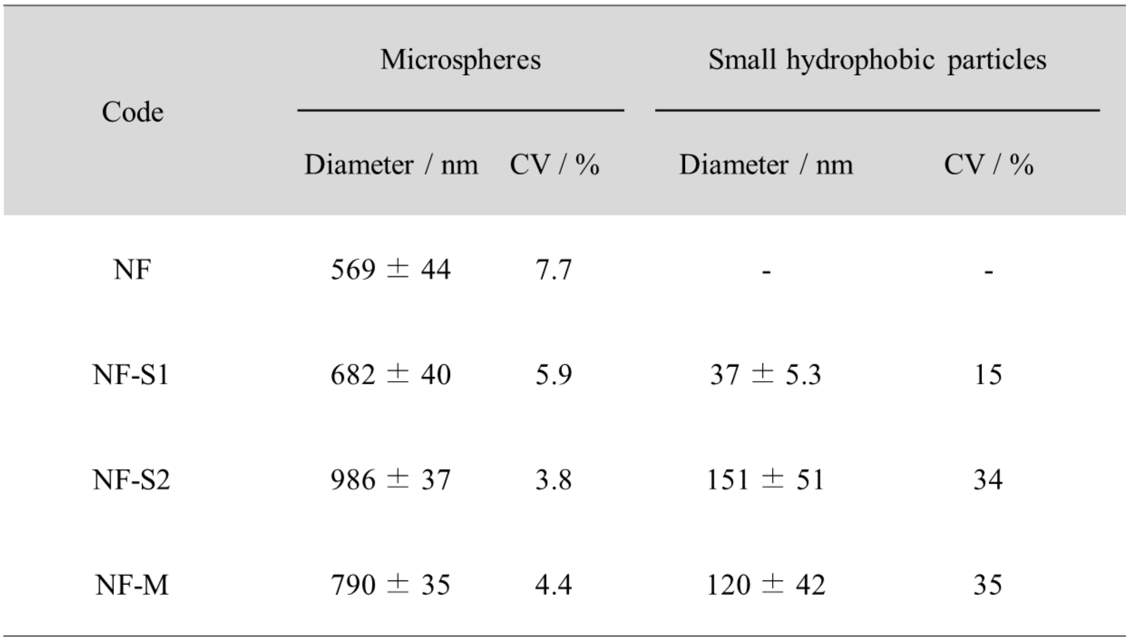
The morphology of the samples was examined by scanning electron microscopy (FE-SEM, Hitachi Ltd., S-5000). For the sample preparation, a diluted particle dispersion (~0.05 wt%) was placed on a polystyrene substrate and dried at room temperature. Then, the dried sample was washed with pure water to remove the sodium salts. The sample substrates were sputtered with Pt/Pd prior to observation (15 mA, 6 Pa, 80 s).

The electrophoretic mobility (EPM) was evaluated on a Zetasizer NanoZS instrument (Malvern, Zetasizer software v. 4.20). For the sample preparation, the particle concentration was adjusted to ~0.005 wt% and the ionic strength to 1 mM using solutions of NaOH, HCl, and NaCl. The EPM data correspond to an average of 20 independent measurements from three independent measurements. For all measurements, the samples were equilibrated for 300 s at the set temperature before measurement.

The obtained emulsions were evaluated with an optical microscope (BX51, Olympus) equipped with a fluorescence system (ramp: U-RFL-T, excitation: 451-485 and 541-565 nm, emission: 500-523 and 584-675 nm) and a digital camera (ImageX Earth Type A-5.0M Ver.3.0.4, Kikuchi-Optical Co. Ltd.). For all microscopy measurements, the emulsions were sampled from the mixed solution with pipette and observed as soon as possible (within 30 min after the homogenization. Prior to the observation, the emulsions were diluted with water or the appropriate oils.

Results and Discussion

Table S1. Diameter of the (nanocomposite) microgels and small hydrophobic particles attached to the microgel surface



Code	Microspheres		Small hydrophobic particles	
	Diameter / nm	CV / %	Diameter / nm	CV / %
NF	569 ± 44	7.7	-	-
NF-S1	682 ± 40	5.9	37 ± 5.3	15
NF-S2	986 ± 37	3.8	151 ± 51	34
NF-M	790 ± 35	4.4	120 ± 42	35

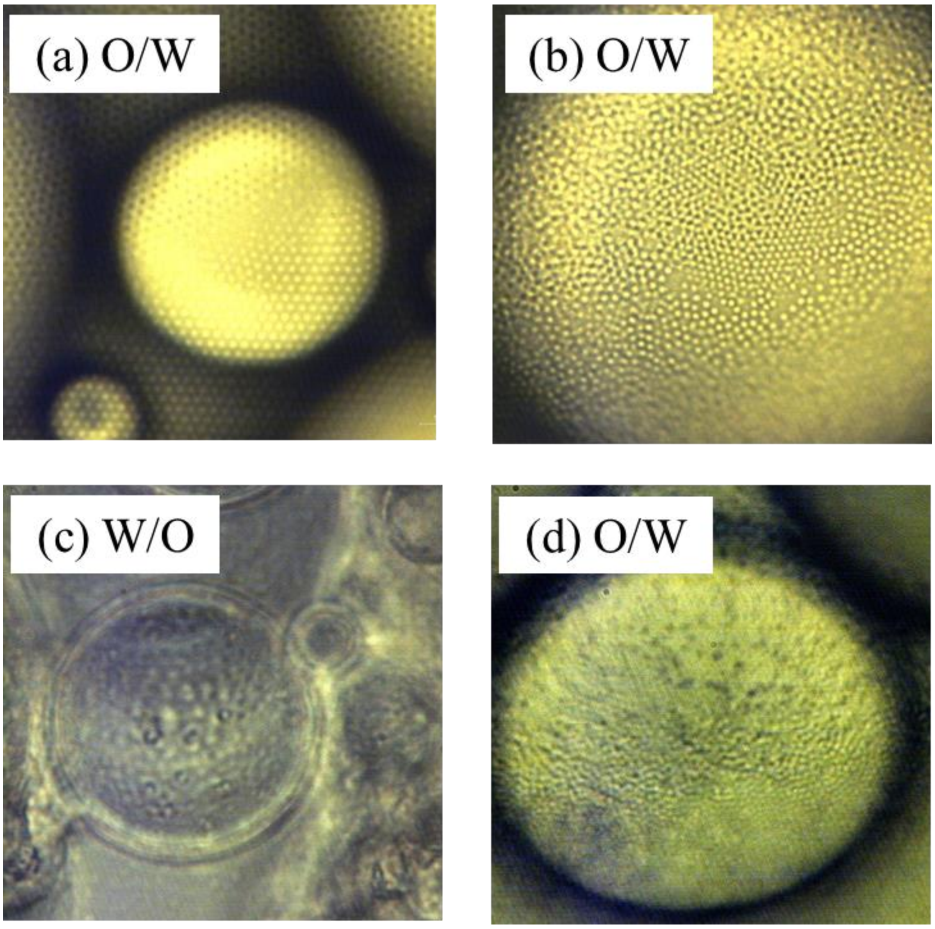


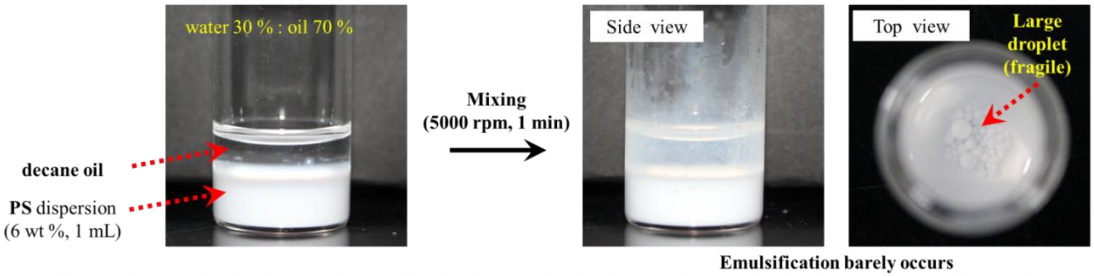
Figure S1. Fluorescence microscopy images of **MS-E**s prepared with (a) **NF** microgels (2 wt%), (b) **NF-S1** nanocomposite microgels (4 wt%), (c) **NF-S2** nanocomposite microgels (6 wt%), and (d) **NF-M** nanocomposite microgels (6 wt%). In this case, the emulsions were prepared by mixing 1 mL of cyclohexane and 1 mL of individual microgel dispersions under basic conditions (pH ≈ 10). The images confirm that all emulsions are covered by the corresponding microgels.

Table S2. Solubility parameters of oils and polymers used in this study

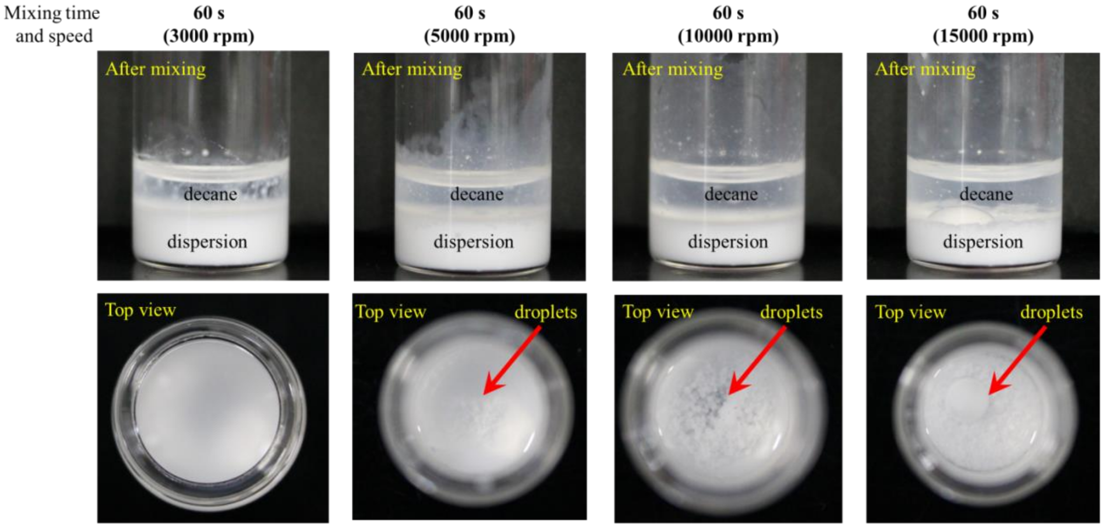
Type	Solubility Parameter [MPa$^{1/2}$]
n-Decane	15.8
Hexadecane	16.4
Cyclohexane	16.8
Styrene	19.0
Octanol	20.9
Pentanol	21.7
Butanol	23.1
polystyrene	18.6
poly (methy methacrylate)	19.6

※ All solubility parameters were taken from a polymer handbook.[3]

(a) Representative photograph



(b) Effect of stirring speed on emulsification



※ Although small amounts of large droplets (fragile emulsion) were formed under certain mixing conditions, most **PS** microspheres did not work as emulsifiers.

(c) Effect of type of oil on emulsification

In the case of cyclohexane

Figure S2. Photographic images of **MS-E**s prepared using **PS** microspheres. The effect of the stirring speed during the preparation of the emulsions on the emulsification behavior in the case of (a, b) *n*-decane and (c) cyclohexane as the oil phase is summarized above. All emulsions were prepared by mixing 0.6 mL of a **PS** dispersion (2 wt%) and 1.4 mL of the oil. Under these conditions, the preparation of particle-stabilized emulsions did not occur.

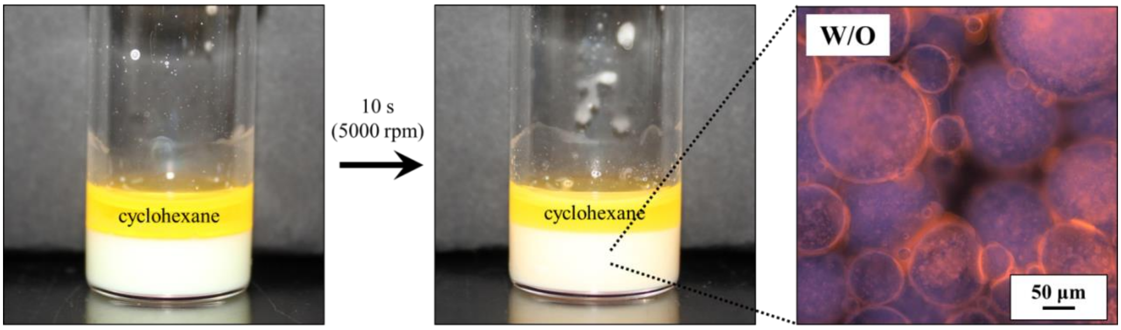


Figure S3. Photographic images of **MS-E**s prepared with **NF-S2** nanocomposite microgels before and after emulsification. The emulsions were prepared by a short homogenization (10 s, 5000 rpm).

Code	Monomer conc. [mM]	Monomer [mol%]			*D*h (pH 3)[nm]	Shell Thickness [nm]
		NIPAm	BIS	FAc	25° C	
PSN	-	-	-	-	380 ± 4	-
PSN-N(10)	10	90	5	5	386 ± 4	3
PSN-N(30)	30	90	5	5	449 ± 1	35
PSN-N(50)	50	90	5	5	652 ± 3	136

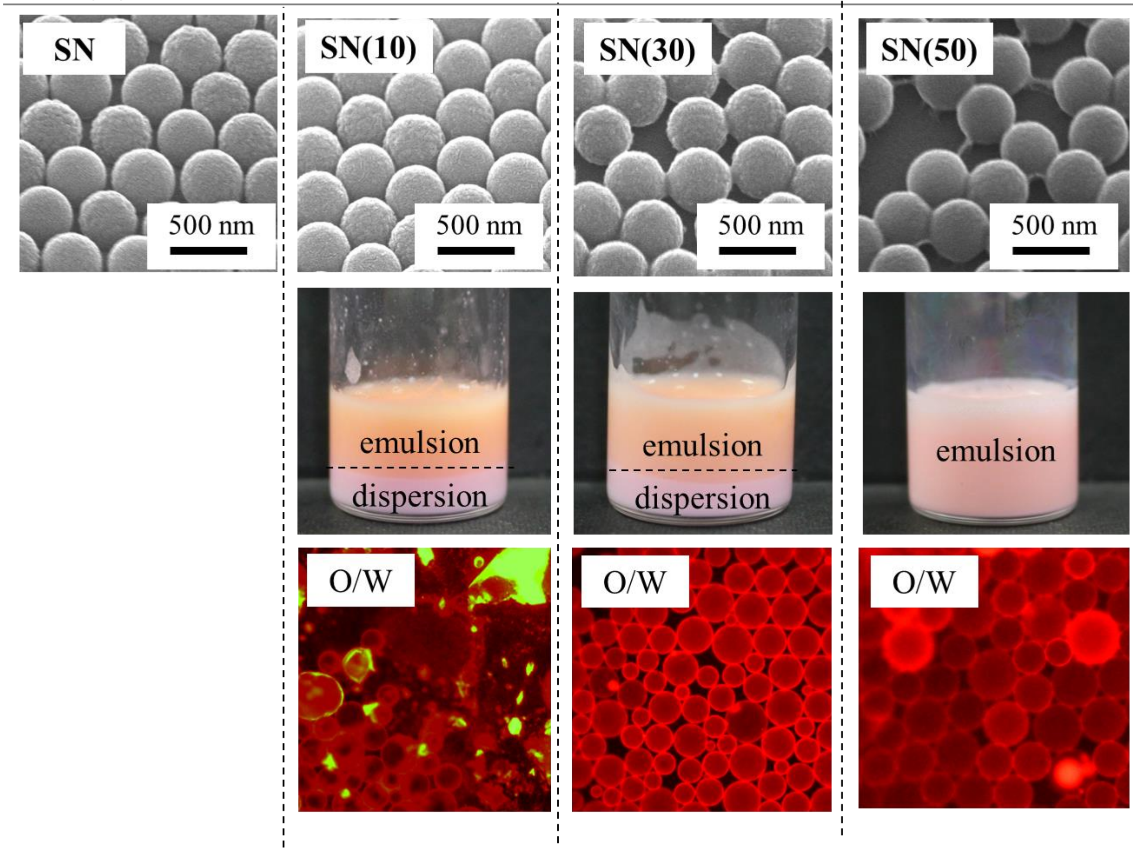


Figure S4. Photographic and fluorescence-microscopy images, as well as FE-SEM images of core–shell microgel-stabilized emulsions using **PSN-N(10)**, **PSN-N(30)**, and **PSN-N(50)** core–shell microgels. The emulsions were prepared with cyclohexane (red, stained with Nile red). A series of core–shell microgels were prepared by precipitation polymerization in the presence of **PSN** microspheres composed of 90 mol% styrene and 10 mol% NIPAm. The polymerization protocol is shown in the table in this figure. The emulsions were prepared under constant stirring (5000 rpm, 1 min) with different microgel dispersions at a fixed concentration.

References

[1] R. H. Pelton, *Adv. Colloid Interface Sci.* **2000**, *85*, 1-33.

[2] C. D. Jones, L. A. Lyon, *Macromolecules* **2000**, *33*, 8301-8306.

[3] Brandrup, J., Immergut, E. H., Grulke, E. A., Abe, A., & Bloch, D. R. (Eds.). (1999). Polymer handbook (Vol. 89). New York: Wiley.