Supporting Information for

Anomalous Dispersion of Magnetic Spiky Particles for Enhanced Oil Emulsions/Water Separation

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Experimental Methods

Absorption of ZnO nanoparticles to magnetic microspheres.

Magnetic microspheres (~1 μm in diameter) containing iron oxide nanoparticles (<10 nm) embedded in polystyrene matrix (carboxyl group conjugated) were pursued from PolySciences, Inc. The microspheres were absorbed with ZnO nanoparticles (<40 nm, Sigma-Aldrich) by incubating the microspheres with the ZnO nanoparticles in water, agitating at 400 rpm for 2 h. The ZnO nanoparticles-absorbed microparticles were centrifuged at 2000 rcf to remove the unabsorbed ZnO nanoparticles, and then washed with DI water. The centrifugation and washing were repeated for at least 4 times to completely remove the unabsorbed ZnO nanoparticles. The resulted microparticles were collected for further steps including either direct functionalization with ODTMS or nanospike growth.

Fabrication of magnetic spiky particles.

ZnO nanospikes were grown on the particle surface through hydrothermal reaction, forming magnetic spiky particles. Aqueous solution containing ZnO nanoparticles-absorbed magnetic microparticles were supplemented with 25 mM zinc nitrate hydrate [$Zn(NO_3)_2 \bullet 6H_2O$, Sigma-Aldrich] and 25 mM hexamethylenetetramine ($C_6H_{12}N_4$, HMTA, Sigma-Aldrich), and then incubated at 80 ^oC for 1 hour with 1000 rpm stirring, resulting in growth of ZnO nanospikes. After reaction, the microparticles were centrifuged and washed with DI water for 3 times.

Microparticles functionalization with ODTMS

The ZnO nanoparticles-absorbed microspheres or spiky particles were functionalized with octadecyl trimethoxysilane (ODTMS, Sigma-Aldrich). Briefly, the particles were firstly re-suspended and washed with anhydrous ethanol, and then re-suspended in anhydrous heptane/ethanol mixture (volume ratio of anhydrous heptane: anhydrous ethanol = 5:1). The particles were mixed with 2% ODTMS in anhydrous heptane (Sigma-Aldrich) supplemented with anhydrous ethanol (volume

ratio of anhydrous heptane: anhydrous ethanol = 5:1). The mixture was stirred at 80 ^{o}C for 12 hours. After reaction, the particles were washed several times with ethanol to remove extra ODTMS. The particles were dried into powders under vacuum and the weight was measured. The particles were still magnetically responsive after these chemical reactions.

Fabrication of Microparticles coated with surfactant

ZnO nanoparticles-absorbed microspheres were functionalized with ODTMS (Smooth-ODTMS). These microparticles were suspended in aqueous solution containing 0.01 M surfactant, cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich). The solution were incubated at room temperature overnight, agitating at 300 rpm. In the next step, the microparticles were washed with DI water to remove unabsorbed CTAB, and collected via centrifugation at 2000 rcf. The washing steps were repeated for at least four times. The surfactant-coated microparticles were dried into powders under vacuum and the weight was measured.

Particle characterization

Particles were re-suspended in ethanol, and drop-casted onto a Si wafer substrate and allowed to dry. Samples were sputtering-coated with Au-Pd, and imaged with SEM system (Zeiss SUPRA 60). For TEM imaging, the particles were suspended in anhydrous ethanol. Then the particles were embedded in resin and sliced. The samples were imaged with TEM system (FEI Tecnai).

Test of Hydrophobic QDs absorption to microparticles

100 µl toluene solution containing CdSe/ZnS core-shell type quantum dots (QDs, fluorescence λ_{em} 630 nm, concentrated to be 5 mg/ml in toluene, Sigma-Aldrich) was injected into 1ml aqueous solution containing spiky-ODTMS, and then agitated vigorously with vortex mixer (VWR). 100 µl resulted solution containing particles was transferred to a glass-bottom 96-wells plate, and was imaged on typical area with confocal fluorescence microscopy (Zeiss LSM).

Contact angle measurement of microparticle film.

Microparticles (Smooth-ODTMS, Spiky-ODTMS, and Smooth-ODTMS/Surfactant) were drop-casted on a glass substrate and allowed to dry at room temperature. The microparticles formed a thin film on the substrate. 5 μl drop of DI water or corn oil (Sigma-Aldrich) was deposited on top of the microparticle thin film. Static Contact angle measurement was conducted with Goniometer measuring system to analyze the wetting properties of the microparticle thin film.

Test of microparticle dispersity in water.

Dried microparticles were placed in a 1.5 ml centrifuge tube. DI water was supplemented to the microparticles, and the solution was agitated at 1500 rpm with vortex mixer (VWR) for 1 min. The particle dispersion was photographed. 200 μl particle solution was transferred to a 96-wells plate. Particle dispersion of typical area was imaged with optical microscopy (Mshot). To further examine particle dispersion and aggregation states, aqueous solution containing microparticles was deposited on porous membrane (Cyclepore). The water was filtered, and the particles were collected on the porous membrane and allowed to dry immediately so that the particle dispersion states were preserved.

Long-term dispersity test.

Particles dispersed in 200 μl aqueous media were placed in 96-wells plate. The particle dispersity was observed with optical microscopy on the first day, and then stored without agitation for another 1 weeks. On day 7, the particle dispersity was imaged again.

Application of microparticles for Absorbing oil spill on water surface.

DI water was added to a petri dish, and then 60 mg corn oil (stained with sudan red dye) was supplemented on top of the water surface. Different microparticles (Smooth-ODTMS, Spiky-ODTMS, and Smooth-ODTMS/Surfactant) of indicated doses were

added to the oil surface carefully. The oil drop was allowed to absorb to the microparticles for 30 min. Neodymium magnet was placed close to the sidewall of the petri disc to attract the microparticle-oil complex. The oil absorption progress was recorded with video camera.

Application of microparticles for cleaning dispersed oil emulsion in water.

2% corn oil emulsion was prepared by mixing corn oil in DI water followed by sonication overnight. Spiky-ODTMS and Smooth-ODTMS/Surfactant were pre-suspended in water by supplementing DI into microparticle powders since they were dispersible in water. Smooth-ODTMS was directly applied as dried powder since it aggregated in water. For both Spiky-ODTMS and Smooth-ODTMS/Surfactant, 40 mg particles were pre-dispersed in 1 ml water, and was supplemented into 1 ml 4% emulsion solution, which ended up to be totally 2 ml 2% emulsion solution versus 40 mg Spiky-ODTMS or 40 mg Smooth-ODTMS/Surfactant. For Smooth-ODTMS, 40 mg dried powders were directly added into 2 ml 2% emulsion solution. The mixture solution was vortexed for 2 min and stood for 30 min, to allow sufficient mixing and absorption of oil emulsion to the microparticles. Neodymium magnet was placed close to the sidewall of the container to attract the particle-oil complex. The upper 200 μl solution was withdrawn to evaluate the water cleaning profiles with optical microscopy. The particle-oil complex was collected and examined with optical microscopy.

S1: Fabrication process of spiky particles and smooth particles with or without surfactant

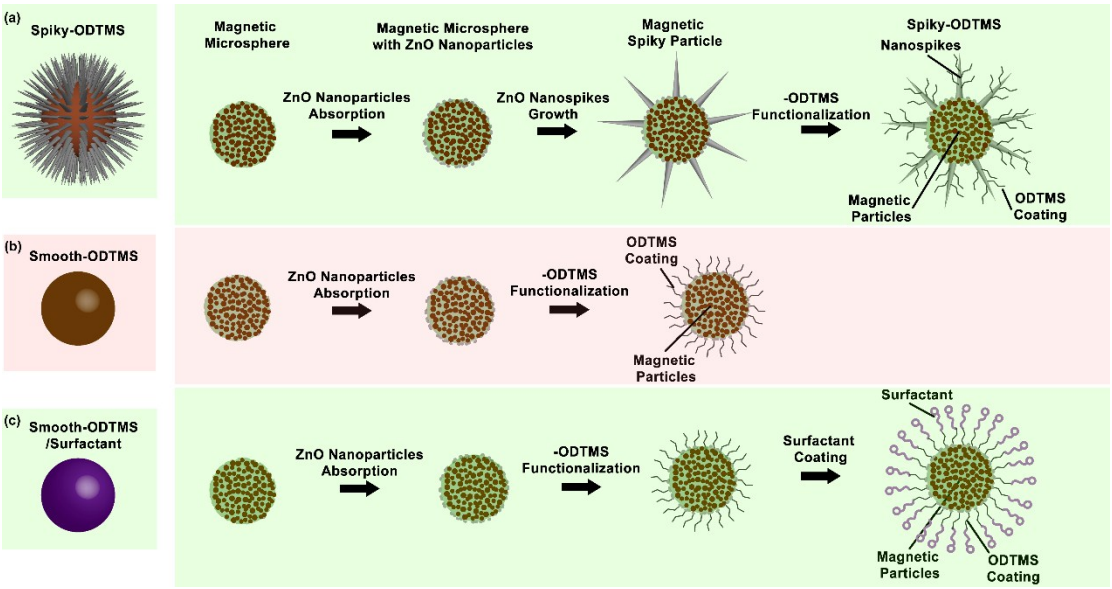

Figure S1. Illustration of the fabrication process of spiky particles and smooth particles with or without surfactant. (a) Spiky particles functionalized with –ODTMS (Spiky-ODTMS); (b) Smooth microspheres with ZnO nanoparticles absorbed on the surface but without nanospikes (Smooth-ODTMS); (c) Smooth-ODTMS coated with surfactant (Smooth-ODTMS/Surfactant).

S2: Magnetic responses of microspheres, spiky particles and Spiky-OTDMS.

To evaluate whether the magnetic responsibility of particles were disrupted by the particle fabrication and functionalization processes, different particles including magnetic microspheres, magnetic spiky particles and Spiky-OTDMS were tested. The particles were dispersed in DI water. When placing a Neodymium magnet close by, the particles moved toward the magnet responsively, and reached to the container sidewall within 2 min, indicating the magnetic responsibility of the particles were not disrupted.

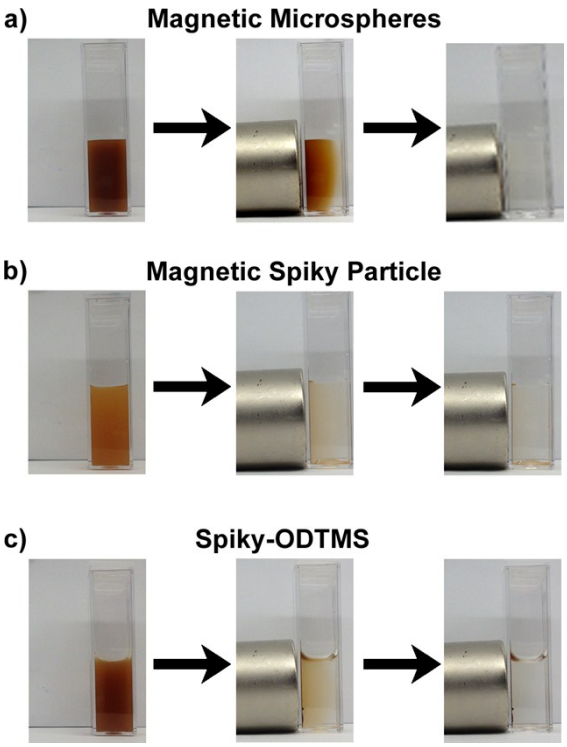

Figure S2. Magnetic responses of different particles including (a) magnetic microspheres, (b) magnetic spiky particles, and (c) Spiky-OTDMS. The particles reached to the container sidewall within 2 min under magnetic attraction.

S3.1: Supplemental information of QDs absorption assay of -ODTMS particles

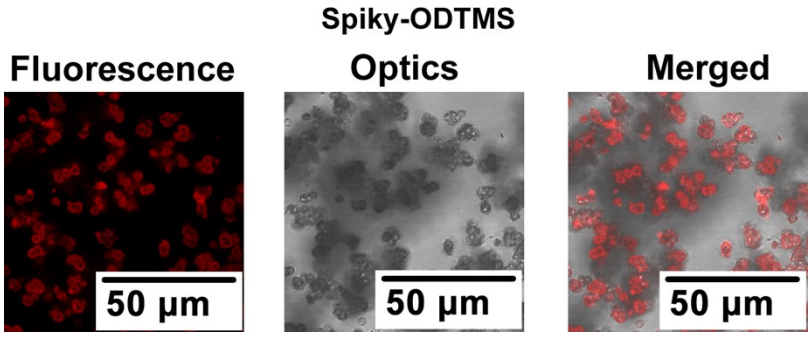

Figure S3.1. Confocal fluorescence images showing the absorption of hydrophobic QDs to Spiky-ODTMS in water. Hydrophobic QDs attached on the particle surface presented red fluorescence signal, indicating particle surfaces were hydrophobic.

S3.2: Hydrophobic QDs absorption by microparticles without ODTMS functionalization

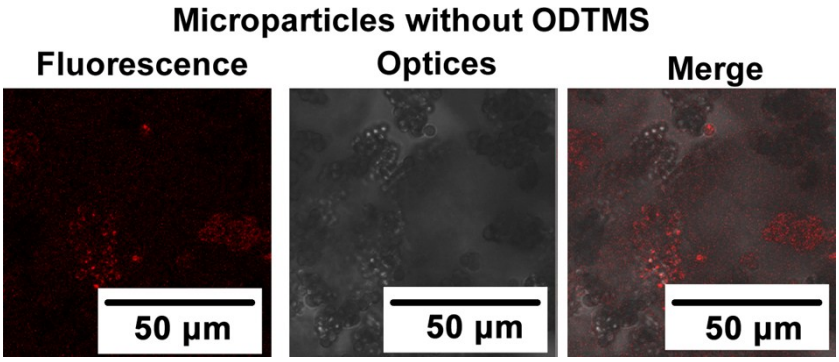

Figure S3.2 The particles after absorbing hydrophobic QDs exhibited weak red fluorescence, indicating some hydrophobic QDs were nonspecifically absorbed to the microparticles, but were at a much lower extent compared to the microparticles with ODTMS functionalization.

S4: Contact angel of water spreading on Spiky particle film without ODTMS

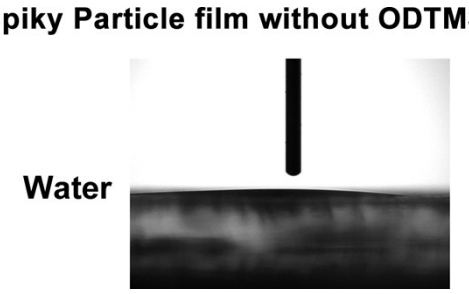

Figure S4. Wetting properties of spiky particle film without ODTMS coating. Optical image of a water droplet spreading on the spiky particle film.

S5.1: Supplemental information of the dispersity of magnetic microsphere in water or in ethanol

The dispersity in water or ethanol of magnetic microsheres with or without hydrophobic coating were studied. These microsphers were not decorated with ZnO nanoparticles. Magnetic microspheres were functionalized to be superhydrophobic by reacting with hydrophobic organic tethers, trimethoxy(octadecyl) silane (ODTMS). The microparticles were incubated with 2% ODTMS in anhydrous heptane solution at 80 °C for 12 hours. After reaction, the microparticles were washed, dried and re-dispersed in water for further testing. Dispersion state of microparticles were characterized with optical microscopy, photography and SEM. Magnetic microsheres

without ODTMS coating can dispere uniformly in water (Figure S5.1a), meanwhile with ODTMS coating cauased sever aggreation of the microspheres in water (Figure S5.1c).

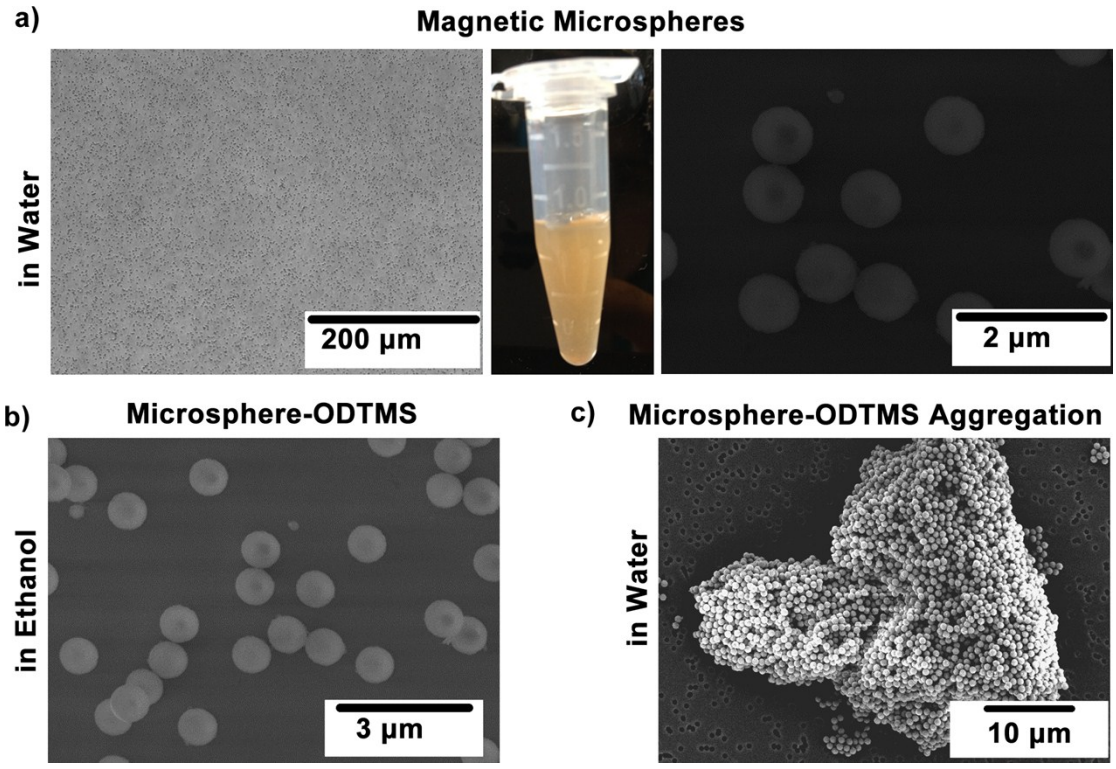

Figure S5.1. The dispersity of magnetic microspheres. (a) Optical, photographic and SEM images showing the dispersion of magnetic microspheres in water. (b) SEM image showing magnetic microspheres coated with ODTMS dispersed in ethanol. (c) SEM image showing microspheres coated with ODTMS aggregated in water.

S5.2. Supplemental information of the magnetic microspheres-ODTMS coated with surfactant.

To evaluate the dispersity of surfactant-coated magnetic microspheres, magnetic microspheres-ODTMS were decorated with surfactant, cetyltrimethylammonium bromide (CTAB). The particle dispersion state was exanimated with both optical microscopy and SEM. The dispersity was observed with SEM imaging by depositing the particles on a porous membrane to preserve the particles' dispersion states. Both SEM and optical images revealed that the magnetic microspheres-ODTMS coated with surfactant exhibited dispersion profiles, shown in Figure S5.2.

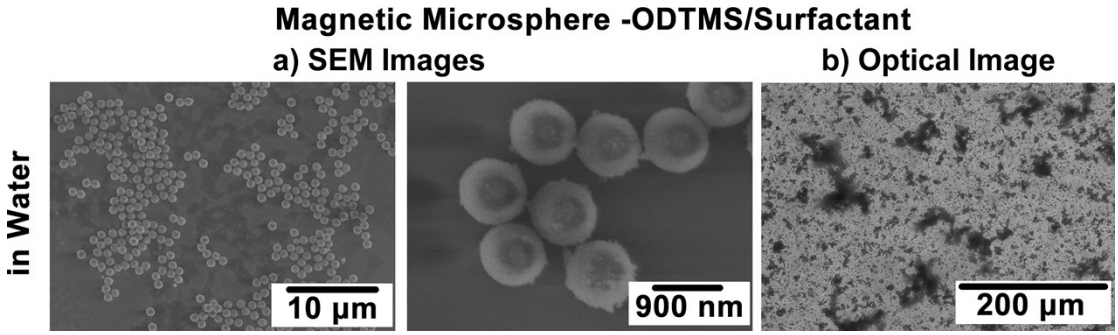

Figure S5.2 (a) SEM and (b) optical images showing the dispersion of magnetic microspheres-ODTMS coated with surfactant.

S6: Oil absorption test for applying sufficient Smooth-ODTMS.

140 mg magnetic Smooth-ODTMS were applied. These particles were able to completely absorb 60 mg oil spill on water surface within 30 minutes. When placing a magnet close by, the Smooth-ODTMS moved toward the magnet responsively, and the particle-oil mixture can be removed.

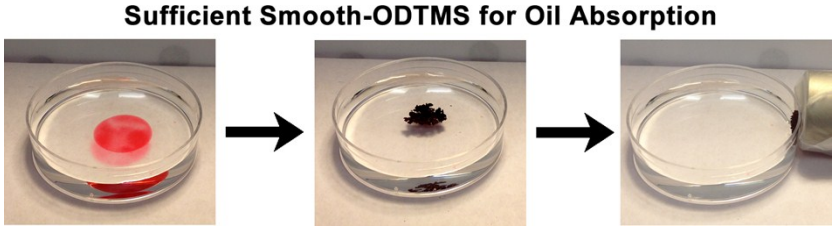

Figure S6. Sufficient (140 mg) magnetic Smooth-ODTMS were applied to completely absorb 60 mg oil spill on water surface. The oil-particle mixture was removed by a magnet.

S7: Mechanical stability of the Spiky-ODTMS after oil absorption

The nanospikes were mechanically stable during the particle fabrication process and the applications of oil absorption. The spiky particles after oil absorption were collected and washed with acetone/ethanol (1:1 mixture) for couple of times. The particles were then imaged with SEM. The particle morphology was shown in Figure S7a and Figure S7b, and it was found that the spiky particles were stable after the oil absorption and washing steps. However, the nanospikes were unstable by intensive sonication for 5 hours, Figure S7c, indicating the spiky particles were not suitable for other applications that requires intensive sonication.

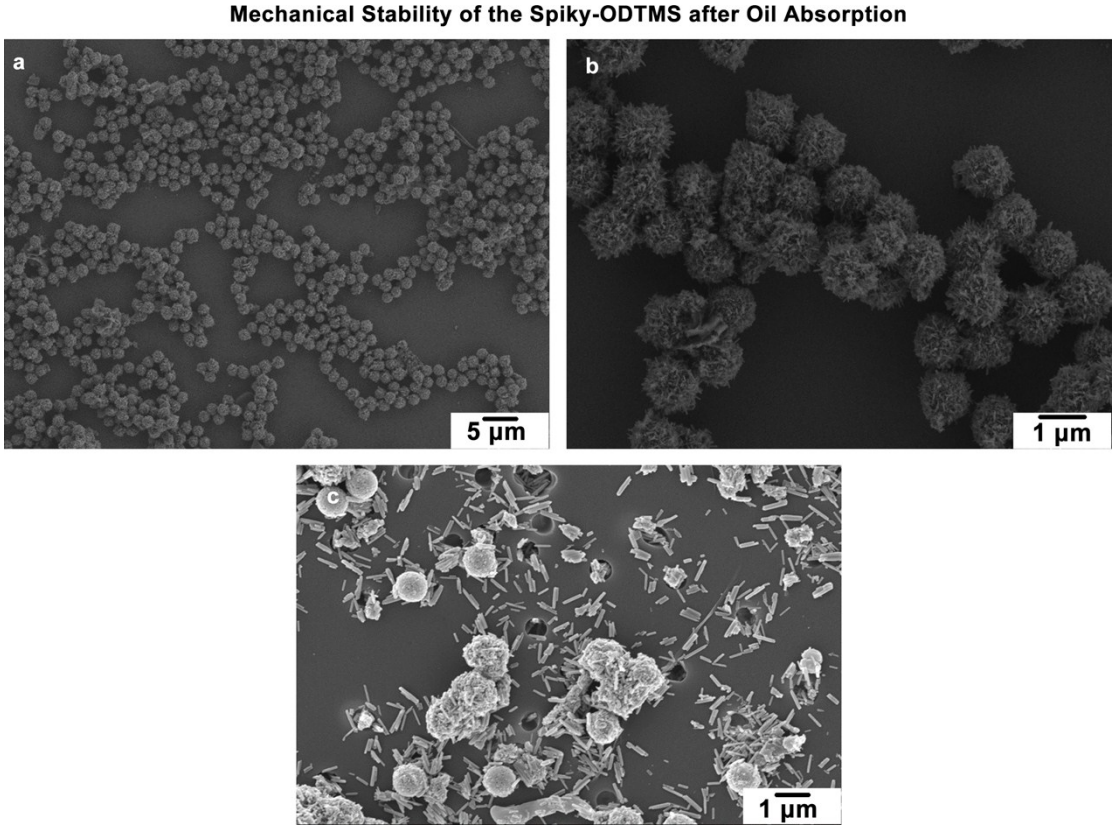

Figure S7. SEM images (a) and (b) showing the Spiky-ODTMS after oil absorption collected and washed with acetone/ethanol (1:1 mixture) for couple of times. (c) SEM image showing the Spiky-ODTMS after oil absorption were unstable by intensive sonication for 5 hours.

S8：The quantitative analysis of the emulsion separation efficiency

The oil was stained with Nile Red, and dispersed in water to form emulsion as described in the main text. The oil emulsion was separated by the magnetic spiky particles. The remaining oils stained by Nile Red in aqueous solution were analyzed with fluorescence spectroscopy.

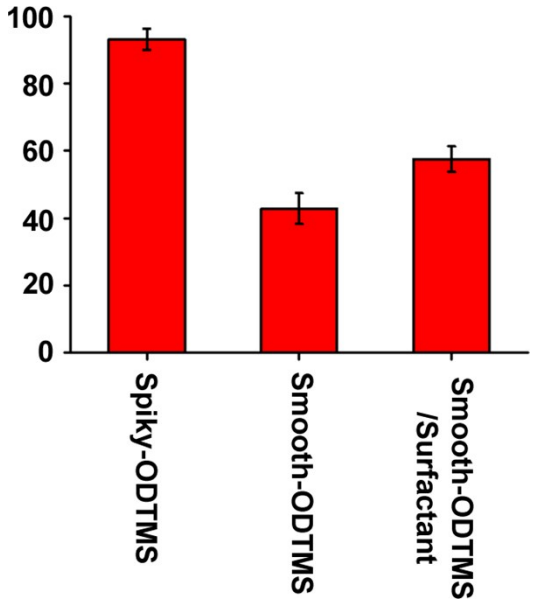

Figure S8. Quantitative analysis of emulsion separation efficiency. Diagram summarizing the emulsion separation efficiency of Spiky-ODTMS, Smooth-ODTMS and Smooth-ODTMS/Surfactant.

S9: Detail process of Oil-water mixture cleaning

Image#(1): 40 mg Spiky-ODTMS were pre-dispersed in 1 ml water in bottle#1.
Image#(2): 1 ml 4% emulsion solution in bottle#2-1.
Image#(3): The 1ml solution in Bottle#1 was added into Bottle#2 to become Bottle#2-2, which was totally 2 ml solution.
Image#(4): the 2 ml solution in Bottle#2-2 was treated with magnetic field.
Image#(5): 1 ml upper water solution was withdrawn to another bottle, bottle#3, to evaluate the water cleaning profile.

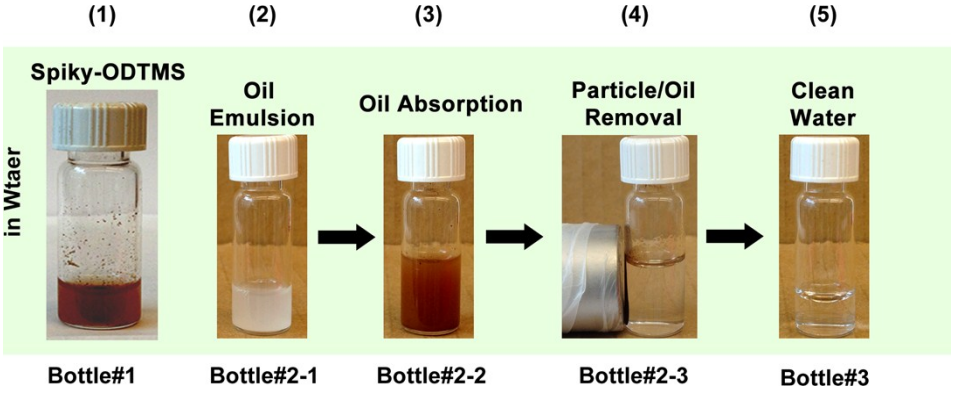

Figure S9. Illustration of Oil-water mixture cleaning process.