Reversible Switching of the Amphiphilicity of Organic-Inorganic Hybrids by Adsorption-Desorption Manipulation

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Materials

Aluminum nitrate nonahydrate (≥ 98%, Sigma-Aldrich), ammonia solution (30% in water, Chem-Supply), stearic acid (95%, Sigma-Aldrich), Tergitol (Type 15-S-9, Sigma-Aldrich), hexane fraction (≥97%, Ajax Finechem), cyclohexane (99.5%, Sigma-Aldrich), octane (≥ 99%, Sigma-Aldrich), decane (≥98%, Sigma-Aldrich), toluene (AR, Fisher Scientific), ethylbenzene (99.8%, Sigma-Aldrich), p-Xylene (99%, Sigma-Aldrich), methylene blue (Sigma-Aldrich), Oil Red O (Sigma-Aldrich), Coumarin 343 X carboxylic acid (Lumiprobe). All chemicals were used as received without further purification. Ultrapure water was used in all experiment (18.2 MΩ·cm, Synergy UV Water Purification System, Merck Millipore).

Synthesis of Al₂O₃ nanofibers

Briefly, 15 g of Al(NO₃)₃·9H₂O was dissolved in 25 mL of ultrapure water. Under vigorously stirring, ammonia aqueous solution (mass fraction 10%) was added dropwise to above solution until the pH reached 5, and kept stirring for one more hour. Afterwards, the produced precipitate was separated by centrifugation, transferred into a stainless steel autoclave and heated at 170 °C for 48 hours. After cooling down, the resulting solid was washed with ultrapure water and then mixed with 20 g of Tergitol. Finally, the mixture was heated at 450 °C for 5 hours to obtain the final products.

SA-Al₂O₃ “hybrid surfactant” and emulsion stabilization

Al₂O₃ aqueous suspensions with various concentrations (expressed as wt% in water phase) were prepared by sonicating Al₂O₃ nanofiber in ultrapure water for 5 minutes. Stearic acid (SA) was dissolved in hexane to obtain solutions with different concentration of SA (expressed as mM in oil phase). Next, the Al₂O₃ aqueous suspension and the SA solution (1.5 mL/1.5 mL) were mixed in a vial. The vial was then sealed and shaken by hand for 30 sec to produce emulsions. Other emulsions with different oil phase were prepared by a similar method. In some cases, for better visualization, methylene blue and Oil Red O were used to color the water phase and oil phase, respectively.

Emulsions observation

The light microscope (LM) images were obtained through observing a water-diluted emulsion placed in the middle of two pieces of glass slides separated by a distance of 1mm. The
emulsion type was identified by observing an emulsion in which the water phase and oil phase were colored by methylene blue and Oil Red O, respectively.

**Contact angle and interfacial tension measurement**

The sessile drop method was used to measure the contact angle of SA-Al$_2$O$_3$ hybrid. For the measurement, 1 g of SA-Al$_2$O$_3$ hybrid was obtained by centrifuging the corresponding emulsions and drying the sediment overnight. Then the SA-Al$_2$O$_3$ hybrid was filled in a steel die and compressed under a pressure of $6 \times 10^8$ N/m$^2$ to obtain a disk (diameter, 13mm; thickness, ca. 1mm). The contact angle measurement was performed on this disk using FTA200 Contact Angle Analyser. Briefly, a drop of water was first dripped on the disk, and then the droplet shape was captured by the camera and analysed through software to give contact angle.

The pendant drop method was used for interfacial tension measurement. Prior to the measurement, an oil phase (3 mL, with or without SA) was first filled in a quartz cuvette, and a pendant drop of water (with or without Al$_2$O$_3$) was formed on the end of a stainless steel needle immersed in the oil phase. Then the images of the drop were taken automatically at a certain frequency and analysed through software to give a series of interfacial tension value during the aging process.

**Fluorescence-labelling experiment**

Fluorescence-labelled stearic acid solution:

The stearic acid solution was fluorescence-labelled by adding small amount of Coumarin 343 X carboxylic acid (denoted as CCA). Toluene was used as solvent and the concentration of CCA in the solution was $2 \times 10^{-3}$ mM.

Fluorescence-labelled Al$_2$O$_3$ nanofibers:

Pristine Al$_2$O$_3$ nanofibers were dispersed in CCA solution ($2 \times 10^{-2}$ mM in ethanol) and stirred for 5 hours to reach adsorption equilibrium. After centrifuging, washing with ethanol and drying, the CCA-labelled-Al$_2$O$_3$ nanofibers were collected.
Adsorption capacity measurement of the SA-Al₂O₃ hybrid foam

A 50 mL beaker with small amount of water was placed on an analytical balance; then a piece of SA-Al₂O₃ hybrid foam was placed on the water surface and its weight was recorded. Oil phase (colored by Oil Red O for easily observing) was dropped onto the water surface drop by drop and adsorbed by the hybrid foam until saturated. The weight of the adsorbed oil was used to evaluate the adsorption capacity of the hybrid foam according to the following equation.

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\text{Weight gain} \, (\%) = \frac{\text{the weight of absorbed oil}}{\text{the weight of hybrid foam}} \times 100\%
\]

Characterization

The morphology of prepared Al₂O₃ nanofiber was studied using a JEOL 2100 transmission electron microscopy (TEM) equipped with a Gatan Orius SC1000 CCD camera and the accelerating voltage of TEM was 200 KV. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra photoelectron spectrometer using mono Al Kα (1486.6 eV) X-ray. The X-ray diffraction (XRD) patterns of the Al₂O₃ nanofiber were obtained on a Philips PANalytical X'Pert PRO diffractometer using Cu Kα radiation (λ = 1.5418 Å) working at 40 mA and 40 kV. The diffraction data were collected from 10° to 90° with a resolution of 0.01° (2θ). The SA-Al₂O₃ hybrid foam was observed using a ZEISS Sigma scanning electron microscopy (SEM) at accelerating voltages of 5 kV. The infrared spectrum (IR) was collected between the wave number of 400 to 4000 on a BRUKER Alpha infrared spectrometer. The interfacial tension and contact angle measurement were performed on a FTA200 Contact Angle Analyser. Nikon Eclipse Ni light microscope and Nikon A1R confocal laser scanning microscopy were used to image the emulsions.
**Figure S1.** Water-hexane interfacial tension without and with Al$_2$O$_3$ in water.

**Figure S2.** The stability of emulsions stabilized by different concentrations of stearic acid: (a) taken immediately after preparation and (b) taken after two days.

**Figure S3.** The stability of emulsions stabilized by different concentration of stearic acid together with 0.33 wt% Al$_2$O$_3$ in water: (a) taken immediately after preparation and (b) taken after one year.
Figure S4. (a) The structure and (b) absorption and emission spectra of the used fluorescence molecule.

Figure S5. FTIR spectra of Al₂O₃, SA and SA-Al₂O₃ hybrid with various adsorption time.
Figure S6. Digital photos of (a) pristine Al₂O₃ fibers and (b) CCA-labelled-Al₂O₃ nanofibers excited under 365 nm UV light.

Figure S7. (a) The confocal image of two kinds of Al₂O₃ nanofibers: (i) the original fluorescence-labelled-Al₂O₃ nanofibers; and (ii) after sonicating for 2 min in oil phase. (b), (c) corresponding fluorescence intensity under different angle of view. The decrease of fluorescence intensity indicating the detachment of SA from Al₂O₃ nanofibers upon sonicating.
**Figure S8.** FTIR spectra of Al$_2$O$_3$ fibers after stearic acid adsorption and sonication. The decrease of peak intensity indicating the detachment of SA from Al$_2$O$_3$ nanofibers upon sonicating.

**Figure S9.** Hexane-water emulsions stabilized by recycled SA-Al$_2$O$_3$ hybrid. The hybrid was thoroughly washed with ethanol to remove physically adsorbed SA.
Figure S10. SEM (a) and TEM (b) images of the 3D SA-Al$_2$O$_3$ foam.

Figure S11. A series of digital photos showing the hydrophobic property of the hybrid foam. When press the hybrid foam into water, it rebounded immediately.