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Robust Liquid Marbles Stabilized with Surface-Modified Halloysite Nanotubes

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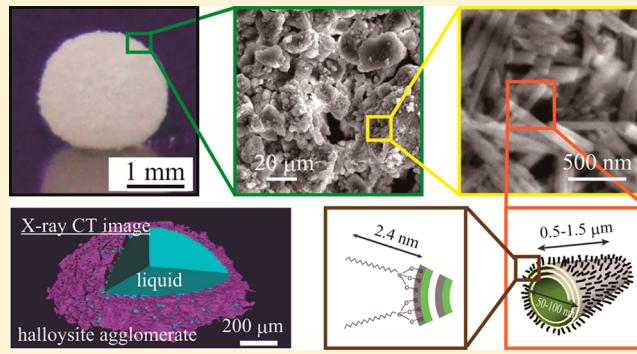
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S Supporting Information

ABSTRACT: We have demonstrated the fabrication of fluorine-free liquid marbles from halloysite nanotube. Halloysite is a naturally occurring inorganic nanotube that has a high aspect ratio, and the surface was modified with octadecyltrimethoxysilane. The surface-modified halloysite formed pincushion agglomerates on the surface of the liquid droplets, which create superhydrophobic surface similar to that of the plant gall surface prepared by aphids. As a result, the liquid marbles showed high mechanical strength upon impact without the use of low surface energy fluoroalkyl or fluorine-modified materials. Our results suggest a new strategy for designing novel materials for liquid marbles inspired by nature.



INTRODUCTION

The manipulation of small quantities of liquids on solid surfaces is of universal importance in miniaturized systems for chemical, electronic, and biological applications.^{1–5} The formation of liquid marble in which micro- or nanoscale hydrophobic solid particles encapsulates a small droplet of liquid is one of the useful way to achieve this goal.^{6,7} Liquid marbles maintain their spherical shape on various substrates and move smoothly over any substrate without leakage of liquid. Many researchers have focused on understanding the unique physical properties as well as demonstrating their potential applications.^{6–23} Liquid marbles have mainly been prepared using low surface energy fluoroalkyl or fluorine-modified particles of a uniform size.

Liquid marble is also found in nature, and insects, such as aphids and whiteflies, prepare liquid marbles to avoid sticking to and drowning in the honeydew droplets that they excrete.^{24,25} They coat the honeydew with a wax secretion that is a mixture of long-chain esters, alcohols, aldehydes, and fatty acids.²⁴ The insects then push the marbles out of the plant galls they inhabit. Interestingly, aphids fabricate liquid marbles utilizing carbon-neutral material that does not have the lowest surface energy like fluorinated materials. Surface wettability is determined by the surface topography and its chemical composition. Because the secreted powdery wax has needlelike morphology, the inner gall surface with the weakly compacted wax needles exhibits high water contact angle over 160°. Therefore, a liquid marble coated by the wax shows high

stability. Here, we have proposed a new strategy for designing liquid marbles inspired by nature. We focused on the unique morphological feature of halloysite nanotube.^{26–31} Because halloysite has submicrometer outer diameter with several hundred micrometers length, modified halloysite formed asymmetric networks or aggregates to show superhydrophobicity. The morphology was investigated by X-ray computed tomography (X-ray CT) and scanning electron microscopy (SEM) observations. Moreover, mechanical stability of the liquid marbles was evaluated by impact tests. The fabrication of liquid marble utilizing carbon neutral materials based on the particle shape, size, and mechanical properties is strongly desired for various bio-related applications such as deliverable capsules, bioreactors, in cosmetics, and for controlled drug delivery system.

EXPERIMENTAL SECTION

Materials. Halloysite nanotubes were gifted from Prof. Yuri Lvov of Louisiana Tech University. *n*-Octadecyltrimethoxysilane was obtained from Gelest Inc. All solvents in this study were purchased from Kanto Chemicals and used without further purification. Poly(tetrafluoroethylene) (PTFE) microparticles (35 μm diameter) were obtained from Sigma-Aldrich Co. LLC.

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Synthesis of ODTMS-Modified Halloysite Nanotubes. ODTMS-modified halloysite nanotubes were obtained as follows: Halloysite nanotubes (1 g) were dispersed in dry toluene (50 mL), and ODTMS (2.2 mL) was added in a glovebox. The mixture was stirred for 90 h at room temperature, and then the modified halloysite was centrifuged and shaken thoroughly with dry toluene, ethanol, water, and acetone repeatedly to remove excess ODTMS. The final product (ODTMS-modified halloysite) was dried at 120 °C for 20 h under vacuum.

X-ray CT Observations. A X-ray microscope at the beamline 20XU (Experimental Hutch II) in the synchrotron radiation facility Super Photon ring 8 GeV (SPring-8) in Hyogo, Japan, was used for 3D structural observations. The intensity of X-ray irradiation was fixed at 12 keV through a double-crystal monochromator. The stage was rotated in every 0.2° steps for 180° with low speed (100 Hz). X-ray images at different angles were recorded using a charge coupled device (CCD) camera, and the effective pixel size was 1.33 μm/pixel. The recorded images were reconstructed to obtain tomograms, which were stacked to generate 3D images. The image analysis was done using Amira 5 software (FEI Visual Science Group).

Impact Tests. The liquid marbles were put on a silicon substrate (unpolished side) that was placed with a certain height, and the marble were dropped to ground by tilting the substrate. To guarantee a quasi-free-falling test, the tilting was precisely controlled at 0.1°/step by a stepping motor (ALS-602-HOM; Chuo Seiki). Another silicon substrate was placed on the ground, and the impact of the liquid marble to the substrate was monitored by capturing the digital images using a high-speed camera (FASTCAM MC2.1, Photron). The image capture was done with 512 × 512 pixels at a frame rate of 2000 frames/s.

Measurements. The thermal properties of unmodified and modified halloysite were analyzed by a PerkinElmer Pyris 1 thermogravimetric analyzer. The sample was heated from 40 to 800 °C with scanning rate of 10 °C/min under N₂ flow of 20 mL/min. FT-IR spectra were recorded on a Bruker Optics VERTEX70 spectrophotometer. Static water contact angle (CA) measurement was performed using a DSA10 Krüss contact angle measurement system equipped with an automatic liquid dispenser and a monochromatic CCD camera. Scanning electron microscopy (SEM) observation was performed using a Hitachi S-4300SE.

RESULTS AND DISCUSSION

Surface Modification of Halloysite Nanotubes. Because the external surface of halloysite nanotubes is similar to silica,^{32,33} the tube surface properties can be tuned by covalently attaching silane compounds to produce organo-functionalized surfaces.^{34–37} We created halloysite with desirable properties of low-energy surface by modifying the surface with a long-chain alkylsilane, *n*-octadecyltrimethoxysilane (ODTMS) (Figure 1). The thickness of the modified

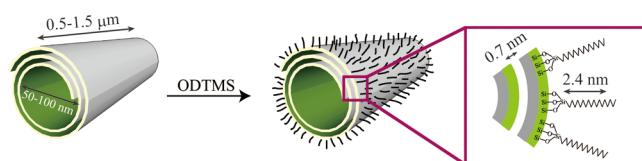


Figure 1. Schematic illustration of the halloysite nanotube surface modified with ODTMS.

organosilane layer was evaluated using an ODTMS-modified silicon wafer as a reference because of the similarity of the external surface of halloysite to an oxidized silicon wafer. The thickness was measured with a spectroscopic ellipsometer (Mass-103FH; Five Lab., Co. Ltd.) as 2.4 ± 0.1 nm, indicating that an alkylsilane monolayer^{38,39} was attached to the surface. The thermogravimetric analysis (TGA) (see Supporting

Information, Figure S1) showed that ~6.4 wt % of the organosilane was immobilized on the halloysite. In the FT-IR spectra of the modified halloysite (Figure S2), the peak positions of CH₂ asymmetric stretching vibrations $\nu_a(\text{CH}_2)$ at 2923 cm⁻¹ and symmetric stretching vibrations $\nu_s(\text{CH}_2)$ at 2853 cm⁻¹ indicated that an amorphous alkylsilane monolayer with a gauche-rich conformation was formed on the halloysite surface. The surface modification was only accomplished on the external surface of the halloysite as confirmed by the water contact angle measurements of the corresponding flat substrates (Figure S3). The inner lumen of halloysite nanotubes that is similar to alumina was intact against ODTMS.

To evaluate the hydrophobicity of the modified halloysite, the water contact angle (CA) was measured by placing water drops (5 μL) on the surface of the molded powder. The powder surfaces were prepared by gently pressing the powders onto an adhesive (Pritt, Henkel) on a silicon wafer.¹² The CA of the original halloysite was less than 10° (Figure 2a), indicating the raw material was hydrophilic.²⁸ After it was modified by ODTMS, the apparent CA increased to 164.1 ± 2.7° (Figure 2d). This value was higher than that of the reference PTFE microparticles with 35 μm diameter (CA 140.3 ± 4.4°, Figure 2b) and ODTMS-modified silicon wafer (CA 102.0 ± 1.0°, Figure 2c). Similar to the inner gall surface made by aphids, roughness-induced superhydrophobicity was achieved on the pincushion surface of halloysite. The water droplets exhibited strong adhesion and high hysteresis on the surface. The water droplet maintained its spherical shape and remained attached to the surface even when the surface was tilted at 90° (Figure 2e) and 180° (Figure 2f). This resembled the rose petal effect; the droplet was in the Cassie impregnating wetting regime to produce high contact angle hysteresis.^{12,40–42} It indicates that the water droplet entered even in the hollows of pincushion surface of needle-like halloysite nanotubes.

Morphology of Halloysite Nanotubes and the Liquid Marble. SEM observations were conducted to evaluate the morphology of halloysite nanotubes. The individual ODTMS-halloysite consisted of nanotubes with a length of 0.5–1.5 μm and an external diameter of 50–100 nm (Figure 3a). No critical difference was observed before and after the surface modification. The ODTMS-modified halloysites were randomly self-assembled to form agglomerates ranging from submicrometers to tens of micrometers (Figure 3b,c). The surface of agglomerates has pincushion structure owing to the needle-like morphology of individual halloysite.

The agglomerated structure was maintained even in a liquid marble. Figure 4 shows the reconstructed 3D image of the water marble obtained using X-ray computed tomography (X-ray CT) at the BL20XU beamline of SPring-8. The liquid marbles were fabricated by placing ~5 μL of the liquid on the modified halloysite powder and gently shaking it. The measurement was done in a sealed capillary tube to reduce the evaporation of water. The modified halloysite formed aggregates with irregular shapes, and it spread randomly over the entire surface of the liquid droplet (Movie S1). The size of agglomerates is almost the same as we observed by SEM before liquid marble formation. Moreover, similar surface morphology of air/solid and solid/liquid interfaces indicates that halloysite agglomerates simply coated water droplet with random orientation (Figure 4b). It revealed that the surface morphology of halloysite agglomerates was remained intact even after the liquid marble formation. In Figure 4, it seems as though inside liquid was exposed to atmosphere. However, it arose from the

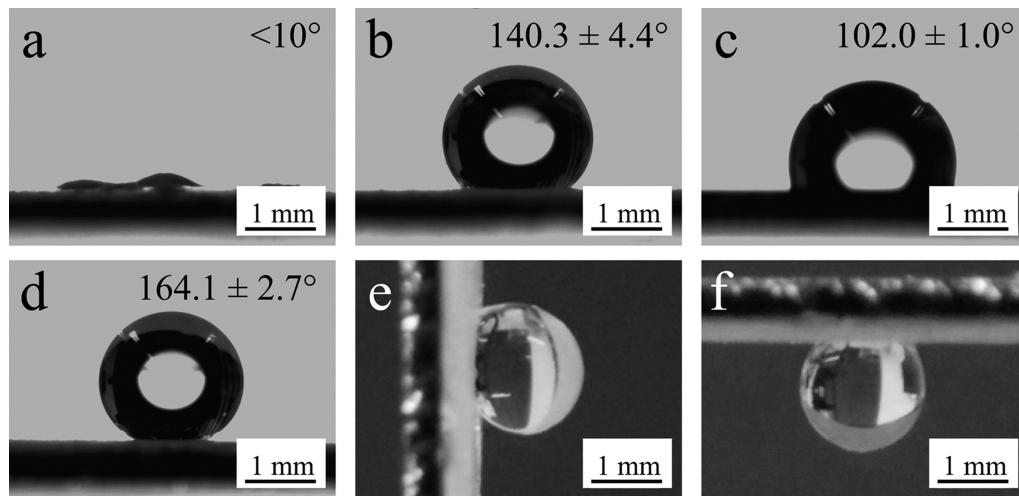


Figure 2. Micrographs of 5 μL water droplets on the surfaces of (a) original halloysite, (b) 35 μm PTFE microparticles, (c) ODTMS-modified silicon wafer, and ODTMS-modified halloysite held (d) horizontally, (e) vertically, and (f) upside down.

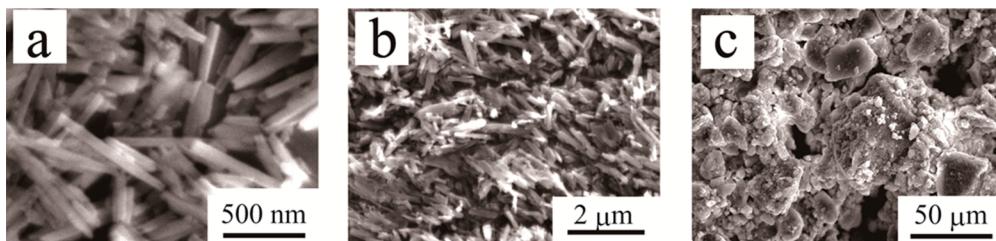


Figure 3. SEM image of ODTMS-modified halloysite nanotubes with different magnification.

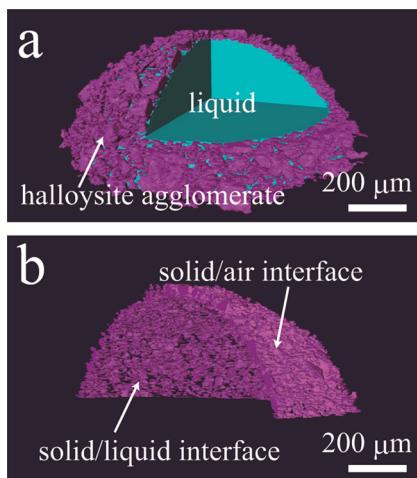


Figure 4. Reconstructed 3D X-ray CT image of water marble stabilized by ODTMS-modified halloysite: (b) is the shell structure in (a).

presence of small agglomerates that were not detected due to the limitation of the X-ray CT resolution. The bigger agglomerates formed a skeleton and the smaller ones filled the gaps. The thickness of shell was estimated to be 70 μm from the cross-sectional image of X-ray CT.

Physical Properties of Halloysite Nanotubes and the Liquid Marbles. Liquid marbles were obtained from various liquids, including water, glycerol, and several ionic liquids with ODTMS-modified halloysite (Figure S4a–d). Considering the interface interaction between the nanoparticles and liquid, the spreading coefficient ($S_{S/L}$) was used to evaluate the formation

of liquid marbles.²⁰ The solid–overliquid spreading coefficient can be defined as follows

$$S_{S/L} = -2\gamma_s + 2\sqrt{(\gamma_L^d\gamma_S^d)} + 2\sqrt{(\gamma_L^p\gamma_S^p)} \quad (1)$$

where γ_L^d and γ_L^p are the dispersive and polar components of the surface energy of a liquid, and γ_s^d and γ_s^p are those of the modified halloysite particles. To evaluate the surface energy of modified halloysite, the ODTMS-modified silicon wafer was used as reference because of the similarity of external surface of halloysite to silica. The values are calculated as 26.9 and 1.5 mN/m for dispersive and polar components from the static contact angle measurements of water and CH_2I_2 as probing liquid. The surface energies of liquids and the corresponding calculated $S_{S/L}$ values are shown Table 1. The positive values of the calculated $S_{S/L}$ indicate that the formation of liquid marbles from these liquids is thermodynamically possible.^{13,20}

Since the wrapping of hydrophobized halloysite alters the surface tension of the liquid droplet, the effective surface tension (γ_e) of the liquid marbles was evaluated by the puddle height of large marbles.¹⁴ The effective surface energy (γ_e) can be calculated by the equation

$$\gamma_e = \frac{\rho g H_{\max}^2}{4 \sin^2\left(\frac{\theta}{2}\right)} \quad (2)$$

where ρ is the liquid density, g is gravitational constant, H_{\max} is maximal marble heights, and θ is the apparent contact angle of the liquid on the powder surface. H_{\max} can be obtained from the photos of large marbles with puddle shape using liquid volume of 500 μL (Figure S5).⁴ Table 2 lists the parameters of density and effective surface energy (γ_e) of liquid marbles

Table 1. Surface Energies of Liquids and the Corresponding Calculated $S_{S/L}$ Values for Liquid Marble Formation

liquids	surface energy (mN/m)				formation
	γ_d^a	γ_p^b	γ	$S_{S/L}^c$ (mN/m)	
water	22.6	50.2	72.8	9.9	yes
glycerol	40.6	22.8	63.4	21.0	yes
dimethyl sulfoxide	29.0	14.5	43.5	8.4	no
ethanol	20.3	1.9	22.2	-6.7	no
1-ethyl-3-methylimidazolium dicyanamide	33.2	26.8	60.0	15.6	yes
1-ethyl-3-methylimidazolium tetrafluoroborate	32.8	25.1	57.9	14.9	yes
1-butyl-3-methylimidazolium tetrafluoroborate	31.4	18.3	49.7	11.8	yes
1-hexyl-3-methylimidazolium tetrafluoroborate	12.4	17.8	30.2	-9.9	no

^aDispersive component. ^bPolar component. ^cDetermined by eq 1.

Table 2. Physical Parameter of Liquid Marbles

liquids	ρ^a (g/cm ³)	H_{\max}^b (mm)	apparent CA ^c (deg)	γ_e^d (mN/m)
water	1.000	4.61	164.1	53.1
glycerol	1.261	4.07	163.7	52.2
1-ethyl-3-methylimidazolium dicyanamide	1.106	3.71	143.8	41.5
1-ethyl-3-methylimidazolium tetrafluoroborate	1.279	3.73	139.8	49.5

^aLiquid density. ^bMaximal marble heights. ^cApparent contact angle of the liquid on the powder surface determined digital camera images.

^dEffective surface energy.

prepared with different liquids. The γ_e values of liquid marbles prepared with water, glycerol, 1-ethyl-3-methylimidazolium dicyanamide, and 1-ethyl-3-methylimidazolium tetrafluoroborate were calculated to be 53.1, 52.2, 41.5, and 49.5 mN/m, respectively. These values were lower than the surface tension of the corresponding pure liquids and the marble coated with PTFE microparticles (59.3 mN/m for water marble). The difference of effective surface tension may provide the difference of mechanical stability of liquid marble owing to the difference of capillary interaction between the solid particles.^{14,21}

Mechanical Stability of Liquid Marble. To further understanding the mechanical stability of liquid marbles, stability of liquid marbles on impact was evaluated by dropping the liquid marbles from a given height. Because kinetic energy of free fall was converted into surface energy, the mechanical stability was simply assessed by comparison of the maximum height before the liquid marble ruptures. The water marbles prepared with ODTMS-halloysite bounced on the silicon wafer with a maximum height of 2.3 cm (Movie S2), which was much higher than the marbles prepared with Janus microspheres (less than 1.0 cm)¹⁹ and slightly higher than for marbles prepared with 35 μ m PTFE microparticles (2.2 cm). The difference was more clear when glycerol marbles were measured (9.0 and 7.1 cm for ODTMS-halloysite and PTFE, respectively). It is obvious that ODTMS-halloysite liquid marble has higher mechanical stability than PTFE liquid marble.

CONCLUSIONS

We have demonstrated that the use of low surface material such as fluorinated material is not the only way to stabilize liquid marbles. A new strategy for the preparation of liquid marbles is possible by learning the designing from nature. The strategy is based on the fabrication of superhydrophobic solid surface by morphological control of surfaces. Natural halloysite nanotubes were modified with a long-chain alkylsilane, ODTMS, and the agglomerates exhibited roughness-induced superhydrophobicity. As a result, liquid marbles showed high mechanical strength upon impact. These halloysite liquid marbles could be useful for deliverable capsules, bioreactors, in cosmetics, and for controlled drug delivery because of the fluorine-free characteristics.

ASSOCIATED CONTENT

Supporting Information

TGA spectra, FT-IR spectra, and static water contact angle data of samples; photographs of liquid marbles; 3D structure of water marble (Movie S1) and bouncing of a liquid marble (Movie S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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