

Superamphiphobic Macroporous Silicone Monolith with Marshmallow-like Flexibility

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A number of researchers have been studying on the creation of hydrophobic and oleophobic surfaces due both to the pure scientific interest and to industrial applications. These studies are becoming to draw increasing attention because of growing demands for applications such as anti-fingerprint touch panels on electronic devices and solar panels which can prevent their output fall from dusts and smears on the surface by the self-cleaning effect.^[1] In nature, many examples of superhydrophobic surface whose water contact angle is above 150 ° such as eyes of mosquitos and lotus leaves,^[1a, 2] and these are important for their survival. Their non-wetting surfaces possess a combination of nano- or micro-scaled roughness^[3] and low surface energy, which are known for the key of creating artificial superhydrophobic surfaces.^[1a] However, most of the superhydrophobic materials can easily be wetted by organic liquids because of lower surface tension of the liquids. Recent years, techniques for creating oleophobic surfaces are under vigorous progress. The promising way to obtain the surface with above 150 ° of organic liquids contact angle is making rough microstructure covered with perfluoro-alkyl groups, which are bound on some kinds of polyhedral oligomeric silsesquioxanes (POSS),^[4] monomeric silanes,^[5] and polymers.^[6] However, the reported technologies to achieve superamphiphobicity are limited in the forms of films and fibers. As far as we know, there have been no reports on monolithic superamphiphobic materials which can be prepared in a wide range of thickness and in any shapes.

We have been recently investigating “marshmallow-like” gels derived from tri- and difunctional alkoxy silanes as co-precursors through a facile one-pot sol-gel reaction.^[7] These silicone-based

macroporous materials have high porosity (> 90 %), flexibility both for compression and bending and in-built superhydrophobicity. The marshmallow-like gels can be used like a sponge for quick removal of organic liquids/oils from oil-water mixtures for environmental purposes and for new solid-phase extraction media in analytical chemistry. By changing the combination of the alkoxy silanes, various kinds of marshmallow-like gels with different functional groups can be obtained. For example, in the case of methyltrimethoxysilane–dimethyldimethoxysilane copolymer system, the obtained gels are composed of the crosslinked polydimethylsiloxane (PDMS)-like molecular structure. They keep the flexible mechanical properties in a wide temperature range from –130 °C to 320 °C evidenced from thermal and mechanical analyses. Moreover, due to their elasticity and bendability even under –196 °C, we can successfully absorb and squeeze-out liquid nitrogen. In the case of (3-mercaptopropyl)trimethoxysilane–(3-mercaptopropyl)methyldimethoxysilane copolymer system, gold ions can be adsorbed on the pore surface due to the mercapto groups.

Here we employed a vinyltrimethoxysilane (VTMS)–vinylmethyldimethoxysilane (VMDMS) co-precursor system to create the first superamphiphobic monolith. The VTMS–VMDMS marshmallow-like gel can be obtained by simple 4 routine steps within half a day; 1) mixing VTMS, VMDMS, urea, and surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) in a dilute aqueous acetic acid solution, and stirring for 60 min at room temperature for acid-catalyzed hydrolysis of alkoxy silanes; 2) transferring the resulting transparent sol to an oven for gelation and aging at 80 °C over several hours to promote the siloxane network formation in a basic condition, which is brought up by the hydrolysis of urea into ammonia; 3) washing with alcohol by hand; and 4) evaporative drying under an ambient condition (Figure 1a). The obtained gel (MG1) shows marshmallow-like flexibility enough to recover their original shape from 80 % uniaxial compression and 3-point bending (Figures 2 and S1). This material possesses superhydrophobic surface whose water contact angle is 153 ° due to the negligible amount of residual hydrophilic silanol groups as characterized by ²⁹Si solid-state cross polarization/magic angle spinning (CP/MAS) NMR (Figure S2).^[8] However, MG1 does not show oleophobicity but absorbs organic liquids quickly like a sponge (Figure 3a) as mentioned before.

To transform the superhydrophobic gel into the superamphiphobic one, the thiol-ene click reaction, which is well-known as a facile and reliable method to bind molecules for the purpose of surface modification as well as in organic synthesis,^[9] has been used. We attached perfluoro-alkyl groups to the rich vinyl groups on the pore surface of MG1 (0.5 g, 6.2 mmol) by soaking in 50 mL of a 2-propanol solution containing 10 v/v % 1*H*,1*H*,2*H*,2-*H*-perfluorodecanethiol (18 mmol, excess) with a catalytic amount of *N,N'*-azobisisobutyronitrile (AIBN, a radical initiator) for 10 h, and characterized surface and microstructure of the obtained gel (MG2) (Figure 1b). By X-ray photoelectron spectroscopy (XPS) survey spectra, the presence of the elements F (F_{1s} at 688.6 eV) and S (S_{2p} at 163.8 eV)^[10] is detected on MG2 (Figure 4a). Consistently with

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



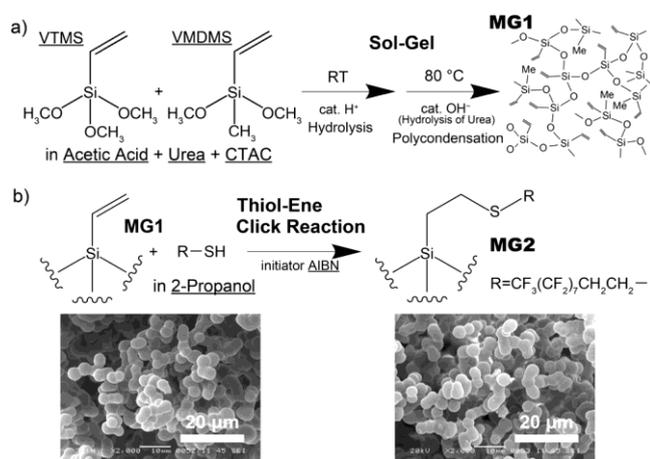


Figure 1. a) One-pot acid-base sol-gel synthesis scheme for the VTMS-VMDMS marshmallow-like gel (MG1). b) Synthetic approach for the oleophobic MG2 by attachment of perfluoro-alkyl groups onto the rich vinyl groups on MG1 pore surface by the thiol-ene click reaction. From SEM observations, no changes are found in the macroporous morphology by the reaction.

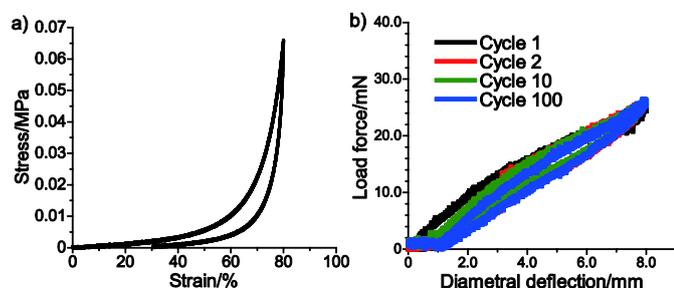


Figure 2. Stress-strain curves of a) uniaxial compression test and b) 100 cycles of 3-point bending test on the sample MG1. In both cases, VTMS-VMDMS marshmallow-like gels perfectly recover their original shape. (See also Figure S1)

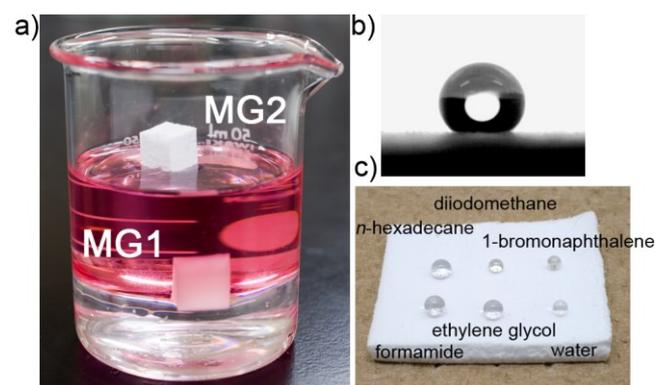


Figure 3. a) The superhydrophobic marshmallow-like gel (MG1) and the superamphiphobic marshmallow-like gel (MG2). MG2 floats on 1,3,5-trimethylbenzene (colored by Oil Red O) by its surface tension, while MG1 absorbs it. The colorless liquid at the bottom is water. b) The contact angle of *n*-Hexadecane is 151°. c) MG2 with droplets of water, ethylene glycol, formamide, 1-bromonaphthalene, diiodomethane and *n*-hexadecane.

the elemental analysis (C, H, F) results, the fluoride content on the surface of MG2 is around 50 atomic %, which indicates that

1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol is well-attached to the vinyl groups, covering the most part of the macropores of MG1. Unreacted vinyl groups are also detected from Fourier transform infrared (FTIR) spectroscopy (=CH₂ wagging at 970 cm⁻¹, C=C twist at 1000 cm⁻¹, =CH₂ scissor at 1400 cm⁻¹, and C=C stretching at 1600 cm⁻¹)^[11] and ¹³C solid-state dipolar decoupling/magic angle spinning (DD/MAS) NMR spectra (Figure 4b and c). Percentage of reacted vinyl groups is only 3-5 % by estimating from the density change of MG1 and MG2 (0.122 g cm⁻³ and 0.157 g cm⁻³, respectively), ¹³C NMR spectra, and elemental analysis, simply because the perfluoro-alkyl groups are attached only onto the vinyl groups on the macropore surface. The rather large perfluorodecanethiol molecules could not permeate into the core of the nonporous micron-sized skeletons. During this surface reaction, there is no change in the microstructure which possesses enough roughness to show high water contact angle (Figure 1b). After the treatment, MG2 acquired superoleophobicity (Figure 3a and Movie S1). The contact angles of water and *n*-hexadecane are 160° and 151°, respectively (Figure 3b and c). Likewise, the surface of monolithic MG2 shows superoleophobicity for ethylene glycol, formamide, diiodomethane and 1-bromonaphthalene (Figure 3c). From these results, it can be concluded that the hydrophobic monolithic macroporous silicone gels bearing vinyl groups on the surface is imparted with oleophobicity by a facile process.

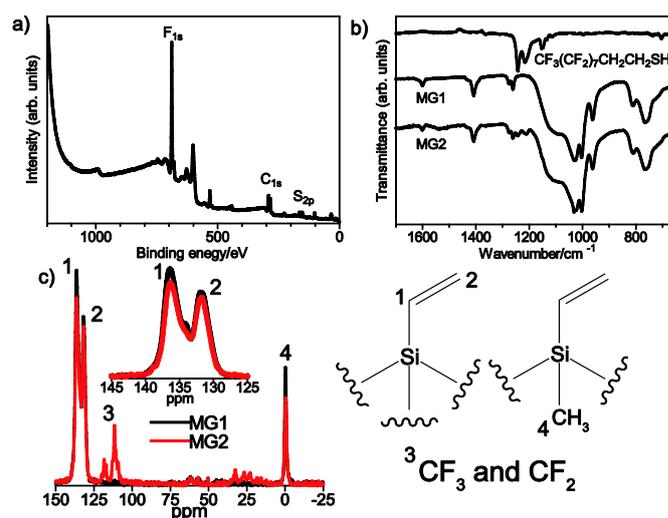


Figure 4. a) XPS survey spectrum of MG2, revealing the presence of F. b) FTIR spectra of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol, MG1 and MG2. c) ¹³C solid-state DD/MAS spectra of MG1 and MG2. Four percent of vinyl groups are reacted by the thiol-ene click reaction. For MG2; ¹³C NMR δ = 0.38 (s, Si-CH₃, overlapped with Si-CH₂), 22.77–32.57 (t, CF₂-CH₂), 50.41 (s, OCH₃), 109.17–118.33 (m, other carbons in CF₃ and CF₂), 131.76 (s, CH=CH₂), 136.31 (s, CH=CH₂).^[14] Two peaks at ca. 60 ppm are spinning sidebands.

Significant features of the marshmallow-like gel including MG1 are not only the flexibility but also the wide controllability in size and shape of the monolith. We obtained MG1 as flexible sheets as well as bulky monoliths, which can be carved into desired shape and size. These features are maintained in MG2 (Movie S1) because MG2 can be obtained from MG1 only by the surface modification without changing the original siloxane network and microstructure. The most important feature of MG2 is superamphiphobicity on any cutting surface. This can be explained by the microstructure of marshmallow-like gels. Marshmallow-like gels have co-continuous

structure derived from the transient structure of spinodal decomposition.^[7, 12] On cutting any face, the fraction of the unmodified cores of intricate micron-sized skeletons on the new surface plane is appreciably low and the modified pore surfaces of the skeletons largely contribute to the oleophobicity. In fact, it is hard to recognize the cross-section of cut skeletons in the SEM image (Figure S3). Thus, non-oleophobicized core parts of the cutting surfaces of MG2 can be ignored and this material keeps superamphiphobicity on any surfaces after cutting into desired shape. Although marshmallow-like gels are not so strong against tensile stress and friction due to their thin skeleton, they can keep their superamphiphobicity for good. By this feature together with low density, the machined MG2 can float on organic liquids such as 1,3,5-trimethylbenzene and *n*-hexadecane by surface tension at least over a week without any change (Figure 3a and Movie S2). These features have not been reported on other materials so far. Thermogravimetry-differential thermal analysis (TG-DTA) result shows that MG2 is stable up to ca. 170 °C (Figure S4). At higher temperature, the macroporous structure was gradually collapsed by the oxidation and degradation of vinyl groups.

In summary, we have successfully obtained the first superamphiphobic monolith with contact angle greater than 150 ° for both water and organic liquids such as ethylene glycol, formamide, diiodomethane, 1-bromonaphthalene and *n*-hexadecane. This material can be facilely obtained by a combination of the simple one-pot sol-gel process and the thiol-ene click reaction. Co-continuous macroporous structure covered with perfluoro-alkyl groups supplies roughness and low surface energy, resulting in superamphiphobicity on any cutting surfaces of the monolith. The superamphiphobic marshmallow-like gel floats on the surface of water and oils for long by surface tension. This unique and outstanding monolithic material is expected to pioneer the scientific and technological interests of three-dimensional superamphiphobic materials. In addition, novel applications to new self-cleaning and antifouling surfaces, gas-permeable separators, medical/biomedical materials, and selective separation media for organic liquid would be developed by carefully tuning the surface energy and roughness of the monolith.^[7a,13] Formability of the material in such as monoliths and sheets/membranes, as well as developing coating films and particles, would allow extended applications in various fields.

Experimental Section

Experimental details can be found in the Supporting Information.

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