Angewandte
Communications

Superamphiphobic Materials

DOI: 10.1002/anie.201304169

A Superamphiphobic Macroporous Silicone Monolith with Marshmallow-like Flexibility**

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A number of research groups have been studying the preparation of hydrophobic and oleophobic surfaces, both for pure scientific interest and industrial applications. These studies are drawing increasing attention because of the growing demands for applications such as anti-fingerprint touch panels on electronic devices and solar panels that can prevent output fall from dust and smears on the surface by the self-cleaning effect.[1] In nature, many examples of superhydrophobic surface exist with a water contact angle of more than 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 microscaled 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 the lower surface tension of the liquids. In recent years, techniques for creating oleophobic surfaces have been vigorously investigated. A promising way to obtain a surface with a contact angle of more than 150° for organic liquids is to make rough microstructures covered with perfluoroalkyl 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 that 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 alkoxysilanes 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 built-in 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 alkoxysilanes, 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 cross-linked polydimethylsiloxane (PDMS)-like molecular structure. They retain the flexible mechanical properties over a wide temperature range from −130 °C to 320 °C, as evidenced from thermal and mechanical analyses. Moreover, owing to their elasticity and bendability even at temperature of 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 by the mercapto groups.

We employed a vinyltrimethoxysilane (VTMS)-vinylmethyldimethoxysilane (VMDMS) co-precursor system to prepare the first superamphiphobic monolith. The VTMS-VMDMS marshmallow-like gel can be obtained by four simple, 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 alkoxysilanes; 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 under basic conditions, which is brought up by the hydrolysis of urea into ammonia; 3) washing with alcohol by hand; and 4) evaporative drying under ambient conditions (Figure 1 a). The obtained gel (MG1) shows enough marshmallow-like flexibility to recover their original shape from 80 % uniaxial compression and 3-point bending (Figure 2; Supporting Information, Figure S1). This material has a superhydrophobic surface with a water contact angle of 153°, which is due to the negligible amount of residual hydrophilic silanol groups, as characterized by ^{29}Si solid-state cross polarization/magic angle spinning (CP/MAS) NMR spectroscopy (Supporting Information, Figure S2).[8] However, MG1 does not show oleophobicity, but absorbs organic liquids quickly like a sponge (Figure 3 a) as mentioned before.

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[**] This work was supported by a Grant-in-Aid for Scientific Research (No. 25·1089 and 24550253) administrated by the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Japan). This study was carried out with the NMR spectrometer in the Joint Usage/Research Center (JURC) at Institute for Chemical Research, Kyoto University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304169.

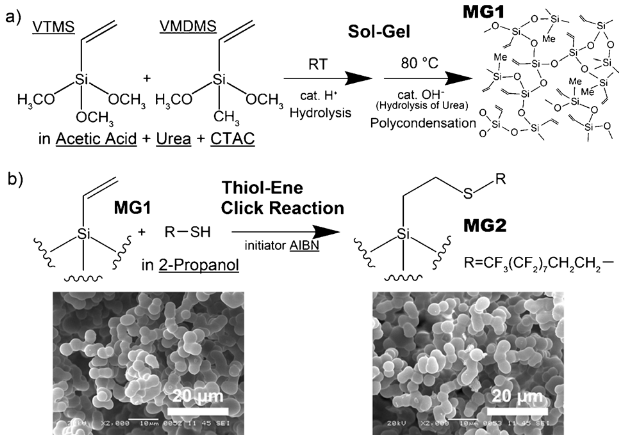

Figure 1. a) One-pot acid–base sol–gel synthesis for the VTMS-VMDMS marshmallow-like gel (MG1). b) Synthetic approach for the oleophobic MG2 by attachment of perfluoroalkyl groups onto the vinyl groups on MG1 pore surface by the thiol–ene click reaction. From SEM observations, no changes are found in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

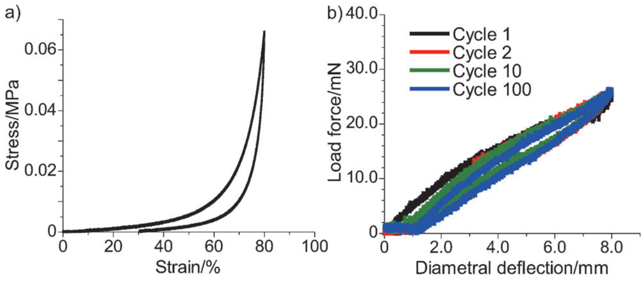

Figure 2. Stress–strain curves of an a) uniaxial compression test and b) 100 cycles of a three-point bending test on the sample MG1. In both cases, VTMS-VMDMS marshmallow-like gels perfectly recover their original shape (see also the Supporting Information, Figure S1).

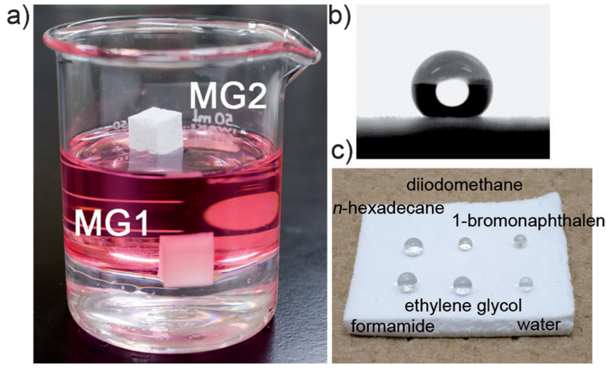

Figure 3. a) The superhydrophobic marshmallow-like gel (MG1) and the superamphiphobic marshmallow-like gel (MG2). MG2 floats on 1,3,5-trimethylbenzene (colored by Oil Red O) by its surface tension, while MG1 absorbs it. The colorless liquid at the bottom is water. b) The contact angle of *n*-hexadecane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

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 perfluoroalkyl 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 1 b). By an 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 4 a). Consistent with the elemental analysis (C, H, F) results, the fluoride content on the surface of MG2 is around 50 atom%, 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 FTIR spectroscopy (=CH_2 wagging at 970 cm^{-1}, C=C twist at 1000 cm^{-1}, =CH_2 scissor at 1400 cm^{-1}, and C=C stretching at 1600 cm^{-1})[11] and ^{13}C solid-state dipolar decoupling/magic angle spinning (DD/MAS) NMR spectra (Figure 4 b,c). The 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), ^{13}C NMR spectra, and elemental analysis, simply because the perfluoroalkyl groups are attached only onto the vinyl groups on the macropore surface. The rather large perfluorododecanethiol molecules could not permeate into the core of the nonporous micrometer-sized skeletons. During this sur-

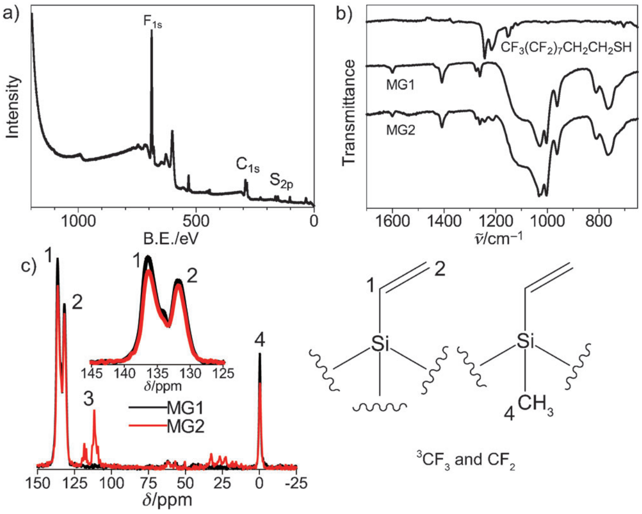

Figure 4. a) XPS survey spectrum of MG2, revealing the presence of F. b) FTIR spectra of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol, MG1, and MG2. c) ^{13}C Solid-state DD/MAS spectra of MG1 and MG2. Four percent of vinyl groups are reacted by the thiol–ene click reaction. For MG2: ^{13}C NMR $\delta = 0.38$ (s, Si-CH_3, overlapped with Si-CH_2), 22.77–32.57 (t, CF_2-CH_2), 50.41 (s, OCH_3), 109.17–118.33 (m, other carbons in CF_3 and CF_2), 131.76 (s, CH=CH_2), 136.31 (s, CH=CH_2).[14] Two peaks at about 60 ppm are spinning sidebands.

face reaction, there is no change in the microstructure, which possesses enough roughness to have a high water contact angle (Figure 1 b). After the treatment, MG2 acquired superoleophobicity (Figure 3 a; Supporting Information, Movie S1). The contact angles of water and *n*-hexadecane are 160° and 151°, respectively (Figure 3 b,c). Likewise, the surface of monolithic MG2 shows superoleophobicity for ethylene glycol, formamide, diiodomethane, and 1-bromonaphthalene (Figure 3 c). 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.

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 (Supporting Information, 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 micrometer-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 (Supporting Information, Figure S3). Thus, non-oleophobized 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 rather brittle against tensile stress and friction owing to their thin skeletons, their superamphiphobicity is perfectly maintained. 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 for at least over a week without any change (Figure 3 a; Supporting Information, Movie S2). These features have not been reported on other materials to date. Thermogravimetry–differential thermal analysis (TG-DTA) result shows that MG2 is stable up to about 170 °C (Supporting Information, Figure S4). At higher temperatures, the macroporous structure was gradually collapsed by 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 obtained in a facile manner 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. Furthermore, 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.

Received: May 15, 2013

Keywords: click chemistry · gels · hydrophobic effect · organic–inorganic hybrid composites · sol–gel processes

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