Hydrophobic Gels

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Facile Synthesis of Marshmallow-like Macroporous Gels Usable under Harsh Conditions for the Separation of Oil and Water**

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The separation of oil and water is an important pursuit for saving endangered environments. In 2010, the Gulf of Mexico oil spill widely and seriously damaged the ocean and coast near the oilfield. The number of similar accidents is increasing with the development of industry, and materials that can reduce environmental pollution are in high demanded. At the same time, in the area of analytical chemistry, the efficient separation of molecules is a key technique, which determines the efficiency and accuracy of chemical analysis and detection. For these purposes, hydrophobic porous materials are in common use, because hydrophobic surfaces effectively adsorb/absorb oily target compounds that are mixed with an aqueous phase. Therefore, many researchers have been studying hydrophobic porous materials and their application as oil/water separation media.[1] Various chemical compositions have been investigated, such as carbon-based materials,[2] metal oxide nanowires (such as manganese[3,4]), biomass nanofibers (such as cellulose[5,6]), organic polymers (such as polyester,[7] polydivinylbenzene, and polythiophene[8]) and hydrophobic macroporous aerogels.[9,10] Other materials based on polydimethylsiloxane (PDMS) or fluorocarbon-coated materials,[3,7,10,11] and the design of a biomimetic rough surface, through the use of etching techniques, to enhance hydrophobicity[6,12] are also widely reported. However, these methods have problems such as complicated and lengthy processes and high costs for reagents and devices, which prevents the use of these materials in practical and commercial applications.

We have investigated hydrophobic porous polymethylsilsesquioxane (PMSQ, $CH_3SiO_{1.5}$) materials, derived from methyltrimethoxysilane (MTMS), consisting of transparent aerogels and xerogels with mesoporous to macroporous monoliths that are created by controlling phase separation in the sol–gel process.[13] Polymethylsilsesquioxane gels have a superhydrophobic surface owing to methyl groups that are directly bonded to silicon atoms; this flexible network structure allows the material to spring back after compression. This mechanical feature allows the preparation of aerogel-like xerogels by ambient-pressure drying. Last year, we first reported bendable, marshmallow-like porous gels derived from a co-precursor system of MTMS and dimethyldimethoxysilane (DMDMS) in almost the same way as PMSQ gels.[14] Marshmallow-like gels not only show compression/reexpansion properties similar to that of PMSQ gels, but also very soft and bendable mechanical features. A high sound absorption property has also been previously reported, owing to the soft networks. The flexiblity and intrinsic hydrophobicity indicate that these materials can be used like a sponge as an adsorption/absorption media for the quick removal of unwanted organic liquids. Herein, we report the outstanding capability of these materials for absorbing organic liquids over a wide temperature range, and discuss the possibility for their application as separation media.

Recently, we succeeded in the preparation of various kinds of marshmallow-like gels derived from tri- and difunctional alkoxysilanes as co-precursors through a facile one-pot reaction. The combinations of alkoxysilanes and the standard synthesis are shown in Figure 1 a. Regardless of the combinations chosen, the synthetic procedure and conditions remain the same, which means that we can design flexible porous gels with different functional groups (for FTIR spectra, see the Supporting Information, Figure S1)[15] without the need for any complicated processes such as chemical vapor deposition, dip coating with PDMS, or additional polymerization of organic groups, all of which are necessary in the above-mentioned reports. To obtain gels, only four simple routine steps are needed: 1) mixing alkoxysilanes, urea, and the surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) in a dilute aqueous acetic acid solution, and stirring for 60 min at RT to promote hydrolysis; 2) transferring the solution to an oven for gelation at 80 °C over several hours; 3) washing with alcohol; and 4) evaporative drying under ambient conditions. Alkoxysilanes with higher hydrophobic organic groups such as 3,3,3-trifluoropropyl lead to macroporous skeletons that are more spherical, but each particle is tightly bound together at the neck, the diameter of which is several micrometers (Figure S2). The bulk body is elastic and bendable without any failure in the structure (Figure S3).

In the case of MTMS–DMDMS copolymers (these precursors are inexpensive and readily commercially available), the synthesis can be completed within a day, even on a multi-liter scale (Figure 1 b); the resulting gels can be formed in any shape desired. Before obtaining the final

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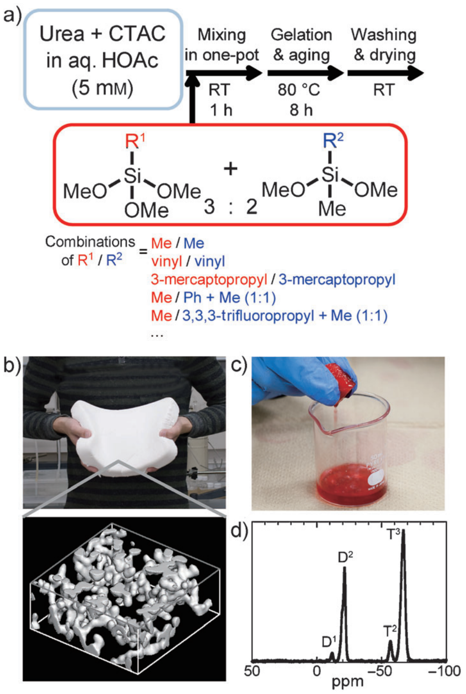

Figure 1. a) Facile synthesis of marshmallow-like gels derived from di- and tri-functional alkoxysilanes as co-precursors. b) The shape of the MTMS–DMDMS (R^1,R^2 = Me) gel produced on a 2.5 L scale, and its 3D microstructure (73.1 × 73.1 × 30.8 µm). c) The gel can be used to absorb organic liquids and then be squeezed out by hand. d) ^{29}Si solid-state NMR spectrum of the MTMS–DMDMS gel.

product, we need to wash out the surfactant and unreacted compounds; the sponge-like flexible nature of the material helps in this process, reducing the work to soaking and squeezing by hand (Figure 1 c). The ^{29}Si solid-state NMR spectrum shows that residual hydroxy groups are virtually negligible in the structure, which indicates that the network formation is complete in a few hours (Figure 1 d).[16] This is a great advantage for an emergency, such as an oil-spill accident, because the gels can be immediately synthesized, even on site.

In addition to the simple synthesis process, MTMS–DMDMS gels have a low density (ca. 0.12 g cm^{-3}, which corresponds to a porosity of >92 %) and superhydrophobicity (contact angle is ca. 153°; see Figure 2 a and Movie S1). The hydrophobicity is caused both by the geometrical rough surface, which is derived from a macroporous structure presumably formed by spinodal decomposition,[17] and by the many methyl groups and relatively few hydroxy groups exposed on the surface. To evaluate the material as an oil/water separation media, we tested its absorption–drying behavior using *n*-hexane as a model organic compound (Figure 2 b). Over ten repetitions, the gel showed stable performance: the gel absorbs ca. 6.2 times its dry weight in *n*-hexane, and no damage is observed. We also performed an *n*-hexane removal test using this material as a sponge (Figure 2 c and Movie S2). All of the *n*-hexane was successfully separated from water easily and quickly, even though there was larger quantity of liquid than could be absorbed at once.

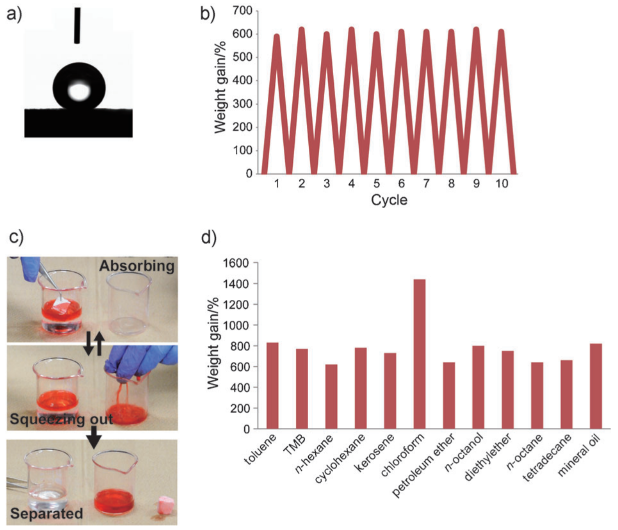

Figure 2. a) Superhydrophobic surface of the MTMS–DMDMS marshmallow-like gel. Contact angle is 152.6°. b) Weight gain during *n*-hexane absorption/drying cycles. c) The marshmallow-like gel can separate *n*-hexane from water (see also, Movie S2). d) Absorption capacities of the MTMS–DMDMS gel for various organic solvents and oils, as indicated by weight gain.

Also, the gels can absorb other organic liquids and still be dried by squeezing-out, even in the case of high-density oils (such as chloroform) and viscous oils (such as mineral oil with a comparable kinetic viscosity (ca. 44.6 mm s^{-1} at 40 °C) to medium crude oil[18]) in the same way as *n*-hexane. The organics are stored in the abundant pores of this material (Figure 1 b and Movie S3[19]), and the weight ratio of absorbed solvent/dried gel depends on the density of the organic compounds (Figure 2 d). Absorbing media specific to the chemical and physical nature of a desired organic compound can be designed both by changing the substituent groups in the precursors and by controlling flexibility and macropore skeleton diameters of this material, which is accomplished by changing the starting composition, such as the precursor ratio and the amounts of urea and CTAC.[14]

Because of the PDMS-like network, MTMS–DMDMS gels show high flexibility over a wider temperature range than conventional organic polymers such as polyurethane and polyethylene. MTMS–DMDMS gels can recover their original shape from 80 % uniaxial compression and a 3-point bending test at RT (Figure 3). To evaluate their thermal

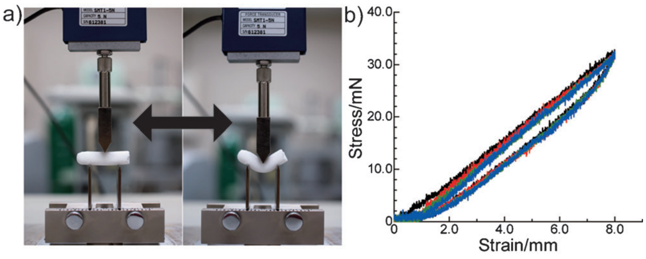

Figure 3. a) Photograph and b) stress-strain curves of a 3-point bending test on the MTMS–DMDMS gel. Cycle 1 (——), cycle 2 (——), cycle 10 (——), cycle 100 (——).

stability, we conducted thermogravimetry-differential thermal analysis (TG-DTA). The result shows that these materials are stable up to ca. 320 °C, whereas the methyl groups in the network are oxidized at higher temperatures (Figure S4). In fact, there was no change in the FT-IR spectra, mechanical properties, or contact angle of water after heat treatment at 315 °C for 24 h. This thermal stability is higher than oil/water separation media based on organic polymers. Moreover, even at low temperatures, the gels show high flexibility. From differential scanning calorimetry (DSC), no obvious glass transition is observed from RT to −130 °C. We could absorb and squeeze out a dry ice/ethanol mixture at ca. −70 °C. The flexibility of the swollen gel was not lost and they completely recovered their original shape after squeezing out the liquid (Figure 4a, strain was completely recovered after measurement). Furthermore, the gel even shows high flexibility in liquid nitrogen (LN_2), although the gel was somewhat hardened (Figure S5 and Movie S4). We could use the gel to absorb and squeeze out LN_2 as if it were water in a sponge (Figure 4b and Movie S5). Thus, MTMS–DMDMS gels can be also used as oil absorbing media in a very low temperature region, such as the polar zone. In fact, kerosene was successfully absorbed and squeezed out at 0 °C in exactly the same way as RT. No other materials have been reported to show high flexibility at such low temperatures except for entangled carbon nanotubes obtained by the "super-growth" method.[20]

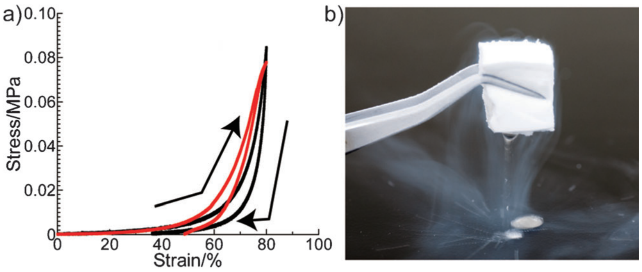

Figure 4. a) Stress–strain curves of the MTMS–DMDMS gel, both dried (——) and swollen with a dry ice/ethanol mixture (——). b) Squeezing out liquid nitrogen.

The functional groups on the marshmallow-like gels can be used for specific adsorption/absorption purposes. For example, in the case of (3-mercaptopropyl)trimethoxysilane-(3-mercaptopropyl)methyldimethoxysilane copolymerized gels, gold ions are adsorbed on the surface by simply soaking in an aqueous tetrachloroauric acid solution (Figure S6). By positioning organic groups other than methyl (such as phenyl and 3,3,3-trifluoropropyl) on the surface, hydrophobicity can be further increased. Owing to the soft and elastic porous structure it would also be possible to create new separation media for solid-phase extraction.[21] We have also succeeded in the synthesis of marshmallow-like materials derived from a bridged alkoxysilane and di-functional alkoxysilane as co-precursors (bis(methyldiethoxysilyl)ethane–DMDMS) with the same process (Figure S7). We will report the unique properties of these gels in greater detail in the near future.

In summary, we have reported the development of a new kind of superhydrophobic medium for the separation of oil and water. These marshmallow-like gels, which are based on polysiloxane networks, are synthesized from various alkoxysilanes, such as tri-, di-functional, and bridged alkoxysilanes, as co-precursors by a facile process and without special conditions. Copolymerization with various types of alkoxysilanes adds functionality to the gels, which allows for the flexible design of surface chemical properties. The obtained MTMS–DMDMS gels display superhydrophobicity and can act as a sponge, removing organic compounds from water by absorbing them and then releasing them upon being squeezed out. The elastic properties are maintained over a wide temperature range, from LN_2 temperatures up to ca. 320 °C, which extends their possible applications to use in harsh environments. The introduction of different functional groups allows for changing of the adsorption/absorption properties, which is advantageous in their use as separation media for different target compounds. Together with high sound absorption properties,[14] these unique multifunctional gels are expected to further extend the practical applications of this class of compounds.

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