DOI: 10.1002/anie.200((will be filled in by the editorial staff))

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

Gen Hayase, Kazuyoshi Kanamori, Masashi Fukuchi, Hironori Kaji and Kazuki Nakanishi*

Oil/water separation is an important topic for saving environments. In 2010, the Gulf of Mexico oil spill widely and seriously damaged ocean space and the coast near the oilfield. The number of similar accidents is increasing with the development of industry, and materials that can reduce environmental pollution are strongly demanded. At the same time, in the area of analytical chemistry, efficient separation of molecules is the key technique, which determines efficiency and accuracy of chemical analysis and detection. For these purposes, hydrophobic porous materials are common and useful because hydrophobic surfaces effectively adsorb/absorb oily target compounds mixed with aqueous phase. Many researchers have therefore been studying hydrophobic porous materials and their application to oil/water separation media.[1] Various chemical compositions are investigated such as carbon-based materials[2], metal oxide nanowires (e.g. manganese[3,4]), biomass nanofibers (e.g. cellulose[5,6]), organic polymers (e.g. 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 biomimetic rough surface by etching technique to enhance hydrophobicity[6,12] are also widely reported. However, these methods have problems such as complicated and lengthy process and high costs of reagents and devices, which prevents those materials from practical applications and commercial uses.

We have investigated hydrophobic porous polymethylsilsesquioxane (PMSQ, $CH_3SiO_{1.5}$) materials from transparent aerogels and xerogels with mesopores to macroporous monoliths derived from methyltrimethoxysilane (MTMS) by controlling phase separation in the sol-gel process.[13] Polymethylsilsesquioxane gels have superhydrophobic surface as prepared due to methyl groups which are directly bonded with silicon atoms, and the flexible network structure allows “spring- back” behaviour against compression. This mechanical feature allows preparation of aerogel-like xerogels by ambient pressure drying. Last year, we first reported bendable porous gels like “marshmallow” derived from a co-precursor system of MTMS and dimethyldimethoxysilane (DMDMS) with almost the same way as PMSQ gels.[14] Marshmallow-like gels not only show the compression-reexpansion property like PMSQ gels, but also very soft and bendable mechanical features. A high sound absorption property has been reported in the previous report because of the soft networks. The flexible property and intrinsic hydrophobicity indicate that they can be used as adsorption/absorption media like sponge for a quick removal of unwanted organic liquids. In this paper, we report outstanding ability of these materials for absorbing organic liquids under a wide temperature range, and discuss the possibility for applications to separation media.

Recently, we have succeeded in the preparation of various kinds of marshmallow-like gels by a facile one-pot reaction derived from several tri- and di-functional alkoxysilanes as co-precursors. The combinations of alkoxysilanes and the common process of synthesis are shown in Figure 1a. In any combinations, it is not necessary to change the synthesis procedure and condition, which means that we can design flexible porous gels which have different functional groups (Fourier transform infrared (FT-IR) spectra are shown in Figure S1)[15] without any complicated processes such as chemical vapour deposition, dip coating with PDMS and additional polymerization of organic groups, which are necessary in the above-mentioned reports. To obtain gels, only 4 simple routine steps are needed; (1) mixing alkoxysilanes, urea and surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) in a dilute acetic acid aqueous solution and stirring for 60 min at RT for hydrolysis, (2) transferring the sol to an oven to keep at 80 ºC for several hours for gelation, (3) washing with alcohol and (4) evaporative drying under ambient conditions. From alkoxysilanes which have higher hydrophobic organic groups, such as 3,3,3-trifluoropropyl, the obtained macroporous skeletons becomes more spherical, but each particle is tightly bonded together at the neck whose diameter is several micrometers (Figure S2). The bulk body is elastic and bendable without any failure in their structure (Figure S3).

In the case of MTMS-DMDMS copolymers (these precursors are not expensive and easily available in the market), the total time of synthesis is within a day even if with a large scale such as several liters (Figure 1b), and the gels can be formed in any desired shape. Before obtaining the final product, we need to wash out the surfactant and unreacted compounds, during which the sponge-like flexible feature can help reducing this work by a soaking-squeezing by hand (Figure 1c). The ^{29}Si solid-state NMR spectrum shows that residual hydroxyl groups are virtually negligible in the structure, which represents the network formation is completed in a few hours (Figure 1d).[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 low density (~0.12 g cm^{-3}, corresponds to porosity > 92 %) and superhydrophobicity (contact angle is ~153 °, Figure 2a and Movie S1). The hydrophobicity is caused both by the

[*] G. Hayase, Dr. K. Kanamori, Prof. K. Nakanishi
Department of Chemistry, Graduate School of Science, Kyoto University
Kitashirakawa, Sakyo-ku, Kyoto, 606-8502 (Japan) E-mail: kanamori@kuchem.kyoto-u.ac.jp

Dr. Masashi Fukuchi, Prof. Hironori Kaji
Institute for Chemical Research, Kyoto University
Uji, Kyoto 611-0011 (Japan)

[**] This study was carried out with the NMR spectrometer in the JURC at Institute for Chemical Research, Kyoto University. Financial supports from Advanced Low Carbon Technology Research and Development Program (ALCA) from Japan Science and Technology Agency (JST) and Grant-in-Aid for Scientific Research (No. 24550253) from Japan Society for the Promotion of Science (JSPS) are acknowledged.

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

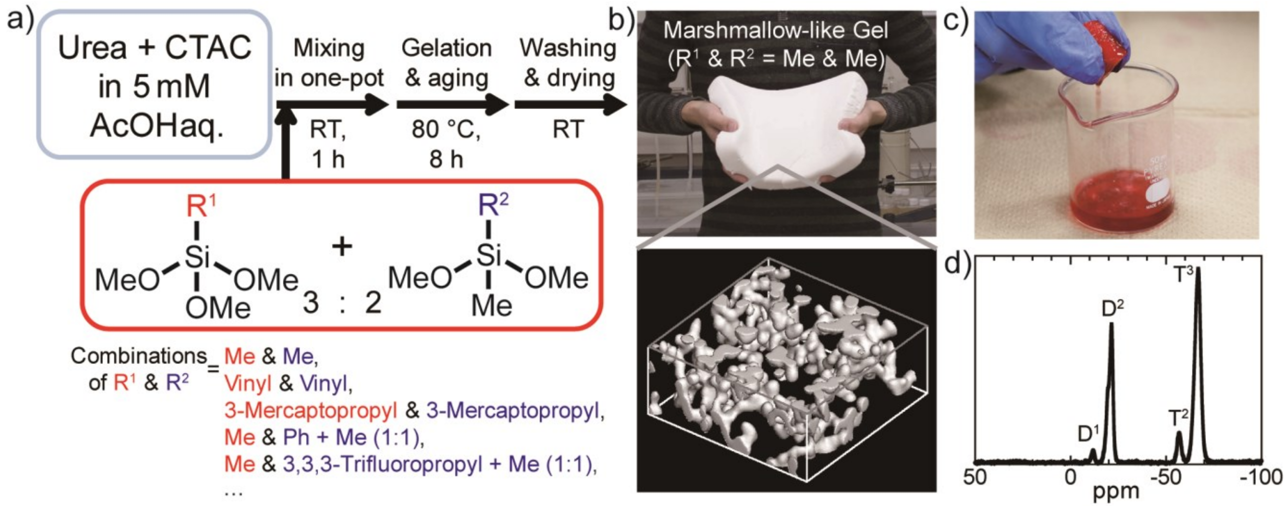

Figure 1. a) Facile synthesis process of marshmallow-like gels derived from di- and tri-functional alkoxysilanes as co-precursors, and b) the shape of the produced MTMS-DMDMS gel of 2.5 L scale and its 3-D microstructure image (73.1 × 73.1 × 30.8 μm). c) The gel can absorb and be squeezed out organic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

geometrical rough surface derived from macroporous structure formed presumably by spinodal decomposition[17] and the rich methyl and few hydroxyl groups exposed on the surface. To evaluate as oil/water separation media, we tested absorption-drying behaviour using *n*-hexane as an organic compound (Figure 2b). During the 10 times repetition, the gel showed the stable performance; the gel absorbs ~6.2 times of *n*-hexane relative to the weight of a dried gel, and no damage is found. We also performed an *n*-hexane-removing test using this material like a sponge (Figure 2c and Movie S2). All *n*-hexane was successfully separated from water easily and quickly, even though there was larger quantity of liquids than that can be absorbed at a single time. Also in the cases of other organic solvents, the gels can absorb and be dried by squeezing-out even in the case of high weight and viscosity oils (Figure 2c). The organic liquids are stored in the abundant pores of this material (Figure 1b and Movie S3[18]), and the weight ratio of absorbed solvent/dried gel depends on density of organic compounds (Figure 2d). We can design absorbing media specific to the chemical and physical nature of the organic compound needed to be absorbed, by changing the substituent groups in the precursors and by controlling flexibility and macropore skeleton diameters of this material by changing the starting composition such as the precursor ratio and amounts of urea and CTAC.[14]

Due to the PDMS-like network, MTMS-DMDMS gels show high flexibility in the wider temperature range than conventional organic polymers such as polyurethane and polyethylene. Gels can recover their original shape from 80 % uniaxial compression and 3-point bending test at RT (Figure 3). To evaluate the thermal stability, we tested thermogravimetry-differential thermal analysis (TG-DTA). The result shows these materials are stable up to ~320 °C, and methyl groups in the network are oxidized at higher temperatures (Figure S4). In fact, there was no change in FT-IR spectra, mechanical properties and 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 under low temperatures, gels show high flexibility. From

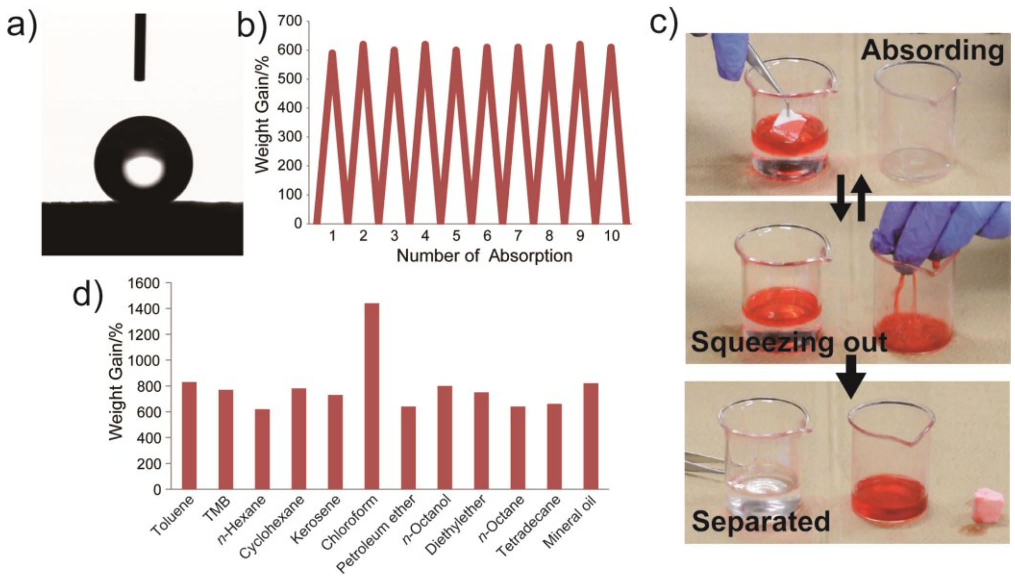

Figure 2. a) Superhydrophobic surface of the MTMS-DMDMS marshmallow-like gel. Contact angle is 152.6 °. b) A series of weight gain during *n*-hexane absorption/drying cycles. c) Marshmallow-like gel can separate *n*-hexane from water (Movie S2). d) Absorption capacities of the MTMS-DMDMS gel for various organic solvents and oils in terms of its weight gain.

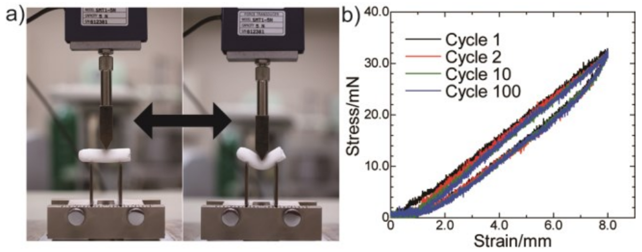

Figure 3. a) Digital camera images and b) stress-strain curves of 3-point bending test on the MTMS-DMDMS gel.

differential scanning calorimetry (DSC), no obvious glass transition is observed from RT to –130 °C. We could absorb and squeeze out dry ice-ethanol at ca. –70 °C. Flexibility of the swollen gel was not lost and completely recovered their original shape after squeezed out the liquid (Figure 4a, strain completely recovered after measurement). Furthermore, the gel shows high flexibility even in liquid nitrogen (LN_2) though the gel was somewhat hardened (Figure S5 and Movie S4). We could absorb and squeeze out LN_2 as if with water and sponge (Figure 4b and Movie S5). Thus, MTMS-DMDMS gels can be also used as oil absorbing media at a very low temperature region such as the polar zone. In fact, we succeeded absorb/ squeezing-out kerosene at 0 °C as well as the case at RT. No other materials which show high flexibility at such low temperatures have been reported except entangled carbon nanotubes derived from the "super-growth" method.[19]

The functional groups on the marshmallow-like gels can be used for specific adsorption/absorption purposes. In the case of (3-mercaptopropyl)trimethoxysilane−(3-mercaptopropyl)methyldimethoxysilane copolymerized gels, for instance, gold ions are adsorbed on the surface by simply soaking in a tetrachloroauric acid aqueous solution (Figure S6). By utilizing organic groups other than methyl (i.e. phenyl and 3,3,3-trifluoropropyl) on the surface, hydrophobicity can be further increased. Owing to the soft and elastic porous structure as well as functionality, it would be possible to create new separation media for solid-phase extraction.[20] We have also succeeded in the synthesis of marshmallow-like materials derived from a bridged alkoxysilane and di-functional alkoxysilane as co-precursors (i.e. bis(methyldiethoxysilyl)ethane-DMDMS) with the same process (Figure S7). We will report unique properties of these gels in the near future in greater detail.

In summary, we report the inception of a new kind of superhydrophobic oil/water separation media. The marshmallow-like gels based on polysiloxane networks are synthesized from a couple of alkoxysilanes such as tri-, di-functional and bridged alkoxysilanes as co-precursors by a facile process without special conditions. Copolymerization with various kinds of alkoxysilanes adds functionality to the gels, which allows a flexible design of surface chemical properties. Obtained MTMS-DMDMS gels have superhydrophobicity and can remove organic compounds from water by absorbing and squeezing-out like sponge. Soft and elastic properties are maintained in a wide temperature range, from LN_2 temperature to ~320 °C, which extends possible applications to under harsh environments. The introduction of functional groups is also available for changing adsorption/absorption properties, which is advantageous for separation media for different target compounds. Together with the high sound absorption,[14] the multifunctional gels with unique properties would further extend practical applications.

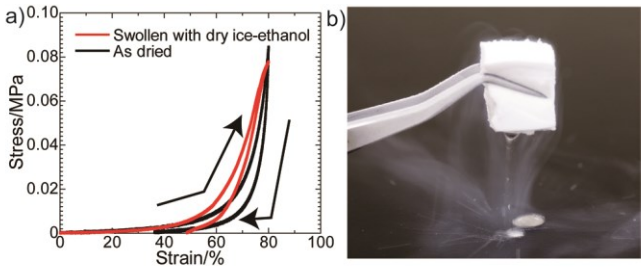

Figure 4. (a) Stress-strain curves of the as-dried MTMS-DMDMS gel and the one swollen with dry ice-ethanol. (b) Squeezing out LN_2.

Experimental Section

Experimental details can be found in the Supporting Information.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: environmental chemistry, hydrophobic effect · gels · organic-inorganic hybrid composites ·sol–gel processes

[1] Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, *Adv. Mater.* **2011**, *23*, 4270.

[2] a) M. Inagaki, A. Kawahara, Y. Nishi, N. Iwashita, *Carbon* **2002**, *40*, 1487; b) H.-W. Liang, Q.-F. Guan, L.-F. Chen, Z. Zhu, W.-J. Zhang, S.-H. Yu, *Angew. Chem. Int. Ed.* **2012**, *51*, 5101.

[3] J. Yuan, X. Liu, O. Akbulut, J. Hu, S. L. Suib, J. Kong, F. Stellacci, *Nat. Nanotechnol.* **2008**, *3*, 332.

[4] J. Lahann, *Nat. Nanotechnol.* **2008**, *3*, 320.

[5] J. T. Korhonen, M. Kettunen, R. H. A. Ras, O. Ikkala, *ACS Appl. Mater. Interfaces* **2011**, *3*, 1813.

[6] A. Tuteja, W. Choi, M. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, R. E. Cohen, *Science* **2007**, *318*, 1618.

[7] J. Zhang, S. Seeger, *Adv. Funct. Mater.* **2011**, *21*, 4699.

[8] M. Nicolas, F. Guittard, S. Geribaldi, *Angew. Chem. Int. Ed.* **2006**, *45*, 2251.

[9] a) A. V. Rao, N. D. Hegde, H. Hirashima, *J. Colloid Interface Sci.* **2007**, *305*, 124; b) J. G. Reynolds, P. R. Coronado, L. W. Hrubesh, *Energy Sources* **2001**, *23*, 831.

[10] M. Ma, R. M. Hill, *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193.

[11] a) M. Jin, J. Wang, X. Yao, M. Liao, Y. Zhao, L. Jiang, *Adv. Mater.* **2011**, *23*, 2861; b) K. Tsujii, T. Yamamoto, T. Onda, S. Shibuichi, *Angew. Chem., Int. Ed.* **1997**, *36*, 1011.

[12] a) X. Yao, Y. Song, L. Jiang, *Adv. Mater.* **2011**, *23*, 719; b) K. Liu, X. Yao, L. Jiang, *Chem. Soc. Rev.* **2010**, *39*, 3240.

[13] a) K. Kanamori, Y. Kodera, G. Hayase, K. Nakanishi, T. Hanada, *J. Colloid Interface Sci.* **2011**, *357*, 336; b) K. Kanamori, M. Aizawa, K. Nakanishi, T. Hanada, *Adv. Mater.* **2007**, *19*, 1589.

[14] G. Hayase, K. Kanamori, K. Nakanishi, *J. Mater. Chem.* **2011**, *21*, 17077.

[15] a) R. Al-Oweini, H. Ei-Rassy, *J. Mol. Struct.* **2009**, *919*, 140; b) W. R. Thompson, M. Cai, M. K. Ho, J. E. Pemberton, *Langmuir* **1997**, *13*, 2291; c) Y.-S. Li, Y. Wang, S. Ceesay, *Spectrochim. Acta, Part A* **2009**, *71*, 1819.

[16] Z. Olejniczak, M. Leczka, K. Cholewa-Kowalska, K. Wojtach, M. Rokita, W. Mozgawa, *J. Mol. Struct.* **2005**, *744*, 465.

[17] K. Nakanishi, *J. Porous Mater.* **1997**, *4*, 67.

[18] H. Jinnai, Y. Nishikawa, H. Morimoto, T. Koga, T. Hashimoto, *Langmuir* **2000**, *16*, 4380.

[19] M. Xu, D. N. Futaba, T. Yamada, M. Yumura, K. Hata, *Science* **2010**, *330*, 1364.

[20] a) M. C. Hennion, *J. Chromatogr. A* **1999**, *856*, 3; b) D. Louch, S. Motlagh, J. Pawliszyn, *Anal. Chem.* **1992**, *64*, 1187.