



# Ionic liquid assisted synthesis of flexible and super-hydrophobic porous gels



Zhiqiao Qin<sup>a</sup>, Yi Fang<sup>a</sup>, Yanji Wang<sup>a</sup>, Huanrong Li<sup>a,\*</sup>, Jinsheng Liang<sup>b</sup>

<sup>a</sup> Hebei Provincial Key Lab of Green Chemical Technology and High Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, PR China

<sup>b</sup> School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China

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## ABSTRACT

Herein we demonstrate the preparation of polysiloxane network-based aerogels through a facile one-pot reaction from co-precursor of trimethoxysilane and dimethoxysilane assisted with a carboxyl-functionalized ionic liquid for the first time. The gels show good absorption performance such as good selectivity, outstanding recyclability, simple recycling route, and robust stability, which make them highly appealing in the application as a sponge for quick separation of oily targets from water by absorption and simple mechanical squeezing. The resultant porous gels are highly flexible and super-hydrophobic, which are much lighter ( $0.075 \text{ g cm}^{-3}$ ) and show larger absorption capacity for n-hexane than those obtained from dimethyl acetic acid.

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## 1. Introduction

The developments of advanced absorbent materials that can achieve oil/water separation efficiently are highly demanded for saving the endangered environment and ecosystem caused by the increasing discharges of industrial oily wastewater and oil leakage [1–3]. Hydrophobic porous materials have demonstrated promising absorption performance towards oils and organic solvent. Therefore, a great number of hydrophobic porous materials have been prepared and their application for oil/water separation have been investigated [4]. So far, both inorganic absorbents and organic polymers have been investigated, such as ultralight carbon aerogels [5,6], porous boron nitride [2], metal oxides nanowires [7–9], organic polymers [10,11] as well as polydimethylsiloxane (PDMS) based organic-inorganic hybrid materials [12,13]. However, drawbacks exhibited by these materials aforementioned such as complicated and time-consuming procedure, high cost, low flexibility and stability as well as poor selectivity and recyclability limit their full exploitation in practical applications. Recently, Hayase reported

polysiloxane-based marshmallow-like gels that can be used as an absorbent for removing oily targets from water in a wide temperature range. The high flexibility of the gels affords a simple and quick oil/water separation by absorbing them and then releasing them upon being squeezed out. The preparation of the flexible gels can be easily realized through a facile one-pot reaction from co-precursor of tri- and di-functional alkoxy silane in a dilute aqueous acetic acid solution [14,15].

Ionic liquids (IL) are organic salts that are totally composed of ions with melting temperature below  $100^\circ\text{C}$ . Remarkable advantages exhibited by ionic liquids with respect to the traditional solvents include negligible vapor pressure, good thermal stability, wide electrochemical window, etc, which provide them great opportunities for application in materials science [16–21]. Interestingly, some special materials of controlled structure, morphology and properties are very difficult to prepare in conventional solvents and they can be obtained in ILs [22–24]. So far, different kinds of materials such as carbon materials [25], polymers [26], nanoparticles [27], porous silica [28], metal-organic frameworks [29] and so forth [30–33] have been prepared from ionic liquids. As far as we know, there are still no reports on the preparation of flexible, hydrophobic and ultralight polysiloxane aerogels assisted with ILs. Herein, we demonstrate the preparation of flexible,

\* Corresponding author. Tel.: +86 22 60203674.

E-mail address: [lihuanrong@hebut.edu.cn](mailto:lihuanrong@hebut.edu.cn) (H. Li).

hydrophobic, ultralight porous gels based on polysiloxane from a diluted carboxyl-functionalized IL solution for the first time. The obtained gels show a lower density and an increased absorption capacity towards n-hexane with respect to the porous gels of the same composition prepared under diluted acetic acid solution. Our study further verifies that attractive properties can be obtained by using IL to replace conventional solvents to prepare materials.

## 2. Experimental sections

### 2.1. Materials

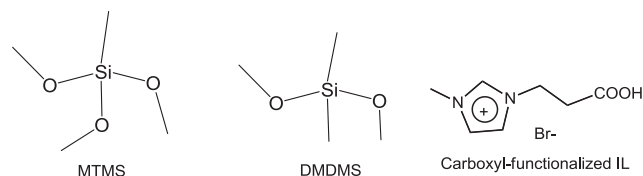
1-Methylimidazole was purchased from J&K, 3-bromopropionic acid was from China National Medicines Corporation Ltd. Urea (99%) and acetic acid were purchased from Tianjin Chemical Reagent Factory. n-Hexadecyltrimethylammonium bromide (CTAB, >99%) was purchased from Sinopharm Chemical Reagent CO., LTD. Methyltrimethoxysilane (MTMS, 95%) and dimethyldimethoxysilane (DMDMS, 98%) were obtained from ALDRICH. The carboxyl-functionalized IL was synthesized and characterized according to the method described in ref34.

### 2.2. Preparation of the flexible aerogels

First, 0.40 g of CTAB, 3.0 g of urea, and 7 mL of aqueous carboxyl-functionalized IL (4 mM) were mixed in a glass sample tube. Then 10.5 mmol of trimethoxysilane and 7 mmol of dimethoxysilane were added under vigorous stirring at ambient temperature, and the stirring was continued for 30 min until the solution was homogeneous. The obtained sol was transferred into a tightly-sealed container, which was placed in a forced convection oven at 60 °C for 7 h to complete gelation and aging. The obtained gels were washed with ethanol by soaking/squeezing by hand several times to remove the residual surfactant and other chemicals. The washed samples were evaporative dried under ambient condition to obtain flexible aerogels. We used conventional liquid acetic acid instead of carboxyl-functionalized IL on the similar system as control experiment.

### 2.3. Measurements

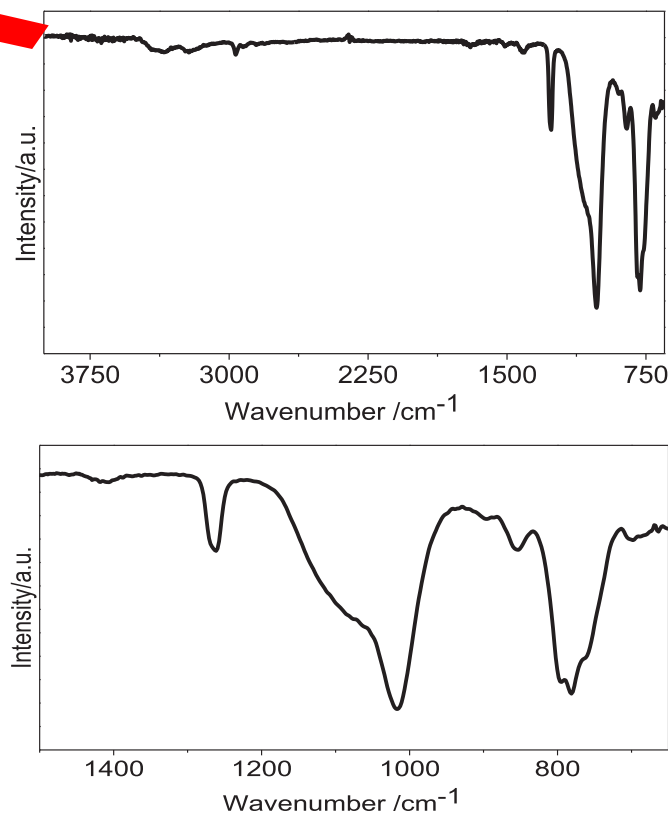
Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer in the range of 400–4000  $\text{cm}^{-1}$ .  $^{29}\text{Si}$  solid state NMR measurement was performed on Varian Infinityplus 300 MHz. Thermogravimetry analysis (TGA) was performed on SDT-TG Q600. In the TGA experiments the samples were analyzed from r.t. up to 800 °C at a heating rate of 10 °C  $\text{min}^{-1}$  with air as purging gas. SEM images were obtained using a FE-SEM (NOVA NANOSEM 450) at an acceleration voltage of 10 kV. Bulk density  $\rho_b$  was obtained by measuring the volume and weight of a carved gel. The porosities  $\epsilon$  (%) were calculated by the equation  $\epsilon = (V_s/V_b) \times 100\%$ , where  $V_b$ ,  $V_s$  are volume of bulk and the skeleton of the aerogels, respectively. Mechanical properties of aerogels were measured by a material testing machine (CMT610) in uniaxial compression test, carved aerogels (typical length  $\times$  width  $\times$  height was 21  $\times$  21  $\times$  15  $\text{mm}^3$ ) were compressed using a load cell of 10 KN with a rate of 4  $\text{mm min}^{-1}$ . For three-point bending tests, samples (typical length  $\times$  width  $\times$  height was 41  $\times$  16  $\times$  13  $\text{mm}^3$ ) with a span of 30 mm and a depth of 10 mm were compressed for 10 times with using a load cell of 100 N at a rate of 5  $\text{mm min}^{-1}$ . Nitrogen-adsorption porosimetry was performed on an ASAP 2020 V3.04H specific surface area and porosity analyzer, a production of Micromeritics Instrument Corporation.



**Scheme 1.** Chemical structure of the precursors and the carboxyl-functionalized ionic liquid.

## 3. Results and discussion

The hydrophobic porous gels were prepared according to the modified procedure described in ref [14]. Methyltrimethoxysilane (MTMS) and dimethyldimethoxysilane (DMDMS) are used as the precursors and their structures are listed in Scheme 1, which are readily commercially available in a competitive price. The carboxyl-functionalized IL employed in this study was synthesized according to the reported procedure [32,33] and the chemical structure of which is also listed in Scheme 1. The mixture of the precursors, urea, n-Hexadecyltrimethylammonium bromide (CTAB) in a diluted carboxyl-functionalized IL solution was stirred for ca. 0.5 h at room temperature to get a homogeneous solution. The gelation was done at 60 °C for several hours and the flexible aerogels were obtained by washing with alcohol and dried at room temperature. The resulting gels can be shaped in any desired shapes. Moreover, they are highly flexible and can be bent freely. FT-IR was firstly employed to characterize the obtained gels to investigate the hydrolysis and condensation of the precursor under the experimental conditions. Fig. 1 reveals that no intense absorption at 960  $\text{cm}^{-1}$  and 1166  $\text{cm}^{-1}$  characteristic for the  $\text{SiOCH}_3$  groups are observed, indicating the hydrolysis of the precursors is totally completed. The strong and



**Fig. 1.** FT-IR spectrum of the flexible aerogel.

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