Superhydrophobic hybrid aerogel powders from waterglass with distinctive applications

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ABSTRACT

Hybrid silica aerogel powders with enhanced superhydrophobicity and very high reaction yield were prepared by a fast co-precursor method at ambient pressure. An inexpensive aqueous sodium silicate solution was used as starting material (waterglass or WG), with hexamethyldisilazane (HMDZ) as organic co-precursor.

The key for successfully achieving such high yields and superhydrophobicity was a systematic tuning of the synthesis parameters (co-precursors and acid catalyst molar ratios) and process conditions (stirring speed, stirring period, aging, washing and drying steps), in close correlation with the reaction mechanism. Using a minimum amount of organic co-precursor, a total yield of ~80% in hybrid aerogels with high lipophilic/hydrophilic ratio, very high water contact angles (~152 ± 2°) and very low densities (~0.120 g cm^{-3}) were obtained. The optimized synthesis conditions consist in HNO$_3$:WG:HMDZ molar ratios of 1.5:1.0:1.5, stirring speed of 120 rpm, only during addition of the catalyst and co-precursor, aging for 5 min and washing with water before drying at atmospheric pressure.

The minimization of the only costly precursor allows envisaging a low-cost large scale production and, moreover, the encapsulation of water droplets within aerogel powder allows proposing distinctive applications, such as water transport at a microscale level.

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1. Introduction

The outstanding properties of silica aerogels encouraged continued efforts for the development of these materials since Kistler's pioneering work [1]. They are highly porous, extremely light (densities in the range 3–500 kg m^{-3}), nanostructured, non-flammable, and excellent thermal insulators (thermal conductivity in the range 0.01–0.02 W m^{-1} K^{-1}) [2].

Moreover, when the applications require stability towards moisture, hydrophobization is essential. Hydrophobic aerogels have been prepared using a wide variety of techniques, all of which seek to replace the hydrophilic hydroxyl groups by surface modification, either during the synthesis (co-precursor methods [3]) or as post-synthesis treatments (vapor phase [4] or silylation methods [5–8]). The unique combination of properties renders hydrophobic silica based aerogels attractive materials for thermal insulation [9], superhydrophobic surfaces [10], environmental clean-up [11] and biological applications [12].

Traditionally, the silica precursors used are either silicon alkoxides (such as tetraethoxysilane or tetramethoxysilane) [13–15] or organically modified alkoxides (such as methyltrimethoxysilane or trimethylethoxysilane) [10,16]. However, these precursors are expensive, an important factor when considering large-scale production. On the other hand, the commonly used supercritical drying techniques, with or without replacement of the solvent by carbon dioxide, have limitations in terms of cost and safety: due to the high pressures and/or temperatures usually involved in the process, to the need of relatively expensive equipment and to complex and long intermediate steps [17]. Besides, the aerogels produced with solvent exchange for carbon dioxide are hydrophilic, therefore needing post-synthesis chemical treatments that usually release environmentally harmful products [2].

For industrial commercialization of hydrophobic hybrid aerogels, it is essential to use low-cost precursors in combination with rapid and inexpensive drying methods. Thus, sodium silicate appeared as an eligible silica precursor and ambient pressure drying as a valid alternative for solvent extraction. In point of fact, the materials obtained by this approach do not correspond to the conventional definition of an aerogel [1], since drying is not

supercritical. Given their properties, they should be named "aerogel like" materials. However, in the last twenty years, a broader definition of aerogel has been adopted, based on the properties rather than on the drying method [18,19]. In the late 1990s, Schwertfeger [20] and Deshpande [21] produced aerogels from sodium silicate with Na⁺ ion exchange, followed by surface chemical modification. However, the numerous solvent exchanging steps which are required render those processes time consuming. Since then, many researchers have focused on developing the synthesis of hybrid aerogels from sodium silicate and drying at ambient pressure [22–27].

Aiming at short processing times and low production costs, Bhagat et al. reported a simple co-precursor method for the synthesis of hydrophobic silica-based aerogel powders, using, as starting material, a sodium silicate aqueous solution or waterglass (WG) without prior ion exchange and, as co-precursor for organic modification, hexamethyldisilazane (HMDZ) and drying at atmospheric pressure [28]. In this process, the surface modifier is directly mixed with the waterglass to achieve a hybrid network. This co-precursor method offers the advantage of a faster surface modification and improved internal hydrophobicity [2].

The aqueous silicate chemistry is well known since the 1980s [2,29], and the mechanism and kinetics of the silylation reaction of a silica surface by HMDZ have been object of thorough theoretical investigation [30] and experimental analysis in different solvents [31]. However, the influence of each synthesis parameter on the mechanism of the hybrid silica formation using HMDZ as co-precursor is still an open field.

In the present work, we sought a greater insight into the details of the reaction between sodium silicate and HMDZ, in order to synthesize superhydrophobic hybrid silica aerogel powders with optimum reaction yield. The role of different process conditions, such as stirring speed, stirring period after HMDZ addition, aging, washing and drying steps was analyzed, as well as the influence of the precursors' molar ratio and catalyst content. To the best of our knowledge, this is the first systematic study on superhydrophobic hybrid aerogel powders prepared under atmospheric conditions.

2. Experimental section

### 2.1. Preparation of the silica aerogel powders

The sodium silicate solution D40 from Solvay Portugal (27.5 wt% SiO_2, 8.5 wt% Na_2O and 1.37 g cm^{-3}) is initially diluted with deionized water to obtain a 5 wt% in SiO_2 precursor, at pH 12. In order to acidify this alkaline solution, nitric acid from Sigma–Aldrich (HNO_3, 65%) is added in variable amounts. This step is intended to activate the molecular silicates in solution to silicic acid (by partial or total protonation of Si–O⁻ centers), resulting in a pH in the range 1–2. Subsequently, hexamethyldisilazane from Sigma–Aldrich (HMDZ, 99.9%) is added, under constant orbital stirring, at room temperature (24–25 °C), with the double role of increasing pH and as co-precursor.

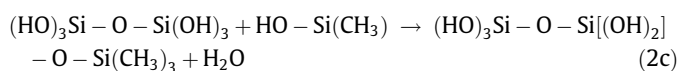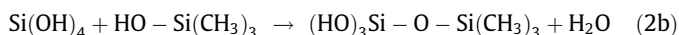As co-precursor, HMDZ undergoes partial or total hydrolysis:

$$(CH_3)_3Si - NH - Si(CH_3)_3 + 2H_2O \xrightarrow{H^+} 2[(CH_3)_3Si - OH] + NH_3 \ (g) \tag{1}$$
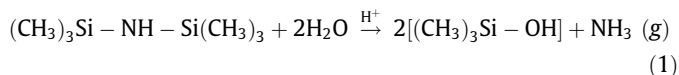
NH_3 is released to the gas phase and pumped.

The partial neutralization with HMDZ initiates condensation reactions and gelation occurs immediately. The reactions that yield the organically modified silica network (ORMOSIL) are condensations and co-condensations between inorganic and/or organically modified species at different stages of hydrolysis and/or condensation. Reactions (2a), (2b), (2c) are examples:

$$Si(OH)_4 + Si(OH)_4 \ \rightarrow \ (HO)_3Si - O - Si(OH)_3 + H_2O \tag{2a}$$
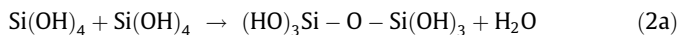
(slow in acidic medium [32], it yields the first inorganic dimer that can further condense);

$$Si(OH)_4 + HO - Si(CH_3)_3 \ \rightarrow \ (HO)_3Si - O - Si(CH_3)_3 + H_2O \tag{2b}$$

$$(HO)_3Si - O - Si(OH)_3 + HO - Si(CH_3) \ \rightarrow \ (HO)_3Si - Si[(OH)_2] - O - Si(CH_3)_3 + H_2O \tag{2c}$$

and so on.

Other condensation reactions may occur as soon as hydrolyzed HMDZ species start to form, although less probable, due to the low concentrations of methylated species present:

$$(CH_3)_3Si - OH + HO - Si(CH_3)_3 \ \rightarrow \ (CH_3)_3Si - O - Si(CH_3)_3 + H_2O \tag{2d}$$
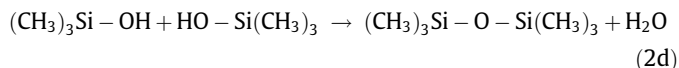
(corresponds to the formation of hexamethyldisiloxane). If any NH3 were still present, the reverse reactions of (1) and (2d) could regenerate HMDZ.

The recently formed gels have different morphologies, depending on the composition of the reaction mixture, on the stirring speed and period, ranging from clouds to plates or even monoliths. Examples are given in Fig. 1.

The gels are aged in the residual solution for different periods. This solution, when there is some left, is then removed in order to stop the reactions. *n*-Hexane (96%, from ACS Basic) is added in a fixed WG:*n*-hexane molar ratio of 1:0.1, to replace any water included in the pores, whose surfaces are expected to be essentially hydrophobic. This exchange proceeds for 3 h, after which the two liquid phases (excess *n*-hexane and displaced pore water) are removed. The silylated hydrogels are dried at ambient pressure in two steps: at 60 °C for 24 h followed by 24 h at 100 °C. The samples are repeatedly washed with water (to remove the NO_3^- and Na⁺ ions) and finally dried under the above conditions, until aerogel powders are obtained. The removal of Na⁺ was confirmed by EDS and the removal of NO_3^- by DRIFTS. This procedure differs from that of Bhagat et al. [28] in essential steps intended to control the reaction yield and the outcoming properties: the aging in residual solution, the removal of this solution prior to the addition of *n*-hexane (when residual solution is left after aging) and the
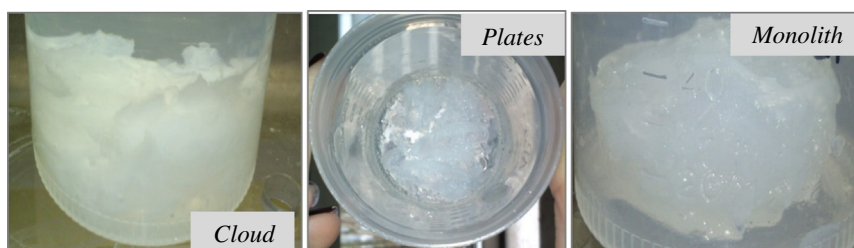

Fig. 1. Different morphologies of the silylated gels.