ELECTROSPINNING OF SILICA NANOFIBERS WITHOUT CARRIER POLYMER FOR ADVANCED ENGINEERING APPLICATIONS

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ABSTRACT

Nanofibrous materials produced via electrospinning are characterized by a high porosity, large specific surface area, and high pore interconnectivity and, therefore, show potential for, e.g., separation and filtration. The development of more inert nanofibers with higher thermal and chemical resistance extends the application field. Silica nanofibrous membranes produced by direct electrospinning of a sol–gel solution without a sacrificing carrier meet these challenging demands. A combination of hydrolysis and condensation reactions of the tetraethoxysilane (TEOS) precursor, results in dense silica nanofibers with superior mechanical properties, without a rough and uneven surface, allowing the use in advanced engineering applications.

Key Words: ELECTROSPINNING, SILICA, SOL-GEL SYNTHESIS, HYDROPHOBICITY, VISCOSITY

1. INTRODUCTION

Electrospinning of polymer nanofibers has been studied extensively and has shown to be possible via stable, reproducible and controllable processes [1]. Studies on ceramic nanofibers are less comprehensive. Ceramic materials are hard and inert and are therefore known for their excellent properties such as high temperature resistance and chemical inertness. These promising characteristics allow ceramic nanofibers to be investigated for various applications such as biological applications, filtration, composites, catalysis, etc [2–4]. Electrospinning is a simple and versatile technique for the production of polymer and ceramic nanofibers. Using electrostatic forces, continuous nanofibers can be obtained having controllable compositions and controllable diameters below 500 nm [5,6].
The combination of electrospinning and the sol–gel technique is relatively recent but has already been used to obtain ceramic nanofibers with various compositions such as SiO_2, TiO_2, Al_2O_3 and ZrO_2. So far, the most common technique to obtain ceramic nanofibers is the electrospinning of solutions containing a sol–gel precursor and an organic polymer, added to control the rheological properties of the solution [7–9]. Afterward, this polymer is removed via a thermal treatment to obtain pure ceramic nanofibers. Recently, our group successfully produced ceramic silica nanofibers without the need of this sacrificing polymer [10–12]. In contrast to other work, in which a well-spinnable organic polymer is mixed with a metal oxide precursors to facilitate the electrospinning process, direct electrospinning of a sol–gel solution of a tetraethyl orthosilicate (TEOS) precursor eliminates the need for a post-production removal of the added organic polymer. This results in dense silica nanofibers with superior mechanical properties, without a rough and uneven surface of the fibers [13,14]. In addition and even more important, it offers the benefits of a simple, more tunable material design.

2. MATERIALS AND METHODS

The sol–gel precursor (TEOS, reagent grade 98 %) was obtained from Sigma-Aldrich and used as received. The catalyst, hydrochloric acid (HCl, 37 %) and solvent, absolute ethanol, were also supplied by Sigma-Aldrich. The sols used for electrospinning were prepared by modifying the procedure reported by Choi et al.[15]. The silica sol was prepared from a mixture of TEOS, ethanol, distilled water and HCl at molar ratios of 1:2:2:0.01. First, TEOS was mixed with ethanol. Secondly, aqueous HCl solution was added to the TEOS/ethanol solution under vigorous stirring with a magnetic stir bar. This solution was heated under stirring at 80 °C until the volume decreased to approximately 1/4th of the initial volume and the desired viscosity was reached. Finally the solution was cooled down to room temperature resulting in a viscous sol.
Prior to electrospinning, the viscosities of the solutions were measured using a Brookfield viscometer LVDV-II.
The electrospinning experiments were executed on a mononozzle setup. The tip-to-collector distance was fixed at 15 cm, the flow rate at 1 mL.h^{-1}, and the voltage was adjusted between 20 and 25 kV to obtain a stable electrospinning process. All the experiments were executed at room temperature of 20 °C ± 2 °C.
The morphology and the diameters of the nanofibers were examined using an FEI Quanta 200F SEM at an accelerating voltage of 20 kV. Prior to analysis the samples were coated using a sputter coater (Emitech SC7620, Au coating).
Contact angle experiments were performed on a DSA 30 Krüss GmbH drop shape analyzer using a droplet of 2 µL demineralized water. Per sample, 10 to 20 measurements were executed.
The cross-linking density of the silica nanofibrous membranes was measured with using ^{29}Si MAS NMR. The spectra were recorded at 74.49 MHz on a Bruker AVANCE400 III-HD WB spectrometer. An overall 20 000 free induction decays were accumulated. The excitation pulse and recycle time were 30° and 10 s, respectively. Chemical shifts were measured relative to a tetramethylsilane standard. Deconvolution of the ^{29}Si MAS NMR spectra was performed with DM2011 software. Peaks were observed centered at −91 ppm for Q^2 species, −101 ppm for Q^3 species, and −110 ppm for Q^4 species.

3. RESULTS AND DISCUSSION

3.1 Electrospinnable viscosity range

Silica nanofibrous membranes were produced via electrospinning of acid-catalyzed sol–gels, derived from TEOS building blocks. The principle of the chemical reactions is shown in **Figure 1**, with in a first-phase hydrolysis converting part of the ethoxy groups of TEOS in hydroxyl groups, also called silanols, and in a second-phase condensation of these silanols, resulting in the formation of silicon-oxygen-silicon bonds. Eventually, this leads in a third phase to a loosely cross-linked, hence, electrospinnable sol–gel solution.

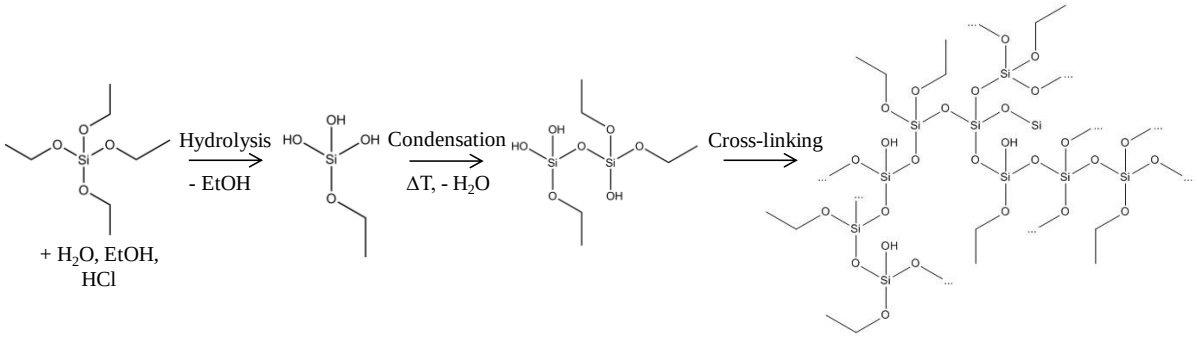

Figure 1. Principle of sol-gel synthesis for the direct electrospinning of silica nanofibers: the first step is an exothermal hydrolysis of the TEOS precursor, after which external heat allows for further condensation, resulting in a loosely cross-linked electrospinnable silica structure.

The viscosity plays a key role in the electrospinnability of solutions. Reproducible electrospun nanofibrous nonwovens are obtained when there is a stable Taylor cone at the tip of the needle

over time (**Figure 2**a-b). In this study sols with different viscosities were to electrospin and were visually evaluated on the presence of a stable Taylor cone. The sols were obtained by changing the heating time of the sols at 80°C. Different viscosities were obtained, which had varying electrospinnabilities, see **Figure 2**c. The electrospinnability at each viscosity is expressed with a number from 1 to 5, where the electropinnability of 4 and 5 is defined as stable electrospinning.

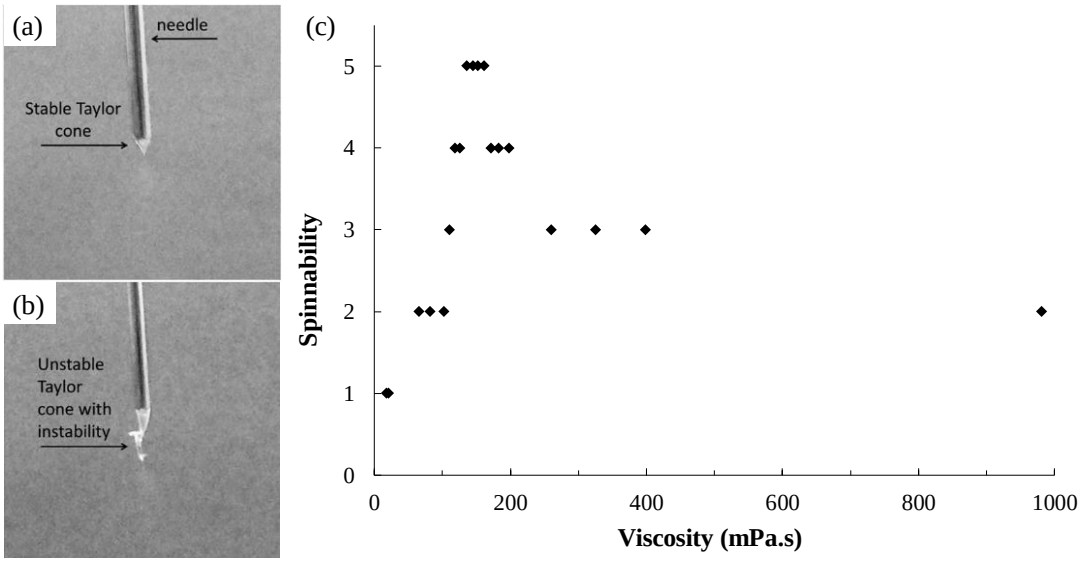

Figure 2. Electrospinnability of TEOS-based sol-gels by following the stability of the Taylor cone over time. Visualization of the Taylor cone: (a) Stable Taylor cone, (b) unstable, branched Taylor cone. (c) Electrospinnability as a function of the viscosity shows an optimal range between 120 and 200 mPa.s.

Table 1. Explanation of the different electrospinnabilities

	Electrospinnability
1	Not electrospinnable
2	Electrospinnable with drops
3	Electrospinnable with a stable Taylor cone for 30 s
4	Electrospinnable with a stable Taylor cone for 1 min
5	Electrospinnable with a stable Taylor cone for 2-5 min

The resulting nanofibers were studied with scanning electron microscopy (SEM), see Figure 3.

3.2 Evolution of hydrophilicity

After electrospinning, the membrane is highly hydrophobic, as confirmed by a stable high (>140°) contact angle (**Figure 4**). Over time, the membrane switches to superhydrophilic (water contact angle < 5°). When stored at room temperature (RT, 20 °C) and 65% relative humidity (RH), the hydrophobic/hydrophilic switch is observed after 4 months. In the case of an RH of 90%, the membrane is superhydrophilic within 15 days. The lower the relative humidity, the longer the hydrophobic nature lasts, as proven by prolonged storage at 25% RH, where the hydrophobicity is maintained for over 8 months (**Figure 4**). Thus, the hydrophobic/hydrophilic switch of the silica nanofibrous membrane can be controlled by the storage conditions, enabling advanced applications that make use of hydrophobic or hydrophilic membranes.

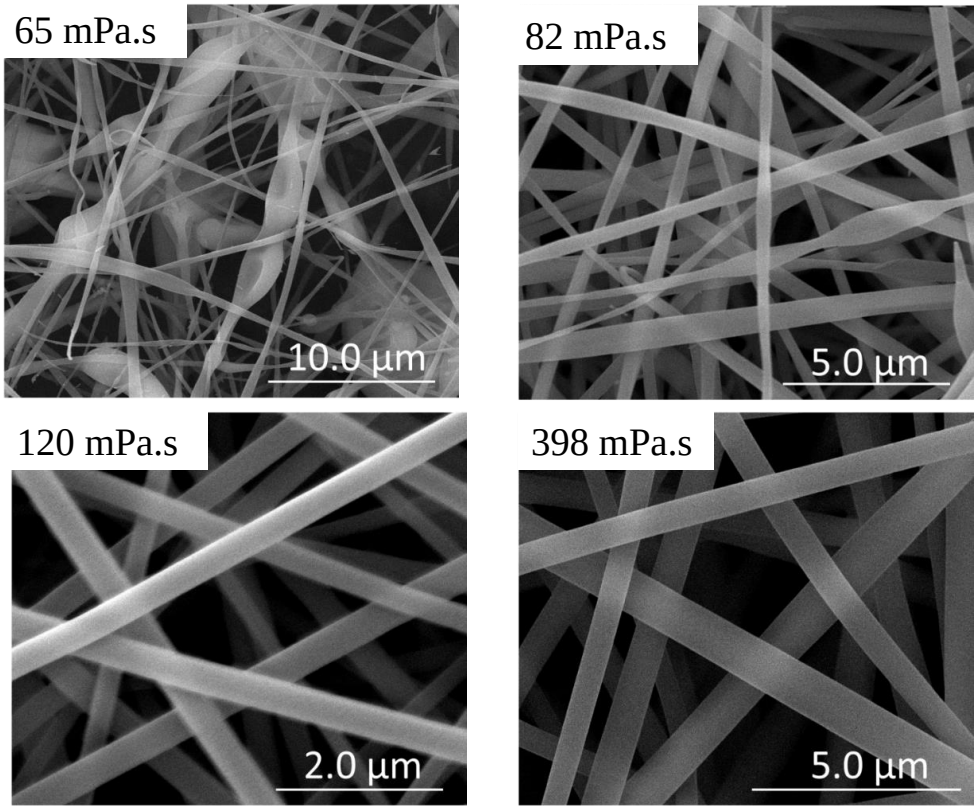

Figure 3. SEM images of silica nanofibers produced by direct electrospinning of a TEOS-based sol-gel system

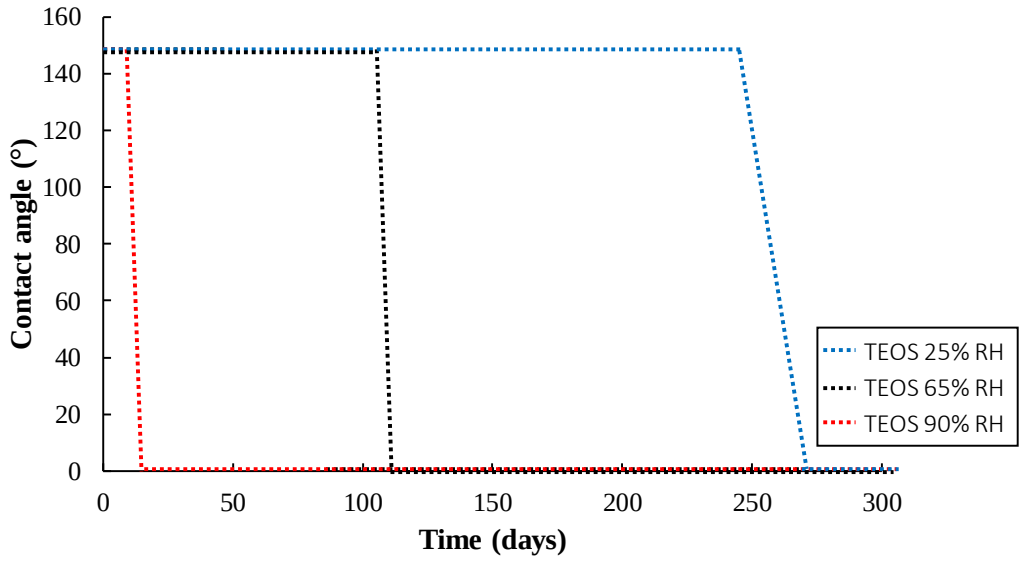

Figure 4. Water contact angle of silica nanofibers stored under controlled conditions of 20°C and 25, 65 and 90% RH. Just after the electrospinning the membrane is highly hydrophobic, with a contact angle around 150°. By storing the membrane under dry conditions, the hydrophobicity can be maintained for several months.

Over time, the remaining ethoxy groups, present due to incomplete hydrolysis in the production of the sol–gel system prior to electrospinning, react with moisture in the air, resulting in removal of the hydrophobic ethyl groups with the formation of silanols instead. At room temperature, this results in a switch from a highly hydrophobic membrane to a membrane with complete and immediate wetting when stored in high relative humidity environments. This hydrophobic/hydrophilic switch of the silica nanofibers is strongly accelerated by applying a

thermal treatment, see **Figure 5**a. In addition, the cross-linking density of the material is increased when applying a thermal treatment above 400°C, as proven with ^{29}Si NMR in **Figure 5**b, by measuring the Q^1–Q^4 species, where Q^1 refers to one Si-O-Si bond, Q^2 to two Si-O-Si bonds, etc. By applying a heat treatment at 500 and 1000°C, there is a significant increase in Q^4 species and a decrease in Q^2 and Q^3 species, and thus a significant increase in cross-linking density due to further condensation of the amorphous silica network.

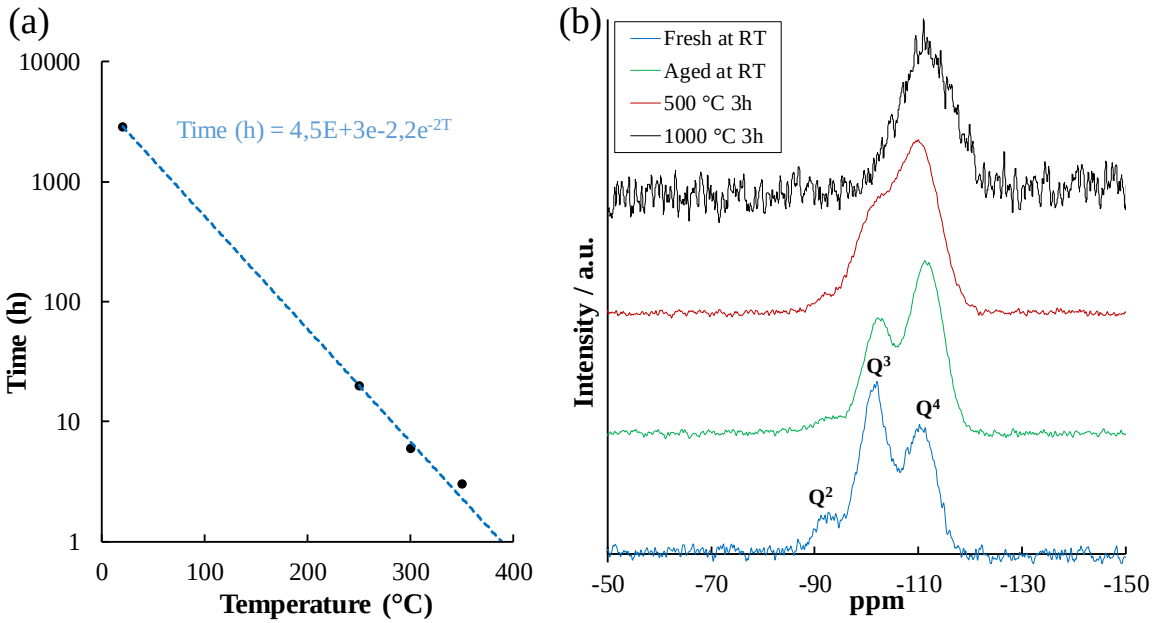

Figure 5. (a) Evolution of the heating time required for obtaining a superhydrophilic membrane as a function of the treatment temperature. The heating time increases exponentially upon lowering the heating temperature. (b) ^{29}Si solid state NMR spectra of a hydrophobic and hydrophilic silica nanofibrous membrane at room temperature and of heat treated membranes at 500°C and 1000°C for 3h. The higher the treatment temperature, the higher the cross-linking density of the molecular structure of the nanofibers.

3. REFERENCES

[1] S. Ramakrishna, *An Introduction to Electrospinning and Nanofibers*, World Scientific, 2005. https://books.google.be/books?id=QHkyRdb2TicC.

[2] C.J. Brinker, G.W. Scherer, Sol-gel science : the physics and chemistry of sol-gel processing, *Academic Press*, 1990. http://www.sciencedirect.com/science/book/9780080571034 (accessed August 31, 2017).

[3] X. Wang, J. Yu, G. Sun, B. Ding, Electrospun nanofibrous materials: a versatile medium for effective oil/water separation, *Mater. Today.* 19 (2016) 403–414. doi:10.1016/j.mattod.2015.11.010.

[4] H. Wu, W. Pan, D. Lin, H. Li, Electrospinning of ceramic nanofibers: Fabrication, assembly and applications, *J. Adv. Ceram.* 1 (2012) 2–23. doi:10.1007/s40145-012-0002-4.

[5] M. Zhu, J. Han, F. Wang, W. Shao, R. Xiong, Q. Zhang, H. Pan, Y. Yang, S.K. Samal, F. Zhang, C. Huang, Electrospun Nanofibers Membranes for Effective Air Filtration, *Macromol. Mater. Eng.* 302 (2017) 1–27. doi:10.1002/mame.201600353.

[6] M.R. Bilad, P. Westbroek, I.F.J. Vankelecom, Assessment and optimization of electrospun nanofiber-membranes in a membrane bioreactor (MBR), *J. Memb. Sci.* 380 (2011) 181–191. doi:10.1016/j.memsci.2011.07.003.

[7] Y. Si, Q. Fu, X. Wang, J. Zhu, J. Yu, G. Sun, B. Ding, Superelastic and Superhydrophobic Nanofiber-Assembled Cellular Aerogels for Effective Separation of Oil/Water Emulsions, *ACS Nano.* 9 (2015) 3791–3799. doi:10.1021/nn506633b.

[8] M.H. Tai, J. Juay, D.D. Sun, J.O. Leckie, Carbon-silica composite nanofiber membrane for high flux separation of water-in-oil emulsion - Performance study and fouling mechanism, *Sep.*

Purif. Technol. 156 (2015) 952–960. doi:10.1016/j.seppur.2015.08.008.

[9] S. Agarwal, A. Greiner, J.H. Wendorff, Functional materials by electrospinning of polymers, *Prog. Polym. Sci.* 38 (2013) 963–991. doi:10.1016/j.progpolymsci.2013.02.001.

[10] J. Geltmeyer, L. Van Der Schueren, F. Goethals, K. De Buysser, K. De Clerck, Optimum sol viscosity for stable electrospinning of silica nanofibres, *J. Sol-Gel Sci. Technol.* 67 (2013) 188–195. doi:10.1007/s10971-013-3066-x.

[11] J. Geltmeyer, J. De Roo, F. Van den Broeck, J.C. Martins, K. De Buysser, K. De Clerck, The influence of tetraethoxysilane sol preparation on the electrospinning of silica nanofibers, *J. Sol-Gel Sci. Technol.* 77 (2016) 453–462. doi:10.1007/s10971-015-3875-1.

[12] E. Loccufier, J. Geltmeyer, L. Daelemans, D.R. D'hooge, K. De Buysser, K. De Clerck, Silica Nanofibrous Membranes for the Separation of Heterogeneous Azeotropes, *Adv. Funct. Mater.* (2018). doi:10.1002/201804138.

[13] Y. Dai, W. Liu, E. Formo, Y. Sun, Y. Xia, Ceramic nanofibers fabricated by electrospinning and their applications in catalysis, environmental science, and energy technology, *Polym. Adv. Technol.* 22 (2011) 326–338. doi:10.1002/pat.1839.

[14] D. Li, J.T. McCann, Y. Xia, M. Marquez, Electrospinning: A simple and versatile technique for producing ceramic nanofibers and nanotubes, *J. Am. Ceram. Soc.* 89 (2006) 1861–1869. doi:10.1111/j.1551-2916.2006.00989.x.

[15] S.-S. Choi, S.G. Lee, S.S. Im, S.H. Kim, Y.L. Joo, Silica nanofibers from eletrospinning/sol-gel process, *J. Mater. Sci. Lett.* 22 (2003) 891–893. doi:10.1023/A.