Synthesis of Porous Inorganic Hollow Fibers without Harmful Solvents

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A solvent-free route is presented for the fabrication of porous inorganic hollow fibers with high surface-area-to-volume ratio. The approach is based on bio-ionic gelation of an aqueous mixture of inorganic particles and sodium alginate during wet spinning. In a subsequent thermal treatment, the bioorganic material is removed and the inorganic particles are sintered together. The method is applicable to the fabrication of various inorganic fibers, including metals and ceramics. The route completely avoids the use of organic solvents, such as N-methyl-2-pyrrolidone, and additives associated with the currently used fiber fabrication methods. In addition, it inherently avoids the manifestation of so-called macro voids and allows the facile incorporation of additional metal oxides in the inorganic hollow fibers.

Organic hollow fibers provide a high surface-area-to-volume ratio^[1] and have found application in, for instance, hemodialysis,^[2] filtration,^[3] desalination,^[4] high-pressure gas separation^[5] and microfluidic devices.^[6] The high surface area of the fibers results from their small radial dimensions, which are achieved by the dry-wet spinning method. In this method, a polymer solution is pressed through a spinneret and led into a coagulation bath, where a non-solvent causes the polymer solution to separate into a solid polymer-rich phase and a liquid polymer-lean phase. The dimensions and cross-sectional morphology of the resulting fibers can be changed via the composition of the spinning solution and the process conditions.^[7,8,9] This method of production of organic hollow fibers via non-solvent induced phase separation (NIPS) is very mature, as is evident from the combined low cost and high quality of hemodialysis membrane modules. Over 100 million of defect-free hemodialysis modules are marketed annually at a selling price of ~15 \$.^[10]

The application landscape of organic hollow fibers is limited by their thermo-chemical and mechanical stability. In this respect, inorganic materials provide superior resistance to abrasion and thermo-chemical degradation and allow greater usability in corrosive environments and under severe operating conditions.^[11,12,13] In recent years, several inorganic hollow fibers have been synthesized, from materials including alumina,^[14,15] yttria-stabilized zirconia,^[16] stainless steel,^[17] nickel,^[18] and

perovskites.^[19] All these fibers have been prepared via a two-step approach. The first step is similar to that of the production of organic hollow fibers and entails dry-wet spinning of a particle-loaded polymer solution. In the second step, the organic polymer is burned out and the inorganic particles are sintered together. Recipes for the particle-loaded spinning solutions have been inspired by the wealth of knowledge that exists for dry-wet spinning of organic fibers. An example of a typical solution in which the inorganic material is dispersed is polyethersulfone dissolved in N-methyl-2-pyrrolidone. Polyethersulfone is an easily available and relatively cheap polymer that allows the use of water as a non-solvent to induce phase separation. The decomposition temperature of polyethersulfone is sufficiently high to allow some necking of the inorganic particles before the polymer is removed. Other polymers are used as well but all require the use of an organic solvent. Particularly suitable are aprotic solvents, such as dimethyl formamide, N-methyl-2-pyrrolidone and dimethyl acetamide. These solvents dissolve a wide variety of polymers and their spinning solutions readily coagulate upon contact with water. Yet, many of these solvents are toxic, hazardous, or environmentally malignant.

Figure 1. Backscattering SEM images of polymer hollow fiber loaded with stainless steel particles, prior to thermal treatment; obtained via phase separation (left); obtained via bio-ionic gelation (right); close up of fiber made by dry-wet spinning (bottom).

In this communication, we present an alternative approach for the synthesis of inorganic hollow fibers. This novel method is based on ionic crosslinking of a biopolymer, here referred to as bio-ionic gelation. The biopolymer is sodium alginate, the sodium salt of the polysaccharide alginic acid that is produced by brown algae and bacteria. It is a linear, unbranched block copolymer consisting of two C-5 epimer uronic acids: 1,4-(b-D)-mannuronic acid (M) and 1,4-(a-L)-guluronic acid (G). When the sodium ions in the polymer are replaced by di- or trivalent cations, the water-soluble alginate forms a stable, water insoluble, three-dimensional gel network.^[20] The gel formation involves interaction between the cations and consecutive

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guluronate residues. Sodium alginates find application in cellular and enzyme encapsulation, photocatalyst immobilization,^[21] food industries,^[22] and drug delivery.^[23]

Figure 2. SEM micrographs of hollow fibers obtained via bio-ionic gelation; prior to thermal treatment (a and c), and sintered (b and d) with 50 vol.% inorganic particle loading of stainless-steel particles (a) and (b); alumina particles (c) and (d).

Bio-ionic gelation has several benefits over NIPS. Firstly, the biopolymer that is used is water soluble, which avoids the use of undesirable organic solvents. Secondly, the viscosity of the spinning solution can be directly regulated via the concentration of the biopolymer, which makes the need for rheology-modifying additives, such as polyvinylpyrrolidone, superfluous. Thirdly, the bio-ionic gelation requires less polymer in comparison with the NIPS process. Consequently, the resulting fibers contain less organic material, facilitating a more effective thermal treatment. Fourthly, bio-ionic gelation inherently circumvents the creation of so-called macro voids in the hollow fiber structure. In NIPS, such macro voids result from the entrapment of the polymer-lean phase in the fiber during the exchange of non-solvent and solvent. The presence of macro voids is often considered to cause a reduced mechanical strength of the fibers. In bio-ionic gelation, there is no creation of a new phase and consequently a macro void free structure is obtained.

Scanning Electron Micrographs (SEM) elucidate the morphology of stainless steel particle loaded fibers that have been prepared by bio-ionic gelation and NIPS prior to sintering (Figure 1). The images clearly show the entrapped stainless-steel particles in the polymer matrix, appearing as bright spots in the contrasting polymer materials. The fiber prepared via NIPS (left in Figure 1) possesses a cross-sectional morphology with distinct macro voids, whereas the fiber prepared via bio-ionic crosslinking (right in Figure 1) exhibits a more homogeneous cross section (picture on right in Figure 1). The feasibility of the continuous fabrication of hollow fibers by wet spinning with bio-ionic gelation is further demonstrated in Figure 2. On the left side in Figure 2, fibers are presented that have been spun with an aqueous sodium alginate solution containing stainless-steel particles (top panels in Figure 2) or alumina particles (bottom panels in Figure 2). Details of the spinning solution compositions are provided in the supporting

information (Table S1). For both types of particles, a round fiber with uniform cross-sectional morphology and an open lumen is obtained. The alumina fiber has a larger diameter and a larger wall thickness in comparison with the stainless-steel fiber. These differences in fiber dimensions are due to the differences in rheology of the two spinning solutions that are caused by the different particle sizes. The alumina particles are smaller, which results in a higher viscosity and a more pronounced shear-thinning behavior of the spinning solution (supporting information Figure S1). For both materials, the fiber geometry persists during thermal treatment (right in Figure 2), except for a reduction in fiber diameter and in wall thickness due to polymer burnout. These observations demonstrate the feasibility to produce a variety of inorganic hollow fibers via wet spinning and bio-ionic gelation.

Figure 3. Nitrogen gas flux and liquid water flux versus transmembrane pressure difference, at 25 °C. Different symbols indicate different fibers, obtained from two different batches that were prepared in an identical manner.

Potential applications of the inorganic fibers include (electro)catalysis, microfluidic devices, and membrane separations. For the last application field the fibers can serve either as support for a thin selective film, or for microfiltration of fluids. The fluxes of liquid water and nitrogen gas through various alumina fibers are presented in Figure 3. The fluxes show linear trends with the inside-out pressure difference over the fiber wall. The water flux is measured up to a pressure difference of 20 bar. This substantiates that the fibers can have sufficient strength to withstand this measured pressure difference. The linear trend indicates that in this pressure range the fibers do not suffer severely from mechanical deformation. The variations in flux, when comparing different fibers, can presumably be attributed to lateral variations in the shape and the inside and outside diameters of the fibers. The alumina fibers are able to separate small particles from an aqueous solution (supporting information, Figure S2). The size of the particles that can be separated by sieving is directly related to the pore size of the fibers, which in turn is directly determined by the size of the inorganic particles used in the fiber synthesis. The pore sizes of the alumina fibers obtained via bio-ionic gelation and NIPS are similar, in the range 200 to 300 nm (supporting information, Figure S2). The pore volume of the fiber obtained by bio-ionic gelation is lower as compared to the NIPS derived fiber, due to the more homogeneous fiber morphology that is inherent to the bio-ionic gelation procedure.

Bio-ionic gelation implicates the introduction of multivalent cations into the inorganic particle loaded biopolymer. During the burnout of the biopolymer, these cations may remain in the fiber, conceivably as an oxide when oxygen is present during thermal treatment. By selecting a cation that is associated with the inorganic particles, for instance Al^{3+} for alumina particles, the introduction of the cation does not have implications for the final chemical composition of the fiber. When other cations are used for gelation, the fiber (surface) chemistry may be altered. Figure 4 shows alumina fibers obtained by bio-ionic gelation, using different multivalent cations. The different colors of the fibers indicate the presence of the different cations. Before thermal treatment the color of the fiber is resembling that of the ionic solution used for the gelation. A solution of CaCl_2 or $\text{Ca}(\text{NO}_3)_2$ is colorless and the oxide of calcium is white. Before and after sintering the presence of calcium will not be apparent from the color of the fiber, but is confirmed by X-ray Photoelectron Spectroscopy (XPS). For the other fibers colorization persists upon thermal treatment, indicating that cations remain in the fibers. The color changes of the fibers made with cobalt and chromium are manifestations of the change in the oxidation state of these cations. The XPS inserts of the fiber outer surface confirm that cobalt and chromium are indeed present before and after sintering. These results demonstrate that our method allows facile alteration of the surface chemistry of the hollow fibers via the introduction of various elements in the bio-ionic gelation process.

Figure 4. Alumina loaded alginate fibers obtained via bio-ionic gelation using various cations, before and after thermal treatment (left and right fibers of pairs, respectively). From left to right: calcium chloride, calcium nitrate, ferric nitrate, cobalt nitrate and chromium nitrate. The insets show XPS spectra

In conclusion, we demonstrate an organic solvent-free method for the fabrication of inorganic porous hollow fibers based on the gelation of a biopolymer. This approach is simple and suitable to fabricate ceramic and metallic hollow fibers and can be extended to different inorganic materials without extensive alterations.

Experimental Section

The details of the materials used, mixture preparation, spinning conditions and sintering program are described in the Supporting Information. The hollow fibers fabrication by bio-ionic

gelation was carried out as follows. Initially, the inorganic powders were dispersed in water, followed by the addition of sodium alginate powder in three steps. The mixture was stirred overnight to obtain a uniform suspension. The mixtures were then transferred to a stainless-steel vessel and degassed under vacuum to remove air bubbles. The vessel was pressurized to 2 bar by nitrogen. This forced the particle-loaded alginate solution out of the spinneret through an air gap of 1 cm, before coming in contact with an aqueous solution of multivalent cations, invoking bio-ionic gelation. The same aqueous solution of multivalent cations was used as the bore liquid. The obtained fibers were dried overnight and sintered. The morphology, microstructure, composition, and thermal evolution of weight of the samples were investigated by SEM (JEOL JSM 5600LV), XPS (Quantera SXM (scanning XPS microprobe from Physical Electronics), and TGA-DTA (Netzsch STA 449 F3). Water and nitrogen flux measurements were performed in dead-end mode with atmospheric pressure at the permeate side. The flow was determined using a balance (water) or a soap film flow meter (nitrogen). For the flow-to-flux conversion, the fiber diameter was determined per batch using SEM, and considered to be representative for the whole batch.

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COMMUNICATION

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