Silica nanotubes and hollow silica nanofibers: Gas phase mineralization, polymerization catalysis and in-situ polyethylene nanocomposites

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ABSTRACT

Gas phase mineralization and mesoscopic replication of polyvinyl alcohol (PVA) nanofibers represents an attractive route to the preparation of silica nanotubes and hollow fibers with independent control of pore diameter and wall size. In the sol/gel gas phase process, PVA nanofibers, produced by electrospinning of aqueous PVA, were encapsulated in a thin silica shell by repeated sequenced feed of $SiCl_4$ and H_2O vapors, followed by thermal degradation of the PVA core at 550 °C. The hollow fiber wall thickness was governed by the number of $SiCl_4/H_2O$ cycles with an average increase of the wall size of 0.7 nm per cycle. In contrast to conventional sol/gel electrospinning and wet sol/gel dip coating, shearing of such hollow silicate nanofibers afforded single silica nanotubes with an average length of a few microns. Aqueous silica sols added together with PVA gave control of the inner pore architectures. Methylalumoxane (MAO) activated silica nanotubes were used as supports for half sandwich chromium (III) (**Cr**) and post metallocene (**Fe**) catalysts for ethylene polymerization and in-situ nanocomposite formation with uniform dispersion of silica nanotubes within the polyethylene matrix. A blend of **Cr** and **Fe** was supported on silica nanotubes to produce melt processable polyethylene nanocomposites with bimodal molecular weight distributions.

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1. Introduction

Going well beyond the scope of hollow silica fibers used in fiber optics [1], there exists a growing interest in silicate 1D nano-materials such as nanotubes and hollow nanofibers with tailor-made architectures and surface functionalities [2]. Highly diversified applications are envisioned, including nanocontainers for drug delivery [3,4], fibers and nonwovens for separation technologies [5–8], color-coding nanotubes for bio-labels [9], high porosity supports with channel-like pores for immobilizing industrial catalysts and enzymes [10,11], and even reinforcing agents for polymer nanocomposites exhibiting improved stiffness/toughness balance combined with high thermal and dimensional stabilities [12,13]. Extensive research has been published on exploiting nanoporous inorganic materials containing many cylindrical interconnected nanopores as supports for immobilizing homogeneous "single-site" catalysts [14,15]. Much less is known with respect to catalysts

supported on hollow silicate nanofibers. Naturally occurring silicate nanotubes such as imogolite and halloysite minerals offer rather limited opportunities of tailoring pore sizes and pore surface chemistry. Therefore, synthetic sol/gel routes are developed using nanometer-scaled rods, wires, tubes, and fibers as templates for the nanostructured replication during mineralization. Several approaches employ sol/gel chemistry combined with mesoscopic replication of soft templates such as cylindrical micelles, obtained by means of self-assembly of surfactants [16,17], amino acid amphiphiles [18] reverse-micro-emulsions [19], metal salts [20], tartrate crystals [21–23], and nanofibrils of gels obtained with organic gelators [24] and tailored peptides [25,26]. Typical hard templates include inorganic anisotropic nanoparticles, which are removed selectively after sol/gel-coating, e.g. by means of selective etching of ZnO nanowires [27], photoetching of CdS nanorods [9], or selective carbon combustion of silica-coated multi walled carbon nanotubes, respectively [28]. The dual template approach combines soft with hard templates to produce silica nanotubes with meso-porous walls [29,30]. The mesoscopic replication of synthetic and natural nanometer-scaled fibers is of great promise with respect to both understanding of the nanostructure replication processes and

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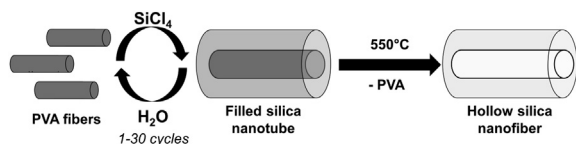
Scheme 1. Preparation of hollow fibers and nanotubes.

the cost-effective fabrication of nanostructured silica [31]. Sol/gel reactions [32,33] as well as atomic layer deposition [34] on cellulose afforded TiO$_2$/cellulose composites for applications in photocatalysis. The prospects of nanofiber-mediated mesoscopic replication are widened considerably by progress made in electrospinning, affording a great variety of nanofibers with diameters of just a few nanometers [35]. While sol/gel electrospinning of tetraethoxysilane (TEOS) polycondensates in acidic ethanol affords dense silica nanofibers [36], the post-electrospinning sol/gel coating of electrospun organic nanofibers enables encapsulation of the nanofibers in silica and formation of core/shell-type nanofibers. In the TUFT ("tubes by fiber templates") process of Greiner and Wendorff, nanofiber templates of degradable polymers such as polylactide were coated by means of chemical vapor deposition, dip coating and sol/gel reactions in order to fabricate inorganic as well as organic nanotubes [37,38]. Frequently, nanofiber formation as well as surface coating by means of sol/gel reactions is accompanied by bonding together large bundles of nanofibers due to extensive interfiber silanol polycondensation, thus producing nonwoven like structures of hollow silica nanofibers. Few approaches exploit electrospinning for heterogenous catalysis, for example, electrospinning of polymer solutions containing transition metal salts and sols has been employed to produce composite nanofibers as supported catalysts for hydrogenation and biocatalysis [39,40]. Very little is known with respect to olefin polymerization on catalysts supported on electrospun nanofibers, synthetic silicate nanotubes, and hollow silicate nanofibers. It is well known that polymerization in the presence of nanoparticles such as carbon nanotubes and functionalized graphenes can produce fine dispersions which are rather difficult to obtain by means of conventional melt blending [41,42]. Here we report on a very versatile process for preparing both hollow silica nanofibers and silica nanotubes with independent control of core size, wall thickness, and aspect ratio. Key step of the hollow silica nanofiber fabrication, as outlined in Scheme 1, is the gas phase mineralization of polyvinyl alcohol (PVA) fibers, prepared by electrospinning, followed by thermal PVA degradation. Upon shearing, silica nanotubes are formed and employed as supports for chromium (III) half sandwich and iron(II) post metallocene catalysts and the in-situ formation of polyethylene nanocomposites during ethylene polymerization.

2. Results and discussion

Polyvinyl alcohol (PVA) nanofibers with average diameter of 195 nm and melting temperature of 218 °C were produced by electrospinning and mineralized by means of sol/gel silica coating in solution and gas phase. Thermal post-treatment of PVA nanofibers for 10 min at 150 °C enhanced both PVA crystallinity (51%) and PVA solvent-resistance, which is important to retain nanofiber architectures during nano templating. In conventional wet sol/gel dip coating, similar to the TUFT process [43], PVA nanofibers were silylated with tetraethoxysilane in ethanol, followed by hydrolysis and silanol polycondensation with aqueous ethanol containing 1wt-% water. Upon thermal degradation of the PVA at 550 °C, nonwoven hollow silica nanofibers with specific surface area of 700 m^2/g were obtained. As is apparent from Fig. 1, sol/gel reactions link together the hollow nanofibers to produce non-wovens. With increasing silica content, silica films were formed between the nanofibers. The resulting non-wovens with very thin silica walls were highly fragile and difficult to handle in heterogeneous catalysis. In contrast, sol/gel coating in gas phase enabled controlled growth of the silica shells without encountering the problem of silica film formation between fibers. At 250 mbar pressure and 20 °C the PVA nanofibers were silylated by exposing them to SiCl$_4$ vapors, followed by subsequent hydrolysis and polycondensation of chlorosilanes in the presence of water vapors directly at the surface of the PVA fibers. Excess reagents and the formed HCl were removed in vacuum in order to prevent side reactions like uncontrolled hydrolysis of the chlorosilane. The individual SiCl$_4$/H$_2$O cycle lasted 5 min and was repeated up to 30 times. Fig. 2 shows the linear correlation between PVA/SiO$_2$ nanofiber weight and the number of cycles with an average weight increase of 4.5 wt% during one cycle. In the corresponding solution process with SiCl$_4$/H$_2$O treatment in ethanol the PVA nanofibers were destroyed. After thermal treatment with temperature increasing from 50 to 550 °C, the PVA was completely degraded, as evidenced by the absence of IR absorption at 3300 cm^{-1} and 1080 cm^{-1} typical for the PVA hydroxyl groups. The analysis of fractured surfaces of fiber bundles by means of environmental scanning electron microscopy (ESEM), displayed in Fig. 1, provides the experimental evidence for the formation of hollow silicate nanofibers.

Upon applying high shear fields by Ultra-Turrax®, only hollow silica nanofibers (HSF) obtained in the gas phase mineralization process readily break up to produce single silica nanotubes with micrometer-scaled length (cf. Fig. 3 left and middle), which is in contrast to the coated SiO$_2$/PVA prepared by dip coating. The silica nanotubes are readily separated from the much larger hollow silica nanofibers, which can be simple removed by centrifugation. As listed in Table 1, a variety of silica nanotubes were prepared. While the diameter of the inner nanotube pores is governed mainly by the
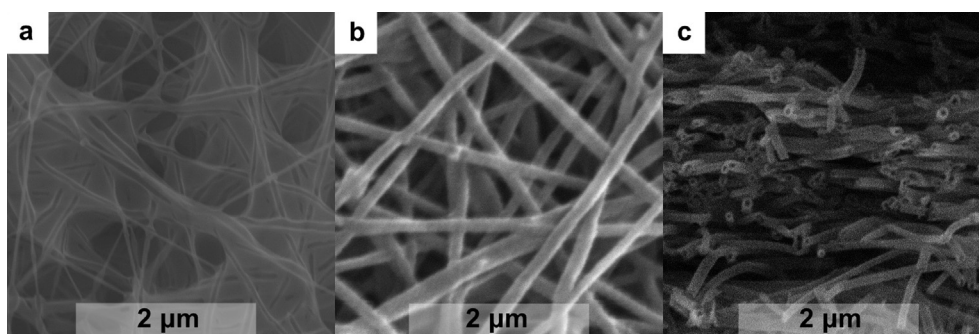

Fig. 1. ESEM images of silica nanofibers prepared by means of dip coating with TEOS/H$_2$O in ethanol (left) and gas phase mineralization with 20 cycles of SiCl$_4$/H$_2$O vapor treatment (middle). Fracture surface of fractured silica nanofiber bundles as obtained in gas phase mineralization (right).