

A simple approach for the synthesis of anisotropic particles by electrospinning

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ABSTRACT

We developed a new and simple approach to fabricate large amounts of anisotropic particles via controlled fragmentation of electrospun nanofibers [1]. Polystyrene nanoparticles were embedded as void precursors in silica fibers by simultaneously electrospinning two dispersions of silica and polystyrene (PS) nanoparticles. After calcination, pure silica fibers with voids were obtained. Subsequent exposure to ultrasound resulted in rod-shaped fiber segments composed of aggregated silica nanoparticles. The morphology, rod-length and dispersity of the fiber segments could be controlled and was dependent on the size and amount of the embedded PS particles.

Keywords: colloid-electrospinning, anisotropic particles

1 INTRODUCTION

The shape of nanoparticles is an important variable for the study of their interaction with biological materials, e.g. their adhesion on cell layers [2-3]. Unfortunately the large scale synthesis of well-defined anisometric particles is usually difficult and performed in batch processes [4]. On the contrary electrospinning is a continuous process. Furthermore, the electrospinning of colloids provides the possibility to immobilize inorganic and organic particles in a fiber forming polymer (template) [5-6]. In case of high particle concentrations this template can be removed either thermally or by solvent extraction without disaggregation of the fiber shape [6]. On the other hand immobilized particles can be degraded leading to porous fibers structures [7]. We investigated the possibility to combine both methods for the synthesis of anisometric particles via controlled fiber fragmentation [1]. Polystyrene nanoparticles were embedded in PVA/silica fibers as precursors for the formation of voids in the fibers by calcination. Silica fibers obtained after calcination were expected to show reduced mechanical integrity at the voids, which provides the opportunity to break them predominately at these voids by a moderate mechanical force. The concept for the preparation of rods is schematically shown in Figure 1.



Figure 1: Formation of silica fibers with voids via calcination of PVA/silica fibers with embedded polymer particles and subsequent exposure to ultrasound.

2 RESULTS AND DISCUSSION

2.1 Generation of silica fibers with voids

Silica nanoparticles (20 nm) were dispersed in an aqueous solution containing equal weight amounts of high molecular weight Polyvinylalcohol (PVA). The resulting dispersion was applied as feed solution in electrospinning experiments yielding (PVA)/silica hybrid fibers with diameters of 448 ± 43 nm. The silica nanoparticles dispersed over the entire fiber surface and within the fiber core, as shown in the cross-section scanning electron microscopy (SEM) micrographs (Figures 3a, Inset). Calcination at 600 °C removed the template polymer completely and reduced the fiber diameter to 305 ± 24 nm without disassembly of the fiber morphology (Figure 3a). To obtain hybrid fibers with embedded PS, aqueous dispersions of PS particles with diameters in the range of 61-558 nm were mixed with the PVA/silica mixture and electrospun under the same conditions. Polymer particles with diameters of 61 ± 16 nm, 102 ± 18 nm, 157 ± 22 nm, and 227 ± 56 nm were synthesized by the miniemulsion polymerization process varying the concentration of the surfactant sodium dodecyl sulfate (SDS). PS particles with sizes of 558 ± 20 nm were achieved by emulsion polymerization. Electrospun PVA/silica nanofibers with embedded PS particles of different size showed varying fiber diameters in the range of 310 - 415 nm prior to calcination (Figure 2). The observation of various fiber diameters can be explained by differences in the viscosity of the feed solutions and the presence of different amounts of sodium dodecylsulfate (SDS), which is inherent to the miniemulsion synthesis that we used. The lowest average fiber diameter was observed in the sample with embedded

61 nm PS particles. These nanoparticles were synthesized with comparatively high amounts of SDS. The presence of the surfactant increased the conductivity and decreased the surface tension of the feed solution, which resulted in intensified stretching of the polymer jet during the electrospinning experiment. The decreased fiber diameters of samples with PS particles compared to pure PVA/silica fibers can be explained by the dilution of the PVA phase in the electrospinning feed which lowered the solution viscosity and increased the stretching of the polymer jet. A direct correlation of the fiber diameter and the PS particle size was not observed.

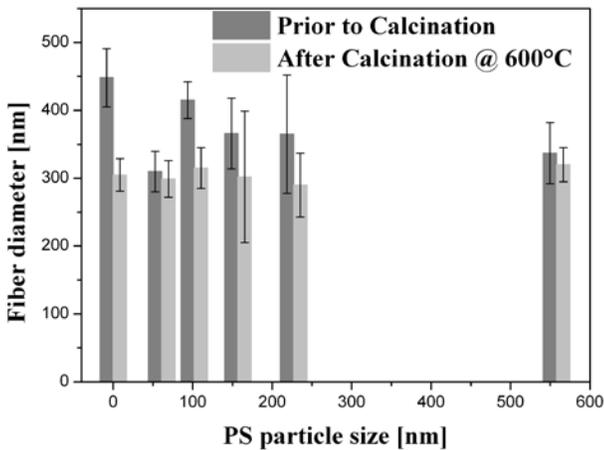


Figure 2: Fiber diameter of PVA/silica hybrid fibers with embedded PS particles prior and after calcination at 600 °C measured from SEM micrographs.

Thermal decomposition of the template polymer PVA and the PS spheres at 600 °C reduced the fiber diameters to 290 - 310 nm and led to creation of holes within the fiber matrix resulting in different fiber morphologies (Figures 3).

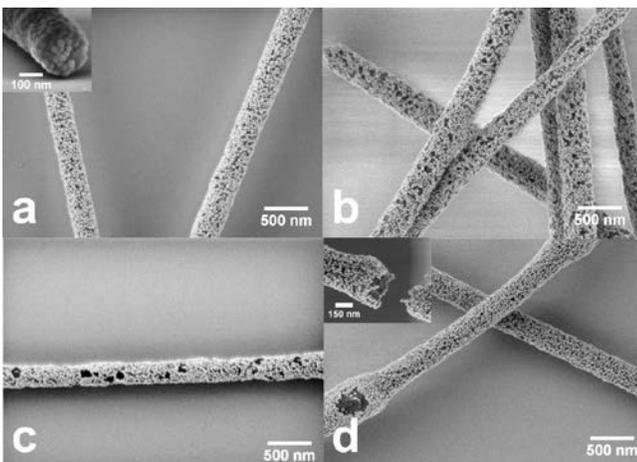


Figure 3: SEM micrographs of silica fibers without (a), and with defects derived from PS particles with diameters of 61 nm (b), 157 nm (c), and 558 nm (d) via calcination.

Silica fibers with previously embedded PS particles of 61 or 102 nm diameter looked perforated (Figure 3b), whereas holes, that were generated due to degradation of 157 and 227 nm polymer particles, covered nearly the whole fiber cross-section (Figure 3c). Thermal removal of the 558 nm spheres left hollow bulges (Figure 3d) which in some cases induced rupture of the fibers resulting in fiber fragments with chalice-shaped ends (Figure 3d, Inset).

In order to explain the formation of holes during calcination, investigations on the thermal decomposition of the PVA/silica/PS fibers in the temperature range of 25 - 700 °C were performed using thermogravimetric analysis (TGA). The obtained decomposition diagrams and derivative TGA curves are displayed in Figure 4. Thermal decomposition of the hybrid fibers occurred in two steps. The derivative curves indicated that the main part of the template PVA degraded in the range of 210 - 310 °C and therefore prior to the PS spheres which started to decompose between temperatures of 310 - 370 °C. This explains the observation that voids within the silica fibers resulting from the PS decomposition were not sealed by melting of PVA and a possible migration of silica particles in the holes. Remaining polymer content was finally removed in a second decomposition step between 400 °C and 560 °C.

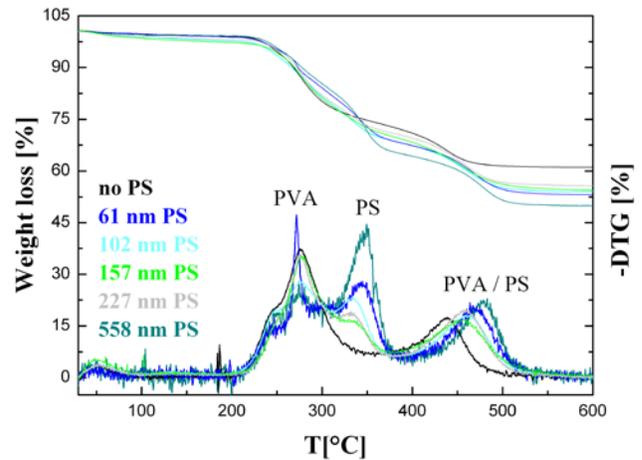


Figure 4: TGA and derivative thermogravimetric (DTG) curves of PVA/silica/PS hybrid fibers.

2.2 Sectioning of silica fibers

After previous dispersion of the calcinated fibers in water by stirring at 300 rpm for 1 h, the effect of ultrasound on the fibers was investigated. Non-uniform silica rods observed after stirring, were further sectioned by applying ultrasound for increasing time intervals. The fiber fragments additionally showed increasing uniformity of their length with increasing ultrasonic treatment. Figure 5 summarizes the measured rod length and their standard deviations in all samples after exposure to ultrasound for 300 s.

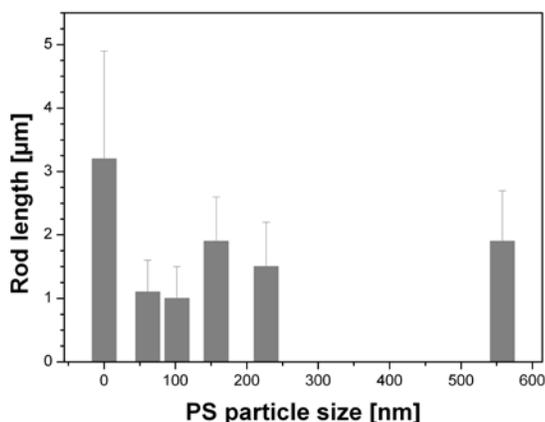


Figure 5: Rod length and dispersity of anisometric silica particles obtained after 300 s ultrasonication.

After 300 s exposure to ultrasound the fibers without voids were broken into rod shaped segments of $2.5 \pm 1.2 \mu\text{m}$ (Figure 6a). Silica rods deriving from fibers with PS particles of 61 or 102 nm sizes showed porous morphologies and were smaller in length ($1.1 \pm 0.5 \mu\text{m}$) (Figure 6b). Fragmentation of fibers with previously embedded 157 and 227 nm PS particles lead to halving of the rod lengths compared to pure silica/PVA fibers. These fiber fragments showed only less or now presence of holes (Figure 6c). In comparison to silica rods derived from fibers without voids (Polydispersity: 0.27) the polydispersity of fiber fragments could be reduced in all samples with voids (0.13 - 0.23). Silica rods with the lowest polydispersity were obtained via embedding of 558 nm PS particles. Fragments obtained here showed chalice-shaped fiber ends and lengths of $1.9 \pm 0.8 \mu\text{m}$ (Figure 6d).

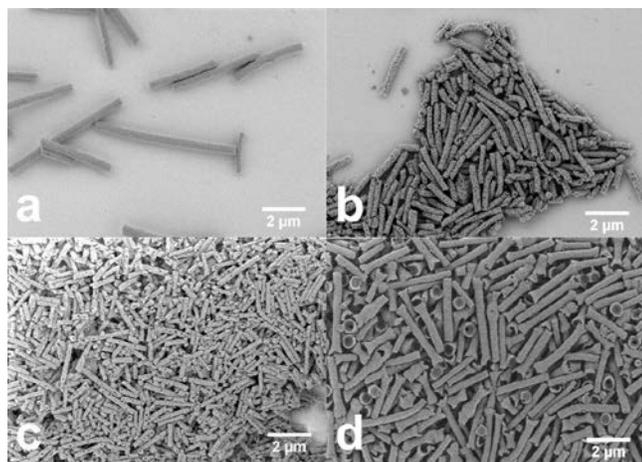


Figure 6: SEM micrographs of anisometric silica particles obtained after 300 s ultrasound exposure of calcined fibers without (a) and with embedded PS particles with diameters of 61 nm (b), 157 nm (c) and 558 nm (d).

We did not observe an effect of the ultrasonic treatment on the fiber diameter, but further exposure to ultrasound for

more than 600 s yielded a mixture of anisometric microparticles and individual spherical 20 nm silica nanoparticles.

Electrospinning experiments using different amounts of embedded 558 nm PS particles strongly indicated, that the length of fiber fragments could be additionally controlled by the inter-particle distance of PS in the as-spun fibers. Silica fibers with higher concentrations of embedded PS spheres showed lower inter-particle distance and increased fragmentation at short ultrasonic treatment periods compared to fibers with lower PS concentration.

3 EXPERIMENTAL PART

Materials: Styrene (99%, Merck) was purified using a column packed with aluminium oxide (Merck) prior to use. Sodium poly(styrenesulfonate) (NaPSS) ($M_w=300\,000 \text{ g mol}^{-1}$, Alfa Aesar), Sodium dodecyl sulfate (SDS) (99%, Carl Roth), 2,2'-azobis-(2-methylbutyronitrile)(V59) (Wako Chemicals), ammonium persulfate (APS, 99%, Acros Organics), hexadecane (99%, Merck), poly(vinyl alcohol) (PVA) (M_w of $125\,000 \text{ g mol}^{-1}$, Polysciences Inc., 88 mol% hydrolyzed) and silica nanoparticles (average diameter: 20 nm, 35.4 wt.% in water, Sigma-Aldrich) were used as received. Demineralized water was used throughout this work.

Preparation of PS particles using miniemulsion: A mixed solution of 6 g styrene and 250 mg hexadecane was added to an aqueous phase consisting of 72 mg SDS and 24 g water and stirred 1 h for pre-emulsification. Afterwards 125 mg V59 was added and subsequently the miniemulsion was prepared via ultrasonication (120 s, 90% amplitude, Branson Sonifier 450 D, 1/2" tip, ice cooling). The polymerization was performed at $72 \text{ }^\circ\text{C}$ for 16 h. Finally the dispersions were filtrated. Varying SDS amounts (360 mg, 18 mg, and 6 mg of SDS) were used to synthesize particles of different size.

Preparation of 558 nm PS spheres via emulsion polymerization: Milli-Q water was stirred at 1000 rpm for 20–30 min at $80 \text{ }^\circ\text{C}$ under argon flow. 15.4 g styrene was added and stirring was continued for 10 min. Afterwards 5 mL of a 0.1 wt.% NaPSS and 5 mL of a 4 wt.% APS aqueous solution were added. Reaction was performed overnight at $80 \text{ }^\circ\text{C}$ at a stirring rate of 700 rpm and under reduced argon flow. After 4 days dialysis and repeated centrifugation at 10 000 rpm and each time redispersion in Milli-Q-water the obtained PS particles were redispersed in water to prepare dispersions with different solid contents (8.8, 10, and 17.5 wt%).

Bi-colloid electrospinning with silica and PS: Silica suspensions with a 34 wt.% solid content were added to 10 wt.% aqueous solutions of PVA (ratio 1:1) and the mixture was stirred with a vortex at 2500 rpm for 3 min to disperse the nanoparticles. Subsequently, varying amounts of PS dispersions with particles of different size were added and dispersed via further stirring. The concentration of PVA

and silica was 77.3 and 69.4 g L⁻¹ for samples without and with PS, respectively. Fibers were electrospun using a commercial platform (ES1a, Electrospinz) equipped with a counter electrode covered with aluminum foil at a constant flowrate of 2.54 mL h⁻¹. The applied voltage was 10 kV and the tip-to-collector distance was held constant at 8.5 cm. Electrospun fiber meshes were calcined for 2 h at 600 °C to completely remove the polymer fraction.

Fiber fragmentation with ultrasound: 3 mg of the calcined fiber material was dispersed in 15 mL of water by stirring at 300 rpm for 1 h. Finally, fibers were further sectioned by ultrasonication for 300 s at 70% amplitude (Branson Sonifier 450 D, 1/4" tip).

Characterization: PS particle sizes were determined using a Nicomp 370 Submicron Particle Sizer. Two measurements were performed and the obtained value was averaged. The morphologies of fibers and fiber fragments were determined on a SEM, working with low voltage (LEO 1530 Gemini, Zeiss). Distribution analysis of the fiber diameter and the particle size observed with SEM were performed using the ImageJ program.

Thermal decomposition of the fibers was investigated with a Mettler Toledo 851 thermogravimetric analyzer. The measurements were carried out in the temperature range between 25 °C and 700 °C at a heating rate of 10 °C min⁻¹ under an oxygen atmosphere with a flow rate of 30 mL min⁻¹.

4 CONCLUSIONS

Anisometric rod-shaped silica particles with either porous or smooth surface or chalice-shaped ends were fabricated in high yields via controlled fragmentation of calcinated silica fibers. The fibers were produced by simultaneously electrospinning two dispersions of silica nanoparticles and PS particles. The morphology and the length of the obtained anisometric silica particles were dependent on the size and concentration of the embedded PS particles as well as on the time of exposure to ultrasound.

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