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Fabrication of Polymer Ellipsoids by the Electrospinning of Swollen Nanoparticles

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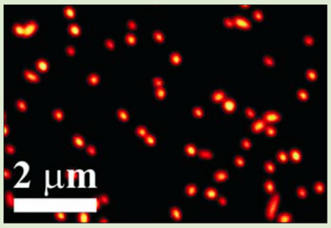
Supporting Information

ABSTRACT: Electrospinning is used to deform originally spherical polymer nanoparticles into ellipsoidal nanoparticles. The polymer nanoparticles are swollen and the dispersion is then electrospun. Under certain conditions, the stretching generated in the electrospinning jet is enough to generate elongated nanoparticles embedded in fibers. The formation of the anisotropic particles is observed by stimulated emission depletion (STED) microscopy performed on fluorescent nanoparticles and by electron microscopy measurements on the nanoparticles recovered after removal of the fiber matrix.



Yunker et al. recently reported a major discovery in the fields of colloid and coatings science. They showed that the coffee-ring effect can be hindered by the addition of a very small amount of polymer ellipsoids upon drying an aqueous colloidal suspension.[1] The only limitation for a facile application of this fundamental result is the fabrication of the ellipsoid particles. They are usually prepared by the so-called film-stretching technique. This technique was already reported more than 20 years ago and consists in the mechanical deformation of a polymer film containing particle fillers of a second immiscible polymer above the glass transition of both polymers. When the film is cooled sufficiently rapidly, the fillers are elongated.[2] Ellipsoids are obtained when spherical particles are stretched,[1−6] but more complicated colloidal structures can also be obtained.[6,7] Particles are recovered after successive washing procedures with hitherto a low yield due to the difficulty to redisperse the particles.[6] Other methods such as crystallization of polymers[8] or self-assembly of block copolymers in nanoconfinement[9] also yielded anisotropic submicrometer particles but with a rather low control on the polydispersity in size of the obtained particles. All of the aforementioned methods have the additional drawback to be batch processes.

The opposite of the film-stretching method, which starts from particles with an aspect ratio of 1 to achieve higher aspect ratios, is the cryosectioning of microfibers,[10] the anisotropic plasma etching of fibers containing particles[11] or the selective disrupting of nanofibers containing voids.[12] The latter method is based on the reduction of an aspect ratio of practically infinite (fibers) to an aspect ratio given by the distance between the voids that were present in the fibers. The nanofibers are fabricated by electrospinning, which is an up-scalable and continuous process. It was already observed that the stretching generated by electrospraying polymer solutions was sufficient to deform polymer microparticles.[13] The authors proposed that the elongated particles were formed when Coulombic fission occurred in the droplets while the solvent is rapidly evaporated. We explore here a new method inspired by the film-stretching method but using the electrospining technique to elongate nanoparticles. It is well known that the polymer jet is stretched during the electrospinning process.[14,15] Greenfeld et al. expressed the compression in the radial direction and the stretching in the longitudinal direction of the polymer chains as a function of the hydrodynamic and elastic forces for the electrospinning of a polymer solution.[15] Initial longitudinal stresses of the order of 10−100 kPa and rates of stretching of the order of 100−1000 s^{-1} due to electrical stretching were estimated to be present when the solution goes from the modified Taylor cone to a thin jet.[14] The stretching in the straight part of the jet is then reduced to 20−100 s^{-1}.[16] The bending instability sets in after this zone and large elongations occur again at rates of ~1000 s^{-1}.[14] Therefore, it is possible to deform polymer particles when they are either in the molten or the swollen states. The latter case is particularly interesting because it would allow the formation of anisotropic particles from polymers with high T_g or T_m or from polymers that degrade before melting. We describe here the preparation of elongated polymer nanoparticles by electrospinning and their characterization by high resolution fluorescence microscopy.

Although high elongation occurs in the electrospinning jet, hard polymer particles do not experience detectable elongation in nanofibers produced by colloid-electrospinning.[17] Therefore, we investigated the possibility to stretch swollen nanoparticles by electrospinning. Fluorescent nanoparticles with sizes of 100 ± 15 nm (Figure 2a) were first prepared by copolymerization of a fluorescently labeled Bodipy-monomer and styrene (Figure S1).[18] The dye was selected because of its high stability and high quantum yield. These characteristics are suitable for stimulated emission depletion (STED) microscopy, which allows the proper estimation of size and shape of fluorescent objects with sizes far below 200 nm.[19] The fluorescent nanoparticles were swollen with various amounts of toluene

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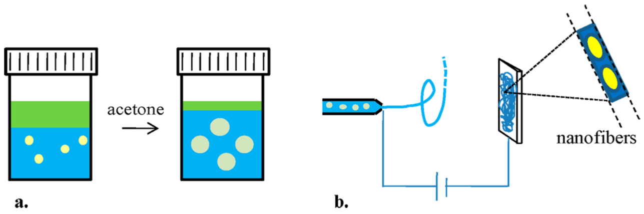

Figure 1. Schematics for (a) the preparation of the swollen nanoparticles. The toluene supernatant (green) is partially transferred in the nanoparticles by adding acetone to the dispersions; (b) electrospinning of the swollen particles to obtain ellipsoids embedded in the fiber matrix.

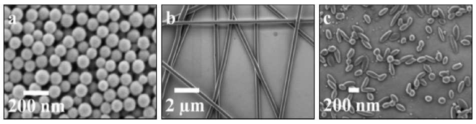

Figure 2. SEM micrographs of (a) the swollen and then colloidal particles, (b) the PVA fibers containing PS nanoparticles, (c) the recovered anisotropic colloidal nanoparticles after removal of the polymer matrix.

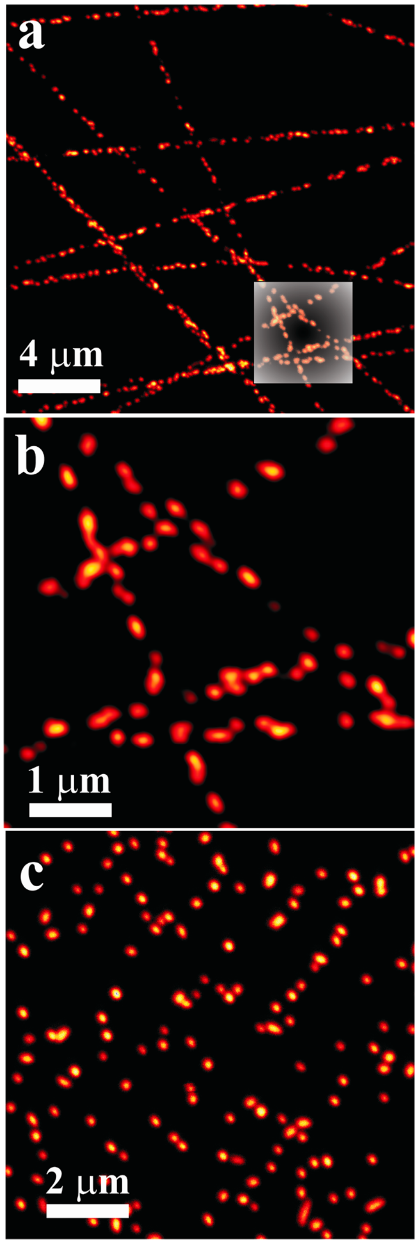

Figure 3. STED images of (a) the particles (CH225A) inside the fibers, (b) selected area (gray area in the Figure 3a), (c) the particles after removal of the PVA matrix.

to obtain deformable particles (Figure 1a). Toluene was added to the dispersion of nanoparticles to form two separated liquid phases. To allow the diffusion of toluene to the nanoparticles, acetone was added before. Acetone is miscible with toluene and water and increases the solubility of toluene in the aqueous continuous phase of the dispersion. This step was found to be necessary because significant swelling of the nanoparticles was not possible without the addition of acetone. The dispersion of swollen particles was mixed with a solution of polyvinyl alcohol (PVA) to build the electrospinning fluid. As for the classical electrospinning of polymer solutions, the accumulation of charges in the fluid due to the high applied voltage induces electrostatic repulsions between the charges that overcome the surface tension of the fluid. In this case, the stretching of the jet provided by the Coulombic interactions elongates the jet of PVA solution and the swollen PS particles. The fiber diameter was chosen to be larger than the diameter of the initial swollen particles so that the stretching occurs more homogeneously along the fiber cross-section compared to a necklace configuration that can be possibly prepared by using particles with diameters larger than the fiber diameters. Smooth fibers were then obtained with a diameter of 279 ± 47 nm (Figure 2b). The nanoparticles are completely embedded in the fibers. Due to the low contrast in electron density between both polymer phases, it is usually difficult to observe polymer nanoparticles in polymer fibers by TEM.[17] Therefore, STED microscopy was used to detect the nanoparticles inside the fibers. The stretching of the swollen particles yielded elongated nanoparticles as shown by STED microscopy (Figure 3). The deviation from spherical morphology could be clearly identified in comparison to samples that could not be successfully stretched. This method of production of anisotropic polymer nanoparticles is convenient since electrospinning is a continuous process and therefore the synthesis can be easily up-scaled. The nanoparticles could be recovered after dissolving the polymer matrix (Figure 2c). The aspect ratio of the recovered and dried nanoparticles was 2.4 ± 0.6.

We varied the initial voltage of 10 kV applied to the dispersion, and lower aspect ratios of 1.8 and 1.5 (Figure S2) were obtained when using higher (20 kV) and lower (5 kV) voltage, respectively. Similarly, a variation of the initial tip-collector distance of 10.5 cm to lower (8.5 cm) and higher (12.5 cm) distances yielded particles with smaller aspect ratios of 1.8 in both cases. As for classical electrospraying and electrospinning, the control of the geometrical properties of the final material is governed by a subtle interplay between physical, chemical, and process parameters. The situation is further complicated by the fact that the electrospinning fluid is biphasic. A qualitative understanding of the consequence of the variation of the aforementioned parameters on the aspect ratio of the nanoparticles needs to consider the rate of evaporation of the toluene from the nanoparticles. There is certainly an optimal rate of solvent evaporation to "freeze" the nanoparticle shape in a nonequilibrium configuration. The stretching is driven by the Coulombic interactions and by the elastic forces whereas the relaxation toward the initial spherical shape is driven by the interfacial tension between the swollen particles and polymer matrix. If the time of evaporation is larger than the relaxation time, the particles return to the spherical shape. On the contrary, a very fast evaporation time does not allow the particles to be stretched because they become too stiff. The polydispersity in size of the obtained nanoparticles is larger than the polydispersity of the initial nanoparticles. This is explained by the bending instabilities occurring in electrospinning[16] that causes inhomogeneity in the stretching of the different elements of the fibers. In principle, this drawback can be corrected by using controlled-electrospinning such as near-field electrospinning[20] or patterned collectors for preparing the fibers.[21]

Not only nanoparticles can be stretched by this method but also nanocapsules. PMMA nanocapsules were prepared by the miniemulsion-solvent evaporation method[9] and subsequently swollen and stretched by electrospinning. In the case of nanocapsules, a much smaller amount of solvent is needed to swell the polymer because the amount of polymer in the shell is lower than in nanoparticles. As for nanoparticles, the elongation of the nanocapsules could be observed with STED microscopy (Figure S3).

We showed here that the electrospinning technique can be applied to deform polymeric emulsions. Elongated nanoparticles and nanocapsules embedded in the fibers were detected by STED microscopy. The aspect ratio was controlled by the electrospinning parameters and the nanoparticles could be recovered by removing the fiber matrix. A limit of the method is the relatively large polydispersity in size compared to the aforementioned film-stretching method. However, our method is particularly interesting because electrospinning is a continuous process. Moreover, polymer particles with high T_g or T_m could be in principle elongated. Finally, the elongated nanocapsules could be used as extrinsic self-healing materials because it was predicted that the healing efficiency increases with the aspect ratio of the containers.[22]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The experimental section, the chemical structures of the two fluorescent dyes, and two STED images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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