## Microliter-Electrospinning: A novel technique to produce micro and nanofibers from biomolecules

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Conventional electrospinning requires highly concentrated solutions of self-assembling molecular units, and also a certain solution volume. The minimum amount of material is thus in the range of 100 mg. However, many biomolecules, especially peptides and proteins, are only available in µg amounts. In order to assess fiber formation potential even from such molecules, or in fact from any other substance, we developed a microliter-electrospinning system, based on an electrified wire. Figure 1.(a) shows the standard system, where ml volumes are fed from a syringe to an electrified metal needle, controlled by a syringe pump or by air pressure. When the electric field between the needle and a flat collector reaches a critical value, a charged jet of solution is ejected from the tip of the needle and undergoes a series of bending instabilities during its passage to the collector. In addition, evaporation of the solvent reduces the diameter of the traveling solution jet and dries the fiber. Figure 1.(b) shows the microliter setup, where the voltage is applied to a platinum (Pt) wire of 0.27 mm diameter, onto which the solution is directly dropped from a micropipette. Building on the same physical processes, the droplet attached to the wire is stretched, causing the formation of a fiber (see figure 2.).

We tested our system with the self-assembling short aromatic peptides diphenylalanine (Phe-Phe) and Gly-Phe, which we already master well [1,2]. Peptides pose a special challenge since the required highly concentrated solutions demand careful selection of solvents. Only then we can achieve entanglement or at least strong interaction, and a stable fiber is formed. We were able to use amounts as small as 5  $\mu$ l, which even at concentrations of 10 wt% contain merely 500 micrograms of material. Of course our system is equally compatible with standard polymer fiber spinning, as shown for polyacrylonitrile (PAN) and other polymers, again from microliter droplets.

Optical microscopy revealed extremely long peptide fibers (see figure 3.), which can only be produced by our method. Raman and infrared spectra [3] provide information on molecular vibrations, and were compared to simulation results of single molecules and of dimers (see figure 4.). The comparison shows that changes in O-H and N-H stretching vibrations are due to hydrogen bonding in the fibers. However, the aromatic residues in the peptide cause  $\pi$ -stacking of the molecules [2,4]. This additional interaction supports assembly to fibers when electrospinning assists the molecular alignment.

## References

- [1] W. Nuansing, A. Rebollo, D. Sedaghat, A.M. Bittner, in prep.
- [2] G. Singh, A.M. Bittner, S. Loscher, N. Malinowski, K. Kern, Adv. Mater., 20 (2008) 2332.
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## Figures



Figure 1. Schematic of the electrospinning system; (a) conventional and (b) microliter-electrospinning.



*Figure 2.* High-speed photography of the fiber formation during microliter-electrospinning (HFIP = Hexafluoroisopropanol, DMF = N, N-dimethylformamide).



*Figure 3.* Optical microscopic images of fibers obtained by microliter-electrospinning (a) Phe-Phe and (b) Gly-Phe.



Figure 4. Raman spectra of a Phe-Phe fiber compared to the calculation result of a single molecule.