Morphological Studies of Electrospray Deposition of Methylcellulose Nanowires

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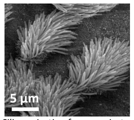
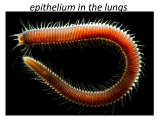
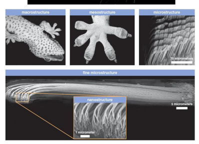
Abstract

Electrospray deposition (ESD) is a versatile coating technology used in micro and nanoscale manufacturing. This process is done by applying an electric field to a solution flowing through a capillary. The build-up of charge in the solution results in a series of "Coulomb fissions" until there is an equilibrium between the surface tension and charge of the droplet. Usually, this results in the formation of spherical shells, as fissions result in a droplet formation that dries, leaving a shell behind. The resulting droplet sizes can be found using an equation that relates the droplet size to the flow rate, density, surface tension, conductivity, and other constants. However, when methylcellulose (MC), a polymer with a lower critical solution temperature (LCST) of ~40C, is sprayed above its LCST, it transitions from a spherical droplet to a nanowire formation. This study focused on relating the nanowire structure's length, diameter, and resulting aspect ratios to different spray variables such as the flow rate, solids content (wt%), molecular weight, and different additives. In doing so, a more optimized wire shape can be found, that being one with a large aspect ratio. In creating this optimized nanowire formation, the surface area of the wire can be increased, making a surface useful in sensor development as well as creating superhydrophobic surfaces.



Cilia projecting from respiratory epithelium in the lungs

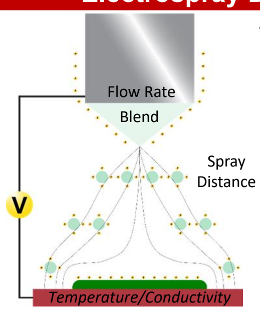




https://en.wikipedia.org/wiki

- Adhesive
- Self-cleaning
- Superhydrophobic

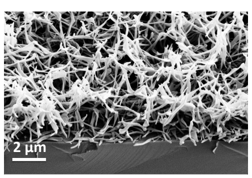
Electrospray Deposition and Morphologies



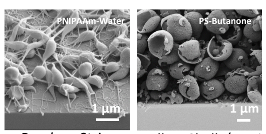
- ESD is a process by which a voltage is passed through a solution, resulting in the solution's dispersal into a uniform spray. The droplets break up into increasingly smaller droplets through a series of "Coulomb fissions" until there is an equilibrium between the surface tension of the droplet and the charge of the droplet.

$$d = \alpha \left(\frac{Q^3 \varepsilon_0 \rho}{\pi^4 \sigma \gamma} \right)^{\frac{1}{6}}$$

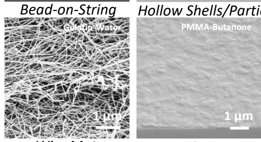
α = Empirical Constant
ε_0 = Dielectric Constant
γ = Surface Tension
σ = Liquid Conductivity
d = Droplet Size
Q = Flow Rate
ρ = Density



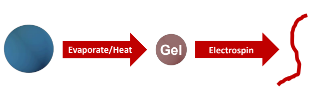
MC Nanowire Forests



Bead-on-String *Hollow Shells/Particles*



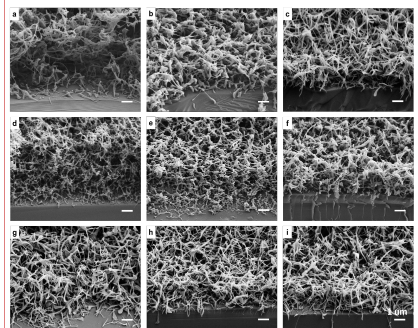
Wire Mats *Film*



- PNIPAAm: Poly(N-isopropylacrylamine)
- PS: Polystyrene
- MC: Methylcellulose
- PMMA: Poly(methyl methacrylate)

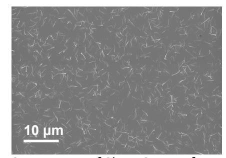
- The viscosity of evaporating droplets increases during MC spray leads to the transition behavior of bead-on-string and wire mats.
- In order to create a model of wire size, parametric MC spray studies were conducted varying flow rate, blend, solids content, molecular weight, and distance.

Parametric Study



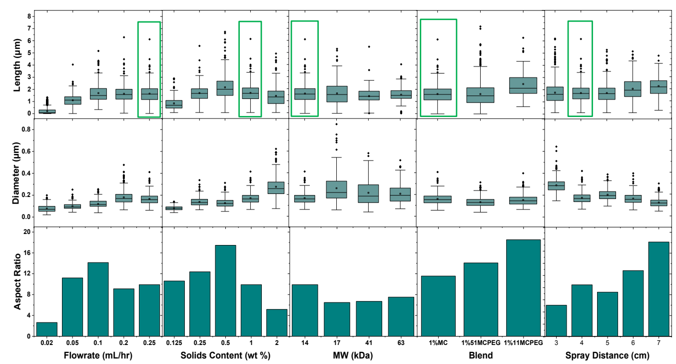
Sprays of 1% MC, 14kDa in 3:2 water:ethanol.
Temperature series: 30C, 40C, 50C, 110C, 0.25 mL/hr for 30 min.
Flow rate series: 0.02 mL/hr, 0.05 mL/hr, 0.15 mL/hr, 0.25 mL/hr.
Spray distance series: 3cm, 5cm, 7cm.
Constant solids in each at 90C for 30min

- MC possesses a lower critical solution temperature (LCST) in water and water:ethanol blends, though the ethanol is predicted to rapidly evaporate. Above the LCST, the MC and water phases separate and gel.
- The length, diameter, and aspect ratio of the sprays were compared in order to quantify the effect of flow rate, solids content, molecular weight (MW) and additives (polyethylene glycol/PEG).



SEM Image of Short Spray of 5:1 MC:PEG blend

- (a-d) MC wires can form remarkably at all temperature, more agglomerated structures of MC wires forms when sprayed below LCST.
- (e-f) The reduction in both length and diameter with reducing flow rate is apparent, and within these trends, the effects of droplet size on evaporation and charge effects
- (g-i) The longer spray distance leads to longer thinner wires



Parametric Study of Nanowire Parameters of Short-Time Sprays (Green indicates standard)

- To optimize the nanowire shape, longer and thinner nanowires, or nanowires with a higher aspect ratio, were desired. This shape would allow the easier, more distributed loading of more useful particles.
- As shown in the figure, a spray of 0.5% 14kDa MC blended in a 5:1 ratio with PEG sprayed at 0.1 mL/hr would result in the best wire structure.

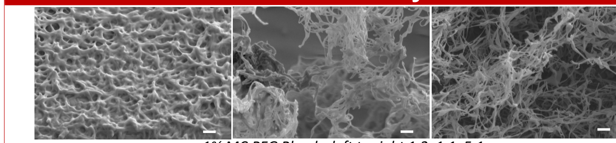
References

[1] L. Lei, D. A. Kovacevich, M. P. Nitzsche, J. Ryu, K. Al-Marzoki, G. Rodriguez, L. C. Klein, A. Jitianu, J. P. Singer, Obtaining Thickness-Limited Electrospray Deposition for 3D Coating, ACS Applied Materials & Interfaces, 2018.

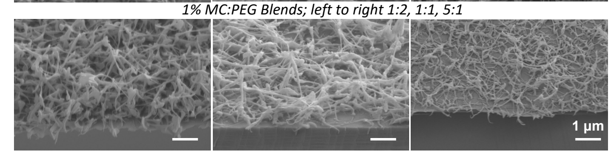
[2] Gañ an-Calvo, A. M.; Da´ vila, J.; Barrero, A. Current and droplet´ size in the electrospraying of liquids. Scaling laws. J. Aerosol Sci. 1997, 28, 249–275

[3] L. Lei, S. Chen, T. Moy, C. Nachtigal, X. Yong, J. P. Singer, in Preparation

Blends Study

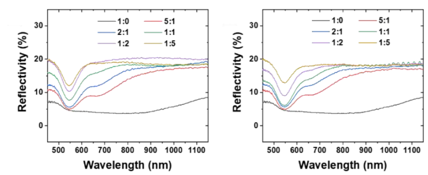


1% MC:PEG Blends; left to right 1:2, 1:1, 5:1



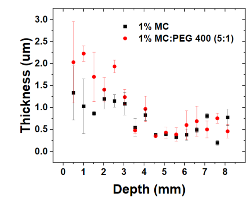
1% MC:Gold Blends; left to right 1:2, 1:1, 2:1

- To adjust the viscosity of sprayed materials, additives were added with MC
- Loading additional PEG reduces the viscosity of sprayed blends, then leads to longer, thinner wires.
- Loading additional plasmonic nanoparticles (gold) opens up the possibility to manufacturing functional wires, with the optical properties adjustable.



Reflectance Graphs of MC:Gold Nanoparticles Sprays and (MC+PEG):Gold Sprays, left to right

- Loading gold alone results in the broadening of the plasmon, indicating agglomeration.
- By loading PEG with gold, the reflectance dips occur at the same spot, resulting in less gold clumping and a more optimized structure.
- The self-limiting ability of NWs enables MC spray to be used in complex 3D coatings



Thickness of MC Spray on 4x4 Hole Array

Conclusion

- As a result of these experiments, the best parameters can be found to optimize wire size and create the most structurally useful wires (largest aspect ratio).
  - Best found: 0.1mL/hr, 0.5%, 14 MW, 5:1 MC/PEG blend
  - Will allow the loading of materials while maintaining more optimal shape
- Blends of conductive and other useful materials shows the change in wire structure as they are loaded.

3D Surface Coating of MC+PEG:Gold on Cypress

Acknowledgments

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