Electrospun Nanofibers with Tunable Electrical Conductivity

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Electrospinning is a convenient method to produce nanofibers with controlled diameters on the order of tens to hundreds of nanometers. The resulting nonwoven fiber mats are lightweight, highly porous, and have high specific surface areas around 1 to 100 m²/g. Combined with the high electrical conductivity of intrinsically conductive polymers, conductive electrospun fiber mats are promising for a variety of applications, such as multifunctional textiles, resistance-based sensors, flexible reversibly hydrophobic surfaces, organic photovoltaics, scaffolds for tissue engineering, and conductive substrates for surface functionalization and modification. Intrinsically conductive polymers, such as polyaniline (PAni), however, are relatively hard to process compared to most other polymers. They have fairly rigid backbones due to the high aromaticity, and are usually available only in relatively low molecular weight forms, so that the elasticity of their solutions is insufficient for it to be electrospun directly into fibers.

Considerable amount of recent work has been reported trying to make electrospun polymeric nanofibers with intrinsically conductive polymers or composites. However, a large fraction of the work only showed the morphology and did not characterize the actual performance of these fibers, nor did they test the variability of the fibers and mats from a wide range of processing conditions and resulting structures. Therefore, this thesis aims to make a comprehensive study of the electrical tunability of electrospun fibers with intrinsically conductive polymers and its composites, to establish a clear processing-structure-property relationship for these fibers and fiber mats, and to test the resultant fibers with the targeted applications such as gas sensing.

We have first developed a reliable method to characterize fiber electrical conductivity using interdigitated electrodes (IDE) and high-impedance analyzers with contact-resistance corrections, and applied to electrospun conductive polymer nanofibers. This method was shown to be reliable and sensitive, as opposed to some of the other methods that have been reported in literature.

Facing with the challenge of overcoming the relatively low elasticity of the conductive polymer solutions to achieve electrospinnability, we have fabricated electrospun fibers of PAni and poly(3,4-ethylenedioxythiophene) (PEDOT), blended with poly(ethylene oxide) (PEO) or poly(methyl methacrylate) (PMMA) over a range of compositions. Pure PAni (doped with (+)-camphor-10-sulfonic acid (HCSA)) fibers were successfully fabricated for the first time by co-axial electrospinning and subsequent removal of the PMMA shell by dissolution. This allowed
for the pure electrospun PANi/HCSA fibers to be tested for electrical performances and its enhancement as well as gas sensing application.

The conductivities of the PANi-blend fibers are found to increase exponentially with the weight percent of doped PANi in the fibers, to as high as 50 ± 30 S/cm for as-electrospun fibers of 100% PANi/HCSA. This fiber conductivity of the pure doped PANi fibers was found to increase to 130 ± 40 S/cm with increasing molecular orientation, achieved through solid state drawing. The experimental results thus support the idea that enhanced molecular alignment within electrospun fibers, both during the electrospinning process and subsequent post-treatment, contributes positively to increasing electrical conductivity of conductive polymers. Using a model that accounts for the effects of intrinsic fiber conductivity (including both composition and molecular orientation), mat porosity, and the fiber orientation distribution within the mat, calculated mat conductivities are obtained in quantitative agreement with the mat conductivities measured experimentally. This correlation, along with the reliable method of fiber conductivity measurement by IDE, presents a way to resolve some of the inconsistencies in the literature about reporting electrical conductivity values of electrospun fibers and fiber mats.

Pure PANi fibers with different levels of doping were also fabricated by co-axial electrospinning and subsequent removal of the shell by dissolution, and shown to exhibit a large range of fiber electrical conductivities, increasing exponentially with increasing ratio of dopant to PANi. These fibers are found to be very effective nanoscale chemiresistive sensors for both ammonia and nitrogen dioxide gases, thanks to this large range of available electrical conductivities. Both sensitivity and response times are shown to be excellent, with response ratios up to 58 for doped PANi sensing of ammonia and up to more than $10^5$ for nitrogen dioxide sensing by undoped PANi fibers. The characteristic times for the gas sensing are shown to be on the order of 1 to 2 minutes. We have also developed a generic time-dependent reaction-diffusion model that accounts for reaction kinetics, reaction equilibrium, and diffusivity parameters, and show that the model can be used to extract parameters from experimental results and used to predict and optimize the gas sensing of fibers under different constraints without the need to repeat experiments under different fiber and gas conditions.

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