Enhanced Plasmonic Activity of Polymer Fibers Through Nanoparticle Doping

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The incorporation of metallic nanoparticles (NPs) into a polymer matrix has been used to enhance and control dissolution and release of drugs, for drug delivery, as antimicrobial agents, for localized heat sources, as mechano-responsive nanocomposites, and for unique optoelectronic applications.[1] Colloidal gold NPs (Au_c) exhibit a plasmonic response that has applications in photothermal energy conversion. Colloidal gold (Au_c) NPs were incorporated into electrospun (ES) polyethylene glycol fibers (Au_c/PEG) to utilize the nanoparticle plasmonic response for localized heating of the polymer. Maximum absorbance of these materials in fiber form was recorded at 504 nm. Au_c/PEG fibers were ES directly onto resistance temperature detectors (RTDs) so that resistance of the materials could be measured. A drawback to Au_c/PEG electrospun mats was a propensity for electrospraying and droplet formation instead of depositing a fibrous mat that could be peeled up from the deposition surface and distributed as a drug-delivery device. To counter this issue polyethylene oxide (PEO; 200,000 MW) was blended with PEG in various ratios to improve polymer viscosity and resultant material properties for distribution, Figure 1. PEG was blended with PEO at a ratio of 3:2 respectively to create a fiber mat that can be peeled from the substrate and exhibited a measurable response to green (532 nm) laser light with an increase in temperature of 7 °C.

Gold nanorods (GNRs) were incorporated into PEG thin films as well, Figure 2. The GNRs used exhibit a tunable longitudinal surface plasmon resonance that depends on the GNR aspect ratio. While Au_c used for this work were sourced commercially, GNRs were synthesized with a novel, secondary (seeded) growth procedure which allows improved control over aspect ratio and size of GNRs. Aspect ratio control during synthesis results in GNRs with resonances tuned between 760 and 820 nm in order to vary interactions with λ_{808nm} activation optical source. Using spectroscopic ellipsometry (J.A. Woollam M-2000 U), the complex optical constants of drop cast films will be determined for calculation of material absorbance. In addition, an infrared camera system will be used to map temperature changes throughout the polymer films. Electron microscopy will be used to quantify fiber mat quality. The suitability of doping ES fibers with plasmonic dopants has important applications ranging from energy conversion, sensing, and drug delivery.

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[1] R.-C. Zhang, D. Sun, R. Zhang, W.-F. Lin, M. M.-M., J. Patel, S. Askari, C. McDonald, D. Mariotti and P. Maguire, *Scientific Reports* 7, 46682 (2017).

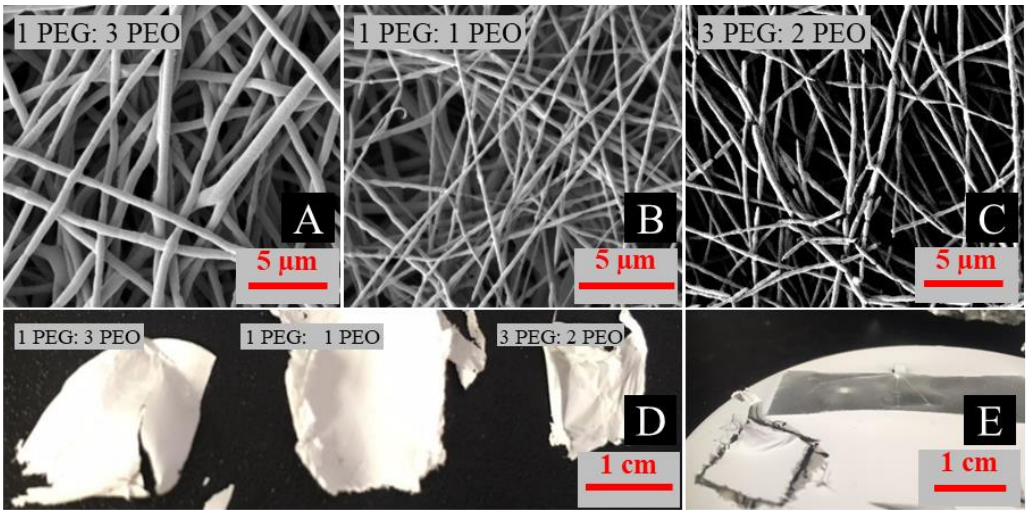

Figure 1: **A-C** SEMs showing PEG:PEO polymer blends prepared at various wt% and electrospun into fibers. **D** Polymer blends shown in **A-C** created fiber mats that could be peeled from the deposition surface for distribution. **E** Image of the deposition plate used to deposit ES fibers directly onto RTDs for temperature measurement with illumination.

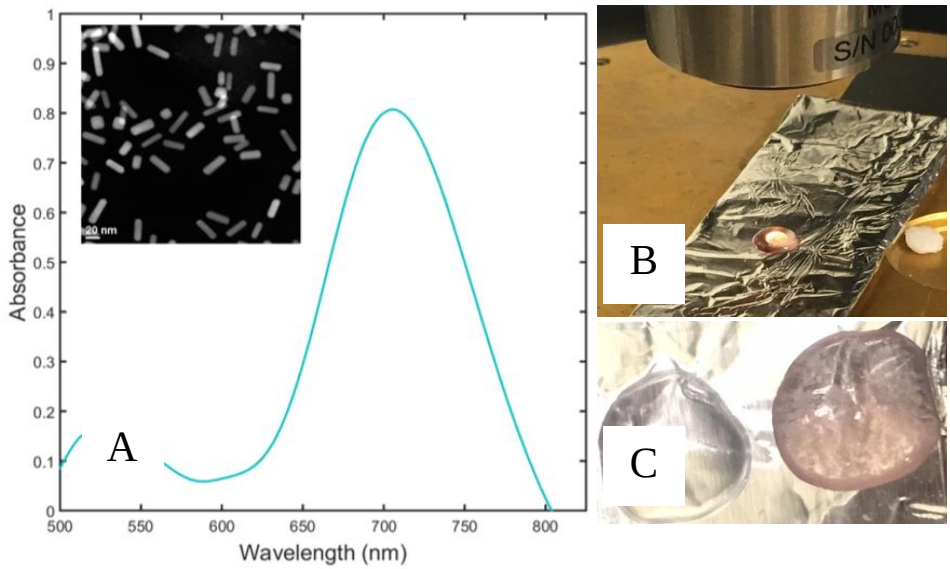

Figure 2: **A** Absorbance spectra for gold nanorods (GNRs) with inset transmission electron micrograph of the nanorods. **B** Image showing microscope interrogation of PEG:PEO polymer doped with gold nanoparticles. **C** Image showing neat polymer on the left and nanoparticle-doped polymer on the right.