Photo-Activation of Sensitized Denitrification Filters

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Nitrate is a frequently occurring ground water pollutant that has significantly increased in concentration over the last century due to fertilizer use in agriculture.[1] Although nitrogen-based fertilizers play a critical role in agriculture, use of these fertilizers has led to nitrate contamination of surface and ground waters. Nitrogen in aquatic environments promotes biological growth and algal blooms, resulting in eutrophication of these waters. Eutrophication, in turn, depletes waters of oxygen. Lack of oxygen in aquatic ecosystems causes death of aquatic animals, and nitrogen oxyanions severely affect human health by reducing nitrate to nitrite in the human gut.

Several water treatment technologies have been examined to address nitrate pollution.[1] While nitrate removal has been predominantly approached by traditional physiochemical and biological treatment processes, these methods have presented drawbacks including high operational and labor costs, large energy requirements, and residual waste production. More recently, technologies that minimize the environmental impact presented by denitrification have been explored. One such technological approach involves development of nanoscale photocatalytic denitrification materials that reduce the footprint of denitrification.

In this work, electrospinning was used to fabricate a denitrification filter with photocatalytic surfaces for nitrate reduction and nanoscale dopants that improve catalytic efficiencies (Figure 1). Polymer fibers in the filter consist of a coaxial structure with a polycaprolactone-poly(3-hexylthiophene-2,5-diyl) (PCL-P3HT) blend core (sensitizer layer) and PCL-polyethylene glycol (PEG) block copolymer shell containing an electron mediator ($Fe^{3+/2+}$). During fabrication, the PEG blocks were dissolved from the shell structure, and the fibers were coated in zirconium oxide nanoparticles (ZrONPs, Figure 2) that had access to the P3HT core through these pores. Efficiency of the filter was improved by doping the polymer shell with metallic nanoparticles that scatter light within the fibers, increasing the rate of nitrate reduction. Using pump-probe microscopy,[2] electron injection from the P3HT sensitizer onto the surface of ZrONPs will be examined and photocatalytic efficiencies will be monitored using a Hepatochem PhotoRedOx Box photochemical system.

[1] H. O'Neal Tugaoen, S. Garcia-Segura, K. Hristovski, P. Westerhoff, "Challenges in photocatalytic reduction of nitrate as a water treatment technology," *Science of The Total Environment*, Vols. 599–600, Pgs. 1524-1551, 2017.
[2] E.M. Grumstrup, M.M. Gabriel, E.E. Cating, E.M. Van Goethem, J.M. Papanikolas, "Pump–probe microscopy: Visualization and spectroscopy of ultrafast dynamics at the nanoscale," *Chemical Physics*, Vol. 458 pp. 30-40, 2015.

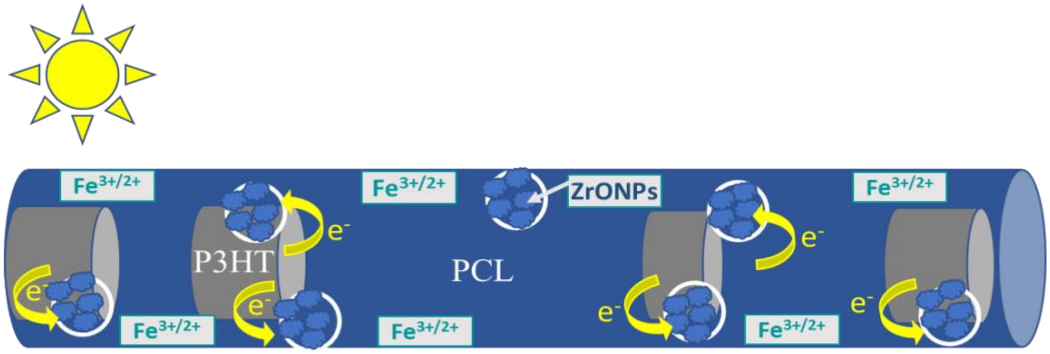

Figure 1. Schematic showing the design of photocatalytic denitrification polymer fibers used in the filter for nitrate reduction. Photons absorbed by P3HT facilitate electron injection from the P3HT to ZrONPs at the polymer surface. $Fe^{3+/2+}$ in the structure acts as an electron mediator, while the reduction reaction occurs at the surface of ZrONPs. Gold or silver nanoparticles doped into the polymer shell will be used to scatter light and improve catalysis efficiencies (not shown).

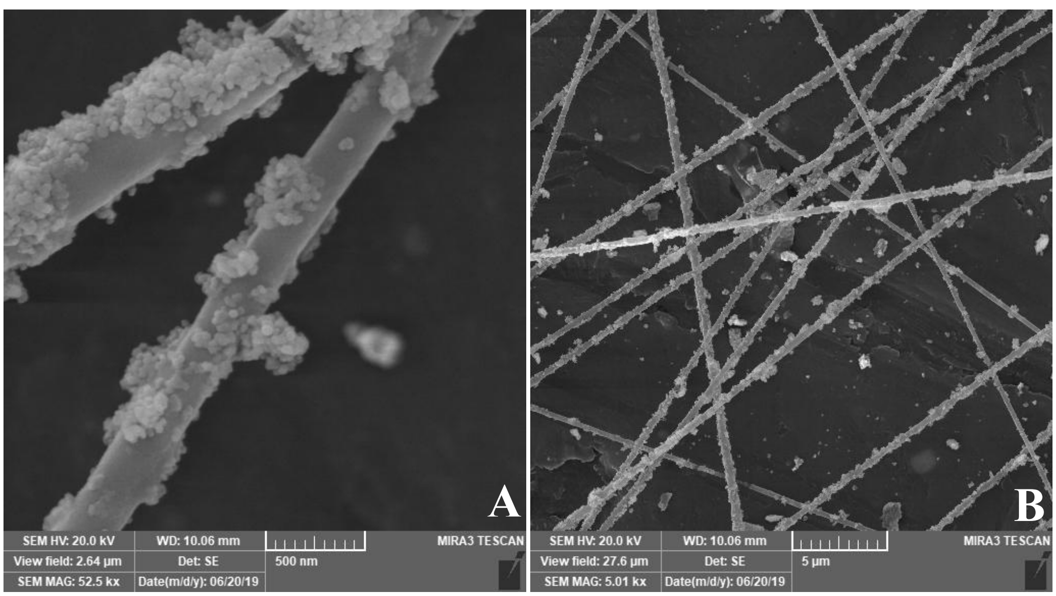

Figure 2. Scanning electron micrographs of electrospun PCL fibers coated in ZrONPs. **A** Magnification of 52.5 kX with scale bar of 500 nm. **B** Magnification of 5.01 kX with scale bar of 5 µm.