Denitrification Through Light Scattering and Photocatalysis by Sensitized Nanofibers

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Nitrogen-based fertilizers play a critical in the high yield production of crops, yet the use of these substances has led to nitrate contamination of surface and ground waters. Nitrate contamination in aquatic environments damages the ecosystems and can negatively affect human health. While nitrate removal has been predominantly approached by physicochemical and biological treatments, these methods have presented drawbacks including high costs, large energy requirements, and residual waste production. Recently, more sustainable processes are being explored including the use of nano-catalysts that promote photocatalytic denitrification with reduced footprint.[1]

In this work, a catalytic electrospun filter that uses photons from natural sunlight to promote reduction of aqueous nitrate is described. The filter was designed to utilize the high surface area of electrospun nanofibers to increase the number of catalytic sites for nitrate reduction and to improve efficiencies through use of polymer composites containing light-scattering dopants. Specifically, the individual fibers consist of a polycaprolactone-poly(3-hexylthiophene-2,5-diyl) (PCL-P3HT) blend core and a PCL - polyethylene glycol (PEG) block copolymer shell (Fig. 1). In the design used, PEG blocks are dissolved from the shell structure and filled with zirconium oxide nanoparticles (ZrONPs) that exhibit stability and an adequate reduction potential for nitrate reduction in water. In this design, sunlight transmitted through the shell layer is absorbed by the P3HT core, leading to electron injection by the core onto the surface of ZrONPs at the fiber-water interface, promoting catalysis. In past work, thin film versions of the photocatalytic fibers were fabricated to determine feasibility of the design (Fig. 2A). Results demonstrated a nitrate reduction of 22 % observed over 8 hr using a Hepatochem PhotoRedOx system (Fig. 2B) and a 540 nm LED.

Following these results, we investigate the fabrication in filter form. Denitrification is quantified using gas chromatography / mass spectroscopy, and fibers is imaged by electron microscopy. Electron injection is monitored by ultrafast pump-probe microscopy.[2] In addition, we add metallic nanodopants (gold spheres) to the shell layer to promote light scattering and examine improved efficiencies of the reaction. Light scattering is quantified using a pixel-by-pixel analysis of images taken through a layer of the shell materials with and without dopants (Fig. 3).

[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.

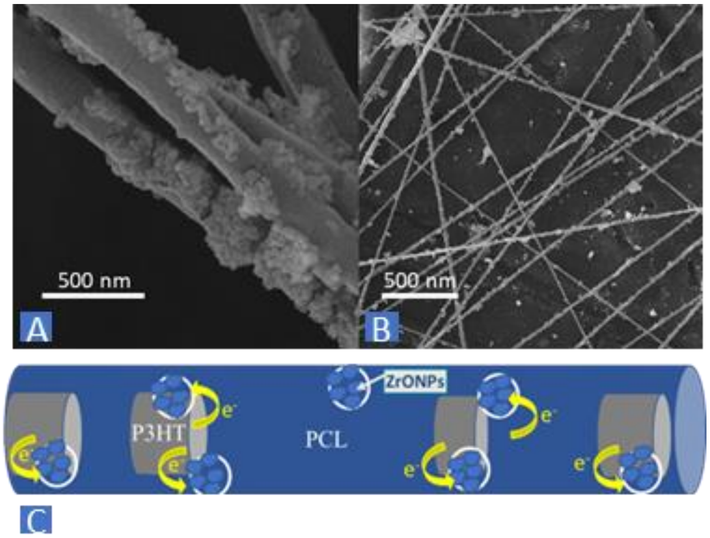

Fig. 1. ***(A-B)*** *SEM micrograph of PCL fibers coated in ZrONPs. Fibers were preliminarily fabricated to provide proof of concept.* ***(C)*** *Graphic showing the photocatalytic denitrification fiber design and concept of electron injection.*

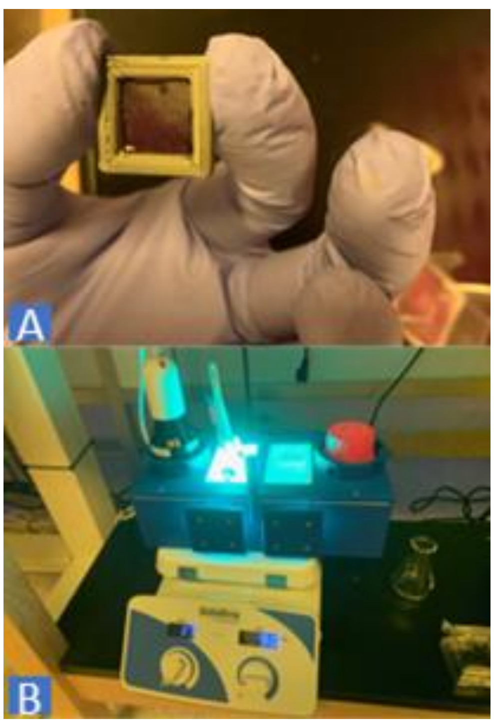

Fig. 2. ***(A)*** *Thin film version of the photocatalytic denitrification fiber structure. The layered film was sealed in a 3D printed frame and backed with a quartz cover slip.* ***(B)*** *Hepatochem PhotoRedOx Box system during testing of the thin film.*

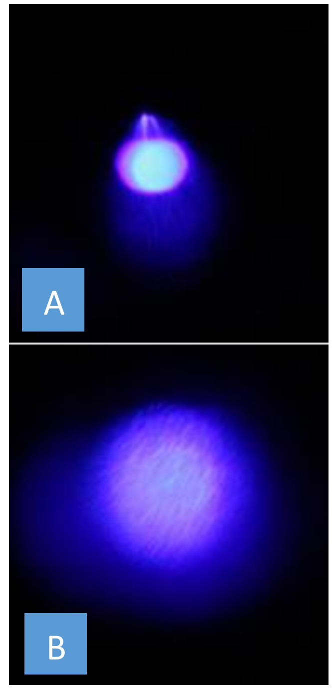

Fig. 3. ***(A)*** *Image of a laser (454 nm) shown through a polymer thin film. The image was analyzed pixel-by-pixel to form an intensity map. (****B)*** *Image of the same laser shown in part A but shown through a polymer thin film containing gold nanodopants. Pixel-by-pixel intensity analysis reveals the light is scattered over a larger area in the image. In the filter, we hope this method will improve photon capture and catalytic efficiencies.*