Nanostructured Sensing Surfaces via Combination of Electrospinning with Electrostatic Layer-by-Layer Assembly.

Xianyan Wang[1], Young-Gi Kim[1], Christopher Drew[1], Bon-Cheol Ku[1], Jayant Kumar[1*], Lynne A. Samuelson[2*]
[1]Center for Advanced Materials, Departments of Chemistry and Physics, University of Massachusetts Lowell, Lowell, MA 01854
[2]Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick MA 01760

Electrospun nanofibrous membranes are of particular interest due to their very large surface area structures.[1] To date, we have demonstrated that fluorescence based sensors fabricated by electrospinning a fluorophor containing polymer, can have 2-3 orders of magnitude higher sensitivities than those from continuous thin films of the same sensing material.[2] Here we report an extension and further improvement of the sensitivities of these sensors by a unique combination of electrospinning with electrostatic layer-by-layer deposition (ELBL) to modify the surface of the nanofibrous membranes with a fluorescent conjugated polymer.

To fabricate these sensors, cellulose acetate (CA) electrospun nanofibrous membranes were first prepared. Then the negatively charged fluorescent conjugated polymer, hydrolyzed poly[2-(3-thienyl)ethanol butoxy carbonyl-methyl urethane] (H-PURET), was electrostatically assembled onto the surface of the CA electrospun nanofibrous membrane using poly(allylamine hydrochloride) (PAH) as the polycation (figure 1).

The morphology of an electrospun membrane of CA is shown in Figure 2. The diameters of the fibers were approximately 100 to 300 nm. The quenching behaviors of these sensors to metal ions Fe^{3+} and Hg^{2+} were studied by the measurement of the fluorescence spectra of the sensing films as a function of different concentrations of the quenchers as shown in Figure 3 for Fe^{3+}. Similar behaviors were observed for Hg^{2+}. For quencher concentrations in the range of 10^{-8} to 10^{-7} mol/l, linear plots between concentration of quencher and I_0/I are obtained showing a Stern-Volmer relationship, with the Stern-Volmer constants (K_{sv}) 5.79×10^6 M^{-1} and 5.67×10^6 M^{-1} for Hg^{2+} and Fe^{3+} respectively. The detection limits were in the range of a few to tens parts per billion.

In summary, we have developed highly sensitive nanostructured sensing surfaces for metal ion (Fe^{3+} and Hg^{2+}) detection by combining electrospinning and ELBL self-assembly techniques for sensor fabrication. The localization of a conjugated polymeric fluorescent tag to the surface of an already high surface area nanofibrous membrane minimized the amount of inactive (embedded) fluorescent indicator, and resulted in significantly improved sensitivities compared to similar systems in which the fluorescent polymer was dispersed throughout the electrospun nanofibers. This approach is extremely versatile and expected to find wide application towards the development of new optical sensors.

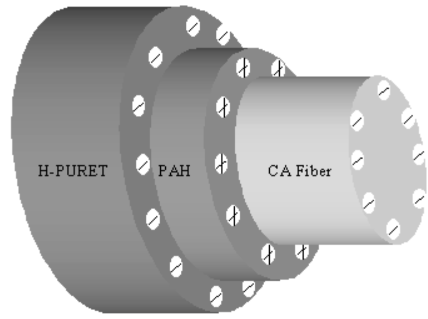

Figure 1. Schematic representations of a H-PURET/PAH thin layer structure on CA electrospun fiber surface (not scaled)

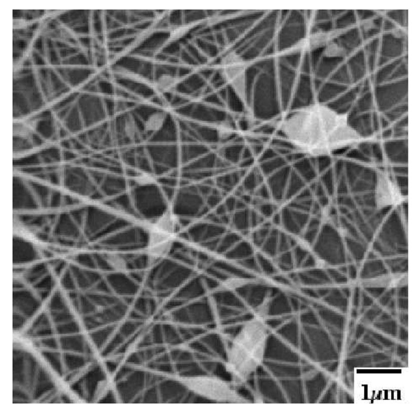

Figure 2. SEM image of the electrospun membrane

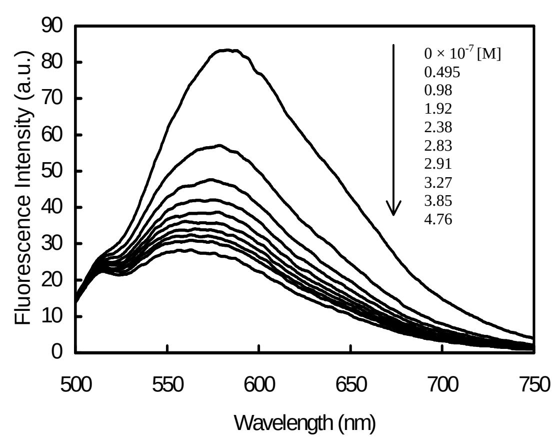

Figure 3. Fluorescence emission spectra of the sensing film with varying Fe^{3+} concentration.

Reference

1. Reneker, D. H.; Chun, I. *Nanotechnology* 7, 1996.
2. Xianyan Wang, Christopher Drew, Soo-Hyoung Lee, Kris J. Senecal, Jayant Kumar and Lynne A. Samuelson, *Nanoletters*, 2(11), (2002).