

Electrospun Nanofibrous Membranes for Highly Sensitive Optical Sensors

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ABSTRACT

The first use of electrospun nanofibrous membranes as highly responsive fluorescence quenching-based optical sensors for metal ions (Fe^{3+} and Hg^{2+}) and 2,4-dinitrotoluene (DNT) is reported. A fluorescent polymer, poly(acrylic acid)–poly(pyrene methanol) (PAA–PM), was used as a sensing material. Optical chemical sensors were fabricated by electrospinning PAA–PM and thermally cross-linkable polyurethane latex mixture solutions. These sensors showed high sensitivities due to the high surface area-to-volume ratio of the nanofibrous membrane structures.

The development of new approaches toward highly sensitive detection techniques remains a major challenge in the field of chemical sensing. It is widely accepted that the sensitivity of a sensor that detects analytes by interacting with molecules on the surface will increase with increasing surface area per unit mass. Therefore, considerable effort has been made to increase the surface area of the sensing interface in chemical sensors.^{1–5} However, these approaches either involve sophisticated synthesis routes or cumbersome fabrication processes. Some of these techniques are also limited to particular materials. Therefore, a new and facile approach for effective and versatile fabrication of high surface area sensor interfaces is still desired.

Recently, the electrospinning technique has been found to be a unique and cost-effective approach for fabricating large surface area membranes for a variety of sensor applications.⁶ Electrospinning is a process by which high static voltages are used to produce an interconnected membrane-like web of small fibers, with the fiber diameter in the range of 10–1000 nm.⁷ This technique can be used with a variety of polymers to produce nanoscale fibrous membranes. Electrospun nanofibrous membranes can have approximately 1 to 2 orders of magnitude more surface area than that found in continuous thin films.⁷ It is expected that this large amount of available surface area has the potential to provide unusually high sensitivity and fast response time in sensing applications.

The pyrene derivative, pyrene methanol (PM) was chosen as the fluorescent indicator because it has a large Stokes shift, high quantum yield, strong absorbance, excellent photostability and lifetime, and is relatively nontoxic.⁸ Covalent attachment of the PM fluorophore to poly(acrylic acid) (PAA) with an appropriate spacer serves to both minimize self-quenching and improve the processibility of the material. Also, similar fluorescence sensing investigation of this material was previously carried out on thin films.⁹ A comparison of these two techniques is expected to show that the sensitivity of the electrospun fabricated sensor would be greatly improved due to the much higher surface area-to-volume ratio than that known for the thin film sensors.

The preliminary results show that the sensitivities of electrospun nanofibrous membranes to detect metal ions (Fe^{3+} and Hg^{2+}) and 2,4-dinitrotoluene (DNT) are 2 to 3 orders of magnitude higher than those obtained previously from the thin film sensors.

The sensing material PAA–PM was synthesized by covalent functionalization of pyrene methanol (PM) into poly(acrylic acid) (PAA) as shown in Figure 1. A solution of 1,1'-carbonyldiimidazole (CDI, 0.45 g, 2.8 mmol) and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 10 mL of *N,N'*-dimethylformamide (DMF) were added to a solution of PAA (MW = 50 000 g/mol) (2.0 g, 28 mmol) in 40 mL of DMF. After stirring the solution at 70 °C until the evolution of carbon dioxide subsided (30 min), a solution of PM (0.65 g, 2.8 mmol) in 15 mL dimethyl formamide (DMF) was added and the solution was stirred at 70 °C for 24 h. The solution was slowly poured with vigorous stirring into ethyl ether to precipitate the polymer. After filtration,

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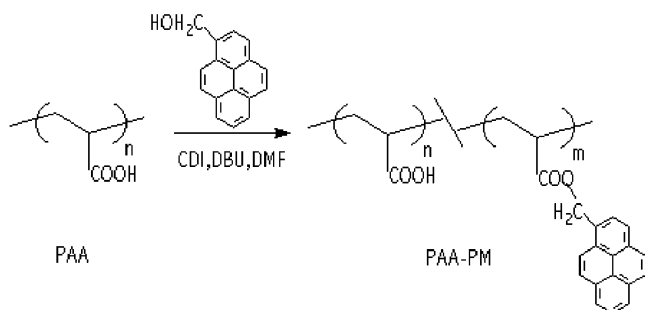


Figure 1. Synthesis scheme for polymer PAA-PM.

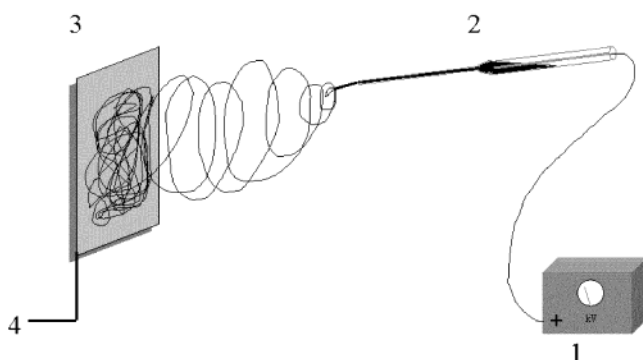


Figure 2. Electrospinning setup (1, power source; 2, polymer spin-dope solutions; 3, collection target; 4, ground).

the obtained solid was washed extensively with ether and acetone and dried in a vacuum oven for 24 h at 25 °C.

Electrospinning was used as a novel and facile method to fabricate optical chemical sensors. Figure 2 shows the electrospinning apparatus used. The spin-dope solution, which consisted of a 18.6 wt % solution of PAA-PM and 36.5% of cross-linkable polyurethane latex (Solucote 1068, Soluol Chemical Company), was dissolved in DMF. A live electrode wire (approximately 0.8 mm) from the DC power source (Gamma High Voltage Research, Inc. model HV ES30P/100) was inserted into the glass pipet which contained the spin dope. The interior diameter of the glass pipet capillary tip ranged from 1.2 to 1.5 mm. The applied electrospinning voltages ranged from 15 to 20 kV. The charged polymer solution overcame the surface tension of the liquid and a stream of polymer jets was produced. The solvent evaporated and very fine fibers were collected on a glass slide. The working distance between the tip of the pipet and the glass slide was typically 15 to 20 cm. The collection time was about 30 to 45 s. The electrospun membranes were dried in a vacuum oven at 70 °C for 24 h. The polyurethane contains a melamine cross-linker that requires a cure time of 60–90 s at 255 °C. The fluorescent polymer was immobilized with the cross-linked polyurethane to form an interpenetrating network structure and a water insoluble sensing membrane.

The electrospun membranes were uniform and exhibited good adhesion and structural stability. The scanning electron microscope (SEM) images of an electrospun membrane of the cross-linked PAA-PM and polyurethane at various magnifications are shown in Figure 3. It is observed that the membrane has a 3-D structure with a random fiber

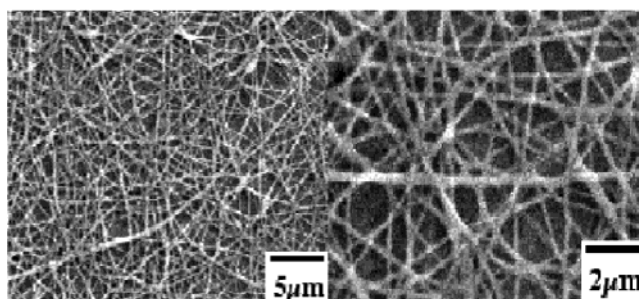


Figure 3. SEM images of electrospun membranes (left, 2000 $\times$; right, 5000 $\times$).

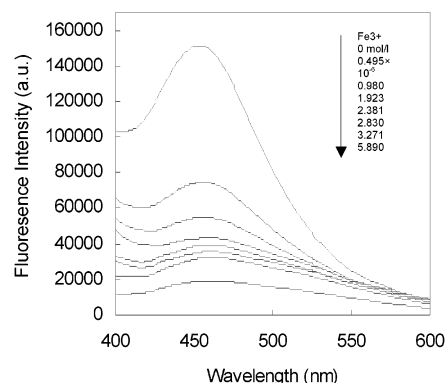


Figure 4. Fluorescence emission spectra of electrospun membranes with varying Fe^{3+} concentrations.

orientation that is evenly distributed on the substrate. The diameters of the fibers were approximately 100 to 400 nm. This type of porous structure of the electrospun membrane provides a surface area-to-volume ratio roughly 1 to 2 orders of magnitude higher than that known for continuous thin films. Further increase of the surface area-to-volume ratio may be achieved by changing the conditions of the electrospinning process such as solvent, concentration, and working distance, which results in either smaller diameter fibers or increased porosity at the fiber surface.¹⁰

Electron-deficient metal cations such as Fe^{3+} or Hg^{2+} and nitro aromatic compounds such as DNT and TNT can serve as quenchers for a fluorophore. In our earlier investigation of a polymer containing a pyrene side group in solution to detect several metal ions such as Ba^{2+} , Ca^{2+} , Fe^{3+} , K^{+} , Zn^{2+} , Hg^{2+} , Cd^{2+} , and Pb^{2+} and an organic nitro compound DNT, it was found that only additions of Fe^{3+} , Hg^{2+} , Pb^{2+} , and DNT had significant effects on the fluorescence intensity and showed efficient quenching.⁹

In this study, similar experiments with electrospun membranes of PAA-PM were carried out. Figure 4 shows a change in fluorescence spectra as a function of different concentrations of ferric ion. It was found that the fluorescence intensities decreased with increasing Fe^{3+} concentration. This fluorescence intensity decrease is expected and believed to be due to the quenching of the PM indicator by Fe^{3+} ions. Similar behavior was observed with Hg^{2+} and DNT. The sensing mechanism of this polymer system has been previously investigated by our group⁹ and is now applied to the electrospun membrane. Here the quenching of fluorescence is due to the interactions of electron-rich PM indicator⁽⁻⁾ and

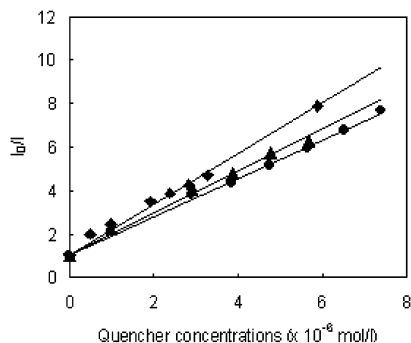


Figure 5. Stern–Volmer plots of electrospun membranes as a function of different quencher concentrations (◆, Fe^{3+} ; ●, Hg^{2+} ; ▲, DNT).

electron deficient quencher⁽⁺⁾, and the degree of quenching depends on the amount of analyte. In a homogeneous medium, such as in solution, the quantitative measure of fluorescence quenching is described by the Stern–Volmer constant, K_{sv} , in eq 4.^{11,12}

$$I_0/I = 1 + K_{sv}[Q] \quad (1)$$

In eq 1, I_0 and I are the intensities of fluorescence in the absence and in the presence of the quencher, respectively. The equation reveals that I_0/I increases in direct proportion to the concentration of the quencher. When all other variables are held constant, the higher the K_{sv} , the lower the concentration of quencher required to quench the fluorescence. In a heterogeneous medium, such as in polymer films, a negative deviation from the linear Stern–Volmer equation occurs at high quencher concentration.^{13,14}

The constant K_{sv} defines the efficiency of quenching and is given by

$$K_{sv} = k_2\tau_1 \quad (2)$$

where τ_1 is the luminescence decay time of the fluorophore in the absence of the quencher ($= 1/k_1$), and k_2 is the bimolecular quenching rate constant. K_{sv} implies two important practical consequences. First, the sensitivity of the quenching process is enhanced by employing fluorophores with long luminescence decay times (τ_1). Second, the sensitivity of the process can be tailored by controlling the quencher diffusion rate to fluorophores via the microstructural properties of the sensing film.

The data obtained by performing a Stern–Volmer analysis in each electrospun sensor are shown in Figure 5. For quencher concentrations in the range of 10^{-6} to 10^{-7} mol/L, linear plots between concentration of quencher and I_0/I are obtained showing a Stern–Volmer relationship. Stern–Volmer constants (K_{sv}) of the electrospun films, calculated from slopes of the plots were found to be 1.1×10^6 (M^{-1}), 8.9×10^5 (M^{-1}) and 9.8×10^5 (M^{-1}) for Fe^{3+} , Hg^{2+} , and DNT, respectively. These values are roughly 2 to 3 orders

of magnitude greater than that obtained previously from the thin film sensors.⁹ The sensitivities of these sensors are in the range of a few to tens parts per billion. The significant enhancement of the sensitivities of the sensors is attributed to the higher surface area of the electrospun membranes.

We have successfully developed nanofibrous thin film optical sensors for metal ion (Fe^{3+} and Hg^{2+}) and DNT detection using the electrospinning technique. As fluorescence quenching-based optical sensors, electrospun films were efficiently quenched by electron-deficient analytes and fluorescence intensities decreased with increasing concentration of analytes. A Stern–Volmer bimolecular quenching relationship was found to hold and was used to determine analyte concentration. Electrospinning is a very promising, facile, and effective technique for fabricating sensor devices. Compared to continuous thin films, electrospun films can offer enhanced reactivity and sensitivity and exciting new opportunities in optical sensors. Further efforts will focus on exploring new sensing materials including fluorescent conjugated polymers, controlling the structural properties of the electrospun membranes, and optimizing the sensitivities for the detection of a variety of analytes both in liquid and vapor phase.

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