

Optical CO₂ Sensing with Ionic Liquid Doped Electrospun Nanofibers

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Received: 28 July 2010 / Accepted: 5 October 2010 / Published online: 14 October 2010
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Abstract The first use of electrospun nanofibrous materials as highly responsive fluorescence quenching-based optical CO₂ sensors is reported. Poly(methyl methacrylate) and ethyl cellulose were used as polymeric materials. Sensing slides were fabricated by electrospinning technique. A fiber-optic bundle was used for the gas detection. CO₂ sensors based on the change in the fluorescence signal intensity of ion pair form of 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS). The sensor slides showed high sensitivities due to the high surface area-to-volume ratio of the nanofibrous membrane structures. The preliminary results of Stern-Volmer analysis show that the sensitivities of electrospun nanofibrous membranes to detect CO₂ are 24 to 120 fold higher than those of the thin film based sensors. The response times of the sensing reagents were short and

the signal changes were fully reversible. The stability of ion pair form of HPTS in the employed matrix materials was excellent and when stored in the ambient air of the laboratory there was no significant drift in signal intensity after 7 months. Our stability tests are still in progress.

Keywords Electrospinning · Electrospun nano fiber · Optical CO₂ sensor · Nano-scale CO₂ sensor

Introduction

The continuous and accurate monitoring of CO₂ levels is of vital importance in environmental monitoring, seawater analysis, medicine and biological processes.

Over the past two decades, the optical CO₂ sensors based on the absorbance or fluorescence changes of pH indicators have been developed [1–10]. Usually they contain a chemically active sensing agent, mostly a pH indicator, at the tip of a fiber or in thin film form which changes the absorbance or fluorescence intensity in response to CO₂. Some of these sensor designs have resulted in commercialization of the products [11–14].

In most of these designs optical chemical sensing of CO₂ is mainly performed with polymer-immobilized pH probes that display analyte dependent optical properties such as absorbance, fluorescence or reflectance. The researchers used a number of polymers and polymer additives to make more sensitive products. The hydrophobic polymers; ethyl cellulose [6, 8, 15–18], silicone [19], poly(1-trimethylsilyl-1-propyne) [20] and sol-gels [21–23] have been employed as matrix materials with or without additives. Oter et al. employed the imidazolium based Room Temperature Ionic Liquid (RTIL) as task specific polymer additive in ethyl cellulose to enhance the solubility of CO₂ as well as the

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stability of the indicator [8]. Wolbeis and co-workers used the ionic liquids together with silicone [20]. In most of these approaches the sensing agent was at the tip of an optical fiber or in thin film form in a flow cell.

On the other hand, in optical chemical sensors, the sensitivity scales inversely with dimensions. Miniaturization attempts and nanotechnology applications allowed improvements in functionality sensitivity, and response time of the sensors. Consequently, nano-scale structures should be combined with optical chemical sensing approaches.

Here we have successfully combined nano-scale electrospun fiber materials with optical sensing technology for CO₂ detection. Electrospinning, the most convenient way to make a nano-scale continuous polymer, uses a high static voltage to draw the fiber from a liquid polymer. As a jet of charged fluid polymer sprays out the bottom of a needle, an electric field forces the stream to spin, stretching the fiber lengthwise so its diameter becomes as little as 10 nanometers. The fiber forms a thin membrane as it hits the electrically conductive substrate below the needle. These electrospun membranes have a unique combination of stretchiness and strength, and are easy to handle, making them suitable for a wide variety of applications. Electrospun nano-fibrous membranes can have approximately 1–2 orders of magnitude more surface area than that found in continuous thin films [24, 25]. It is expected that this large amount of functional surface area has the potential to provide unusually high sensitivity and fast response time in sensing applications.

In this paper matrix materials of poly(methyl methacrylate) and ethyl cellulose were used together with ionic liquids. Optical nano-fibrous membrane chemical sensors were fabricated by electrospinning technique. The ion pair form of HPTS was chosen as the fluorescent indicator because it has large Stokes shift, high quantum yield, strong absorbance, excellent photostability and lifetime. Additionally, similar fluorescence sensing investigation of this material was previously carried out on thin films [6, 8, 20]. The electrospun nano-fibers were characterized using scanning electron microscopy (SEM) and their average diameter was evaluated.

Experimental

The pH and CO₂ sensitive fluorescent dye, 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt was from Fluka and used in the ion pair form. The ion pair was prepared by the reagent tetraoctyl ammonium bromide (TOABr) which was obtained from Sigma. The polymers ethyl cellulose (EC) and poly(methyl methacrylate) (PMMA) were from Acros and Aldrich, respectively. Tetraoctyl ammonium hydroxide

(TOAOH) was from Fluka; in the form of 20% solution in methanol. The plasticizer, dioctyl phthalate (DOP) was from Aldrich. The ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) was supplied from Fluka. Cylinders of carbon dioxide and nitrogen gas of 99.99% purity were obtained from Linde Gas, Izmir, Turkey. All solvents and chemicals were of analytical grade and purchased from Merck, Fluka, and Riedel. The schematic structures of the employed ion pair and the ionic liquid were shown in Fig. 1.

Apparatus

The homogeneous PMMA or EC solutions were placed in a 1 ml plastic syringe fitted with a metallic needle of 0.4 mm of inner diameter. The syringe is fixed vertically on the syringe pump (Top Syringe Pump Top-5300) and the electrode of the high voltage power supply (Gamma High Voltage ES30) was clamped to the metal needle tip (See Fig. 2). Steady state fluorescence emission and excitation spectra were measured using Varian Cary Eclipse Spectrofluorometer with a xenon flash lamp as the light source. For instrumental control, data acquisition and processing the software package of the spectrofluorometer was used.

Preparation of Electrospun Nano Fibers

Electrospinning was used as a novel fast and simple method to fabricate optical chemical sensing agents. The electrospinning conditions were optimized in order to form nodal-free PMMA or EC based continuous nano-fibers by varying the concentrations of, plasticizer, PMMA or EC and RTILs in the solutions. The concentration of RTIL was varied from 5% up to 50% w/w, with respect to the PMMA or EC matrices. We find that the presence of the RTILs in the PMMA solutions facilitates the electrospinning of nodal-free nano-fibers from the lower polymer concentrations and this behavior is attributed to the high conductivity and proper viscosity of the RTIL doped precursor polymer solutions.

The resulting composites were prepared by mixing 240 mg of polymer (PMMA or EC), 192 mg of plasticizer (DOP), 48 mg of RTIL, 6 mg of dye and 200 μL of

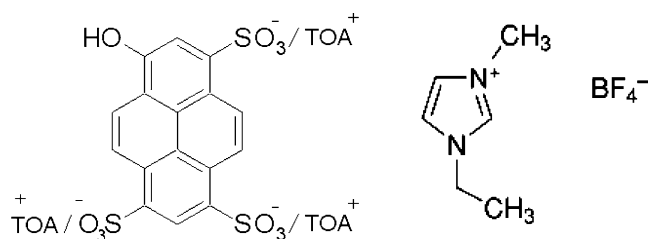


Fig. 1 The schematic structures of the employed ion pair and the ionic liquid

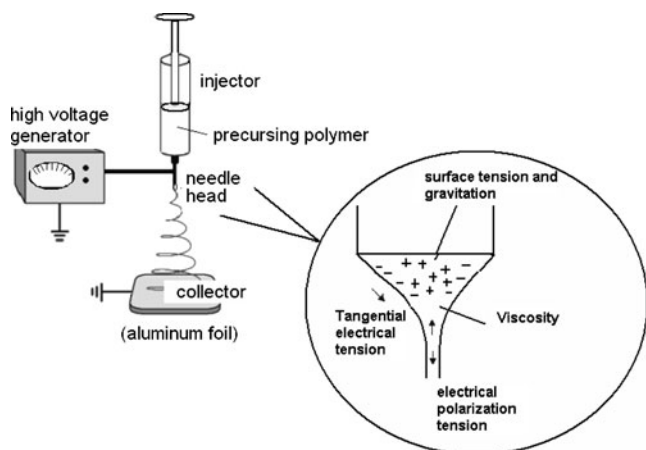


Fig. 2 Schematic structure of the electrospinning apparatus

TOAOH in Toluene:DMF (80:20) or DCM: EtOH (25:75) solvent systems.

The polymer solution was taken in a hypodermic syringe and an electric potential of 20 kV was applied between the needle of the syringe and a substrate in the form of an aluminum foil. The distance between the needle and the electrode was 10 cm while the diameter of the needle was 0.40 mm. The solution flow rate was maintained at 0.5 mL/h using a syringe pump. The charged polymer solution overcame the surface tension of the liquid and a stream of polymer jet was produced. The solvent evaporated and very fine fibers were completely coated on the clean aluminum foil. The surface morphology of the nano-fibers was studied using

SEM instrument (6060-JEOL JSM). The nano-fibers on aluminum substrate were cut into proper size, fixed in the flow cell and the excitation or emission spectra were recorded.

Thin Film Preparation Procedures

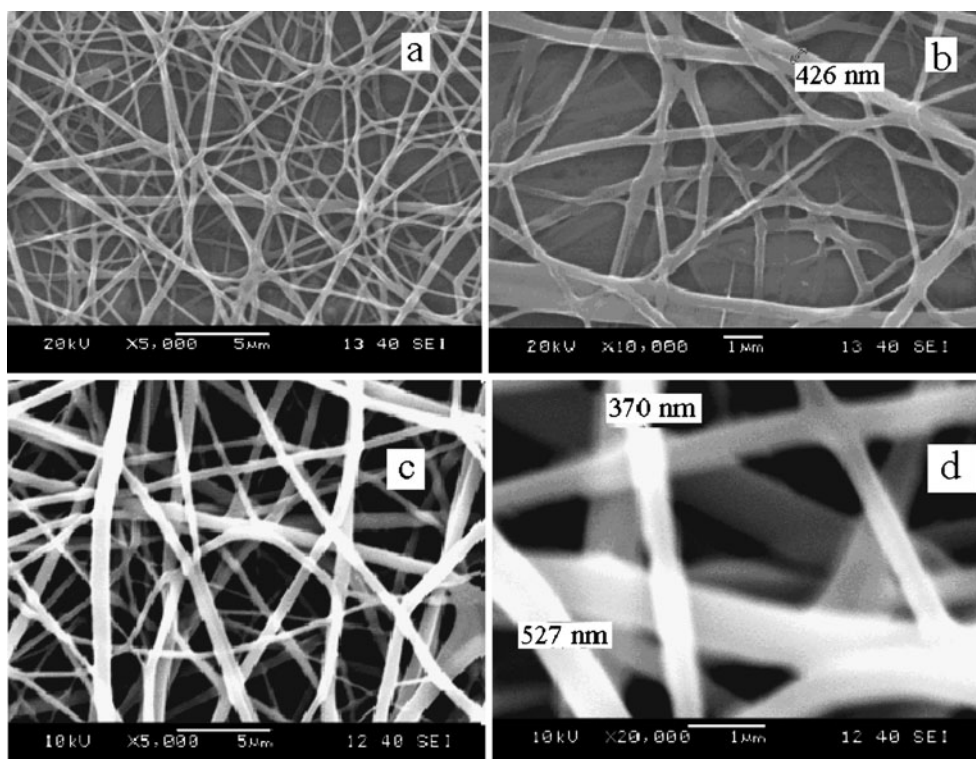
The thin films were prepared by mixing of 240 mg of polymer (PMMA or EC), 192 mg of plasticizer (DOP), 48 mg of IL, 6 mg of dye and 200 μ L of TOAOH in Toluene:DMF (80:20) or DCM: EtOH (25:75) solvent systems. Prior to the experiments, the employed cocktails were completely converted to the basic form. The resulting mixtures were spread onto a 125 μ m polyester support (Mylar TM type) with a spreading device. Thickness of the films was measured using Tencor Alpha Step 500 Profilometer and found to be 5.11 μ m. This result was an average of eight measurements and exhibited a Standard deviation of ± 0.081 .

Each sensing film was cut to 1.2 cm diameter, fixed in the flow cell, and the excitation or emission spectra were recorded.

Synthesis of Ion Pair

The ion pair between anionic form of the HPTS and the tetraoctylammonium counterion (TOA^+) has the composition (HPTS)/(TOA)₃ (Fig. 1) and was prepared according to the following literature method [26]: 200 mg of the trisodium salt of HPTS and the equivalent amount of TOABr

Fig. 3 SEM images of electrospun membranes a and b; PMMA based, c and d; EC based nanofibers ($\times 5000$, $\times 10000$ and $\times 20000$)



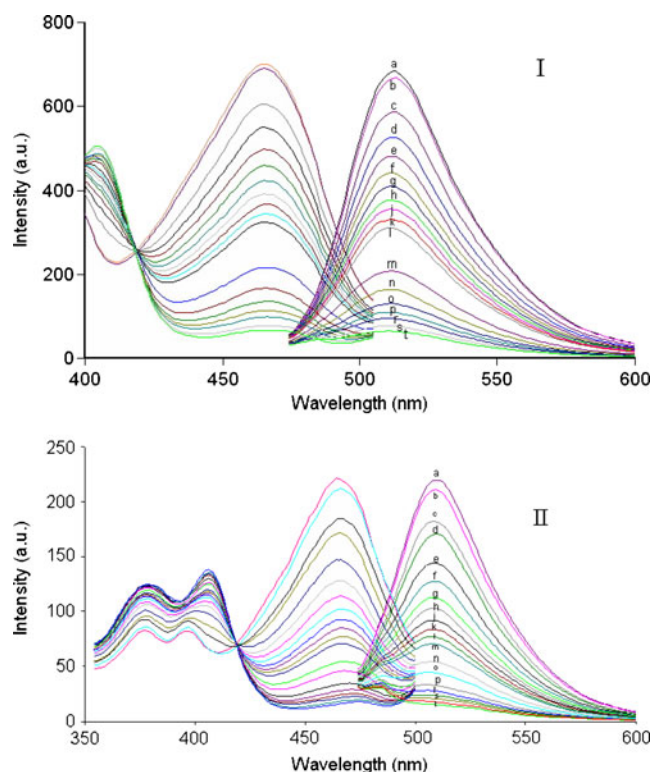


Fig. 4 Excitation and emission spectra of electrospun fibers I: ion pair form of HPTS in EC, II: in PMMA after exposure to certain concentrations of CO₂ ($\lambda_{\max}^{\text{ex}}$ 465 nm, $\lambda_{\max}^{\text{em}}$ 513 nm), a: initial, b: 1% CO₂, c: 2% d: 3%, e: 4%, f: 5%, g: 6%, h: 7%, i: 8%, j:8% k: 9% l: 10% m:20% n: 30% o:40% p: 50% r:60% s:80% t:100% CO₂

(628 mg) were dissolved in 30 mL of water containing 1% sodium carbonate and 30 mL of CH₂Cl₂, respectively, and were mixed in a separatory funnel. After a few minutes the ion pair was completely extracted from the aqueous phase into the organic phase. The organic phase was washed three times with 0.05 M NaOH and separated. After the evaporation of organic solvent under vacuum, the ion pair was obtained. The ion pair is less subject to leaching from the polymer matrix than the HPTS sodium salt owing to its greater affinity to the EC or PMMA matrices.

Carbon Dioxide-Sensing Studies

Gaseous CO₂ and N₂ were mixed in the concentration range 0–100% in a gas diluter (Sonimix 7000A gas blending system). The output flow rate of the gas mixture

was maintained at 250 mLmin⁻¹. Gas mixtures were introduced into the sensor agent-containing flow cell via a diffuser needle under ambient conditions either directly or after humidification of the gas. The humidification of the gaseous was accomplished by bubbling the gas stream through thermostated wash bottles filled with water at 25°C at constant relative humidity level of 100%.

Results and Discussion

RTILs as Polymer Electrolytes

In the electrospinning process, the polymer solution is changed by its surface tension at the end of the needle. When a sufficiently large electric voltage is applied, the solution at the tip of the needle becomes stretched to form a cone because of coupled effects of the electrostatic repulsion within the charged droplet and attraction to a grounded electrode of opposite polarity. As the strength of the electric field is increased, the charge overcomes the surface tension, and at a critical point, fine jet is ejected from the apex of the cone. In order to perform this process, the polymer solution should have a certain electrical conductivity. On the other hand, to achieve true electrical conductivity in polymers one must add compatible electrically conductive additives into the polymer. In this report, we have demonstrated that it is possible to electrospin the EC and PMMA composite fibers in presence of non-volatile room temperature ionic liquid; EMIMBF₄. The employed RTIL was chosen as polymer electrolyte due to its high ionic conductivity, high thermal and chemical stability, non-volatile, non-flammable and low toxicity characteristics [27].

Apart from ionic conductivity, the IL also enhances photostability of the HPTS in the polymer matrix acting as a sink for acidogenic species from the ambient air of the laboratory [7, 8, 23].

The electrospun membranes exhibited good adhesion to the aluminum substrate. The scanning electron microscope (SEM) images of electrospun membranes of the EC and PMMA at various magnifications are shown in Fig. 3. It is observed that the membrane has a 3-D structure with a random fiber orientation that is evenly distributed on the substrate. The diameters of the fibers were between 370 to 527 nm. In addition to these, it can be seen the same figures

Table 1 The fluorescence spectra related characteristics of electrospun PMMA and EC nanofibers and thin films

| Indicator dye | Matrix /form | $\lambda_{\max}^{\text{em}}$ (nm) | $\lambda_{\max}^{\text{ex}}$ (nm) | Stoke's shift (nm) |
|---------------|------------------|-----------------------------------|-----------------------------------|--------------------|
| HPTS/TOAOH | EC /electrospun | 513 | 465 | 48 |
| HPTS/TOAOH | PMMA/electrospun | 510 | 466 | 44 |
| HPTS/TOAOH | EC / thin film | 513 | 466 | 47 |
| HPTS/TOAOH | PMMA/ thin film | 510 | 466 | 44 |

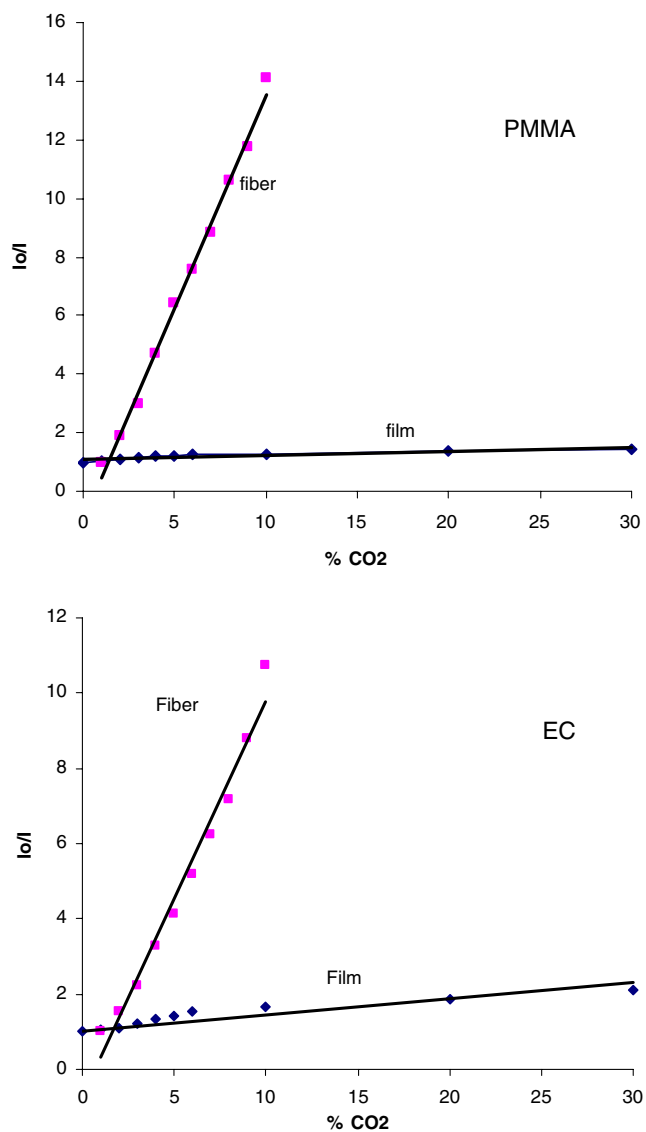


Fig. 5 Gathered Stern Volmer plots of the electrospun nano-fibers and continuous thin films

that the diameters of some nanofibers were smaller than these values. For instance, some nanofibers possess approximately 400 nm.

This type of nano-structure of the electrospun membrane provides higher surface area-to-volume ratio 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 composition, viscosity, concentration, temperature, humidity and working distance, which results in either smaller diameter fibers or increased porosity at the fiber surface [28].

Sensing Mechanism for CO₂

In our earlier investigations, ratiometric response of ion pair form of 1-hydroxy-3,6,8-pyrenetrisulfonate (HPTS) to

gaseous CO₂ was evaluated in ionic liquid doped ethyl cellulose based continuous thin films [8]. It was found that exposure to carbon dioxide caused reversible and high relative signal changes in fluorescence intensity of HPTS. The employed additive; EMIMBF₄ provided enhanced stability, repeatability; wide linear dynamic working range (between 0 and 100% CO₂) and better spectral characteristics allowing ratiometric measurements with more precise data.

In this study, similar experiments with electrospun membranes of PMMA and EC were carried out. Figure 4I and II shows the change in fluorescence spectra of electrospun materials as a function of different concentrations of carbon dioxide.

Most of the CO₂ sensing films contain the ion pair form of HPTS and the quaternary ammonium base (TOAOH) in a polymer matrix. TOA⁺OH⁻ is usually added as a counter ion stabilizing the anionic (deprotonated) form of the HPTS in the lipophilic matrix. In such designs, the sensing scheme is based on two processes, the first being the diffusion of CO₂ through the membrane into the sensing region, the second being the reaction of the wet gas with anionic and highly fluorescent HPTS phenolate anion [6, 8, 20, 36]. The gaseous carbon dioxide dissolves in the trace amounts of water present in the matrix forming carbonic acid, which interacts with the deprotonated form of the indicator. In these sensors the indicator is functional owing to the water content of the ion pair. In our case two different mechanisms are being effective for carbonic acid formation; the well known water content of the ion pair and the trace amount of water encapsulated in the ionic liquid. Therefore, effective hydration of CO₂ and subsequent protolysis decreases the fluorescence intensity of HPTS at 513 nm (See Fig. 4I and II) and converts highly fluorescent HPTS anion (Dye⁻) into the less fluorescent HPTS (Dye) form. The water content of the 1-butyl-3-methylimidazolium tetrafluoroborate has been reported to be 690 ppm after drying of the liquid for 15 h at 343 K [29]. During experimental studies the water content of the EMIMBF₄ was not altered.

Additionally, the [BF₄]⁻ ion of the RTIL also catalyzes bicarbonate formation according to the following mechanism. [EMIM]OH moieties are produced by anion exchange with the present TOAOH in the sensing composition. The ([EMIM]OH) acts as a buffer-like system by neutralization with the hydrated CO₂ or carbonic acid (H₂CO₃). The resulting product is [EMIM]HCO₃. Formation of such a buffer-like system tunes the sensitivity of the sensor and enhances the long-term stability of the indicator since it slowly acts as a sink for acidic species [8]. Therefore the well known hyperbolic response [3, 4, 36] of the (HPTS)/(TOA)₃ in ethyl cellulose matrix becomes more linear. Another acceptable reason for choosing this material is the remarkable solubility of CO₂ in water-miscible ionic liquids, which is approximately 10–20 times that in conventional solvents, polymer matrices, or water [30–32].

Table 2 The Stern Volmer plot related calibration characteristics of PMMA and EC based electrospun nanofibers and thin films

| Indicator dye | Matrix /form | Conc. range (CO ₂ %) | Linear regression equation | Regression coefficient (R ²) |
|---------------|----------------------------|---------------------------------|----------------------------|------------------------------------------|
| HPTS/TOAOH | EC/ electrospun nanofiber | 1–30 | y=1.0486x+0.7322 | 0.9765 |
| HPTS/TOAOH | PMMA/electrospun nanofiber | 1–30 | y=1.4491x+0.9785 | 0.9939 |
| HPTS/TOAOH | EC / thin film | 1–30 | y=0.0437x+1 | 0.8123 |
| HPTS/TOAOH | PMMA/ thin film | 1–30 | y=0.0121x+1.1007 | 0.8011 |

Emission Based Response of EC and PMMA Nanofibers

The fluorescence spectra related characteristics of the electrospun nanofibers and thin films were shown in Table 1.

The EC and PMMA doped HPTS exhibited similar spectral response for CO₂ in thin film form. The acquired spectral data from electrospun membranes were typical and were very similar with spectral characteristics of both the solution phase and thin film form (See Figs. 4 and 5). Since the aluminum foil was completely covered with electrospun nano fibers there were no observable scattering effects in the emission spectra.

In a homogeneous medium, such as in solution, the quantitative measure of fluorescence quenching is described by the Stern-Volmer constant, K_{SV} ,

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

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 directly proportional to the concentration of the quencher. When all other variables are kept 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 [33, 34]

The data obtained by gathering Stern-Volmer analysis for each electrospun and continuous thin film are shown in Fig. 5. For quencher concentrations in the range of 1 to 30%, linear plots between concentration of quencher and I_0/I are obtained showing an excellent Stern-Volmer relationship.

Stern- Volmer constants (K_{SV}) of the electrospun films, calculated from slopes of the plots were found to be 1.4491 (%⁻¹) and 1.0486 (%⁻¹) for PMMA and EC based nanofibers respectively.

These values are 120 and 24 fold greater than that obtained from the continuous thin film sensor slides of PMMA and EC, respectively (See Table 2). K_{SV} values reveal important practical consequences. The sensitivity of the quenching process is enhanced by controlling the quencher diffusion rate to fluorophores via the nano-structural properties of the sensing films.

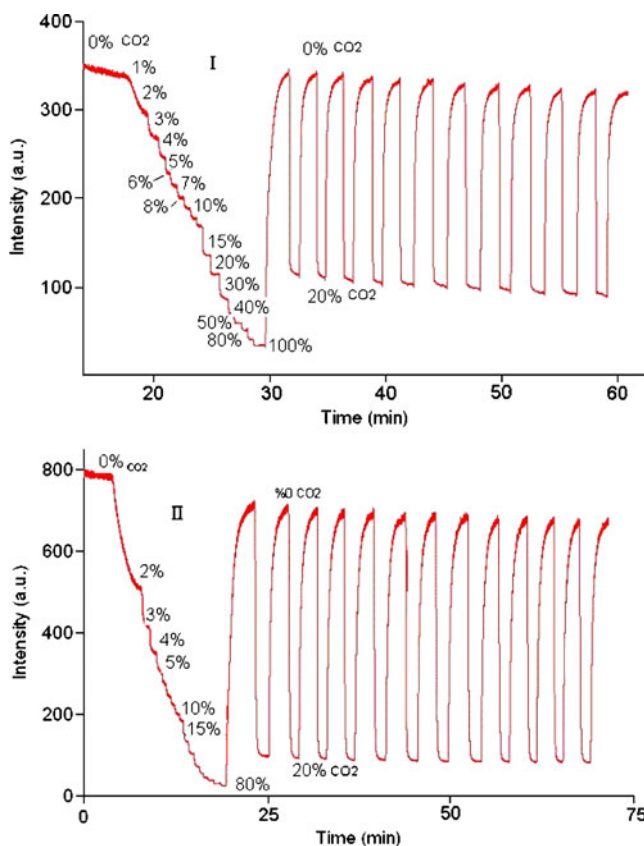
In most of the previous designs, the response of the sensors was hyperbolic, with greater sensitivity at low

carbon dioxide concentrations, which is typical of this type of pCO₂ sensors [35, 36].

In this work, the ordinary least-squares OLS regression model was employed for a linear fit of the calibration curves. The response of the sensors was linear, with greater sensitivity at low carbon dioxide concentrations. The linear regression results for both membranes yielded a linear response with coefficients of regression (R²) of 0.9939 and 0.9765 for PMMA and EC, respectively.

Response, Recovery and Stability Studies

The tested sensor compositions exhibited large relative signal changes and good sensitivity to gas-phase carbon dioxide. The response and recovery-related data of the

**Fig. 6** Emission based kinetic response of ion pair form of HPTS in I: EC, II: PMMA to gaseous CO₂

sensing cocktails with EC and PMMA based nano-fibers were acquired by recording the emission intensity signals during exposure to 0.0–10% CO₂ and 0–60% CO₂, respectively (See Fig. 6). At each time the reagent phase was regenerated with pure gaseous nitrogen (99.99%).

The sensor compositions resulted in quite high relative signal changes of approximately 90% and 95% in the direction of a decrease in emission intensity at $\lambda^{\text{em}}_{\text{max}} = 513$ nm. The τ_{90} response times (the time to achieve 90% of the overall signal change) in-EC and PMMA were in the range 15–20 s on exposure to 0.0–10% CO₂. The initial signal intensities for both compositions could be completely recovered after switching in the concentration range 0.0–10% CO₂. A slight drift was observed after the 2nd cycle. Between the 1st and 10th cycles the level of reproducibility of upper signal levels were 358 ± 4.03 and 734 ± 3.04 ($n=10$) for EC and PMMA respectively. The regeneration time was approximately 2 min. The response and recovery time, varying between one and 5 min, includes the equilibration time for the protonation-deprotonation reaction and the dead volume of the gas tubes, rather than the true response time of the sensor slides.

The stability of ion pair form of HPTS in the employed matrix materials was excellent and when stored in the ambient air of the laboratory there was no significant drift in signal intensity after 7 months. Our stability tests are still in progress.

Conclusion

Electrospinning looks like a promising, simple, and an effective method for fabricating optical chemical sensor devices. This article demonstrates how the sensitivity of micrometer-scale thin film coating on a planar surface can be manipulated by nanometer-scale features on the latter.

Electrospun films provide high porosity; large surface area and consequently high gas permeability when compared to continuous thin films. With respect to continuous thin films, electrospun films can offer enhanced sensitivity and reactivity in optical chemical sensing. Further efforts will focus on exploring new sensing materials and polymer compositions, controlling the nano-scale size of the electrospun membranes, and optimizing the sensitivities for the detection of a variety of analytes.

Acknowledgment Financial support from the Tubitak Münir Birsal Vakfi is acknowledged. Funding this research was provided by Scientific Research Funds of Dokuz Eylül University (projects; 2005 KB Fen 18 and 2007 KB Fen 24) and the Scientific and Technological Research Council of Turkey (TUBITAK).

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