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Tuning oxygen sensitivity of ruthenium complex exploiting silver nanoparticles

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ABSTRACT

In this study, we utilized silver nanoparticles (Ag NPs) along with ionic liquids as additives for fabrication of polymeric oxygen sensitive fibers. Plasticized polymethyl methacrylate and ethyl cellulose (EC) were used as matrix materials. Fibers and porous films were produced by electrospinning technique. Oxygen induced spectral response of the fluorescent tris(2,2′-bipyridyl) ruthenium(II) chloride ($Ru(bipy)_3^{2+}$) was followed as the analytical signal. Utilization of silver nanoparticles in electrospun polymeric fibers for oxygen sensing purposes resulted with many advantages such as tuned sensitivity, linear calibration plot for larger concentration ranges, increased surface area and enhancement in all sensor dynamics. Linearity of the calibration plot for the offered composition was superior with respect to the previously reported ones. When stored at the ambient air of the laboratory there was no significant drift in intensity after 12 months. Our sensitivity and stability tests are still in progress.

1. Introduction

Accurate measurements of oxygen levels are of great importance in environmental and biomedical analysis as well as industrial processes [1]. Today electrochemical and optical sensing strategies have intensively been used for detection of gaseous or dissolved oxygen. The optical chemical sensing approach offers some advantages over electrochemical strategy like shorter response time, easy fabrication, low cost and suitable sensitivity. Most of the optical oxygen sensors work on the principle of luminescence quenching of different types of organic dyes in oxygen permeable solid matrices. These organic dyes are pyrene and its derivatives [2], pyrenebutyricacid, quinoline and phenanthrene [3], transition metal complexes of osmium [4], rhenium [5,6], platinum [7,8], palladium and iridium [9,10], ruthenium [11–17], polypyridine complexes and metalloporphyrins [18]. Covalently assembled monolayer of 61-(*p*-hydroxyphenylmethano) fullerene molecules has also been used for oxygen sensing [19]. Among these dyes, the ruthenium(II) polypyridine complexes have been the most intensively utilized dye. They produce metal-to-ligand charge transfer excited states which are readily quenched by oxygen. Rochea et al. reported enhanced luminescence for the ruthenium dye in trimethoxysilane (TEOS) xerogel spin-coated on a gold surface. However, the offered design was highly sensitive only in low O_2 environment [11]. Wu and coworkers investigated the oxygen sensing properties of Ru(II) complexes on mesoporous structures. Approximately 90% of the luminescence of the sensor was quenched upon exposure to 10% of oxygen [14]. In another work, functionalized $[Ru(Phen)_3]^{2+}$ based dyes in mesoporous silica matrix were tested for oxygen sensing purposes. The calibration plots were nonlinear within the measured oxygen concentrations [15]. Not only the ruthenium based dyes but also other transition metal complexes and porphyrin derivatives developed to date exhibit nonlinear calibration data or Stern–Volmer plots especially for the large working ranges [3–18,20–25]. This is due to the uncontrollable high sensitivity of the exploited dyes towards oxygen. It is obvious that, modeling the calibration related data with linear, quadratic, exponential, and other functions is possible. However, extrapolation or interpolation of quadratic data requires much more computation power with respect to the linear ones. Such kind of calibration plots and the Stern Volmer plots require some algorithms for linearization.

On the other hand, recently, fabrication of mesoporous, micro and nano-scale matrix materials and their usage for gas sensing purposes have been studied [2,6,7,9,13–17,20–25]. Their porous

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structure with enhanced surface area, the feasibility of modification and reliable entrapment of fluorescent dyes within the cavities make them useful as solid matrix materials for the design of optical chemical sensors [25]. Besides, the development of micro and nanomaterials will support the design of new sensors, which represent enhanced analytical characteristics such as small size, robustness, low limit of detection values and enhanced relative signal change. To date, we see that previous work about the sensing of gaseous oxygen with nano or micro-materials are mainly based on the sol gel silica formation or precipitation and micro-emulsion methods for polymers. The ruthenium complexes were intensively used in silicone [3], sol–gel [26–30], ORMOSILs (organically modified silicates) or in modified ORMOSILs [12,31,32]. A detailed comparison of the performances of such optical oxygen sensors in terms of matrix materials, sensitivity, working range and detection limit has been reported earlier [25]. In the light of the literature information, fabrication of new, transparent, meso or micro-porous materials and nano-scale matrices can be concluded as a promising area in optical chemical sensing of oxygen.

On the other hand it is known that presence of the conducting metallic surfaces like gold and silver is effective on emissive spectral properties of nearby fluorophores. Gryczynski et al. investigated effects of metallic silver particles on the emission properties of $[Ru(bpy)_3]^{2+}$ on silver island films [33]. In another recent work influence of metal nanoparticles on fluorescence properties of Ru dye was investigated in solution phase. The samples containing different sizes of silver and gold nanoparticles were titrated with varying concentration of the fluorescent dyes of tris (2,2-bipyridyl) dicholoro ruthenium and other fluorophores [34].

These studies encouraged us to investigate effect of silver nanoparticles on oxygen sensing properties of the Ru complex. In this study, we have successfully fabricated nano-silver doped fiber materials and nano-porous film structures of polymers via electrospinning method for sensitive chemical optical detection of O_2(g). By this way, we succeeded to tune the uncontrollable intensive response of the ruthenium dye observed even in low concentrations of oxygen and enlarged the linear working range. As far as we know, this is the first study with silver doped-electrospun fibers and meso-porous polymers on oxygen sensing. Effects of presence of silver nanoparticles on oxygen sensing were tested and evaluated by steady state and lifetime based measurements in terms of sensitivity, stability and calibration characteristics.

2. Experimental

2.1. Materials

All solvents were of analytical grade and purchased from Merck, Fluka, Sigma and Riedel. The O_2 sensitive fluorescent dye, tris(2,2-bipyridyl)ruthenium(II) chloride and plasticizer, dioctyl phthalate (DOP) were supplied from Aldrich. Ethyl cellulose (EC, ethoxy content of 48%) and polymethyl methacrylate (PMMA) were purchased from Organics. The room temperature ionic liquid (RTIL) and 1-butyl-3-methylimidazolium tetrafluoroborate was from Fluka. Silver nitrate ($>$99% $AgNO_3$) and sodium borohydride (99% $NaBH_4$) were purchased from Merck and Aldrich Chemical Companies, respectively. Ultra pure water was used in preparation of silver nanoparticles. Glassware was cleaned by soaking in alcoholic KOH. Oxygen and nitrogen gas cylinders were of 99.9% purity and obtained from Gunes Company, Izmir, Turkey.

2.2. Instrumentation

The steady state florescence measurements of the sensor films and fibers were recorded by using Varian Cary Eclipse spectrofluorometer. Fluorescence lifetimes were measured by time resolved fluorescence spectrometer of Edinburg Instruments of FLS920 which works on the principle of time correlated single photon counting (TCSPC) method. The samples were excited with a pico-second pulsed diode laser at the wavelength of 468 nm, at a frequency of 10 MHz. The excitation and emission slits were set to 5 nm. During measurements, the Instrument Response Function (IRF) was obtained from a non-fluorescing suspension of a colloidal silica (LUDOX 30%, Sigma Aldrich) in water, held in 10 mm path length quartz cell and was considered to be wavelength independent. The lifetime parameters were recovered by reiterative convolution (reconvolution) with a weighted, nonlinear least-squares method using the measured IRF and emission decay data. The reduced chi-squared values and plots of weighted residuals were used to determine the 'goodness of fit' between the calculated and measured decay curves. In all cases the calculated chi square values (χ^2) were less than 1.2 and the residuals trace symmetrically distributed around the zero axes.

The programmable syringe pump (Top Syringe Pump Top-5300) and the high voltage power supply (Gamma High Voltage ES30) were used for fabrication of electrospun fibers or films. The surface morphology of the fibers and films were studied using scanning electron microscope (SEM) instrument (FEI QUANTA FEG 250). Size distribution analysis of the silver nanoparticles was performed with a Zetasizer instrument in dispersed form in triethanolamine (Malvern Instruments Ltd.) X ray diffraction patterns of the fabricated Ag NPs were determined with XRD instrument from Thermo Scientific. The diffraction patterns were recorded from 30 to 90° at a speed of 2°/min. The XPS analysis of the Ag NPs was performed with Al-$K\alpha$ irradiation of a Thermo-Scientific instrument. The device was calibrated according to gold; $4f_{7/2}$. A 10^{-8} mbar of vacuum was applied and 20 scans from a single point were recorded. Pass energy and energy step size values were reported as 150 eV and 1 eV, respectively.

2.3. Gas sensing studies

The gases, O_2 and N_2were mixed in the concentration range of 0.0–100.0% in a Sonimix 7000 A gas blending system. The out-put flow rate of the gas mixture was maintained at 550 mL min^{-1}. Gas mixtures were introduced on the sensing agents via a diffuser needle under ambient conditions. Real time excitation and emission spectra of sensing materials were recorded upon exposure to certain concentrations of oxygen.

2.4. Preparation of silver nanoparticles

Colloidal silver nanoparticles were synthesized according to the literature method [35] and briefly summarized here. A large excess of sodium borohydride was used to reduce the ionic silver and to keep the silver nanoparticles apart from each other in a coordinated form. A 10 mL volume of 1.0 mM silver nitrate was added dropwise into the 30 mL of 2.0 mM sodium borohydride solution in an ice bath under magnetic stirring. Color of the colloidal solution turned pale yellow after the addition of 2 mL of silver nitrate and following purple and finally gray color when all of the silver nitrate had been added. Later the water content of the sol was evaporated under vacuum and dried silver nanoparticles dispersed in triethanolamine for size distribution analysis.

Zetasizer instrument derived size distribution results of diluted Ag nanoparticles have been shown in Fig. 1.

Here the basic chemical reaction is given in Eq. (1) and shows the reduction of silver by sodium borohydride:

$$AgNO_3 + NaBH_4 \rightarrow Ag + 2H_2 + 1/2B_2H_6 + NaNO_3 \qquad (1)$$