Published in final edited form as:

Anal Chem. 2012 February 7; 84(3): 1402–1407. doi:10.1021/ac2024816.

Hybrid Oxygen-Responsive Reflective Bragg Grating Platforms

Ka Yi Yung^{1,a}, Huina Xu^{2,a}, Ke Liu^{2,a}, Gregory J. Martinez¹, Frank V. Bright^{1,*}, Michael R. Detty¹, and Alexander N. Cartwright²

¹Department of Chemistry, Natural Sciences Complex, University at Buffalo, The State University of New York, Buffalo, NY 14260-3000, USA

²Department of Electrical Engineering, Bonner Hall, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA

Abstract

Oxygen responsive sensor platforms were fabricated by pin printing tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ([Ru(dpp)₃]²⁺) doped sols onto wavelength tuned reflective Bragg gratings. In an epi-luminescence configuration, these Bragg gratings (Gr) were designed to reflect selectively the O₂ responsive [Ru(dpp)₃]²⁺ emission toward the detector to enhance the detected signal magnitude. The xerogel based sensors were formed onto: (i) glass (XGI), (ii) directly on top of the grating (XGrGI), or (iii) on the glass substrate opposite the grating (XGIGr). The results show that all sensors exhibit linear, statistically equivalent O₂ sensitivities and the XGrGI platform yields up to an 8 fold increase in relative detected analytical signal (RDAS) in comparison to the control (XGI) platform.

INTRODUCTION

An ideal chemical sensor should be simple, require little/no power, exhibit high selectivity and sensitivity toward the target analyte, offer low target analyte detection limits, high signal-to-background, high analytical signal and minimum signal drift. In reality, it is extremely rare to realize sensors that fulfill all the aforementioned criteria.

O₂ is an important target analyte in biological¹, environmental² and industrial³ settings. Over the years, many research groups have reported O₂ responsive optical sensors.⁴ Bright and co-workers have described O₂ responsive, xerogel based optical sensors that exhibit linear response profiles and high sensitivity.⁵ To improve overall detectability, these types of sensors have been formed atop frustrated optical cones.⁶ Accuracy and precision have also been improved by creating arrays of xerogel based sensor elements co-doped with two different luminescent reporters in concert with artificial neural network assessment strategies.⁷

Other researchers have been developing reflective Bragg gratings for sensing applications.⁸ For example, Kim et al. reported an O₂ responsive reflective Bragg grating by immobilizing tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ([Ru(dpp)₃]²⁺) directly *within* the grating.^{8f} Unfortunately, this platform exhibited an attenuated, non-linear O₂ response profile.^{8f}

Ohulchanskyy et al. have investigated the chemistry and photophysics of novel tetramethylrosamine dyes that exhibit increased singlet oxygen production upon

* Author to whom all correspondence should be directed (voice: 716-645-4180; chefvb@buffalo.edu).

^aShared first author position

photoexcitation.⁹ These dyes have characteristics that are potentially attractive for Bragg grating development.

In this paper, we report an integrated sensor platform that exploits a wavelength tuned Bragg grating that selectively reflects the analyte dependent, xerogel based sensor luminescence toward the detector. We compare the O₂ sensitivity and relative detected analytical signal (RDAS) from [Ru(dpp)₃]²⁺ doped class II xerogel sensor arrays formed onto (i) glass (XGI), (ii) directly on top of the grating (XGrGI), or (iii) on the glass substrate opposite the grating (XGIGr).

THEORY SECTION

Luminescence Quenching

If luminescent reporter molecules are sequestered within a homogeneous microenvironment and challenged by a quencher (Q), the Q dependent change in luminescence can be described by the Stern-Volmer expression:^{4a, 5, 7, 10}

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

where I_0 and I are the steady-state luminescence intensity in the absence and presence of quencher, respectively, K_{SV} is the Stern-Volmer quenching constant, and $[Q]$ is quencher concentration. In the context of the current research, K_{SV} represents the sensor sensitivity.

Bragg Grating

A Bragg grating can be fabricated by using one-step holographic recording to form an optical interference pattern within a thin photopolymer-containing solution.^{8,11} In this research, a laser beam creates the optical interference pattern by total internal reflection within a thin pre-polymer solution. Where there is constructive interference within the pre-polymer solution, polymerization and crosslinking proceed rapidly. Subsequent UV exposure drives solvent molecules or liquid crystals to migrate and re-arrange toward those regions where destructive interference occurred.^{8a, 8c, d, 8f, 8e} The grating spacing (Λ) is given by:^{8a, 8f, 11}

$$\Lambda = \frac{\lambda_{\text{Bragg}}}{2n_{\text{ave}} \sin \Phi} \quad (2)$$

$$\Phi = \sin^{-1} \left\{ \left(\frac{n_{\text{prism}}}{n_{\text{pre}}} \right) \times \sin \left[\left(\frac{\pi}{4} \right) - \sin^{-1} \left(\frac{1}{n_{\text{prism}}} \sin \frac{\theta \times \pi}{180} \right) \right] \right\} \quad (3)$$

In these expressions λ_{Bragg} is the Bragg reflection wavelength and n_{ave} , n_{prism} , and n_{pre} are the average grating refractive index after fabrication, the coupling prism refractive index, and the pre-polymer solution refractive index, respectively. θ represents the angle between the laser beam and the coupling prism normal.

Predicted Improvements in Detected Analytical Signal

Le Moal et al.¹² have developed a dipole approximation based model to simulate the behavior of a submonolayer of luminescent reporter molecules adsorbed onto a dielectric layer with thicknesses ranging from 1 nm to several hundred nanometers atop a semi-infinite reflective layer in an epi-luminescence geometry. Although not a perfect match for our platform geometries, the Le Moal model exhibits many of the salient features of our

platform. In an epi-luminescence geometry, under optimal conditions with a collection objective having a numerical aperture 0.1–0.2 (4×), the RDAS in the Le Moal platform resulting from improvements in excitation and emission enhancement and collection is 28-fold in comparison to an equivalent luminescent reporter layer on bare glass.

EXPERIMENTAL SECTION

Chemicals and Materials

The following reagents were used: Rose Bengal (RB) (95%), 1-vinyl-2-pyrrolidinone (NVP) (99%), *N*-phenylglycine (NPG) (97%), docusate sodium salt (AOT) (99%), formamide (99.5%), dipentaerythritol penta-/hexa-acrylate (DPHPA), and toluene (99.5%) (Sigma Aldrich); [Ru(dpp)₃]Cl₂·5H₂O (GFS Chemicals); liquid crystal (TL213) (EMD Chemicals); tetraethylorthosilane (TEOS) (99.9%) and *n*-octyltriethoxysilane (C8-TriEOS) (>95%) (Gelest); HCl (ACS grade) (J.T. Baker); and EtOH (200 proof) (Decon Laboratories). All reagents were used as received. Deionized water was prepared by using an AmeriWater purification system (Metro Group) to a specific resistivity of at least 18 MΩ-cm.

Pre-cleaned glass microscope slides (Corning) served as substrates.

N-(6-(dimethylamino)-9-phenyl-3*H*-selenoxanthen-3-ylidene)-*N*-methylmethanaminium chloride (tetramethylrosamine-selenium, TMR-Se) was synthesized following literature protocols.¹³

[Ru(dpp)₃]²⁺ Doped Sol Preparation

The O₂ responsive xerogel used in this research was based on a formulation previously developed in our laboratories.^{5b, 7} This particular xerogel was selected because it exhibits a good O₂ *K_{SV}* value and a linear Stern-Volmer response. Briefly, a sol was prepared by mixing, in order, TEOS (1.45 mL, 6.5 mmol), C8-TriEOS (2.05 mL, 6.5 mmol), EtOH (2.52 mL, 44 mmol) and HCl (0.800 mL of 0.1 M HCl, 0.08 mmol). This sol was capped and magnetically stirred under ambient conditions for 1 h. A luminophore-doped sol was prepared by mixing 0.273 mL of 25 mM [Ru(dpp)₃]²⁺ (in EtOH) with 6.82 mL of the aforementioned sol. A blank sol was prepared by omitting [Ru(dpp)₃]²⁺. These sols were capped and mixed for 2 min by a touch mixer and stored in the dark under ambient condition for 24 h before use.

Sensor Array Fabrication

Xerogel-based sensor arrays with appropriate blanks were formed onto clean glass (Gl) slides and Bragg gratings (Gr) coated onto glass slides via pin-printing^{6,7} (Cartesian Technologies) by using a 200 μm diameter solid tungsten pin (Point Technologies) (Figure 1). The center-to-center distance between pin-printed features was fixed at 450 μm. Figure 1A depicts how the sensor elements and blanks are arranged on the surface of bare glass and the Bragg grating coated glass. This configuration allows us to assess simultaneously the response from each platform without any changes in positioning or adjustments to the detection system/settings. Figure 1B illustrates the three platform geometries that were evaluated in this research: XGl – xerogel formed on clean glass (control); XGlGr – xerogel formed on the glass substrate with the Bragg grating formed on the opposite side of the glass substrate; and XGrGl – xerogel formed directly on the Bragg grating.

Pre-polymer Solution Preparation

Table 1 lists the pre-polymer solution compositions that we developed to create the RB and TMR-Se based reflective Bragg gratings. These formulations are derived in part from pre-polymer solutions previously described in the literature.^{8, 11}

Instrumentation

Figure 2A illustrates the optical system that was used to create the Bragg reflection gratings.^{8f} Briefly, a CW laser (532nm, Verdi-6, Coherent Inc.) served to activate the photoinitiators (RB, TMR-Se). The laser beam passes through a spatial filter and is collimated by a biconvex lens (50.0 mm dia, 5 cm focal length). Twenty microliters of pre-polymer solution (Table 1) is sandwiched between two clean glass microscope slides. The grating thickness is controlled by using 8 μ m spacers positioned between the glass slides. One microscope slide is attached to a 45°-90°-45° BK-7 prism by using index matching oil. The laser beam incident angle (θ) is maintained at 0°. The solution sandwiched between the glass slides is exposed to the laser beam for 60 s at 30 mW/cm². The resulting λ_{Bragg} depends on θ , n_{prism} , n_{pre} and n_{ave} (Eqns. 2 and 3). After the grating is formed, it is post-cured for 18 h by full illumination with an Hg lamp (100W, Sylvania). Afterwards one glass slide is removed to facilitate solvent evaporation; the grating tends to adhere well to one glass slide. The Bragg grating reflection wavelength center and reflection window width are determined by using a diode array UV-Vis spectrometer (8452A, Hewlett Packard) with the beam trajectory normal to the grating surface. This orientation properly matches the epi-luminescence geometry.

Figure 2B illustrates the epi-luminescence microscope system; the XGI, XGIGr and XGrGI platforms are mounted within a custom built flow cell with the reflective Bragg grating positioned normal to the excitation beam and the xerogel elements always facing the microscope objective. The system consists of a 445-nm diode laser (Crystalaser), a 25.4 mm dia f/2 plano-convex lens, an optical fiber, and an epi-luminescence microscope (BX-40, Olympus) with a 4 $\times$ microscope objective (Olympus). The microscope filter cube contains a 442.5-nm bandpass filter (442.5BP15, Omega Optics) to clean up the excitation beam, a dichoric long pass filter (490 nm) (490DRLP, Omega Optics) and a 515-nm longpass emission filter (515 EFLP, Omega Optics). The microscope is also equipped with a multi-spectral imaging module (Nuance FX, CRi). The sensor array data are recorded by collecting epi-luminescence images between 560 nm and 700 nm in 10 nm increments.

Stern-Volmer quenching data was recorded as a function of O₂ concentration (0–100%, 20% increments) by using a pair of precision mass flow controllers (PC1NP1U1V_1A, Sensirion).

Emission spectra from each photoinitiator dissolved in EtOH were measured by using a steady state spectrofluorimeter (8100, SLM).

Scanning electron microscope (SEM) images were measured with an Auriga FIB-SEM (Carl Zeiss Nanotechnology Systems).

Data Analysis and Statistics

Results represent the average of 15 replicate sensor elements and the corresponding blanks from 5 of each platform type ($n = 75$ for each platform). The appropriate xerogel blank was always the closest in space to a particular xerogel sensor element within a given platform. This minimizes problems with non-uniform epi-illumination. The relevant signals were recovered by integrating the detected signals from 300 μ m diameter areas centered at each sensor element and blank coordinate. Results are reported as the mean and measurement standard deviation. All results were assessed for statistical significance by using ANOVA at the 95% confidence level with pairwise comparison (Holm-Sidak test) ($p < 0.05$ being significant). In all cases the power of performance test exceeded 0.99.

RESULTS AND DISCUSSION

Figure 3A presents typical transmission and emission spectra for the RB Bragg gratings, emission spectra from dilute RB in EtOH, and the emission spectrum from $[\text{Ru}(\text{dpp})_3]^{2+}$ sequestered within the class II xerogel. For completeness, Figure 3B presents representative data for the TMR-Se system. Several aspects of these data merit further elaboration. First, the measured λ_{Bragg} for the RB Bragg grating is centered at 625 nm and the full width at half maximum (FWHM) is 54 nm. Second, the measured λ_{Bragg} for the TMR-Se Bragg grating is centered at 650 nm and the FWHM is 16 nm. This is interesting given that the optical platform for creating these two Bragg gratings is identical. The difference in center wavelength must arise from refractive index differences (n_{pre} , n_{ave}) in the two grating formulations leading to differences in Λ (see Eqns. 2 and 3). Typical SEM micrographs of RB and TMR-Se Bragg gratings are presented in Figure 4. Fast Fourier transform (FFT) analysis shows that the RB and TMR-Se Λ are 225 ± 13 nm (relative standard deviation (RSD) = 5.8%) and 207 ± 3 nm (RSD = 1.5%), respectively. As expected, the grating spacing RSD is directly related to the Bragg reflection bandwidth. We propose that the narrower bandwidth seen for the TMR-Se Bragg grating in comparison to the RB grating (ca. 3 fold wider) arises in part from differences in the RB and TMR-Se intersystem crossing rates which are known to differ by up to 130-fold depending on solvent;¹⁴ TMR-Se is thus more effective at creating reactive products that induce photopolymerization in comparison to RB. Although, the intersystem crossing rates within these multicomponent per-polymer solutions is unknown, the known differences in homogeneous solutions could explain why the TMR-Se based reflective Bragg grating exhibits a Λ with significantly less variance in comparison to the RB based grating. Third, there is significant autofluorescence from each Bragg grating type arising from residual RB and TMR-Se fluorescence from within the grating. Thus, the grating itself contributes a background emission. The RB and TMR-Se Bragg grating emission peaks are at 580 nm and 605 nm, respectively. Fourth, the $[\text{Ru}(\text{dpp})_3]^{2+}$ luminescence occurs from 550 to 670 nm, peaking at 610 nm. Fifth, a significantly larger fraction of the $[\text{Ru}(\text{dpp})_3]^{2+}$ emission is reflected by the RB based Bragg grating in comparison to the TMR-Se based Bragg grating. Finally, the TMR-Se Bragg grating autofluorescence overlaps more with the $[\text{Ru}(\text{dpp})_3]^{2+}$ luminescence in comparison to the RB grating.

Figure 5 presents typical angle-dependent transmission spectra for a RB Bragg grating. Although not exploited in the current research, these results demonstrate that the effective λ_{Bragg} can be adjusted more than 100 nm simply by changing the grating angle with respect to the excitation beam trajectory (α). However, despite the ability to tune the reflection window by over 100 nm, there can be a significant loss in reflection efficiency when one moves away from the traditional epi-geometry ($\alpha = 0^\circ$). Over a small α window (0° to $\sim 20^\circ$), the reflection wavelength can be shifted ~ 20 nm with negligible loss in reflectance efficiency.

Figure 6 presents a typical false-color image at 610 nm from a RB based XGrGI and XGI (control) array in the presence of 50% O_2 . (The donut shaped printed features arise from sub-optimal printing conditions. These are cosmetic and do not affect the analytical results.) Inspection of this image illustrates two key points. First, the Bragg grating exhibits spatially non-uniform autofluorescence. This result helps explain why our initial efforts to carry out experiments without imaging yielded highly irreproducible results and non-linear Stern-Volmer plots (not shown); different regions of the same sample behaved differently and it proved impossible to create and position proper Bragg grating blanks to accurately correct for the grating autofluorescence. Second, the autofluorescence contribution at 610 nm is on the order of 10% of the total signal when the sensor is challenged with 50% O_2 . As the O_2 concentration approaches 100% and the sensor emission is quenched, the Bragg grating

autofluorescence can exceed 70% of the total signal. If not properly addressed, this autofluorescence can seriously bias the sensor response. Third, the detected analytical signal from sensor elements positioned on the XGrGI portion of the array are clearly substantially greater (i.e., brighter) in comparison to the detected signal from the same sensor elements located on the XGI portion of the array.

Figure 7 presents typical false color total emission (560–700 nm) and wavelength specific (610 nm) images for XGI, XGrGI, and XGIGr platforms using RB and TMR-Se Bragg gratings under identical experimental conditions (laser illumination, exposure time, 100% N₂). Several aspects of these data merit additional discussion. First, the XGI autofluorescence is the lowest of all platforms investigated. This is not surprising given that there is no residual dye in the glass substrate. Second, the RB based Bragg grating shows the largest autofluorescence. This arises because the RB luminescence quantum yield is significantly greater in comparison to TMR-Se luminescence quantum yield.⁹ Third, the XGIGr platforms appear to be largely the same, save for the background autofluorescence, and very similar to the XGI platform. Fourth, the XGrGI platforms show significant increases in the detected signals from the xerogel sensor elements. These last two observations demonstrate that the sensor element must be in close proximity to the reflective Bragg grating to realize selective reflection of the omni-directional sensor luminescence toward the detector. Simply forming a sensor element on a platform with a reflective Bragg grating does not necessarily yield any advantage unless the sensor and Bragg grating are in close proximity. As discussed by Le Moal et al.,¹² signal enhancement should depend on the distance between the reflective surface and luminescent reporters and the wavelength within the dielectric medium (i.e., $\lambda_{\text{emission}}$, n_{ave}).

Table 2 summarizes the recovered K_{SV} and the RDAS (i.e., $\text{RDAS} = \text{DAS}_i / \text{DAS}_{\text{XGI}}$) for each sensor platform geometry studied in this research. The recovered Stern-Volmer plots (not shown) are rigorously linear between 0 and 100% O₂ (i.e., Eqn. 1 is applicable) ($r^2 > 0.996$, intercept = 1.03 ± 0.04). This is not the case unless one can properly address the Bragg grating autofluorescence, which can contribute significantly and is heterogeneous across the Bragg grating face. The recovered K_{SV} values are statistically equivalent ($p > 0.65$), indicating that the sensors *per se*, behave independently of the underlying platform when proper blank correction measures are taken. The RDAS results show that the detected analytical signal (best to worst) is as follows: XGrGI (RB) > XGrGI (TMR-Se) > XGIGr (RB) = XGIGr (TMR-Se) = XGI. Hence, the XGrGI geometries are superior, arising from the ability of these platforms to reflect selectively the sensor element emission toward the detector. There is no advantage over bare glass realized when using the XGIGr platforms, demonstrating the importance of the sensor element and grating proximity. The superiority of the XGrGI (RB) platform arises primarily from its ability to reflect a larger fraction of the sensor element total emission toward the detector despite the RB Bragg grating exhibiting the largest autofluorescence background of the platforms tested.

CONCLUSIONS

We have successfully demonstrated the integration of xerogel based chemical sensors with wavelength tunable reflective Bragg gratings. These new platforms do not alter the intrinsic sensor response profile and they provide up to 8 fold improvement in the detected analytical signal reaching the detector. The improvement in detected signal is, however, not yet fully optimized. Complete optimization will require a better match between the sensor element emission and λ_{Bragg} , the reflection bandwidth and a decrease in the autofluorescence from the Bragg grating. Implementing reflective Bragg gratings in concert with optical sensors of the type described in this paper could provide researchers with an inexpensive pathway to use less sophisticated/lower power demanding detectors (e.g., CMOS (complementary metal

oxide semiconductor) vs. CCD) and/or light sources (e.g., LEDs vs. lasers), lowering system costs and power demands.

Acknowledgments

We thank James Sentementes from CRI for his help in image analysis, Nadine Kraut for her help in schematic artwork. We also acknowledge the generous support by National Science Foundation and the National Institute of Health.

REFERENCES

1. Sen, CK.; Semenza, GL. Oxygen Sensing, in *Methods in Enzymology*. Vol. Vol. 381. San Diego: Academic Press; 2004.
2. Sojka, RE.; Oosterhuis, DM.; Scott, HD. *Handbook of Photosynthesis*. 2nd ed. Boca Raton, FL: CRC Press; 2005. p. 299-314.
3. Whiffin VS, Cooney MJ, Cord-Ruwisch R. *Biotechnol. Bioeng.* 2004; 85(4):422–433. [PubMed: 14755560]
4. (a) Amao Y, Ishikawa Y, Okura I. *Anal. Chim. Acta.* 2001; 445(2):177–182. (b) Apostolidis A, Klimant I, Andrzejewski D, Wolfbeis OS. *J. Comb. Chem.* 2004; 6(3):325–331. [PubMed: 15132591] (c) Kneas KA, Xu W, Demas JN, Degraff BA. *Appl. Spectrosc.* 1997; 51(9):1346–1351. (d) MacCraith BD, O'Keeffe G, McEvoy AK, McDonagh CM, McGilp JF, O'Kelly B, O'Mahony JD, Cavanagh M. *Opt. Eng.* 1994; 33(12):3861–3866. (e) Mak CSK, Pentlechner D, Stich M, Wolfbeis OS, Chan WK, Yersin H. *Chem. Mater.* 2009; 21(11):2173–2175. (f) McEvoy A, McDonagh C, MacCraith B. *J. Sol-Gel Sci. Technol.* 1997; 8(1):1121–1125. (g) Oar MA, Dichtel WR, Serin JM, Fréchet JMJ, Rogers JE, Slagle JE, Fleitz PA, Tan LS, Ohulchanskyy TY, Prasad PN. *Chem. Mater.* 2006; 18(16):3682–3692. (h) O'Riordan TC, Buckley D, Ogurtsov V, O'Connor R, Papkovsky DB. *Anal. Biochem.* 2000; 278(2):221–227. [PubMed: 10660466] (i) Payne SJ, Fiore GL, Fraser CL, Demas JN. *Anal. Chem.* 2010; 82(3):917–921. [PubMed: 20050641] (j) Ciriminna R, Pagliaro M. *Analyst.* 2009; 134(8):1531–1535. [PubMed: 20448915]
5. (a) Bukowski RM, Ciriminna R, Pagliaro M, Bright FV. *Anal. Chem.* 2005; 77(8):2670–2672. [PubMed: 15828809] (b) Tang Y, Tehan EC, Tao Z, Bright FV. *Anal. Chem.* 2003; 75(10):2407–2413. [PubMed: 12918984]
6. Holthoff WG, Tehan EC, Bukowski RM, Kent N, MacCraith BD, Bright FV. *Anal. Chem.* 2004; 77(2):718–723. [PubMed: 15649078]
7. Tang Y, Tao Z, Bukowski RM, Tehan EC, Karri S, Titus AH, Bright FV. *Analyst.* 2006; 131(10):1129–1136. [PubMed: 17003861]
8. (a) Hsiao VKS, Kirkey WD, Chen F, Cartwright AN, Prasad PN, Bunning TJ. *Adv. Mater.* 2005; 17(18):2211–2214. (b) Hsiao VKS, Lin TC, He GS, Cartwright AN, Prasad PN, Natarajan LV, Tondiglia VP, Bunning TJ. *Appl. Phys. Lett.* 2005; 86(13):1311–1313. (c) Hsiao VKS, Yong KT, Cartwright AN, Swihart MT, Prasad PN, Lloyd PF, Bunning TJ. *J. Mater. Chem.* 2009; 19(23):3998–4003. (d) Hsiao VKS, Zheng YB, Betz H, Kiraly B, Yan W, Lloyd PF, Bunning TJ, Cartwright AN, Huang TJ. *Journal of Nanotechnology in Engineering and Medicine.* 2010; 1(4):041011-5. (e) Maskaly KR, Hsiao VKS, Cartwright AN, Prasad PN, Lloyd PF, Bunning TJ, Carter WC. *J. Appl. Phys.* 2006; 100(6):066103. (f) Kim SJ, Chodavarapu VP, Cartwright AN, Swihart MT, Bunning TJ. *Sens. Actuators B.* 2008; 130(2):758–764.
9. Ohulchanskyy TY, Donnelly DJ, Detty MR, Prasad PN. *J. Phys. Chem. B.* 2004; 108(25):8668–8672.
10. (a) Baker GA, Wenner BR, Watkins AN, Bright FV. *J. Sol-Gel Sci. Technol.* 2000; 17(1):71–82. (b) Chen X, Zhong Z, Li Z, Jiang Y, Wang X, Wong K. *Sens. Actuators B.* 2002; 87(2):233–238. (c) Choi MMF, Xiao D. *Anal. Chim. Acta.* 2000; 403(1-2):57–65. (d) Chu CS, Lo Y-L. *Sens. Actuators B.* 2007; 124(2):376–382. (e) Douglas P, Eaton K. *Sens. Actuators B.* 2002; 82(2-3):200–208. (f) Koo Y-EL, Cao Y, Kopelman R, Koo SM, Brasuel M, Philbert MA. *Anal. Chem.* 2004; 76(9):2498–2505. [PubMed: 15117189] (g) Lakowicz, JR. *Principles of Fluorescence Spectroscopy*. Third edition. Singapore: Springer; 2006. (h) McDonagh C, Kolle C, McEvoy AK, Dowling DL, Cafolla AA, Cullen SJ, MacCraith BD. *Sens. Actuators B.* 2001; 74(1-3):124–130. (i) Vasil'ev VV, Borisov SM. *Sens. Actuators B.* 2002; 82(2-3):272–276. (j) Wolfbeis OS, Oehme

- I, Papkovskaya N, Klimant I. *Biosens. Bioelectron.* 2000; 15(1-2):69–76. [PubMed: 10826645] (k)
Xu H, Aylott JW, Kopelman R, Miller TJ, Philbert MA. *Anal. Chem.* 2001; 73(17):4124–4133.
[PubMed: 11569801]
11. Xu H, Liu K, Yung KY, Bright FV, Cartwright AN. Heterogeneous integration of polymer porous photonic bandgap structure with xerogel based biochemical sensors. *Mater. Res. Soc. Symp. Proc.* Cambridge University Press. 2011
12. Moal EL, Fort E, Lévêque-Fort S, Cordelières FP, Fontaine-Aupart MP, Ricolleau C. *Biophys. J.* 2007; 92(6):2150–2161. [PubMed: 17172306]
13. (a) Brennan NK, Donnelly DJ, Detty MR. *J. Org. Chem.* 2003; 68(8):3344–3347. [PubMed: 12688818] (b) Detty MR, Prasad PN, Donnelly DJ, Ohulchanskyy T, Gibson SL, Hilf R. *Biorg. Med. Chem.* 2004; 12(10):2537–2544.
14. (a) Stracke F, Heupel M, Thiel E. *J. Photochem. Photobiol. A: Chem.* 1999; 126(1-3):51–58.(b) Larkin JM, Donaldson WR, Foster TH, Knox RS. *Chem. Phys.* 1999; 244(2-3):319–330.(c) Cramer LE, Spears KG. *J. Am. Chem. Soc.* 1978; 100(1):221–227.

Figure 1. Schematic of [Ru(dpp)₃]²⁺ doped xerogel based microarrays formed onto Bragg gratings and glass. (Panel A) Overall geometry for xerogel based sensor elements, xerogel blanks, Bragg grating, and glass substrate. (Panel B) Cross-section view of [Ru(dpp)₃]²⁺ doped xerogel based sensor elements and xerogel based blanks formed onto glass (XGI) (control), on glass substrate opposite the Bragg grating (XGIGr), and directly on the Bragg grating (XGrGI).

Figure 2. Instrumentation used to create and assess the hybrid sensor-Bragg grating platforms. (Panel A) Holographic single beam reflective Bragg grating fabrication system schematic. (Panel B) Multispectral imaging epi-luminescence system schematic.

Figure 3.

Typical Bragg grating transmission and normalized emission spectra, normalized photoinitiator emission spectra in EtOH, and normalized xerogel sequestered [Ru(dpp)₃]²⁺ emission spectra. (Panel A) RB. (Panel B) TMR-Se.

Figure 4.
Typical high resolution SEM images of RB and TMR-Se gratings.

Figure 5. Angle-dependent transmission spectra for a RB based Bragg grating. The angle (α) represents deviation from the transmission beam being normal to the Bragg grating surface.

Figure 6. False-color image at 610 nm from an O_2 responsive sensor array and blanks in the XGrGI and XGI (control) geometries (RB grating) in the presence of 50% N_2 .

Figure 7.

False color total emission and 610 nm images from O_2 responsive sensor arrays and blanks in the XGI, XGrGI, and XGIGr geometries in the presence of 100% N_2 . RB and TMR-Se based Bragg grating results are shown. All instrument acquisition parameters are identical for each platform so signals can be readily compared.

Table 1

RB and TMR-Se based solution compositions used to form reflective Bragg gratings.

Grating	Substance	Weight %	Weight (g)
RB	DHPHA	41.4	8.77×10^{-1}
	Formamide	26.7	5.66×10^{-1}
	NVP	19.1	4.06×10^{-1}
	AOT	11.9	2.53×10^{-1}
	NPG	0.630	1.33×10^{-2}
	Rose Bengal	0.200	4.30×10^{-3}
TMR-Se	DHPHA	43.3	3.66×10^{-1}
	Toluene	19.6	1.66×10^{-1}
	LT312	19.5	1.64×10^{-1}
	NVP	16.4	1.39×10^{-2}
	NPG	0.980	8.30×10^{-3}
	Tetramethylrosamine-selenium	0.150	1.30×10^{-3}

Table 2

Recovered Stern-Volmer constant (K_{sv}) and relative detected analytical signal (RDAS) for each sensor platform evaluated.

Platform	K_{sv} (%O ₂ ⁻¹)	RDAS ^{a,b}
XGI	0.13 ± 0.01 (r ² : 1.00)	1.0 ± 0.1
XGrGI (RB)	0.15 ± 0.03 (r ² : 0.998)	7.6 ± 0.5
XGIGr (RB)	0.12 ± 0.02 (r ² : 0.998)	1.0 ± 0.1
XGrGI (TMR-Se)	0.16 ± 0.04 (r ² : 0.998)	4.3 ± 0.3
XGIGr (TMR-Se)	0.10 ± 0.01 (r ² : 0.998)	1.0 ± 0.1

^{a)} Relative detected analytical signal (= DAS_i/DAS_{XGI}).

^{b)} Conducted under 100% N₂.