

Oxygen Detection via Nanoscale Optical Indicators

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Abstract—Oxygen plays a ubiquitous role in terrestrial biological processes such as respiration and chemical process, i.e. oxidation-reduction reactions. We have developed an optical technique for monitoring oxygen in both gas and liquid phases utilizing nanoscale metal-halide clusters immobilized in a porous matrix. The sensor monitors the luminescence intensity or lifetime from inorganic hexanuclear molybdenum chloride clusters ($\text{Mo}_6\text{Cl}_{12}$) which is efficiently quenched by ground state $^3\text{O}_2$. Control of the material properties of the matrix at the nanometer scale is required for fast quantitative output from our reflection mode fiber based sensor. For aqueous applications we can monitor dissolved oxygen in the 0.2–17 mg/L range at temperatures of 10–25 °C. The sensor output was validated using a commercial electro-chemical sensor and the Stern-Volmer fit is linear over the entire measurement range. In the gas phase our device can monitor oxygen with a response time, t_{95} , of 30s in the 0.1 – 21 % range.

I. INTRODUCTION

Real-time detection of oxygen in liquids and gases is important for a variety of chemical and biological processes ranging from industrial process control to aquaculture. The family of molybdenum chloride clusters are unique optical indicators as their specificity to oxygen is governed by quantum mechanics, i.e. the fact that the ground state of O_2 is a spin triplet state. We have developed techniques to disperse

the cluster in polymeric and sol-gel matrices in order to accommodate a range of different applications.

II. OPTICAL INDICATOR

A. Photophysics

A schematic of the nanoscale molybdenum chloride lumophore, $\text{Mo}_6\text{Cl}_{12}$, is shown in Fig. 1. From x-ray crystallography: $a=11.24 \text{ \AA}$, $b=11.28 \text{ \AA}$, $c=14.08 \text{ \AA}$ with four clusters per unit cell [1]. When dissolved in solution the clusters exist in the form $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4\text{L}_2$ where L is either a solvent molecule or another ligand. The reaction pathway for quenching of the luminescence by $^3\text{O}_2$ is shown in the lower portion of Fig. 1. Absorption of an ultraviolet (UV) photon through the broad absorption band (300–400 nm) leaves the cluster in an excited electronic state from which it can either emit a red photon (600 – 900 nm) or be quenched by a molecule with a triplet ground state such as oxygen. The wide absorption band allows for the use of an inexpensive UV light emitting diode (LED) with a color glass filter as the excitation source. The luminescence signal is easily detectable by simply integrating over the broad emission band due to the long cluster lifetime ($>100 \mu\text{s}$) and large Stokes. Simple filtering techniques are used to separate pump and probe beams.

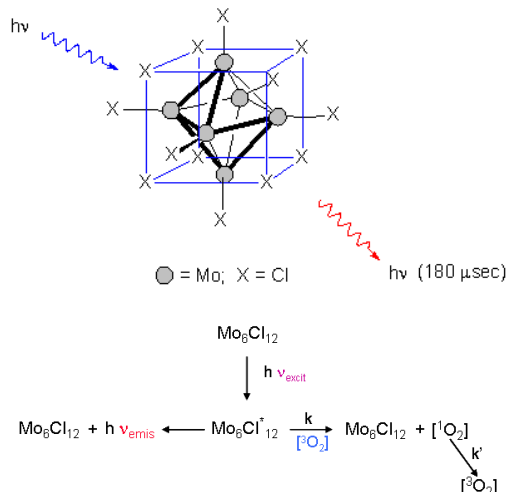


Figure 1: Molybdenum chloride nanoscale optical indicator. From x-ray crystallography: $a=11.24 \text{ \AA}$, $b=11.28 \text{ \AA}$, $c=14.08 \text{ \AA}$ with four clusters per unit cell. Reaction pathway for quenching of the luminescence by $^3\text{O}_2$.

The quenching of either the luminescence lifetime or intensity is expected to follow the Stern-Volmer equation:

$$I_0/I \text{ or } \tau_0/\tau = 1 + k_{\text{SV}} [\text{O}_2] \quad (1)$$

where I_0 or τ_0 are the unquenched intensity or lifetime and k_{SV} is the Stern-Volmer constant. In solution, using a solvent such as acetonitrile, it is relatively simple to disperse the lumophore as a monomer and obtain a linear Stern-Volmer relationship.

B. Sensing Film

Our goal is to monitor oxygen levels in gas phase and aqueous solutions. To this end we immobilize the molybdenum chloride clusters in an oxygen permeable matrix to form a sensing film. The sensing film is then either coated on the end of an optical fiber or on a UV transparent substrate. A bifurcated optical fiber brings the excitation radiation to the sensing film and transmits the signal photons back to the detector. The challenge in synthesizing the sensing film is to disperse the Mo lumophores as monomers within the support matrix to avoid deleterious cluster-cluster interactions, which severely compromise the optical efficiency of the sensing film. We have developed techniques to disperse the acetonitrile complex of $\text{Mo}_6\text{Cl}_{12}$ or the salt $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ in polymer [2] and sol-gel [3] binders such that self quenching is not an issue; This was demonstrated by measurements of the luminescence lifetime, luminescence intensity and the quenching rate constant of the sensing film.

III. OXYGEN DETECTION

A. Gas-phase measurements

Data from our reflection mode fiber optic oxygen sensor for gas phase monitoring of oxygen is given in Fig. 2 [2]. The molybdenum chloride clusters were dispersed in a

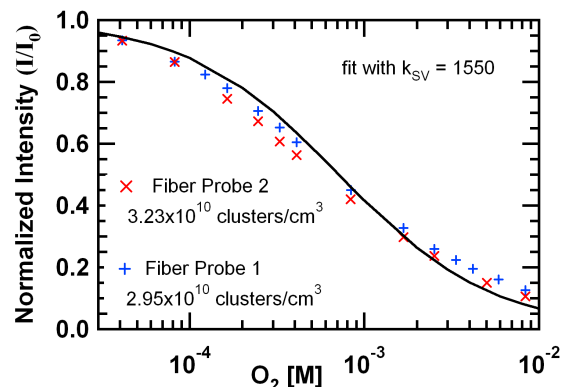


Figure 2: Measurement of the oxygen concentration in gas phase for two reflection mode fiber optic probes from 0.1 to 21.0 % O_2 . The fit to the Stern-Volmer equation for two different cluster concentrations shows the lack of deleterious cluster-cluster interactions.

polymer matrix and the composite was dipped coated on the far end of a UV transparent quartz fiber. Shown in Fig. 2 is the normalized signal (with respect to I_0 the sensor signal in the absence of oxygen) intensity as a function of oxygen concentration over 2.5 orders of magnitude, from 0.1 - 21 % oxygen. The sensor can cleanly resolve changes of 0.1% absolute oxygen concentration in the 0-1% range, changes of 0.5% absolute oxygen concentration in the 1-4% range, and changes of 1% absolute oxygen concentration in the 4-10% range. The upper bound of the sensor switching time was determined to be 30 s. This is not the intrinsic response time of the sensor but an upper bound set by the response time of the gas mixing system used to characterize the device. From the known oxygen permeability of the polymer matrix and the measured sensor film thickness we estimate a lower bound to the sensor response time to be 1 s.

Fig. 2 shows the normalized sensor output for two different concentrations of the nanoscale lumophores, 2.95 and 1.31×10^{19} clusters/ cm^3 for Fiber Probe 1 and 2 respectively. The solid line is a least squares fit to Eq. (1) with $k_{\text{SV}}=1550$. Although the two fiber sensors differ in cluster concentration by a factor of 2, they have essentially the same normalized response characteristic. This data demonstrates that the photophysics of the Mo optical indicator are not adversely affected by immobilization in the polymer matrix and self quenching is not an issue.

B. Dissolved oxygen sensing

Measurements of dissolved oxygen (DO) in water are given in Fig. 3. In this case the molybdenum cluster salt, $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, was dispersed in a hydrophobic polymer matrix and drop coated onto a quartz slide. The sensor substrate with the film facing outward is mounted a water tight sensing head and a 1m bifurcated optical fiber bundle makes intimate contact with the backside of the substrate. The luminescence lifetime was monitored using a compact commercial

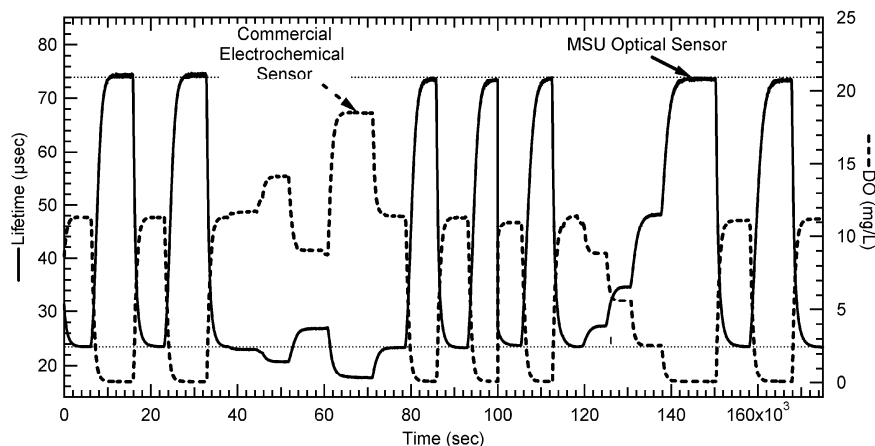


Figure 3: Measurement of the dissolved oxygen (DO) concentration in water at 10 °C. Validation of the optical sensor signal by a commercial electro-chemical device.

fluorometer [4]. The measurements were made in a water tank, while externally varying the oxygen concentration between zero and 100% saturation (~11 mg/L at 10 °C). The water bath was maintained at 10 °C.

The luminescence lifetime was monitored while varying the DO level during seven cycles between 0 and 11 mg/L. The output of our optical sensor signal was validated using a commercial electro-chemical oxygen sensor in the same water tank. The dashed lines are a guide to the eye, and demonstrating the reproducibility of our oxygen sensor over 7 measurement cycles. In addition data from random steps at 13, 8, 18, 5 and 2 mg/L were obtained. A linear fit of τ_0/τ to the Stern-Volmer was obtained over the entire measurement range from 2 to 17 mg/L. The linearity of the normalized luminescence lifetime over this wide concentration range demonstrates that the Mo-indicators have been dispersed as monomers in the polymer matrix, such that self quenching is not a problem for DO measurements. From a practical point of view the linearity of the Stern-Volmer fit is particularly important for development of a commercial device as it allows for a two point calibration of the sensing film. We are developing this DO sensor for 24/7 monitoring

of oxygen for aquaculture applications in collaboration with our commercial partners.

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