

Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants

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ABSTRACT

A reflection mode fiber optic oxygen sensor that can operate at high temperatures for power plant applications is being developed. The sensor is based on the $^3\text{O}_2$ quenching of the red emission from hexanuclear molybdenum chloride clusters. High temperature measurements of the emission of clusters in sol gel films show that the luminescence intensity from the films follow a $1/T$ relationship from room temperature to 150 °C, and then declines at a slower rate at higher temperatures. The large number of photons available at 230 °C is consistent with simple low cost optics for fiber optic probes based on the emission from clusters in sol gel films.

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LIST OF GRAPHICAL MATERIALS

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INTRODUCTION

Maximizing the efficiency of the combustion process requires real-time control of the correct fuel/oxygen ratio. This requires the ability to sense oxygen levels over a broad range of concentrations with fast response times. Mussell, Newsham, and Ruud previously reported preliminary studies of the synthesis and optical properties of $\text{Mo}_6\text{Cl}_{12}$ -based clusters relevant to this project ^[1-4]. Mussell described the synthesis of the molybdenum clusters, and Newsham gives a good account of the properties of neutral $\text{Mo}_6\text{Cl}_{12}$ clusters and their salts, in both solution and a sol gel matrix. Newsham's data indicate that the photophysical properties of the clusters are maintained in sol gel matrices. To prepare a fiber optic sensor based on $\text{Mo}_6\text{Cl}_{12}$, Ruud dispersed $\text{Mo}_6\text{Cl}_{12}$ in poly[1-trimethylsilyl-1-propyne] (PTMSP), and used a dipping technique to immobilize the composite at the cleaved end of a silica optical fiber. Ghosh and co-workers ^[5] demonstrated a fast room temperature fiber optic sensor based on oxygen quenching of the luminescence from the PTMSP/ $\text{Mo}_6\text{Cl}_{12}$ composites. While the PTMSP support is adequate for room temperature applications, is unable to withstand the high temperatures associated with combustion in a power plant. To improve the sensor's high temperature performance, we are replacing PTMSP with a thermally stable sol gel matrix that should be able to withstand the higher temperature requirements of the power plant combustion process. The idea of using a sol gel as the support matrix for high temperature oxygen sensor application is not new. Remillard and coworkers have shown that a sol gel supported copper based oxygen sensor can be used in a combustion process ^[6]. With these facts in hand, we anticipate promising results from our design.

EXECUTIVE SUMMARY

One of the critical parameters in a high temperature sensor based on luminescence quenching is the stability of the lumophore, and the temperature dependence of the luminescence, i.e. having enough photons at high temperatures to enable practical sensing. Previously we had reported preliminary luminescence data for a Mo-cluster/sol-gel film from room temperature to ~200 °C. We now have extended the data to 230 °C in flowing N₂ (purity 99.999%), and have tested the long term stability of the lumophore. High temperature measurements of the emission of molybdenum clusters in sol gel films show that the luminescence intensity from the films follow a 1/T relationship from room temperature to 150 °C, and then declines at a slower rate at higher temperatures. The large number of photons available at 230 °C is consistent with simple low cost optics for fiber optic probes based on the emission from clusters in sol gel films. Of note is that the measurements were made on a film that was ~1 year old that had been thermally cycled to T.>200 ° several times. Despite the repeated cycling, the luminescence intensity of the film had not diminished,

EXPERIMENTAL

Materials.

All glassware was oven-dried prior to use. Acetonitrile (Spectrum Chemical Company, HPLC grade) was dried over CaH_2 and distilled prior to use. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%) and hydrochloric acid (CCI, electronics grade) were used as received. Molybdenum dichloride (Cerac, Inc.) was purified as described elsewhere.^[7] The acetonitrile complex of $\text{Mo}_6\text{Cl}_{12}$ was prepared by placing dry, purified $\text{Mo}_6\text{Cl}_{12}$ (100 mg) into a cellulose Soxhlet extraction thimble. After assembling the Soxhlet apparatus and flushing the system with nitrogen, the $\text{Mo}_6\text{Cl}_{12}$ was extracted with 250 mL of dry acetonitrile for one week. Concentration of the resulting clear yellow solution to 10 mL gave an orange-yellow solution of the acetonitrile complex (cluster concentration $\sim 2 \times 10^{-3}$ M). Suprasil – W1 quartz microscope slides ($3'' \times 1'' \times 1$ mm) were obtained from Heraeus Amersil and were cut into $1.25 \text{ cm} \times 2.45 \text{ cm}$ pieces. Slides were handled with gloves and tweezers in order to minimize surface contamination.

Preparation of the potassium salt of $\text{Mo}_6\text{Cl}_{12}$. ($\text{K}_2\text{Mo}_6\text{Cl}_{14} \cdot 2\text{H}_2\text{O}$)

KCl (5 mL of a solution prepared by dissolving KCl (1.0077g, 13.5 mmol) in 50 mL of 6M HCl) was added to a stirred solution of $\text{Mo}_6\text{Cl}_{12}$ (25 mL, 2.05×10^{-3} M) in 6M HCl in an Erlenmeyer flask. The resulting yellow solution was concentrated to 15 mL by boiling on a hot plate with stirring. The solution was slowly cooled to room temperature on the hot plate, stoppered, and placed in a refrigerator. The resulting yellow needles were collected by gravity filtration through Whatman medium-fast filter paper. The crystals were then placed onto several pieces of filter paper and allowed to dry under ambient conditions, to give 28.4 mg of bright yellow crystals.

Direct application of clusters to slides (direct method – not sol-gel)

A solution of 7.1 mg of the acetonitrile complex of $\text{Mo}_6\text{Cl}_{12}$ in 3.0 mL of acetonitrile (2.4 mg/mL) was prepared in a 4 mL auto sampler vial from Kimble Glass, Inc. Slides cleaned using method #2 were dried under a stream of nitrogen and then dipped into the solution. The slides were withdrawn slowly and placed horizontally into a 4 mL Kimble vial that had been pre-dried in an oven at $\sim 200^\circ\text{C}$. The solvent was allowed to evaporate until it appeared dry to the eye, and then was further dried under a stream of nitrogen. The slides were placed into a small vial and then transferred to an oven that had been equilibrated in air at the desired temperature. After 1 hour, the slides removed and their luminescence and quenching characteristics were characterized.

Optical microscopy of thin films

Polarized optical microscopy images were acquired using a Nikon Optiphot2-Pol equipped with a Sony Hyper HAD CCD-IRIS/RGB color video camera (model DXC-151A). The camera was connected to a PC using a Sony camera adapter (model CMA-D2). The images were viewed using a Sony Trinitron color video monitor. Images were taken using Hauppauge computer works Win/TV software (version 2.4.17052).

Fluorescence measurements

The fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The system includes a single Czerny-Turner excitation spectrometer with a 1200g/mm ruled grating blazed at 330nm and a single Czerny-Turner emission spectrometer with a 1200g/mm holographic grating blazed at 630 nm. The excitation optics consists of a 450W ozone free Xe lamp, followed by a 270-380 nm bandpass filter (Oriel 1124). A Si photodiode is used to continuously monitor the lamp signal. The detection optics consists of 603.2 nm long wave pass filter (CVI) followed by a multi-alkali photo multiplier tube (Hamamatsu R928) with photon counting electronics. Data processing was performed using the Datamax (version 2.2) software package supplied with the instrument. Spectra were obtained by exciting at 313 nm and scanning the emission monochromator from 550 to 850 nm.

The measurements of the $\text{Mo}_6\text{Cl}_{12}$ emission from Mo-cluster / sol-gel composite films, as a function of temperature were made in the same quartz cuvette described above. A platinum microheater (part 32 208 172 from Heraeus Sensor Technology) was attached with a thermally conducting silver print (GC 22-202 from GC Electronics) to the backside of the quartz slide. The silver print is allowed to cure for at least one hour in air at 100. °C. Electrical connection to the Pt heater was made by microwelding 5 mill thick Cu wire to the 5 mill thick legs of the Pt microheater. The electrical leads were then threaded through the septum. The microheater was powered with a regulated voltage supply. We determined the heater temperature by monitoring the heater resistance, and using the resistance versus temperature curves for a standard 100 ohm Pt thermometer. Prior to the experiments in the SPEX fluorimeter, a curve of temperature as a function of heater power was obtained with the same gas flow as that was used during the actual experiments. Measurements of the sol-gel immobilized and directly attached clusters were made in the same manner. The film-coated side of the quartz slide was irradiated at an angle of $\sim 66^\circ$ with a 90° angle maintained between the excitation beam and detector. The slides were purged in-situ and care was taken not move the excitation spot between measurements in the different gas environments.

RESULTS AND DISCUSSION

One of the critical issues in developing a fiber optic oxygen sensor based on luminescence quenching is to devise a porous support that adheres well to the fiber probe. For spectroscopic work, an additional requirement is access to large area films (1×2 cm) that are uniform and have minimal scattering. A major effort in the third quarter was to establish the conditions that lead to optical quality films for spectroscopy, and translate those conditions to optical fibers.

Immobilization of clusters in sol gel films on surfaces and fibers.

One problem characteristic materials prepared by sol gel synthesis is their propensity to fracture during curing. This problem can be understood by considering the changes in the structure of sol gel matrices as they cure. The chemistry of the sol gel process involves the condensation of tetraethoxysilane (TEOS) in the presence of either an acid or a base catalyst and solvent. As TEOS hydrolyzes and loses ethanol, the silanols generated by hydrolysis condense to form the “sol”. At some point in the process, the sol solution is spread on the surface of a substrate by dip or spray coating. Solvent evaporation plus the hydrolysis and condensation of residual alkoxysilanes complete the process. If the substrate is non-adhesive, the film (often termed a monolith if it is too thick to be considered to be a film) shrinks both laterally and in thickness, and if done under near-equilibrium conditions where the rates of condensation and evaporation are uniform throughout the material, the film or monolith is transformed into a homogeneous solid. Thin films deposited on fibers or planar substrates for optical experiments must have good adherence to the substrate. For these cases, condensation and drying develops substantial strain in the material, often exceeding the yield stress of the material. Such films crack, and upon release of the strain, delaminate from the surface. The likelihood of such failures increases as the films are made thicker.

In anticipation of the need to immobilize clusters on fibers and to obtain high quality films for optical experiments, we carried out a systematic evaluation of cleaning and deposition procedures that lead to high quality films. We examined a range of surface preparation techniques and found that the choice of surface preparation did not correlate with the likelihood of a film cracking. However, film thickness did correlate with cracking, with thinner films far less likely to crack. An interesting example of this phenomenon is shown in a series of slides prepared by dip coating clean slides into a sol gel solution. The sol gel film was deposited on both sides of the substrate and then the substrates were stored horizontally in small vials and allowed to dry. All of the films on the top side of the substrate (see *Figure 1*) cracked within 24 hours, while those on the bottom of slide did not. The crucial difference was that the film on the bottom face of the substrate was in contact with the walls of the vial allowing a portion of the film to flow from the slide to the wall, effectively thinning the film. These slides are shown in the micrographs in *Figure 1*.

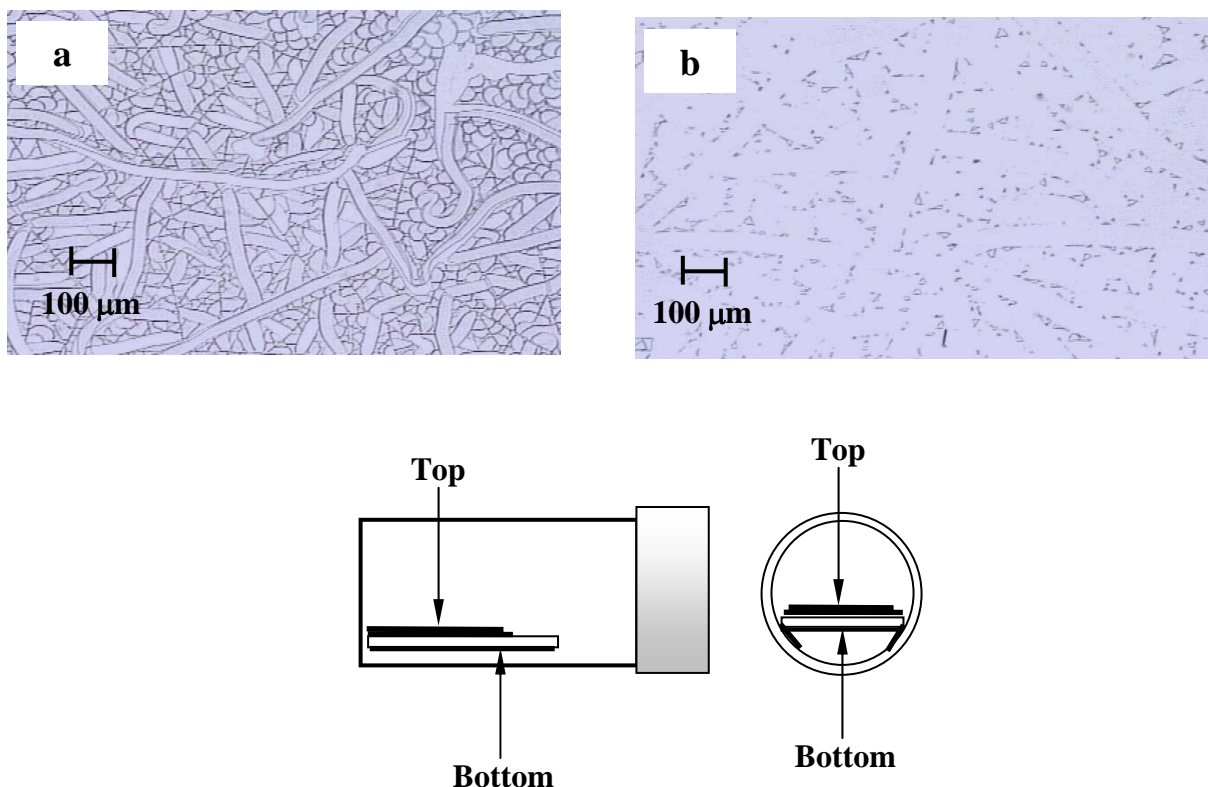


Figure 1. Optical micrographs of the surfaces of slides coated with sol gel films. (a) Top face of a slide showing the characteristic cracking pattern of thick films. (b) after applying and removing tape. Note that while nearly all of the film has been removed, the original pattern can be inferred from residual fragments of the sol gel film. The schematic at the bottom left defines the orientation of the film while drying.

Panel a shows the dried film deposited on the top side of the substrate. During the drying process, the stress induced by the drying led an interesting and extensive pattern of cracking. The cracked film has poor adhesion to the surface. As shown in panel b, applying tape to the surface followed by peeling the tape from the surface removes nearly all of the sol gel film.

Direct adsorption of clusters from solution

Since, the high temperature optical properties of molybdenum clusters can in principle, be accessed from a thin film of clusters directly attached to a surface, we tested various dip coating methods for depositing thin films on quartz slides using variations of a scheme reported by Shriver et al.^[8] We successfully prepared thin uniform films from solutions of $\text{Mo}_6\text{Cl}_{12}$ in acetonitrile. Surprisingly, these films proved to be thermally unstable compared to the bulk material, and to clusters embedded in sol gel films that we had previously prepared. In short, our observations were consistent with degradation stemming from the reaction of the silanol terminated surface of the quartz substrate and the cluster with an onset at temperatures $<200^\circ\text{C}$. We were able to rule out the possibility that the degradation was related to the high surface to volume ratio of the

clusters in the thin films by comparing thermal gravimetric analyses on clusters that had been pulverized to have a high surface to volume ratio than clusters used in previous experiments. No differences in thermal stability were observed between the two samples, thus pointing to the enhance degradation being a surface phenomenon.

Measurement of $\text{Mo}_6\text{Cl}_{12}$ luminescence as a function of temperature.

One of the critical parameters in a high temperature sensor based on luminescence quenching is the stability of the lumophore, and the temperature dependence of the luminescence, i.e. having enough photons at high temperatures to enable practical sensing. Previously we had reported preliminary luminescence data for a Mo-cluster/sol-gel film from room temperature to $\sim 200^\circ\text{C}$. We now have extended the data to 230°C in flowing N_2 (purity 99.999%), and have tested the long term stability of the lumophore. The data, shown in **Figure 3**, are the integrated signal intensity (i.e. integrating all the luminescent photons in the 580-850 nm emission band from a sol gel film containing $\text{Mo}_6\text{Cl}_{12}$. The data were collected non-sequentially, i.e., the film was not simply heated and the data collected, but instead the temperature of the sample was varied in a somewhat random fashion. As described earlier, sample heating was carried out by attaching platinum heaters to the back face of the substrate. The measured luminescence intensity follows an approximately $1/T$ relationship from room temperature to 150°C , and then declines more slowly at higher temperatures. At the highest temperature measured, (230°C) the absolute number of photons leads to a signal to noise ratio >5 , ensuring that no special optics will be required fiber based detection of oxygen at high temperatures. Similar measurements on sol gel films containing $\text{K}_2\text{Mo}_6\text{Cl}_{12}$ are in progress.

Of note is that the measurements were made on a film that was ~ 1 year old that had been thermally cycled to $T.>200^\circ$ several times. Despite the repeated cycling, the luminescence intensity of the film had not diminished, but instead had increased. While the reason for the change in luminescence is not certain, it is likely related to the continued evolution of the sol gel matrix.

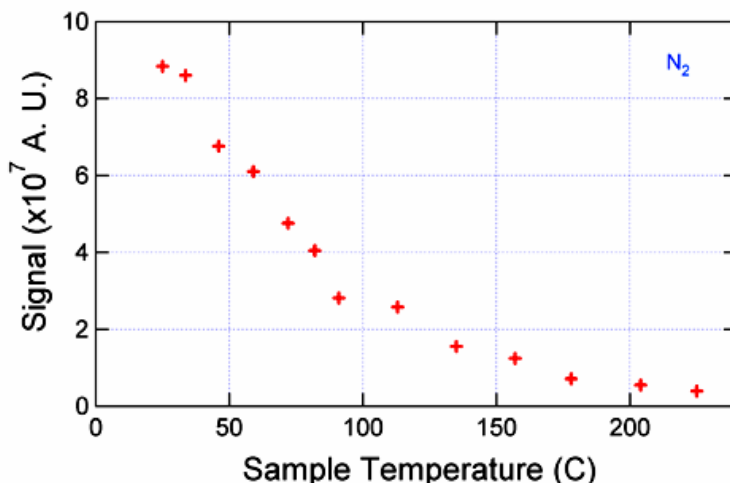


Figure 2. Integrated luminescence intensity (580 - 850 nm) of Mo-cluster/sol gel composite film 15F as a function of temperature. The measurements were taken in flowing nitrogen. The data were collected non-sequentially with respect to temperature.

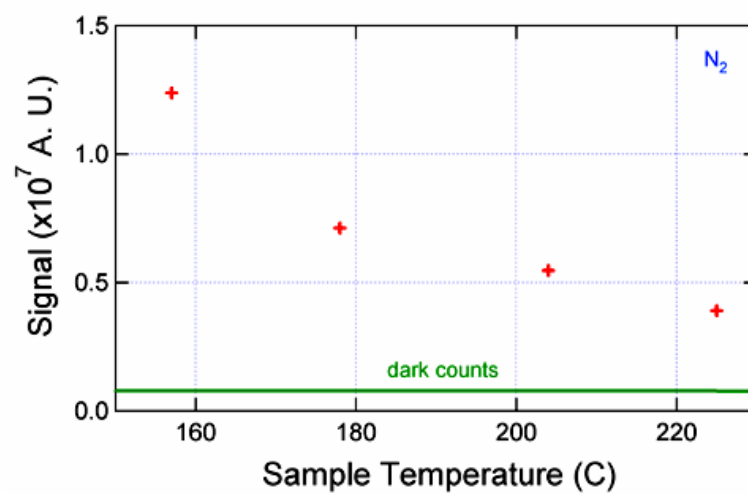


Figure 3. Data of Figure 4, expanded to show the high temperature signal intensity. The dark counts from the photomultiplier, shown in green, leads to a signal to noise ratio >5 .

CONCLUSIONS

We have defined the experimental parameters that lead to uniform sol gel films containing molybdenum clusters. The films have no cracking and exhibit excellent adhesion to substrates. Molybdenum clusters were successfully immobilized in sol gel films at the end of optical fibers. As with planar substrates, thick films crack and failed mechanically, but thin films were uniform and robust.

High temperature measurements of the emission of clusters in sol gel films show that the luminescence intensity from the films follow a $1/T$ relationship from room temperature to 150 °C, and then declines at a slower rate at higher temperatures. The large number of photons available at 230 °C is consistent with simple low cost optics for fiber optic probes based on the emission from clusters in sol gel films.

REFERENCES

- [1] R. D. Mussell, Ph. D. thesis, Michigan State University (East Lansing), **1988**.
- [2] M. D. Newsham, Michigan State University (East Lansing), **1988**.
- [3] M. D. Newsham, M. K. Cerreta, K. A. Berglund, D. G. Nocera, *Mater. Res. Soc. Symp. Proc.* **1988**, 121, 627.
- [4] C. J. Ruud, Ph. D. thesis, Michigan State University (East Lansing), **1999**.
- [5] R. N. Ghosh, G. L. Baker, C. Ruud, D. G. Nocera, *Appl. Phys. Lett.* **1999**, 75, 2885.
- [6] J. T. Remillard, J. R. Jones, B. D. Poindexter, C. K. Narula, W. H. Weber, *Appl. Opt.* **1999**, 38, 5306.
- [7] J. C. Sheldon, *J. Chem. Soc.* **1960**, 1007.
- [8] L. M. Robinson, H. Lu, J. T. Hupp, D. F. Shriver, *Chemistry of Materials* **1995**, 7, 43.

BIBLIOGRAPHY

None.

LIST OF ACRONYMS AND ABBREVIATIONS

Moly Oil – $\text{Mo}_6\text{Cl}_{12} \cdot 2\text{CH}_3\text{CN}$ in acetonitrile

HCl – Hydrochloric Acid

MeOH – Methanol

CH_3CN – Acetonitrile

TEOS – Tetraethyl orthosilicate