

Sol-Gel based Optical Ammonia Gas Sensor

Susanne Widmer^{1,2}, Marko Dorrestijn¹, Edwin C. Constable², Lukas J. Scherer¹

¹Empa, Swiss Federal Laboratories for Material Science and Technology,
Laboratory for Protection and Physiology,
Lerchenfeldstr. 5, St. Gallen, Switzerland

Correspondence: susanne.widmer@empa.ch

²University of Basel, Department of Chemistry,
Spitalstr. 51, Basel, Switzerland

Abstract

State of the art gas sensors usually are hand-held devices. The development of a gas sensor system based on flexible polymer optical fibers, which finally can be integrated into textiles, would increase sensor wearability. As a model system, sol-gels with different mixtures of coumarin and fluorescein were coated on PMMA plates, which were exposed to gaseous ammonia. Significant differences in fluorescence intensity were observed for different dye mixtures. First sensor measurements with dye-doped sol-gel coated PMMA plates showed response to gaseous ammonia.

Key words: Ammonia sensor, polymer optical fibers, sol-gel, coumarin, fluorescein

Introduction

In recent years, various optical fiber based evanescent gas sensor systems have been reported [1-3]. The use of sol-gel materials as a porous support material has emerged as a promising means to produce glass fiber based chemical sensors [1,3]. However, glass fibers are too brittle to be integrated into textiles. Our aim is to coat dye doped sol-gels onto flexible polymer optical fibers (POFs) [4]. Flexible sol-gels can be obtained using organic modified silicates (ormosils) as the precursors instead of common orthosilicate precursors [5]. For proof of concept, sol-gels doped with coumarin (Cou) and fluorescein (FI) dyes were prepared and spin coated on poly(methyl methacrylate) (PMMA) plates. Coumarin and fluorescein were chosen in combination, since this system exhibit a large Stoke shift due to the Förster resonance energy transfer (FRET) and a high quantum yield [6].

The sensitivity of the resulting xerogel films towards gaseous ammonia was measured with a gas sensor setup built in-house. Best dye mixtures and most efficient emission wavelength to detect gaseous ammonia were found using fluorescence spectroscopy.

Experimental

Gas-sensing sol-gels were produced by adding ormosil precursors, fluorescein (FI) and coumarin (Cou) to ethanol. The gelation was acid catalyzed. The PMMA plates were coated

with sol-gel, followed by drying to form xerogel coated PMMA plates.

For fluorescence spectroscopy measurements, plates were pinched into a microtitre plate. The xerogels were exposed to gaseous ammonia by adding aqueous ammonia solutions into the wells.

For gas sensor measurements, coated plates were placed into a gas sensor setup (Fig. 1).

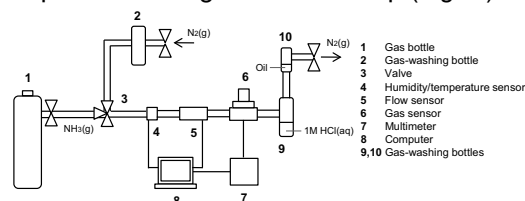


Fig. 1. Gas sensor setup

Results and Discussion

Best emission intensities for Cou and FI and Cou/FI mixtures were found by excitation at 375 nm and 481 nm, respectively. Cou xerogels emitted with one band centered at 447 nm whereas FI xerogels emitted with a main band at 540 nm and a slight shoulder at 520 nm, which corresponds to the anionic and dianionic forms [7] (Fig. 2). For Cou/FI mixtures, different spectra were obtained which is due to FRET. For fluorescence spectroscopy studies, the same conditions as in the sensor system were imitated by exposing xerogels to water vapour and gaseous ammonia. Water vapour had no significant effect on the absorption/emission wavelengths or fluorescence intensity. In Cou/FI

mixtures, the Cou emission at 447 nm, as well as FI emission at 518 nm were almost entirely quenched when exposed to gaseous ammonia (Fig. 2).

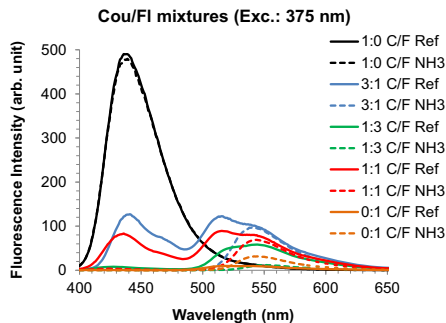


Fig. 2. Emission spectra (excitation at 375 nm) of Cou/FI mixtures. Ref: xerogel coated plates with corresponding dye mixture. NH₃: sol-gel coated plates exposed to 1.3% NH₃(aq).

The spectra revealed that excitation at 375 nm and detection of emission at 400–500 nm gave the highest response signals. Further fluorescence experiments on different ratio of Cou/FI in the sol-gel showed that the 1:1 Cou/FI mixture is a promising candidate for sensing ammonia gas (Fig. 3).

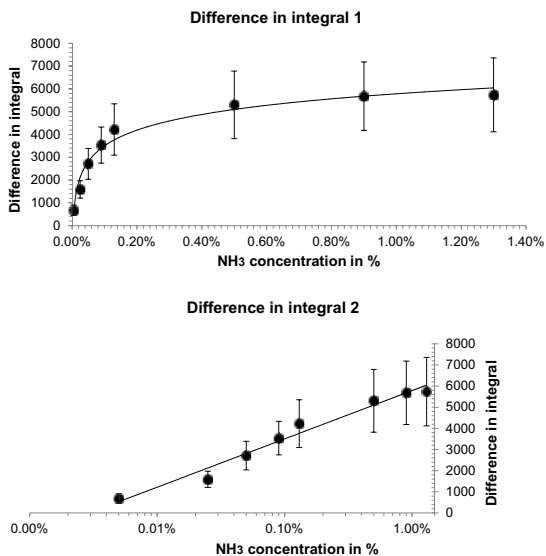


Fig. 3. Emission peak area vs. NH₃ concentration for Cou/FI=1:1 (linear and semi-log plots). The peak area is defined as the increase in the integral of the emission spectrum from 408–460 nm.

The trend is approximately – although not strictly – logarithmic. The exposure to different concentrations of ammonia of only Cou or FI doped xerogels showed limited sensitivity when excited at 375 nm respectively 481 nm and no trend could be observed. This finding indicates that the FRET between the dyes played an important role in the sensing mechanism. High

dye concentrations did not lead to higher fluorescence emission due to self-quenching. Gas sensor measurements were performed on a 1:1 Cou/FI xerogel (Fig. 4).

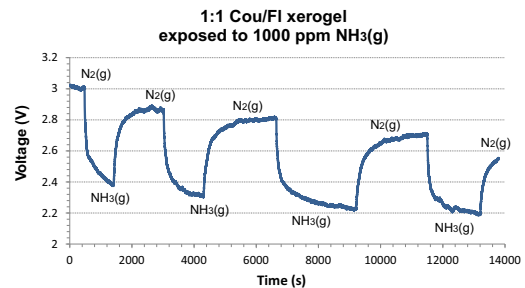


Fig. 4. Gas sensor measurements on 1:1 Cou/FI xerogel on PMMA. The plate was illuminated at 375 nm from the top. A band pass filter allowed light from 408–460 nm reaching the perpendicular installed detector. By turning the valve it could be alternated from N₂(g) to NH₃(g) (1000 ppm).

The sensor measurements confirmed the usefulness of the ormosil-PMMA system as a sensor system. The decrease in fluorescence at 440 nm due to the presence of ammonia leads to a fast decrease in voltage. The detection limit was below 100 ppm. The effect is reversible and reproducible when the sensor is flushed with N₂(g). A baseline shift was observed which is may be caused by irreversible adsorption of a certain ammonia amount from the xerogel and/or from thermal drift of the electronics. An undoped xerogel was measured as a reference that did not show any decrease or increase in voltage when exposed to gaseous ammonia.

Conclusion

PMMA plates coated with dye doped sol-gels were used as a model for POF ammonia gas sensing. Optimal Cou/FI mixtures and excitation/emission wavelengths were found using fluorescence spectroscopy leading to a linear NH₃ response. First measurements with a gas sensor device showed sensitivities of low ppm values. Once the sensor system has been optimized, it will be applied to POFs. The final integration of this technology into textiles will lead to higher sensor wearability. This platform technology can be applied to detection of other toxic industrial chemicals (TICs) and chemical warfare agents (CWAs) to protect employees in chemical industries and first responders.

Acknowledgements

We gratefully thank J. Gschwend and his workshop team for the implementation of our sensor designs.

References

- [1] S. T. Lee, et al, *Journal of Optics A: Pure and Applied Optics* 3, 355-359 (2001); doi:10.1088/1464-4258/3/5/307
- [2] Y. Huang, S. Tao, *Journal of Sensor Technology* 1, 29-35 (2011); doi: 10.4236/jst.2011.12005
- [3] B. D. Gupta, S. Sharma, *Optics Communications* 154, 282-284 (1998); doi: 10.1016/S00304018(98)00321-6
- [4] M. Dorrestijn, et al, *The 14th International Meeting on Chemical Sensors*, Nürnberg, Germany, 448-449 (2012); doi: 10.5162/IMCS2012/5.2.5
- [5] Y. Hu, J. D. Mackenzie, *Journal of Materials Science* 27, 4415-4420 (1992); doi: 10.1007/BF00541574
- [6] D. M. Goodall, D. R. Roberts, *Journal of Chemical Education* 62, 711-714 (1985); doi: 10.1021/ed062p711
- [7] R. Sjöback, J. Nygren, M. Kubista, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 51, L7-L21 (1995); doi: 10.1016/0584-8539(95)01421-p