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Colorimetric CO and NO_2 Gas Sensors for Fire Detection

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Abstract:
We present the development of a novel CO and NO_2 sensing principle using gasochromic materials. The sensor set-up works with a very low power consumption to enable their usage in commercial fire detection systems. CO and NO_2 are both typical fire indicating gases. For the detection of CO we used a binuclear rhodium complex. NO_2 can be detected using the chinonime dye N,N,N',N'-tetramethyl-phenylene-diamine. Both dyes were embedded into a highly porous polymer and deposited on planar optical waveguides by spin coating. The capability of the developed sensors was shown in a real fire lab, regarding different standardized test fires.

Key words: gas sensor, evanescence field, colorimetric sensor, fire detection

Introduction

Reliable fire detectors are very import for everyday's life. Most commercial detection devises are so-called scattered light sensors. In case of a fire, the light of a LED gets diverted on fume particles and is focused on a photo detector. This causes the fire alarm. The principle bases on the assumption that all fires produce fume particles. These detectors are low-priced and work for many years, but they have other disadvantages. An alarm can not only be caused by a fire, also by other particle producing events like cooking, hot shower etc. To detect fires with higher probability, it's important to detect typical fire gases like carbon monoxide (CO) and nitrogen dioxide (NO_2). Both gases are very toxic and shouldn't appear in rooms under normal conditions. Requirements for commercial fire detectors are that they are low-cost and low-power and work with a battery for up to ten years. This is unfortunately not realizable using commercial affordable metal-oxide gas sensors.

In this publication we present an alternative measurement principle to detect CO and NO_2 reversible in fire typical concentrations without interfering sensitivities to other gases.

Experimental

The improvement is the detection of CO and NO_2 using a colorimetric effect.

As gasochromic material for CO detection we used a binuclear rhodium complex embedded into a porous ethyl cellulose matrix. The complex has been characterized in [1]. The performance of a congeneric Rh-complex to CO has been described in [2]. The complex has been synthesized analogue to [1], fig. 1 shows the reaction of the rhodium complex to CO.

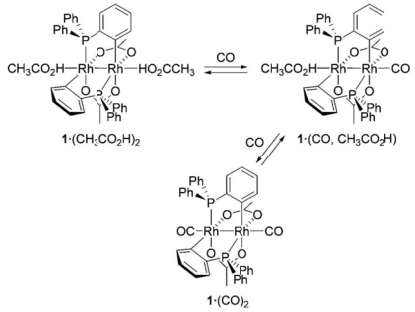

Fig. 1. Reaction of the rhodium complex to CO. This reaction induces a color change from violet to yellow [3].

For NO_2 detection we investigated N,N,N',N'-tetramethyl-phenylene-diamine (TMPD). TMPD, also called *Wurster's blue*, is a chinonime dye, which was embedded into a polyvinyl chloride (PVC) matrix. Fig. 2 shows the reaction of TMPD (left) to NO_2. The centered molecules are two different forms of the radical cation, which is blue. A second oxidation step reacts to the colorless di-cation (right). The equilibrium lies on the side of the blue cation [3].

Spectroscopic measurements have been performed with both dyes. The spectra were recorded using a *Perkin Elmer Lambda 900* spectrometer. On the basis of the spectra it's possible to determine the region of maximum wavelength shift due to gas exposure.

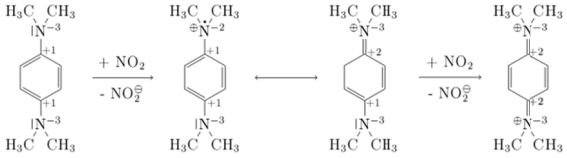

Fig. 2: Reaction of TMPD (Wurster's blue) to NO_2. The TMPD (left) gets oxidized to a blue cation. Another oxidation steps generates the colorless di-cation (right). The equilibrium lies on the first oxidation step (middle).

Laboratory tests

Fig. 3 shows the transmission spectra of both dyes during gas exposure. The Rh-dye was embedded into an EC-matrix and exposed to 240 ppm CO at 40% r.H. in ambient air. The exposure leads to an increasing of the maximum transmission at 485 nm, resp. to a decreasing at 560 nm. TMPD was embedded into a PVC –matrix and exposured to 5 ppm NO_2 at 40% r.H. in ambient air. The gas generates three new minimums at 456 nm, 568 nm and 622 nm.

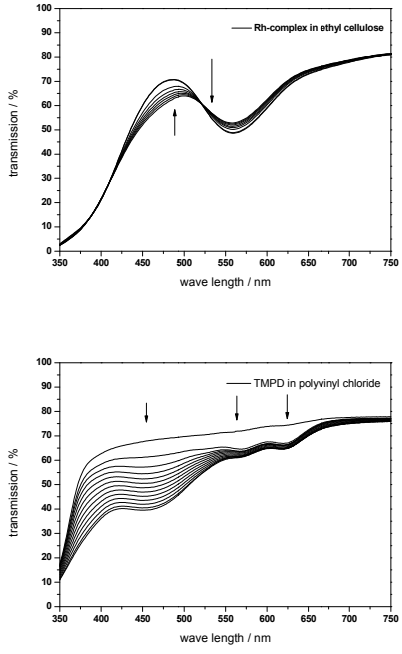

Fig. 3. Above: transmission spectra of Rh complex to 240 ppm CO at 40%r.H. in ambient air. Down: reaction of TMPD to 5 ppm NO2 at 40% r.H. in ambient air.

Sensing principle

The sensors work after a colorimetric principle. Thereby, the color of a dye changes due to gas exposure. This principle is widely used in so-called Dräger gas tubes® [4].

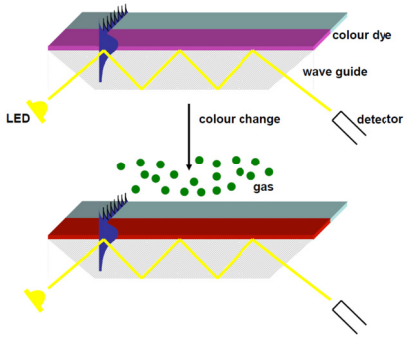

Fig. 4: Sketch of the microscope slide. The lower half is covered with the gasochromic dye. The light of an LED is coupled into one end of the waveguide and travels trough it under TIR before it is focused onto a photo detector. Changes in the color of the dye, due to a gas reaction can be detected by changes in the out-coupled light.

But, in comparison to these gas tubes, a sensor has to work independently without the assistance of an operator. Our measurement principle bases on changes in the evanescence field of the dye. To detect this, the dye gets deposited on planar optical waveguides. The used sensing principle has been already described in detail in [5]. A sketch of the colorimetric sensing principle is shown in fig. 4; fig. 5 shows the realized sensor with integrated electronic for signal processing.

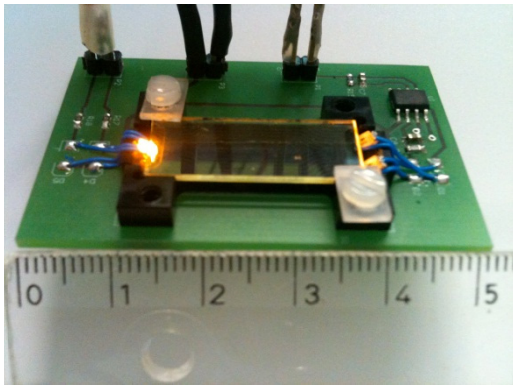

Fig. 5: Photograph of the developed sensor set-up. The implemented sensor is deposited with the TMPD dye. The usage of SMD electronics minimizes the set-up tremendously.

It was our aim to use only sensor for both gases. The transmission spectra show, that the highest shift in transmission is in the area about 460 nm. Due to this fact we integrated a blue LED (λ_{max}= 470 nm) in the system.

Real fire tests

With the developed sensor set-up real fire gas measurements were performed. The test fires were carried out in a 240 m^3 fire lab, analogue to the standardized test fires in EN 54. These test fires differ in their fire material and in consequence in their gas composition. We regarded the two test fires TF 2 and TF 6. TF 2 is a wood based smoldering fire with low heat development, but smoke emission. Compared to this, TF 6 is an ethanol liquid fire with strong heat development but without any smoke emission. TF 6 is a perfect example of the need of gas based fire detectors [6]. The results of these test fires to the colorimetric sensors are shown in fig. 6 resp. fig. 7.

The dyes were spin coated for 20 sec. with 2000 RPM on 1 x 3.8 cm^2 big optical wave guides. The dyes had a resulting thickness of 1 µm for TMPD, resp. 1.6 µm for the Rh-complex.

Fig. 6 shows the reaction of the Rh-complex to TF 2. During the test, beech wood was heated up, till it started to smolder. After 37.3 min the CO concentration reaches 86 ppm. The colorimetric sensor changes his output signal about 18 mV from 271 mV to 253 mV. After ventilation the sensor needs 4.7 min to reach again its T_{90} value. The actual CO concentration was recorded with a Binos 100 [7] gas analyzer.

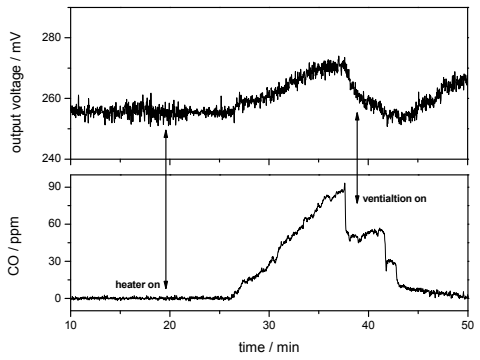

Fig. 6. Reaction of the Rh-dye to TF2. The output signal of the colorimetric sensor is analogue to the reference CO sensor.

The TMPD dye was exposed to TF 6. According to EN 54, the NO_2 concentration can reach up to 2 ppm. The recorded measurement is shown in fig. 7. For fire generating, 2.53 liters ethanol were inflamed. After burning for 10 minutes the following gas concentrations are detectable: CO: 4.68 ppm; CO_2: 8110 ppm; NO: 1785 ppb and NO_2: 695 ppb. The output voltage of the colorimetric sensor decreases from 503 mV to 158 mV during NO_2 exposure. This is a signal change of 69%. After 10 minutes the fire was extinguished and the room was ventilated. After 24 minutes the sensor reaches his T_{90} value again.

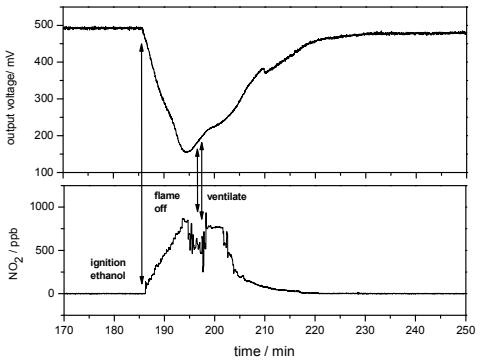

Fig. 7. Reaction of TMPD to TF6. The output signal of the colorimetric sensor is analogue to the reference NO_2 sensor.

Conclusion

We presented the development of colorimetric gas sensor; especially regarding two different dyes to detect the fire indicating gases CO, resp. NO_2. Both dyes were embedded into polymer matrices and deposited on optical waveguides by spin coating. UV/VIS measurements showed the color change of both materials in the blue wavelength area. A demonstrator was built up, to perform real fire tests. The sensors were exposed to the two standardized test fires TF 2 and TF 6. Both dyes show an excellent gas depending behavior. The measured sensitivities are 0.2 mV/ppm(CO) for Rh, resp. 494 mV/ppm(NO_2) for TMPD.

We have shown, that these colorimetric sensors a promising alternative to commercial low-cost gas sensors for reliable fire detection.

Acknowledgements

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