COLORIMETRIC MATERIALS FOR GAS SELECTIVE SENSING IN LOW-POWER APPLICATIONS

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ABSTRACT

One approach to realize selective chemical sensors is the integration of colorimetric materials as gas sensitive substances. Color changes, due to the reaction with the target gas, can be detected optically. These kinds of sensors offer various advantages, such as fast response times and the use of simple instrumentation. Being selective, reliable and energy-saving, the integration into different low-power applications such as fire detectors, RFID-labels or energy autarkic systems and sensor networks is possible. Therefore a low-cost and fully reversible sensor system capable to detect CO, NO_2, NH_3 and C_2H_4 at low concentrations in air was developed.

KEYWORDS

gasochromic color dyes, absorption based measurement, selective gas detection, low-power application

INTRODUCTION

The investigation of color dyes for sensing has a very long history. The most prominent representatives are surly pH indicator stripes, which are used for the determination of the pH value of liquids. Next to pH stripes there are other commercially available chemosensitive sensors. Gas sensitive color dyes, further called gasochromic dyes, are chemically known since many years.

Often sensors do not need a high accuracy, but a compact setup, long-term stability, low energy consumption and low fabrication costs. Chemosensitive sensors, in combination with a suitable measurement technique, enable such a development for manifold applications, like fire detectors, environmental monitoring, control of perishable goods, biomedicine etc.

In this presentation we will give an overview of the gasochromic detection of CO, NO_2, C_2H_4 and NH_3, concerning different color dyes, measurement principles and their advantages and disadvantages.

STATE OF THE ART

One gasochromic reaction of CO was already described by Martinek in 1928 [1]. He detected CO in air and blood using iodine pentoxide, which changes its color from white to brown. The detection limit was determined to be 10 ppm. Unfortunately this reaction is irreversible, so it is not suitable for the application in many fields. Other frequently used color dyes are palladium compounds like palladium chloride or palladium ammonia molybdate [2]. Other CO sensitive dyes are metal-complexes like porphyrines. The most famous CO sensitive porphyrine is the “color dye” of our blood – hemoglobin. Another complex, with reported high selectivity features, is an iron pincer complex. As solid state, the color changes from yellow to red, in solution from yellow to blue. The reverse reaction takes five minutes at 100°C, which is far too long for many sensing applications [3] We investigated another complex family, which was first described by Esteban in 2010 [4]. It is a binuclear rhodium complex, which can bind up to two CO molecules in axial position. The reaction principle was already described in [5].

As for CO detection, there are a lot of different gasochromic materials to detect NO_2. The first published and mostly cited gasochromic proof of NO_2 was described by Saltzman et al. in 1954 [6]. Due to their chemical nature, many metal complexes are also suitable. The working group around Spichiger-Keller published investigations on NO_2 sensitive membranes. They consist of a Co(III)-cobyrinate and chrome ionophore. In contact with NO_2, the chrome ionophore gets protonated to a Nile blue derivate. This leads to a reversible color change from blue to yellow. The Co(III)-cobyrinate catalyzes the reaction resulting in decreasing reaction constancy [7, 8]. This sensing mechanism was pushed to develop a low-power gas sensor for fire gas detection. Therefore the membranes were deposited on photo detectors and arranged as an array of always four detectors surrounding a red LED. The measurement range was described between 25 and 800 ppb NO_2. Yet the dye could not be used due to the low chemical stability of the dye above 50°C. Next to this there are a couple of further complexes with chromosensitive behavior described in [9, 10]. The gasochromic reactions of chinonimine color dyes to NO_2 were described by Alexy in 2006 [11]. He detected the color change of N,N’-diphenyl-1,4-phenylendiamine, o-dianisidin, N,N’-diphenylbenzidine and N,N,N’,N’-tetramethyle-p-phenylene diamine (TMPD) in transmission. Long term stabilities of about one year were stated. The detection limit is below 0.1 ppm. We investigated TMPD, which is also known as Wursters blue [12].

The chemosensitive proof of NH_3 is certainly one of the first. Already in 1976 David et al. reported on the gasochromic detection of gaseous ammonia. They coated quartz cylinders with ninhydrin and polyvinylpyrrolidone. By this they reached detection limits in the lower ppb range. Unfortunately this reaction is irreversible and not suitable for gas sensors. Guiliani et al. coated capillaries with pH-sensitive oxacine perchlorate and used them as optical waveguides. This detection is reversible for ammonia concentrations between 60 and 1000 ppm. Often the pH-indicator dye

bromophenol blue is used [13, 14]. Due to its high sensitivity to NH_3 and easy handling, we used this dye throughout the experiments described in this paper. A detailed overview on the state-of-the-art on pH-based ammonia sensors is given in [15].

The gasochromic reaction of ethylene was by now rarely described. The use of molybdenum blue can be found in [16-18]. Due to the reduction form Mo(VI) to Mo(V) in ethylene atmosphere, the indicator changes its color from light yellow to blue. Palladium (II) can be used as catalyst.

SENSOR SETUP

One opportunity is to measure absorption changes in the reflected light of the chemosensitive probe. Fig. 1 shows the setup. The sample is illuminated by a light source, which can simply be an LED, and the reflected light can be measured by a photo detector. In this case the sample has to be prepared as a planar solid. In combination with NH_3 sensitive dyes this principle was described by [19]. The color of the LED depends on the spectral range of the color change of the dye. In both cases, the detectable signal is often very small, although the color change is clearly visible. In case of UV/VIS-measurements, the sample will be measured only once - regarding the law of Lambert-Beer, it is obvious that the thickness of the probe is crucial. By measuring the reflected light as in fig. 1, only changes at the surface of the dye are detected. Changes inside the sample are not captured.

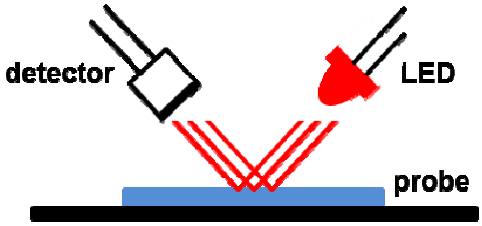

Figure 1: Measurement setup to detect gas dependent color changes of a dye by the reflected light of a LED.

One way to improve the sensitivity of the sensor system is to apply waveguide based measurements. Here, the color dye is deposited onto an optical waveguide. The light of an LED is coupled into one end of the waveguide and passes through it under the conditions of total internal reflection (TIR). The color change of the sensitive dye can be detected by absorption changes inside the layer and by changes in the evanescent field. After coupling out, the light is focused on a photo detector. Changes in the dye induce direct changes in the intensity of the light. Compared to measurements in transmission, the waveguide principle has much lower detection limits, caused by the longer optical path. As in the case with reflection-based measurements, the LED should cover the spectral range of the color change. This measurement principle has already been described in [13]. To be independent from environmental influences, a reference channel is embedded additionally.

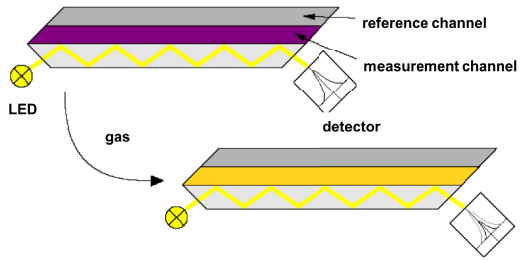

Figure 2: Sketch of the gasochromic sensor, consisting of a planar optical waveguide, covered with the chemochromic film.

EXPERIMENTAL

For CO detection we adapted a binuclear rhodium compound (Rh-C), which was first described in 2011 [4]. It is capable of changing its color by ligand exchange when exposed to CO in synthetic air. Even at very low CO concentrations a reversible color change from purple to yellow can be observed within minutes (fig.3). For NO_2 detection, we investigated the color dye N,N,N',N'-tetramethyl-phenylene-diamine (TMPD). This is a chinonimin dye, which changes its color from brown to blue already at NO_2 concentrations of 100 ppb. Any basic material can be detected optically with pH indicators, which change their color depending on the actual pH-value. This principle can be adapted for the sensing of ammonia in the low ppm range. A color change of ethylene can be detected with a solution of ammonium molybdate with palladium catalysts. The reaction with ethylene leads to reversible color changes from limpid to blue up from 2 ppm C_2H_4 (fig. 5).

We investigated the reflection behavior of the rhodium complex. Therefore we diluted the color dye in ethanol and stirred it with silica gel. After reaching a homogeneous mixture, the solution was dried in air for 24 hours. Thereby we get colored silica gel. This gel can be integrated into our measurement setup, as shown in fig. 1.

For all transmission-based measurements we embedded the color dyes, which are usually a powder, in a polymer matrix. This matrix has to fulfill the following requirements: high porosity for diffusion of the target gases, inert to environmental influences like humidity, temperature and radiation, inert to the colorimetric material and ideally the same solvent as the dye. Possible polymers are poly vinyl chloride (PVC), polydimethylsiloxan (PDMS), ethyl cellulose (EC) and/or poly methylmethacrylate (PMMA). Each dye/polymer combination is unique and has to be determined individually. The liquid sensitive matrix can be deposited onto the waveguide by dip- or spin coating.

RESULTS

In the following we will give an overview of the results of our work and selected measurements will be shown. The color change of the binuclear rhodium complex is shown in figure 3. It is deposited on silica gel during exposure to 200 ppm and 1000 ppm in synthetic air with 50% relative humidity. The according measurement is shown in figure 4.

Figure 3: Color change of the binuclear rhodium complex deposited on silica gel during exposure to 200 ppm and 1000 ppm in synthetic air with 50% relative humidity.

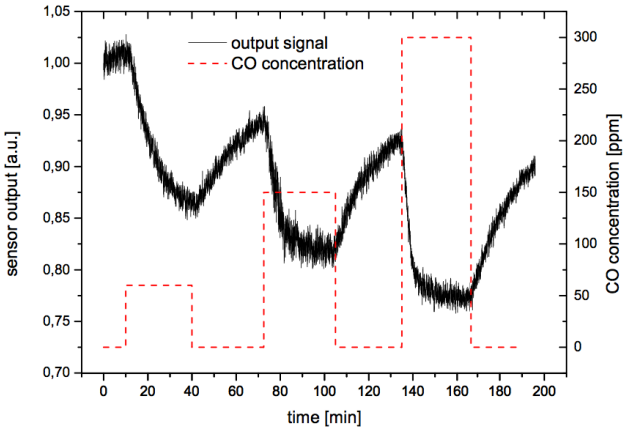

Figure 4: Reaction of the rhodium complex, adsorbed on silica gel, during exposure to 50, 150 and 300 ppm CO in synthetic air.

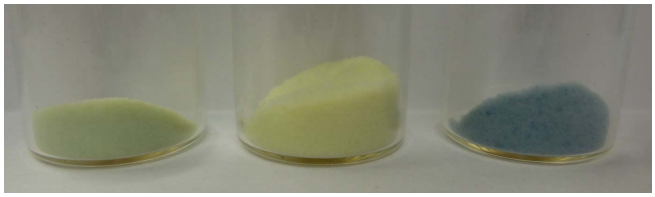

Figure 5: Color change of MO7:Pd before (b) and after (c) the exposure to 20 ppm ethylene. After the gasochromic reaction, the probe was rinsed with synthetic air for another 20 minutes, to reach the original state again (a). The measurement was performed in synthetic air with 40% r.H.

The C_2H_4 sensitive dye MO7:Pd was adsorbed on silica gel, similar as the rhodium complex. The gasochromic reaction to ethylene is shown in figure 5. In this case, the probe was exposed to 10 ppm C_2H_4 for 20 minutes (c). Afterwards the same probe was rinsed with synthetic air for another 20 minutes. The reverse reaction is shown in (a). This measurement was performed in synthetic air with 40%r.H. To compare the results, (b) shows the probe before any exposure to the target gas. The gasochromic color change from bright yellow to blue is clearly visible. Figure 6 shows the measurement, recorded with a Perkin Elmer Lamda 900 UV/VIS spectrometer. Figure 7 shows the absorption changes of TMPD to different concentrations of NO_2 between 500 ppb and 4 ppm as changes in the output signal of the photodiode. This measurement was performed using a planar waveguide setup. Different concentrations of NO_2 can be detected. In contrast to the gasochromic reaction of the rhodium complex to CO, the reaction of TMPD has an irreversible part. Depending on the application, this dye might be not useful. The gasochromic reaction of bromophenol blue (BPB) is shown in figure 8. The color dye was deposed to 1 ppm, 5 ppm and 10 ppm NH_3, in synthetic air with 40% r.H. This measurement was also performed using an optical waveguide setup. The dye was embedded into an ethylcellulose matrix. The sensor responds to all concentrations, with response times between four and ten minutes depending on the concentration. The detection limit of this sensor can be estimated in the lower bbp range.

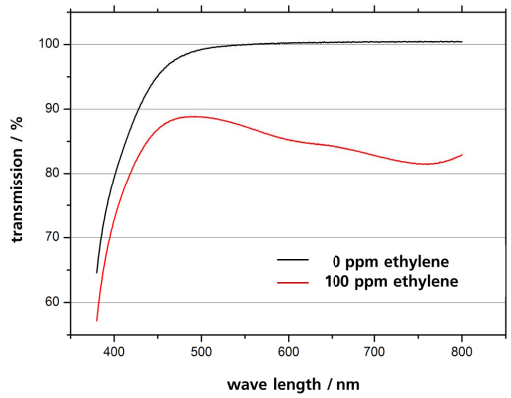

Figure 6: Transmission spectra of Mo_7:Pd (solved in chloroform) before and after the reaction to 100 ppm ethylene in the visible range.

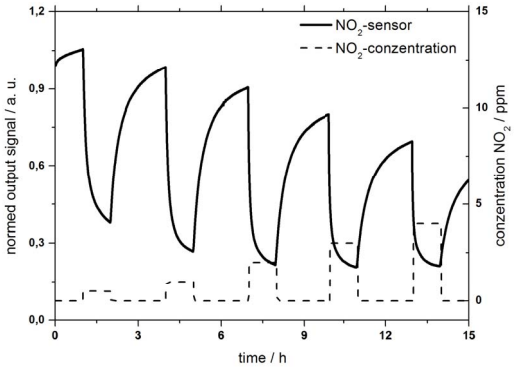

Figure 7: NO_2 dependent measurement of TMPD in PVC, realized with a planar optical waveguide setup. The sensor was exposed to 0.5 ppm, 1 ppm, 2 ppm 3 ppm and 4 ppm NO_2, each for one hour.

Table 1 gives an overview of the color dyes, their measurement range to the target gases and the wavelength of the maximum absorption changes.

Colorimetric Material	Target gas	Measurement range	Max. absorption
Rhcomplex	CO	10 – 10000 ppm	480 nm
TMPD	NO_2	100 ppb – 5 ppm	460 nm
pH indicators	NH_3	0,5 – 50 ppm	560-630 nm
MO_7:Pd	C_2H_4	2 – 100 ppm	750 nm

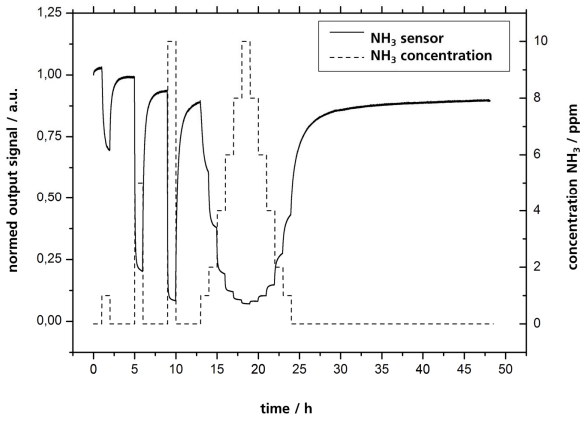

Figure 8: Reaction of bromophenol blue to different concentrations of NH_3 between 1 ppm and 10 ppm. The measurements were performed using a waveguide principle

CONCLUSION

In this paper we give an overview of different gasochromic materials for the detection of CO, NO_2, NH_3 and C_2H_4. The materials were investigated using spectroscopic techniques. Two different options of sensor setups were described. Waveguide based measurements are very sensitive, due to their long optical path length, but suffer from long-term stability due to the usage of polymers as matrices. Reflection based measurements have the advantage of being independent to a polymer matrix, but only near-surface changes are detectable. The selection of a suitable sensor setup has to be done individually depending on the application and requirements.

We have shown that gasochromic color dyes enable sensitive and selective gas sensing. A summary of the investigated materials, their target gases, measurement range and maximum adsorption change is given in table 1.

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