

# Screen-Printable Colorimetric Sensors for the Monitoring of Toxic Gases in Ambient Air

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## I. SUMMARY AND MOTIVATION

We present a fast and simple method to monitor toxic gases in ambient air based on a visible color change of a printed paper sensor, which can be evaluated using a camera (e.g. smartphone) or naked eye. This study focuses on the development of gas-sensitive pastes for the processing of the colorimetric material by screen printing. Indicators for the detection of ammonia ( $\text{NH}_3$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ) and formaldehyde ( $\text{CH}_2\text{O}$ ) were examined in closer detail. The sensing properties of the respective indicator towards the target gas was characterized via UV/Vis spectroscopy in reflection.

## II. ADVANCES OVER PREVIOUS WORKS

When dealing with gases a lack of risk awareness, insufficient information or even human error are ubiquitous. For this reason, the monitoring of toxic gases is very relevant in many areas, especially in terms of occupational safety but also for the control of environmental and chemical processes. Colorimetric sensors offer a good low-cost and low-power alternative for fast and selective detection of toxic gases in the surrounding air.



Fig. 1. Schematic illustration of the sensor principle. Colorimetric disposable sensor for the determination of toxic gases in the ambient air.

Figure 1 illustrates the sensor principle of a disposable colorimetric paper sensor. The sensor consists of a paper/plastic substrate on which the gas-sensitive material is deposited by means of printing processes. Ideally, the colorimetric material responds selectively to only one target gas with a characteristic color change. To protect the sensor against environmental influences and aging it should be packaged gas-tight after the print. If the sensor is used, the selective color change due to the contact with the target gas can be evaluated contemporarily. This measurement principle enables a simple and simultaneous analysis of the target gas concentrations in complex gas

mixtures. The content of the present study examines the gas-sensitive behaviour of indicators for the detection of  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and  $\text{CH}_2\text{O}$ .

## III. RESULTS AND METHODOLOGY

A white paper coated with poly(*p*-phenylene oxide) (PPE) served as substrate for the sensor manufacture. The substrate has an acidic pH value and is well suited for the evaluation by camera due to its pronounced matt surface. For the manufacture of a screen-printable paste, the color dyes were dissolved in ethanol and embedded into an ethyl cellulose matrix (ethoxyl content 48%, ALDICH Chemistry, St. Louis, MO, USA) using tributyl phosphate ( $\geq 99.0\%$ , SIGMA-ALDRICH, St. Louis, MO, USA) as plasticiser. In addition, various printing aids were investigated with respect to their influence on the gas-sensitive behaviour of the colorimetric layer. The color change was characterised by UV/Vis spectroscopy (Perkin-Elmer Lambda900, Perkin-Elmer, Waltham, MA, USA) with a setup for diffuse reflection (Praying Mantis, Harrick Scientific Products Inc., Waltham, MA, USA) to different gas and humidity concentrations. The general description of the gas measurement station is given in [1].

For the detection of  $\text{NH}_3$ , the commercial available pH indicator bromocresol green (indicator grade, AppliChem, Darmstadt, Germany) was investigated as color dye. The indicator reacts reversible with  $\text{NH}_3$  and changes color from yellow via green to deep blue in the pH range 3.8-5.4.

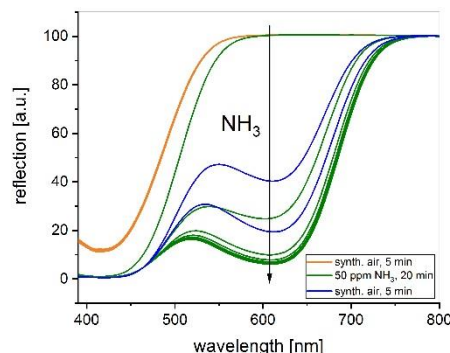


Fig. 2. UV/Vis spectra (in reflection) of the embedded  $\text{NH}_3$  indicator on PPE coated paper to 50 ppm  $\text{NH}_3$  and a relative humidity of 40% at room temperature. Recording of 15 measurement cycles every 2 min.

Figure 2 shows the color change of the developed  $\text{NH}_3$  paste to 50 ppm  $\text{NH}_3$  exposed for 20 min. The recording consists of

15 spectra with a time lag of 2 min. Before and after the exposure of the target gas, the measurement chamber was flushed with synthetic air for 5 min, respectively. After 1 min of gas exposure, the sensor has already reached 80% of the final signal (@ 610 nm). The sensor has also a fast back reaction. After flush with synthetic air for 1 min, the sensor has already reached again 18% of its initial signal (@ 610 nm) and is suitable for the indication of the actual gas concentration over several weeks.

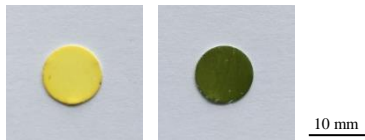


Fig. 3. Color change of embedded  $\text{NH}_3$  indicator on PPE coated paper before (left) and after (right) exposure to 50 ppm  $\text{NH}_3$  for 20 min.

Figure 3 shows the significant color change of the  $\text{NH}_3$  sensitive layer from yellow to green before and after exposure to 50 ppm  $\text{NH}_3$  for 20 min.

For the monitoring of  $\text{H}_2\text{S}$ , a copper complex was synthesized from copper(II) chloride ( $\geq 99.99\%$ , trace metals basis, ALDRICH Chemistry, St. Louis, MO, USA) and the azo dye 1-(2-pyridylazo)-2-naphthol (H-PAN) (indicator grade, SIGMA-ALDRICH, St. Louis, MO, USA) in a molar ratio of 1:1 according to literature [2,3] and characterized by FTIR spectroscopy and STA measurements [4]. The reflection spectra in Figure 4 illustrates the color change of the  $\text{H}_2\text{S}$  sensitive layer to 8 ppm  $\text{H}_2\text{S}$ . The target gas was exposed for 20 min, before and afterwards the gas measurement chamber was flushed with synthetic air for 5 min, respectively. For the measurement, 15 spectra were recorded every 2 min.

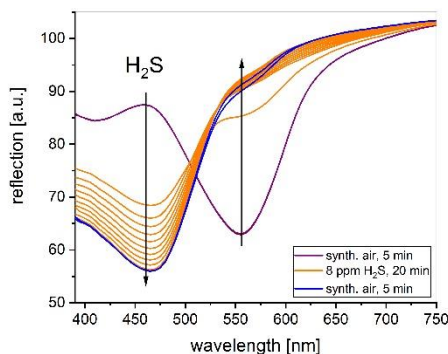


Fig. 4. UV/Vis spectra (in reflection) of the embedded  $\text{H}_2\text{S}$  indicator on PPE coated paper to 8 ppm  $\text{H}_2\text{S}$  and a relative humidity of 40% at room temperature. Recording of 15 measurement cycles every 2 min.

After  $\text{H}_2\text{S}$  exposure for 1 min, the sensor has already reached 76% of its final value (@ 555 nm). If the gas measurement chamber is flushed with synthetic air after the  $\text{H}_2\text{S}$  exposure, the sensor reached only 4% (@ 555 nm) of its original value after 1 min. Although the indicator is reversible, it is well suited for a disposable dosimeter application, to monitor the maximum exposed gas concentration of a defined period.

The pictures in Figure 5 show the color change from pink to yellow due to exposure of 8 ppm  $\text{H}_2\text{S}$  for 20 min.

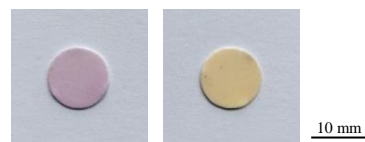


Fig. 5. Color change of embedded  $\text{H}_2\text{S}$  indicator on PPE coated paper before (left) and after (right) exposure to 8 ppm  $\text{H}_2\text{S}$  for 20 min.

The color dye 4-Amino-3-penten-2-one (97%, ALDRICH Chemistry, St. Louis, MO, USA) was selected as colorimetric material for the detection of  $\text{CH}_2\text{O}$ . It forms a fluorescent dye, which becomes visible only after contact with the target gas. The reaction of the enaminone group of the color dye with  $\text{CH}_2\text{O}$  leads to a change in the chromophore, visible as color change from colorless to neon yellow [5].

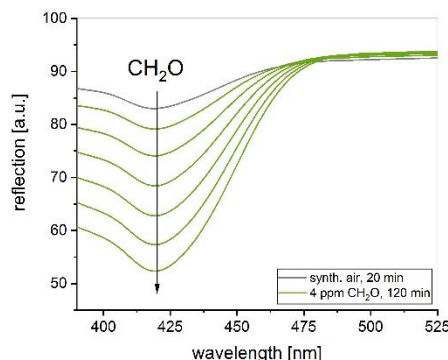


Fig. 6. UV/Vis spectra (in reflection) of the embedded  $\text{CH}_2\text{O}$  indicator on PPE coated paper to 4 ppm  $\text{CH}_2\text{O}$  and a relative humidity of 40% at room temperature. Recording of 7 measurement cycles every 20 min.

Figure 6 shows the reflection spectra of the  $\text{CH}_2\text{O}$  sensitive layer to 4 ppm  $\text{CH}_2\text{O}$ . The measurement consists of 7 spectra recorded in intervals of 20 min.  $\text{CH}_2\text{O}$  was exposed for 120 min, before the gas exposure the gas measurement chamber was flushed with synthetic air for 20 min. After end of gas admission, the  $\text{CH}_2\text{O}$  sensor layer has not yet reached its final value. This indicator is reversible, but it is due to its very slow back reaction (within days) great for a disposable dosimeter application.

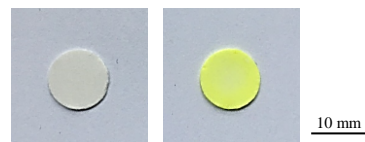


Fig. 7. Color change of embedded  $\text{CH}_2\text{O}$  indicator on PPE coated paper before (left) and after (right) exposure to 4 ppm  $\text{CH}_2\text{O}$  for 120 min.

Pictures of the color change from colorless to neon yellow due to the impact of 4 ppm  $\text{CH}_2\text{O}$  are shown in Figure 7.

Our investigations illustrate the properties of printable disposable indicators to monitor toxic gases in ambient air based on visible color changes. With regard to their inexpensive preparation and evaluation, these sensors can be useful for many chemical, environment and industrial applications.

## REFERENCES

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