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Colorimetric Detection of Oxygen in Food Packaging

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Summary:
We present a simple method to monitor the oxygen (O_2) concentration within food packages based on a UV resettable colorimetric indicator. The basis is a material combination of the redox color dye methylene blue (MB) with a titanium dioxide (TiO_2) nanopowder and glycerol. The work comprises different paste approaches suitable for screen printing and discusses the influencing factors to achieve the desired sensor properties based on investigations in an application-related scenario.

Keywords: Colorimetry, screen-printing, oxygen, food packing, optical gas sensor.

Background, Motivation and Objective

Approximately 12 million tons of food waste are generated in Germany every year, 52% of them in private households [1]. According to the Federal Ministry of Food and Agriculture, a targeted halving of the food waste in private households could save six million tons of CO_2 equivalents of greenhouse gas emissions annually. The generation of waste through discarded food is therefore not only associated with an immense economic loss, but also indispensable for the pursuit of rational climate and resource protection, which is a social task. Looking at the situation globally, it is assumed that a total of 1.3 billion tons of the food produced is not used every year [2]. According to estimates, the resulting total damage amounts to around 2.6 trillion US dollars, which corresponds to around 4% of global gross domestic product [2]. The food industry must deal with an increasingly complex, globalized environment of legal regulation and standards. With increasing use of additives in agriculture and animal husbandry, the risk of leaving residues in plant or animal products that are harmful to the health of consumers increases, too. Statistics show that the cause of 43% of all foodborne infections in Germany cannot be identified [3]. Increasing complexity of the value chain and increasing output per production facility complicate the traceability in the case of contaminated food. Furthermore, the distribution process also poses a risk to the quality of the food. Examples for this are a lack of compliance within the cold chain or violations of hygiene standards. However, independent from the multitude of influencing factors food quality could be monitored with the help of an integrated gas sensor. The goal of this work is the development of a printable, colorimetric gas sensor label (O_2, H_2S, amines, etc.), which gives a general description of the packaging's gas composition und thus on the condition of the product (see Fig. 1.).

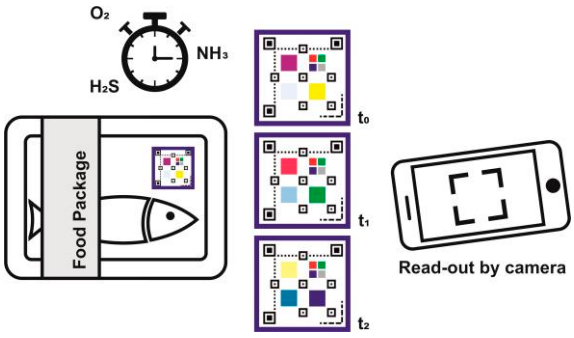

Fig. 1. Scheme of the sensor principle with three different colorimetric indicators. The integration of the colorimetric layers into a machine-readable pattern and the incorporation of a color reference enables an assessment of the color change that is independent from the illumination and the camera used.

In the present work the material development was focused on the example of an O_2 indicator. The shelf life of most packaged foods is affected by the presence of O_2. This gas leads to oxidation-related spoilage, accelerates the microbial growth of aerobics microorganisms, and is therefore excluded or reduced as far as possible in the protective gas atmosphere. To extend the shelf life, a reliable monitoring of the O_2 concentration could contribute to capture the current state of the goods.

Description of the New Method

Main challenge for the development of an O_2 indicator is the presence of O_2 in nearly every environment. Many goods are very sensitive to

O_2, and the packaging materials used show different barrier properties as well as a certain O_2 level of the already sealed packaging. The aim of this work is the development of a colorimetric indicator for the detection of O_2 that allows the time at which the measurement starts to be determined and that presupposes that "low" O_2 concentrations are negligible over the planned measurement period. As a part of this work an approach based on methylene blue (MB), titanium dioxide (TiO_2) and glycerol is used as gas sensitive material for the detection of O_2. The detection method is based on a photo-induced reduction of the redox dye MB to its leuco form, which in turn can be oxidized to its blue condition again by the presence of O_2 [4]. This method allows the sensor to be handled in an O_2 environment. Packed with the goods in a protective gas atmosphere, the measurement can be stated by resetting the gas sensitive layer with UV light. After the reset, the package is covered with a UV blocking foil to avoid a reverse reaction of the gas sensitive material through the given lighting conditions. For the manufacture of the gas sensitive layer different paste approaches were pursued. For the manufacturing of the paste, MB (indicator grade, Roth) and TiO_2 nanopowder (AEROXIDE TiO_2 P25, Evonik) were wet grinded in a planetary ball mill (PM 100, Retsch) using different solvents for the respective paste approach. Additives (defoamer, dispersant and thixotropic agent) were added to support the milling process to form a homogeneous paste structure on the one hand and to support the printing process on the other. Finally, glycerol (≥99.5%, Sigma-Aldrich) was added to the raw dispersion. To characterize the printability of the pastes, measurements were performed using a rotational rheometer (KINEXUS lab+, Netzsch) to determine the viscosity and the thixotropy of the pastes. A printing process was developed on a precision screen-printing machine (Thieme Lab 1000, Thieme GmbH & Co. KG) using a 120-30 PE mesh for the prints. Fig. 2 shows a 1-layer print by the example of a paste approach based on propylene glycol. The printed sensor layers were characterized by UV/Vis spectroscopy and in-situ readout station, which allows to analyze the color change via RGB values recorded with a camera. The in-situ readout station enables the indicators to be measured in a real-world perspective from 5 °C and is, in addition, coupled with a mass spectrometer to define the exact O_2 entry into the measurement chamber used to simulate food-packaging. Fig. 3 shows the sensor response of the exemplary selected layer towards 20% O_2 measured by UV/Vis spectroscopy. The respective camera images can be seen in Fig. 4.

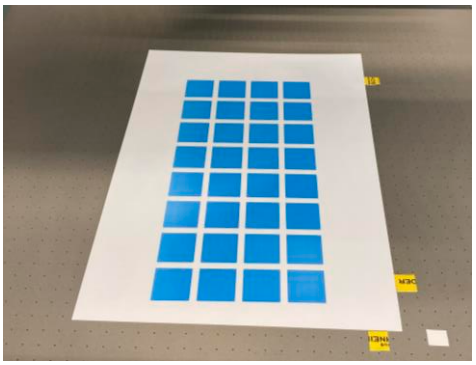

Fig. 2. Colorimetric sensor layers on A4 sheet.

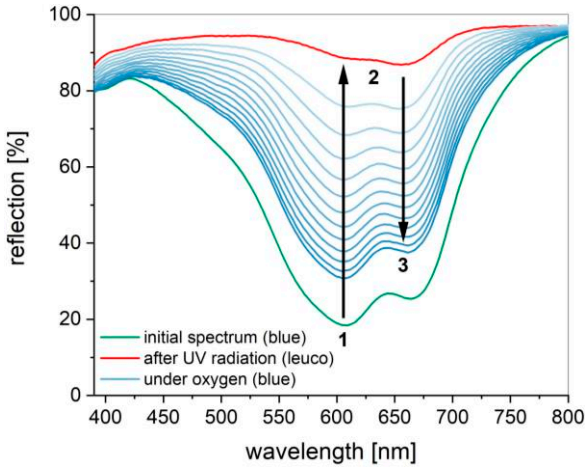

Fig. 3. Change in spectrum of the O_2 sensitive layer under the influence of 20% O_2 for 1 hour at room temperature and a relative humidity of 40%. Recording of the spectrum every 5 minutes.

Fig. 4. Screen-printed sensor layer at ambient condition (1), after rest with UV light under N_2 (2) and after exposure to 20% O_2 for one hour (3).

Results

Within this work we developed and characterized colorimetric sensor layers for the detection of O_2 in food packages over a defined period (~weeks). For the manufacture of the sensors, different screen-printing pastes were developed and characterized with respect to printability, sensitivity towards O_2, possible interfering gases and the influence of relative humidity.

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