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Monitoring the quality of raw poultry by detecting hydrogen sulfide with printed sensors

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ABSTRACT

Food quality and safety are controlled by legislation and monitored both by food industry players and regional and national authorities in a food supply chain. The need for more precise estimation of shelf life and faster results from food pathogen tests has resulted in the development of novel food quality sensors. Intelligent food packages are the concept toward traceability and real time monitoring of food. Herein we present the usage of printed and low-cost copper acetate-based sensors for monitoring the quality of raw broiler meat. The sensor operates by detecting hydrogen sulfide (H_2S) as an end product of the microbial metabolism. The sensors responded to H_2S at +6 °C accumulated in modified atmosphere, packaged broiler meat. A concept of the sensor platform, in which the sensor is combined with a printed planar coil antenna and printed capacitor to construct a wirelessly readable printed resonance circuit, is also presented. The sensor is suitable for large-scale production, which could make it inexpensive enough to be integrated in a low-cost retail food package.

1. Introduction

The total production of food for human consumption in Europe and North America is about 900 kg/year per capita and about one-third of that – i.e. 280–300 kg/year – is lost throughout the food supply chain. A remarkable amount of wastage, about 40%, occurs at retail and consumer levels of the food supply chain in wealthy industrialized countries [1]. A large proportion of food is being discarded in unopened packages either by retailers or consumers, because the use-by date has been passed. According to Regulation (EU) No 1169/2011, microbiologically highly perishable foods need to be labeled with the use-by date. The Codex Alimentarius defines the use-by date as “the date after which the product should not be consumed. It is determined from the date of production, utilizing the product shelf life and building in a margin of safety as determined by the manufacturer” [2]. Shelf life is the “period during which the product maintains its microbiological safety and sensory qualities at a specific storage temperature” [2].

Defining the use-by date is a challenging task, because the shelf-life of products depends on many variables which cannot be fully controlled, like the quality of raw material, hygiene level of manufacturing process and storage temperatures, etc. Manufacturers often set the use-by date according to the lowest quality raw material normally used for the product, with some margin for temperature abuse. This means that the majority of food packages are fit for consumption even shortly after the use-by date. However, they cannot be sold by the retailer and are thus being discarded. This is frequently a necessary precaution for ready-to-eat products, especially if *Listeria monocytogenes* are able to grow in the food. However, for raw meat stored at refrigerating temperatures and cooked before consumption, it is often the sensory quality rather than a pathogen risk which limits shelf-life. In these cases, the suitability of meat for human consumption could be determined by a sensor indicating the sensory quality of meat.

Many types of chemical sensors and biosensors have been developed for monitoring food quality and safety. These sensors measure, e.g. freshness, pathogens, carbon dioxide, oxygen, pH and the combined effect of time and temperature [3–5]. Freshness and microbial spoilage are often indirectly monitored by gas sensors, which detect volatile or gaseous compounds resulting from microbial growth, e.g. CO_2, amines, ammonia, ethanol and H_2S. Sensors

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integrated in food packages and combined with a suitable communication method would be able to monitor the food throughout the food supply chain and provide information about the quality of the product.

The rate of bacterial spoilage of raw poultry, in the manner of other microbiologically perishable foods, depends on the growth rate, concentration and metabolism of bacteria proliferating in food. Food is spoiled when the level of any bacterial metabolite exceeds the human sensory threshold. For raw poultry, it is often the sulfur containing bacterial metabolites that limits shelf life [6–8]. Under modified atmosphere packing (MAP) conditions, hydrogen sulfide (H_2S) has been determined to be one of the prominent volatiles released during the spoilage of raw poultry [6–8].

The sensor cost has to be minimized for inexpensive food packages. Another requirement is the easiness of reading the sensor information so that the package can interact with the user. Wireless measuring and battery-free operation are beneficial properties for the sensors, and passive radio-frequency identification (RFID) technology can fulfill these demands. However, the RFID sensor tags with embedded transponder chips can still be considered too expensive to be used in low-price retail product packages [9]. Cheaper options are chipless sensor systems. They are based on measuring the change on the resonance frequency or impedance of an RLC (R = resistance, L = inductance, C = capacitance) -resonance circuit. The circuit works as an inductively coupled device and can be wirelessly read using frequencies specific for high-frequency RFID (HF-RFID) or electronic article surveillance (EAS) technologies, for example [10,11]. In the food industry and related logistics, it is possible to use application-specific reader devices to receive information. The embedded near-field communication (NFC) property of many mobile phones could provide an option for reading the state of the RLC circuit for consumers.

The H_2S sensors presently available can be divided into three major categories: semiconductor metal oxide sensors, electrochemical sensors and optical sensors [12]. Current research aims for the development of robust and cost-effective H_2S sensors with enhanced sensitivity and stability as well as the ability to operate consistently under harsh environmental conditions. However, most of the commercially available H_2S sensors are either too expensive or cannot be integrated into a food package in any convenient manner, or do not show long-term stability under MAP conditions.

Amongst the various materials, copper acetate (CuAc) has been recently introduced as an easily processable material with an excellent sensitivity toward hydrogen sulfide (H_2S) gas [13–17]. CuAc films printed on paper substrate have been shown to directly react with H_2S gas to form copper sulfide (CuS) [14,17]. This has been shown to result in a significant and irreversible change in resistance of the film at room temperature with relatively low (1–20 ppm) H_2S concentrations. The large change in resistance is attributed to a direct conversion of insulating CuAc to a semiconducting (p-type) CuS. Chemiresistor-type sensors based on CuAc nanoparticles showing more than eight orders of magnitude change in resistance when exposed to H_2S on ppm level have been previously demonstrated [14,15,17]. In addition, good repeatability and long-term stability of printed CuAc-based H_2S sensors in ambient conditions have been reported earlier [17].

In this study, we have successfully used printed paper and plastic-supported resistive sensors based on copper acetate (CuAc) for monitoring volatile H_2S compounds produced by broiler meat spoilage under modified atmospheric conditions. In the broiler meat experiments, MAP conditions similar to that of consumer package were replicated in a laboratory environment. Sensor structures were fabricated on a plastic substrate using a commercial flexible printed circuit board (PCB) process to test the mass-scale manufacturing possibilities. The sensor was combined with a printed planar coil antenna and a printed capacitor to construct an inexpensive, wirelessly readable printed RLC-sensor. A commercial wireless EAS-reader was used to receive the on/off-response from the fabricated RLC-sensor. Bacterial levels (end-point) in broiler meat were analyzed in order to relate the sensor responses to the microbiological quality of the meat.

2. Materials and methods

2.1. Fabrication of inkjet-printed CuAc-based H_2S sensors on paper

The sensors consisted of interdigitated silver (Ag) or gold (Au) electrodes and an inkjet-printed CuAc layer on a multilayer curtain-coated [17,18] or laboratory-coated paper substrate [19]. Examples of interdigitated electrode structures are given in Appendix Fig. A.1. Inkjet printing was performed using a Dimatix Materials Printer (DMP-2831, FUJIFILM Dimatix, Inc., Santa Clara, USA) equipped with a cartridge (DMC-11610) that consisted of 16 nozzles with a nominal droplet size of 10 pL. Silver electrodes were inkjet-printed using silver nanoparticle-based ink (SunTronic U5603, Sun Chemicals), as presented previously [17]. The ink (40 wt% of Ag) was printed with drop spacing of 30 μm. Dodecanethiol-protected gold nanoparticles (AuNPs) were synthesized, following the procedure reported by Hostetler et al. [20]. The AuNPs (15 wt%) were dispersed in xylenes and inkjet-printed on a multilayer laboratory-coated paper substrate with drop spacing of 30 μm using a custom waveform and a 27 V firing voltage [21,22]. The electrodes were sintered using an infrared (IR) drier (IRT systems, Hedson Technologies AB, Sweden) to obtain conductive electrodes (resistivity, Au: $1.6 \times 10^{-7}\ \Omega\,m$ [18], Ag: $1.4 \times 10^{-7}\ \Omega\,m$ [23]). The sensor structure was completed by printing two layers of 0.1 M CuAc solution in water/ethylene glycol/isopropyl alcohol (8:1:1 volume ratio) upon interdigitated electrodes, with drop spacing of 25 μm. Besides the sensors, colormetric indicators were manufactured on a paper substrate by printing three uniform layers of CuAc on the paper substrate (Appendix Fig. A.2). Colorimetric indicators (print area: 10 mm × 10 mm) were used for visual inspection of H_2S exposure during and after the broiler meat spoilage experiments.

2.2. Fabrication of CuAc-based H_2S sensors on PET substrate

The H_2S sensors were fabricated also on plastic (polyethylene terephthalate, PET) substrate (Appendix Fig. A.1C). The PET-based sensors were fabricated completely, except for the application of the active sensor material, in a commercial roll-to-roll circuit manufacturing process. In addition to the interdigitated sensor structures, the parallel-connected RLC-sensor structures – consisting of the interdigitated sensor, planar coil antenna and parallel plate capacitor – were manufactured on a PET-based film. In the manufacturing process, the first conductor layer was realized by etching the conductive structures on the copper-coated PET film. The thickness of the PET film and copper layer were 50 μm and 18 μm, respectively. The copper fingers in the active area of the sensors and contacting pads were protected against oxidation by electroplating them with gold. Consecutive layers of nickel and gold were applied by electroplating on the copper surface. The purpose of the nickel layer was to provide better adhesion for gold. To minimize the amount of gold as protecting material, other parts of the copper structure were protected by screen-printing a polymer insulator layer having a thickness of 15 μm upon it. Screen-printed silver was used to realize the conductive structures of the second conductor layer in RLC-sensors. An additional insulator layer of 10 μm was applied in the places where the two conducting layers overlapped in the structure, in order to avoid the formation of