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Short communication

A simple laminated paper-based sensor for temperature sensing and imaging

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ABSTRACT

We describe a low cost optical temperature sensor that is simple to manufacture. The sensor is constructed by simple soaking of paper in a solution of the temperature sensitive luminescent indicator Ru(phen)$_3$ and subsequent lamination of the dried paper. Lamination prevents O_2 diffusion to the indicator and thus eliminates O_2 cross-sensitivity. The temperature sensitivity was up to −2% change in luminescence lifetime per K, a t_{90} response time of 10 s. Besides luminescence lifetime based measurements, the sensor is well suited for ratiometric imaging with simple RGB cameras, where the temperature dependent red luminescence can be referenced by the blue luminescence of the optical brightener in the paper.

1. Introduction

Temperature is one of the most fundamental parameters in applied and basic science. Precise measurement of temperature is needed in fields as diverse as meteorology, aquatic biology, environmental science, production technology, biotechnology and medicine to name only a few.

Numerous temperature sensing principles have been developed, ranging from classical liquid-filled glass thermometers that are based on the thermal expansion of liquids [1] over thermistors and thermocouples based on the Seebeck effect [2] to optical temperature sensors [3].

Optical temperature sensing principles and materials, especially based on temperature-dependent changes in indicator luminescence, were recently reviewed [4]. Metal–ligand complexes (e.g. Ru(phen)$_3$) [5–8] and lanthanide complexes (e.g. Eu(tta)$_3$) [9] are among the currently most promising indicators for optical temperature measurements. As these indicators show a strong cross sensitivity to molecular oxygen (O_2) that effectively quenches the luminescence of such complexes [4], it is necessary to incorporate them into polymers with a very low O_2 permeability. As the number of such polymers is limited (see Table 12 in Ref [4]), finding a compatible polymer – indicator – solvent mixture can be tedious and sometimes not even possible. This limitation often leads to additional synthetic steps like e.g. lipophilization of the indicator [8].

New synthetic solutions toward sensitive temperature probes and suitable polymers are constantly presented [10,11] but often involve complicated manufacturing procedures and/or expensive readout systems limiting a more widespread availability and application. Besides having favorable measuring characteristics such as long-term stability, sensitivity and specificity to the analyte, sensors need to be cheap and easy to use in order to enable widespread use and eventually make it into everyday products and technology [12].

In this paper, we present a new low cost optical temperature sensor that can easily be constructed by simply laminating a piece of indicator soaked paper. The sensor material exhibits very good signal stability, no cross-sensitive to other analytes (e.g. O_2), and is well-suited for ratiometric temperature imaging with commercial RGB cameras.

2. Materials and methods

Dichlorotris(1,10-phenanthroline)ruthenium(II) hydrate (Ru(phen)$_3$) was purchased from Sigma–Aldrich (www.sigmaaldrich.com). If not stated otherwise, distilled water was used throughout the experiments. Normal photocopy paper

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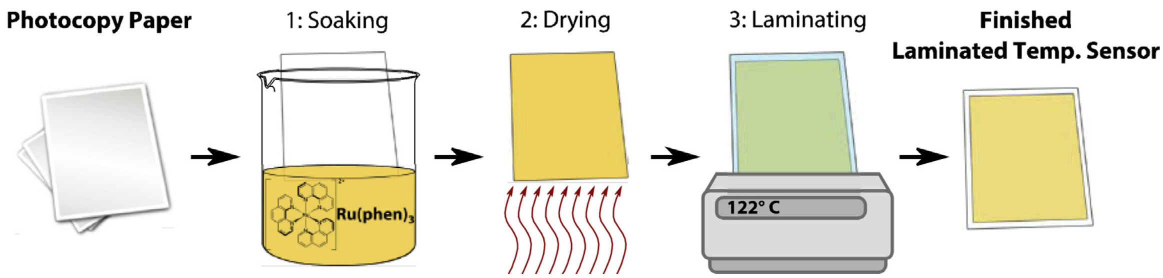

Fig. 1. Visual summary of the three-step sensor production. Simple soaking of photocopy paper, subsequent drying and lamination result in a fully functional temperature sensor foil.

was taken from the office printer (Plano® universal 80 g/m^2, www.papyrus.com). Laminating pouches (A4, 2 × 100 μm, clear) were obtained from GBC (www.gbceurope.com).

2.1. Sensor construction

The sensor was constructed by simply soaking a piece of copy paper (normally 10 × 10 cm) in an aqueous solution of Ru(phen)$_3$ (20 mg of indicator in 100 ml of water) for around 5 min. Subsequently, the stained paper was dried in a heating cabinet at 60 °C. The dry piece of now orange-colored paper was placed in a laminating pouch and laminated in an available office lamination machine (GMP LAMINART-13LSI; lamination temperature of 122 °C and speed setting 2). After lamination, the sensor is ready to use.

2.2. Sensor characterization

Emission spectra of the sensor were recorded using an ocean optics QE65000 fiber optical spectrometer (oceanoptics.com) equipped with a 2 m long PMMA fiber (2 mm in diameter). Luminescence lifetime measurements were performed using a miniaturized phase fluorimeter (pH mini from PreSens, modulation frequency 44.64 kHz, www.presens.de). Ratiometric imaging was done with an RGB SLR setup [13] consisting of a SLR camera (EOS 1000D, Canon, Japan) combined with a macro objective (Macro 100 f2, 8 D, Tokina, Japan) equipped with a 455 nm long pass filter (uqgoptics.com). Excitation of sensor particles was achieved with a 405 nm multichip LED combined with a bandpass filter (NT43-156, Edmundoptics.com). The LED was powered by a USB-controlled LED driver unit for fluorescence imaging applications (available from http://imaging.fish-n-chips.de). Image acquisition control of the SLR and LED was done with the software look@RGB (http://imaging.fish-n-chips.de).

2.3. Image analysis

Acquired images were split into red, green, and blue channels and analyzed using the freely available software ImageJ (http://rsbweb.nih.gov/ij/). In order to obtain temperature images, the following steps were performed: First the red channel (temperature sensitive emission of Ru(phen)$_3$) and blue channel (emission of the optical brightener in the paper) images were divided using the ImageJ plugin Ratio Plus (http://rsb.info.nih.gov/ij/plugins/ratio-plus.html). Afterwards, the obtained ratio-image was fitted with the previously obtained calibration curve using the Curve Fitting tool (linear fit).

2.4. Sensor calibration

A sensor piece was taped to the side wall of a 10 L aquarium filled with water of known temperature as checked with an electric thermometer (testo 110; www.testo.de). After equilibration for a few minutes, imaging and/or lifetime measurements were performed. Images were analyzed at three different regions of interest.

3. Results and discussion

The well-known and extensively studied luminescent indicator dye dichlorotris(1,10-phenanthroline)ruthenium(II) hydrate (Ru(phen)$_3$) [14,15] is used for O$_2$ sensing [16–18], but is also one of the most sensitive temperature indicators on the market (see Table 11 in Ref. [4]). In contrast to many other comparable indicators, this dye is commercially available and very photostable [17]. For temperature sensing purposes, Ru(phen)$_3$ normally gets incorporated into polymers with low O$_2$ permeability in order to overcome the inherent O$_2$ cross sensitivity of the indicator. As Ru(phen)$_3$ itself is hydrophilic, a lipophilization step [16] is normally needed in order to dissolve the indicator in nonpolar polymers like poly(acrylonitrile) (PAN) or poly(vinyl chloride) (PVC). Although the synthetic operations to get a lipophilic indicator are not very complex, they might already be challenging for labs that are not used to handling organic solvents or common purification steps. In contrast, our new approach does not need organic solvents at all. In fact, Ru(phen)$_3$ is the only needed chemical besides water. Simply soaking a piece of paper with an aqueous solution of Ru(phen)$_3$ and subsequent lamination of the dried paper is all it takes to obtain an operating optical temperature sensor foil. As Ru(phen)$_3$ is very soluble in water, the staining via soaking process is very effective. The sensor construction is summarized in Fig. 1.

Oxygen cross sensitivity is a main complicating issue of luminescence based temperature sensors, but lamination of the colored paper appears to totally eliminate the problem. Commercial laminating pouches consist of two poly(ethylene terephthalate) (PET) sheets that are coated with poly(ethylene) (PE) at the inside. Due to the heat treatment, the PE melts and permanently glues the two sheets together.[1]. Due to their low O$_2$ permeability, PET foils are routinely used as sensor support in planar sensors [19]; including O$_2$ sensors [20,21]. We thus assumed that the lamination process would provide a good isolation of the Ru(phen)$_3$-soaked paper from O$_2$. We tested this assumption by measuring the luminescent lifetime of the laminated sensors in air saturated and anoxic water. We started with air saturated water at a temperature of 293.15 K and after an hour added sodium sulfite in order to deoxygenate the water (checked with an O$_2$ sensor). The setup was left at constant temperature over the weekend and the phase shift was constantly recorded. After more than 2 days in anoxic water the phase shift (lifetime) has not increased. While for the dissolved Ru(phen)$_3$ the lifetime more than doubles when deoxygenated the lifetime of the dye inside the produced temperature sensor remained stable.

The temperature dependence of the indicator luminescence showed a linear relationship (Fig. 2). As sensor preparation via

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[1] Personal communication with GBC.