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Abstract

Swelling Behavior of an Ethanol-Sensitive Hydrogel Immobilized on a Plasmonic Sensor Substrate †

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Abstract: Refractive index-sensitive plasmonic sensors are suitable for the on-site detection of fluid parameters in process engineering applications. The functionalization of optically sensitive nanostructured surfaces with stimuli-responsive hydrogels enables the selective determination of parameters of complex liquids. Thereby, the degree of swelling of the hydrogel gives indications to liquid parameters like pH or molecule concentrations. In this study, the influence of the swelling degree of an immobilized ethanol-sensitive hydrogel on the sensor signal is investigated. The application of both a measuring and reference area allows differentiation of the refractive index change induced by the swelling effect from the refractive index change of the analyte due to concentration changes.

Keywords: plasmonic sensor; hydrogel; ethanol sensing; on-site detection

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1. Introduction

There is a high demand for measuring devices used on-site in the process industry for the continuous determination of fluid parameters, especially in the pharmaceutical, food and biotechnology industries. This is because the permanent determination of, for instance, molecule concentrations, is important for process control and influences the quality assurance of the products. Refractive index-sensitive sensors, such as the plasmonically active gold substrate used here, provides real-time feedback on a continuously changing composition of the process liquid. If the detection of a single parameter is required, functionalization of the sensor substrate with a hydrogel is a suitable option. Hydrogels are three-dimensional polymer networks that change their swelling degree in response to a stimulus. Because of swelling, the ratio of the polymer network and the absorbed fluid changes. In this study, an ethanol-sensitive hydrogel is used to investigate the influence of the swelling behavior on the optical sensor signal to show the possibility of separating the influences of swelling from refractive index change and to demonstrate future applicability.

2. Materials and Methods

2.1. Synthesis and Determination of the Swelling Degree of the Ethanol-Sensitive Hydrogel

For the hydrogel solution, 15 vol% of monomer acrylamide and 0.44 mol% of crosslinker N,N′-methylenebisacrylamide were dissolved in double-deionized water and subsequently 0.44 mol% of lithium phenyl 2,4,6-trimethylbenzoyl phosphinate as photoinitiator was added.

For the determination of the swelling degree, 150 µL of the hydrogel solution was polymerized under UV light (2.3 W/cm^2, 3 min), resulting in a 650 µm thickness. The volume change of the bulk hydrogel between 0 and 100 vol% ethanol was determined through thickness measurement by focus determination of a light microscope and area measurement by image evaluation.

2.2. Plasmonic Sensor Substrate and Sensor Setup

A plasmonic sensor substrate was used which exhibits optically sensitive nanostructured areas. For the investigation of continuously flowing fluids, the substrate is integrated in a flow cell. In addition to fluidic components, the measuring system also contains optical components (light source, spectrometer) which enable the detection of the optical transmittance signals from the plasmonically active surfaces. The measuring area is covered with a functionalized hydrogel (4 µm thickness). The additional usage of a non-functionalized reference area allows the differentiation between changes in the swelling degree of the hydrogel and refractive index changes of the analyte as a function of concentration changes therein. This is important for future detection of single substances in complex liquids containing more than two different chemical species which influence the refractive index. Here, aqueous solutions in the range between 0 and 60 vol% ethanol were studied.

3. Discussion

The volume change of a hydrogel covalently bound to the substrate (on one side) shows different behavior than the optical transmittance signal thereof as a function of the ethanol concentration. The plasmonically active, nanostructured gold substrate has a high sensitivity to the refractive index change in proximity of the sensor surface only. Therefore, only swelling states that extend 50–100 nm into the hydrogel volume are considered [1]. In other words, unlike the swelling curve, it is not the change in refractive index over the entire volume of the hydrogel attached to the substrate that is detected, but only the change in refractive index at the interface with the sensor substrate.

Under these conditions, measurements using measuring and reference area in a concentration range up to 40 vol% ethanol showed that the refractive index change of the analyte alone has a stronger influence on the sensor signal than is induced by the swelling of the hydrogel. Only above 40 vol% does the swelling degree of the hydrogel dominate and the measuring area show a higher sensitivity to the ethanol concentration change. This is an important finding for understanding hydrogel as a sensor material in plasmonic sensors and paving the way for further application to sense multiple substances.

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