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Development of Conductive Molecularly Imprinted Polymer Blends for VOC Sensing

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Summary:
We synthesized molecularly imprinted polymers for the templates heptanal and 2-propanol. Blends of the polymers with the conductive polymer P3HT proved suitable as receptor layers on both QCM and chemiresistors. Both types of sensors provide concentration dependent signals for the respective analyte. In comparison the QCMs can detect lower concentrations than the chemiresistor.

Keywords: molecular imprinting, conductive polymers, quartz crystal microbalance, chemiresistor, volatile organic compounds

Background, Motivation an Objective

Molecularly imprinted polymers (MIPs) are synthetic materials that contain binding sites for selectively rebinding the target analyte. [1] Herein, conductive MIP blends serve as receptor layers on quartz crystal microbalance (QCM) sensors as well as chemiresistors. QCM is a mass-sensitive sensor based on the piezoelectric properties of quartz. [2] Chemiresistors can detect volatile organic compounds (VOCs) in the gas phase through thin conductive polymeric films. Adsorption of the analyte causes the films to swell which results in a change in electric resistance. [3] Conductive MIP blends have already proven useful sensor materials to detect limonene on QCMs and chemiresistors. [4] We now intend to extend the applications to other compounds. The analytes in this case are VOCs that have been identified as biomarkers in the exhaled air of breast cancer patients. [5] Those sensors could be preliminary work towards applications in non-invasive early detection of diseases via breath analysis. Alternatively, they could serve as a stepping stone to other conductive MIP systems for VOC monitoring purposes.

Description of the New Method or System

This short paper presents the results obtained with conductive MIPs as sensor materials for detecting heptanal and 2-propanol, respectively. For heptanal detection MIPs based on the functional monomer N,N-dimethylacrylamide (DMAA) and the crosslinker ethylene glycol dimethacrylate (EGDMA) were developed. MIPs for the detection of 2-propanol are based on polyurethane (PU) containing diphenylmethane 4,4'-diisocyanate, bisphenol A and phloroglucinol. Both are blended with the conductive polymer poly(3-hexylthiophene-2,5-diyl) (P3HT). One electrode of the dual-channel QCM sensors is coated with the imprinted conductive blend (MIP) via spin-coating. The second electrode is coated in the same way with the corresponding non-imprinted polymer (NIP) and acts as the reference. Both electrodes of the chemiresistors are coated with the MIP blends. The reference electrode is covered with a tape prior to the measurement. All sensors are tested in gas flows containing different concentrations of the respective analytes. Selectivity tests with other VOCs were performed.

Results

QCMs coated with the conductive polymer blends can detect heptanal in gas phase in a range of 250-1000 ppm (Figure 1). Blending the MIP with P3HT increases the average sensor response for 1000 ppm heptanal from 5 to 8 Hz/10 nm polymer layer compared to pure MIP. Selectivity tests with other volatile organic compounds suggest selectivity towards the desired analyte.

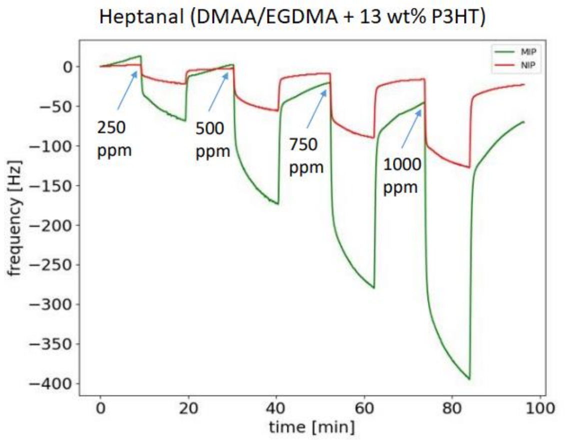

Fig. 1. QCM measurement at different heptanal concentrations. (DMAA/EGDMA containing 13 wt% P3HT).

The blends also proved suitable for use in a chemiresistor (Figure 3). On average 1000 ppm heptanal leads to a reversible shift of 0.5% in the sensor response.

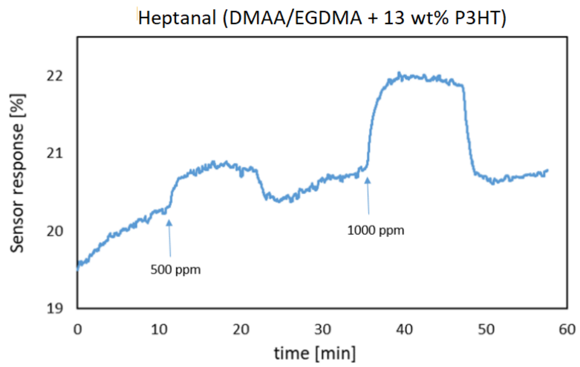

Fig. 2. Chemiresistor measurement at different heptanal concentrations. (DMAA/EGDMA containing 13 wt% P3HT).

The conductive polyurethane blends can detect 2-propanol in the range 500-2000 ppm with similar signal intensities as the pure MIP. 1000 ppm 2-propanol lead to a reversible frequency shift of 1 Hz/10 nm polymer.

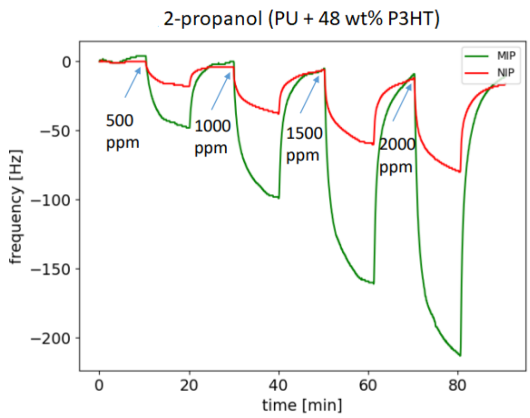

Fig. 3. QCM measurement at different 2-propanol concentrations. (PU containing 48 wt% P3HT).

The chemiresistors coated with the polyurethane blends so far only react to concentrations above 1500 ppm (Figure 4). 2000 ppm of the analyte cause a sensor response of 0.1 %.

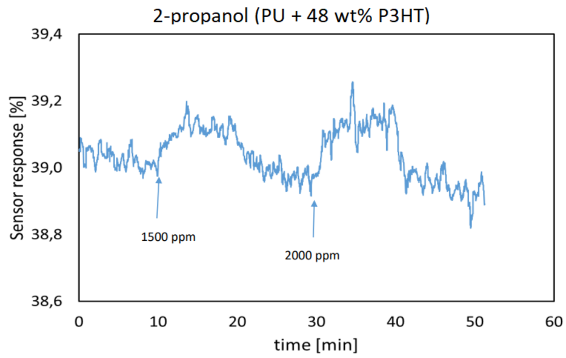

Fig. 4. Chemiresistor measurement at different 2-propanol concentrations. (PU containing 48 wt% P3HT).

Based on this, our future focus will be the improvement of the signal intensity, as well as increasing the signal/noise ratio of our chemiresistor devices.

The combination of simple chemiresistors with conductive MIPs was proven successfully and bears huge potential with respect to the simplicity of the system and its broad applicability.

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