



Abstract UV Light Stereoselective Limonene Sensor Using Electrospun PVP Composite Nanofibers [†]

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Abstract: This study explored the design of an innovative stereoselective S-(-)-limonene sensor according to the molecular imprinting polymer (MIP) strategy using UV light to generate in situ polymer cross-linking. A conductive composite nanofibrous fabric of polyvinylpyrrolidone (PVP), polyacrylic acid (PAA) and carbon nanotubes (MWCNTs) was deposited on purpose in a single step by electrospinning onto interdigital microelectrodes. The nanostructured layer was investigated by microscopy (SEM, TEM, AFM) and infrared transmission measurements (FTIR). The resulting sensing features (carried out in environmental air) seemed to be mainly dependent on the peculiarity of the nanostructure and the phenomena occurring at the interfaces between the cross-linked PVP–PAA/cavity shape and MWCNTs. Furthermore, the specificity of the host–guest interaction was proven by the sensitivity, selectivity and stereoselectivity of the sensor when exposed to similar monoterpenes ((\pm)- α -pinene and (\pm)-linalool) and the enantiomer of limonene (R(+)), respectively.

Keywords: electrospinning; limonene; MIP; nanocomposite sensors; UV light-induced polymer cross-linking

1. Introduction

Detecting terpene vapors emitted by plants has proven to be an efficient way to monitor plant growth status, providing information about plant pest attacks, abiotic stress and other diseases [1]. The creation of molecular imprinting polymers (MIPs) is one of the most investigated strategies in the literature for developing terpene chemical sensors. MIP techniques typically consist of the polymerization of monomers or polymers in the presence of template molecules and the following generation of functional cavities upon removal of these molecules, thus leaving highly specific active sites [2]. The combination of the excellent selectivity of MIPs due to their recognition properties, like those of natural receptors, and the ability of electrospinning (ES) technology to produce diverse forms of fibrous assemblies with remarkable specific surface area and high porosity [3] enables one to design enhanced sensing platforms taking advantages from both the technologies. This study used the combination of these two technologies to fabricate an innovative, highly specific ES/MIP-based conductive sensor for S(-)-limonene by blending PVP and PAA as carrier polymer and cavity generator, respectively, S(-)-limonene as template molecule and MWCNT as conductive reinforcement.



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2. Materials and Methods

PVP (Mw 1,300,000), PAA (Mw 450,000), MWCNT, S(-)-limonene (96%), R(+)-limonene (97%) and (\pm)-α-pinene (98%) and (\pm)-linalool were purchased from MERK. Absolute ethanol and N-N Dimethylformamide were reagent-grade. Sol A: PVP/EtOH_{abs} (C: 120 mg mL⁻¹), Sol B: PAA/EtOH_{abs} (C: 78 mg mL⁻¹) and Sol C: MWCNT/DMF (0.2%wt.) [4] were prepared. Electrospinning solution was obtained by mixing A, B and C (5:0.5:0.2, *v:v:v*) and S(-)-limonene (0.017%, v%) under magnetic stirring at room temperature. Measurements of VOCs were carried out in air under dynamic mode (MKS flowmeters; 5 replicates) at room temperature and 50% RH.

3. Discussion

Figure 1A,B shows TEM and SEM images, respectively, of the nanocomposite fibers after UV irradiation (500 W, ~5 min) and terpene washing-off ($Ø_m = ~450$ nm) with ethanol. The layer appeared highly porous, with smooth nanofibers housing MWCNT mainly in the innermost part. FTIR analysis reported an evident difference among samples depending on UV irradiation, confirming that this treatment induced in situ polymer cross-linking in the electrospun composite nanofibers. The resulting insolubility of UV-treated fibers in common organic solvents also confirmed such an outcome. No electrical signal was recorded in the sensor before template molecule removal, while the washing off of S(-)-limonene by solvent provided imprinted nanofibers to detect it. Sensor exposure to increasing concentrations of both S(-)- and R(+)-limonene (Figure 1C) showed a marked difference in sensitivity ($S_{S(-)lim} > 3.5 S_{R(+)lim}$), thus demonstrating its stereoselectivity. Furthermore, only a few nonspecific interactions appeared to regulate the interplays with other terpenes, like α -pinene ($S_{\alpha-pin}$: 0.00055 ppm⁻¹) and linalool (S_{lin} : 0.00095 ppm⁻¹), pointing out the effectiveness of the MIP strategy proposed. Studies on the effects of humidity, temperature and other chemical interferents are underway.



Figure 1. (**A**) TEM and (**B**) SEM of one and a network of the treated nanocomposite fibers, respectively; (**C**) response curves of the ES-MIP-sensor to increasing concentration of S(-)- and R-(+)-limonene (ranging between 5 and 165 ppm).

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