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Abstract

Housing Molecularly Imprinted Polymer Nanoparticles in Polyvinylpyrrolidone/Multiwall Carbon Nanotube Nanofibers to Detect Chiral Terpene Vapors †

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Abstract: This study proposes a two-step process to design a chiral sensor combining MIP (molecularly imprinted polymer) and electrospinning technologies. First, stereoselective S(-)-limonene molecularly imprinted polymer nanoparticles (MINPs) were fabricated and dispersed into polyvinylpyrrolidone–carbon nanotube (PVP-MWCNT) conductive nanofibers to cover resistive interdigitated electrodes (IDEs). The electrical and sensing performances of the resulting sensor confirmed its capacity to discriminate and quantify the two limonene enantiomers. The sensor's response to terpene gases appeared completely reversible, probably due to the peculiarity of the nanostructure. The sensor characteristics were influenced by the polymer matrix's composition ratio, the cavity shape and the interfaces with carbon nanotubes. The morphological properties of the nanofibers were investigated by microscopy (optical, SEM, TEM and AFM).

Keywords: electrospinning; limonene; stereoselectivity; MIP; nanoparticles; sensors

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1. Introduction

Biomarkers are molecules produced by animals or plants that ideally allow us to predict a clinically relevant endpoint or intermediate outcome that is difficult to observe. For example, monoterpenes like limonene, α-pinene and linalool are known to be biomarkers for humans, animals and plants.

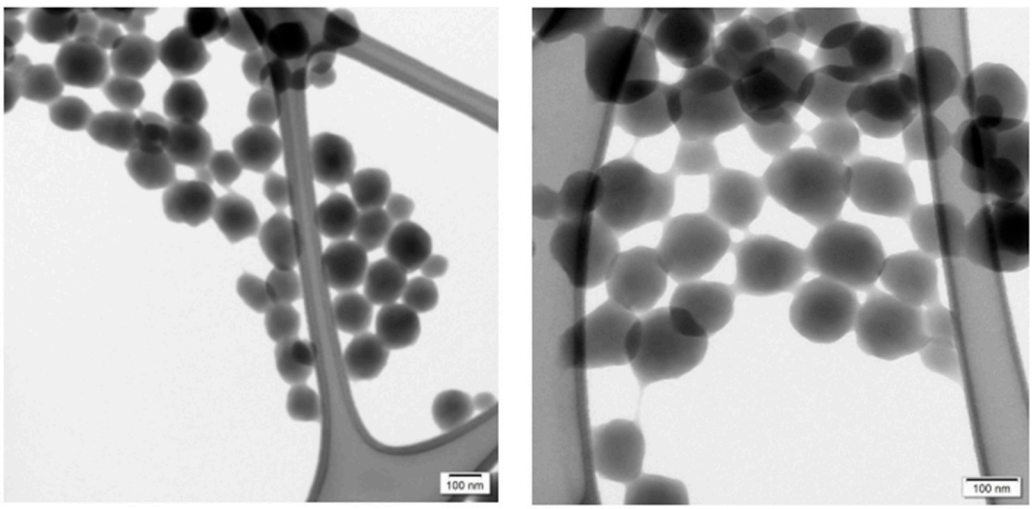
MIP techniques typically consist of the polymerization of monomers or polymers in the presence of template molecules and the subsequent generation of functional cavities upon the removal of these molecules, thus leaving highly specific active sites [1]. On the other hand, adding a specifically tailored molecular recognition capability to electrospun materials is expected to be highly beneficial for designing a selective sensor [2]. However, integrating these two technologies has proven to be quite challenging, mainly due to the different processing methodologies that characterize the two approaches [3]. Conversely, the dispersion of MINPs inside polymer nanofibers sounds fairly straightforward upon separating the technological processes. Hence, tailoring each process's parameters enables one to achieve optimized final architectures and efficient recognition performances. In this preliminary study, S(-)-limonene-templated MINPs were prepared and dispersed in polyvinylpyrrolidone (PVP) nanofibers housing multiwall carbon nanotubes (MWCNTs) to design a stereoselective sensor. In fact, PVP has a high electron cloud density on the pyrrolidone ring, thus providing good dispersion stability for NPs with polar groups and active hydrogen atoms.

2. Materials and Methods

PVP (Mw 1300000), MAA (methacrylic acid), EGDMA (ethylene glycol dimethacrylate), AIBN Azobisisobutyronitrile), MWCNT, S(-)-Limonene (96%) and R(+)-Limonene (97%) were purchased from Merck. Absolute ethanol, N-N Dimethylformamide, Acetonitrile and Cyclohexane were reagent-grade (Merck). MINPs were obtained via the thermal polymerization of MAA in the presence of S(−)-Limonene, using EGDMA as crosslinking agent, AIBN as a free radical initiator and acetonitrile as a solvent. In order to obtain nanoparticles, the polymerization was carried out at 60 °C for 6 h, using an excess of solvent and following a sonication step. S(-)-Limonene was extracted by washing the particles with cyclohexane using sonication and centrifugation, while the supernatant was reserved for analyses. These steps were repeated four times. For electrospinning, an MINP solution was prepared by mixing the PVP solution with an MWCNT dispersion in DMF (0.7%wt) prepared using a previous described procedure [4]. Fibers produced using MINP dispersion in DMF instead of MINP dispersion as control. A NINP dispersion was also prepared as in the MINP procedure but without the target molecule. After deposition, the electrospun nanofibers (ESNFs) were irradiated for 5 min with UV light (500 Wat) to strengthen (via cross-linking) the fabric and make it insoluble in common organic solvents.

3. Discussion

The NINPs (Figure 1A) were more regular and rounder (<100 nm diameter) than the MINPs, which showed a diameter size ranging between 50 and 200 nm (Figure 1B). The electrospun NINP and MINP nanofibers were collected for 5 min on customized IDEs placed on a rotating, grounded cylinder to achieve a fibrous network composed of rough and earthworm-like nanofibers due to the loaded NPs. When the sensors were exposed to the same amount of limonene enantiomers, linalool and alpha pinene (15 ppm in air), MINP-ESNF-sensor showed a higher electrical change to S(-)-limonene in comparison to the other terpenes (Figure 2A), suggesting it was mainly due to the phenomena happening at the interfaces between the cross-linked PVP, the MINP cavity shape and the MWCNTs. Could be observed that NINP-ESNF was substantially unresponsive to the same concentration of S limonene. Therefore, the proposed two-step strategy is a promising chance to create a new generation of stereoselective sensors for chiral biomarkers.



(**A**) (**B**)

Figure 1. (**A**) TEM image of a cluster of NIMPs (bar: 100 nm) and (**B**) MINPs (bar: 100 nm).

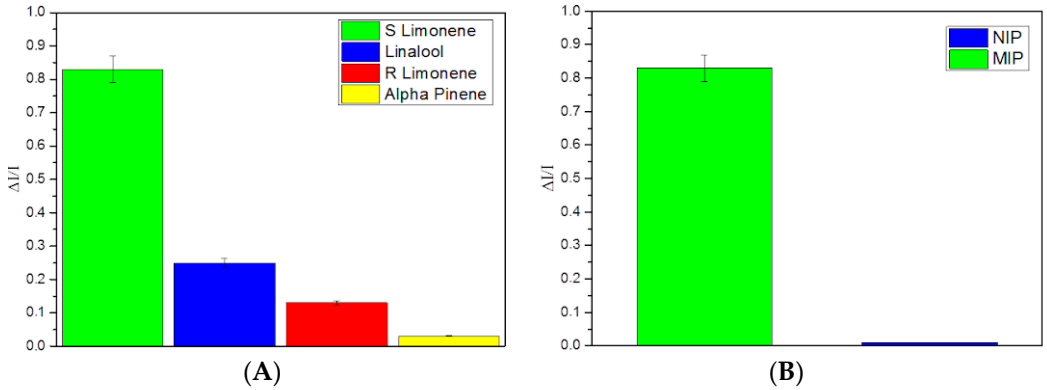


Figure 2. (**A**) MINP-ESNF sensor response when exposed to 15 ppm of vapors of the enantiomers of limonene (S and R_), linalool and alpha pinene (**B**) MINP-ESNF and NINP-ESNF sensor response when exposed to 15 ppm of vapors of S limonene.

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