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# An overview of biomimetic optoelectronic noses based on various biological sensing materials and surface plasmon resonance imaging

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**Abstract**—Inspired by mammalian olfactory system, electronic noses (eNs) are promising alternatives for the reliable and rapid analysis of volatile organic compounds (VOCs). As for sensing materials, so far the materials most often used are inorganic or organic. Nevertheless, various biological materials are emerging in recent studies such as peptides, hairpin DNA, peptide nanostructures, etc. Concerning transduction system, surface plasmon resonance imaging (SPRi) is particularly interesting for eN development. Since this technique allows to monitoring binding events in label-free and real-time by providing temporal responses with kinetic information, with capacity for simultaneous detection on a multiplexed sensor array. Therefore, the combination of such a detection system with novel biological sensing materials could lead to the development of original biomimetic optoelectronic noses with improved performances in terms of sensitivity and selectivity.

**Keywords**— *electronic nose, biological sensing materials, peptide, volatile organic compounds, surface plasmon resonance imaging*

## I. INTRODUCTION

In the last decades, electronic noses (eNs) have been considered as promising alternatives for the reliable and rapid analysis of volatile organic compounds (VOCs) with potential applications in a wide range of domains. However, from an industrial point of view, the eN suffers from significant drawbacks related to their performance that forbade this technology the bright future that it was initially promised. Most existing eNs are based on a small number of non-specific sensors each functionalized with chemical layers. To date, conducting polymer composites (e.g. carbon black/insulating polymer matrix), conducting polymers (polypyrrole, polythiophene, polyaniline, etc.) and metal oxides (n-type including zinc oxide, tin dioxide, titanium dioxide and iron (III) oxide and p-type including nickel oxide, cobalt oxide, etc.) are the most commonly used sensing materials in the eNs [1]. In particular, almost all commercial eN systems are based on these sensing materials.

The initial hope was to approach the ability of human nose by increasing the number of individual sensors. However, the problem is that the information gained by adding additional sensors rapidly saturates. Since these sensing materials suffer from a general lack of selectivity for VOC analysis on the basis of simple physical adsorption. In fact, the unequalled performance of the human nose has turned out to be not only

the great diversity of sensing receptors, about 400 different types of olfactory receptors (ORs) compared to 10 - 50 sensors generally used in eNs, but their selectivity and their unsurpassed sensitivity for some odorant molecules. Consequently, an enhancement in selectivity and capabilities of the eNs by increasing the number of sensing receptors is possible only if these additional sensing receptors can deliver new and supplementary information.

In this context, new sensitive materials with good sensitivity and selectivity are under development, for instance, based on thin layers, synthetic receptors and molecularly imprinted polymers. One particularly interesting tendency is using small organic and biological molecules as building blocks with the help of surface chemistry and nanomaterials. The general idea is to use small, simple and easily-accessible molecules as building blocks; then to make them self-assemble onto sensor surfaces via appropriate surface engineering. This gives a nanometer-scale organic or biological thin film, such as self-assembled monolayers (SAMs). The composition, structure, and physicochemical properties of the monolayers can be varied and tuned rationally according to applications. Different laboratories in the world have adopted this strategy. For instance, Hossam Haick's group used monolayers of silane or thiol with various physicochemical properties as sensing materials [2, 3]. The group of Charlie Johnson used monolayers of single stranded DNA (ssDNA) as sensing materials for development of VOC sensors [4, 5].

Another biomolecule family has great potential as sensing materials for the detection of VOCs is peptide. [6] The diverse physicochemical properties and chemical robustness make peptides particularly interesting for such applications. Thanks to recent advances in peptide synthesis, short peptides or polypeptides can be chemically synthesized, recombinantly made in cells or plants with little difficulty. Moreover, based on biomimetic approaches with the help of phage display and molecular simulation, it is possible to tune the binding properties of peptides for VOCs. [7, 8] Finally, in a recent published work, it was shown that short peptides can self-assemble into nanostructures such as nanofibers, which could further increase sensor diversity. [9]

In the last decade, we have focused on the development of biomimetic optoelectronic noses using biomolecules as sensing materials and an original optical system, surface plasmon resonance imaging (SPRi), as transduction system. Herein, an overview of their development will be given.

## II. OVERVIEW OF BIOMIMETIC OPTOELECTRONIC NOSES

### A. Surface plasmon resonance imaging for analysis of VOCs in gas phase

SPRi has been largely used for the development of biosensors and biochips for monitoring binding events in liquid phase. While we were the first to use SPRi for VOC analysis in gas phase and to explore its potential for eN development [6]. Indeed, SPRi is ideal for such application since it allows to monitoring binding events in label-free and real-time by providing temporal responses with kinetic information, with capacity for simultaneous detection on a multiplexed sensor array.

We have studied and optimized different optical parameters for the improvement of detection sensibility of SPRi for gas sensing. It was shown that the surface sensitivity of SPRi is dependent on the wavelength of the light source [10]. In the range of 530 nm to 740 nm, the SPRi sensitivity increases as the wavelength increases. For example, with the wavelength of 740 nm, the obtained optoelectronic nose was able to reliably detect 1-butanol at very low concentration (10 ppb). In another study, we have investigated the impact of the prism geometry on SPRi sensitivity [11]. All these studies allow us to validate SPRi as an efficient system for gas sensing.

### B. Biomimetic optoelectronic noses based on various biological sensing materials

In a previously reported study, short peptides with varied physicochemical properties (hydrophobic, hydrophilic, charged, neutral, etc.) were used as sensing materials. They were deposited on the gold surface of SPRi prism by a non-contact microspottor and formed self-assembled monolayers thanks to the thiol-gold chemistry. It was shown that the obtained biomimetic optoelectronic nose was very efficient and versatile for the analysis of VOCs from diverse chemical families. Thanks to SPRi, the generated temporal responses provided supplementary discriminatory information compared to a simple equilibrium response used by most existing eNs. Based on them, the good performance of the eN was exemplified by its ability to discriminate between VOCs differing by a single methylene group [6] and even between chiral molecules demonstrated in another study. [12] Furthermore, the eN exhibited very good repeatability and stability upon repeated use and prolonged storage. It is important to mention that our SPRi technology has been valorized by a local company, which has succeeded in miniaturizing the system into a portable device for odor analysis.

As mentioned before, peptides can be further modeled and virtually screened in order to obtain better selectivity and specificity to VOCs of interest. Indeed, using virtual screening 'in silico' testing of VOC - peptide binding can be carried out in a fast and low-cost way. One of our collaborators has developed this approach to identify short peptides with good sensitivity and selectivity for VOCs. Besides, they have also designed and selected several hairpin DNA (hpDNA) for gas sensing by computational screening. The shape of these sequences was very interesting because it maximized the

orientation of the binding element (via the stem) using the loop as a sensitive element. Both their short peptides and hpDNA were integrated into SPRi chips [8]. Thanks to the complementarity of their binding properties, the obtained optoelectronic nose has very good selectivity, being able to discriminate not only between VOCs of different chemical families, but also VOCs of the same family with very similar structures.

In a very recent study, we developed a novel paradigm in order to diversify the structural heterogeneity of sensing elements using a single peptide as building block to obtain different binding properties for VOCs. [9] To do so, we have designed a surfactant-like peptide CG<sub>7</sub>-NH<sub>2</sub>, with a cysteine as head group and seven repetitive glycine residues as the tail group where the C-terminal is amidated. Such a peptide is able to self-assemble into various supramolecular nanostructures (nanofibers, globular aggregates, etc.) under certain experimental conditions. In this study, by tuning pH and water content of peptide solutions, we successfully fabricated a five-element biohybrid sensor array, containing morphologically and physicochemically heterogeneous "biohybrid" surfaces with immobilized hierarchical peptide nanostructures surrounded by self-assembled monolayers of the peptide. The obtained optoelectronic nose has excellent sensitivity, which was benchmarked for hexanoic acid and phenol, with a LOD of <1 and 6 ppb, respectively.

## III. CONCLUSION AND PERSPECTIVES

Through this overview, we demonstrate that peptides have great potential as sensing materials for eNs thanks to their chemical robustness, diverse chemistry, capability to form nanostructures and their homology to natural ORs. Their integration into SPRi chip led to the development of original biomimetic optoelectronic noses with excellent performances in terms of sensitivity and selectivity.

Very promisingly, based on biomimetic approaches with the help of molecular simulation and phage display, peptides can offer promising alternatives for ORs with high sensitivity, selectivity and much better stability. In the future, we aim to develop a new methodology for eNs, by taking inspiration from human nose, which uses the combination of two types of recognition principles. Indeed, among about 400 different types of ORs, some ORs are "narrowly tuned" and thus specific to few odorants while the others are "broadly tuned" and cross-reactive to many odorants. It is such a combination that gives the human nose extraordinary capacity of discriminating over 10,000 of different odors. In contrast, the existing eNs employ solely the cross-reactive principle, and never the combination of the two. Therefore, in the future we will combine these two recognition principles on the same chip for designing and developing a new generation of biomimetic eNs with greatly improved performances.

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