Bi-Dimensional MIP Composites

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Deposition of thin MIP layers over different substrates, i.e. metal chips, silicon-based supports, carbon-based materials or semiconductors

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1. Metal Chips

The use of metal chips and, in particular, gold slides was popularized from the surface plasmon resonance (SPR) technique, although they have been applied to other types of detection. In this kind of devices, it is very important to obtain a surface imprinting and a control of the thickness of the polymer layer to increase the reproducibility of the measurements. There are several techniques that allow an exhaustive control of the thickness of the polymer onto the substrate. These polymerization techniques are not only used in this type of material but are applied to most of the hybrid materials discussed in this article.

One of the simplest approaches to prepare MIP films of controlled thickness consists of depositing the pre-polymerization mixture on a substrate and spreading it homogeneously in a step prior to its polymerization. In this sense, the spin-coating technique allows a nanometric control of the thickness of the obtained layers [1]. Dibekkaya et al. [2] modified SPR chip surfaces with an MIP for the detection of cyclic citrullinated peptide antibodies (anti-CCP), using anti-CCP/AAm (acrylamide) pre-complex for the synthesis of the polymer. By this method, a nanofilm was produced as monolayer. The sensor recognition was evaluated against an immunoglobulin M and against bovine serum albumin (BSA), showing that, due to the presence of the anti-CCP/PAAm complex, there was only recognition of the analyte. It was demonstrated the possibility of reusing the sensor up to 4 times obtaining the same recognition signal, although it is possible to observe that the recovery to base line was lost with time. Ayankojo et al. [3] prepared a hybrid organic-inorganic MIP film over a gold slide for amoxicillin detection. Hybrid materials consisting of inorganic and organic components can be formed at the nanoscale and integrated on a sensor to yield uniform thin films. This technique results in a better analytical sensitivity and selectivity due to rapid mass transport, easy access of analyte molecules to the binding sites and faster recognition. This sensor allowed analyte detection in the pico- and nanomolar concentration level, remarkable when compared to other studies on amoxicillin detection by MIP-based sensors. It was found that there was no cross-reactivity against other antibiotics, structurally similar or not. However, some competition was observed for the binding sites by ampicillin, although the signal generated was low enough to be considered as a true competition.

The thickness of the polymer layer can also be controlled by confining the pre-polymerization mixture between two flat materials and applying continuous pressure during the polymerization process. One of these materials usually acts as a substrate or support for MIP while the other can be functionalized with the template molecule. This method is known as micro-contact imprinting, resulting in a surface imprint of the polymer [4]. This approach is particularly useful for the imprinting of high molecular weight species, such as biomolecules [5] or microorganism [6]. In this case, the polymer is immobilized on the gold surface using monomers with double bonds or molecules that allow the direct bonding of the MIP during polymerization. However, the use of these techniques does not allow an exhaustive control of the thickness of the MIP film. Kidakova et al. [7] prepared an SPR sensor for BSA detection by the combined use of controlled/living radical polymerization. This technique allows the control of the composition and thickness of the MIP films by using a surface initiator (called an iniferter) that also attached the film to the surface, avoiding problems related to external factors.

2. Silicon-Based Slides

Silicon-based materials are of great interest in the development of optical sensors. In particular, slides made of SiO_2, both glass and quartz, allow surface modifications with silanes helping to anchor the polymer and other molecules to the surface and the functionalization of the sensor. Moreover, their transparency makes them an excellent waveguide and window for interrogation with a multitude of spectroscopic techniques [8].

It is common to functionalize the surface of the support with double bonds so that the polymer remains attached after the reaction. In the case of SiO_2, silanes containing this functionality are widely used, such as 3-(trimethoxysilyl)-propyl-methacrylate (MPS) [9]. Chang et al. [8] described a fluorescent sensor chip for indole-3-butyric acid. Pre-polymerization mixture was poured over a quartz chip previously silanized with MPS to obtain a MIP coating. With this sensor extraction recoveries were observed to be higher than 91% at μg g^{-1} concentration level. In the cross-reactivity studies it was found that structural analogues were recognized by MIP, albeit in a lower proportion than analyte, demonstrating the influence of shape on selectivity. This chip was designed to be used in an online system as a flow cell.

3. Other Conductive Substrates

Electrodes based on metals, semiconductors and carbon derivatives have gained great importance in recent years in the development of sensors based on MIPs. Although their use has always been relegated to the development of electrochemical sensors it is possible to use them as optical sensors due to electrochemiluminescence (ECL) [10], a kind of luminescence in which radiative emission is obtained from an electrochemical reaction in solution. This method requires no irradiation and problems such as scattering or light source instability are avoided. Moreover, ECL affords the electrochemical regeneration of some reactants at the electrode surface and emission in ECL occurs near the electrode surface, which affords finer control [11]. It is worth to state that in this type of sensors a light-emitting species are necessary by means of the participation in an electrochemical reaction. The most common are luminol and Ru complexes, such as *tris*(2,2′-bipyridine)ruthenium(ii) complex, $[Ru(bpy)_3]^{2+}$ [12], although other elements such as quantum dots (QDs) [13] or up-conversion nanoparticles (UCNPs) are currently being applied [14].

Due to the very nature of the support material, the most commonly used technique for the generation of polymer films is electropolymerization, in which the precursor mixture is deposited on partially conductive substrates, generating the MIP layer by applying an electric current. The monomers must polymerize after the application of certain voltages, although it is also common to use linear copolymers π-conjugated that interact with the template and favour electrical conductivity [15]. However, it is possible to apply other techniques for the development of sensors, such as direct deposition of the MIP on the electrode, polymerization of the material after depositing the pre-polymerization mixture on it or mixing the MIP physically with the electrode material.

One approach is the incorporation of the electroluminescent species into the electrode itself [16]. They prepared a $[Ru(bpy)_3]^{2+}$/MWCNTs/nano-TiO_2-Nafion electrode on which the MIP selective to bisphenol A was deposited. Including MWCNTs/nano-TiO_2 nanohybrids into the Nafion film could provide an excellent basis for effective immobilized $[Ru(bpy)_3]^{2+}$ and improve the electrochemical and ECL properties of the complex. This sensor achieved a low detection limit, the best to date for the analyte compare with other analytical methods and showed that there was no cross-reactivity regarding other endocrine disrupters, demonstrating its applicability in water samples.

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