



Review

Molecularly imprinted polymer nanoparticles in chemical sensing – Synthesis, characterisation and application



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ABSTRACT

During the last years, artificial nanostructured materials attracted increasing scientific interest due to some remarkable properties such as high surface-to-volume ratio, low cost and straightforward preparation and handling. Among others, such materials show high potential for highly selective recognition in different fields of Analytical Chemistry, such as chemical sensor design. Carrying forward the approach of molecular imprinting from bulk/thin film to nanoparticles is one possible way to actually achieve that goal. Recent years have hence seen substantial increase in the number of MIP nanoparticle publications. This review gives a detailed overview of established precipitation and microemulsion methods for synthesising molecularly imprinted polymer (MIP) nanoparticles (NPs) as well as giving an outlook on improving those by “living” polymerisation techniques to achieve controlled geometry and thickness as well as post-synthesis functionalisation. Besides these techniques, novel solid-phase imprinting approaches have recently emerged that show high potential for automatically synthesising MIP NP and transferring the protocols to large-scale production at reduced costs. In terms of sensor application, MIP NPs lead to appreciable sensitivity and selectivity. Moreover, nano-composite materials can be tailored to include additional functionality such as magnetic and semi-conductive cores. Within optical sensors, implementation of quantum dots (QDs) as optosensing material with a MIP shell even allows for fluorescence detection of non-optically active analytes. Sensitivity can be substantially improved by introducing Surface Plasmon Resonance (SPR) and Surface-Enhanced Raman Scattering (SERS), which have recently been successfully combined with MIP NPs and are promising chemical and biological sensors. Finally, MIP NPs have also proven very useful as plastic antibodies in pseudo-immunoassays.

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Contents

1. Introduction	145
2. Synthesis of MIP NPs – polymerisation methods	145
2.1. Precipitation polymerisation	145
2.2. Emulsion polymerisation	147
2.3. Template synthesis approach	147
2.4. Iniferter polymerisation	147
2.5. Automated reactors	148
3. Synthesis of core–shell NPs and nanoparticle composites	148
3.1. Functionalisation and grafting of core NP surfaces	149
4. Sensor applications	149
4.1. Electrochemical sensors	150
4.2. Optical sensors	151
4.3. Surface plasmon resonance (SPR)	153
4.4. Surface-enhanced Raman scattering (SERS)	153

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5. Pseudoimmunoassays.....	153
6. Summary and outlook.....	153
References.....	154
Biographies.....	157

1. Introduction

As a matter of principle, analytical methods require selective and sensitive recognition of the respective target analyte. Nature for instance applies antibodies, receptors, or enzymes for that purpose. However, for actual technological application, those are often limited in terms of ruggedness and cost-effectiveness. To overcome these limitations, synthetic receptors have been proposed and are now commonly applied [1–3]. Molecular imprinting is one way to achieve such artificial recognition. The concept was established in 1972 by Wulff and Sarhan, when they investigated a new method to introduce functional groups with specified stereochemical properties into polymers. They achieved this by introducing template molecules during polymerisation [4], finally leading to what they then called “host–guest polymerisation”. This straightforward strategy enables chemists to generate synthetic polymers that are selective towards a specified template via complementary non-covalent binding sites, based for example on ionic, hydrophobic or hydrogen bond interactions. After complete polymerisation, the template is removed resulting in recognition sites within the polymer matrix [1,2,5,6]. Fig. 1 summarises the principle of molecular imprinting.

Generally, MIPs are straightforward to synthesise and significantly reduce costs when compared with natural antibodies. They are highly stable and reveal remarkable mechanical properties. Furthermore, the method of molecular imprinting can be applied to a wide range of analytes making it possible to design sensors targeting small molecules, such as drugs, pesticides, peptides and sugars, as well as larger organic compounds and bio-analytes, such as viruses, erythrocytes and immunoglobulins [7,8]. They also allow for generating tailor-made polymers in such cases when a biological receptor cannot be found [2,9,10]. However, MIP can be further improved by introducing nano-sized structures, either by blending them with NPs, e.g. to increase sensitivity [11] or by synthesising MIP NPs. Obviously, the latter reveal much higher surface-to-volume ratio than thin films and thus also substantially larger total surface area per weight unit of polymer. Due to their geometric features, they provide better accessibility of recognition sites for the analyte as well as a lower mass-transfer resistance. Besides improved binding kinetics, the template species can be more easily removed from nanoparticles leading to reduced template leaching when applying those MIP [12,13]. Finally, when comparing MIP NPs obtained by solid-phase synthesis to natural antibodies, the artificial matrix turned out to excel in several properties: MIP NPs are 4–200 times less expensive, show much longer lifetime (up to several years), are more robust towards higher temperatures, and are easily regenerated and sterilised [3].

2. Synthesis of MIP NPs – polymerisation methods

Imprinted particles in micrometre dimensions are generally obtained by grinding the imprinted polymer monolith. This procedure leads to particles of somewhat irregular shape and size. Thus, they have to be sieved to obtain the desired particle size which inherently leads to low yields [14] and thus makes them unsuitable for standard industrial manufacturing and production processes. Therefore, there is a need of straightforward, cheap, easy and

generally applicable syntheses of MIP particles leading to narrow size distribution with high yield. Furthermore, several novel application scenarios of MIPs require smaller diameters in the nanoscale range [15,16]. To reach this, generally speaking high cross-linker ratios between 60 and 90% are applied to increase MIP NP formation at early stages of polymerisation [17]. It also turned out that photo-initiated polymerisation leads to better recognition properties in the final MIP, than thermal initiation, because increasing polymerisation temperature decreases selectivity and cross-linking [18,19]. In the majority of cases, free radical polymerisation is applied, because it provides a wide range of monomers and fine control of reaction conditions. Additionally, a wide variety of photo initiators is available on the market [20]. However, it is difficult to control size, shape and size distribution of particles during free radical polymerisation. This limitation can be reduced by making use of controllable “living” radical polymerisation (LRP) [21]. Table 1 summarises different polymerizations strategies and their respective outcomes.

2.1. Precipitation polymerisation

Precipitation polymerisation leads to quick, straightforward and cheap syntheses of monodisperse spherical polymer particles in high yield and purity. This synthetic method was first applied in 1999 to obtain MIP NP [22], because it resulted in materials that turned out superior to ground monoliths both in terms of selectivity and load capacity. Precipitation polymerisation is achieved by cross-linking polymerisation in highly diluted monomer solutions containing the respective template species. This continuous phase is a nonsolvent for the formed polymer beyond a critical molecular weight and results in spherical MIP with diameters of a few micrometres and below [14,22,23]. The idea of “post-dilution polymerisation” was first reported by Wulff *et al.* aiming to increase selectivity and economise template. They suggested diluting the pre-polymerised polymer after initial polymerisation time and continuing polymerisation to obtain nanogels [8,24]. Another precipitation polymerisation approach induces polymerisation in concentrated monomer solutions and to stop it before the gelation point is reached by diluting the oligomer solution. This method was successfully applied for TiO₂ sol–gel NPs precipitated with water [25]. In the case of biospecies as the template, first an aqueous oligomer solution is pre-polymerised in the presence of the template. For NP formation, a small amount of pre-polymer is added to a poor solvent for the polymer [26–30] (typical ratio 1:100; in this case the bulk polymerisation process is terminated early to lead to NP). In order to realise surface imprinting, the template can be covalently immobilised onto polymeric NPs followed by precipitation polymerisation to form a MIP shell around the core [31]. A detailed monograph about recent developments in MIP NPs by surface imprinting technique is provided by Ding *et al.* [32]. Another method is to perform precipitation polymerisation in aqueous media containing surfactant at very low concentration to avoid the use of organic solvents. In this way peptide MIP NPs could successfully be synthesised. The polymers include hydrogen-bonding, charged and hydrophobic functional monomers [33]. Recently, a new material design concept for protein imprinted NPs was reported, namely thermally responsive copolymer NP hydrogels. The affinity of such hydrogels towards the template decreases with increasing temperature protecting the

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