Nanostructured materials with biomimetic recognition abilities for chemical sensing

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Modern Materials Science takes some pride in implementing – sometimes complex – functionality into man-made matrices to make them suitable for a wide range of technological applications. Among other fields, materials being able to selectively and sensitively recognize species in their environments have become a strong focus of interest: Recognition is one of the key aspects of life governing a wide range of biological functions including immune reactions, but also catabolic and anabolic enzymatic processes to name the most important ones. Implementing such properties into an artificial material requires designing its functional and sterical features on the nanoscale finally leading to truly biomimetic setups.

From the material chemist's point of view, affinity interactions constitute one of the most straightforward possibilities for chemical sensing. It could already be shown that MoS_2 nanoparticles interact with organic thiol vapors in air [1]. For understanding the underlying mechanisms better, they were coated on piezoelectric transducers, namely so-called quartz crystal microbalances (QCM). When exposed to different analytes, they yield a very distinct response pattern, as can be seen in the front column of data in Figure 1: the highest responses are achieved for octane thiol and butane thiol, respectively. For octane and the other analytes, the responses are at least a factor of two (butane thiol) and 25 (octane thiol) lower. Especially the selectivity between octane and octane thiol, respectively, is a strong indicative that recognition is indeed governed by the thiol functionality. Being a "soft" group on the Pearson hardness scale, further material optimization should focus on this parameter e.g. by changing the metal in the substrate material to Cu instead of Mo. Figure 1 shows the outcome of this approach, namely an almost threefold increase in sensor response for the thiols. This factor is lower for octane and one for the other analytes supporting the strategy of optimized affinity.

Besides functionality, also sterical parameters can be addressed by smart materials structuring. Molecular imprinting [2] (see also Fig. 2) is a template-assisted strategy that leads to recognition cavities either in the bulk or on the surfaces of highly cross-linked polymer. The smallest possible analytes for their synthesis are given by metal ions. In this case, monomers that can form coordinative bonds allow for designing systems selectively interacting with bivalent copper ions, as can be seen from the QCM sensor responses summarized in Figure 2. Clearly, the imprinted material prefers the own template compound over all cross-reacting ones. This is even more remarkable keeping the fact in mind that there are only minute differences in the ionic radii of the compounds under observation.

The method has proven very powerful also for volatile organics and their mixtures [3]. Further increasing the size of the analyte towards biospecies, the properties of molecularly imprinted polymers (MIP) can directly be compared to natural systems. An example for this is the imprinting with WGA lectin, a surface protein that plays an important role in infection pathways. In this case, the natural receptor group is an oligosaccharide with a glucosamine moiety. By adding a suitable linker group (p-nitrophenol reduced to the amine and then linked to cysteine), the receptor can be immobilized via self-assembled monolayers on a QCM surface yielding appreciable sensor characteristics. When comparing them to Molecularly imprinted polymers towards the same analyte, one can see that the nanostructured polymer yields selectivity that is only a factor two lower than the natural system. This generally speaking marks the way towards actual artificial antibodies.

Inherently, the systems are also suitable for being applied for microorganisms. MIP for E. coli [4] on QCM are sufficiently robust to be applied over extended periods of time. Additionally, their interactions with the analyte are reversible. This makes them highly feasible tools for sensing immediately in bioreactors. During baceterial growth, the respective sensors indeed yield population-dependent sensor signals that can be vailidated by light microscopy. In contrast to antibodies, these artificial matrices can be regenerated and reused.

Summarizingly, rationally structuring materials on the subnano- to micrometer scale results in biomimetic interaction behavior combined with the technological strengths of man-made substrates.

References

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Figures

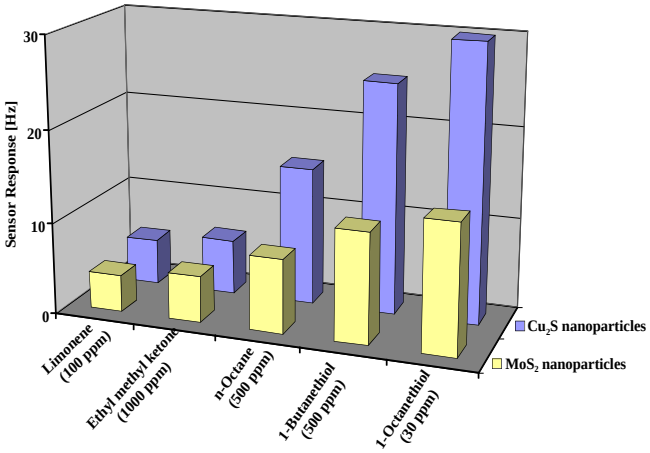

Fig. 1: QCM selectivity pattern of two different metal sulphide nanoparticles

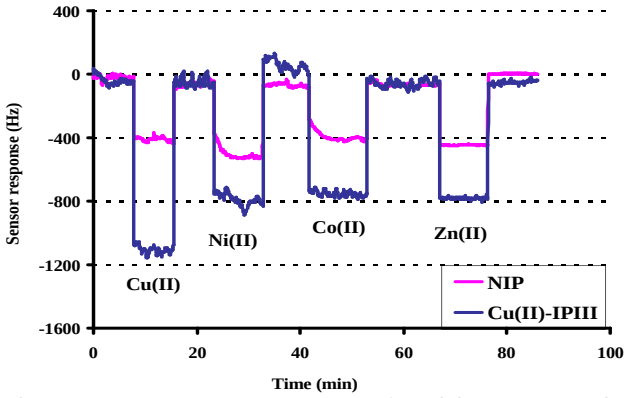

Fig. 2 QCM sensor responses of Cu(II) MIP towards competing bivalent ions.

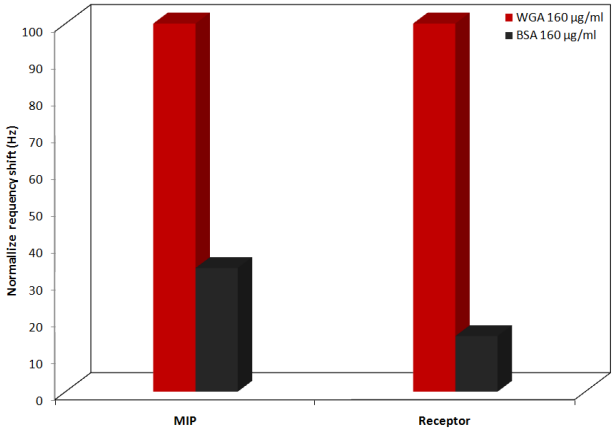

Fig. 3 Selectivity Pattern of Natural receptor analogue and WGA MIP, respectively.