Characterization of highly versatile micrometer sized sensor particles using different microscopical techniques

Klaus Koren[1,2], Günter Mistlberger[1], Armin Zankel[2], Peter Pölt[2] and Ingo Klimant[1]

1. Institute of Analytical Chemistry and Food Chemistry, A-8010 Graz, .
2. Austrian Centre for Electron Microscopy and Nanoanalysis , A-8010 Graz,

korenk@sbox.tugraz.at
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Real-time monitoring of chemically and biologically important parameters, like oxygen and pH, is of great interest not only in science, but also in industry. Knowing the exact level of these parameters can, e.g., elucidate bottle necks in metabolic pathways, control chemical reactions, or it can also be useful for improving large scale bio-processes.

During the last decade optical sensors have became very powerful tools in analytical science and are more and more replacing classical methods (classical analytical labs and electrochemical sensors) in research and industry. Among the different types of optical sensors nano- and micro-particle based sensors are constantly gaining importance [1]. Those highly versatile sensors consist at least of a polymeric matrix and an analyte sensitive dye. Due to their reduced sizes compared to bulk optodes the diffusion distance of the analyte towards the sensitive dye is very small, which significantly decreases the response time of such sensors. Furthermore additional functionalities can be achieved by e.g. binding biological species such as enzymes.

Recently, several groups reported on the incorporation of superparamagnetic nanoparticles into optical sensor particles [2, 3]. This enables the magnetic separation and remote control of the sensor particles, which is useful for many applications, such as in situ sensor spot formation [4].

Here we present a very promising method for large scale production of magnetic optical sensor particles (MOSePs). Spray-drying of a “cocktail” (including the polymer, a sensitive dye and magnetite nanoparticles in an organic solvent) yields micro-particles (3-30µm) (Figure 1). Characterization of the analytical properties of such particles showed astonishing results. Although the particles are large, compared to nano sensor particles with diameters of ca. 100nm, they respond extremely fast to varying analyte concentrations [5]. Moreover, the Stern-Volmer plots of τ_0/τ and I_0/I have almost identical and linear slopes for pO_2 = 0-1013 hPa, which indicates that all dye molecules are equally accessible by the quencher and there is a high probability of single exponential decay, a rare phenomenon in optical sensors (Figure 2a).

To understand why the analyte-diffusion is accelerated, SEM images of the particles were collected (Figure 1). The entire surface of the particles was littered with small pores (10-100nm in diameter). Cross-sections of the particles were investigated in the TEM in order to study the interior of the particles (Figure 2b). Those studies indicated a hollow structure with a shell thinner than 1µm.

TEM images show that the incorporated magnetite nanoparticles are not distributed homogeneously inside the particle shell. Those inhomogeneities were investigated using the highly versatile method of in-situ ultramicrotomy in the ESEM [6].

Combining all these results it was possible to better understand the formation of the particles and optimize the synthetic route. This example clearly demonstrates how important

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it is to characterize sensor particles at the nanometer scale, in order to entirely understand the processes involved in the synthesis as well as the response of the sensor.

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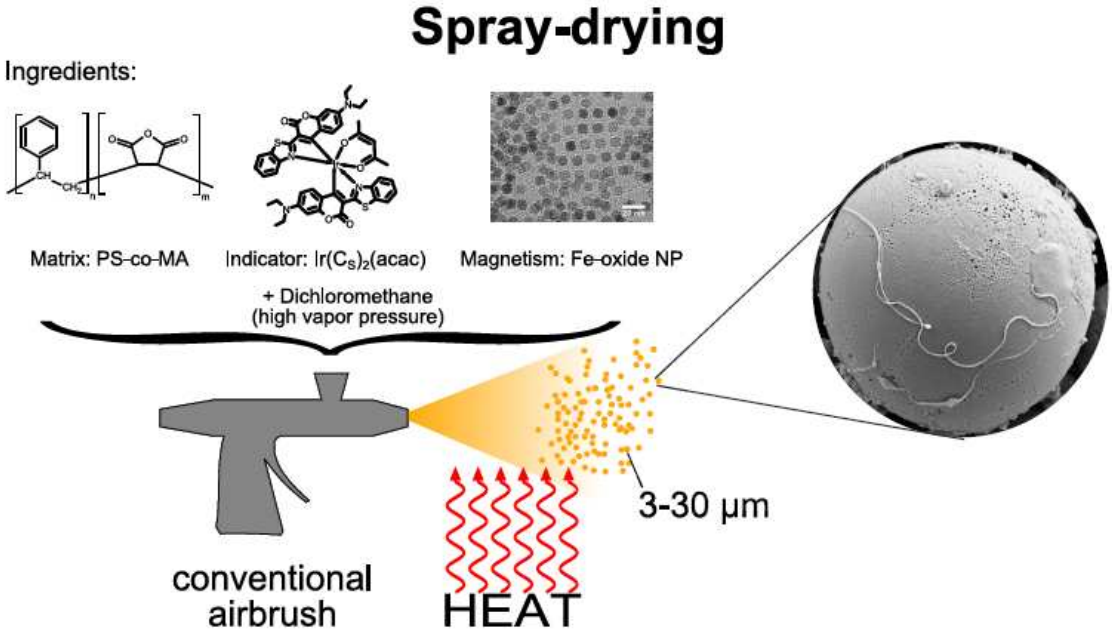

Figure 1. Synthetic strategy towards micrometer scale sensor particles; Polymer, dye and magnetite nanoparticles are dissolved/dispersed in dichloromethane and sprayed though an airbrush into a heated container. The insert displays the structure of the porous particles.

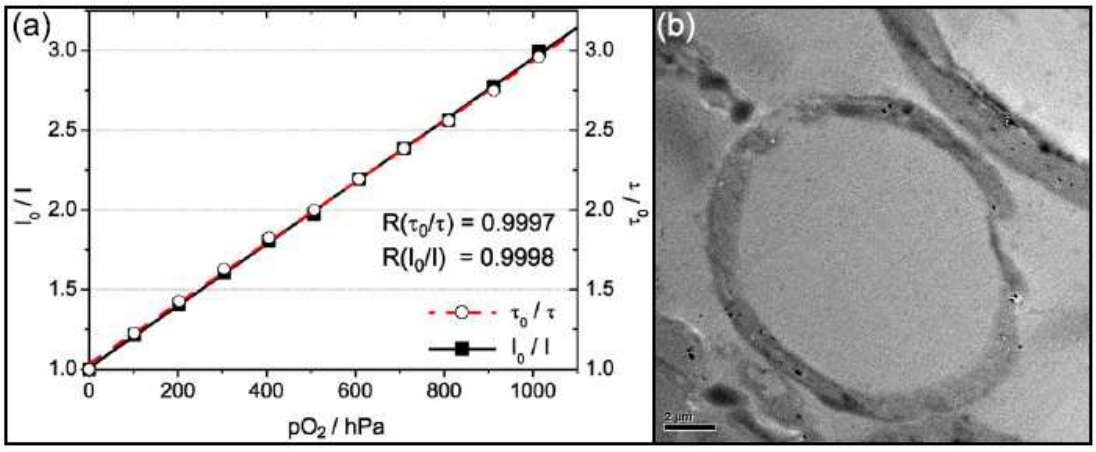

Figure 2. (a): Stern-Volmer plots of τ_0/τ and I_0/I have almost identical and linear slopes for pO_2 = 0-1013 hPa. This is a quite rare phenomenon in sensor chemistry that only can be understood by knowing the exact structure of the particles. (b): TEM cross-section of a particle shows the hollow structure.

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