Chemiresistors Based on Gold Nanoparticle Supercrystals: Sensing Mechanism Studied by in Situ GISAXS

Natalia Olichwer, Andreas Meyer, and Tobias Vossmeyer

Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany

Natalia.Olichwer@chemie.uni-hamburg.de

Assemblies of ligand stabilized gold nanoparticles have demonstrated remarkable potential for vapor sensing applications. The main features of gold nanoparticle based chemiresistors are their high sensitivity, adjustable selectivity, fast and reversible responses, low power consumption and the tunability of their underlying electrical properties.[1,2] It is generally accepted that the sensing mechanism involves (at least) both swelling and sorption induced changes in permittivity. While swelling leads to higher resistivities, due to increased tunnel distances between neighboring particles, an increase in permittivity counteracts, and sometimes even over-compensates, this effect.[3]However, repeatedly, findings have been reported which are difficult to explain by this model.[4] Thus, to enable the rational development and target specific optimization of such sensors, a deeper and more quantitative mechanistic understanding is indispensable. On the experimental side, this requires measurements enabling the correlation of the chemiresistive response with the actual change in interparticle distance and the absolute amount of sorbed analyte. As shown previously, swelling of ordered nanoparticle assemblies can be probed *in situ* via grazing incidence small angle x-ray scattering (GISAXS).[5,6] Here, we use GISAXS to study simultaneously swelling and resistive responses of supercrystals assembled from dodecanethiol stabilized gold nanoparticles. Additionally, the mass uptake due to analyte sorption was quantified using quartz crystal microbalances. When exposed to toluene, 4-methyl-2-pentanone or 1-propanol vapors, with concentrations ranging from 1000 to 10000 ppm, the supercrystals responded with a fast reversible increase in resistance and interparticle distance. All three measurements revealed the same trend concerning the selectivity, which was controlled by the solubility match between the dodecanethiol ligand and the solvent. The measurements allow us to test and further develop the above mentioned model. Further, it was observed that contaminants originating from the particle synthesis can have a considerable effect on the lattice constants, the swelling and the chemiresistive responses.

[1] F. J. Ibañez, F. P. Zamborini, Small, **2** (2011) 174.
[2] N. Olichwer, E. W. Leib, A. H. Halfar, A. Petrov, T. Vossmeyer, ACS Appl. Mater. Interfaces, **11** (2012) 6151.
[3] Y. Joseph, A. Peic, X. Chen, J. Michl, T. Vossmeyer, A. Yasuda, J. Phys. Chem. C, **34** (2007) 12855.
[4] A. W. Snow, M. G. Ancona, D. Park, Langmuir, **44** (2012) 15438.
[5] Y. Wan, N. Goubet, P.-A. Albouy, N. Schaeffer, M.-P. Pileni, Langmuir, **44** (2013) 13576.
[6] M. C. Dalfovo, L. J. Giovanetti, J. M. Ramallo-López, R. C. Salvarezza, F. G. Requejo, F. J. Ibañez, J. Phys. Chem. C, **9** (2015) 5098.