Experimental report

14/02/2018

Proposal: 9-12-470 **Council:** 4/2016

Title: Determining the porphyrin shell ofZnO nanoparticles in situ

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: ZnO with porphyrins

Instrument	Requested days	Allocated days	From	To
D11	3	1	03/10/2016	04/10/2016

Abstract:

Dye sensitized solar cells are of high importance in solar cell research. The main functional part of them is a layer of semiconductor nanoparticles, which are covered with a dye. To obtain highly efficient cells the linkage between porphyrin and ZnO nanoparticles is of interest. We recently followed the stabilization of ZnO nanoparticles by the combination of in situ SAXS and SANS in dependence of time and temperature and in a further study we investigated the ligand exchange of the initially stabilizing acetate by simple catechol molecules. With this knowledge we want to analyze by the help of SANS (in combination with lab-SAXS) the exchange of acetate by different porphyrin dye molecules. Therefore, we intend to perform measurements of the starting ZnO solution, after absorption of different porphyrin concentrations and washed ZnO-porphyrin samples for two different porphyrins. For all samples the SLD of the solvent will be matched to the SLD of the ZnO core, so that the coherent signal will be originating only from the porphyrin shell. The in total 42 samples have to be measured for 1.5h each. Thus, we apply for three days of beamtime at the high-flux instrument D11.

Experimental Report for proposal 9-12-470: Determining the porphyrin shell of ZnO nanoparticles in situ

Dye sensitized solar cells are of high importance in solar cell research.[1] The main functional part of these cells is a layer of semiconductor nanoparticles, which are covered with a dye. The dye is used to harvest light and the semiconductor nanoparticles act as electron transport medium. To obtain highly efficient solar cells the linkage between porphyrin and the ZnO nanoparticles is of interest.[2] We recently followed the stabilization of ZnO nanoparticles prepared by the sol-gel method from zinc acetate by the combination of in situ SAXS and SANS in dependence of time and temperature.[3]

Differently substituted Cobalt-Tetraphenylporphyrins with carboxylic anchor groups were used, which are shown in Figure 1. SANS curves were obtained for all ligand-exchange reactions and the samples were also measured at our in-house SAXS instrument (Figure 1, bottom). The corresponding SAXS and SANS curves were fitted simultaneously and analyzed for their ligand shell(Figure 1, bottom right).

By additional UV/Vis experiments the amount of porphyrin added to ZnO nanoparticles was determined and thus, the amount of acetate could also be revealed. As it is shown in Figure 3, the number of porphyrin, which adds to the ZnO surface is very similar for all porphyrins used.

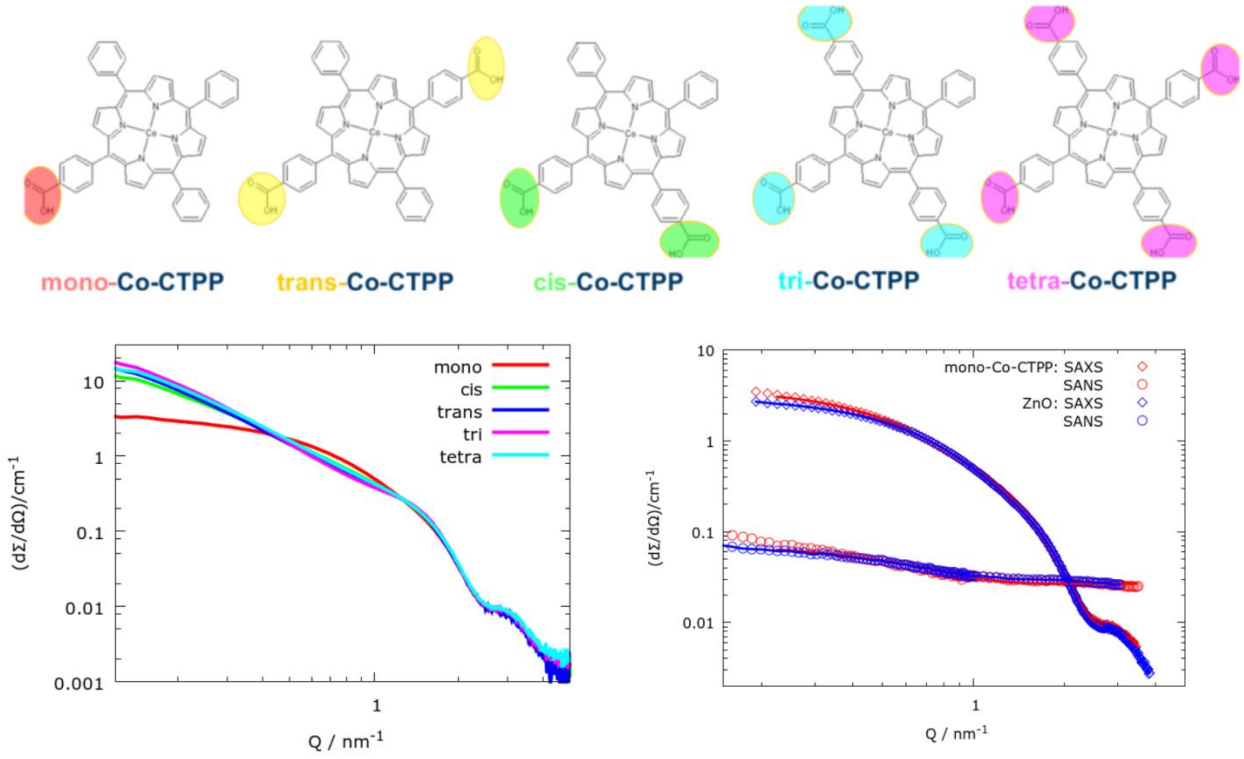

Figure 1: Top: Used Cobalt-Tetraphenylporphyrins, bottom left: SAXS curves of ZnO NPs after decoration with different porphyrins. Bottom right: SAXS and SANS curves

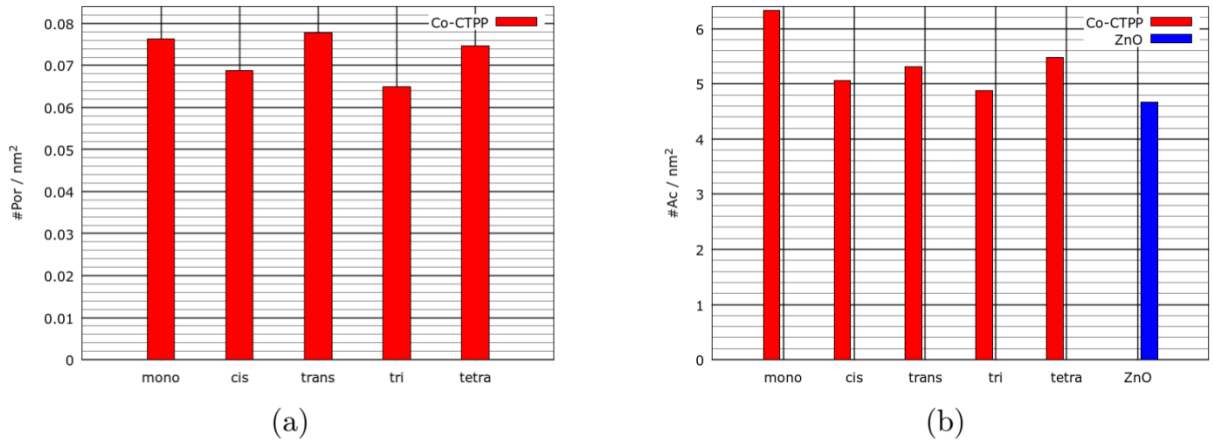

Figure 2: a) Porphyrin and b) acetate coverage of the ZnO NP-surface.

In addition, no significant differences in the acetate coverage could be determined. Due to an increase in the mean size of the NPs upon porphyrin addition, the decorated NPs show a higher acetate coverage compared to the undecorated NPs.

Literature:

[1] B. O'Regan, M Grätzel, *Nature*, **1991**, 353, 6346
[2] H. Saarenpää *et al.*, *J.Phys.Chem.C*, **2012**, 116, 2336
[3] T. Schindler *et al.*, *Langmuir*, **2015**, 31, 10130