ESRF	**Experiment title:** ASAXS study of „Pd bionanocatalysts“	**Experiment number**: SC-1134
Beamline: ID 1	**Date of experiment**: from: 12/05/2003 to: 17/05/2003	**Date of report**: 01/03/2004
Shifts: 11	**Local contact(s)**: Bruno Jean, Peter Boesecke	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Barbara Aichmayer [1]*, Oskar Paris [2]*, Gerald A. Zickler [2]* and Peter Fratzl [2]

1) Institute of Metal Physics, University of Leoben and Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, A-8700 Leoben, Austria

2) Max Planck Institute of Colloids and Interfaces, Department of Biomaterials, D-14476 Potsdam, Germany

Report:

In the framework of the EU project BIO-CAT* we investigate Pd particles which are deposited onto S-layer proteins. S-layers are crystalline bacterial cell surface layers which form highly regular two-dimensional arrays [1]. TEM (Transmission Electron Microscopy) investigations of metallized S-layers showed a regular arrangement of metal particles, which were situated in the pores of the protein [2, 3]. SAXS (Small Angle X-ray Scattering) experiments with lab equipment indicated a change of the protein structure caused by the metal loading.

With the aid of ASAXS (Anomalous SAXS) we intended to separate the scattering contribution of the palladium from the signal of the biological material in order to characterize the Pd particles and the loaded organic template. Unfortunately, during our experiment at the ESRF, we had to deal with several problems. On the one hand, the high energy of the Pd K edge (24.350 keV) could only be reached with an improvised and hence quite unstable setup. On the other hand, the structure of our samples was strongly influenced by the synchrotron radiation (SR). Therefore, we could not succesfully perform the ASAXS measurements we had planned to do.

Nevertheless, the experiments at ID1 led to some very useful results regarding the SR induced formation of Pd particles on S-layer proteins. After we had discovered that exposure to the synchrotron beam changed the scattering signals of our samples, we performed a series of time-dependent measurements. We collected one frame after the other at the same sample position and observed an inrease of the small angle scattering intensity corresponding to the formation of nanosized particles. The obtained effect was proven to be reproducible. Changing the sample position and repeating the measurements led to the same development of the small angle scattering signal. This behavior was observed for different kinds of samples including two types of S-layers with different concentrations of Pd. An example for the increase of the scattering intensity with increasing exposure time to SR is given in Figure 1. The length of the scattering vector Q is given by $Q=4\pi\sin\theta/\lambda$, where λ is the wavelength and 2θ is the scattering angle. Figure 2 shows the evaluated size of the built particles (Porod radius) and their volume fraction as a function of exposure time. The Porod radius is defined as $R_p=\tilde{I}/P$, where $\tilde{I}$ is the integral intensity and P is the Porod constant.

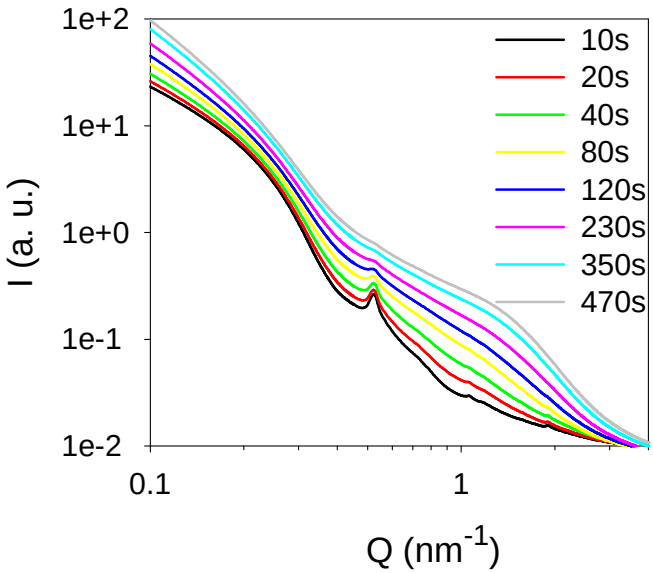

Fig. 1: Intensity I vs. scattering vector Q for different exposure times to synchrotron radiation. (Pd on S-layer of Bac. sph. NCTC 9602)

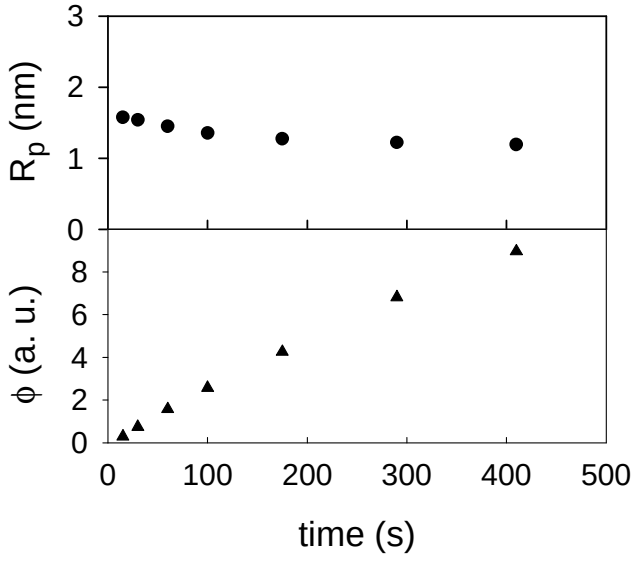

Fig. 2: Porod radius R_p and volume fraction ϕ vs. exposure time to synchrotron radiation. (Pd on S-layer of Bac. sph. NCTC 9602)

Whereas the volume fraction of the particles increased dramatically with increasing exposure time to SR, the size of the particles remained rather constant. No coarsenining occurred. From this behaviour, we conclude that the S-layer protein stabilizes the small particles which have a Porod radius of approximately 1.2 - 1.5 nm. As a result of the experiment, we are currently modifying our sample preparation (the chemical reduction of Pd salt) in order to produce stable samples consisting of metallic Pd particles with a diameter similar to the one we observed for the particles built in the synchrotron beam. Complementary to SAXS measurements, we investigate our samples with neutrons in order to avoid the strong influence that was observed for SR.

*This work is supported by the European Union (contract No. G5RD-CT-2002-00750).

[1] Sleytr, U.B., Sára, M., Pum, D. and Schuster, B. (2001). *Progress in Surface Science* **68**, 231-278.
[2] Mertig, M., Wahl, R., Lehmann, M., Simon, P., Pompe, W. (2001). *Eur. Phys. J. D* **16**, 317-320.
[3] Wahl, R., Mertig, M., Raff, J., Selenska-Pobell, S., Pompe, W. (2001). *Advanced Materials* **13**, 736-740.