| ESRF | **Experiment title:**<br>Structural studies of gold clusters and nanowires in mesoporous alumina using SAXS/WAXS | **Experiment number**:<br>CH-810 |
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Our EU-funded research network CLUPOS is working on the positioning of nano-materials in confinements with regular spacings in order to evaluate their future applications in nano-electronics [1].

Alumina membranes fabricated by an electrochemical anodic oxidation of aluminium metal, contain parallel cylindrical pores packed in a hexagonal array with wall thickness comparable to pore diameter. The pores are perpendicular to the membrane surface and their size is controllable as a function of the voltage within the diameter range 5 – 100 nm [2]. The membranes have found application as a template for metallic nanowires [3] and as a substrate for growing carbon nanotubes [4]. The pores of these alumina membranes are ideally suited to grow electrochemically different metal nanowires to fabricate a new type of supported and insulated one-dimensional "quantum wire".

In the first part of our experiment we used Small-angle X-ray scattering to characterise the pore dimensions as well as their relative arrangement in the empty as well as in the metal filled alumina membrane. The nano-structure of the membranes has been primarily investigated by electron microscopy on ultramicrotomed films but this technique views only the surface structure for a limited area. The SAXS technique is a convenient alternative to the use of electron microscopy allowing a more complete characterisation of these new materials.

Measurements have been made for several membrane samples grown under different voltages featuring different pore sizes. The change in the SAXS profile has been studied as a function of the orientation of the membrane to the incident beam. When the membrane axis is parallel to the incident beam, the intensity profile shows oscillatory shape. Figure 1a shows the SAXS pattern of a 40V alumina membrane featuring pore diameter of 48nm. Those concentric rings result from the disordered hexagonal lattice (with a smooth preferential orientation), times the form factor a single channel (circular aperture which gives rise to a Bessel function in the Fraunhofer approximation).

Four orders of diffraction are seen in the Fraunhofer rings, measured over six orders of magnitude. If the membrane is rotated the two-dimensional pattern exhibits an asymmetric structure. This structure changes systematically in shape from a ring structure pattern to a set of vertical spots when the membrane is edge-on to the beam. Figure 1b shows a typical pattern for a 40V membrane. The adjustment of the membrane axis to give a symmetric ring pattern is found to be very sensitive and confirms that the independent cylinder axes of the pores are very well aligned. Additional structure displayed on the inner rings relates to the distribution of the pores of the sample. A radial summation has been made for the ring structure of figure 1a and is shown as a log plot in Figure 2.

The present results provide a preliminary demonstration in the use of SAXS for detailed studies of the three-dimensional nature of these membranes (length and diameter of the channels, lattice parameter of the hexagonal lattice, quality of the alignment, etc). A full quantitative analysis of the patterns should provide more information and provide a powerful method for the characterisation of these systems, including the distribution of the encapsulated material.

In the second part of our experiment we have then used WAXS technique to study the structure of two ligand-stabilised gold clusters $Au_{55}(PPh_3)_{12}Cl_6$ and $Au_{55}(T_8\text{-}OSS\text{–}SH)_{12}Cl_6$ as well as two nanowires of gold confined in two alumina membranes grown under 20V and 60V presenting pore sizes of 24 and 72 nm respectively.

Figure 3 shows the WAXS data of the two ligand-stabilised gold clusters as well as the nanowires grown by electroplating in the 20 V and the 60V alumina membrane with a gold foil taken as a reference. In the case of the nanowire the X-ray beam was parallel to the pores. The pattern of the nanowire could be indexed with the fcc gold structure but the peaks beyond the first one were found to be very weak at large angles. The pattern of the two clusters showed a broad peak around 2θ = 39° corresponding mainly to the 111 reflection. This is a larger angle than for the bulk, confirming the shorter Au-Au distances in the clusters found already in our EXAFS work.

The WAXS gives further evidence for the fcc structures of these $Au_{55}$ clusters. Simulations of X-ray diffraction patterns have shown that icosahedral gold clusters would give rise to a clear additional feature. The diameters of the two ligand-stabilised clusters were determined by measuring the fwhm of the peaks and using the Scherrer formula.

Gold nanowires grown in the 60V and in the 20V membrane were found to be composed in average of crystallites of respectively 8.6 and 7.1 nm diameter. Both show the same fcc structure and Au-Au distance as the bulk metal confirming our EXAFS results The crystallites have an elongated shape with several crystallites occupying the pore diameter. The shape and the very small size of the crystallites could explain the very low Debye-Waller factors found in our EXAFS analysis [5].

A preliminary test using WAXS on one cobalt nanowire sample which already shown remarkable magnetic properties [6] allowed us to point out very strong preferred orientation of its structure [7].


[1] see the network homepage: www.clupos.lth.se

[2] Hanaoka, T.-A.; Heilmann, A.; Kröll, M.; Kormann, H.-P.; Sawitowski, T.; Schmid, G.; Jutzi, P.; Klipp, A.; Kreibig, U.; Neuendorf, R. *Appl. Organometal. Chem.* **1998**, 12, 367.

[3] T.Kyotani, private communication; J. C. Dore, A.Burian, T.Kyotani and V.Honkimaki, in preparation,

[4] R. E. Benfield, D. Grandjean, J. C. Dore, M. Kröll,; G. Schmid, D. Le Bolloc'h, T. Kyotani, manuscript in preparation.

[5] Benfield, R. E.; Grandjean, D.; Pugin, R. ; Sawitowski T.; Kröll, M.; Schmid, G., submitted for publication.

[6] Paulus, P.; Luis, F.; Kröll, M.; Schmid, G.; de Jongh, L. J. submitted for publication.

[7] R. E. Benfield, D. Grandjean, J. C. Dore, Z. Wu, M. Kröll,; T. Sawitowski, G. Schmid, to be submitted (10th International Symposium on Small Particles and Inorganic Clusters, Atlanta, USA, October 2000.

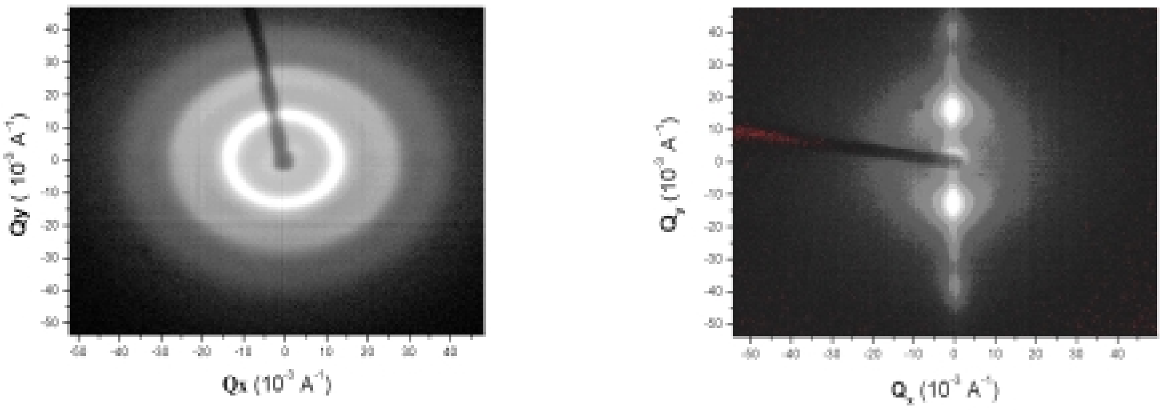
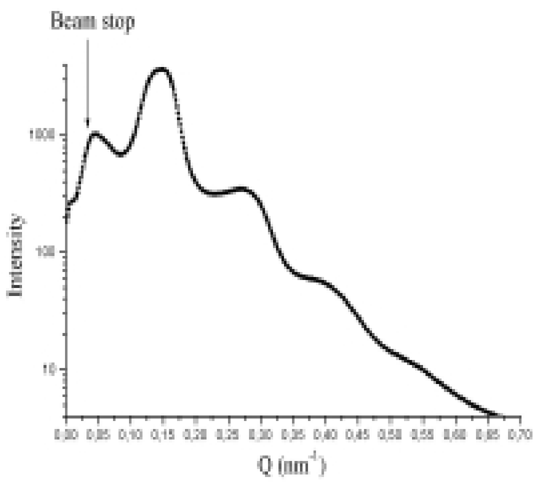




**Figure 1** :SAXS patterns showing ((a) left) the concentric rings of a 40V alumina membrane face-on to the beam; ((b) right) the set of vertical spots of a 40V membrane edge-on to the beam.



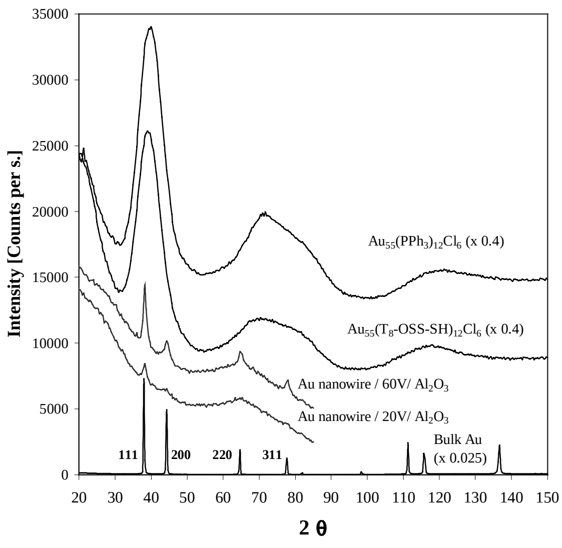




**Figure 2 (left)** :Radial summation for the ring structure of figure 1a shown as a log plot.

**Figure 3 (right)** :WAXS data of the two ligand-stabilised gold clusters as well as the nanowires grown by electroplating in the 20 V and the 60V alumina membrane with a gold foil taken as a reference.