



	Experiment title: Structural evolution of nanostructured metal oxide and organosilica thin films by chemical solution deposition monitored by SAXS	Experiment number: 26-02-488
Beamline: BM-26B ‘Dubble’	Date(s) of experiment: From: 18-9-2009 To: 22-9-2009	Date of report: 1-10-2009
Shifts: 12	Local contact(s): dr. G. Portale	
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Report: (max. 2 pages)

The chemical solution deposition technique is a highly flexible method for the fabrication of mixed metal oxide and hybrid organic/inorganic thin films from liquid precursor solutions, nanoparticle dispersions and sol-gels [1]. This technology holds great promise for energy-efficient molecular separation membranes [2], as well as for future low-cost printable electronics, sensors and MEMS applications. The solutions that are used for patterning and thin film formation consist of a mixture of metal organic or organosilica precursors, stabilizing agents and solvents. The precursors and stabilizing agents associate into small physically and/or chemically bonded fractal aggregates of 1-10 nm diameter, one order of magnitude smaller than the dimensions of the targeted structures. These sol particles can be turned into thin films and nanopatterns after deposition, drying and thermal consolidation. While a complex relation exists between the various parameters of a sol-gel process and the obtained nanostructure, the final structure is determined to a great extent by the applied drying procedure. Detailed understanding of the drying stage is therefore required to allow effective tailoring of these nanostructured devices.

Network formation during drying is determined by three main factors. One involves the intrinsic reactivity of the precursors, one the concentration increase of the various reactants upon solvent evaporation, and one the actual surface charges in the sol, determined by both the colloidal structure and the presence of additional charged species (e.g. acids). In order to understand these processes and allow tailoring of the nanostructure, we need to systematically assess which factors dominate at what stage, and how these influence the structure.

The high intensity of a synchrotron beam is ideal for studying the rapid structural evolution on a second-to-minute scale, using SAXS to study the drying process of a thin layer. In this way, a deeper understanding of network formation during rapid drying can be acquired with broad applicability. We specifically focused on functional hybrid and oxidic microporous and mesoporous materials that can be used as membranes for energy-efficient molecular separation. These are prepared from silane, organosilane and metal alkoxide precursors, and combine molecular separation selectivity with exceptional structural stability [2]. We have used SAXS to tune the structure of colloidal sols for membrane coating [3]. Better understanding of the processes during the drying stage will allow further improvement of the nanostructure, and thus of membrane separation performance. We aimed at studying the formation mechanism of nanostructured materials upon in-situ drying. The influence of processing variables on size and shape of the colloids in solution was assessed, as well as the relation between colloidal structure, crystallite formation and porosity. We can thus distinguish

physically- (solvent evaporation) from chemically (ageing) induced network formation, and acquire information on the evolution of crystallinity and porosity in drying films.

We have carried out Small-angle X-ray scattering (SAXS) measurements at the DUBBLE beamline BM-26B on (organo)silica sols with various stages of development. We obtained data at short detector distance and studied silica colloidal sols with different bridging groups, sols from metal alkoxides, and sols from monofunctional triethoxysilane precursors. By combining SAXS with other techniques, such as DLS (which determines the hydrodynamic radius of the sol particles), we can obtain a full description of the effect of the organic groups on the development of the structure. We varied independently the catalyst concentration, the type of catalyst, the hydrolysis ratio and the silane concentration for sols that were introduced in thin-walled glass capillaries. The applied beam energy was 16 keV, and the sample-detector distance 1.5 m.

Thanks to optimized slit settings and focusing on the beam stop and efficient assistance by our local contacts, a high resolution could be obtained. We experienced a very stable beam delivery throughout the experiment. Excellent reproducibility of the scattering patterns was found, enabling observation of reactant- and catalyst-dependent development of sols, and structural evolution of as-dried films.

The drying step is a very important but almost unexplored stage in the preparation of a sol-gel derived material. The greater part of our experiments were devoted to in-situ drying experiments, for which a special setup had been developed by Guy Eeckhaut and Wim Bras, which we were kindly allowed to use. We successfully attempted in-situ drying experiments of sols using this setup, at various temperatures.

The drying experiments show that a colloidal organosilica sol can form either a microporous or a mesoporous network, in which the type of catalyst (acid or base) and its concentration during drying play a crucial role. The exact conditions are strongly dependent on the electronic structure of the precursor. For all precursors, the formation of porosity additionally depends on the availability of water, the degree of network condensation and the drying temperature. In addition, we investigated how ionic and nonionic surfactants affect the formation of ordered structures during drying. Leaching out of these surfactants will similarly lead to mesoporous structures. Understanding the development of porosity upon drying is highly relevant for the further development of molecular separation membranes.

The obtained results will allow us to better understand how the colloidal network develops during drying, as well as to relate synthesis conditions to the membrane pore structure and separation performance. Tailoring of the recipe for membrane development can thus be greatly accelerated and will allow a broadening of the application window for molecular separation membranes.

References

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