TEM Characterisation of SBA-15 and Au Nanoclusters

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Introduction

Monolithic meso-/macroporous organo-silica materials with several hierarchical levels from the molecular- to the macroscale are prepared from a phenylene-bridged ethylene glycol-modified silane (bPhGMS) through sol-gel processing [1]. The resulting structures are compared with those grown from ethylene glycol-modified silane, EGMS, which leads to a purely inorganic network. [2]. In both cases Pluronic P123 is used as structure directing agent for the ordered mesopores. The macromorphologies of the resulting networks evolve due to phase separation during the hydrolysis and condensation and are frozen in by the sol-gel transition. Both systems exhibit narrow pore-size distributions and high surface areas (500-1000 m^2g^{-1}), which makes them promising candidates for numerous applications, e.g. catalysis, (bio-) immobilisation and separation, adsorption, sensing and optoelectronics.

The network structures were studied by a combination of CTEM and electron tomography. It is shown that the macroscopic networks of the three samples are similar with respect to the mesopore orientation. Systematic differences in the portion of disordered mesopores are found. The interplay between meso- and macrostructure allows for drawing conclusions on the formation mechanism. A model is presented which could explain the observed differences from the formation process. The results are supported by complementary in-situ time-resolved Small-angle X-ray scattering SAXS measurements of the gel formation.

Moreover we demonstrate that the simultaneous synthesis of the silica networks and functional noble metallic nanoparticles, here Au, is possible.

Literature:1. D. Brandhuber, H. Peterlik, and N. Hüsing, small 2006, **2**, 4, 503
2. D. Brandhuber, V. Torma, Chr. Raab, H. Peterlik, A. Kulak, and N. Hüsing, Chem. Mater. 2005, 17, 44262
3. Ch. Yu, J. Fan, B. Tian, and D. Zhao, Chem. Mater. 2004, 16, 889

Sample Series

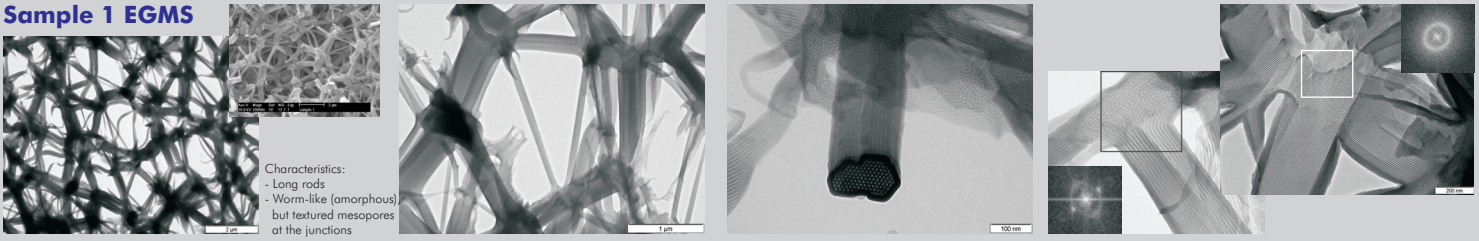
Synthesis

Sample	Si-precursor	Surfactant	Si [wt-%]	pH	H2O [wt-%]	Gelation time [min]
1	EGMS	P123	8	1	110	70
2	bPhGMS	P123	5.8	2.5	110	30-40
3	bPhGMS	P123	5.3	2.5	90	45
4	EGMS	P123	Au source: $HAuCl_4$			

Characterisation

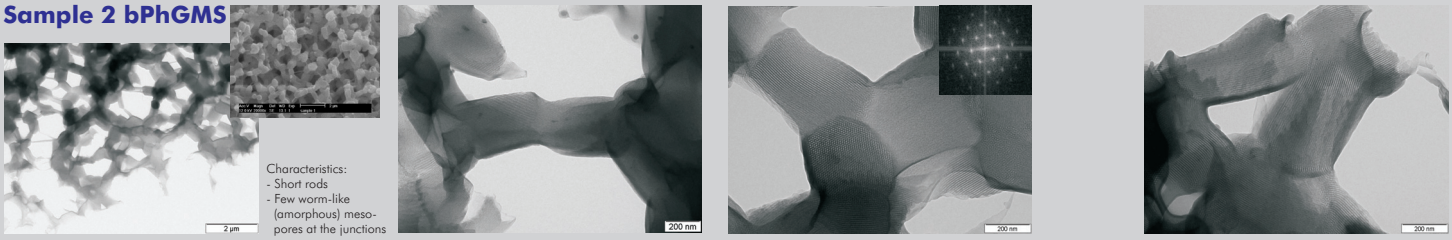
Sample	Lattice constant [nm] SAXS	Pore diameter [nm] BET	Wall thickness [nm] SAXS & BET	Aspect ratio From spot checks
1	13.7	6.8	6.9	20:1 - 5:3
2	12.5	7.5	5.0	7:1 - 1:1
3	12.9	7.7	5.2	1:5 - 1:6
4	13.6	6.9	6.7	not determined

Sample 1 EGMS



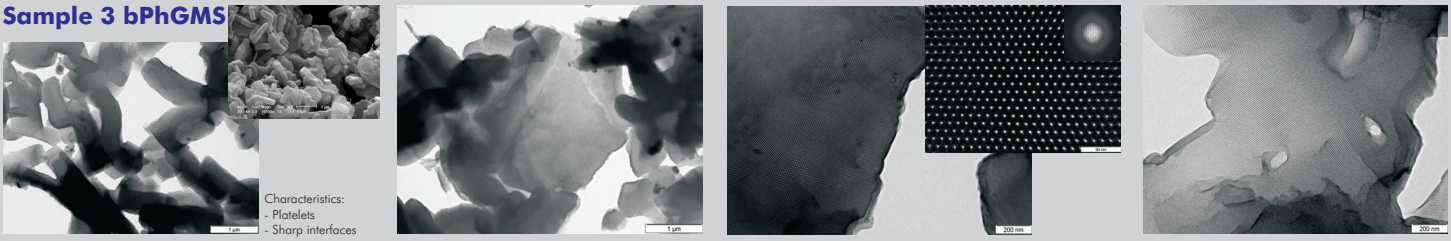
Characteristics:
- Long rods
- Worm-like (amorphous) but textured mesopores at the junctions

Sample 2 bPhGMS



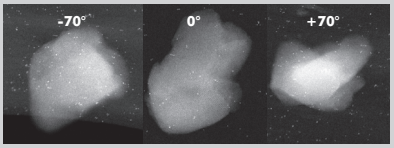
Characteristics:
- Short rods
- Few worm-like (amorphous) mesopores at the junctions

Sample 3 bPhGMS

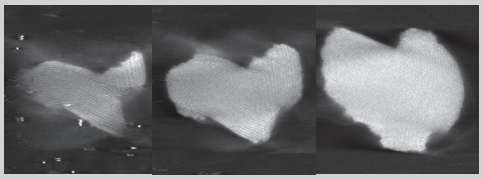


Characteristics:
- Platelets
- Sharp interfaces

Tomography on sample 2

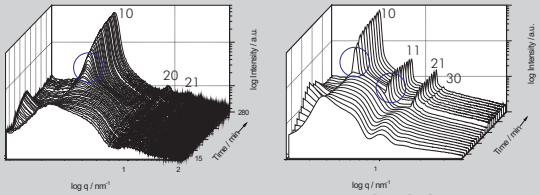


Tilted particle



Z-slices of the reconstructed particle

Growth model



EGMS - similar to sample 1 **Sample 3 bPhGMS**

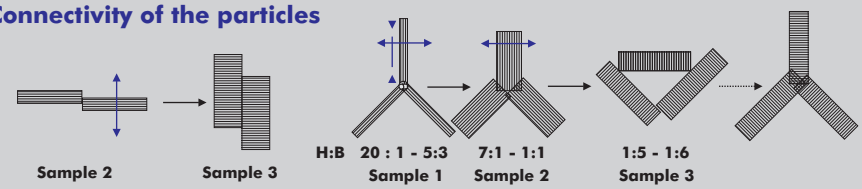
In-situ SAXS measurements on the gel kinetics were performed at the SAXS beamline Elettra (Trieste, Italy, EGMS) and Id02 at ESRF (Grenoble, France, bPhGMS). In time-resolved SAXS curves of both systems a rise and decrease in intensity was observed at low-q. This suggests that both materials grow from a disordered intermediate phase which vanishes at the moment of mesopore formation.

The curves display significant differences in the evolution of the structures. The time at which the mesostructure starts to form is much longer in case of the EGMS system. The final gel consists of long rods with high aspect ratio and disordered but textured worm-like mesopores at the junctions of the rods. In the bPhGMS system phase separation, mesostructure formation and gelation takes place much faster, the interplay leading to gel-networks with low aspect ratio such as thick rods (sample2) or platelets (sample 3). The portion of worm-like pores at the particle junctions decreases with the aspect ratio, i.e. with the formation velocity.

Questions for future research:

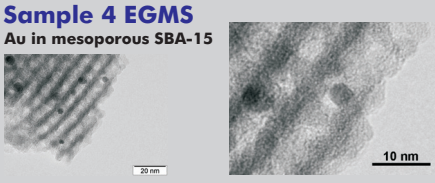
1. Is the pH value the only reason for the two velocities of the mesostructure formation process?
2. Does the mesostructure formation velocity influence the morphology of the particles or are the particles only determined by the morphology of the separated phase? Can we conclude from the macromorphology to the growth direction?
3. Are the diesordered worm-like pores in sample 1 (altered) residuals of the intermediate phase?

Connectivity of the particles



Sample 4 EGMS

Au in mesoporous SBA-15



Conclusion

Interconnected networks with hierarchical pore structures were produced in a sol-gel process from EGMS and bPhGMS and characterised by CTEM in combination with electron tomography. Complementary in-situ SAXS measurements provided time resolved informations about the structure formation. For the TEM measurements we used a novel method of embedding the 3D networks. By this approach it was possible to study the mesopore structure with respect to the macromorphology.

All samples formed similar networks with respect to the relative mesopore orientation in the gel network while the junctions differed significantly between EGMS and bPhGMS samples. EGMS samples showed interparticle junctions with a core of disordered but textured worm-like mesopores. The observation of worm-like mesopores is in aggreement with Yu.[3] The bPhGMS samples showed relatively sharp interfaces. The interconnected mesoporous particles differed in their aspect ratio. The lower the aspect ratio the lower was the content of disordered mesopores. Samples grown from bPhGMS exhibited a lower aspect ratio than EGMS samples. The mesopore formation in sample 3 occurred much faster than in the EGMS sample. Moreover, in this work we demonstrated the simultaneous synthesis of hierarchical mesoporous silica supports with the functional noble metal nanoparticles.

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