Summary

The development of new materials with tailored structure and properties has given an impetus to new research directions in materials science. Different ways to control the structure down to the nanometer scale are being extensively studied. There are various methods to build up nanostructured systems: atomic deposition, mechanical milling, chemical methods, and gas-aggregation techniques. Each of these techniques has its own pro’s and con’s. A proper selection of the appropriate method has to be made based on the fundamental and applied requirements.

Processing of nanoparticles and characterization of their structure are the main objectives of the research presented in this thesis. We use both experimental and theoretical approaches to investigate the influence of experimental conditions on nanoparticles size, morphology and composition. Controlling these parameters opens remarkable opportunities to develop materials with a specific functionality more efficiently. The first part of this work focuses on the production of nanoparticles in a so-called cluster source, whereas the second part is dedicated to the research of nanoparticles formation in flames. Siloxanes present in biogases convert into silica nanoparticles upon combustion. In most cases this effect is undesirable since it results in the contamination and eventual failure of the gas operating equipment. A systematic research has been performed to study the effect of experimental conditions on formation process.

We started this project with the design and assembly of experimental setup to produce nanoclusters (Chapter 2). It is based on the gas aggregation technique, where magnetron sputtering is a source of atoms. The computer based control system enables us to run experiment fully automatic. This, in turn, provides a high reproducibility especially for short deposition times. The overall design of the cluster source, containing thermal and e-beam evaporators, 4-axis heated and electrically isolated sample stage, separate pumping units for every chamber, additionally available vacuum ports makes the setup efficient and versatile, allowing a wide range of experiments to be performed. The second part of Chapter 2 focuses on the experimental setup used to study nanoparticles formation in flames at well-defined laboratory conditions. It has two main sections, i.e. concerning the gas handling system and sampling system. The former is built to simulate the presence of siloxanes in biogas by the addition of siloxane-containing liquid to the
methane/air mixture and feeding to the burner. A broad range of siloxane concentrations can be simulated by changing the configuration of the flow controllers and type of siloxanes. The working principle of the sampling system is based on thermophoresis. Multiple experiments followed by probe modifications allowed us to fabricate the thermophoretic probe for sampling with high spatial resolution. We have shown that probe construction can significantly affect the precision of nanoparticle sampling in flame.

Nanosized dimensions of particles require not only sophisticated processing techniques but also highly advanced techniques for its characterization (Chapter 3). Transmission electron microscopy (TEM) was used as the primary tool to investigate the structure of nanoparticles. Scanning electron microscopy (SEM) was employed to observe surface microstructure of samples collected from the heat exchanger. We utilized quantitative X-ray microanalysis on both TEM and SEM to determine the chemical composition. Quantification of TEM micrographs was done using image processing and analysis techniques.

We have formulated a physical model of nanocluster formation from a supersaturated atomic vapor in an inert gas flow (Chapter 4). It shows that the evolution of nanocluster size distribution is governed through several concurrent processes. Computer simulations using this model predict that due to high diffusion mobility, monomers and small cluster are deposited to walls, while diffusion for larger clusters is dominated by convective transport mechanism. As a result, a fraction of large clusters can survive diffusional loss to inner walls. Aggregation of fractal-like nanoclusters results in a broad size distribution.

Nanoclusters synthesis by a gas aggregation technique was presented in Chapter 5. We used in-house built experimental setup for this purpose and hence several tests were performed to explore its capabilities and to find the influence of experimental conditions. Results have shown that agglomerates formation takes place already in the aggregation chamber; so as to understand the kinetics of cluster formation we focused our research on processes inside the aggregation chamber. Experimental results for two kinds of gases and two different pressures were used to validate the model of cluster formation which has been formulated in Chapter 4. A good agreement has been obtained between the experimental data and predictions of the model. This confirms that the model can be used as a practical tool in planning future experiments with nanoparticles production in our experimental setup and similar installations.

Chapter 6 is devoted to the formation of silica nanoparticles in flame. We investigated this phenomenon by simulating presence of siloxane in biogas thru addition of hexamethyldisiloxane (L2) to the methane/air mixture. TEM analysis has
shown the large influence of L2 concentration on the morphology and size of silica particles. At L2 concentration of 270 ppm random collisions of nanoparticles leads to agglomerates with the fractal-like structure, whereas at lower concentration (50 ppm) most of the collected nanoparticles were spherical. The silica particle size increases with siloxane concentration. We observed that at higher temperatures the sintering process occurs more rapidly resulting in the formation of spherical structures. The mean size of particles also increased at a higher temperature, which is attributed to a decreased viscosity and higher energy collisions. Combination of TEM examinations with the theoretical analysis allowed us to find the conditions for the formation of silica fractal-like aggregates. The proposed model was able to capture the effects of the system parameters on the onset of silica aggregate formation and evolution of PSD.

Combustion of siloxane-containing biogas in a typical domestic boiler was investigated in Chapter 7. Experiments demonstrated that substantial silica layers are formed in the heat exchanger leading to a decrease in performance and eventual failure of the appliance. The theoretical description formulated in Chapter 4 was used as a base for developing a model of silica deposition. It is shown that the mass flux of silica to heat exchanger surfaces is not sensitive to particle coagulation process and particle size distribution. The model predicts that clogging of heat exchanger by silica deposition during combustion of siloxane-containing gas is a linear function of time and siloxane concentration. The maximum allowable silicon content in biogases can be determined by extrapolating the results from short-term tests. This avoids the need to perform time consuming long-term tests at very low siloxane concentrations. Since the thickness and density of silica layers formed on internal parts of gas-burning equipment depend on the morphology and the size distribution of silica particles, these results are useful for the elaboration of silicon specifications for equipment utilizing biogas.