

Gas-Phase Synthesis of Highly-Specific Nanoparticles on the Pilot-Plant Scale

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ABSTRACT

Highly-specific nanoparticles provide promising properties for current and future applications as the size dependence of their properties allows to tailor materials for specific applications [1-3]. The synthesis of particles in the size regime of a few nanometers follows two different routes, the wet-chemical synthesis route that usually yields materials grown by thermodynamic control and the gas-phase synthesis processes, which allow a kinetic control of nanoparticle formation. The second route is favored for the formation of doped nanoparticles and nanocomposites. However, industrial nanoparticle production is frequently carried out by cost-effective flame processes with high throughput [4]. The quality of the resulting materials is limited and often agglomerates with a broad size distribution are formed. Highly specific nanomaterials are often available in minute quantities and therefore, subsequent processing steps to generate nanoparticulate composites cannot be studied.

Keywords Nanoparticles, Particle Synthesis, Silicon, Pilot-Plant

1 PILOT PLANT SET UP

We designed a unique pilot-plant scale particle synthesis facility enabling for three different synthesis routes using either a hot-wall reactor (HWR), a flame reactor (FLR) or a plasma reactor (PLR). In these reactors the energy required for precursor decomposition is provided by either an electrical heat source, a flame, or a microwave-supported plasma. Figure 1 shows a schematic and a photo of the pilot plant. The pilot plant exhibits a base area of about 60 m² and an overall height of 7.2 m, containing a multi level lab with a floor space of about 180 m².

The HWR and the FLR are located on the third level. In these reactors the process gases and the precursor gases are injected at the top of reactors via complex nozzles. After the precursor decomposition and the particle formation, the particle-laden hot gases are delivered to the second level. While precursor materials in the FLR are being burned by a natural gas flame under the presence of oxygen, the precursors in the hot-wall reactor are decomposed by convective heating at temperatures up to 1100°C. The microwave-supported plasma reactor is located on the ground level of the pilot plant. In this reactor all gases are injected at the

bottom via a nozzle into the reaction zone, where the energy delivered by a microwave feeds a plasma and keeps it burning for the duration of synthesis. In all synthesis reactors the overall gas flow with adjustable mixtures of inert process gases and gaseous precursors can reach values up to 200 l/min. The pumping unit is located on the ground level, while the exhaust gas post-combustion system is situated in an intermediate level above the pumps.

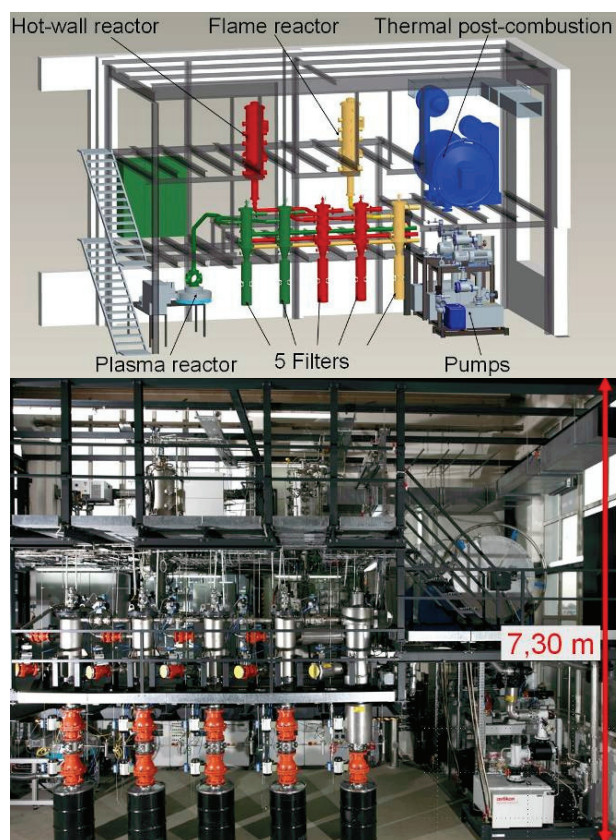


Fig. 1: Schematic (top) and image (down) of 3-level nanoparticle synthesis plant: Filter system in front of the image on the ground level; reactors on the first and second level

Figure 2 a-c shows the different types of gas-phase reactors in more detail. All reactors provide several ports that can be equipped with quartz windows to allow for on-line laser diagnostics of the synthesis process and the formation of particles. In each of the independently operating reactor

systems the particle-laden gases are delivered to the filter system, which is located on the second level of the pilot plant area.

The PLR and HWR can operate in a continuous mode, due to their individual double filter system. The particles are filtered alternately by one of the filter cartridges, while the other one can be released from collected particles and prepared for further operation. Additionally, this system enables to separate particles, which are generated in the first minutes of production process from those particles, which are synthesized later under stable operating conditions.

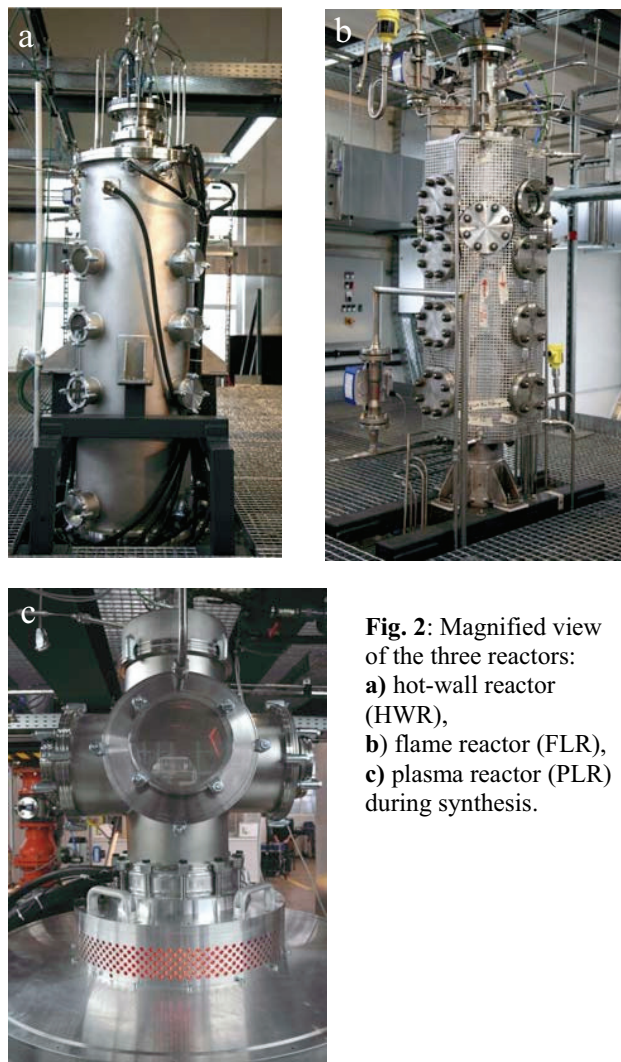


Fig. 2: Magnified view of the three reactors:
a) hot-wall reactor (HWR),
b) flame reactor (FLR),
c) plasma reactor (PLR) during synthesis.

1.1 On-line diagnostics

For an *in-situ* analysis of the synthesis process and the particles morphology highly sophisticated on-line diagnostic measurement set-ups are required. In recent years, laser diagnostics has proved to be a very powerful tool for the

on-line analysis of combustion processes [5]. Strategies that have been developed for combustion diagnostics can often be modified for applications in other reactive gas-phase flow systems. Consequently, the pilot-plant is equipped with on-line laser diagnostic techniques and on-line gas analysis systems. Laser-induced incandescence (LII) can be used for the monitoring of the particle and aggregate size during different stages of the formation processes and as well for on-line monitoring of the final particle size, which allows adjusting and varying the product parameters during synthesis [6]. Using a particle mass spectrometer (PMS) during the gas phase synthesis the size of generated particles can be monitored on-line [7]. Furthermore, for the analysis of the gas and flame temperatures within the FLR a laser induced fluorescence (LIF) system is installed. The obtained data are used as input for simulations of the combustion process.

The overall chemical process of the decomposition of precursor materials is continuously monitored by a quadrupole mass spectrometer (QMS) to ensure the complete conversion of the chemical starting materials.

1.2 Off-line diagnostics

Several standard off-line diagnostics methods are available at IUTA and associated research groups. Typically, electron microscopy techniques (SEM and TEM) are used to characterize the particle morphology and the state of agglomeration, while high-resolution transmission electron microscopy (HR-TEM) is performed on selected materials to study details of the material structure. The received on-line and off-line measurement results are compared to BET measurements, which yields off-line results of specific surfaces and thus particle sizes within one day. The structure and the crystallinity of the generated nanoparticulate powder are usually observed by X-Ray Diffraction (XRD) measurements. Using Scherrer's equation the crystallite size of the multi-domain particle ensemble is calculated and compared to HR-TEM investigations.

2 SYNTHESIS OF SILICON NANOPARTICLES

In this paper we present two synthesis routes for silicon nanoparticles. First, the generation process in the PLR will be visualized by images and second, results of the synthesis of nanoparticulate silicon in the HWR will be shown. Both reactor types enable for the synthesis of non-oxide materials, due to the fact, that gaseous precursor materials and process gases without oxygen content can be used.

2.1 Microwave-Supported Plasma Reactor

In this reactor all gases are injected at the bottom via a complex nozzle into the reaction chamber, while the energy delivered by microwave radiation at 915 MHz ignites a plasma and keeps it burning for the duration of synthesis.

For the synthesis of silicon nanoparticles in the microwave-supported plasma reactor, first, a mixture of Hydrogen and Argon is injected into the reaction zone to ignite and stabilize the plasma before the synthesis. After the stabilization process, Monosilane (SiH_4) as precursor is additionally injected into the system. This step directly changes the color of the plasma emission from deep blue to orange-red. Figure 3 shows images of the plasma without and with the presence of silicon nanoparticles in the system.

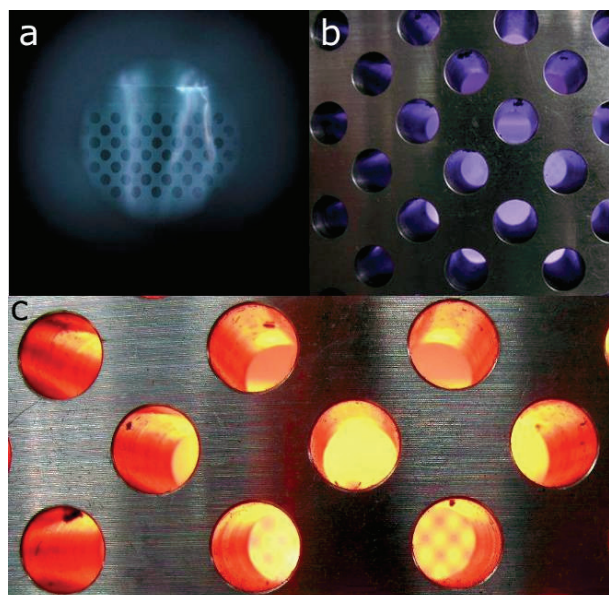


Fig.3: **a** and **b**: Hydrogen/Argon Plasma in the reaction chamber of the microwave-supported plasma reactor. **c**: Hydrogen/Argon with Silane during the synthesis of silicon nanoparticles

2.2 Si nanoparticles from the hot-wall reactor

The silicon nanoparticles are synthesized by thermal decomposition of SiH_4 in a hot-wall reactor at temperatures of 1000°C , while the process pressure is varied in the range from 15 to 100 kPa. The resulting material is characterized directly after the synthesis using specific surface measurements (BET). The measurements reveal an increase of the specific surface with decreasing synthesis pressure. Si particles generated at pressure of 100 kPa exhibit a specific surface of $21 \text{ m}^2/\text{g}$ corresponding to a particle diameter of 120 nm, while BET measurements on particles synthesized at 15 kPa reveal a specific surface area of $44 \text{ m}^2/\text{g}$ corresponding to particle diameter of about 60 nm. Figure 4 shows the particle diameter as a function of the synthesis pressure.

To characterize the structure of the materials XRD measurements are performed. Figure 5 shows the received diffraction pattern, which proofs the presence of a silicon crystallite structure, due to Bragg angles, which are in agreement with the bulk values. The position of the (111)

maximum is calculated by a Lorentzian fit. Using the fitting results we calculated a crystallite size of 13 nm within the nanoparticles. Furthermore, a shift of the maxima of the Bragg reflexes to smaller angles compared to the bulk values can be observed. From this displacement a decrease of the Si lattice constant can be estimated.

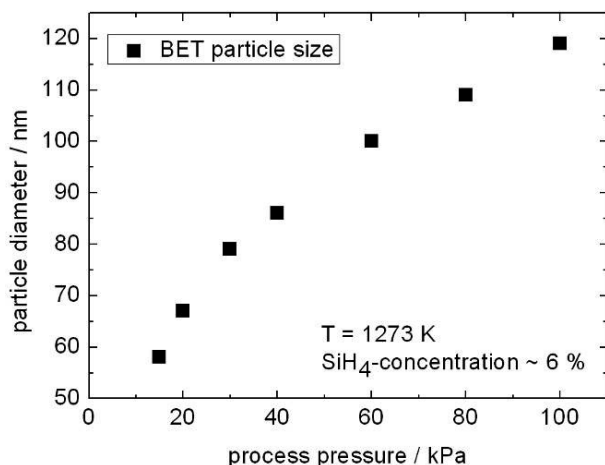


Fig 4: Si particle size as a function of the process pressure for particles generated at 1273 K with a total precursor concentration of 6 % Silane in a Hydrogen/Nitrogen mixture.

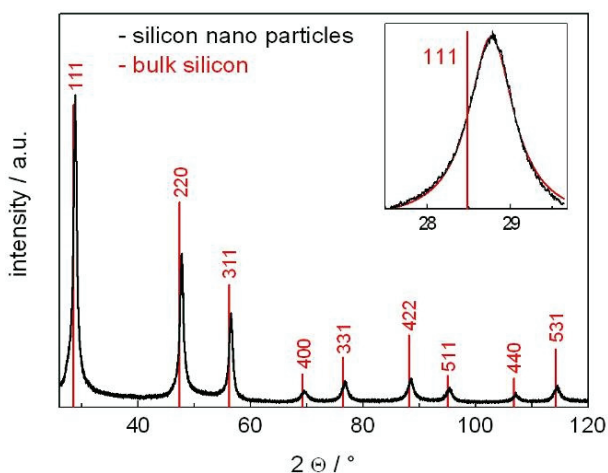


Fig 5: X-ray diffraction measurement of Si nanoparticles. The red peaks indicate the position of the Bragg angles for bulk material. The intensity of these peaks is normalized to the maximum of the (111) reflex. The inset shows a magnification of the (111) reflex and the Lorentzian fit (red).

HRTEM and TEM analysis confirm the crystalline structure throughout the particles, an oxygen content of $\sim 5 \text{ atom\%}$ in the sample, but do not indicate the presence of a distinctive SiO_2 shell. Furthermore, HR-TEM investigations reveal a crystallite size of 12 nm, which is in good agreement with XRD analysis. Figure 6 shows a TEM image of Si nanoparticles. Typically, the particles are agglomerated and the resulting particle assemblies exhibit diameters of up to $1 \mu\text{m}$ and more.

Scanning electron microscopy (SEM) investigation is performed on the nanoparticulate powder material. For SEM analysis the particles are dispersed in acetone and droplet of the suspension is put on a p-doped silicon substrate.

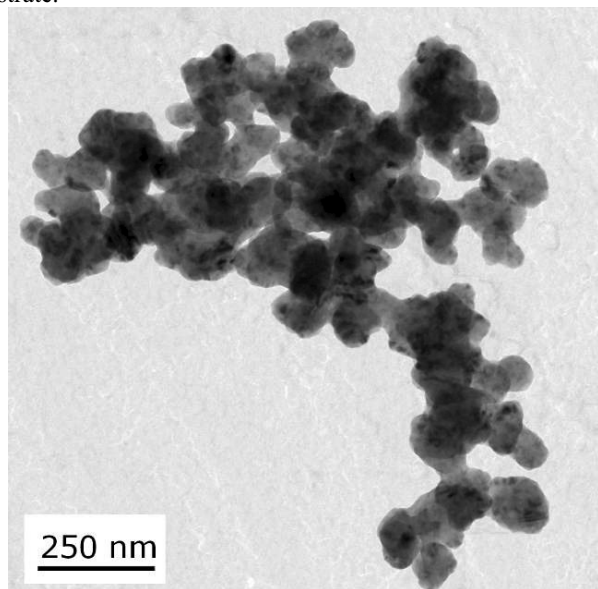


Fig. 6: TEM image of Silicon nanoparticles

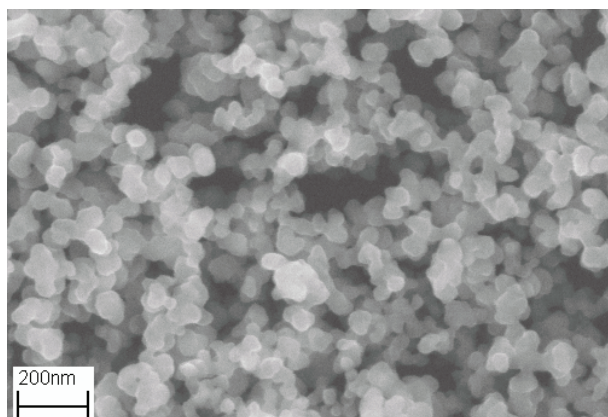


Fig 7: SEM image of Silicon nanoparticles

Figure 7 shows a SEM image of the Si nanoparticles. The analysis reveals a homogenous thin film of particles with mainly distinct grain boundaries. The size distribution of the particles is in the range of $\sigma = 1.3$, as it is expected for the hot wall synthesis route.

3 HANDLING OF NANOPARTICULATE POWDER

The production rate of nanoparticulate material in the pilot-plant can be increased up to the kg/h range. Therefore, the handling of the generated powder material must be optimized to fulfill pre-industrial standards and scientific re-

quirements. Additionally, a continuous extraction of particles from the filter system under inert conditions during the synthesis must be possible. Therefore, a polyethylene (PE) hose, which is welded at the bottom, is rolled on and fixed at an outlet branch below the filter. The powder is released from the filter cartridge and falls into a lock, where the material is purged with gaseous nitrogen. After purging and opening the lock, the particles fall into the bottom-welded PE hose. After the collection of particles, the hose is sealed by welding above the collected powder. To separate the welded nanoparticulate powder, the PE hose is cut directly in the joint. With this method we create flexible bags with nanoparticles without nanoparticle exposure during the synthesis and the filling procedure.

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REFERENCES

- [1] F. E. Kruis et al., J. Aerosol Sci. **29**, 511-535 (1998).
- [2] K. Wegner et al., Powder Technology **150**, 117-122 (2005).
- [3] T. Hülser et al., Sens. & Act. B **109**, 13-18 (2005).
- [4] P. Roth, Proc. Combust. Inst. **31**, 1773-1788 (2007).
- [5] C. Schulz, Z. Phys. Chem. **219**, 509-554 (2005).
- [6] A.V. Eremin et al., Appl. Phys. B **83**, 449-454 (2006).
- [7] P. Ifeacho et al., Proc. Combust. Inst **31**, 1805-1812 (2007).