Nano-Silicon and Non-Oxide Ceramics Synthesis via Gas-phase Sodium Reduction Aerosol Reactor

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The largest volumes of nano-particles in consumer products include carbon black for reinforcement applications (e.g. tires), silicon dioxide (SiO_2) as rheology agent (e.g. silicones) and titanium dioxide (TiO_2) in pigments and photocatalysts. All of those are manufactured on large scale via gas-phase aerosol synthesis. Such flame processes, however, are usually run under oxidizing conditions and result in oxide particles. The production of pure metal or non-oxide ceramics (e.g. nitrides or carbides) in a gas phase reactor under reducing conditions, however, has so far not been investigated much. Here, a scalable and flexible gas-phase sodium reduction reactor platform was used to synthesize pure silicon, tin-doped silicon, silicon carbide, titanium nitride and titanium carbide. Potential applications of such materials are plentiful and include capacitors, Li-ion batteries, catalysts, hard coatings, 3D printable materials and thermoelectrics just to name a few.

Pure silicon nano-powder was successfully synthesized on the Na-Reduction reactor at different production rates as high as 30 g/h. The produced powders were analyzed by nitrogen adsorption, transmission and scanning electron microscopy, X-ray diffraction, inert gas fusion analysis and glow discharge mass spectroscopy. Silicon particles had a BET surface area in the range of 23 to 44 m^2/g after salt removal. TEM image analysis show aciniform aggregates of silicon particles with a relative homogeneous primary particle size distributions. The silicon was protected by a relative thin 2-3 nm passivation layer established during the washing step resulting in an oxygen content of less than 3 wt.% O, lower than commercially available nano-silicon and therefore suitable for manufacturing of Li-Ion batteries. Tin-doped samples were prepared with nominally 5 and 10 at.% Sn each. The resulting powders exhibited a surface area of 28 and 16 m^2/g after salt removal, respectively. The tin appeared to both decorate the silicon surface with small (5-20 nm) Sn crystals and be present as individual larger (>50 nm) particles.

Different non-oxide ceramic materials were synthesized on the Na-Reduction reactor. While synthesis of titanium nitride was achieved by adding pure nitrogen to the $TiCl_4$ feed, this approach was not successful to synthesize silicon nitride. For the carbides CCl_4 was premixed with the respective silicon or/and titanium chlorides resulting in the formation of silicon and titanium carbide upon reaction with sodium. Surface areas achieved were in the range of 32 (TiN) to 280 m^2/g (SiC) and are dependent on material composition and synthesis conditions.

The gas-phase sodium reduction is a new and viable synthesis platform for metal, ceramic or composite particles of high surface and offers a path to a scalable manufacturing technique.

Topic area: Nanoparticle Synthesis & Applications – “Dry synthesis”

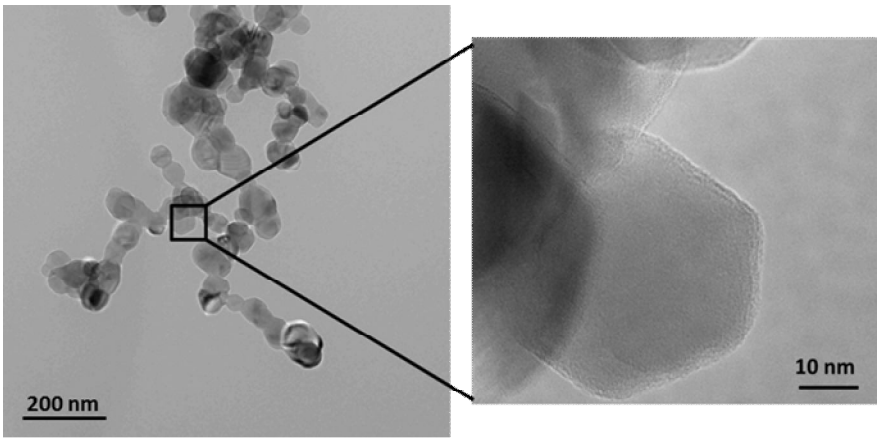

Figure 1: TEM image of a silicon sample produced in the gas-phase Na-reduction reactor. Right side shows high resolution image of the uniform and thin (ca. 2 to 3 nm) oxide passivation layer after removal of the NaCl.

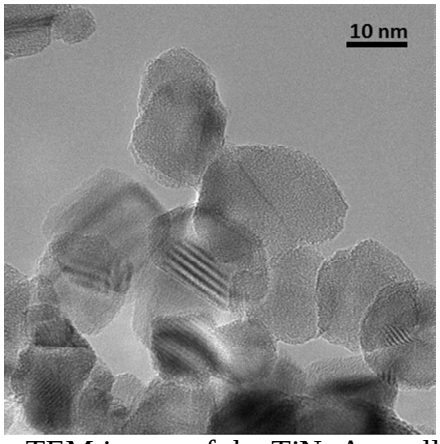

Figure 2: High resolution TEM image of the TiN. A small fraction of the particles appear to be amorphous rather than crystalline.

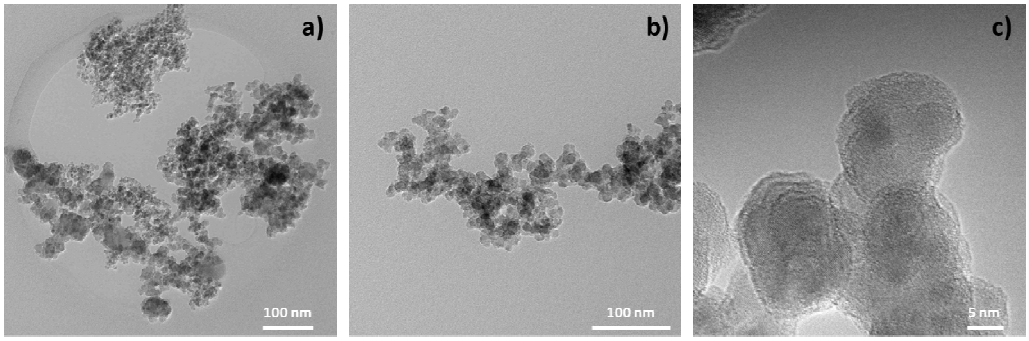

Figure 3: TEM images of silicon carbide made by gas-phase Na-reduction. The powder consists of small but highly aggregated primary particle with a few bigger particles present (a). Agglomerate size (a and b) seems to be in the range of a few hundred nanometer while the primary particle show a relative broad size distribution ranging from 50 nm down to ca. 10 nm (c).