Tungsten nanoparticles generated in an atmospheric pressure plasma jet

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Background
Atmospheric pressure plasma sources have proven to be a cost and space efficient technology for the preparation of various nanostructures. However, synthesis of high melting point metal nanoparticles remains an ongoing challenge. In this work, tungsten nanoparticles are synthesized by the HelixJet atmospheric pressure plasma source using a tungsten wire as a source material and an oxygen free argon plasma. This offers the opportunity to fabricate a wide range of nanoparticles in terms of particle size, morphology and chemical composition in a single preparation step.

Methods
Tungsten nanoparticles were synthesized in an atmospheric pressure plasma jet (APPJ) with helix electrodes (HelixJet) and a metal wire inserted into the plasma. The metal wire was heated by the interaction with the plasma. The vaporized material is carried in the gas stream and condensates to form nanoparticle nuclei. The synthesized nanoparticles were measured with a commercial scanning mobility particle sizer (SMPS) spectrometer. The morphology and the crystal structure of the resulting particles were analyzed by bright field transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Energy dispersive X-ray spectroscopy (EDX) combined with scanning TEM was used to gain local information on the chemical composition of the particles.

Results
TEM along with SAED and EDX showed monocrystalline tungsten nanoparticles with an average size of 14 nm, consisting of beta-tungsten with a thin oxygen-rich layer on the surface. The composition of such particles was studied with EDX profiling and analyzed using a so called sub-shell approach revealing that the core of the particle is composed of pure tungsten while the approximately 1.5nm surface layer has a tungsten to oxygen ratio of around 1:9. When increasing the plasma power, the average size of the nanoparticles also increased. The weakest plasma power used led to nanoparticles of average size of 12 nm. As the working gas flow rate increased, the time spent by the nanoparticles in the plasma decreased and the resulting size decreased. For the highest flow rates, when the residence time dropped to 0.4 s, the resulting particles had a thick oxide layer on the surface, while for the lowest flow rates with residence times above 1.8 s, the resulting particles were composed mainly of alpha-tungsten. Nanoparticles agglomerate into clusters, which are then measured by SMPS. The resulting size spectrum was fitted and individual peaks were sequentially assigned to agglomerates with increasing number of particles. It turns out that the SMPS measures the mobility of agglomerates as if they were larger particles than their actual size given by the sum of individual volumes or masses of particles in the agglomerate, making them to appear significantly larger.

Conclusion
Synthesis of monocrystalline tungsten nanoparticles with an average size as low as 12 nm and with a fairly uniform distribution has been shown. The HelixJet APPJ gives the possibility to prepare nanoparticles of high melting point materials and due to its versatility allows to prepare particles with complex morphology (alloys, oxides, core shells).

Keywords:
Tungsten nanoparticles, Atmospheric plasma