Mechanisms of SnO_2 nanoparticle formation: An *in situ* total scattering study

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By means of *in situ* X-ray total scattering and pair distribution function (PDF) analysis, we have elucidated the formation and growth mechanisms in the hydrothermal synthesis of SnO_2 nanoparticles from aqueous solutions of $SnCl_4 \cdot 5H_2O$.[1] The analysis of the data reveals that when the tin(IV) chloride precursor is dissolved, chloride ions and water coordinate octahedrally to tin(IV), forming aquachlorotin(IV) complexes of the form $[SnCl_x(H_2O)_{6-x}]^{(4-x)+}$ as well as hexaaquatin(IV) complexes $[Sn(H_2O)_{6-y}(OH)_y]^{(4-y)+}$. Upon heating, ellipsoidal SnO_2 nanoparticles are formed uniquely from hexaaquatin(IV). The total scattering data show that the nanoparticle size and morphology (aspect ratio) are dependent on both the reaction temperature and the precursor concentration, and particles as small as ~2 nm can be synthesized. Analysis of the growth curves shows that Ostwald ripening only takes place above 200 °C, and in general the growth is limited by diffusion of precursor species to the growing particle. The *c*-parameter in the tetragonal lattice is observed to expand up to 0.5% for particle sizes down to 2–3 nm as compared to the bulk value. SnO_2 nanoparticles below 3–4 nm do not form in the bulk rutile structure, but as an orthorhombic structural modification, which previously has only been reported at pressures above 5 GPa. Thus, adjustment of the synthesis temperature and precursor concentration not only allows control over nanoparticle size and morphology but also the structure.

[1] Jensen K. M. Ø., Christensen M., Juhas P., Tyrsted C., Bøjesen E.D., Lock N., Billinge S.J., Iversen B.B.. *J. Am. Chem. Soc.*, 2012, 134 (15), 6785

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