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Growth Regimes of Hydrothermally Synthesized Potassium Tantalate Nanoparticles

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Nanoparticles have a broad range of applications, from increasing the efficiency of heterogeneous catalysis to creating the next generation energy storage devices. Hydrothermal synthesis is a popular technique because it yields highly pure, monodisperse nanoparticles spanning a wide range of chemical compounds, directly made possible due to the increased solubility of the reagents at elevated temperatures and pressures. Despite many studies modelling the growth thermodynamics and kinetics of colloidal nanoparticles, few exist for hydrothermally synthesized oxide nanoparticles [1, 2]. Continuum methods, such as the kinetic and thermodynamic Wulff construction, predict the equilibrium nanoparticle shapes [3, 4]. While popular for modelling oxide nanoparticles, these methods do not explain what is happening to the nanoparticles during growth.

This study uses secondary electron (SE) imaging in a scanning transmission electron microscope (STEM) to study the kinetic growth of potassium tantalate (KTO) nanoparticles synthesized hydrothermally. In kinetic growth, the rate of growth is dependent on both the diffusion of atoms to a growing surface and the nucleation of a terrace on that growing surface [4]. Here, these rate limitations result into two different growth regimes: nucleation of stepped terraces and "smoothing" of the nanoparticle facets. SEM images taken in a STEM are capable of distinguishing between the two growth regimes by resolving these terraces.

The KTO nanoparticles were made according to the synthesis developed by Goh et al., where Ta_2O_5 and a KOH solution are added to an autoclave and heated to 150 °C for different lengths of time between 1-4 hours [5]. Powder X-ray diffraction (XRD) was performed using a Rigaku DMAX diffractometer. A Hitachi HD-2300A STEM was used to characterize the product with the secondary electron detector.

Figure 1 shows XRD patterns of the synthesis products after different lengths of time. Based on the observed diffraction peaks, the reactants are almost completely converted to KTO after 2 hours of synthesis time. SEM images of the cuboidal KTO nanoparticles after different synthesis times are shown in Figure 2. In Figures 2a-d, the observed nanoparticle facets are not completely flat and are instead populated with numerous terraces. After 2 hours of synthesis, the facets appear completely smooth (Figure 2e) and similar in appearance to the final product after 4 hours (Figure 2f).

These stepped terraces exhibit the two different growth regimes of the KTO nanoparticles. As described above, the growth of nanoparticles is dependent on the nucleation of a terrace on an existing surface and the diffusion of atoms to that surface. A high rate of terrace nucleation will result in very rough facets, as observed in Figures 2a-d. The increasing smoothness from Figure 2a to Figure 2e suggests that the terrace nucleation rate is decreasing as the synthesis progresses. Furthermore, the dominating growth mechanism changes from terrace nucleation to facet "smoothing" at some point between 1 and 2 hours. In this regime, atoms diffusing from the solution to nanoparticle surfaces are attaching to the terraces rather than nucleating a new terrace. This behaviour suggests a change in the energy barrier for nucleation versus the energy of adding a new atom to the terrace compared to the previous regime, or that there may be other mechanisms at play, such as Ostwald ripening.

For a more complete study of these two growth regimes, the areal step density on KTO nanoparticle surfaces were counted from SEM images by applying stereology. The trends observed show a transition between the nucleation and "smoothing" regimes, in addition to showing how SEM imaging has utility in studying these types of growth behaviour in nanoparticles due to its sensitivity to surface morphology and high resolution in a STEM.

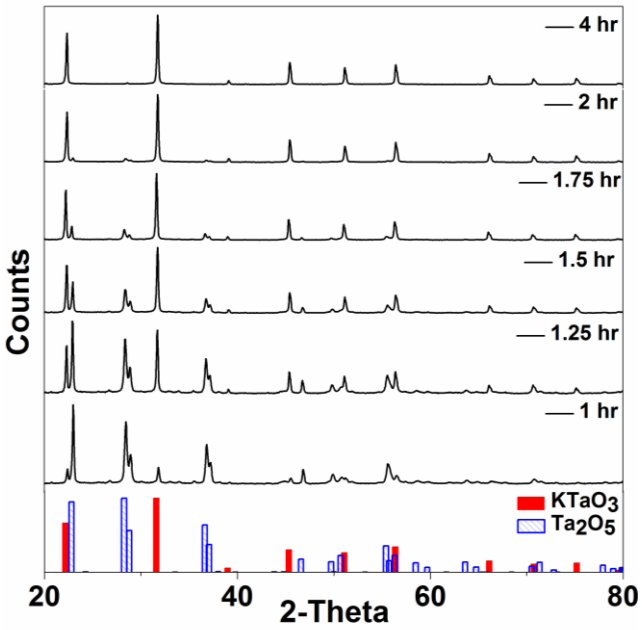

Figure 1. X-ray diffraction patterns of potassium tantalate nanoparticles after 1-4 hours of heating in a hydrothermal vessel.

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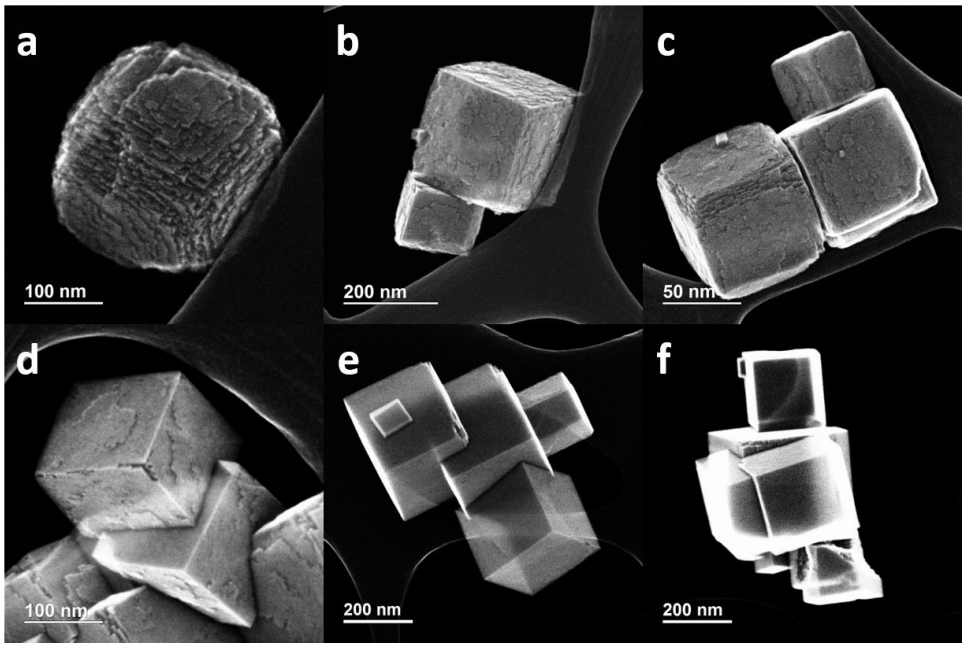

Figure 2. SEM images of KTO nanoparticles after being synthesized in the hydrothermal vessel for (a) 1 hour, (b) 1.25 hours, (c) 1.5 hours, (d) 1.75 hours, (e) 2 hours, and (f) 4 hours.

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