Nanomaterials, Environment, Nanotoxicology & Health

MIM.3.036 Investigating the formation mechanism of three-dimensional mesocrystalline rutile nanospheres synthesized by the resin-gel method.

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Three dimensional hierarchical mesocrystalline rutile nanospheres, synthesized using various methods, are not a new find in study of titanium dioxide nanoparticles [1,2]. Resin-gel is a modification of the Pechini method for the fabrication of mixed metal oxide nanoparticles [3]. The underlying principle is the addition of a long chain coordinating polymer to a stable solution of metal ions thus forming a gel [3]. It is believed that the after complete solvent evaporation, the metal-polymer complexes are held in positions apart from each other as a consequence of binding to the long chain polymer [3]. Flame induced ignition of the resin causes scission of the polymer chains and results in the aggregation of the metal complexes to form nanoparticles. Resin-gel is a beneficial technique as it has the potential to form single phase, nonstoichiometric, multi-metal oxides within a single reaction step. Previous work based on investigating the effect of polymer chain length, stoichiometry, heating rate and the effect of citric acid gave rise to the concept of the formation of a polymer reaction chamber within which metal ion complexes aggregate to form anatase. Anatase then transforms into rutile single crystals that grow anisotropically forming 3D rutile superstructures.

The aim of this study was to investigate the formation of rutile superstructures using an interrupted resin-gel synthesis technique and rationalise the cause of their formation using the new hypothesis of resin-gel.

Polyethylene glycol (PEG) of different average molecular weights was incorporated in a 1:1 stoichiometric ratio with TiCl₄ in excess distilled water. Concentrated nitric acid was added to allow for complete dissolution of the metal ion precursor in water. Following complete solvent evaporation under incandescent lamps, each resin was heated gradually in glazed alumina crucibles in a sand bath. Periodically during the heating step, a thin, aluminium rod was rapidly inserted into selected crucibles and rapidly removed. The captured drop of hot wax was transferred directly onto a holey carbon copper TEM grid. Upon reaching the auto-ignition point, each sample was ignited using a Bunsen burner and selected waxes were collected using the described aluminium dipping technique. The residual sample after the burn was collected and calcined at 773 K for one hour to remove the formed carbon material that had coated the particles. XRD analysis was performed to determine phase purity using the Spurr and Myers equation [4] and particle size analysis was performed using the instrumentally corrected Scherrer equation with K = 0.91. A Tecnai Spirit 120 kV and JEOL 3011 300 kV were used to image selected samples.

XRD analysis showed that low PEG molecular weights favoured the formation of small amounts of rutile and high PEG molecular weights allowed for the formation of greater amounts of rutile (figure 1). A curious observation was that no polymer resulted in the formation of phase pure material. As was expected, calcination caused an increase in the amount of rutile formed. The exception to this trend occurred for the 400 and 1500 g/mol PEG molecular weights that exhibited a decrease and no increase in the amount of rutile formed postcalcination respectively. This is an unexpected result as anatase irreversibly converts to the more stable rutile phase at elevated temperatures [5]. The error bars associated with the 400 g/mol PEG is however significantly large and hence accounts for the unusual data. Figure 2 illustrates the increase in particle size post-calcination. This is due to effects such as sintering during the calcination process. The large error bars are consistent with resin-gel being a thermodynamically favoured synthetic technique that lacks kinetic control and hence particle size is difficult to tailor. HRTEM revealed that the nanospheres were composed of nanowires originating from an apparently common point (figure 3a). It was also noted that the tips of each wire (figure 3b) were significantly more ordered than the points at which they make contact with the sphere (figure 3c). This suggests that the nanowires grow from a common point. The rutile phase was confirmed by comparing calculated and experimentally determined power spectra. This comparison also confirmed growth of the nanowire along the (001) direction as was documented by Hu et al [2]. TEM analysis of the partially synthesized titania revealed the presence of numerous cone-type structures in most samples (figure 4a). It is believed that these structures were formed as a result of the polymer chains unwinding to form sheets during the synthesis and these sheets then folded around themselves during the heating step. Figure 4b shows an expanse of polymer that appears to have formed an enclosure containing metal particles. This is consistent with the new polymer reaction chamber hypothesis. These chambers formed a common nucleation site for the conversion of anatase to rutile crystals and due to their high energy (001) surface, the rutile continued to grow along this direction. Figure 4c was generated from a sample during ignition and shows the presence of crystalline material arranged in a circular manner consistent with the shape of the polymer in figure 4b; adding further evidence to the proposed hypothesis.

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Figure 3. (a) rutile nanosphere composed of nanowires; (b) tip of a nanowire and (c) base of a nanowire including calculated and experimentally determined power spectra



Figure 4. (a) PEG 'cone' structure; (b) formation of polymer reaction chambers; (c) formation of crystalline material in a circular pattern