Type of presentation: Poster

MS-5-P-3174 HRTEM studies of crystalline growth to unlock the formation mechanisms of titania nanodandelions

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Titania in the rutile phase is able to form self-assembled, mesocrystalline, three dimensional superstructures [1,2]. These dandelions are formed by hierarchical arrangements of nanorods aligning radially on a common axis and have been documented during different synthetic routes [1,2]. The cause of rutile dandelion formation and the crystallinity of the structure at the common point have yet to be described.

In this study a form of rutile dandelions have been prepared using resin-gel synthesis. This technique involves addition of a long chain coordinating polymer to a stable solution of metal ions in the presence of a solvent [3]. The classic theory of resin-gel is that metal ions are held apart by the polymer until ignition of the resin causes polymer degradation and forces the metal ions to agglomerate and form a metal oxide. The strength of this technique lies in its ability to form homogeneous non-stoichiometric mixed metal oxides nanoparticles. Evidence supporting the formation of a polymer reaction chamber has previously been reported [4].

The primary aim of this study was to use HRTEM coupled with cryo ultra-microtome to obtain crystalline information about the dandelion superstructure and polymer chambers as they formed during the ignition stage of the resin-gel synthesis.

$TiCl_4$ was added to distilled water containing HNO_3. The solution was added to a stoichiometric quantity of polyethylene glycol with a molecular weight of either 3000 or 10000 g/mol. After complete solvent evaporation, the resins were heated until auto-ignition. Formvar coated TEM grids were used to sample the molten intermediates at different points during the ignition in an attempt to view the forming reaction chamber. Selected samples were cured in a resin before being sliced using cryo ultra-microtome with the intention of obtaining superstructure slices.

The results showed carbon lattice fringes surrounding growing nanoparticles supporting the reaction chamber hypothesis. Nanorod tips were either rounded or tapered to a point with various faces presenting at the tips. Imaging the common point of the nanorods showed several ‘seed points’ that gave rise to fragments of the superstructure. These fragments then formed the dandelion. Using the generated information, understanding of the polymer reaction chambers within the gel is obtained allowing for the formation of either anatase, rutile nanorods or mesoporous dandelions.

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Acknowledgement: The authors wish to thank Dr. James Wesley-Smith from the Council for Scientific and Industrial Research (CSIR) for the use of the Jeol JEM 2100 HRTEM.

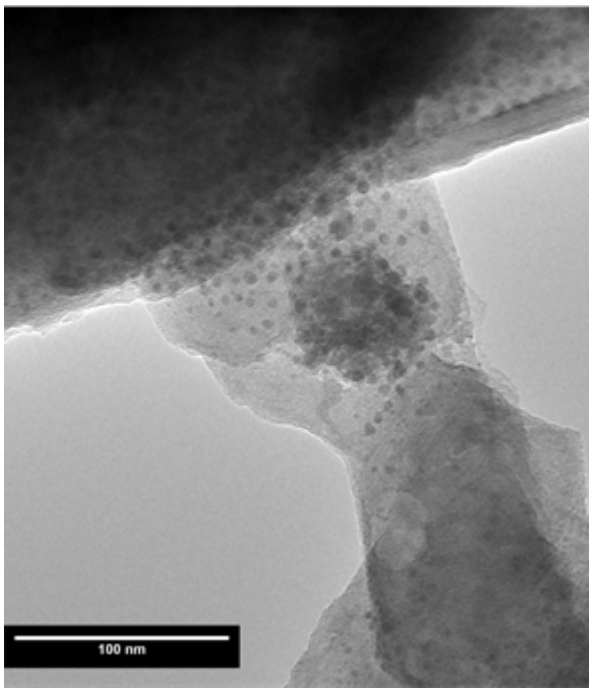

Fig. 1: Polymer surrounding growing nanoparticles during the early stages of heating.

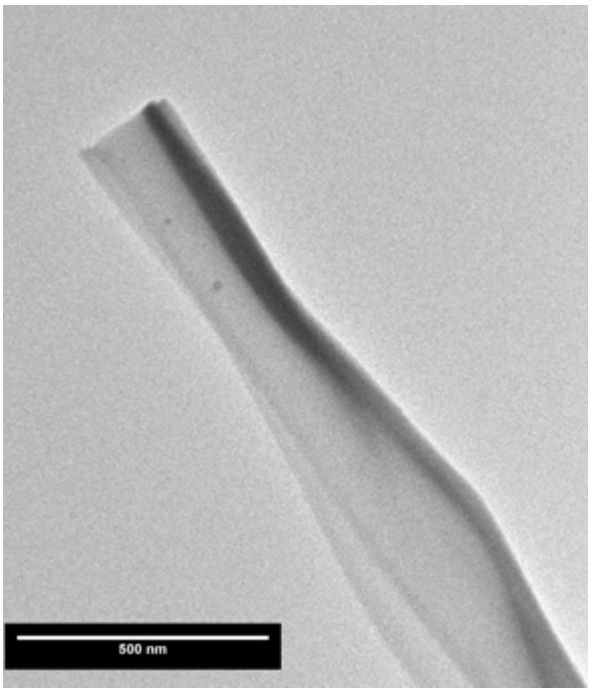

Fig. 2: Polymer sheets begin to wrap around growing particles after heating for a while.

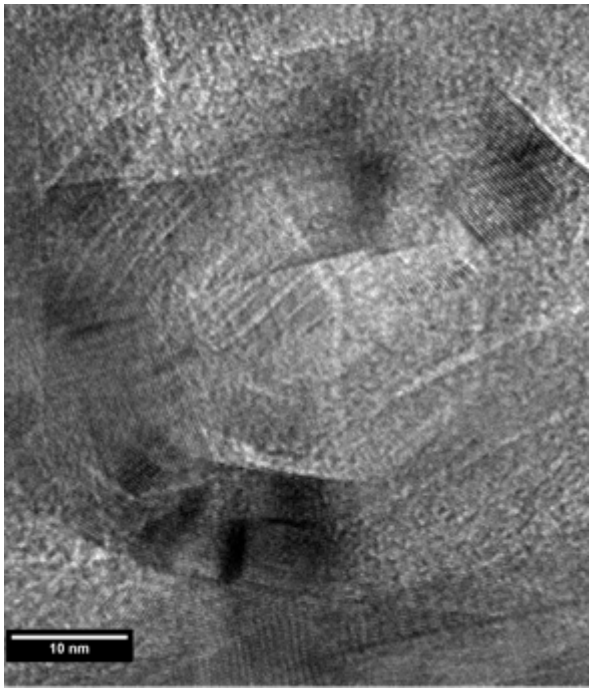

Fig. 3: Formation of a crystalline carbon reaction chamber.

Fig. 4: Ruitle nanodandelion formation with several seed crystals at the common point.