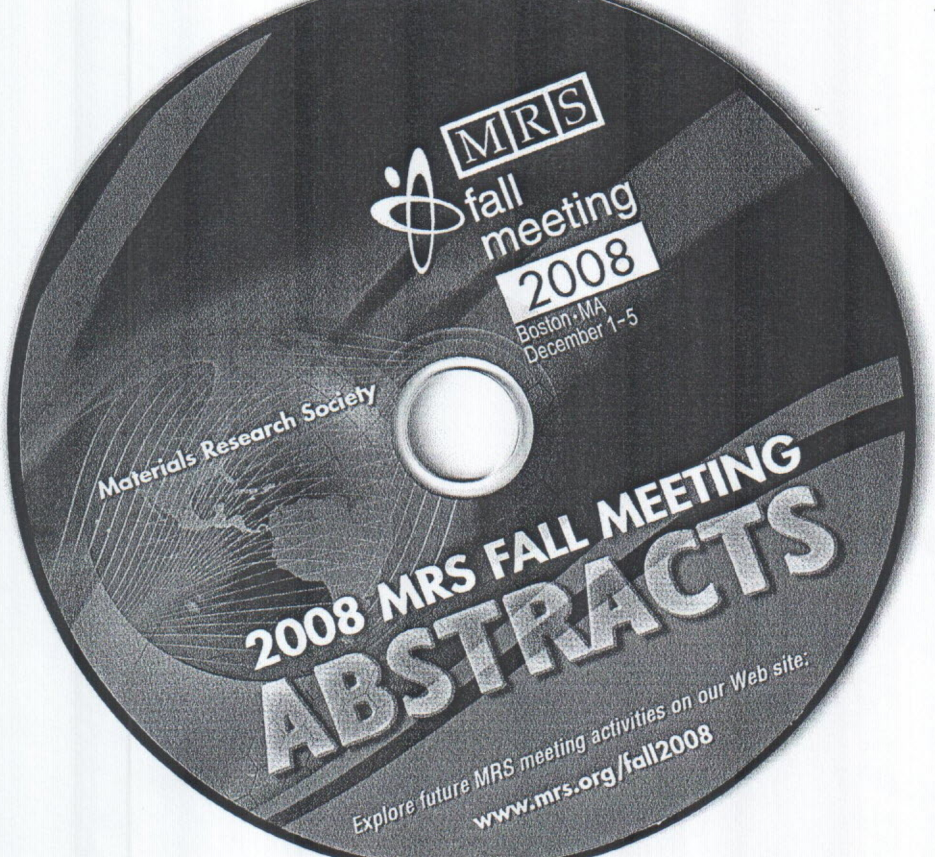
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Phase Transformation in Titania Nanocrystals by the Oriented Attachment Mechanism: The Role of pH Medium.

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Nanoparticle growth mechanisms have received much attention in recent years, especially in view of the importance of controling nanostructural sizes and morphologies. In-depth investigations into classical nanoparticle coarsening processes (Ostwald ripening, OR) have demonstrated the importance of proper control in this stage of the synthesis so that the desired nanostructures can be obtained. However, the Oriented Attachment (OA) mechanism has been highlighted as a common step in nanocrystal growth, even in systems with high solubility (when OR is expected). The influence of this mechanism on the anisotropy of oxide nanocrystals has been investigated, and a wide range of distinct nanostructures are reportedly formed through this mechanism. However, although the role of this mechanism in nanoparticle morphology is well understood, investigations into other implications are still incipient. One of these aspects is the mechanism's influence in phase control, an important variable, particularly in systems with many polymorphs, and one that is frequently disregarded. The role of the growth mechanism in phase control can be understood in terms of its influence on the total distribution of the facets, which can be attained by tailoring anisotropic structures (since the OA mechanism is related to this aspect). Its influence is interpreted as the modification of the Area/Volume relation in the formed particles, favoring phase transformation or not according to the crystallographic planes exposed after the event. However, the surface energy of each plane is strongly influenced by the presence of counterions in the medium. As an example, in the synthesis of TiO_2 nanoparticles, it has been shown that the presence of common ions in the synthesis environment, such as Cl^- or organic chains from the precursors, can alter phase stability. In order to obtain a representative system for TiO_2 with minimal interferences, we have developed a clean synthesis using metallic Ti and hydrogen peroxide as precursors, crystallized in a conventional hydrothermal apparatus. This system can offer some insights concerning the influence of surface energy in the OA mechanism and its importance for adequate phase control of nanoparticles during synthesis. The results revealed the evolution of the crystal morphology dictated by the conditions of pH, which shows a strong dependence on the surface conditions, i.e., surface energy. The occurrence of the OA mechanism as an important way to modify the morphology and, hence, the distribution of surface energy, confirmed that the mechanism can accelerate some phase transitions, albeit with interference of the pH medium in terms of how the mechanism affects the final particle morphology and direction of crystalline growth. Finally, the importance of the mechanism was also apparent in an extremely basic condition, indicating a possible correlation with the formation of hydrogen titanate nanostructures.

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