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Characterization of Anatase Nanoscale Thin Film Structures Synthesized from Hydrothermally Treated Titanium (IV) Butoxide

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ABSTRACT

Titanium (IV) *n*-butoxide was hydrothermally treated at 110^0C for various times to yield the anatase TiO2 (a-TiO2). Thin films were subsequently formed by the flow coating technique to yield submicronic films constituted by nanometric sized titania particles. The uniform sized TiO2 phase was characterized by XRD and HRTEM. Increasing the hydrothermal reaction time increased the average particle size within the nanometric range. Measurements of lattice fringe dimensions showed that crystallographically controlled attachment of discrete particles also called oriented alignment grown nanocrystals was the mechanism responsible for crystal growth.

Introduction

The development and control of semiconductor titania nanostructures is currently an area of intense interest because of the applications in photovoltaics, photocatalysts etc.. However, there are many barriers to overcome if nanostructures are to become widely applicable due to the high reactivity of the crystalline surfaces (1,2). Many approaches such as anodized aluminum oxide (AAO), sol-gel (3-5), various electrodeposition methods,(6-7) electrochemical anodic oxidation of pure titanium sheets,(8-9) and chemical treatment of fine titania particles (10-11) have all been used to produce titania nanostructures. Regarding the preparation of anatase TiO2 nanoparticles a number of methods have been used such as microemulsion, chemical precipitation, hydrothermal crystallization, and sol–gel (12-16).In the present work the characterization of titania nanostructures is discussed as related to the isothermal synthesis reaction time, it is also believed that understanding solution pH effects on assembly and coarsening kinetics in titania systems may enable improved control of nanoparticle properties.

Experimental

Titanium (IV) *n*-butoxide (Merck) precursor and solvent ethanol in an acidic medium were hydrothermally treated at 110^0C for various times to yield the anatase TiO2 (a-TiO2) following the flow sheet shown in fig.1. The TiO2 products were characterized by X-ray diffraction analysis using a Siemens D5000 Cu Kα radiation 1.54 at 20 kV, and a TEM Philips TECNAI 20 super Twin, at 200 kV on HRTEM mode.

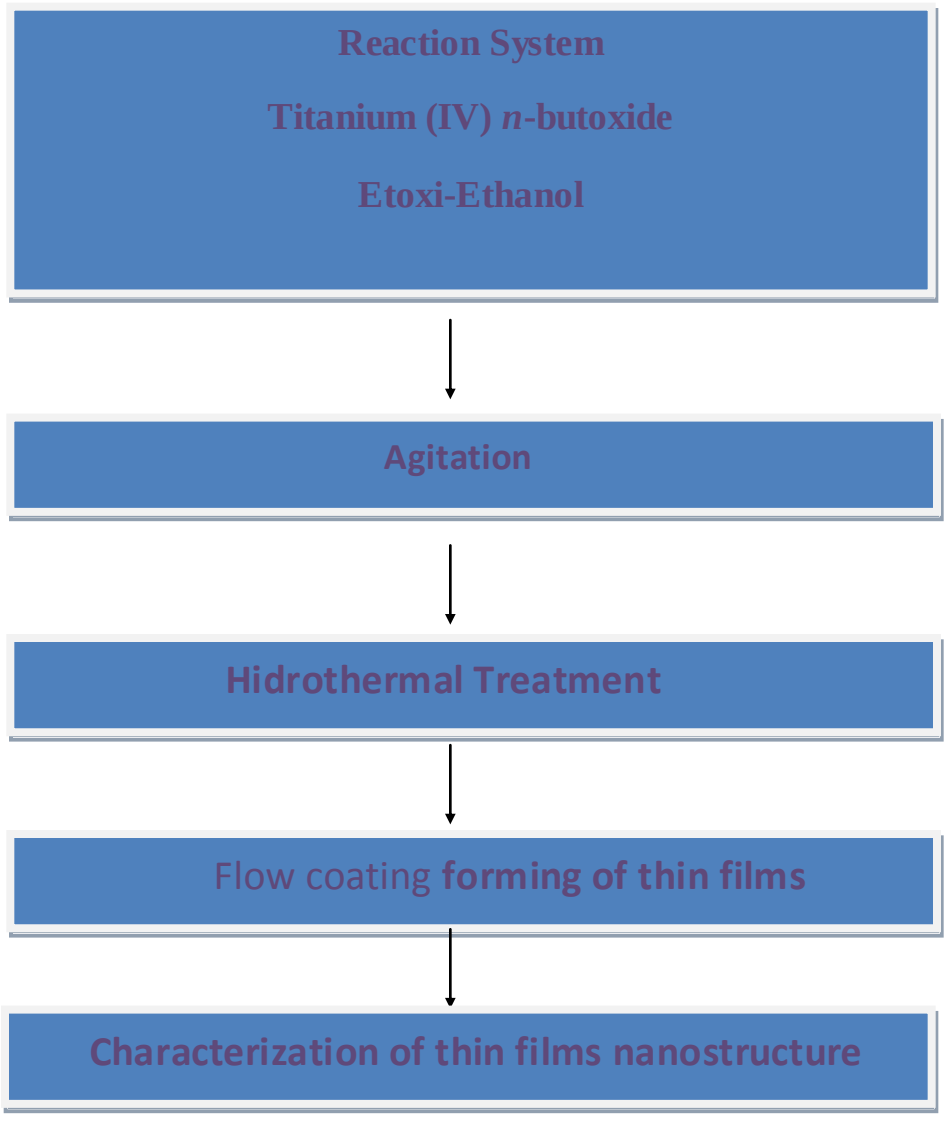

Fig.1 Experimental scheme leading to thin films characterization

Results and Discussion

Fig.2 is a TEM dark field composite image for specimens hydrothermally treated at 110^0C for various times. It can be seen that crystal size in fig.2a is about 5 nm for 10 hrs. growing up to 11 nm when doubling treatment time. Increasing the treatment time up to 60 hrs., the larger crystal grows up to 12 nm. Therefore it appears that that crystal growth is not so sensitive to time of treatment which can be advantageous in attempts to control grain growth. A commonly measured crystal size of 5 nm was computed by HRTEM in fig.3, again and in general it was observed that increasing the hydrothermal reaction time increased slightly the average particle size within the nanometric range for most of the specimens. It is also shown by the same fig.3 that crystallinity increases as treatment time progresses as evidenced by the fft insets on the corresponding micrographs. Shortest time treatments, 8 hrs. (fig.2a) gives rise to partially crystalline specimens in which the (101) plane is the only one plane that crystallizes out in various directions. Fig.2d by contrast shows an extended crystallization through the (101), (103), (004), (200), (105), (213) diffracting planes. Fig.3d shows that the planes (101) and (004) do not have straight continuity besides having varying contrast along the nanocrystal, this is a characteristic (1) of crystallographically controlled attachment of discrete particles also called oriented alignment grown nanocrystals which is a crystal growth mechanism that relies on the minimization of the surface energy of the system. X Ray diffraction also shows evidence on the crystallinity evolution by fig.4 for amorphous specimens just hydrolyzed as compared to those partially crystalline that were subject to short times (8hrs.) of hydrothermal treatment. Fig.4B is a JCPDS standard from a different precursor for comparison.

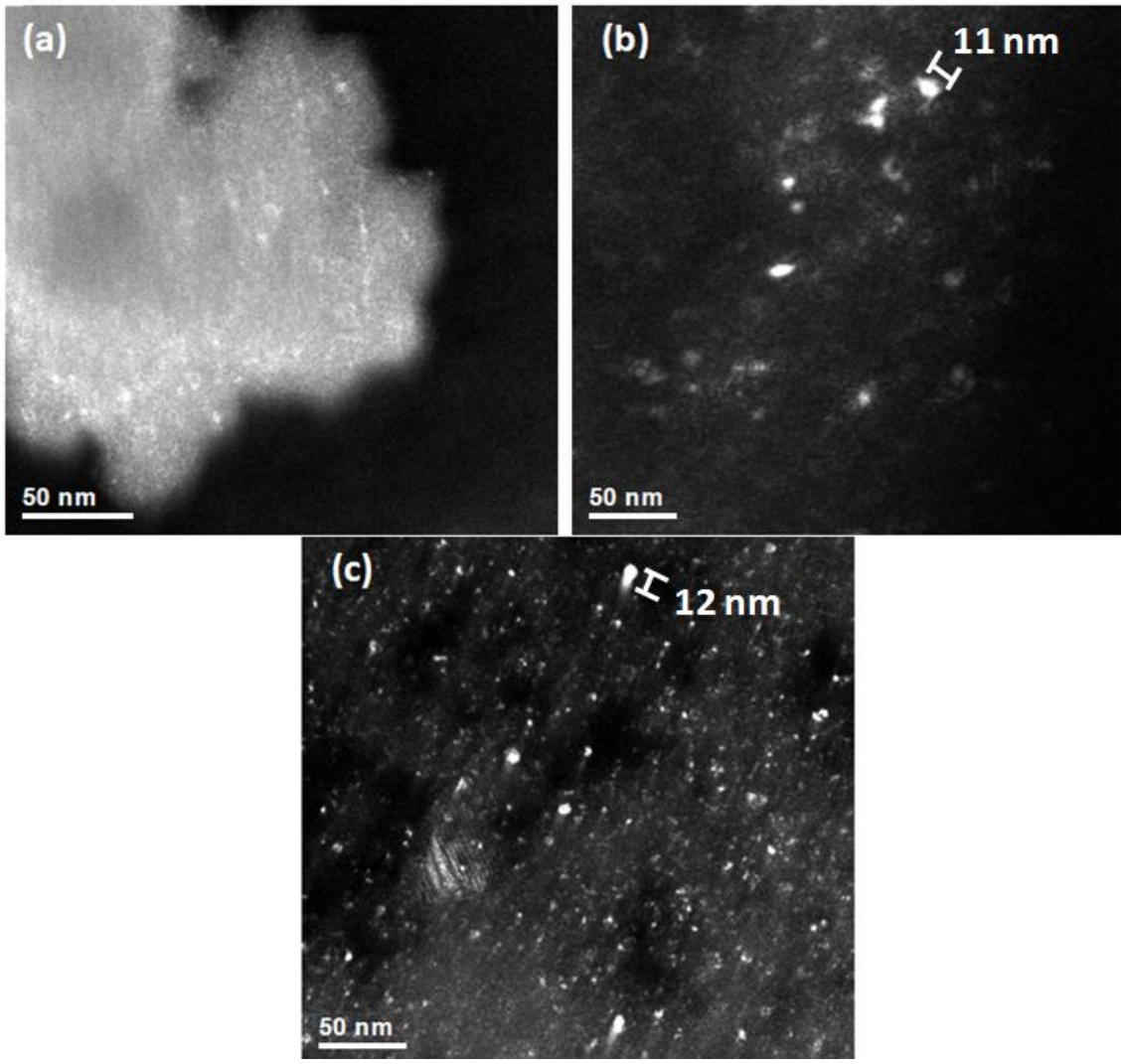

Fig.2 TEM Dark field images formed out of diffracting spots showing grain size evolution in hydrothermally treated specimens for a) 10, b) 20 and c) 60 hrs.

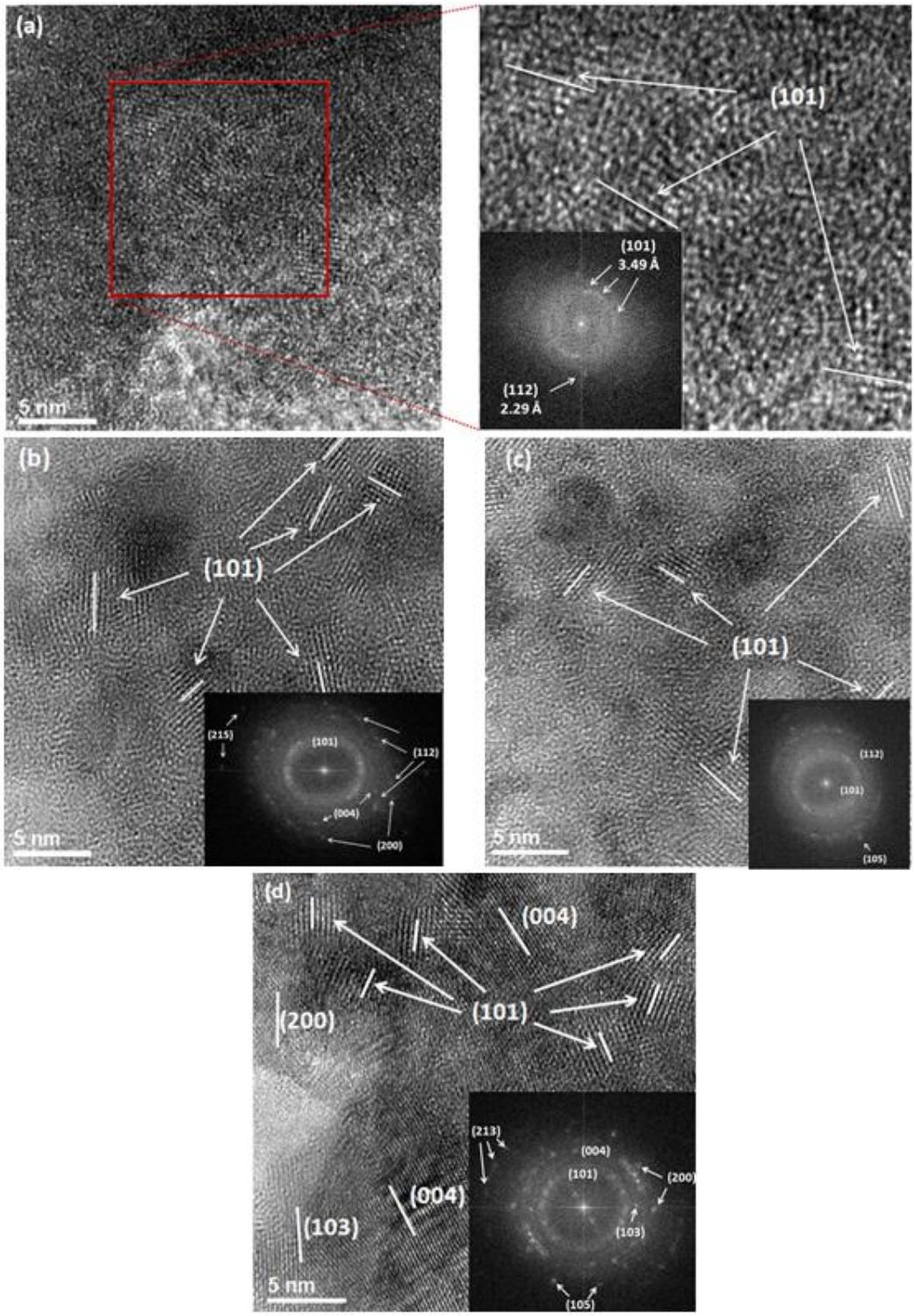

Fig.3HRTEM of hydrothermally treated samples for *(a) 8, (b) 20, (c) 40 and (d) 60 hrs. at 110°C*

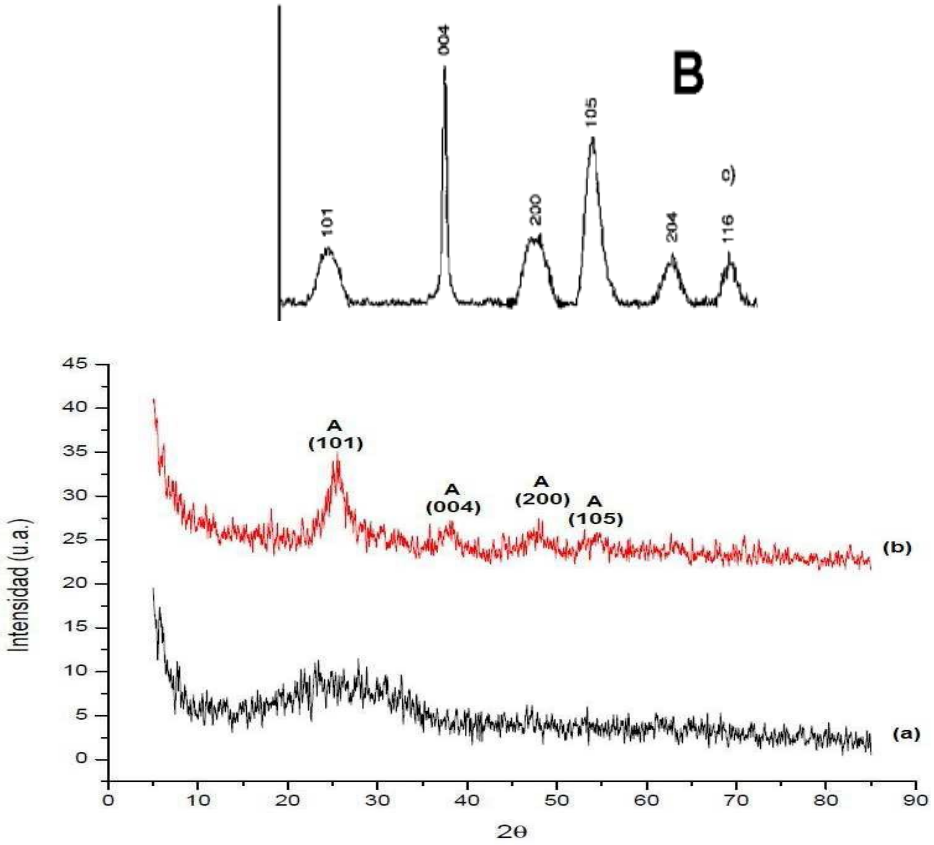

Fig.4 X Ray Diffraction of samples subject to a) hydrolysis b) Hidrothermally treated at 110°C for 8 hrs.. **B** Standard anatase spectra is included for comparison.

Conclusion

Non aggregated one dimensional anatase nanoparticles were syntehsized out of titanium (IV) n-butoxide hydrothermally treated at 110^0C for times up to 60 hrs.under acidic conditions. HRTEM observations and measurements of lattice fringe dimensions showed that crystallographically controlled attachment of discrete particles also called oriented alignment grown nanocrystals was the mechanism responsible for crystal growth.

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