# Evolution of TiO<sub>2</sub> Nanostructures from Nucleation to Nanorods by Hydrothermal Growth Method

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#### Abstract

The growth of  $TiO_2$  nanostructures by hydrothermal growth method with a controllable average growth rate is demonstrated. Experimental evidences to clarify the evolution of  $TiO_2$ nanostructures, from the nanowires coarseness by homogeneous nuclei composition, occurrence of parallel-growth and coherence neighboring nanowires to form nanotapes/nanosheets, and final to nanorods during HTG growth, are reported and discussed.

## 1. Introduction

TiO<sub>2</sub> nanowires (NWs) grown on a transparent fluorine-doped tin oxide (FTO) substrate has been widely used as a photoanode for dye-sensitized solar cells (DSSCs) [1-2]. In 2009, Liu. *et al.* first grew TiO<sub>2</sub> nanorods (NRs) on an FTO substrate and the effect of substrate, initial reaction condition, solution acidity and surfactants or salts on the morphology of NRs were discussed [2]. Although TiO<sub>2</sub> nanostructures open a new era for functional devices applications, the crystal growth mechanism, especially for the evolution of TiO<sub>2</sub> nanostructures among different morphologies using hydrothermal growth (HTG) method, is still inexplicit, which may hinder the development of TiO<sub>2</sub> nanostructures studies and design [3-5]. Thus, it is practically important to explore the evolution of TiO<sub>2</sub> nanostructures among different morphologies.

#### 2. Experimental Procedure

Ti(IV) n-butoxide (TNBT) is an analytical grade solution, which was used as the main precursor for TiO<sub>2</sub> nanostructures synthesis. An FTO glass was used as the substrate, it was cleaned ultrasonically using acetone, isopropyl alcohol, and then dipped into DI water, and final dried under N2 flow. Different TNBT molar concentrations (9.83, 49.16 and 98.32 mM) were prepared, through dipping into constant volume ratio of DI water and HCl (30: 30 (mL)). The mixed chemical solutions were put into a 60 ml Teflon-lined container, and an FTO substrate was also placed in the bottom of the container with the growth plane inclined and downwards. Finally, the stainless-steel autoclave was put into an oven to synthesize TiO<sub>2</sub> nanostructures at 150°C for designed growth times (hr). The surface morphologies of the prepared  $TiO_2$ nanostructures were characterized by SEM (JEOL JSM-7001). The powder X-ray diffraction (XRD; Bruker AXS Karlsruhe) analysis was carried out to identify the TiO<sub>2</sub> crystal phases. The evolution of TiO<sub>2</sub> nanostructures from homogeneous nucleation (nanoparticles, NPs) to form nanowires (NWs), and each NWs cohered to form nanotapes (NTs)/nanosheets (NSs) were examined by TEM (JEOL JEM-2100) analysis.

### 3. Results and discussion

Figures 1 show the SEM images of  $TiO_2$  nanostructures evolving from nucleation, NWs/NTs/NSs and final to NRs, which were synthesized at different precursor concentrations (mM) and growth times. Figures 1(a) and 1(b) show the SEM images of heterogeneous nucleation sites and continuous channel-like film formation at 9.83 mM TNBT (8 hr) and 49.16 mM TNBT (1 hr), respectively. As shown in Fig. 1(c)~(e), it is seen that the TiO<sub>2</sub> NWs were randomly and possible epitaxially grown on the boundaries of FTO grains initially and then enlarged or bundled in the final state. Liu *et al.* [2] elucidated that TiO<sub>2</sub> NWs may epitaxially grow on the grains' surface of FTO, but they didn't show any evidence.



Fig. 1 SEM images of the evolution of TiO<sub>2</sub> nanostructures.

Figures 1(f)~(h) show the TiO<sub>2</sub> nanostructures evolution at double TNBT concentration (98.32 mM). In making comparison between Figs. 1(e) and 1(f), it is very interesting to find that the recipes of 49.16 mM for 6 hr and 98.32 mM for 2 hr could result in a very similar morphology of TiO<sub>2</sub> nanostructures. The average growth rates of the length (L) and diameter (D) of TiO<sub>2</sub> nanostructures were evaluated from Figs. 1(c)~(h) and shown in Fig. 2(a), which are 361 and 56 nm/hr for 49.16 mM TNBT and 262 and 19 nm/hr for 98.32 mM TNBT, respectively. When the concentration of precursor was doubled, both the L and D growth rates increased. Moreover, the D growth rate in 98.32 mM TNBT is near triple more than 49.16 mM condition, which comes from the coalescence phenomena of NWs parallel-growth. Powder XRD was carried out to clarify the crystal phases and crystallinity shown in Fig. 2 (b). The relative signal intensity of crystal face (002), (200), (101), and (110) increase with time, which are all consistent with the theory calculation [6] which indicates the surface energy of a rutile lattice is on the order of  $E_{(110)} < E_{(100)} <$  $E_{(101)} < E_{(001)}$  [6]. It reveals that TiO<sub>2</sub> nanostructure has the fast [001] growth rate due to the higher surface energy. Note that all XRD peaks are in good consistent with the tetragonal rutile TiO<sub>2</sub>

file (JCPDS No. 21–1276). Figures 3(a) and 3(b) illustrates schematically the evolution of  $TiO_2$  nanostructures.



Fig. 2 (a) Averaged growth rate and (b) powder XRD analysis of TiO<sub>2</sub> nanostructures.



Fig. 3 Schematic diagram showing the evolution of TiO<sub>2</sub> nanostructures.





The rough FTO surface causes the growth of TiO<sub>2</sub> NWs randomly. Neighboring NWs might combine together and grow along preferential growth direction [001] through the oriented attachment (OA) growth mechanism [7]. Figure 3(c) shows schematically the formation of the NWs and NTs in the early stage. First heterogeneous nuclei were formed and enlargement by classical Ostwald Ripening (OR) growth mechanism. In our experiment, homogeneous nuclei (NPs) were also formed in the solution to promote TiO<sub>2</sub> nanostructures coarsened and NWs formed. Then, parallel-growth of neighboring NWs cohered to form NTs/NSs. Figure 4 (a) shows the TEM image of NWs parallel-growth and each immature NWs are composed of random arrangement of homogeneous nuclei. It can be clearly seen in HRTEM image on the top portion of NWs as in Fig. 4(b), random and non-identical orientation nanoparticles (NPs) were combined to form NWs. Thus, we conjecture the random arrangement of NPs were combined to form NWs, and crystal orientation finally tuned to the same in the follow-up growth, and result in single crystal NWs, NTs, and NSs. Also, as shown in Fig. 5(a) for the

same growth condition, it is evident that there are about  $3\sim4$  mature NWs parallel-growth combined to form NTs. When growth time was increased to 4 hr, NSs were formed through combining many NTs (Fig. 5(b)). Figures 5(c) and 5(d) show the HRTEM images of the top and bottom portion of TiO<sub>2</sub> NSs. It can be seen that whole NSs have the same crystal orientation. The corresponding SAED patterns by Fast Fourier Transform (FFT) of HRTEM images also confirm that both the top and bottom portion of the NSs have the same crystal orientation with the [001] as the preferential growth direction.



Fig. 5 TEM analysis of (a) low magnification image of NTs, and (b) NSs. HRTEM images of the (c) top and (d) bottom portion of NSs.

#### 4. Conclusion

The growth of TiO<sub>2</sub> nanostructures by HTG method with a controllable average growth rate has been demonstrated. SEM images to clarify the evolution evidences of the TiO<sub>2</sub> nanostructures from nucleation, NWs/NTs/NSs, and to NRs have been reported and discussed. HRTEM images reveal the evidences of the immature NWs coarseness by composed of many homogeneous nuclei (NPs) and the coherence within the parallel growth of neighboring NWs should be responsible for the evolution of TiO<sub>2</sub> nanostructures during HTG growth. The details of each parallel-growth NWs cohered to form NTs/NSs, and final to NRs evolution have also been elucidated in this work.

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