

In Situ TEM Study of the Annealing of Titania Nanotubes for Use as Novel Electrochemistry Based Water Purification Devices

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Access to clean, potable water is a significant world-wide problem. Approximately 1-2 billion people lack a safe source of drinking water according to the World Health Organization, with *E. coli* as one of the primary bacterial contaminants. Recently, Beeman, *et al.* described a novel, point-of-use, electrochemically-based purification device, which consisted of defect laden titania nanotubes on a titania support [1]. In aqueous media, the electrocatalytic production of radical species on the surface of defect rich TiO₂ nanotubes was found to initiate cellular death in waterborne pathogens such as *E. coli* [2,3]. The titania nanotube arrays are synthesized anodically on titanium supports and are initially produced as amorphous structures. Amorphous TiO₂ nanotubes are electrical insulators and reductive annealing is required to create a defect rich polycrystalline structure in the nanotubes which has the necessary conductivity to operate as electrochemical devices. Reductive annealing in a 2 % H₂ (balance N₂) at 500° C has been shown to produce an optimal number of defects in anatase phase crystallites within the nanotubes [4]. To date, this transformation has not been studied under real-time reaction conditions. This study presents the first in situ TEM study of the annealing of titania nanotubes in a reductive atmosphere. Utilizing a Protochips, Inc., Atmosphere 200 gas cell device, we performed in situ TEM on TiO₂ nanotubes dispersed on Atmosphere E-chips. A JEOL JEM-2800 FEG S/TEM operated at 200 kV was used for imaging. Annealing was performed while flowing a 2% H₂ (balance N₂) gas mixture with a nominal pressure of 100 Torr held throughout the experiment. The temperature was ramped from room temperature up to 1000° C, stopping at several temperatures for imaging and holding at critical points. Figure 1 shows four different images of a cluster of TiO₂ nanotubes taken at key temperatures. At 300° C (a), the structure is initially amorphous, as can be seen from the lack of any diffraction contrast in the image. After holding at 300° C for approximately 5 minutes, the onset of crystallization can be seen (b). The wall structure of the nanotubes can be seen to be defined by numerous crystallites of anatase phase TiO₂. Above 300° C, electron transfer from hydrogen molecules to oxygen in the TiO₂ lattice leads to oxygen atom abstraction, and vacancies in the lattice [5]. The promotion of oxygen vacancies and other structural defects lowers the resistivity of the TiO₂ through the creation of delocalized electrons [6]. Heating to 500° C shows continued production of defects within the now crystalline structure (c). Further heating to 600° C (d) and higher temperatures, promotes the production of additional defects as well as rutile phase crystallites and sub-stoichiometric phases of titania known as Magneli phases. The in situ TEM results will be presented in the context of earlier work, which looked at the change in density of states (DOS) and electronic band structure of titania phases during annealing treatment using density functional theory (DFT) [4]. Additional considerations will be discussed regarding the differences in the nucleation of crystallites and phase changes in single nanotubes vs. clusters of nanotubes. The role of the titania support in promoting structural changes in the nanotubes during higher temperature annealing will also be presented, as well as the degradation of nanotube morphology [7, 8].

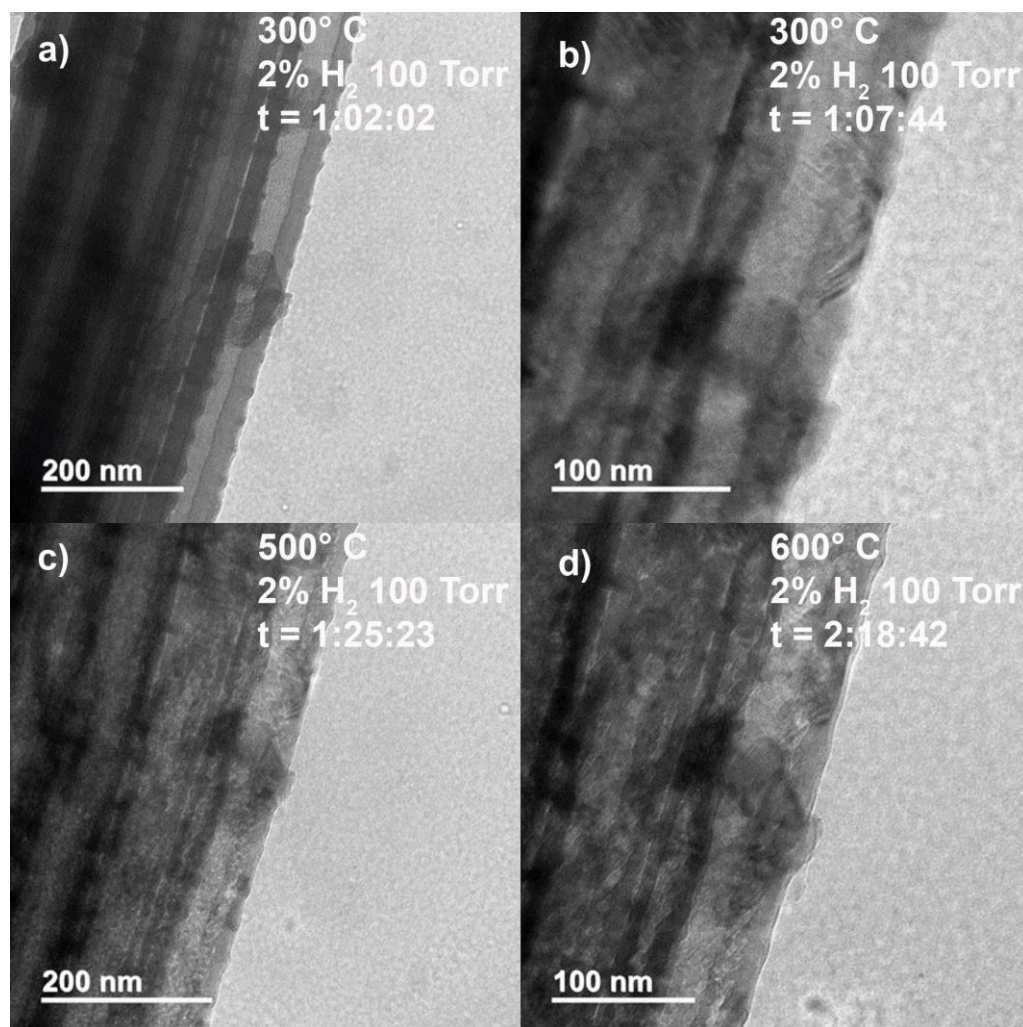


Figure 1. In situ annealing in 2% H₂ (balance N₂) of TiO₂ nanotube cluster. (a) Amorphous (as produced) nanotubes at 300° C. (b) Onset of crystallization at 300° C after ~5 min hold. (c) Continued production of crystallites and defects at 500° C. (d) Additional defect production at elevated temperature, 600° C.

References

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