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In-situ Environmental TEM Study of Phase and Morphological changes of TiO_2 Nanotubes under Different Heat Treatments

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TiO_2 is known to be a photo catalytically active material. The photocatalytic activity of TiO_2 may vary depending on the phase and composition, which is affected by heat treatment conditions. We are using TiO_2 nanotubes for solar fuel reactions and in order to get superior performance, we want to understand and improve the quality of the tubes. In the present work, we are focusing on understanding the phase and morphological changes in the nanotubes under various *in-situ* and *ex-situ* heat treatments and annealing environments. We employ environmental transmission microscopy (ETEM) to investigate morphological changes during *in-situ* annealing.

Self-organized TiO_2 nanotubes were synthesized [1] by anodization of polished and cleaned Ti foils in fluoride mediated ethylene glycol solvent, using a Pt foil as cathode. The as synthesized tubes were cleaned in distilled water and annealed in ambient atmosphere at different temperatures to produce tubes composed of different percentages of anatase and/or rutile. The tubes were characterized by XRD, SEM and TEM techniques. *In-situ* ETEM studies were performed on as-prepared tubes in the presence of 1 Torr of air under different annealing conditions.

Figure 1 (a-d) shows the SEM images of tubes annealed in air at different temperatures in *ex-situ* condition (760 torr) along with the XRD. The onset of tube disintegration is noticed at ~600^{o}C and at 800^{o}C the tubes are completely destroyed. As-prepared tubes are amorphous, and the tubes annealed at 280^{o}C are predominantly anatase. Both anatase and rutile phases exist at 600^{o}C and complete transformation to rutile takes place at 800^{o} C. Figure 1e, shows a high resolution TEM image of TiO_2 nanotube annealed at 280^{o}C along with the Fast Fourier Transformations (FFT) from regions 1 and 2. Though XRD shows the formation of anatase at 280^{o}C, from figure 1e there is still a lot of amorphous phase that has not been transformed to anatase, as shown in the FFT from region 1. Figure 2e shows a colorized image of the nanotube showing the distribution of anatase and amorphous phase derived from diffractogram analysis of the high resolution TEM image. We are also using EELS to quantitatively measure the different phases fractions (amorphous, anatase and rutile) present in the tubes under different heat treatments by using EELS. [2]

Figure 3(a-c) shows the *in-situ* ETEM images of nanotubes in the presence of 1 Torr of air at different temperatures. No change in the tube morphology was observed at 450^{o}C. At 650^{o}C the tubes are destroyed leaving behind a skeleton of nanoparticles. Figure 3d shows the in-situ EELS O K-edge from the tube at 800^{o}C, which shows the nanotube is anatase. This *in-situ* result showing anatase at 800^{o}C is different from the *ex-situ*; this may be due to the difference in gas pressure. We are currently focusing on understanding the effect of gas pressure and gas environment on the anatase to rutile phase transformation. *In-situ* ETEM experiments under

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different gas environments and pressures will be presented and the mechanisms of phase and morphological changes will be discussed in detail.

References

[1] C.A. Grimes et al., *TiO_2 Nanotube Arrays: Synthesis, Properties, and Applications*, Springer, 2009

[2] G. Bertoni et al, Ultramicroscopy, 106 (2006) 630.

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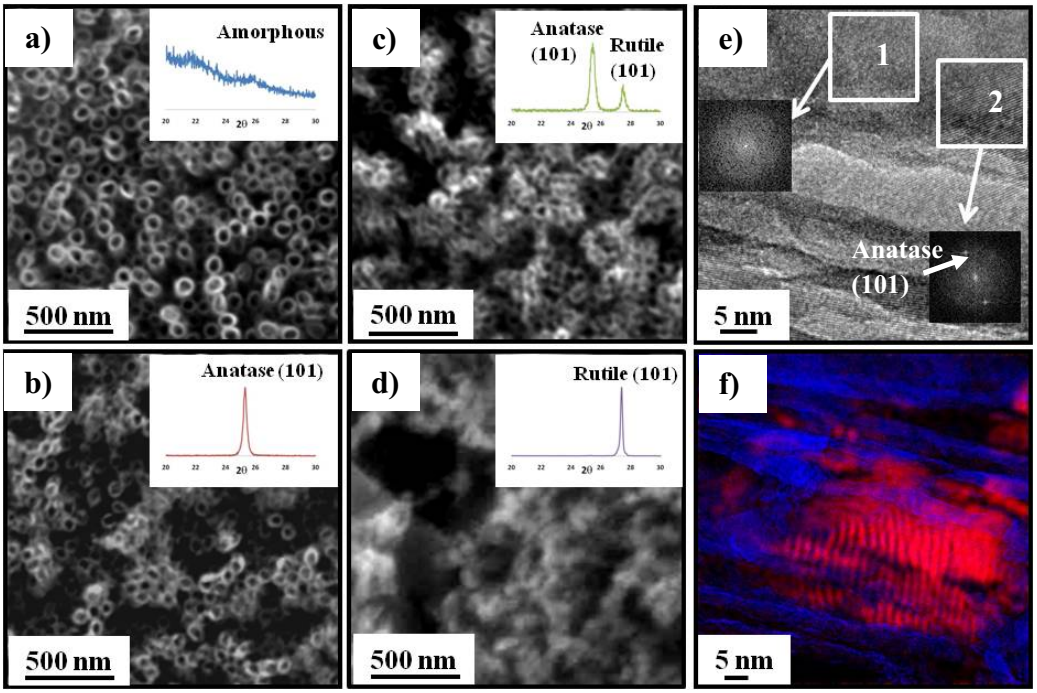

FIG. 1. SEM images of tubes annealed at different temperatures a) as-prepared b) 280°C c) 600°C d) 800°C. e) High resolution TEM image of tube annealed at 280°C with Fourier transform of anatase and amorphous regions (inset). b) Colorized image of a tube showing the distribution of anatase (red) and amorphous (blue) regions.

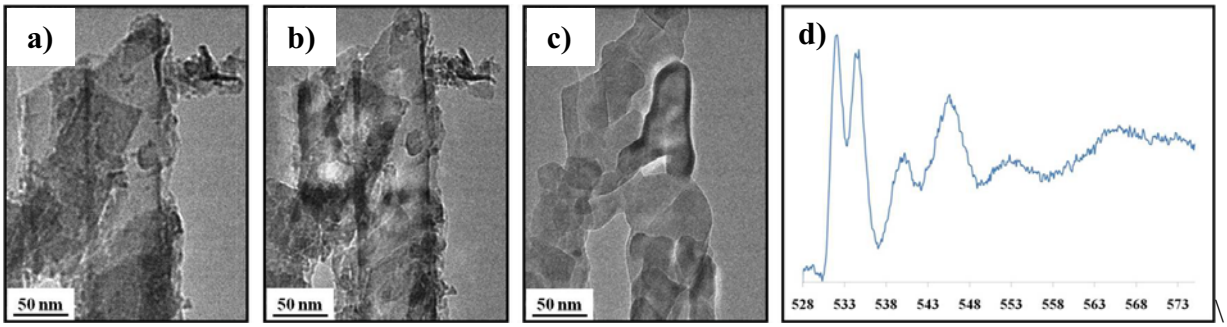

FIG. 3. *In-situ* ETEM images of evolution of tubes in 1 Torr of air at different a) 25°C, b) 450°C, c) 600°C.

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