Effect of annealing temperature on structural and bonded states of titanate nanotube films

I. INTRODUCTION
After the report of Kasuga et al., 1 titanium dioxide and/or titanate nanotubes, with large specific surface area and pore volume, have gained promising and important prospect due to their fascinating microstructures and excellent properties. Using a simple hydrothermal treatment of crystalline TiO$_2$ particles with NaOH aqueous solution, high quality nanotubes with a uniform diameter of ~10 nm with a surface area >400 m$^2$/g are reported widely.1-5 The technology has reached to a level to improve the yield, reduce the production cost, etc. Improvement of the properties such as photocatalytic activities, 6 sensing behavior, and application in lithium batteries 8 is not anymore a difficult task with the present level of research in titanate nanotubes. Vast data are available on the formation/growth mechanism of this kind of nanotubes. However, the issues such as structure stability and their corresponding crystalline phases at various calcination temperatures from a practical application point of the view still need to be addressed.

Considering the large specific surface area, high pore volume, and unique morphology, the obtained nanotubes can offer a possibility to design various TiO$_2$-related materials by post-treatment methods such as hydrothermal post-treatment methods, controlled calcination, plasma treatment, conversion of tubes to nanoparticles, functionalization of these nanotubes, etc. These methods need to be investigated for the possible improvement of the performance/utilization of titanate nanotubes for various application/device fabrications. Few reports are available on the post hydrothermal treatment of the titanate nanotubes. Therefore information on the effect of the annealing temperature on the phase transition and morphological change of the titanate film is very less. For example, Wang et al 9 reported that with increasing annealing temperature, the optical band gap and phase structure change for the titanate nanotube powder prepared by ion exchange. Yu at al. 10 observed that the photocatalytic activity of the titanate nanotube powder
increases with calcination in comparison with the P25 powder, and especially at 400 and 500 °C. it exceeded by three times the P25 activity. Calcination at a higher temperature results in a major phase transition from anatase to rutile, hence a great reduction in photocatalytic activity. However, these two and other reported studies were focused on the effect of calcination on the titanate powder (not film form), whereas no information is available on what happens when the titanate films are calcined at various temperatures. It would be interesting to alter the properties of the film as it can then be applied directly for the device testing. With this aim, we report here the effect of the annealing temperature on the phase transition and morphological changes of the titanate film. The annealed titanate films can bring important and unexplored features of these nanotubes in the film form for devices such as photoelectrodes, dye-sensitized solar cells, lithium-ion batteries, etc.