TEM characterization of TiO_2 nanotube templates for DSSCs.

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TiO_2 nanotubular layers have been recently investigated as an alternative template material for dye-sensitized solar cells [1-3]. These layers are anodically grown in fluoride containing organic electrolytes. The mechanism of growth is supposed to be similar to the well known case of porous alumina [4-6]. Knowledge on the growth mechanism of nanotubular TiO_2 in order to further optimize the formation of TiO_2 nanotube arrays as a scaffold for efficient dye sensitized solar cells can be already gained by using transmission electron microscope (TEM) that offers more information about the morphology of the nanotubes.

The purpose of the visit was TEM sample preparation and characterization of nanotubular layers prepared in the Erlangen lab. The nanotubular layers were grown at different growth conditions (electrolyte, anodization potential) on sputter deposited Ti-metal films containing thin W- marker layers on an aluminum substrate.

Sample preparation for TEM investigations was conducted using two methods. The first method was scraping the TiO_2 nanotubular layer off the substrate and dispersing it on a TEM grid. The second method used was cutting ultra thin (25 nm) slices of the nanotubular layers employing an ultramicrotome. Prior to ultramicrotoming the samples were embedded in epoxy resin. After shaping the specimens with a glass knife the ultra thin slices were cut using a diamond knife and successively transferred on a TEM grid. It should be mentioned that the ultramicrotome method is the only method to prepare highly defined cross sections of TiO_2 nanotubes and that it can be only performed on thin sputtered metal layers on an aluminum substrate.

Figure 1 shows SEM images of a TiO_2 nanotubular layer made in Erlangen and TEM images of the same sample prepared with the scrape off method.

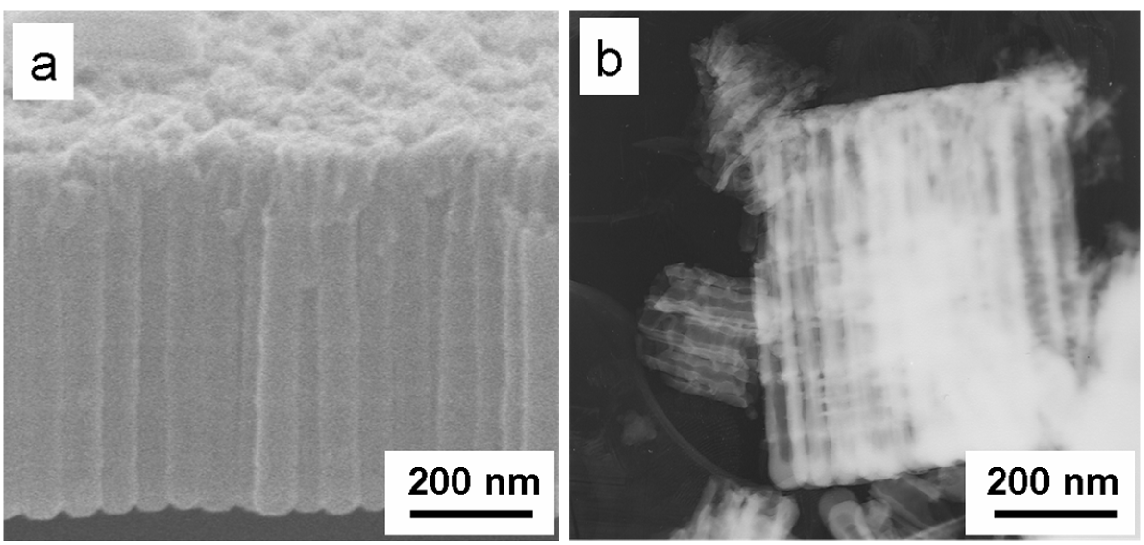

Figure 1: (a) SEM images of a TiO_2 nanotubular layer made in Erlangen and (b) TEM image of the same sample prepared by the scrape off method

It can be clearly seen that a TEM image of the TiO_2 nanotubular contains significantly more information on the morphology of the tubes than a SEM image. For example the barrier layer thickness and the wall thickness of the tubes can now be easily obtained, see also figure 2.

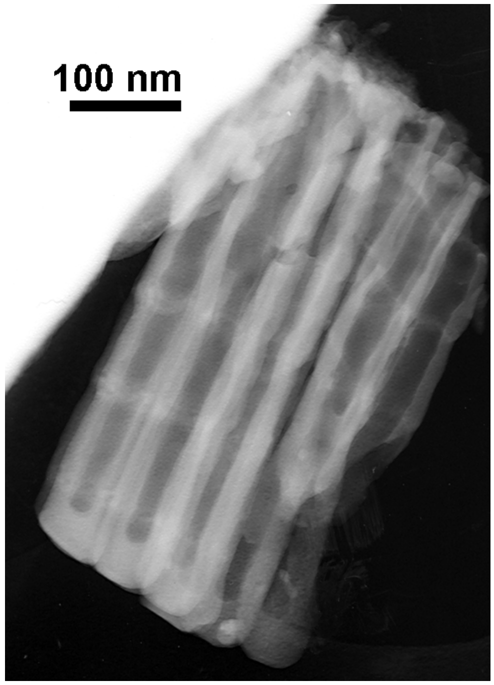

Figure 2: TEM image of TiO_2 nanotubes prepared by the scrape off method

Looking at nanotubes grown at different voltages a dependency of the barrier oxide thickness with the anodization potential can be found. The thickness of the barrier oxide layer increases from 20 nm at an anodization potential of 40 V to 40 nm at an anodization potential of 150 V. Even more detailed TEM images were obtained when the samples were prepared by the ultramicrotome method. In Figure 3 a cross-sectional image of a nanotubular layer prepared by the ultramicrotome is shown. The overall thickness of the cut cross section is about 25 nm.

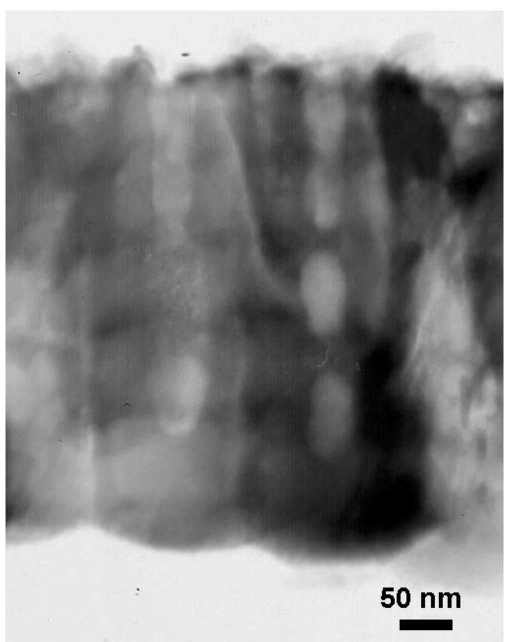

Figure 3: TEM image of TiO_2 nanotubes prepared by the ultramicrotome method

In the ultramicrotomed cross-section additionally two different layers in the tube walls/bottoms are visible. The tungsten layers which are part of the multilayered sputter structure and hence part of the TiO_2 nanotubular structure can be clearly seen as dark belts in the TEM images while in the SEM image (see figure 1a) only a little change in the morphology can be found.

The results obtained show that TEM imaging offers much more detailed information on the morphology and composition of the TiO_2 nanotubes. Depending on the preparation method different features of the nanotubes, like barrier layer and tube wall thickness, marker distribution, marker layer spacing and double layered structure could be investigated.

An extensive systematic investigation of the features traced during this short visit, combined with other analytical methods can be used to provide an insight in the mechanism of tube formation and will help to further optimize TiO_2 nanotubular layers as a scaffold for dye sensitized solar cells.

The author would like to thank all people involved especially Prof. George E. Thompson for the obliging supervision at the Corrosion and Protection Centre in Manchester. The European Science Foundation is gratefully acknowledged for funding this research.

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