doi:10.1017/S1431927615009484 Paper No. 0869 Microsc. Microanal. 21 (Suppl 3), 2015

Microscopy Guided Design of Radial *p-n* Junction in Single TiO_2 Nanotubes

Miaofang Chi,[1] Mina Yoon,[1] and Parans Paranthaman[2]

[1.] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831.
[2.] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

Engineering one-dimensional nanostructures in the axial direction is of great importance to researchers in energy harvesting fields, as utilizing materials with such a unique configuration could potentially introduce significant efficiency improvements for use in future solar energy conversion, storage, and nanoelectronic devices [*1-3*]. In 2007, the Lewis group proposed an interesting solar cell configuration consisting of radial *p-n* junction nanorods that exhibited a considerably improved cell efficiency compared to traditional planar solar cells [*4*]. Such a configuration decouples the direction of incident light and the proximity of generated charge carriers to the *p-n* junction. Vertical alignment of many cylindrical junctions facilitates the transport of photon-generated minority carriers to the junctions, and therefore, greatly increases carrier collection efficiency, as well as enhanced tolerance to radiation damage, defects, and impurities. Further advantages are anticipated with nanotube structures for solar energy conversion based on recent theoretical calculations, which showed that nanohole arrays (aligned nanochannels in a Si matrix) provide better light absorption compared to nanowire arrays due to the high density of waveguide modes [*5*]. Anodic TiO_2 nanotube arrays (NTA) have been studied extensively such that their radial physical properties can be tailored by incorporating an additional layer having different physical properties. These layers are either incorporated on the inner or outer walls of the nanotubes [*6,7*]; however, the synthesis of well-controlled and reproducible axial *p-n* junctions with desirable properties at a relatively low cost for NTAs remains a challenge.

Previous reports of the microscopy characterization of TiO_2 nanotubes summarized observations regarding general morphological parameters, such as crystallinity/phase, size/diameter, length, and wall thickness. A detailed analysis of the surface atomic structure, however, has not been studied in detail since it has been assumed that TiO_2 nanotubes have the same rolled structure as observed for carbon nanotubes [8]. Current electron microscopy work has revealed that anodic TiO_2 nanotubes are single crystal tubes with clear surface facets. The TiO_2 outer walls are consistent with (110) and (100) surface facets, as shown in Figure 1, e.g., four {110} and two {100} outer wall surfaces comprise a near-hexagonal morphology. In contrast, the inner surface/wall is characterized by a relatively smooth, curved surface that has essentially formed by many adjoining small facets (1-2 atomic layers). Internal strain in the radial direction was determined by analyzing a series of high-resolution STEM images using geometrical phase analysis (GPA) analysis. The inner walls are under a compressive strain that gradually transitions to a tensile strain at the outer tube walls. Furthermore, the atomic termination and electronic structures at the inner and outer wall surfaces/facets were different, as evidenced by analysis of the EELS Energy Loss Near Edge Structure (ELNES), as shown in Figure 2. For example, the first pre-peak of the Ti-L_3 edge (labeled "A" in Figure 2b, which arises from the $2p_{3/2}$ Ti to the t_{2g} molecular orbital MO transition), is more pronounced in the spectrum from the outer wall compared to that from the inner wall. Although the corresponding pre-peak splitting of the O-K edge is not clearly visible, peak "b" of the O-K edge, which can be directly correlated to the hybridization of O 2p orbitals and Ti 4s/4p orbitals, is notably different [9]. These electronic structural differences will be correlated to their atomic structures and be discussed in detail in our presentation. Furthermore, distinctive chemical activities are associated with different surface terminations, as predicted by first principle theoretical calculations.

Results from microscopy studies can offer direct structural input for designing novel coaxial *p-n* junctions that can exploit the unique chemical properties provided by tailored inner and outer wall structures and chemistry. This concept was recently validated experimentally where it was shown that elements such as Nb, Sr, and Cr, can be used to preferentially dope specific locations and establish internal junctions. [10]

References:

[1] LJ Lauhon *et al*, Nature **420** (2002) p. 57.
[2] BZ Tian *et al*, Nature **449** (2007) p. 885.
[3] LF Shen *et al*, Journal of Physical Chemistry Letters **2** (2011) p. 3096.
[4] BM Kayes, HA Atwater, and NS Lewis, Journal of Applied Physics **97** (2005) p. 1678.
[5] SE Han and G Chen, Nano Letters **10** (2010) p. 4692.
[6] DA Wang *et al*, Journal of Materials Chemistry **20** (2010) p. 6910.
[7] SP Albu *et al*, Advanced Materials **20** (2008) p. 4135.
[8] SM Liu *et al,* Chemistry of Matererials 14 (2012) p.1391.
[9] E. Stoyanov *et al,* American Mineralogist 92 (2007) p. 577.
[10] Research supported by the Laboratory Directed Research and Development (LDRD) program at Oak Ridge National Laboratory (ORNL). Microscopy was conducted at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

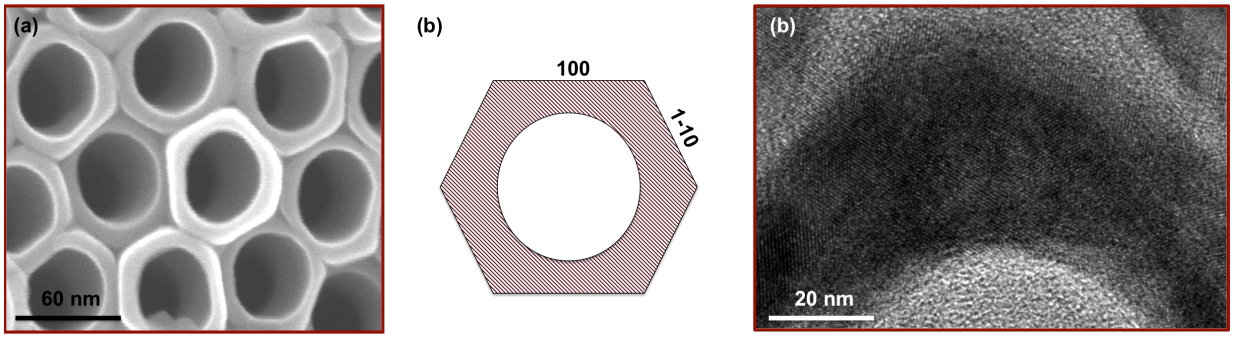

Figure 1. (a) SEM image of an aligned array of anodic TiO_2 nanotubes. (b) Schematic figure of the morphology of TiO_2 nanotubes exhibiting {100} and {1-10} surface facets. (c) High-resolution TEM image showing different surface atomic structure at inner and outer walls.

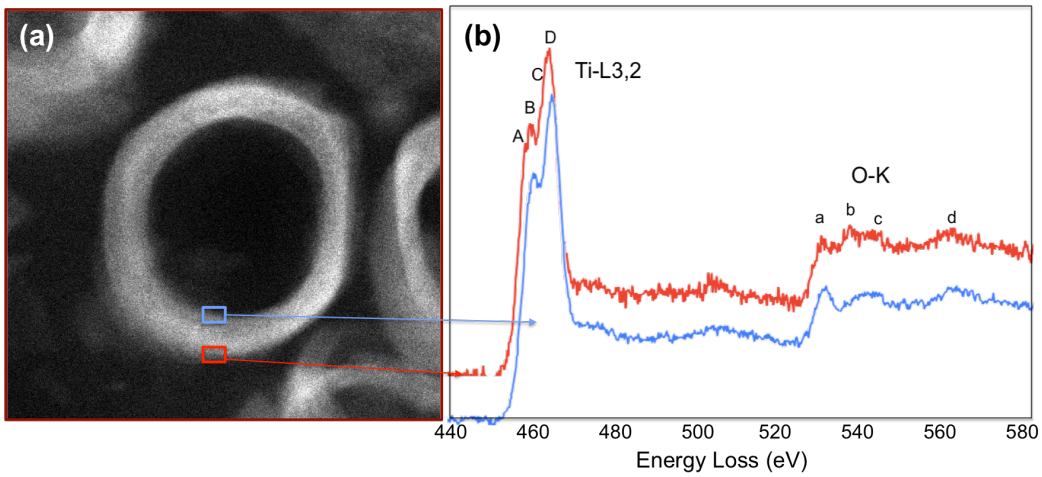

Figure 2. (a) STEM image of a cross-sectioned TiO_2 nanotube; (b) comparison of the EELS spectra acquired from inner (blue) and outer (red) nanotube walls.

https://doi.org/10.1017/S1431927615009484 Published online by Cambridge University Press