Magnetism-Processing Correlations in Anodized Titania Nanotubes

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Titania nanotubes have gained attention in the past few years due to interesting phenomena associated with their semiconducting behavior and very large surface area.[1] Promising applications of titania nanotubes include water splitting using solar radiation to create hydrogen for use as a fuel. Further, if magnetism could be induced in titania, in combination with its semiconducting behavior, there would be a potential for employing these nanostructures in prospective spintronics devices, for instance, in instant-on-computers. In such devices the spin degree of freedom would be used along with the electron charge in developing. While nominally pure titania nanotubes are expected to be non-ferromagnetic, recently magnetic behavior has been observed in these nanostructures that appears to be related to the conditions of crystallization from their as-made amorphous state, such as the annealing environment and temperature.[2] Understanding the relationships between the magnetic properties, crystalline structure and tubular morphology is important to better enhance the performance of these novel materials in multifunctional applications.

In this work, nominally-pure titania nanotubes were synthesized from Ti foil (99.7% pure) by electrochemical anodization and then processed in different conditions to attain a crystalline anatase structure. Annealing was carried out in a tube furnace to induce crystallization of the free-standing nanotubes in different purging gases (O_2, H_2 and Ar, flow rate of 70 cm^3/min) from 280 to 450 °C for two hours with heating and cooling rates of 1 °C/min. Information concerning the structural stability, crystallization character, and transport properties of the as-synthesized and annealed nanotubes were obtained by morphological (scanning and transmission electron microscopy (SEM)), structural (x-ray diffractometry (XRD)) and magnetic (superconducting quantum interference device (SQUID)) probes. Prior to carrying out the magnetic measurements, pulverized free-standing nanotubes were mounted in empty quartz tubes followed by sealing with an oxygen-propane flame under vacuum.

Regardless of the annealing atmosphere, increasing the annealing temperature gradually developed a crystalline anatase structure. XRD confirmed an expanded lattice structure as well as enhanced crystal growth in the oxygen-deficient annealing environment (Fig. 1). Based on the annealing gas, a change in magnetism was observed in nanotubes, with the oxygen-annealed sample exhibiting the lowest weight-normalized moment and the hydrogen-annealed sample exhibiting the highest, compared to the as-synthesized amorphous nanotubes (Fig. 2). The magnetic data are analyzed by decomposition of the magnetic susceptibility response into Pauli and Curie-Weiss paramagnetic components, indicating presence of two types of magnetic phases in the nanotubes. The highly crystalline, defect-rich sample that was annealed in reducing environment (H_2) presented higher paramagnetic signal, indicative of more metallic-like behavior, which may result in an improved semiconducting behavior and thereby, enhanced catalytic performance.

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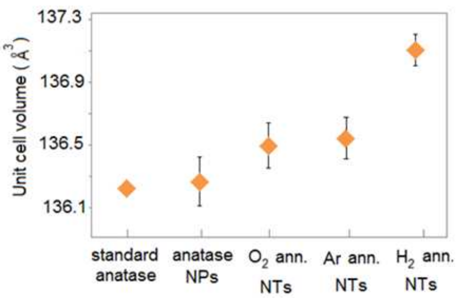

Fig. 1. Anatase unit cell volume.

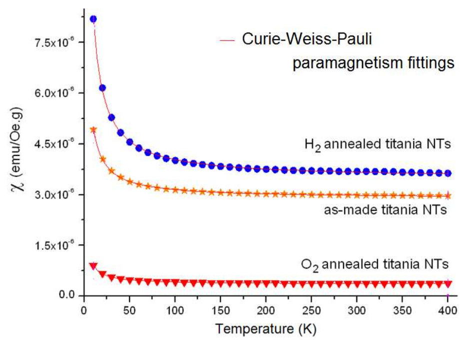

Fig. 2. Magnetic susceptibility of the titania NTs.

References:
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