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Towards understanding electronic structure of high aspect-ratio TiNT arrays

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One-dimensional ordered arrays of semiconducting materials are of great interests owing to their wide ranges of industrial applications, such as solar cell, gas sensor, photocatalytic water splitting, and photocatalytic degradation of pollutant. Highly orientated TiO_2 nanotube (TiNT) arrays with a length of a few hundred nanometers can be fabricated by electrochemical anodization method from a Ti foil in aqueous hydrofluroric acid solution. The ordered arrays of one-dimensional TiO2 architectures that provide a path for charge collection and access to the solution, can largely improve light harvesting and enhance the absorption of light. However, the fabricated TiNT arrays film exhibits the close-end bottom near the substrate. This restricted their feasibility and hindered the TiNT arrays from the practical applications. In this study, a simple, low-cost and environment-friendly method with unsophisticated experimental procedure was used to obtain high aspect-ratio free-standing open-ended anodic TiNT films. The bottom caps were removed chemically by oxalic acid with various etching time (0-16 hrs). The resulting open-ended structure allows the photons and the reactants easy access to the nanotube-array surface as well as superior electron-collecting efficiency. However, to well control the TiNT films in various applications requires better understanding its fundamental properties, such as band gap, local atomic structure and electronic structures. Synchrotron-based x-ray spectroscopies are powerful tool to investigate the electronic structure both in conduction and valence band, as well as the local atomic structure. Hence, the x-ray absorption near edge structure (XANES), resonant inelastic x-ray scattering (RIXS), extended x-ray fine structure (EXAFS), and scanning photoelectron microscopy (SPEM) were utilized. Synchrotron-based x-ray spectroscopic results revealed that the electronic and atomic structures at top of the TiNT are different from those at the bottom and on the sidewall. Further, the growth mechanism is also suggested in this study.