Functional Materials

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TiO_2 nanotubes arrays as active material for energy harvesting and storage devices

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TiO_2 nanotubes (NTs) are nowadays attracting increasing interest in applications such as dye-sensitised solar cells (DSCs) as they offer the possibility to modify the standard architecture based on mesoporous layers of TiO_2 nanoparticles by introducing vertically aligned nanostructures, characterised by a large sensitised surface area and anatase crystalline structure, able to improve the charge percolation through the anode because of the strongly interconnection of the nanocrystals [1,2]. The same nanostructures are also attracting interest as anodes in Li-ion batteries. In fact, TiO_2 represents an alternative anode material to graphite, due to its high specific surface area and pore volume, to the reduced cost and to the reduced environment impact [3,4].
In this work we report on the morphological, structural and functional characterization of vertically aligned TiO_2 nanotubes arrays prepared by anodic oxidation. Two different annealing procedures are presented.

In the first procedure, TiO_2 nanotube arrays with different lengths were fabricated by anodic oxidation of Ti foil, followed by an annealing step in furnace 450°C for 30 minutes. Stoichiometry, crystalline phase and morphology of the TiO_2 NTs were investigated by means of TEM, FESEM, Energy Dispersive Spectroscopy (EDS) and X-ray diffraction, evidencing the formation of a highly ordered 1D NT array, with a pure anatase crystalline structure (figure 1).

Free-standing NTs membranes were detached by the metal substrate to be tested as photoanodes in DSC (1) and as anodes in Li-ion batteries (2) [refs].

1) Transparent photoanodes were fabricated transferring the membranes on FTO/glass sheet with an adhesion layer made of TiO_2 nanoparticle (NP). DSCs were assembled employing a microfluidic housing system. The cell performances and the electron transport properties as a function of the tubes length were characterized by I-V electrical measurements, incident photon-to-electron conversion efficiency, electrochemical impedance spectroscopy and open circuit voltage decay. A comparison with the charge transport properties evaluated in nanoparticle-based photoanode showed an increase of the electron lifetime and the diffusion length, yielding an overall power conversion efficiency up to 7.56% [5].

2) The electrochemical response in laboratory-scale lithium cells with TiO2 NTs as anode was highly satisfying, showing good stability and capacity retention after prolonged cycling along with improved durability (> 1100 cycles). High surface area, short diffusion path and fast kinetics of the TiO_2 nanotube arrays are considered to be responsible for the noticeable electrochemical performance [4].

Due to the high annealing temperature (450°C), not compatible with the most common polymeric substrates, TiO_2 nanotubes cannot be used for the fabrication of flexible devices. However, the flexibility is becoming a key characteristic for future devices, because it can provide devices able to adapt to different configuration.

In the second procedure, low temperature water treatment is proposed as a way to overcome this limitation, obtaining the crystallization starting from amorphous metal-oxide nanostructures [6]. In the present work, this easy approach is improved exploiting water vapour as phase transformation environment in order to crystallize the amorphous TiO_2 NTs layer (figure 2) and open the way to future highly-efficient TiO_2 NTs based flexible photoanodes. Stoichiometry, crystalline phase and morphology of the TiO_2 NTs were investigated by means of TEM, FESEM, EDS and X-ray diffraction, in order to put in evidence the characteristic of the TiO_2 nanotubes before and after the water vapour treatment and confirm the successful crystallization of the nanostructures.

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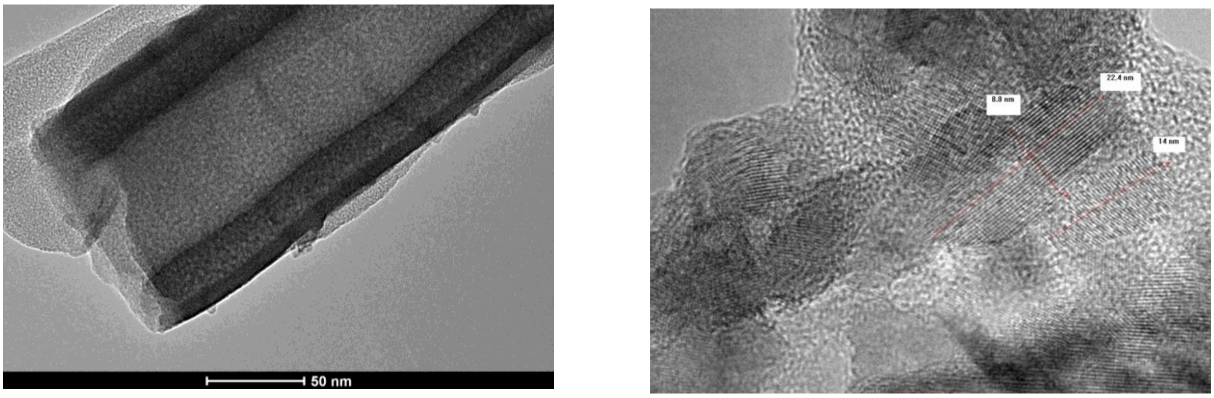

Figure 1. TEM and HRTEM images showing the morphology and the crystalline quality of TiO_2 NTs annealed at 450°C for 30 minutes

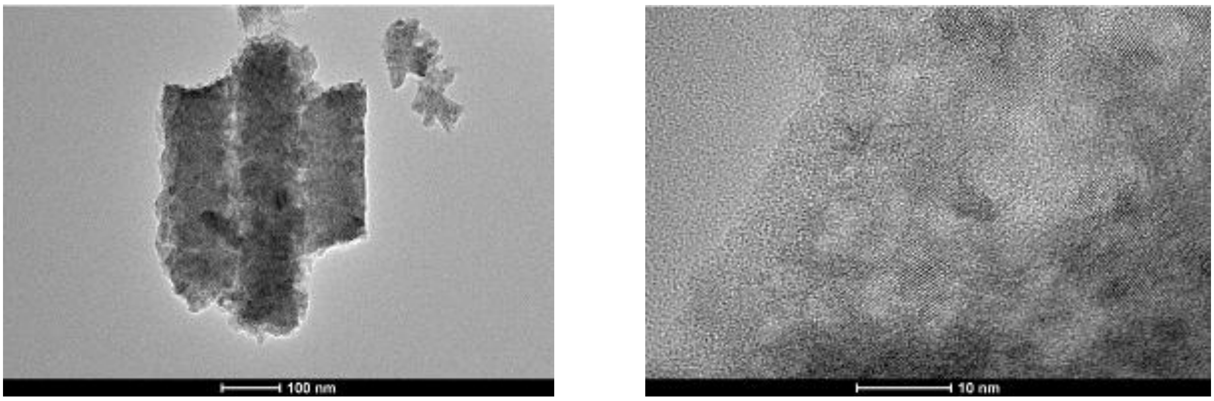

Figure 2. TEM and HRTEM images showing the morphology and the crystalline quality of TiO_2 NTs treated with water vapour