

Thickness and order enhancement in arrays of TiO₂ nanotubes through a simple electropolishing pre-treatment

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The highly-ordered TiO₂ nanotubes (NTs) have gained much importance for application in hydrogen production by water splitting and dye-sensitized solar cells (DSCs). The DSCs have a great potential to be an alternative device for conventional photovoltaics due to their low cost and easy fabrication [1,2].

The TiO₂ NTs arrays must have a high-aspect-ratio configuration to obtain higher conversion efficiency. The photoelectrochemical behaviour of TiO₂ (anatase) with different nanoarchitectures (such as nanoparticles, nanowire, nanofiber, nanotubes [3]) and the same active surface area (or thickness) has been studied and applied to DSCs to overcome the limitation of TiO₂ nanoparticle structure. Recently a new architecture has been in focus, among these structures: the TiO₂ nanotube arrays have received a great attention due to their one dimensional structure to provide a direct path for electrons. However, the efficiency of TiO₂-nanotube-based DSCs is 6.89%, which is still lower than that of TiO₂-nanoparticle-based DSCs (~10%). The geometry of the nanotubes depends on different anodizing parameters (electrolyte type and concentration, pH, time, applied potential) that determine the tube features (length, pore diameter, wall thickness, etc.).

We synthesized TiO₂ NTs arrays by electrochemical anodization of a Ti foil (two-electrode cell) in fluoride ion containing baths in combination with non-aqueous organic polar electrolytes including ethyleneglycol or glycerol. These Ti foils were biased with an anodization potential of 60 V for 17 h at room temperature. We then obtain highly self-ordered arrays of TiO₂ NTs, with a length of 100 micron, an outer diameter of ~200 nm. The NT arrays morphology was characterized by scanning electron microscopy (SEM). The study of current density transients [$j(t)$] monitored during the anodization process allowed us to probe the different stages of the nanotubes formation. We also concentrate our study on the NT growth quality, i.e. the influence on the nanotubes length of: the type of electrolyte organic solvent, the Ti pre-treatment prior to the anodization, and the electrolyte concentration. In the first case, by simply changing the organic solvent of the electrolyte we can pass from a 6 μm NT length (glycerol) to an 70 μm length (ethylenoglycol). In the second case, by using the same electrolyte three times the 17 h we can see a decreasing in the NT length corroborated with the current density transients decrease. Finally, prior to the anodization we perform an electropolishing pre-treatment in the Ti foil (in a H₂SO₄/HF solution, with an applied potential of 15V during 4 min). We found that such process allows the growth of NTs of enhanced length (larger than 100 μm , i.e. an increase larger than 50% when compared with the as-rolled sample). The topography of the electropolished Ti surface was investigated by Atomic Force Microscopy. After the electropolishing, the Ti surface revealed a dimple-pattern structure (and a surface roughness decrease) that enhances the NTs growth and thus allows to obtain a higher NT length. The subsequent anodization of the dimpled Ti surface led to an increase in the array structural order. The structural analyses of the TiO₂ NTs, was performed using X-Ray Diffraction. The corresponding diffraction patterns showed the as-prepared nanotubes are amorphous. We carried out a systematic study of different annealing temperatures to obtain the Anatase phase isolated. The NTs crystallize in Anatase phase after a proper annealing at 400 °C (with O₂).

References

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