Ain Shams University
Faculty of Engineering
Design and Production Engineering

Nanostructured Materials for Solar Fuel Production

A Thesis submitted in partial fulfillment of the requirements of the degree of

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(Design and Production Engineering)

by

Mostafa Mamdouh Abd-Allah Omar

Bachelor of Science in Mechanical Engineering
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Faculty of Engineering, Ain Shams University, 2012

Supervised By

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Statement

This thesis is submitted as a partial fulfillment of Master of Science in Mechanical Engineering, Faculty of Engineering, Ain shams University.

The author carried out the work included in this thesis, and no part of it has been submitted for a degree or a qualification at any other scientific entity.

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Thesis Summary

Finding a sustainable, clean energy source is considered the most important challenge facing the scientific community in the 21st century, and since the sunlight is the most sustained, abundant energy source on earth, many research efforts have been directed towards utilizing solar energy in different fields. Photoelectrochemical (PEC) water splitting is one of the most studied routes for solar fuel production at which sunlight is used directly to split water into hydrogen and oxygen.

However, till now, no single material can satisfy all the requirements for a high efficient PEC water splitting. Challenges such as large band gap, stability, and cost still hinders the application of PEC water splitting on a larger scale. Of the different candidate materials for water splitting, immense research efforts have been exerted on TiO_2 to make them efficient photoanodes, owing to their stability, suitable band edge positions, and low cost. Nevertheless, their large band gap is still a major problem.

The main aim of this thesis was to make use of nanostructuring, morphology tuning, and alloying to overcome the pure TiO_2 challenges *via* the fabrication of complex oxide nanotubes. Different one-step potentiostatic anodization conditions for a Ti-Nb-Zr alloy were investigated aiming to synthesize Ti-Nb-Zr-O nanotubes. A formamide-based electrolyte containing NH_4F was used in the anodization. The effect of anodization potential and time were thoroughly studied.

FESEM, XRD, Raman Spectroscopy, XPS, and EDX were used to characterize the morphology, crystallinity, and composition of the synthesized nanotubes. In addition, the optical and PEC properties were investigated *via* Linear Sweep Voltammetry, Chronoamperometry, and Mott-Schottky analysis. A micro-mechanical model was built and verified using the FESEM images to further understand the kinetics of the nanotubes growth.

NTs with diameters up to 507 nm and lengths up to 36 μm were successfully fabricated. It was found that with the increase of the anodization potential, the diameters and length of the nanotubes increased. On the other hand, increasing the anodization time was found to have almost no effect on the nanotubes diameter, although it led to increase

in the nanotubes length. In addition, anodization at 100 V for 2 hours led to the formation of multipodal nanotubes.

The growth kinetics of the nanotubes were studied at 40V. Nanotubes growth can be considered as 2 main stages. First, a stage with a fast growth rate which was calculated to be 2.8 nm/sec, and a second steady-state stage with a growth rate of 0.198 nm/sec.

The micro-mechanical model suggested that the multipodal (MP) nanostructure formation is owed to bending and fusion of discrete NTs. This theoretical model considered NTs as a bottom-fixed cantilever, and was used to analyze the preconditions required for the formation of MP nanostructure. The model findings suggest that bending only occurs when the net forces acting on the NTs overcome the NTs stiffness as it passes a critical length which can be calculated as a function of the modulus of elasticity, 2^{nd} moment of area, and the surface tension of the electrolyte. Refractive indices calculations showed that MPNTs have a graded refractive index, being max. at the bottom oxide layer and decreases as we get closer to the air at the top of the tubes. This gradient increase light scattering probability, which in turn enhanced its light harvesting characteristics.

As a proof, the photoelectrochemical properties of the MPNTs annealed in air showed a 9-fold enhancement in the photocurrent density compared to conventional compact NTs. This enhancement is ascribed to the MP morphology with its graded refractive index as well as easier charge transport. Mott-Schottky analysis demonstrated a positive shift in the flat band potential for the MPNTs when compared to the compact counterpart as well as double charge density. Further verification was obtained by removing the multipodal portion of the NTs via sonication, the sonicated samples showed significantly lower photocurrent. H_2 annealed samples showed the same trend confirming that this improvement is related to the presence of the MPNTs and independent of the annealing condition.

Hence, fabricating multipodal nanotubes from metal oxides can be considered as a promising route for engineering the complex metal oxides to enhance their performance for PEC water splitting.

KEYWORDS: Complex oxides, nanomaterials, multipodal nanotubes, anodization, water splitting.

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