Materials Science in Semiconductor Processing 93 (2019) 252–259

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

# Hierarchical rutile/anatase $TiO_2$ nanorod/nanoflower thin film: Synthesis and characterizations

Shervin Daneshvar e Asl[a,b], Ailar Eslami Saed[c], Sayed Khatiboleslam Sadrnezhaad[a,c,*]

[a] Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran
[b] Department of Chemistry, National University of Singapore, Singapore
[c] Advanced Bionanomaterials Laboratory, Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

ARTICLE INFO

*Keywords:*
Nanoflower
Nanorod array
Rutile/anatase $TiO_2$
Hydrothermal
Aqueous chemistry

ABSTRACT

Hierarchical $TiO_2$ nanorod/nanoflower thin film was synthesized on fluorine doped tin oxide glass via hydrothermal and aqueous chemistry methods. According to field emission scanning electron microscopy results, the thin film was crack-free and uniform. Primary nanorods had an average diameter of 95 nm and a length of 2 µm. They were perpendicular to the substrate owing to the $TiO_2$ prenucleation. Growth of the nanoflowers on the nanorods could increase both the specific surface area and roughness. X-ray diffraction and Raman spectroscopy showed that the nanorods were rutile; while the nanoflowers were anatase. Efficient electron transfer from anatase to rutile could therefore occur. According to the diffuse transmittance spectroscopy examination, the light harvesting rate was ameliorated and the band gap energy reduced to 2.83 eV. This was attributed to the $F^-$ doping the sample during synthesis. The enhancement of the photoelectrochemical activity allowed substitution of the $TiO_2$ nanorod/nanoflower thin film for the traditional $TiO_2$ nanorods usually used in solar cells, sensors, and photocatalytic systems.

## 1. Introduction

Semiconductor materials have received much attention in recent decades due to their application potential in solar energy conversion and environment purification [1–6]. Among them, titanium dioxide ($TiO_2$) has some superiorities such as appropriate band edge position, high redox potential, high photocatalytic activity, desirable photoabsorption, photocorrosion resistance, chemical/thermal stability, being environmentally friendly, and low cost, which made it one of the most promising materials in fabrication of novel systems [7–11]. Solar cells [12,13], photocatalysts [14–16], catalysts [17,18], gas sensors [19–21], molecular sensors [22,23], and lithium batteries [24,25] are some of titanium dioxide applications.

Photoelectrochemical performance of $TiO_2$ strongly depends on factors like morphology, phase structure, crystallite size, and amount of surface hydroxyl groups [26–29]. $TiO_2$ morphology directly influences specific surface area, surface crystalline planes, molecular absorption characteristics, and electron mobility. These parameters are effective factors on efficiency of solar cells photoenergy conversion, sensors sensitivity, photosystems luminescence intensity, and photocatalytic effects [30]. Therefore, $TiO_2$ micro/nanostructures improvement is vital for diverse applications. In recent years, unique $TiO_2$ micro/nanostructures have been synthesized via different methods and evaluated. Nanosheet [31], nanowall [32], nanorod [33], nano/microsphere [33,34], nanotube [34], nanotree [35], skeleton structure [36], microsponge [37], nanoworm [38], nanopillar [39], leaf-like mesostructure [40], micropetal [41], and nanostar [42] are some examples of these structures.

The main restriction of $TiO_2$ is the recombination of photogenerated electrons and holes [43]. One-dimensional nanostructures offer high rate of charge carriers transportation due to providing direct pathways for these photogenerated charge carriers movement [44,45]. That, in turn, can increase photoelectrochemical activity of material. Albeit, one-dimensional nanostructures don't have sufficient surface area and light harvesting [46], and as a result, introduction of a three-dimensional (3D) nanostructure can be much promising. Besides, an advantage of biphasic $TiO_2$ structure is that different positions of valence/conduction bands energy levels of anatase and rutile phases lead to generated charge carriers separation [47]. Actually, simultaneous presence of these two phases presents a better photoelectrochemical activity than that of just one phase. Meanwhile, biphasic $TiO_2$ structure provides usability of both phases characteristics. To exemplify, rutile has a better chemical stability, higher refractive index, and lower band gap energy [48], yet anatase proposes larger specific surface area,

* Corresponding author at: Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran.
*E-mail addresses:* sh.dan4@student.sharif.edu (S. Daneshvar e Asl), aylar.eslami@aut.ac.ir (A. Eslami Saed), sadrnezh@sharif.edu (S.K. Sadrnezhaad).

https://doi.org/10.1016/j.mssp.2019.01.012
Received 20 November 2018; Received in revised form 6 January 2019; Accepted 10 January 2019
1369-8001/ 