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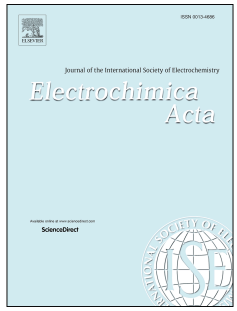

Band-gap narrowing and electrochemical properties in N-doped and reduced anodic TiO_2 nanotube arrays

Naeimeh Sadat Peighambardoust, Shahin Khameneh Asl, Raheleh Mohammadpour, Shahab Khameneh Asl

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Band-gap Narrowing and Electrochemical Properties in N-doped and Reduced Anodic TiO_2 Nanotube Arrays

Naeimeh Sadat Peighambardoust[1], Shahin Khameneh Asl[1], Raheleh Mohammadpour[2], Shahab Khameneh Asl[1]*

[1] *Department of materials engineering, Faculty of Mechanical Engineering, University of Tabriz, Tabriz 51666-14766, Iran*
[2] *Institute for Nanoscience and Nanotechnology, Sharif University of Technology, Tehran 14588-89694, Iran*

**corresponding author: Khameneh@tabrizu.ac.ir*

Abstract

Electrochemical activity of TiO_2 nanotube arrays (NTAs) is restricted by a wide band gap of TiO_2. To overcome this restriction, we considered systematic research on two effective methods of doping of TiO_2 NTAs such as the N-doping and electrochemical reductive doping and predicting the proper application of them. Band gap narrowing was occurred from 3.16 eV for undoped TiO_2 NTAs to 2.9 and 2.7 eV at N-doped and self-doped TiO_2 ones respectively. The electrochemical responses of the TiO_2 NTAs before and after doping were examined by cyclic Voltammetry (CV) curve. To understand the electrochemical behavior of the undoped and doped TiO_2 NTAs, electrochemical impedance spectroscopy (EIS) was used and three equivalent circuit models were also built. The results showed that the undoped TiO_2 NTAs is not strictly capacitive but a small quantity of N in TiO_2 remarkably decreases the surface resistance of TiO_2 electrode. In contrast, self-doped TiO_2 NTAs resistance is reduced to very negligible contents of 0.0001322 Ωcm^{-2}, that not only self-doped sample becomes to completely capacitive but also, it leads to the semiconductor nature of TiO_2 NTAs transforms to semi-metallic one, and the two orders of enhancement in capacitance of blue TiO_2 NTAs are very astonishing and it has outstanding potential for applications like supercapacitors as the electrochemical response of the self-doped TiO_2 NTA sample was found to be a content of about 7 mF cm^{-2} that it is improved about 20 times compared with undoped one. Furthermore, it was found that doping of TiO_2 NTAs with nitrogen atoms increases the carrier density about 2.82×10^{21} and self-doped TiO_2 NTAs show the higher carrier density about 1.14×10^{25} compared with N-doped NTAs. These finding help to understand the mechanism of doping in two different methods and select the best one in relevant applications.

Keywords: electrochemical properties, cathodic polarization, blue TiO_2 nanotubes, N-doped TiO_2 nanotubes, supercapacitor

1. Introduction

Electrochemical anodization of titanium is one of the best methods to synthesis TiO_2 NTAs due to easily adjust of the characteristics of TiO_2 NTAs like the wall thickness, the tube diameter and length by varying the anodization parameters. Hence TiO_2 NTAs have attracted notable recent attention because of plain fabrication, large specific surface area and highly ordered structures [1-3]. Because of these significant features of TiO_2 NTAs, they have been extensively employed in various applications including supercapacitors [4], lithium/sodium ion batteries [5], solar cells [6], photocatalysts [7] and hydrogen production through water splitting systems [8].