



Red Shift in the Light Absorption Threshold of Anodic TiO₂ Films Induced by Nitrogen Incorporation



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ABSTRACT

Titanium foils were anodized in ammonium containing and ammonium free solutions in order to check the possibility of inducing nitrogen incorporation into anodic TiO₂ films. XPS spectra confirmed the presence of O-Ti-N bonds on the surface of the anodic films prepared in ammonium baborate electrolytes. In order to evidence the effect of nitrogen incorporation on the light absorption threshold, photoelectrochemical behavior of as-anodized and high temperature annealed films as a function of the anodizing electrolyte composition were investigated. A photocurrent tail at energies lower than the mobility gap of TiO₂ appeared for those films prepared in ammonium containing electrolytes which became more evident after thermal treatment. It is suggested that a red shift of the light absorption threshold of titanium oxide occurred due to nitrogen incorporation during film formation.

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1. Introduction

Since the pioneer work of Honda and Fujishima in 1972 on photo-splitting of water by TiO₂ electrodes [1], electrochemistry of titanium oxide has become one of the most interesting subjects for researchers trying to utilize this semiconducting material in several applications such as energy conversion [2,3] and photocatalysis [4,5]. The main drawback of TiO₂ is that its wide band gap (3.0–3.2 eV) only allows a small fraction of sunlight to be absorbed. Efficient use of solar energy needs band gap modification of TiO₂ in order to better respond to the visible part of the solar spectrum. Several strategies have been used to make titanium oxide more photo-responsive. Sensitizing by applying organic dyes on the oxide surface seems to be one of the solutions [2,6] although with some limitations including degradation or detachment of dye from the surface of oxide. A lot of work has been done to modify TiO₂ band gap via changing its electronic structure by incorporating some ions as dopants into the oxide. Early attempts made by transition metals ion doping finally revealed that it sometimes has inferior effect as recombination sites for photogenerated electron-hole pairs [7,8].

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Asahi et al. [9] showed, by calculation of density of states (DOS), that substitutional doping of TiO₂ by non-metals such as F, N, C, S and P in anatase increases its visible light response. Because of more comparable radius size of nitrogen and oxygen ions, nitrogen was considered as the most effective dopant due to the overlap of N2p and O2p orbitals forming some states above TiO₂ valence band and eventually leading to band gap narrowing. Although some authors have shown that nitrogen doping forms localized states above the valence band edge and does not extend the valence band of TiO₂ [10], it has been shown that nitrogen doping increases photoresponse of titanium oxide in the visible spectrum. Accordingly, there have been several reports in the literature trying to show that the absorption edge of titanium oxide can be manipulated by incorporation of non-metals and particularly nitrogen [11–13] using different techniques.

In previous works, it was shown that it is possible to prepare transitional metal oxynitrides via anodizing valve metals such as Nb [14–16] and Ta [17] in ammonium containing aqueous solutions at room temperature. In the present work, we try to study the possibility of nitrogen doped TiO₂ formation via anodization of Ti in ammonium containing aqueous solutions. Photocurrent Spectroscopy (PCS) and X-ray Photoelectron Spectroscopy (XPS) were used to confirm the presence of nitrogen in the films and to study its influence on the enhancement of photocurrent produced under photon energies lower than the absorption threshold of TiO₂.

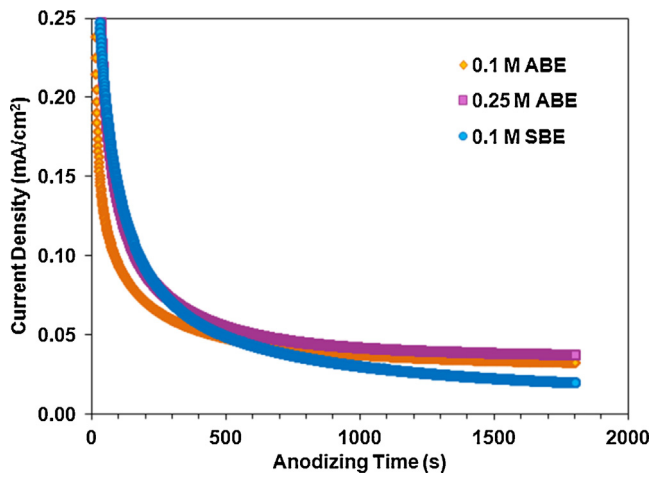


Fig. 1. Current density versus anodizing time for Ti foils polarized for 30 minutes at 5 V in 0.1 and 0.25 M ammonium baborate and 0.1 M sodium borate electrolytes.

2. Experimental

Titanium foils (Aldrich, purity >99.7%) with 0.127 mm thickness were cut into small discs of 11 mm diameter and etched in a mixture

of hydrofluoric acid (39.5%), nitric acid (69.0%) and deionized water (1:1:3 vol.) for 15 seconds, then ultrasonically cleaned in acetone and ethanol for 5 minutes each and finally rinsed with deionized water. Samples were used immediately after being dried in air. To form barrier layers on titanium, 0.1 and 0.25 M ammonium baborate and 0.1 M sodium borate solutions (pH~9) were used as anodization electrolytes. Anodizing was conducted in a three-electrode configuration using a platinum mesh as the cathode and a saturated silver/silver chloride (Ag/AgCl) reference electrode. Potential was applied suddenly and kept constant at 5 V for 30 minutes during anodization. Some of the samples were directly annealed after the anodizing at 450 °C in air for 1 hour to study the effect of high temperature annealing on their photo-electrochemical behaviour. Photo-electrochemical characterizations were conducted in a quartz cell using 0.5 M sulphuric acid electrolyte, a platinum wire counter electrode and a saturated Ag/AgCl reference electrode. The experimental set-up employed for the photo-electrochemical investigations is described elsewhere [18,19]. It consists of a 450 W UV-Vis Xenon lamp coupled with a motorized monochromator (Kratos), which allows monochromatic irradiation of the specimen surface through the electrochemical cell's quartz window. A two-phase lock-in amplifier (EG&G) was used in connection with a mechanical light chopper (frequency: 13 Hz) in order to separate the photocurrent from the total current circulating in the cell. In order to measure photocurrent at visible region a light filter with

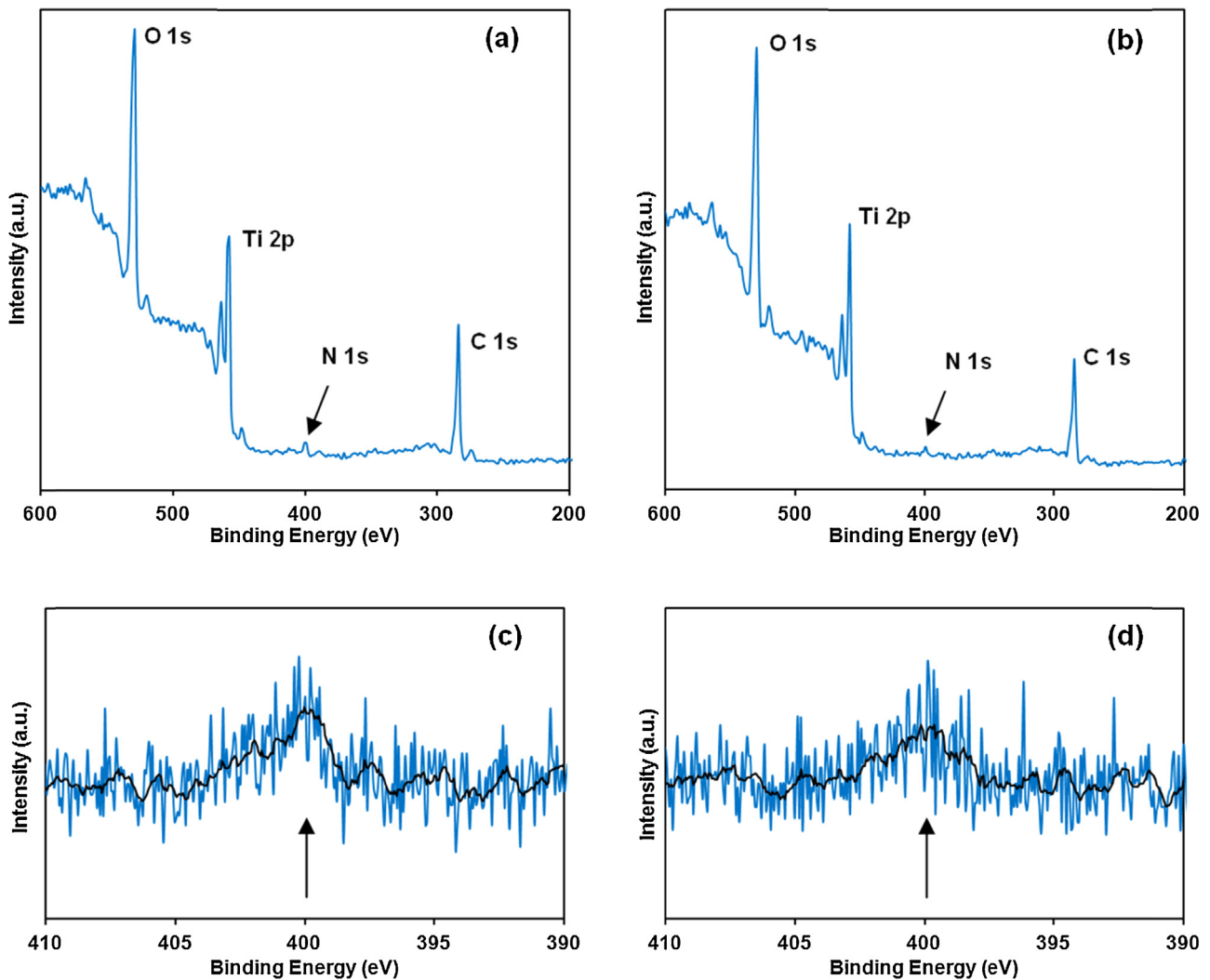


Fig. 2. X-ray photoelectron spectra for films formed in (a) 0.1 M and (b) 0.25 M ammonium baborate. N1s peaks for films formed in (c) 0.1 M and (d) 0.25 M ammonium baborate.

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