International Conference on Renewable Energies and Power Quality (ICREPQ'18)
Salamanca (Spain), 21th to 23th March, 2018
Renewable Energy and Power Quality Journal (RE&PQJ)
ISSN 2172-038 X, No.16 April 2018

Effect of nitridation temperature on TiO_2 nanotubular structure and its photoelectrochemical performance

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Abstract

To improve light absorption in the visible region and to improve photoelectrochemical (PEC) response; herein, we have presented the doping of titanium dioxide (TiO_2) nanotubes with nitrogen. TiO_2 nanotubes have been heat treated under the ammonia environment at different temperatures for 3 h. The characterization was carried out using field emission gun scanning electron microscopy, (FEG-SEM), visible ultraviolet (UV-Vis) spectrophotometry. The photoelectrochemical tests of the samples were carried out in a Na_2S/Na_2SO_3 (aq) solution. It was found that the nitrogen doping of titanium dioxide in temperature above 600 °C collapses the tubular structure and decreases the PEC performance. On the other hand, PEC performance improving was obtained from the sample nitrided at the lower temperatura which is related to the formation of lower defects in the structure of TiO_2 nanotubes.

Key words

Anodizing, Nanotubes, Titanium dioxide, Photoelectrocatalysis, Nitridation

1. Introduction

Increasing environmental problems, limiting fossil resources and geopolitical dependence on oil are enormous challenges for our society. The problems of increasing energy demand and the population growth [1] warrant to develop systems producing renewable energy that is abundant, emission-free and sustainable. In this context, the most interesting way is to convert solar energy to other forms of energy, since the Sun constantly bombards a sufficient energy to sustain society over any foreseeable future [2]. Solar to hydrogen production is a promising way to convert solar energy into hydrogen fuel. It is a clean mechanism that offers great potential to meet clean energy requirements [3]. The use of hydrogen as an energy source can contribute to the balance of the energy matrix and alleviate dependence on polluting energy sources. In photoelectrochemical hydrogen production, an adequate semiconductor is used that is stable and is capable of water splitting reaction. It is necessary to develop materials that exhibit high photo-induced catalytic activity and high surface area, once the photocatalytic reactions occur on the surface of the electrodes [3], [4]. In recent years, the use of nitrogen-doped titanium dioxide (TiO_2) nanotubes have attracted significant technological and scientific interest because of their unique properties, such as large specific surface area, and excellent photoelectrochemical activities.

Titanium dioxide (TiO_2) is a semiconductor with a bandgap of ~ 3.2 eV; therefore, it can only be excited by UV light (wavelength <380 nm). It has been found that N-doping of TiO_2 is a promising approach to improve light absorption and photocatalytic performance [1]. In order to improve its absorption towards the visible light region and to obtain a good photocatalytic performance, it is interesting to dope it with nitrogen. In this way, the oxygen of TiO_2 is replaced by nitrogen, which causes its valence state to be altered by decreasing the bandgap of TiO_2, thereby, increasing the light absorption to the visible region [5], [6], [7].

In this work, we present a study on the doping of titanium dioxide (TiO_2) nanotubes with nitrogen and investigate photoelectrochemical response of titanium dioxide (TiO_2) nanotubes doped with nitrogen by varying the nitridation temperature. The samples were characterized by scanning electron microscopy with field emission gun (FEG-SEM), visible ultraviolet (UV-VIS) spectrophotometry. The Photoelectrochemical measurements are performed in a redox couple of Na_2S/Na_2SO_3.

2. Materials and methods

https://doi.org/10.24084/repqj16.466

A. Preparation and characterizations

To obtain modified crystalline structures the as-anodized amorphous TiO_2 nanotubes [8] were doped with nitrogen, by heat treatment under ammonia environment that was carried out in a muffle furnace (SANCHIS). The nitridation was carried out at 400°, 500° and 600 °C at a flux rate of 100 mL/min of gas mixture (5: 95, NH_3: Ar). The heating and cooling rate of the furnace was fixed to 10 °C / min. In order to obtain the bandgap energy value, UV-Vis diffuse reflectance spectrophotometry was performed using Agilent Cary 5000 spectrophotometer equipped with integrating sphere accessory. The diffused reflectance was transformed to the absrorbtion using Kubelka Munk function [9]. The field emission gun-scanning electron microscopy (FEG-MEV) images were obtained by the microscope MIRA3 by TESCAN operated at 15 kV. Photoelectrochemical behavior was evaluated by linear sweep voltammetry at a sweep rate of 10 mV/s by chopping the incident light in the time interval of 5 sec in dark and under light illumination. TiO_2 nanotubes were used as working electrode, Pt wire as the counter electrode and Ag/AgCl as a reference electrode. These measurements were performed using potentiostat (AUTOLAB, model PGSTAT 100N) in an aqueous solution of 0.35 M de Na_2SO_3 e 0.24 M de Na_2S. The Xe-lamp (Oriel) was used as a light source and the incident light was filtered through AM 1.5G filter and the intensity was calibrated to 100 $mW.cm^{-2}$ (1 Sun) using a photodiode of know responsivity.

3. Results and discussion

Figure 1 displays the FEG-SEM images of the sample before and after the heat treatment at 500 °C under the ammonia gas flux. It can be seen that the top of the tubes before the nitridation process is smooth, however, after nitridation the structure is modified. The top seems rougher. Unlike the literature where nanotubes at 500 °C under air environment does not show any morphological change here we can observe a significant change [10]. This can be related to the modification of the TiO_2 structure. In addition, in the literature for other materials such changes are also observed due to the nitridation process itself and these changes are related to the density difference that occurs due to nitrogen doping and hence material exhibit different density after nitridation as compared to its starting oxide material [10].

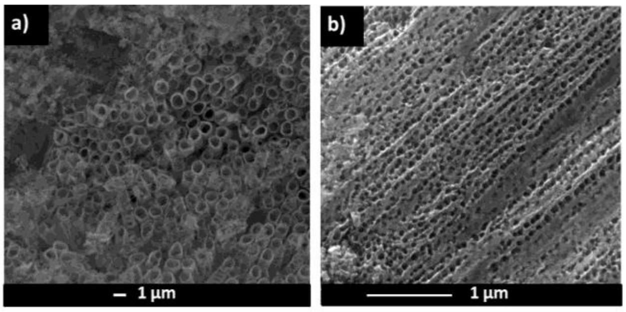

Figure 1: FEG-SEM images of the nanotubes a) before and b) after the heat treatment at 500 °C under de NH_3 environment.

In order to calculate the bandgap and to understand the influence of N-doping on the absorption properties of TiO_2 nanotubes UV-VIS absorbance measurements were performed from the samples doped with nitrogen at different temperatures during the heat treatment in NH_3 atmosphere for 3 h. In figure 2 we can see that the nitridation temperature clearly affects the absorption properties of TiO_2 nanotubes. The sample doped with nitrogen at 500 °C presented higher absorbance in comparison to the other temperatures. Interestingly, the sample doped with nitrogen at 600 °C presented a lower order absorbance along with an abrupt increase in absorption towards lower energy values. These results show that upon increasing the heat treatment temperature, intermediate states are generated in the bandgap of TiO_2. Depending on the position of these states inside the bandgap they may either enhance or decrease the photoelectrochemical performance from these samples [3].

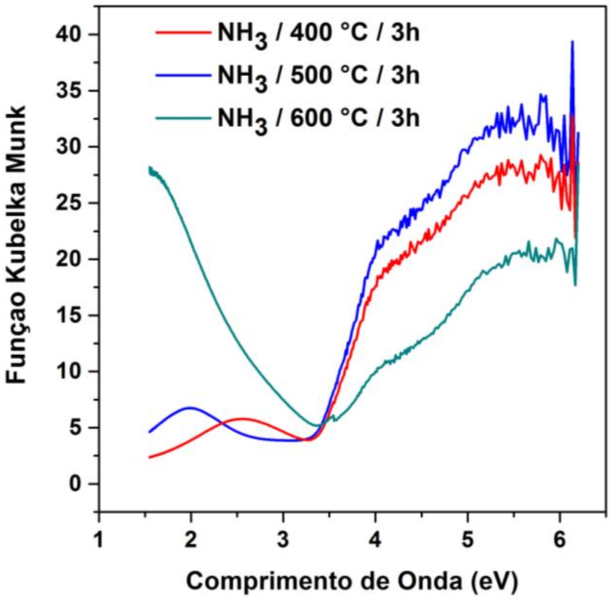

Figure 1: UV-VIS spectra of samples treated under NH_3 atmosphere at different temperatures.

The literature reports TiO_2 requires photon energy of about 3.2 eV to activate it; which corresponds to the UV radiation [11]. We have calculated the bandgap from the UV-Vis spectrophotometry (figure 1) these values are compared in table 1. It can be seen the bandgap values do not change much as compared to the reported values of undoped TiO_2. Based on that we expect that TiO_2 nanotubes possess a rigid structure to dope with nitrogen in the current form of doping.

Table 1: Calculated Bandgap values of the samples treated under NH_3 atmosphere at different temperatures.

Sample	Bandgap (eV)
NH_3 / 400 °C / 3h	3.2
NH_3 / 500 °C / 3h	3.1
NH_3 / 600 °C / 3h	3.3

Figure 2 shows the linear sweep voltammetry (LSV) curves of doped TiO_2 samples at different temperatures under NH_3 atmosphere. To evaluate the light activated response of the samples, the LSV was performed in light incidence and light blocking after every successive five second. It is possible to observe that all the samples present photocurrent response in the presence of light, and when the light is chopped the photocurrent disappears. When irradiating the system with a sufficient photon energy that is equal or greater than the bandgap, the electrons from the conduction band jumps to the valence band of the semiconductor. For N-type semiconductors, the applied biasing is such that these electrons move towards the counter electrode. The holes that are generated in the semiconductor move towards the surface of the semiconductor where they oxidize the nearby species. Since, we are using here the redox couple, that oxidizes before the water oxidation; therefore, in the current study oxygen is not produced. On the other hand, hydrogen is produced on the counter electrode [3], [12].

Hence, the photocurrent produced here is the result of the chemical reaction that occurs on the working electrode and as well as on the counter electrode. Furthermore, figure 3 clearly indicates the influence of the nitridation temperature on the photocurrent response. The lowest performance is obtained from the TiO_2 nanotubes doped with nitrogen, by heat treatment under ammonia environment at 600 °C and it is in accordance to the result obtained in the UV-vis analyses (figure 2)., where the sample heat treated at 600 °C clearly indicates an absorption shoulder at lower photon energies. These results indicate that for photoelectrochemical hydrogen production doping TiO_2 with N at higher temperature creates intermediate bandgap states that act as recombination states for electron-hole pairs. Therefore, we suggest that in order to obtain improved photocurrent TiO_2 should be heat treated under ammonia at low temperature.

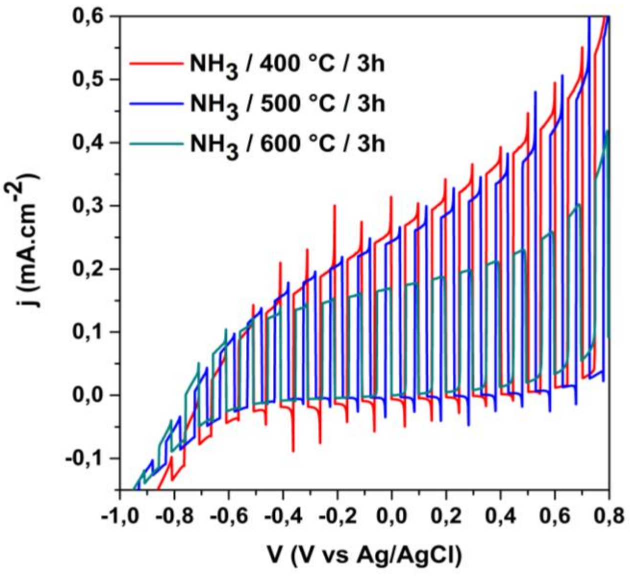

Figure 3: Linear sweep voltammetry curves of N-doped TiO_2 nanotubular electrodes under simulated irradiation (AM 1.5 G, 1 Sun) at a rate of 10 mV/s with an interval of five seconds of light chopping.

4. Conclusion

In this work, we have synthesized TiO_2 nanotubes by anodization process. In order to dope these amorphous nanotubes with nitrogen, we have heat-treated the samples under the ammonia environment. We have found that the heat treatment temperature strongly influence the morphology and the light absorption from TiO_2 nanotubes under ammonia environment, which has a direct effect on the photoelectrochemical performance of the electrodes. Based on the results obtained in the present work it can be concluded that the sample that underwent thermal treatment in ammonia atmosphere at lower temperature is a promising photoelectrode. On the other hand, higher temperature treatment creates intermediate states that act as a recombination centers for photogenerated electron-hole pairs, and hence the photocurrent decreases. Therefore, in order to obtain higher current and lower defects, it is necessary lower heat treatment temperature to dope amorphous TiO_2 nanotubes with nitrogen. TiO_2 nanotubes doped with nitrogen can be applied in dye sensitized solar cells and other titanium dioxide based heterostructures.

Acknowledgement

This work was carried out with the support of CAPES, a Brazilian Government entity focused on Human Resources formation. We also thank PGMAT/UCS, for carrying out the FEG analysis.

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