Improved photoanode structure based on anodic titania nanotube array covered by TiO$_2$-NPs/nanographite composite layer for ETA-cells

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Abstract. This work is devoted to the morphology and electrical properties optimization of flexible photoanodes based on anodic titanium oxide nanotubular arrays (TiO$_2$-NTAs) for solar cells with extremely thin absorbing layer (ETA-cells) by TiO$_2$-nanographite thin composite layer formation on the TiO$_2$-NTAs surface. First, the carbon doped TiO$_2$-NTAs were synthesized by annealing of the as-anodized TiO$_2$-NTAs in argon without foreign carbonaceous precursor. The residual ethylene glycol absorbed on the nanotube wall during anodization serves as the carbon source and the C species are uniformly distributed along the entire nanotube to form the C-TiO$_2$ NTAs. Further decorating of C-TiO$_2$-NTAs surface by TiO$_2$ nanoparticles to form the TiO$_2$-nanographite (NG) composite layer with high conductivity and increased photoanode effective area showed improved ETA-cells performance.

1. Introduction

Due to structural, optical, and chemical properties, anodic titanium oxide nanotubular arrays (TiO$_2$-NTAs) is a promising material for photoanodes in lightweight and flexible dye-sensitized solar cells (DSSCs) and solid-state solar cells with extremely thin absorbing layer (ETA-cells) [1]. However, one of the disadvantages of using titanium dioxide layers in the photoelectric converters is its low electrical conductivity, which reduces the charge carriers collecting efficiency. To reduce the TiO$_2$-NTAs resistance various conductive particles commonly are used to introduce them to TiO$_2$-NT structure. For example, modification TiO$_2$-NTAs with carbon by thermal annealing in acetylene produces TiO$_2$-NT arrays with semimetallic conductivity [2]. But using carbon-containing precursor gases requires high temperatures (600 °C or above) and does not allow obtaining a uniform coating along the tube depth.

Previously, Schmuki and al. [3] has been found that walls of TiO$_2$ nanotubes formed in ethylene glycol based electrolytes have a multilayered structure and one of these layers, located on the TiO$_2$ nanotube inner surface, is saturated by carbonaceous products of electrochemical reactions.

In this paper, we use the presence of the inner layer as a carbon source for its further conversion to covering nanographite ultrafine layer, by heat treatment in an argon atmosphere. Further decoration of
modified TiO$_2$-NTAs surface by TiO$_2$ nanoparticles forms the TiO$_2$-nanographite (NG) composite layer with improved conductivity and increased photoanode effective area.

2. Experiment

2.1. TiO$_2$-NTAs formation

For photoanode structures the TiO$_2$-NTAs were prepared by electrochemical anodization of Ti metal foils in an ammonium fluoride (NH$_4$F) - ethylene glycol (EG) solution. The electrolyte was EG containing 0.3 wt.% NH$_4$F and 2 vol.% H$_2$O. Anodization was performed at 60V for 1 hour. The anodized samples were rinsed in deionized water, dried in air stream, and then annealed for an hour at 500°C in a tube furnace in air ambient (TiO$_2$-NTAs/air) and in Ar atmosphere (TiO$_2$-NTAs/Ar). The morphology, structure, and composition of the samples were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), energy-dispersive x-ray (EDS) and Raman spectroscopy. Processes occurring during samples heat treatment were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Studies carried out at a heating rate of 5°C/min in air and argon streams.

2.2. TiO$_2$-NG composite layer and ETA-cell formation

For the TiO$_2$-NG composite layer formation, annealed TiO$_2$ nanotubes were immersed in 0.2 M TiCl$_4$ solution for 1 hour and then annealed in air at 350°C for 30 min.

For ETA-cell formation, In$_2$S$_3$/In$_x$Pb$_{1-x}$S light absorber layer was deposited on TiO$_2$-NTAs/air and TiO$_2$-NTAs/Ar by SILAR method [4]. First, the substrates were immersed sequentially in the 0.01M InCl$_3$ and 0.01M Na$_2$S*9H$_2$O water solutions for 35 cycles. Then 10 ml of the 0.1M Pb(CH$_3$COO)$_2$ was added to indium chloride solution and additional 15 cycles were done.

After SILAR process the samples were dried in airflow and annealed in air at 130°C for 30 min. On the top of In$_x$Pb$_{1-x}$S absorber layer the CuSCN holes conductor was deposited on heated up to 80°C substrates by impregnation from a 0.05M CuSCN solution in dipropylsulfide. For CuSCN layer deposition, custom-made capillary system with thermo-stabilized table was used to improve the drop contact between solution and the substrates.

Finally, ZnO:Ga transparent conductive electrodes with the thickness of 500 nm were formed on the top of the solar cell structure by magnetron sputtering.

3. Results

3.1. TiO$_2$-NTAs Thermal analysis

By thermogravimetry (TG) and differential scanning calorimetry (DSC) methods it has been found that during obtained structures heating in the air stream, at the temperature range of 300-400°C two exothermic peaks are observed (figure 1a), accompanied by a large loss of weight. At a temperature about 300°C exothermic peak should correspond to oxidation of carbon to CO and CO$_2$ with heat release due to the combustion reaction. Second exothermic peak at 380°C corresponds to crystallization of the amorphous structure of TiO$_2$-NTAs.

On DSC curve for TiO$_2$-NTAs heated in argon stream a sloping hump at the temperature range of 200-300°C and sharp peak near 350°C (figure 1b) are observed. First small low-temperature exothermal
peak arise most probably from dehydration and the small degree of crystallization from anodized hydrated titania to anatase TiO\(_2\) [5] as well as partial decomposition of EG. Larger exothermal peak can be contributed to TiO\(_2\) crystallization, total EG decomposition and graphite phase formation. Observed exothermal peak appeared at temperature lower than at the same experiment but in the air stream due to overheating of the system during combustion reaction. These results are confirmed by obtained Raman and XRD spectra (figure 2).

![Figure 1.](image1.png)

**Figure 1.** (a) DSC and TGA curves for TiO\(_2\)-NTAs heated in air stream; (b) DSC curve for TiO\(_2\)-NTAs heated in argon stream.

### 3.2. Chemical and structural analysis

Phase composition of the samples after thermal post-treatment by XRD showed the strong presence of crystalline phase of anatase type. That has also been confirmed by Raman spectroscopy (figure 2b). However, both methods show the presence of carbon in the graphite phase on samples annealed in argon.

![Figure 2.](image2.png)

**Figure 2.** (a) XRD spectra acquired from TiO\(_2\)-NTAs/air and TiO\(_2\)-NTAs/Ar. (b) Raman shift acquired from TiO\(_2\)-NTAs/air and TiO\(_2\)-NTAs/Ar.

For Raman spectra the peaks positions 393 cm\(^{-1}\), 504 cm\(^{-1}\), 615 cm\(^{-1}\) which correspond to anatase vibronic states were found in both samples. Along with this, in TiO\(_2\)-NTAs/Ar the sample peaks at
1198 cm\(^{-1}\), 1378 cm\(^{-1}\) and 1579 cm\(^{-1}\) appeared. They are attributed to carbon modifications (D and G - lines). Such modes perfectly describe the graphite type compounds and confirmed by peak position 27 (20, deg.) on XRD spectra.

From EDS results (table 1) it can be seen that almost all carbon removed from the TiO\(_2\)-NTA after annealing in air stream. The opposite situation for TiO\(_2\)-NTA annealed in argon atmosphere is observed. In this case, the carbon percentage content is practically unchanged as compared with not annealed sample, what also clearly coincides with other research methods.

| Atomic, %          | C   | O     | F     | Ti   |
|--------------------|-----|-------|-------|------|
| TiO\(_2\)-NTA/as is| 8.18| 45.92 | 10.18 | 35.72|
| TiO\(_2\)-NTAs/air | 1.20| 68.22 | 0     | 30.58|
| TiO\(_2\)-NTAs/Ar  | 15.21| 55.90 | 0     | 28.61|

In addition, TiO\(_2\)-NTAs electrical properties studies have been performed. It has been found that the electrical conductivity of the sample TiO\(_2\)-NTAs/Ar increases more than an order than TiO\(_2\)-NTAs/air that is consistent with the results described in [6].

3.3. Morphology

FE-SEM images of TiO\(_2\)-NTAs annealed in air and argon are presented in figure 3.

![Figure 3. Morphology of TiO\(_2\)-NT layers after thermal post-treatment in different ambient: (a) TiO\(_2\)-NTAs heated in air stream; (b) TiO\(_2\)-NTAs heated in argon stream.](image)

By comparing the titanium oxide nanotubular layers annealed in inert and oxidizing atmospheres strong differences in morphology are observed. Thus, after thermal treatment in argon stream, nanoparticles are observed on the outer and inner titania nanotubes wall surfaces. Presumably these nanoparticles formed from carbon rich layer appeared at inner surface of TiO\(_2\) nanotube walls during the TiO\(_2\)-NTAs formation by anodizing in organic-based electrolytes. In this case, as opposed to
calcination in air stream, carbon not oxidizes to CO$_2$, but constitutes graphite phase nanoparticles at TiO$_2$-NTAs walls surfaces.

3.4. Characterization of the ETA-cells

Test structures of solar cells (ETA-cells) have been formed on the obtained samples and their current-voltage characteristics (CVC) and main electrical characteristics were measured.

CVCs (figure 4) were obtained with custom-made test bench. As the light source Newport solar simulator with irradiation power of light that incident on the sample - 100mW/cm$^2$ was used.

![Figure 4](image-url)  
**Figure 4.** C-V curves of ETA-cells based on TiO$_2$-NTAs with different post treatment procedure (1) TiO$_2$-NTAs; (2) TiO$_2$-NTAs/TiO$_2$-NPs; (3) C-TiO$_2$-NTAs/TiO$_2$-NPs.

Analysis of the CVCs shows that TiO$_2$-NTAs with TiCl$_4$ treatment enhances efficiency of ETA-cell dramatically due to the healing of structural defects occurring during the formation and annealing of TNTs, such as cracks, fractures, nanotubes detached from the substrate, etc. Also, this treatment procedure increases the effective light absorption area by forming TiO$_2$ nanoparticles assemblies on the walls of TiO$_2$-NTs.

At the same time, combining the treatment of the TiO$_2$-NTAs with TiCl$_4$ and the heat treatment in argon atmosphere, which allows to reduce the structure series resistance significantly by increasing the photoanode conductivity due to graphite nanoparticles formation, increases the ETA-cell efficiency in 2 times (table 2) in comparison with ETA-cell with photoanode, which was annealed in air.

| Table 2. Main characteristics of obtained ETA-cells based on TiO$_2$-NTAs with different post treatment procedure |
|---------------------------------------------------------------|
| Structure | $U_{oc}$, V | $J_{sc}$, $\mu$A/cm$^2$ | $\eta$, % | FF, % |
|----------------|---------|-----------------|-------|------|
| TiO$_2$-NTAs   | 0,211   | 116             | 0,06  | 25,5 |
| TiO$_2$-NTAs/TiO$_2$-NPs | 0,371   | 735             | 0,76  | 27,8 |
| C-TiO$_2$-NTAs/TiO$_2$-NPs | 0,547   | 697             | 1,52  | 39,8 |

As a result, ETA-cells based on TiO$_2$-NTAs photoanodes with TiO$_2$-NG composite layer showed improved efficiency compared to solar cells with TiO$_2$-NTAs photoanodes annealed on air.
Conclusions

In the present work a comprehensive comparative analysis of the TiO$_2$-NTAs samples annealed in oxidizing and inert atmospheres was performed. The calcination process features of nanotubular titania containing a carbon-rich layer in different environments were investigated. It is found that carbon located in the body of titanium oxide nanotubes during annealing in an inert atmosphere is not oxidized to carbon dioxide, as in the case of air ambient or other oxidizing atmospheres, but forms crystalline graphite nanoparticles on the inner and outer nanotube wall surfaces. The contribution of the modified photoanode based on TiO$_2$-NTAs with increased conductivity on the solar cells with extremely thin absorbing layer efficiency was rated. Measurements of current-voltage characteristics of the obtained ETA-cell experimental samples showed efficiency increase in two times with carbon doped modified nanocomposite photoelectrode.

Acknowledgments

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