Effect on the optical and structural properties of TiO<sub>2</sub> rutile nanorods by ammonia treatments for direct photoelectrochemical hydrogen production systems

Santiago Ampudia Vásquez
Cristian Fàbrega, Institut de Recerca en Energia de Catalunya (IREC)

Abstract — Titanium dioxide nanorods were successfully grown over conductive substrates via hydrothermal method and subsequently treated through an ammonia annealing process. Compared to pure TiO<sub>2</sub> nanorods, ammonia treated samples exhibited enhanced photoelectrochemical response in both UV and visible region. By means of IPCE and XPS measurements was determined that such an improvement in the UV region was promoted by the introduction of hydroxyl groups on the titania surface.

Index Terms — 5. Nanostructured materials: ammonia treatment, nanorods, titanium dioxide, water splitting

I. INTRODUCTION

HYDROGEN is a carbon-free alternative fuel that avoid non-desirable pollutant sub products and results in total combustion. Fujishima and Honda [1] demonstrated the possibility to get hydrogen fuel by water splitting using a solar-driven titanium dioxide photoelectrode cell (PEC). As alternatives, conventional semiconductors like Si, GaAs, InP, CuInSe an CdS showed impressive efficiencies as PECs but their low stability in water solutions and/or high cost hinders their use for such applications [2].

Titanium dioxide is a wide band gap semiconductor with important applications in photovoltaic [3] and photocatalysis [4]. To date, rutile TiO<sub>2</sub> nanorods synthesized by hydrothermal method have shown the best performance among the reported non-assisted photoanodes for hydrogen production [5] yielding also promising results for dye sensitized solar cells (DSSC’s) [6]. Moreover, rutile TiO<sub>2</sub> nanorods have been considered to be one of the most reliable candidates for scaling lab results up to a prototype level since its synthesis is highly reproducible using low-cost and mass-production methods. However, there is still a big challenge regarding the optimization of electrical, optical and photocatalytic properties of this nanostructured titanium.

One way to overcome the titania limitations is to introduce additives to the surface, going from noble metals through transition metals and different nonmetal anions [7-10]. In the case of noble metals, they presented relatively good performance when were loaded on titania surface, however their cost and availability limits its commercial use. As some simulation studies predicted [11], transition metals have been traditionally considered as the best candidates to improve TiO<sub>2</sub> optical properties. Even so, the main issue with transition metals, as some authors showed, is the affection in their photocatalytic activity [12]. Up to now, the most promising process to improve the efficiency in TiO<sub>2</sub> have been the introduction of nonmetals additives, particularly nitrogen [13, 14]. Notwithstanding the large efforts that have been spent in studying this topic, the origin of such enhancement is still in question. While some authors argued that this improvement lies on the bandgap narrowing caused by the substitution of nitrogen on oxygen sites others consider that vacancy formation inherent to nitrogen doping is responsible of such activity [15, 16].

In this work, we present an hydrothermal synthesis of titanium dioxide nanorods in rutile phase that were subsequently treated through an ammonia annealing process to improve the water splitting performance of the material derived from the increment of the photocatalytic activity of the exposed surface. We determined the optimal working temperature conditions to obtain the maximum efficiency. From Incident photon-to-current efficiency and x-ray photoelectron spectroscopy data, we demonstrated that the ammonia treatment increased the efficiency in the visible part of the spectrum, but above all in the UV range.

II. EXPERIMENTAL SECTION

A. Materials preparation

Titanium oxide nanorods have been grown directly over conductive FTO surface by hydrothermal process [17]. FTO glass pieces (2 x 2cm) were first cleaned in a isopropanol, acetone and water solution (1:1:1) by sonication for 15min, another 15min of sonication with water and finally dried under nitrogen stream. FTO glasses were prepared the very same day of synthesis to avoid any kind of unknown contamination.

The preparation of FTO glass pieces was held by covering 0.5 x 2cm of the FTO surface with Kapton film to avoid nanorods growth over this area and keeping an electrical contact access. These glass pieces were deposited in a Teflon-lined stainless steel autoclave (125ml, Parr Instrument Co.). The chamber was filled with 60ml of HCl 50% and 1ml of...
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titania butoxide (Fluka) as titania precursor, the reactor was heated up at 150°C and was kept to this temperature for 20 hours. The cooling process was performed using a water bath until room temperature. The as-prepared samples were cleaned by sonication in water, dried under nitrogen stream and finally post treated at 400°C for 2 hours to eliminate any chloride present in the nanorods surface [18].

The final treatment of the titania nanorods was carried out using ammonia gas in a tubular furnace at different temperatures (200, 300, 400 and 500°C) for two hours with a ramp temperature of 5°C/min. To control the ammonia-titania interaction during treatment, NH3 flow was cut after the dwell time and was changed to nitrogen flow to prevent any overtreatment of the surfaces during cooling time. The samples were identified as TNR-X, were X correspond to the treatment temperature. One blank sample was used as reference to all characterization analysis.

B. Characterization

TiO2 nanorods morphology was observed with a Zeiss Serie Auriga Field Emission Scanning Electron Microscope (FESEM). Structural characterization was performed in a D8 Advance Bruker X-ray diffraction (XRD) equipment with a Cu Kα radiation source working at 40kV and 40mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI equipment 5500 Multitechnique model with the Al Kα radiation (1486.6 eV). Optical transmission spectra were recorded with a Perkin Elmer UV-Vis-NIR Lambda Spectrometer. The pontentiodinamyc (I-V) behavior was determined with a PARSTAT 2273 (Princeton Applied Research) pontentiotstat in a three reference configuration, using a platinum mesh as a counter electrode and Ag/AgCl as reference electrode. All photoelectrochemical experiments were carried out in a 1M NaOH electrolyte and using a 150W Xenon lamp equipped with AM0 and AM1.5 as light source to conduct. Incident photon-to-current efficiency (IPCE) measurements were conducted under the same experimental conditions of the photoelectrochemical measurements but at 0 V vs Ag/AgCl and using a monochromator as excitation source.

III. RESULTS AND DISCUSSION

A. Morphological and structural properties

TiO2 nanorods arrays were obtained after 20 h of hydrothermal synthesis, with a high degree of density and vertically aligned (fig. 1a). SEM images show tetragonal nanorods in the order of 1-2µm length, 100-200nm width and composed by strongly compacted bundle of smaller squared fibers (fig. 1b). The cross-section SEM image revealed that nanorods were not completely vertical probably because of the roughness of the FTO layer (fig. 1c). Finally and after the oxygen and ammonia annealing treatments, no morphological changes were detected by SEM (not presented here) in any of the samples.

X-ray diffraction (XRD) measurements (fig. 2) revealed that nanorods grown with rutile crystal structure (JCPDS No. 21-1276) with small traces of TiO2 anatase polymorph (JCPDS No. 21-1272). It is worthwhile to note, that there are some missing peaks from the rutile pattern in our XRD spectra confirming that these nanorods growth in a preferential orientation [2]. Furthermore, several SnO2 peaks corresponding to the FTO in the glass substrate (JCPDS No. 41-1445) were detected also in the form of rutile phase, suggesting that the FTO layer acted as seed for the TiO2 nanorod growth and ensuring an almost perfect interphase thanks to the matching of both rutile structures. As a matter of
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the fact, a peculiar and interesting peak no identified appeared between SnO$_2$ and TiO$_2$ (101) peaks that can be attributed to a solid solution of Sn and Ti oxides formed in the interphase of FTO/nanorods. It also could be assigned to the formation of Ti$_2$O$_3$ (JCPDS No. 10-0063) but is less probable than solid solution proposed since the intensity of the measured peak is quite high to detect the substoichiometric titanium dioxide by means, for example, of XPS, which, as discussed below, was not disclosed.

B. Optical and photoelectrochemical properties.

UV-vis evaluation of the samples revealed that transmittance presented an inflexion point around 410 nm which corresponds to an energy bandgap of 3.0 eV (fig. 3a). In the case of the blank (TNR) and TNR-200 we can see that the ammonia treatment did not influence in the final transmittance behaviour. However, for temperature above 300°C, the treatment induced an extension of the absorption to the visible region. When the temperature reached 500°C the absorption was extended across the wavelength spectra in study. From transmittance spectra derivative can be observed a shifting to lower bandgap energies until 400°C and then an increase due to the exceeding ammonia exposure that produce presumable nitration of the TiO$_2$ surface (fig. 3b) [19].

To investigate the effect of ammonia treatment all samples were evaluated by means of PEC measurements [20]. I-V curves within a potential range of -0.9 to 0.5 V vs Ag/AgCl are presented in figure 4a. By analysing these data, it was observed that photo-current densities of the treated nanorods samples were at least two times higher than density of TNR with just an exception in TNR-500 which presented a current density lower than the TNR-200, 300 and 400. The photo-current density of TNR increased with the applied potential and reached a saturated current of 0.32 mA/cm$^2$ at 0.25 V vs Ag/AgCl. On the other hand, TNR-200, TNR-300 and TNR-400 presented a higher slope of the photo-current density and an onset potential of -0.78 V vs Ag/AgCl, and a steady behaviour at a lower potential of -0.37 V vs Ag/AgCl. The negative shift of the saturation potential showed the improvement in the efficiency of charge separation and transportation present in ammonia treated nanorods samples in comparison with TNR sample.

The photoelectrochemical efficiency ($\eta$) of the TiO$_2$ nanorods arrays were calculated as [21]...
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Table 1. Summary of radiation performance of TiO<sub>2</sub> nanorods arrays

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>ɳ(%)</th>
<th>V&lt;sub&gt;max&lt;/sub&gt;(vs Ag/AgCl)</th>
<th>V&lt;sub&gt;OCP&lt;/sub&gt;(vs Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNR</td>
<td>0.19</td>
<td>-0.326</td>
<td>-0.791</td>
</tr>
<tr>
<td>TNR-200</td>
<td>0.46</td>
<td>-0.410</td>
<td>-0.775</td>
</tr>
<tr>
<td>TNR-300</td>
<td>0.47</td>
<td>-0.330</td>
<td>-0.796</td>
</tr>
<tr>
<td>TNR-400</td>
<td>0.47</td>
<td>-0.396</td>
<td>-0.717</td>
</tr>
<tr>
<td>TNR-500</td>
<td>0.24</td>
<td>-0.168</td>
<td>-0.689</td>
</tr>
</tbody>
</table>

\[ \eta(\%) = j_p \left( \frac{E_{rev} - E_{app}}{t_o} \right) \times 100 \]  

(1)

where \( j_p \) is the photocurrent density (\( mA/cm^2 \)), \( E_{rev} \) is the standard reversible potential (\( E_{rev} = 1.23 \) V) and \( E_{app} = E_{meas} - E_{oc} \) is the applied potential (\( E_{meas} \) is the electrode potential vs. Ag/AgCl of the working electrode at which photocurrent was measured under illumination (\( I_o \) in mW/cm<sup>2</sup>) and \( E_{oc} \) is the electrode potential vs. Ag/AgCl of the same working electrode under open circuit conditions, under the same illumination and in the same electrolyte). The efficiency concept evolved reaching more than the double of TNR efficiency (from initial 0.19% to a maximum of 0.47%, see table 1). TNR-500, not only displayed the lowest efficiency among ammonia treated samples but the highest needed voltage to reach the maximum (fig. 4b). This tendency can be attributed to both an increase in the recombination centers on surface and a poor charge separation due to ammonia treatment at temperatures around 500°C. Another important aspect to remark, is the shifting on the open circuit voltage (OCP see table 1) to less negative values. The OCP correspond to the flat band potential condition and so it is related to the situation of the Fermi level in equilibrium with the electrolyte. The observed shifting of the OCP in TNR-500 suggests that Fermi level is further from conduction band than the rest of ammonia treated samples, which implies a lower charge carrier’s density.

To understand the interaction between photoactivity and light absorption of TiO<sub>2</sub> nanorods arrays treated at different temperatures, we have investigated their photoactivity as a function of incident light wavelength. In contrast to photocurrent density obtained under white light illumination, incident-photon-to-current-conversion-efficiency (IPCE) is a better parameter to typify the photovoltaic efficiency because it is possible to discriminate the efficiency as a function of wavelength and is independent from the light sources and filters used in the measurement [22]. The IPCE by definition is calculated from [23]

\[ \text{IPCE} = \frac{I_{\text{photocurrent}}(\text{electrons/cm}^2/s)}{I_{\text{photon}}(\text{photons/cm}^2/s)} \]  

(2)

If the intensity of the monochromatic light (\( I_{\text{photon}} \)) is recorder with a power meter equipped with a thermopile detector or calibrated silicon photodiode, IPCE as a function of \( \lambda \), expressed as a percentage is calculated as [24]

\[ \text{IPCE (\%)} = \frac{1240 \times I_{\text{photocurrent}}(\mu A/cm^2)}{I_{\text{photon}}(\mu W/cm^2)} \times 100 \]  

(3)

All treated samples demonstrated an improvement in the conversion efficiency in the UV range with respect to the TNR IPCE output (fig. 5a). The most outstanding performance can be appreciated on TNR-300 and TNR-400, suggesting that the optimal treatment temperature is around 300-400°C. On the other hand, TNR-500 showed that around this temperature the IPCE output started to decrease around near UV region which confirm the tendency of blue shift on the bandgap observed in UV-Vis spectra. TNR-300 and 400 exhibited an IPCE activity (fig. 5b) in the visible range suggesting that ammonia treatment introduced photocatalytic active intra bandgap levels. In contrast, TNR-500 also showed visible range activity but this intra bandgap levels did not contribute to the photocatalytic activity.

To justify the increment in photocatalytic activity in the UV region some authors had demonstrated that exist a fundamental step previous to the water splitting process,
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Fig 6. High resolution XPS spectra of the O1s region to appreciate the oxygen related contributions and hydroxyls groups behavior with temperature (insert).

consisting in the formation of surface hydroxyls groups which intermediate in the water photo-oxidation reaction. To detect these hydroxyls groups, samples were submitted to an XPS study. Figure 6 presents the high resolution spectra of the O1s region where it can be appreciated at least two contributions, one of them with a binding energy of 529.3 eV attributable to the Ti—O bond. A second contribution is located in a binding energy of 531 eV, usually assigned to surface hydroxyls groups [25]. In fact, by means of deconvolution simulation of the O1s XPS signal was founded a third contribution corresponding to C—O groups around 532.2 eV.

As appreciated in the insert of figure 6, the relative amount of hydroxyl groups increase with temperature treatment reaching a maximum value at 400°C while the oxygen corresponding to the Ti—O bonds decrease. TNR-500 exhibited the same amount of hydroxyl groups as TNR; instead a different kind of surface bonds was established. Effectively, at higher temperatures in ammonia atmosphere has been reported that TiO$_2$ surface presents nitrogen bonds species [13]. The high resolution XPS N1s spectrum (fig 7) presented a strong signal at 400 eV in all samples which is usually attributed to $\gamma$-N state of chemisorbed molecular N$_2$ [19]. However, TNR-500 presented a shoulder around 398 eV which different authors have been assigned either to substitutional nitrogen [26] or TiN [27].

IV. CONCLUSIONS

In summary, TiO$_2$ nanorods were synthesized by hydrothermal method and subsequently treated in temperature controlled ammonia atmosphere to improve water splitting performance. XRD data confirmed that crystal structure was rutile polymorph with preferential orientation. No structural changes were detected after ammonia treatment. The UV-Vis spectra showed an introduction of a new band absorption in the visible region for the ammonia treated samples. PEC measurements exhibited a maximum efficiency of 0.47% for TNR-300 and TNR-400 samples. By means of IPCE was demonstrated that the increment of efficiency of the samples principally came from the increasing performance in the UV range. XPS studies showed that the increment of this performance was produced by the action of the surface hydroxyls groups induced by the ammonia treatment. Finally, an excess on the temperature in ammonia treatment leads to the formation of undesirable recombination centers and nitrogen species which reduced the overall performance.

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