Relation between different crystal orientations and the surface energies in TiO_2-based photoanodes for water splitting: an EBSD microscopy - Raman Spectroscopy study

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Titanium Dioxide (TiO_2) is one of the most studied binary transition metal oxide in the last 40 years. Its nontoxicity, good stability and low production cost have allowed this material to be used in a wide range of applications including conventional areas (such as cosmetics, paintings and sun cream) but also in the development of functional materials including photoelectrochemical cell, photocatalysis, photovoltaic cells, lithium ion batteries and biomedical treatment to name few. In the scope of energy and environment, the control of the TiO_2 phase, size, shape and defects in films has led to very encouraging progresses in this area. However, while the bulk study of powder samples has been intensively done, the development of microscopic techniques is imperative to fully characterise and improve the site specific properties of these TiO_2-based films.[1] In this work, we studied different crystal orientations studies by means of both bulk X-ray diffraction (XRD) and electron backscatter diffraction and the results were compared with Raman spectroscopy. The last technique was used to study surface structures, spatial uniformity and defect formation by means of the intensity ratio between different vibration modes.

A wide range of oriented rutile nanorods were synthesized by hydrothermal synthesis at 150 °C for 12 h in an electric oven. During the synthesis, a piece of FTO glass was placed in the reactor and in order to obtain different crystal orientations, different Ti precursors were used in the presence/absence of additives (HF, H_2O_2 or NaF, Figure 1). After synthesis, the FTO substrate was removed, rinsed extensively with deionized water and allowed to dry in ambient air. Thermal calcination (600 C for 2 h, 5 C/min) was carried out for all the samples and they are identified according to the principal diffraction reflection observed. Crystal, morphological and composition analyses of the resulting films were conducted by XRD, FESEM, Electron Backscatter Diffraction (EBSD) and Raman spectroscopy. Photoelectrochemical (PEC) measurements were carried out in a standard three-electrode configuration using platinum mesh, Ag/AgCl (3.0 M KCl) and the as-prepared samples (counter, reference and working electrodes respectively) using 1 M NaOH as the electrolyte and a Xenon lamp to provide 100 mW/cm^2 illumination, equivalent to 1 sun.

The XRD results are shown in Figure 1 show different preferential orientation of the crystals which could be evidenced by the orientation maps showed below the XRD for each sample in Figure 1. Finally, raman spectroscopy analysis involved the determination of different intensity ratios between the symmetric stretching mode (E_g) and the anti-symmetric bending mode (A_{1g}) for the rutile phase. This ratio is intimately related to the different energies on the surface.[2] It was observed that the films with a higher E_g/A_{1g} intensity ratio had a larger increase in photocurrent efficiency than did the samples with a lower E_g/A_{1g} ratio. This work showcases the combination of different microscopic and spectroscopic techniques in the characterization of TiO_2 photoanodes.

References

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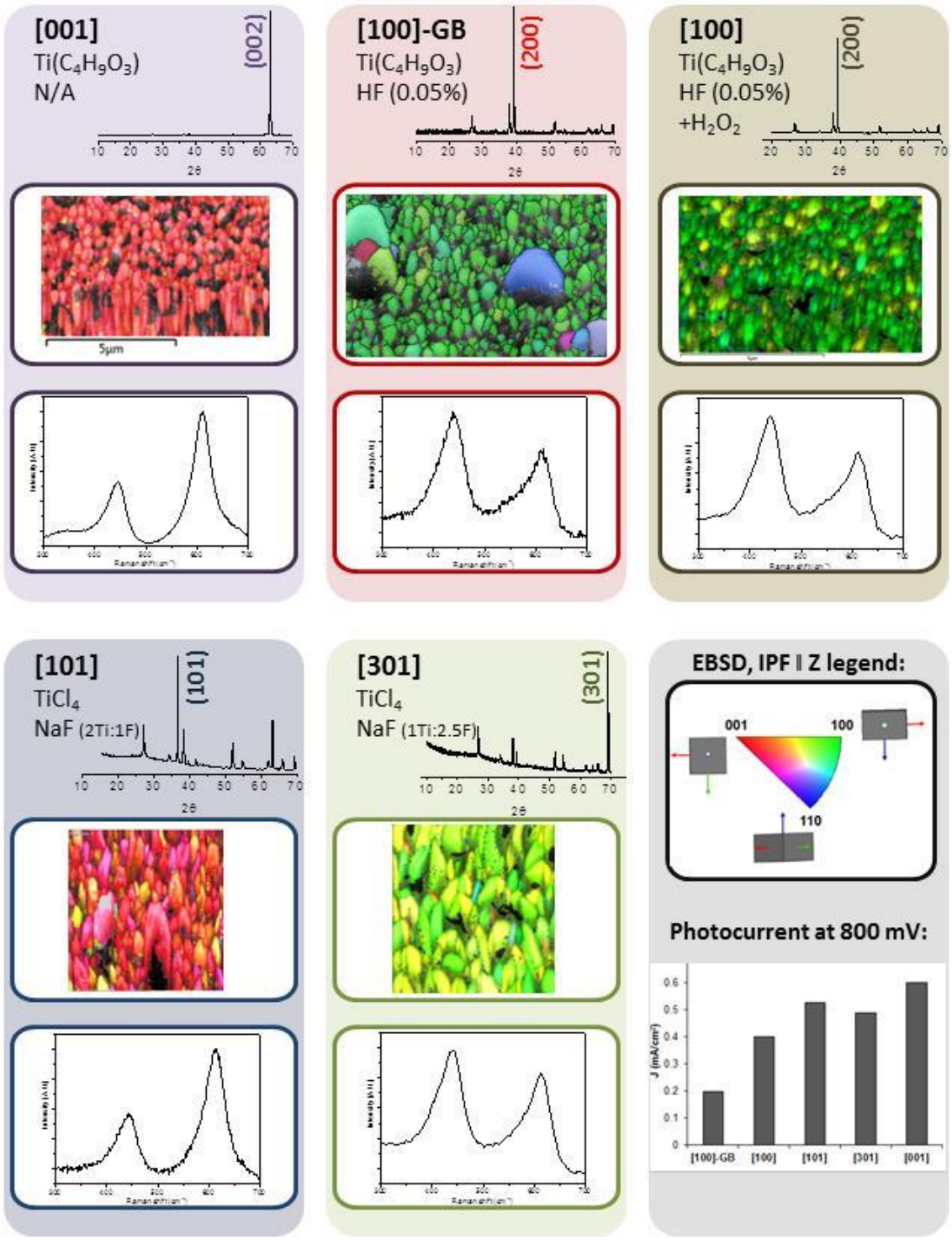

Figure 1. Characterization of rutile TiO_2 photoanodes for water splittings with different crystal orientations: X-ray diffractogram, Orientation map (IPF Z), raman spectra and their photoelectrochemical efficiency determined as the photocurrent measured at 800mV vs Ag/AgCl (3M).