

Advanced Microscopic and Spectroscopic study of the activity of TiO₂ photoanodes for water splitting: A crystal orientation insight

Ballestas Barrientos, A.¹, Li, X.¹, Lee, J.², Yick, S.³, Masters, A.¹ and Maschmeyer, T.¹

¹ Laboratory of Advanced Catalysis for Sustainability, School of Chemistry, University of Sydney, Australia, ² SYDNEY ANALYTICAL – Vibrational Spectroscopy at The University of Sydney, Australia, ³ CSIRO Manufacturing, P.O. Box 218, Lindfield, NSW 2070, Australia

Titania (TiO₂) has proved to function as an effective catalyst for the photoelectrochemical evolution of H₂ as well as for the treatment of polluted air and water. However, the functional application of TiO₂ is strongly influenced not only by the presence of different polymorphs, but also by the orientation of supported crystals and the different facets of TiO₂ crystals that are exposed.¹ This work showcases the application of crystal and facet engineering combined with a set of characterization techniques (Electron Backscatter Diffraction or EBSD, site-specific HRTEM and Raman microscopy) to provide otherwise unobtainable insights in the development of materials for photoelectrochemical driven water splitting. Among the techniques used, EBSD was employed in conjunction with site-specific FIB-SEM/HRTEM in order to determine the different crystal orientations present in each film. Moreover, the surface energy across the surface of the films was mapped by means of Raman microscopy, confirming the formation the crystal defects with different orientations and higher surface energies. These results were also analyzed in the light of the photoelectrochemical (PEC) activity for water splitting measured using Electrochemical Impedance Spectroscopy (EIS).

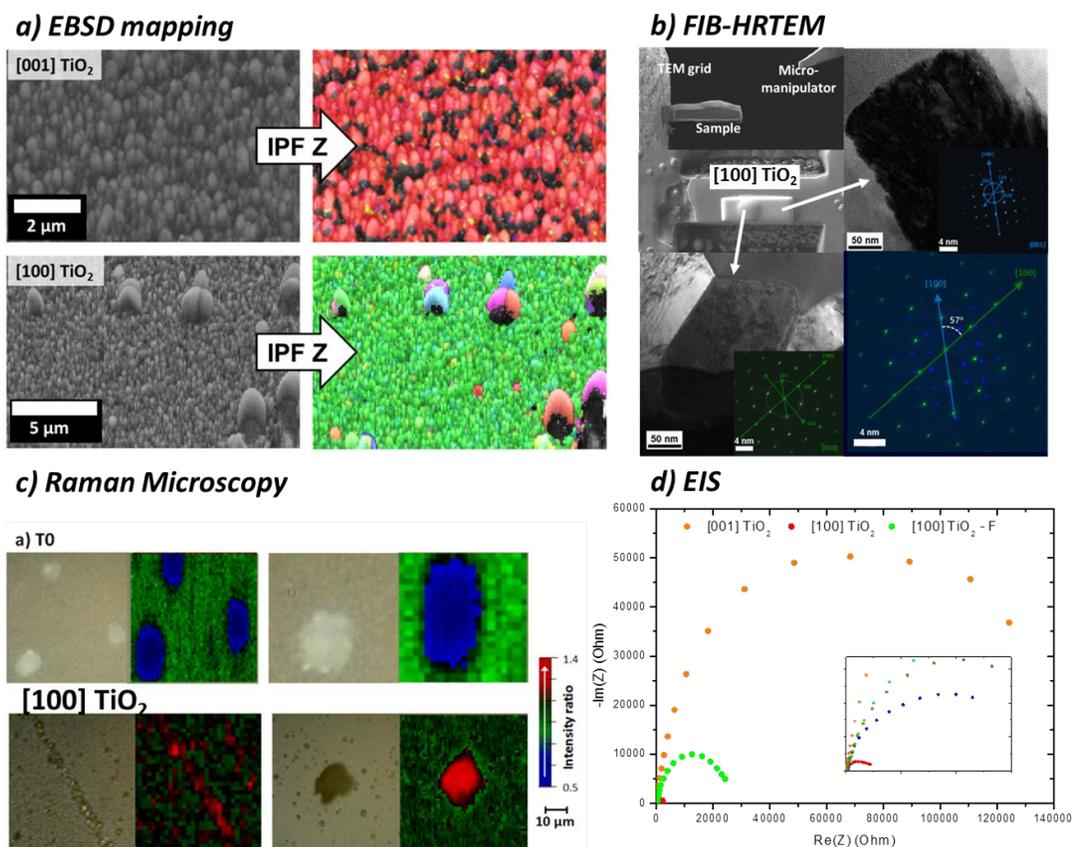


Figure 1. Orientation map (Inverse Pole Figure parallel to the Z axis, IPF \parallel Z, a), FIB-SEM/HRTEM (b), raman spectroscopy (c) and photoelectrochemical study (Nyquist plot, d) of rutile TiO₂-based photoanodes consisting of nanorods with two different crystal orientations namely, the [001] nanorod array and the newly synthesized [100] nanorod array.

TiO₂ films were hydrothermally deposited on FTO glass using titanium(IV) butoxide as a starting material in the presence of a fixed amount of a 1:1 HCl:H₂O solution and different amounts of aqueous HF, the mixture was then heated at 150 C for 12 h in a Teflon-lined autoclave under autogenous pressure. In the absence of HF, [001] oriented rutile TiO₂ nanorods were preferentially obtained. By adjusting the concentration of HF, the formation of [100] oriented rutile TiO₂ nanorod arrays was achieved for the first time, as confirmed by EBSD and HRTEM (Figure 1a and 1b respectively). Further Electrochemical Impedance Spectroscopy (EIS, Figure 1d) and Raman Microscopy (Figure 1c) study demonstrated that, contrary to the anatase phase, the presence of F-ions does not have a detrimental effect on the photoelectrochemical activity of Rutile TiO₂. Additionally, silver nanoparticles (Ag NPs) were photodeposited on the films with different TiO₂ crystal orientations. These films were then characterised using SEM, EBSD (Figure 2a) revealing that the Ag NPs were present at the grain boundaries of the TiO₂. The photoelectrochemical efficiency (Figure 2b) of the Ag - TiO₂ films were tested and compared with a highly oriented Ag - TiO₂ polycrystalline film that possessed negligible index of crystal boundary defects. No detectable enhancement of the PEC activity was observed after Ag NPs deposition on highly oriented TiO₂ films, whereas the photocurrent increased 50 % after Ag NPs photodeposition on the TiO₂ films with high indices of crystal boundary defects. These results, in conjunction with the microscopic study, suggest that Ag NPs photodeposited on grain boundaries and at high energy facets improve the interaction between these noble metal nanoparticles and the TiO₂ polycrystalline film.

Conclusions

The synthesis of rutile TiO₂ crystals on an FTO substrate was performed using HF at very low concentration as a directing agent. Their characterization using microscopic techniques allowed us to determine their different crystal orientations and to detect the presence of crystal defects with different surface energies. These results translated into their individual photoelectrochemical activities and their further enhancement using photodeposited Ag particles, that showed a strong dependence on which crystal facets were exposed.

References

¹*Chem. Rev.* 2014, 114, 9559–9612

Acknowledgements

The authors acknowledge the facilities and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Australian Centre for Microscopy & Microanalysis at the University of Sydney. We also thank the Sydney Analytical of the University of Sydney and the Commonwealth Scientific and Industrial Research Organization (CSIRO). A.R.B.-B. also thanks the Australian Government Department of Education and Training for an Endeavour International Postgraduate Research Scholarship under the Grantee ID 4448_2015.

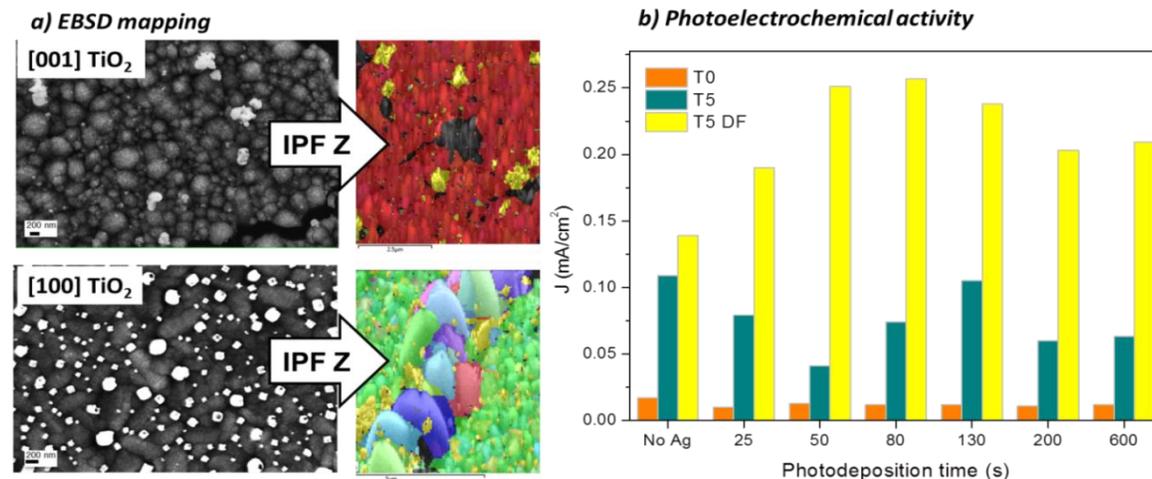


Figure 2. Orientation map (IPF || Z, a) obtained for TiO₂ samples after photodeposition of silver particles and their corresponding photocurrents (b) measured at 800 mV vs Ag/AgCl (3.0 M)