Order of Magnitude Increase in Photocatalytic Rate for Hierarchically Porous Anatase Thin Films Synthesized from Zinc Titanate Coatings

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ABSTRACT: In this paper we report on the use of aerosol assisted chemical vapor deposition (AACVD) to form thin films of the zinc titanate phases using zinc acetate and titanium isopropoxide as precursors in methanol solution. Analysis by XRD and XPS found that through variation in experimental conditions we have been able to synthesize films of zinc titanate with composition of Zn_2TiO_4 or $Zn_{0.3}Ti_{2.7}O_{4.94}$, which adopt the spinel and pseudobrookite structure respectively. In addition, we have also formed hybrid films of Zn_2TiO_4 with either $ZnTiO_3$ or ZnO. Using a technique previously reported with powders, the mixed ZnO and Zn_2TiO_4 films were treated with acid to produce porous Zn_2TiO_4 which, through reduction and vapor leeching of zinc, were converted to hierarchically porous thin films of anatase TiO_2. This conversion was monitored by XRD. Analysis of photocatalytic activity of the hierarchically porous titania, using dye and stearic acid degradation tests, found a factor of 12 to 14 increase in rates of photocatalysis over conventional TiO_2 thin films. Finally we are able to report a maximum formal quantum efficiency for stearic acid degradation of 1.76×10^{-3} molecules per photon.

SUPPORTING INFORMATION

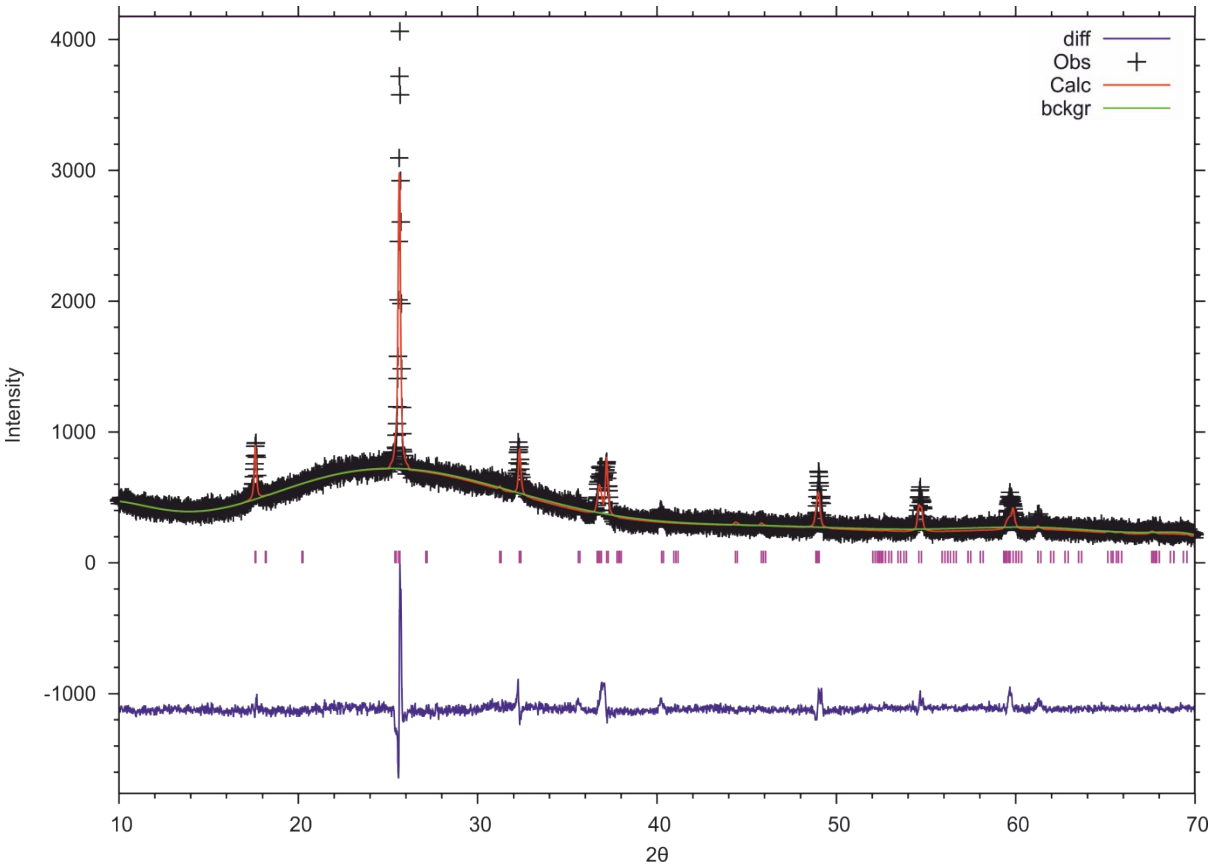


Figure S1. X-ray diffraction pattern and Rietveld fit taken from the front spot of the 1:1 film. Tick marks indicate the position of the peaks for pseudobrookite structured zinc titanate.

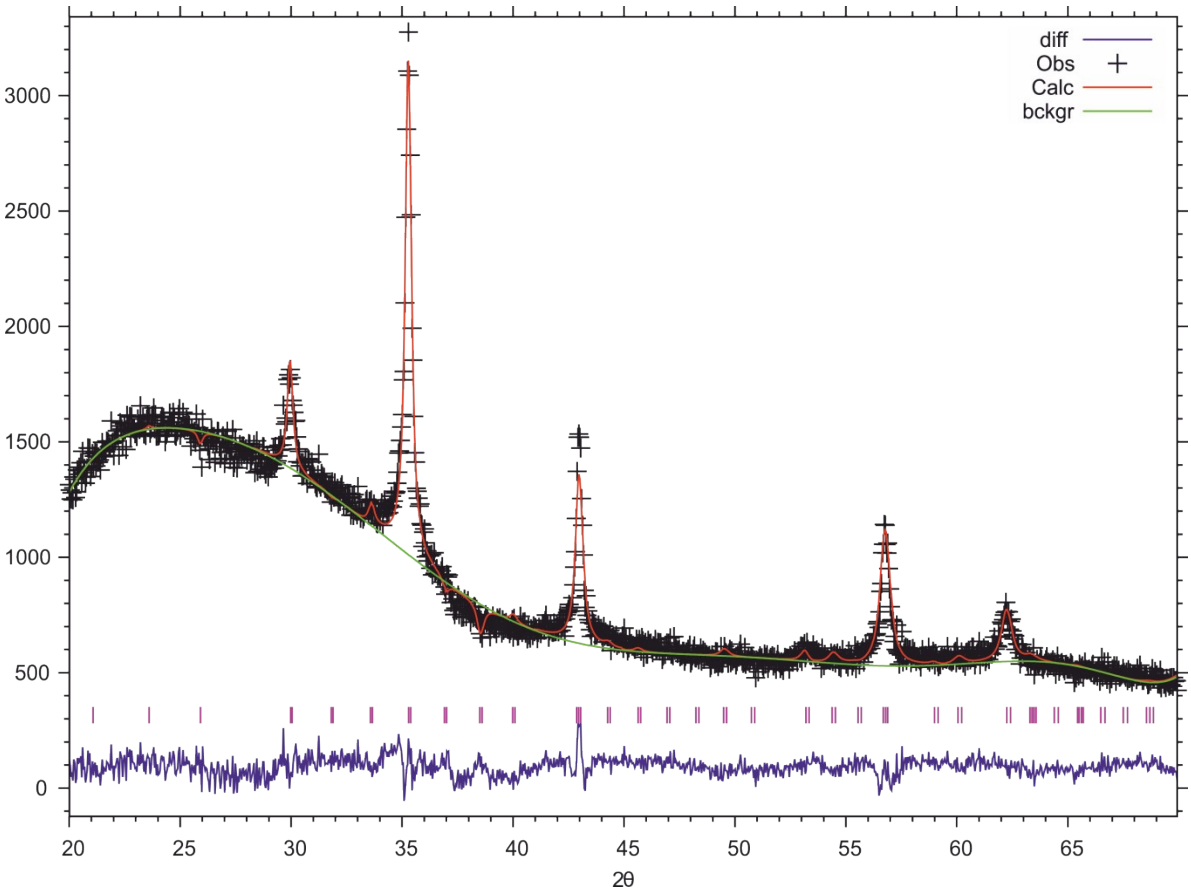


Figure S2. X-ray diffraction pattern and Rietveld fit taken from the rear spot of the 1:1 film. Tick marks indicate the position of the peaks for tetragonal Zn_2TiO_4.

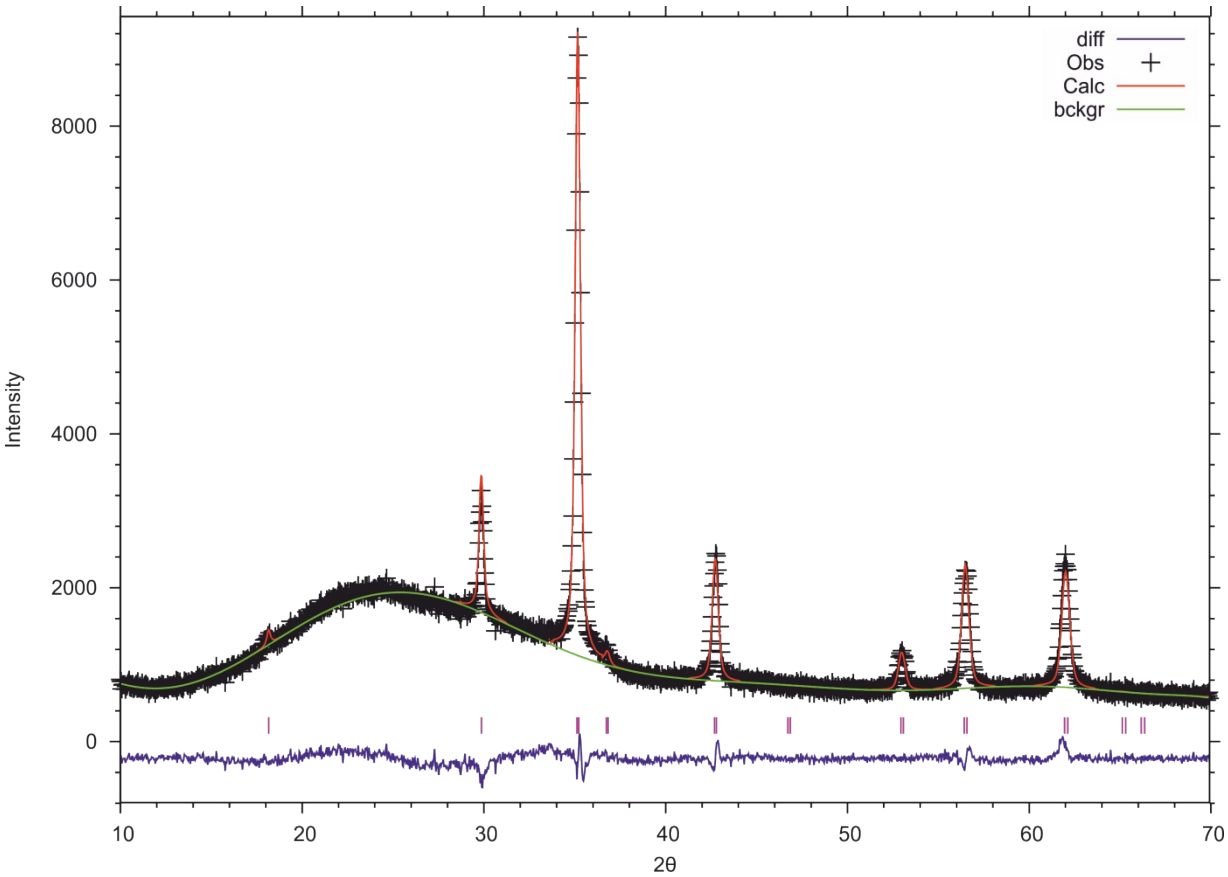


Figure S3. X-ray diffraction pattern and Rietveld fit taken from the front spot of the 2:1 film. Tick marks indicate the position of the peaks for cubic Zn_2TiO_4.

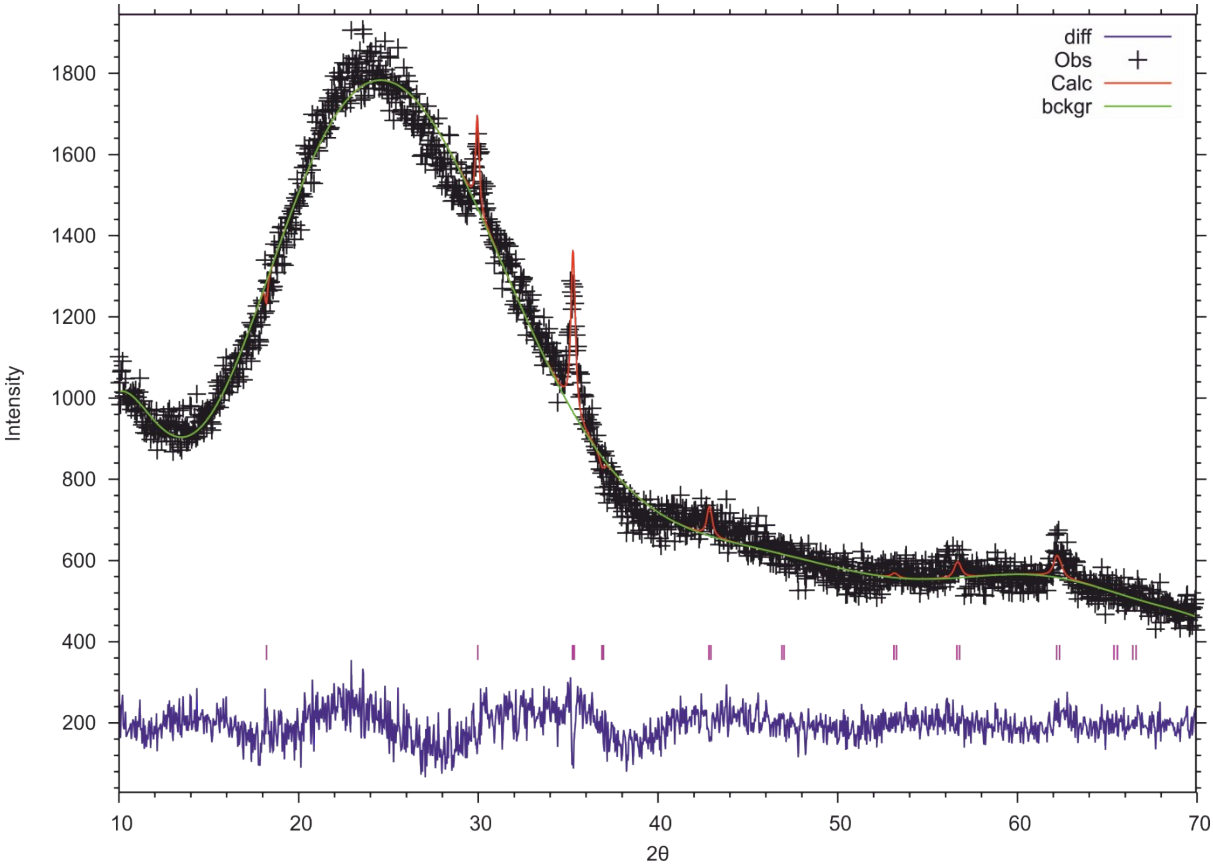


Figure S4. X-ray diffraction pattern and Rietveld fit taken from the rear spot of the 2:1 film. Tick marks indicate the position of the peaks for cubic Zn_2TiO_4.

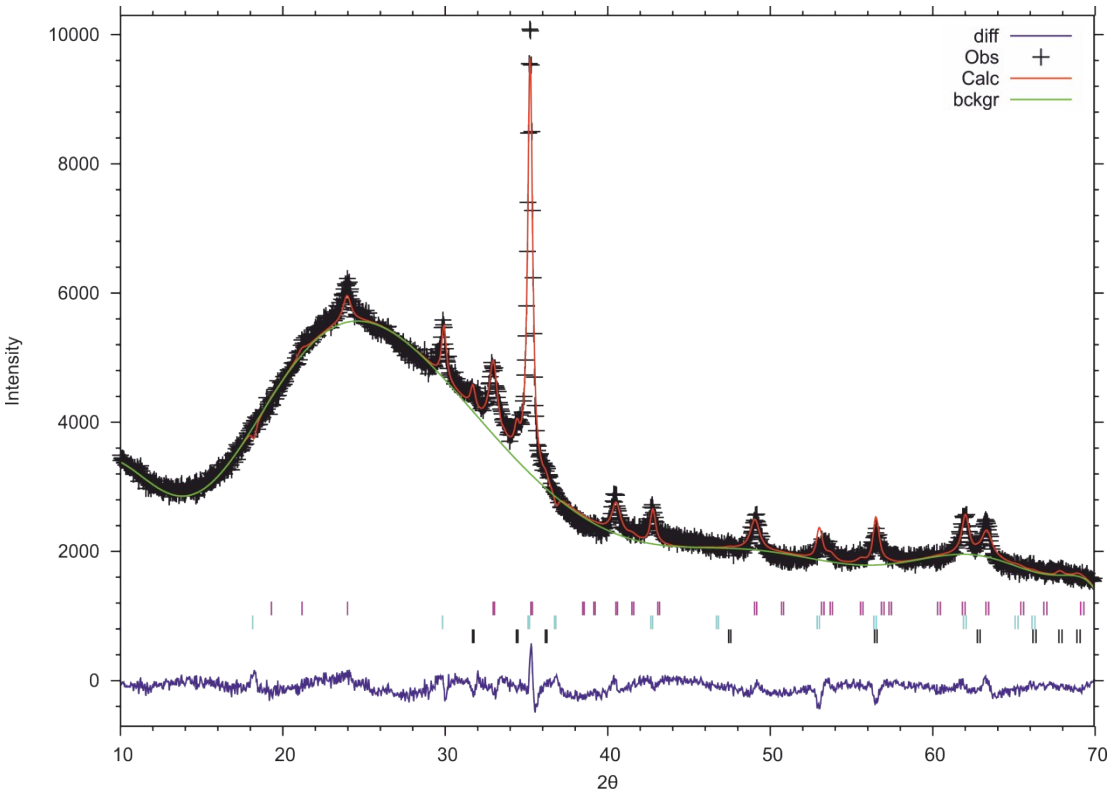


Figure S5. X-ray diffraction pattern and Rietveld fit taken from the front spot of the 3:1 film. The top (pink) tick marks indicate the position of the peaks for $ZnTiO_3$, the middle (cyan) tick marks indicate the position of peaks for cubic Zn_2TiO_4, while the lowest (black) tick marks represent the position of peaks for ZnO.

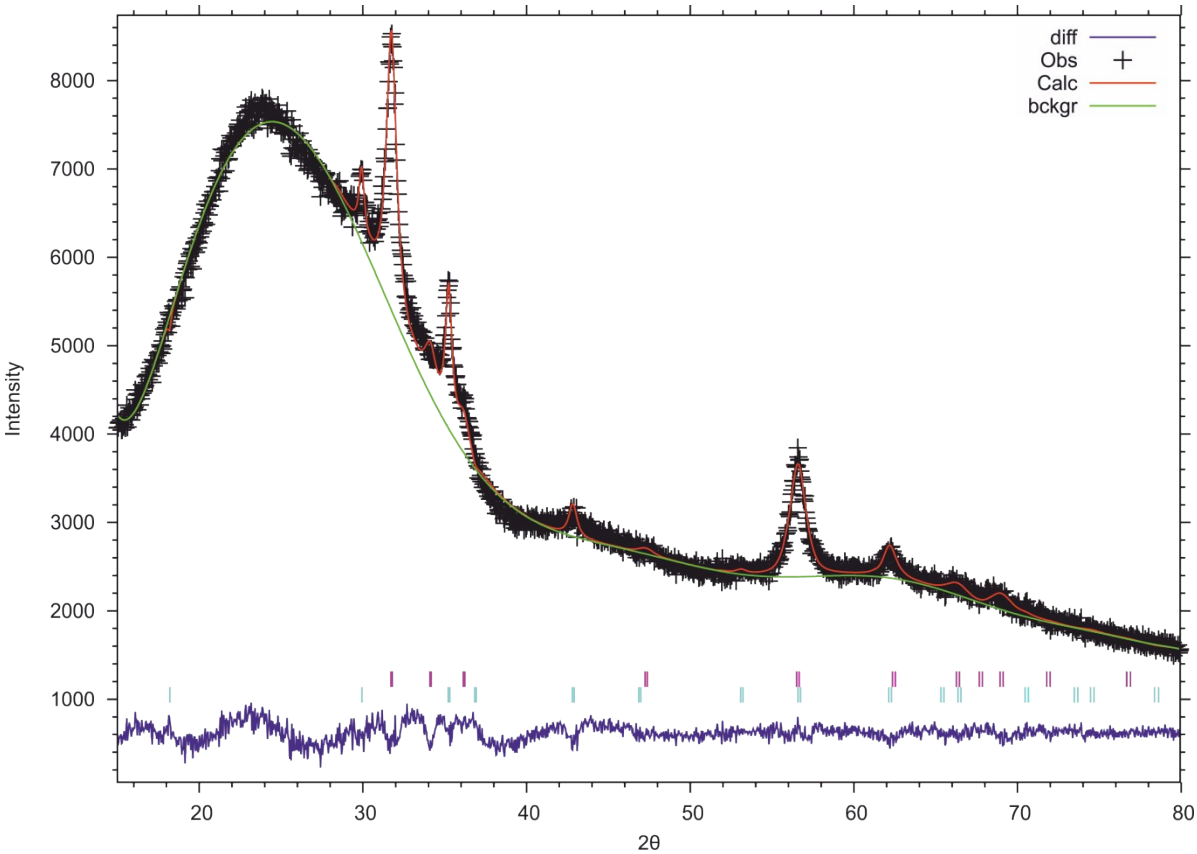


Figure S6. X-ray diffraction pattern and Rietveld fit taken from the rear spot of the 3:1 film.

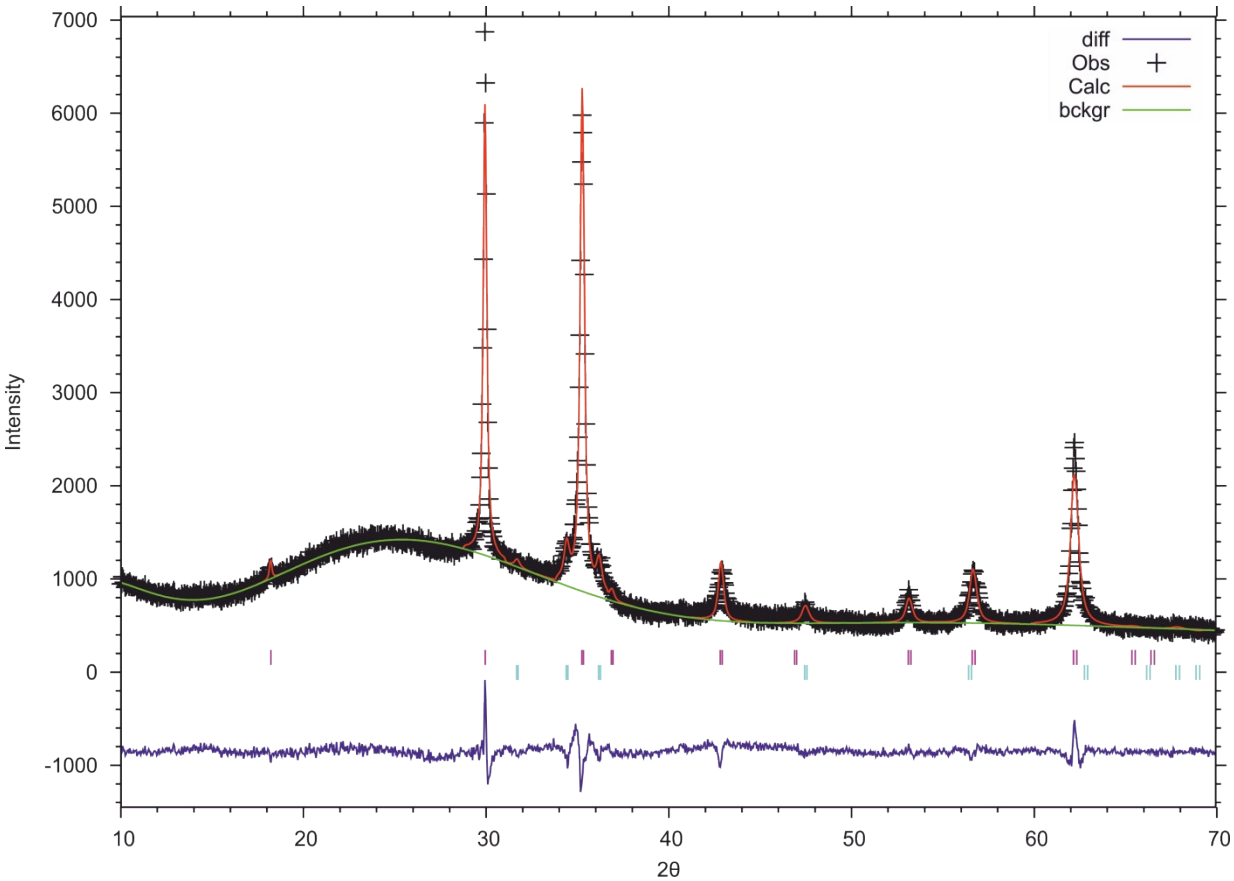


Figure S7. X-ray diffraction pattern and Rietveld fit taken from the front spot of the 4:1 film. The top (pink) tick marks indicate the peaks for cubic Zn_2TiO_4, while the lower (cyan) tick marks are for ZnO.

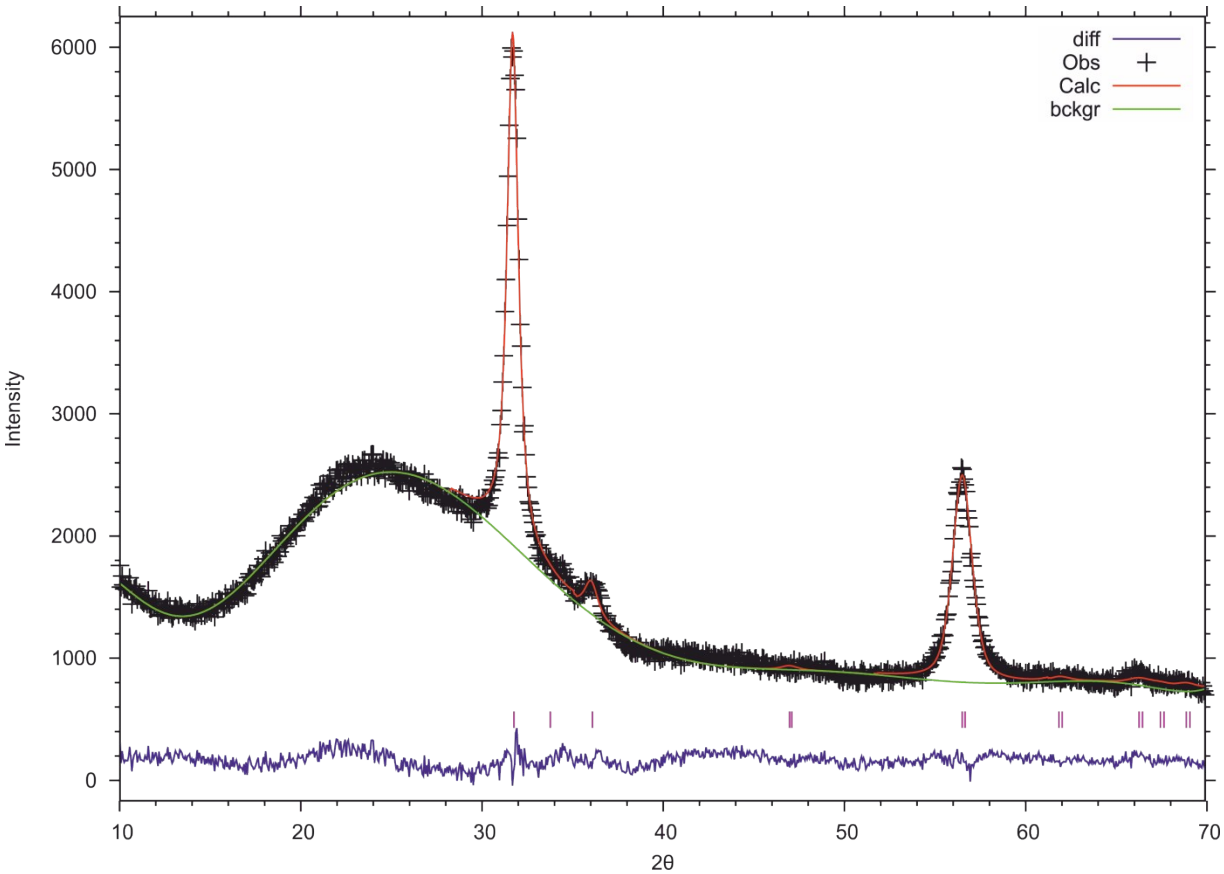


Figure S8. X-ray diffraction pattern and Rietveld fit taken from the rear spot of the 4:1 film. Tick marks indicate the position of the peaks for ZnO.

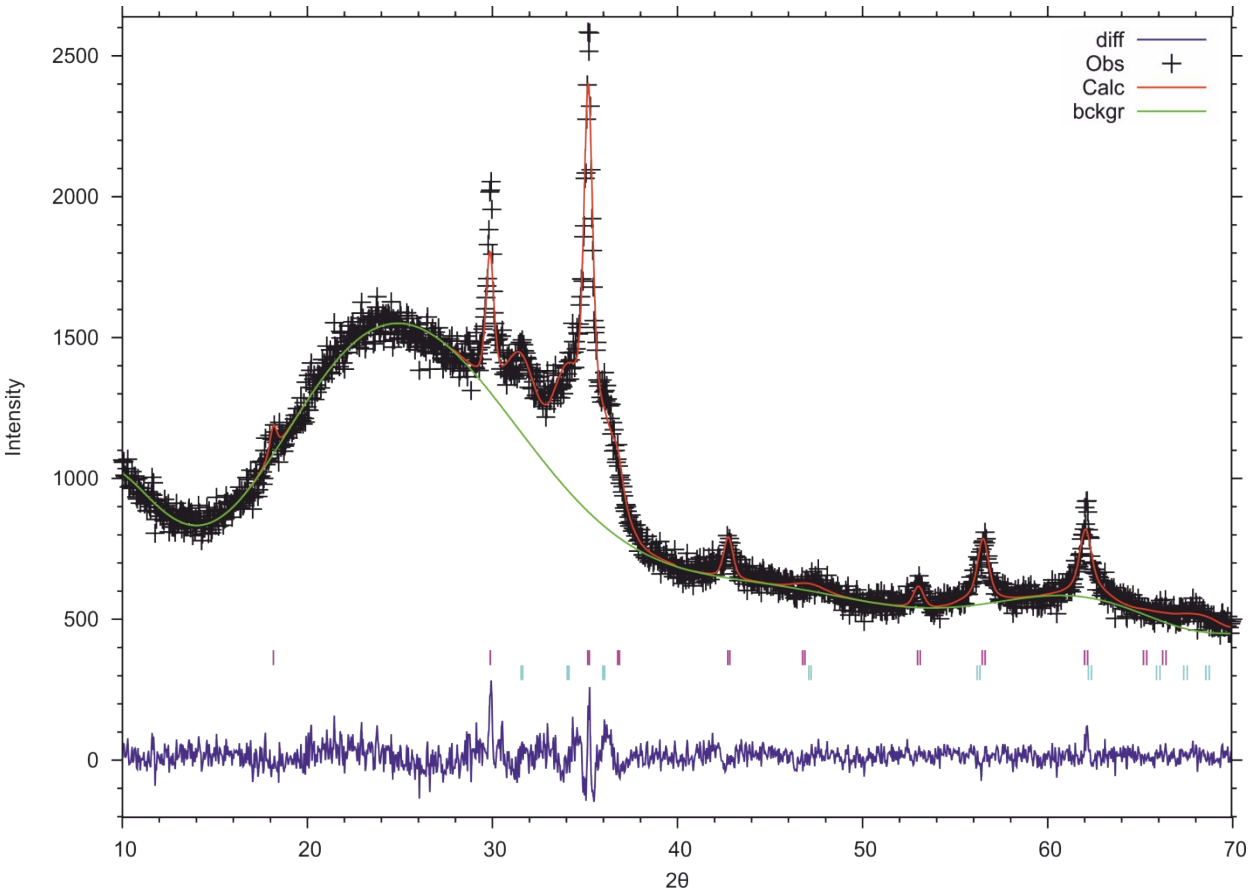


Figure S9. X-ray diffraction pattern and Rietveld fit taken from thefront spot of the 5:1 film. The top (pink) tick marks indicate the peaks for cubic Zn_2TiO_4, while the lower (cyan) tick marks are for ZnO.

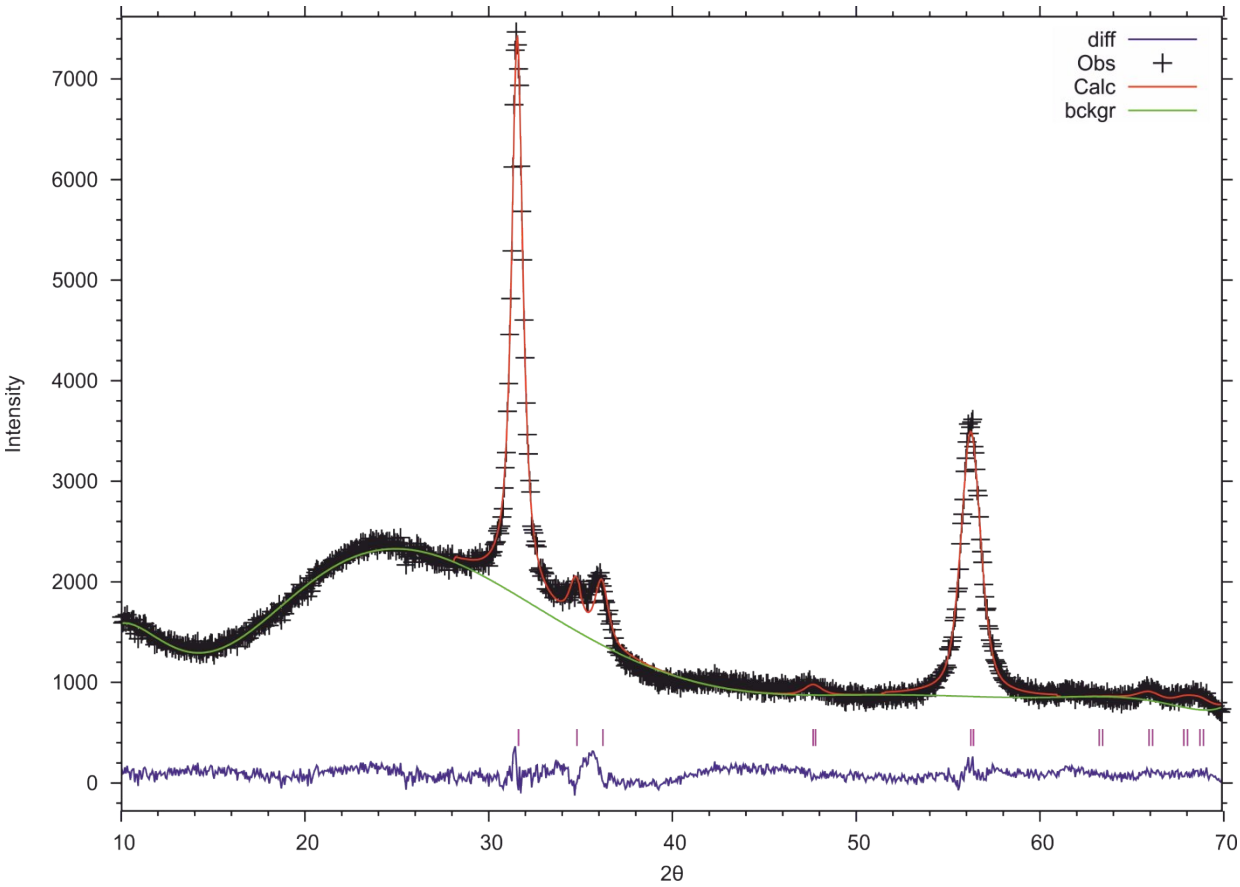


Figure S10. X-ray diffraction pattern and Rietveld fit taken from the rear spot of the 5:1 film. Tick marks indicate the position of the peaks for ZnO.

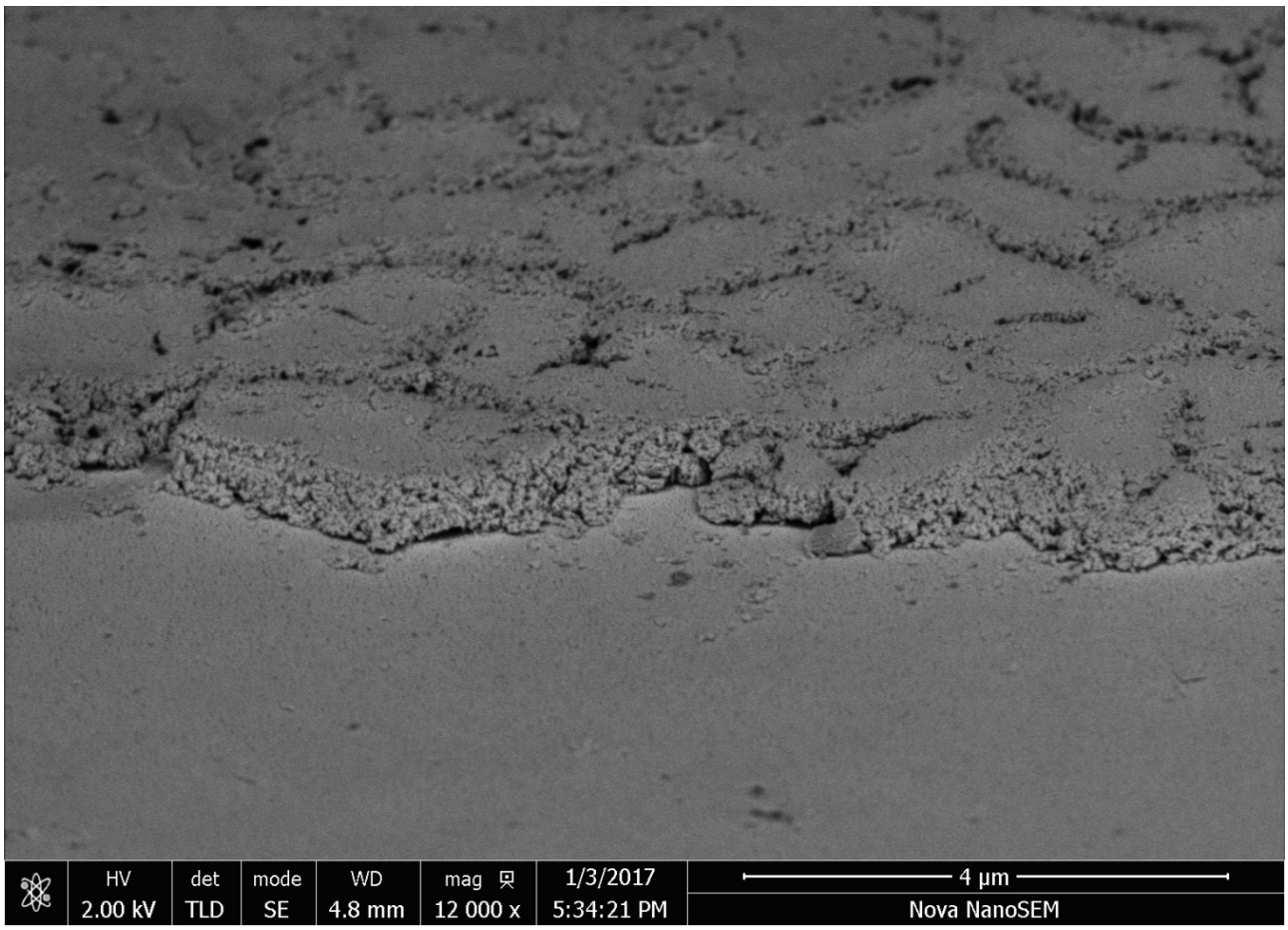
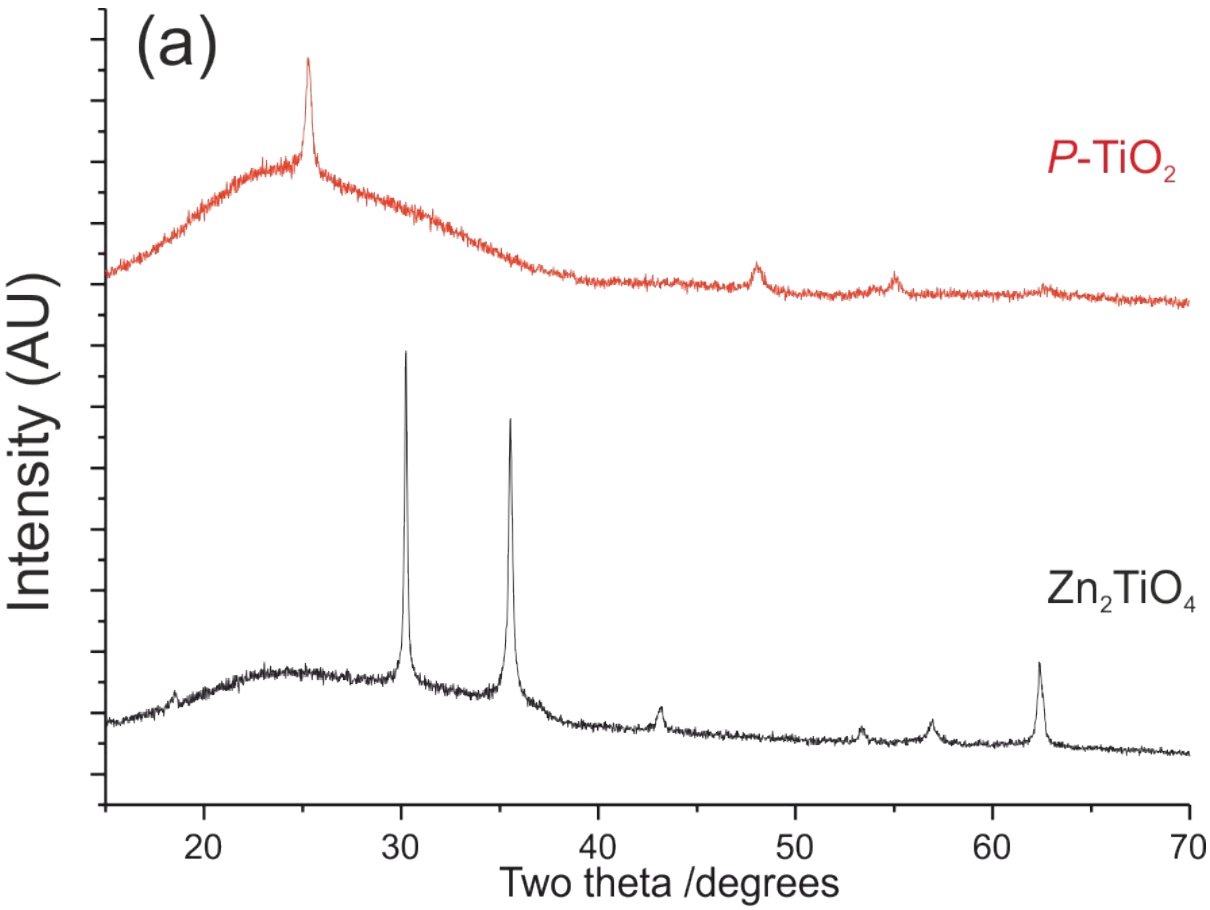


Figure S11. Side-on, or cross-section SEM image of the hierarchically porous *HP*-TiO_2 sample, showing porous structure is found across the depth of the film.



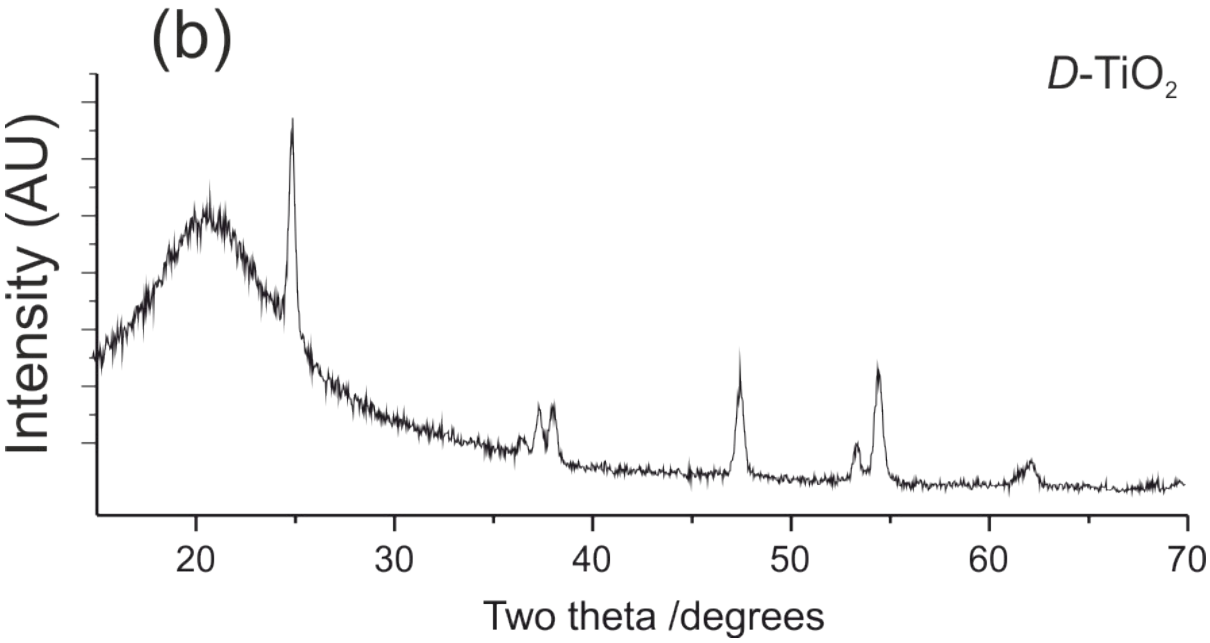


Figure S12. (a) X-ray diffraction pattern of the Zn2TiO4 film, and after conversion through H_2/N_2 reduction to the porous titania sample, *P*-TiO_2. (b) The XRD pattern of the as-made dense titania film, *D*-TiO_2