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 $\text{Zn}_2\text{TiO}_4$ or $\text{Zn}_{0.3}\text{Ti}_{2.7}\text{O}_{4.94}$, which adopt the spinel and pseudobrookite structure respectively. In addition, we have also formed hybrid films of $\text{Zn}_2\text{TiO}_4$ with either $\text{ZnTiO}_3$ or $\text{ZnO}$. Using a technique previously reported with powders, the mixed $\text{ZnO}$ and $\text{Zn}_2\text{TiO}_4$ films were treated with acid to produce porous $\text{Zn}_2\text{TiO}_4$ which, through reduction and vapor leaching of zinc, were converted to hierarchically porous thin films of anatase $\text{TiO}_2$. 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 $\text{TiO}_2$ thin films. Finally we are able to report a maximum formal quantum efficiency for stearic acid degradation of $1.76 \times 10^{-3}$ 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$_2$TiO$_4$. 
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$_2$TiO$_4$.

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$_2$TiO$_4$. 
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$_2$TiO$_4$, 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$_2$TiO$_4$, 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 the front spot of the 5:1 film. The top (pink) tick marks indicate the peaks for cubic Zn$_2$TiO$_4$, 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 Zn$_2$TiO$_4$ 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$_2$. 