Supporting Information for

Pore Orientation Effects on the Kinetics of Mesostructure Loss in Surfactant Templated Titania Thin Films

Saikat Das^a, Suraj Nagpure^a, Ravinder K. Garlapalli^a, Qingliu Wu^b, Syed Z. Islam^a, Joseph Strzalka^c, Stephen E. Rankin^{a,*}

^a Chemical & Materials Engineering Department, University of Kentucky, Lexington, KY ^b Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL ^c Advanced Photon Source, Argonne National Laboratory, Argonne, IL

* Author to whom correspondence should be addressed. E-mail: <u>srankin@engr.uky.edu</u>. Tel: +1-859-257-9799



Figure S1. Comparison between predicted and experimental d-spacing values for the proposed indexing of titania thin films (60 nm thick) on unmodified substrate after aging (Fig. 2a) using a combination of parallel rectangular symmetry (C2mm) and orthogonal hexagonal symmetry.



Figure S2. GISAXS patterns of titania thin films (60 nm thick) on (a) unmodified and (b) modified substrate at room temperature (22.5 °C) before being calcined at 500 °C with a 40 °C/min ramp rate.



Figure S3. 1D line cut of the in-plane (100) diffraction peak for titania thin films (60 nm thick) on both unmodified and modified substrates derived by integrating the GISAXS patterns of Fig. S2 along the q_z direction from 0.05-0.06 Å⁻¹.



Figure S4. GISAXS patterns of titania thin films (60 nm thick) on (a) unmodified substrate just after reaching a final calcination temperature of 550 °C with a 40 °C/min ramp rate, (b) unmodified substrate after heating at 40 °C/min to 550 °C and holding at that temperature for 60 min, (c) modified substrate just after reaching final calcination temperature of 550 °C with a 40 °C/min ramp rate and (d) modified substrate after heating at 40 °C/min to 550 °C and holding at that temperature for 60 min. (c) modified substrate just after reaching final calcination temperature of 550 °C with a 40 °C/min ramp rate and (d) modified substrate after heating at 40 °C/min to 550 °C and holding at that temperature for 60 min. All the samples were aged at 4 °C for 2 h before calcination. The films are oriented horizontally (in the xy plane) relative to the incident beam for this experiment. As is evident from the patterns, no significant change in the intensity of the diffraction spots was seen after holding the titania films for 60 minutes for titania films on either unmodified or modified substrate.



Figure S5. GIWAXS pattern of titania thin films (60 nm thick) on (a) unmodified substrate and (b) modified substrate after calcination at 600 °C with a 40 °C/min ramp rate and holding at that final temperature for 60 minutes.



Figure S6. Normalized (100) diffraction peak height measured from line cuts of GISAXS patterns over q_z values from 0.06-0.07 Å⁻¹ from *in situ* GISXAS data of titania thins films during isothermal treatment at 550 °C after heating at a ramp of 40 °C/min.



Figure S7. Plot to determine *k* parameter using the integrated Avrami equation with n = 0.89 for titania thin films (250 nm thick) on P123 modified substrate during calcination at 400 °C.



Figure S8. Plot to determine *n* and *k* parameters of the Avrami equation at different ramp rates to reach a final calcination temperature of 500 °C. These titania thin films were 250 nm thick films and prepared on P123 modified substrates.