Electronic Supplementary Information (ESI)

Vertically Oriented Hexagonal Mesoporous Zirconia Thin Films by Block Copolymer Templating

Annamária Mikó, A. Levent Demirel and Mehmet Somer*

Chemistry Department, Koç University, Rumelifeneri Yolu, Sariyer 34450, İstanbul, Turkey

Materials and Methods. Block copolymer templating and evaporation induced self assembly were used to synthesize mesoporous zirconia. Polyethylene oxide based block copolymer Pluronic F127 (Pluronic F127 (poly(ethylene oxide)$_{106}$–poly(propylene oxide)$_{70}$–poly(ethylene oxide)$_{106}$, $PEO_{106}PPO_{70}PEO_{106}$) was purchased from Sigma-Aldrich. The polymer had average molecular weight of 12500 gmol^{-1}. Zirconium(IV) oxychloride octahydrate was used as the inorganic precursor and was obtained from Riedel-de Haën in analytical reagent grade. The solutions were prepared in mixture of ethanol and double deionized water at 40-90 volume % of water. Pluronic F127 was first dissolved in ethanol. Zirconium salt was then added to the solution and finally the water was introduced to the system. The final concentration of Pluronic F127 was 0.2-50 mgml^{-1} and that of zirconium salt was 0.25 M. The films were spin coated on silica, glass or gold coated glass substrates at 40-60 % relative humidity at 20-35 ^{o}C. Spin coating was done at rotation speed of 2000 rpm for 120 s using Specialty Coating System, INC. spin coater. Spin coated films had thicknesses less than 200 nm. Thicker films (thickness ~500 nm or more) were solvent casted on 16 cm^2 quartz substrate at 40-60 % relative humidity at 20-35 ^{o}C. The post treatment of the hybrid samples took place in a humidity controlled chamber for 3-5 minutes at 21-35 ^{o}C. The samples were then aged at 50 % relative humidity for 5-10 days at 21-35 ^{o}C. **Figure S1** shows the process steps and the required conditions for each step to obtain vertically oriented hexagonal mesoporous zirconia thin films.

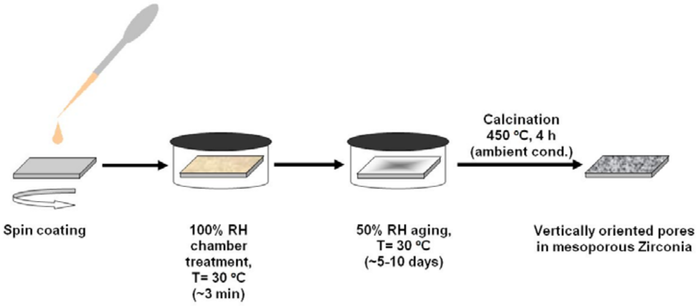

Figure S1. The process steps and the required conditions for the preparation of vertically oriented hexagonal mesoporous zirconia thin films.

The as prepared and calcined films were characterized by NT-MDT Solver P47 atomic force microscope in tapping mode using ultrasharp silicon cantilevers (force constant 48 Nm^{-1}). The AFM images were analyzed with the software Nova 1.0.26 RC1. The transmittance measurements were conducted by T80 + UV/VIS Spectrometer (PG Instruments Ltd.) in the wavelength range 1000-200 nm. The X-ray diffraction measurements were conducted using

Hubert G9670 powder diffraction equipment with germanium monochromator and CuK$_\alpha$ radiation. GISAXS measurements were done by Bruker D8 Discover XRD^2 using IμS CuK$_\alpha$ source, vertical goniometer, Huber centric Eulerian cradle, parallel beam Montel mirror and VANTEC 500 2D detector at 0.4° incident angle and 300 s data collection time. Zeiss Ultra plus field emission microscope was used for scanning electron microscopy (SEM) analysis.

Equilibration of the film morphology with water vapour. The hybrid phase films immediately after coating had poor optical transparency which improved upon water vapour treatment. **Figure S2** shows the transmittance in the wavelength range of 200-1000 nm for an as-prepared solvent cast film of ~500 nm thickness and the same film after ~3 min water vapour treatment followed by vacuum drying for 2 hours at 30 °C. The transmittance increased from 27 % to 95 % upon water vapour treatment and stayed nearly constant above the wavelength of 260 nm. The decrease in transmittance below 260 nm for both spectra is due to the absorption of $ZrOCl_2 \cdot 8H_2O$ at 199 nm. The slowly aged films were stable and maintained their transparency even after keeping at room temperature for more than 2 months.

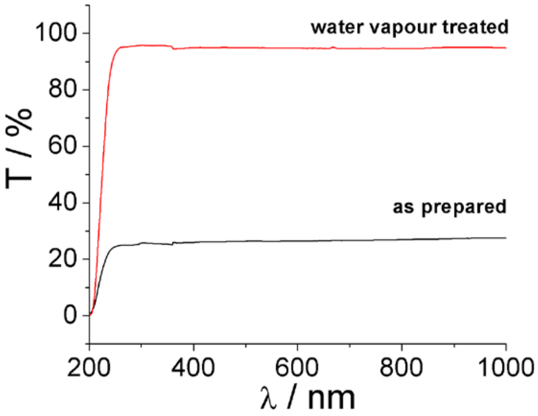

Figure S2. UV-Visible spectra of as-prepared and water vapour treated hybrid phase films after vacuum drying at 30 °C for 2 hours. Film thickness was ~500 nm.

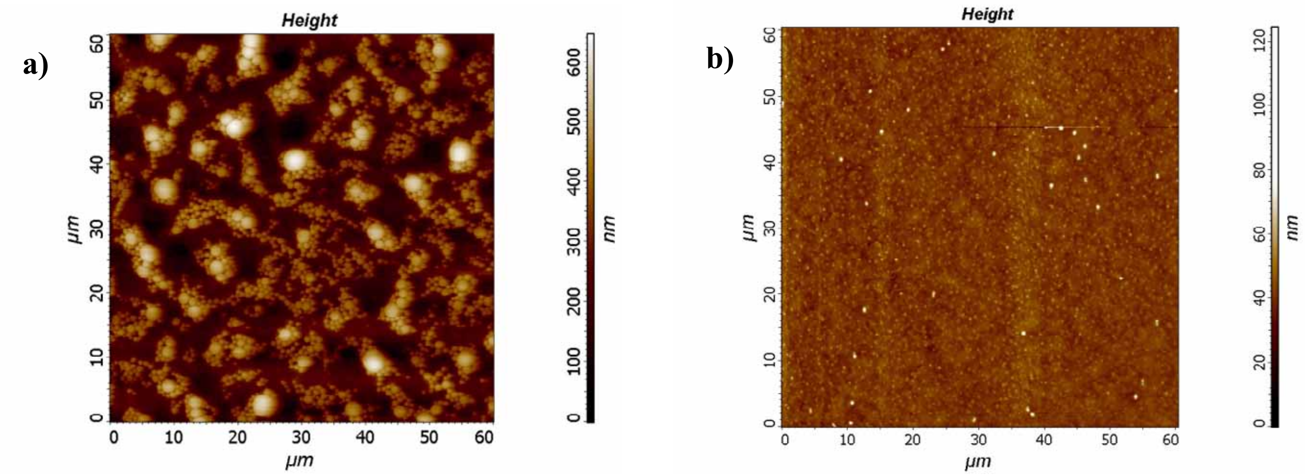

Figure S3. AFM height images of ~150 nm thick spin coated hybrid phase films (a) as-prepared, (b) after ~3 min water vapour treatment at 30 °C.

The effect of water vapour treatment on the surface morphology of the films has been observed by Atomic Force Microscopy (AFM) measurements. **Figure S3** shows 60 µm x 60 µm area height images of ~150 nm thick spin coated hybrid phase film before (**Figure S3a**) and after (**Figure S3b**) water vapour treatment at 30 °C. The as-prepared film had disordered surface morphology and exhibited rms surface roughness of ~350 nm. Water vapour treatment smoothened out the film surface and resulted in an rms surface roughness of ~42 nm.

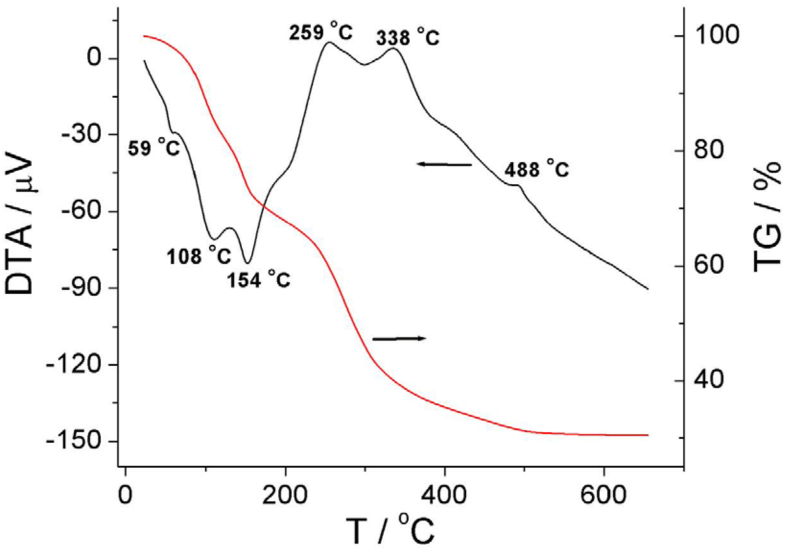

Figure S4. Differential thermal analysis and thermogravimetric analysis data of the hybrid mesophase. The heating rate was 10 °Cmin^{-1}, the measurements were conducted at 200 mlmin^{-1} synthetic air flow. As the temperature was increased from 25 °C up, three endothermic peaks were first observed in the DTA/TG curves. The first event corresponds to the melting of the polymer at ~59 °C and did not cause significant changes in the thermogravimetric data. The second (~108 °C) and the third (~154 °C) endothermic process caused ~35% mass loss which was due to the removal of the water from inorganic salt and of the adsorbed water from the mesophase. Increasing the temperature further resulted in three exothermic peaks. The two broad peaks at ~259 °C and ~338 °C with a total mass loss of ~40% correspond to the decomposition of the polymer to CO and CO_2. The small peak at ~488 °C, without any mass loss, can be attributed to the change of the amorphous structure to crystalline zirconium oxide.

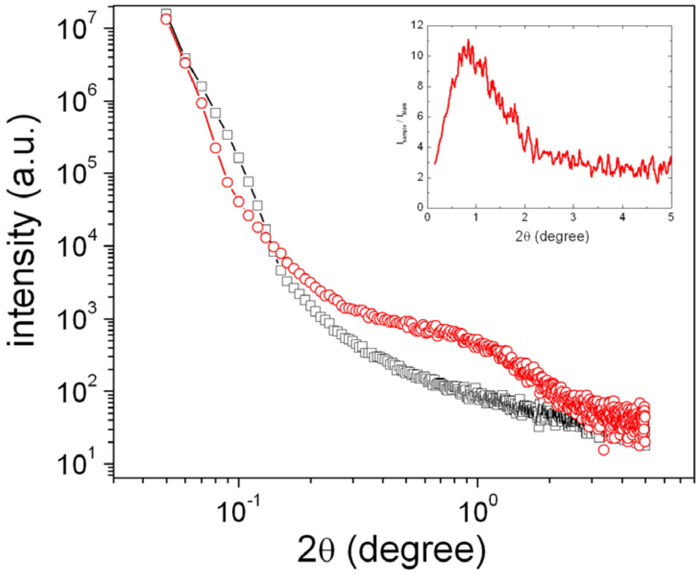

Figure S5 (a). SAXS data of the bulk mesoporous ZrO_2 powder (circles) together with the reference data of a blank capillary (squares). The inset shows the ratio of the intensities. The SAXS peak seen at $2\theta = 0.84^o$ corresponds to d = 10.5 nm.

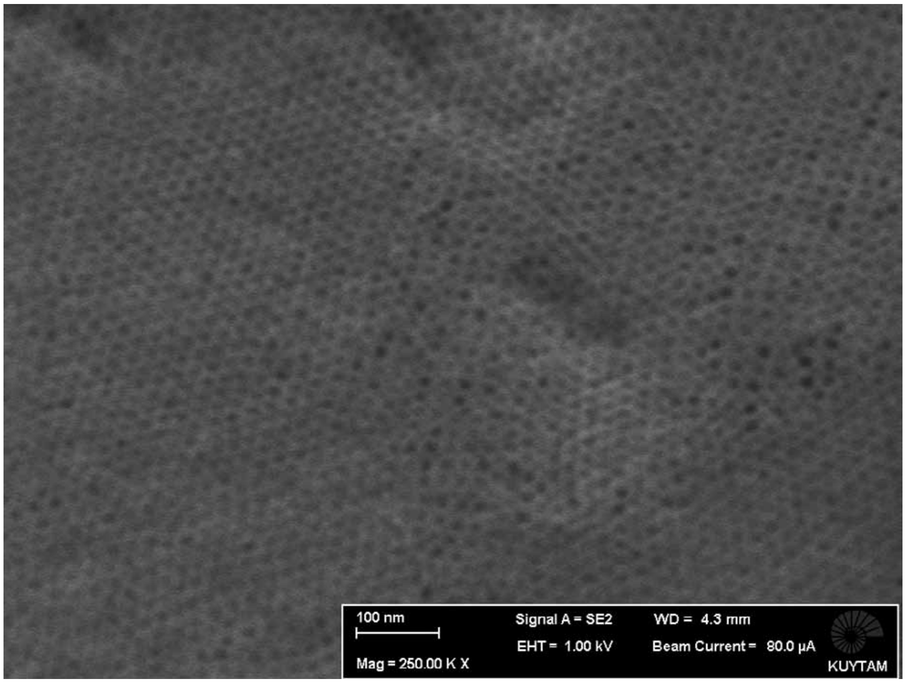

Figure S5 (b). SEM image of the top surface of a ZrO_2 film (air/film interface) prepared at $T_a \sim T_{wvt} \sim T_{aging} \sim 32\ ^oC$. The average pore diameter has been measured as ~10 nm.

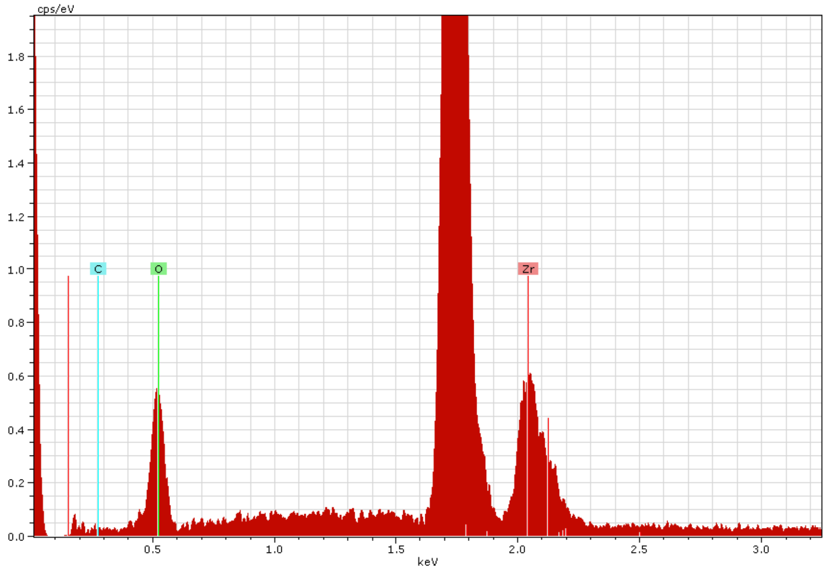

Figure S5 (c). Energy Dispersive X-ray Spectrum of the ZrO_2 film seen in Figure 5(b). Zirconium and oxygen peaks were observed as expected. Any carbon peak was not observed in calcined samples. The major Si peak comes from the silicon substrate.

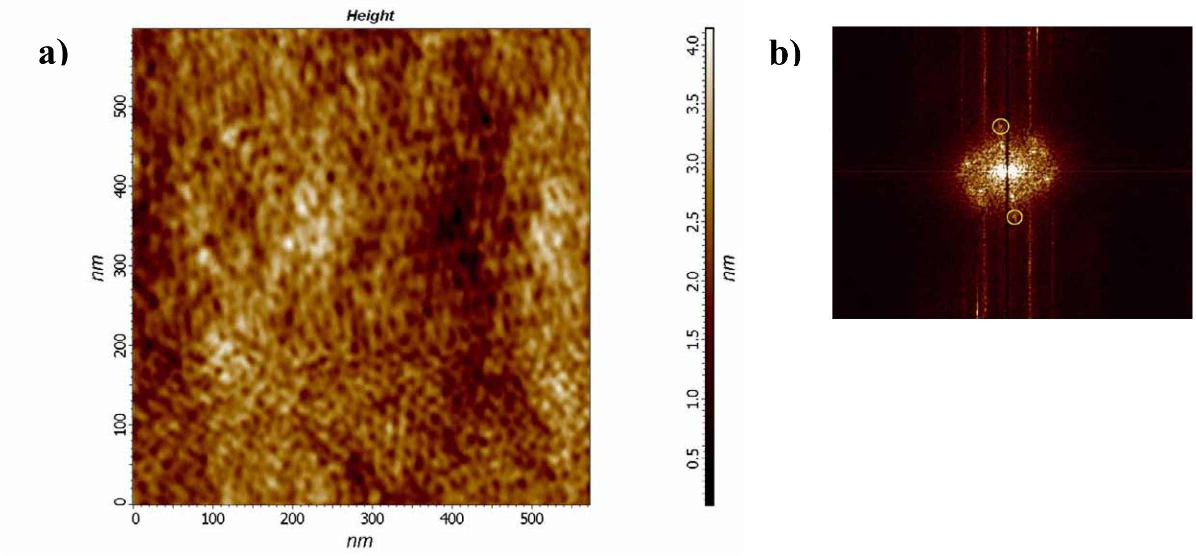

Figure S6. (a) Atomic Force Microscopy height image of ~150 nm thick ZrO_2 film (spin coated; calcined at 450 ^{o}C for 4 h) showing a mixture of horizontal and vertical orientations of the cylindrical pores. The film was spin coated from a solution at 21 ^{o}C followed by water vapour treatment also at 21 ^{o}C. The film was then aged at 50 % relative humidity at a temperature of 35 ^{o}C. (b) Fast Fourier Transform of the height image in (a) indicating the presence of hexagonal morphology together with elongated structures.

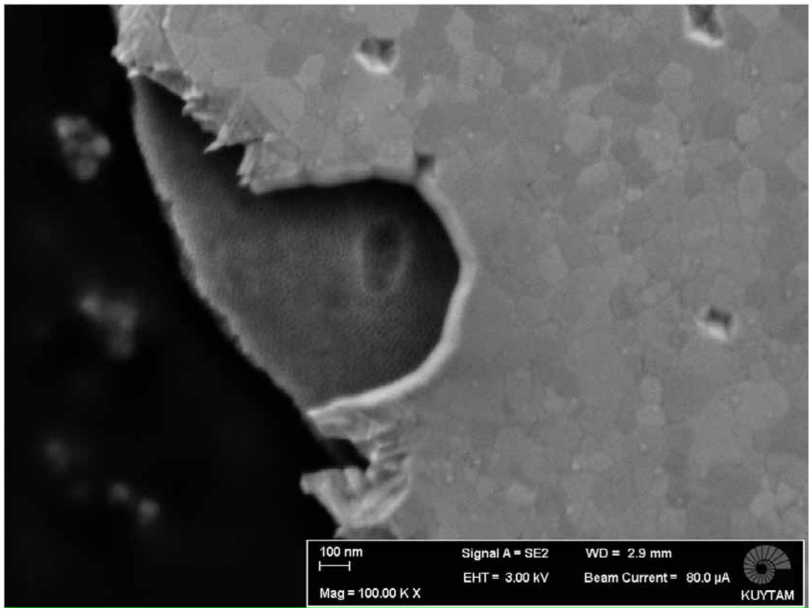

Figure S7. SEM image of the bottom part of a ZrO_2 film (film/substrate interface) prepared at $T_a \sim T_{wvt} \sim T_{aging} \sim 32$ °C. The hybrid mesophase was spin casted on gold coated glass substrates and then the film was calcined at 450 °C for 4 h. The calcined film was lifted off the substrate by a sticky carbon tape together with the gold layer. The holes (~ 1 µm in diameter) where the gold layer stayed on the glass substrate were used to image the bottom part of ZrO_2 films. The gold film is seen brighter in contrast at the right half of the figure. The grains of the deposited gold are also clearly seen. The tips of the cylindrical pores are seen at ZrO_2/gold interface indicating vertical orientations of the cylindrical pores.

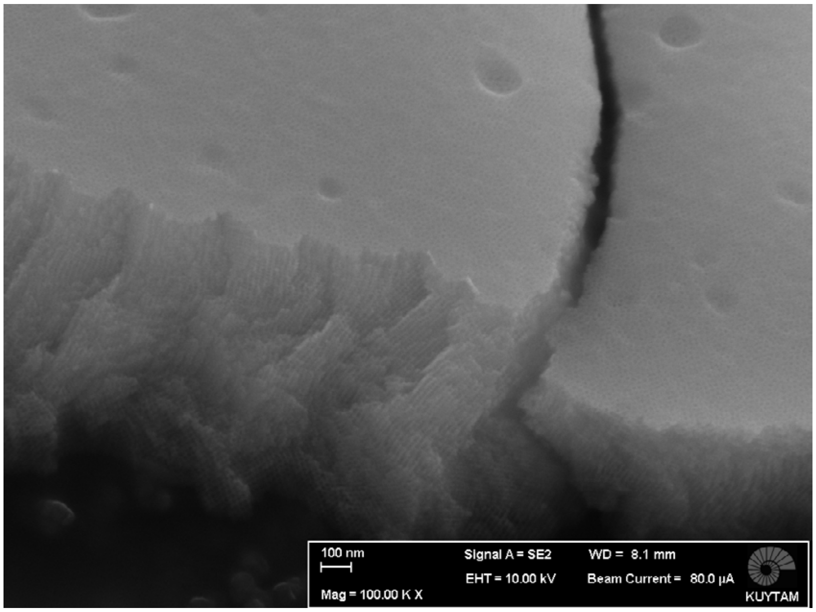

Figure S8. SEM image of the bottom part (film/substrate interface) of the ZrO_2 film of Figure S7 after tilting. The hexagonal cylindrical morphology is clearly seen at the bottom surface together with the vertically oriented cylindrical pores. Note that the cross-sectional area is not well-defined due to the mechanism of peeling-off by a sticky carbon tape.