Toward Ordered Mesoporous Rare-Earth Sesquioxide Thin Films *via* Polymer Templating: High Temperature Stable *C*-type Er_2O_3 with Uniform 16 nm Diameter Pores and Fine-Tunable Crystallite Sizes

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Electronic Supplementary Information

Experimental procedure

Materials

$ErCl_3 \cdot 6H_2O$ (99.9 %), glacial acetic acid (99.99 %), ethanol, and 2-methoxyethanol were purchased from Sigma-Aldrich. $H[(CH_2CH_2)_{0.67}(CH_2CHCH_2CH_3)_{0.33}]_{89}(OCH_2CH_2)_{79}OH$, referred to as KLE, was used as structure-directing agent.

Synthesis of 3D mesoporous *C*-type Er_2O_3 thin films

Both 225 mg of $ErCl_3 \cdot 6H_2O$ and 50 mg of KLE diblock copolymer are dissolved in a mixed solvent of ethanol (0.9 mL), 2-methoxyethanol (0.9 mL), and glacial acetic (0.25 mL). Once the solution is clear, thin films can be produced *via* dip-coating on polar substrates, including quartz and Si(100). Optimal conditions include relative humidities of 11-13 % and constant withdrawal rates of 1-10 mm/s. For best results, the films are aged at 300 °C for 12 h and then heated in air using a 50 min ramp to 800 °C followed by another aging for 5 min.

Characterization

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were taken with a CM30-ST from Philips and a MERLIN from Carl Zeiss, respectively. X-ray diffraction (XRD) measurements were carried out on an X'Pert PRO diffractometer from PANalytical instruments. Grazing incidence small-angle X-ray scattering (GISAXS) patterns were collected at the German synchrotron radiation facility HASYLAB at DESY on beamline BW4 using a MarCCD area detector and a sample-detector distance of ~1820 mm. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a VersaProbe PHI 5000 Scanning ESCA Microprobe from Physical Electronics with monochromatic Al-Kα X-ray source and a hemispherical electron energy analyzer. The electron takeoff angle to the sample surface was adjusted to 54°. The C1s signal from adventitious hydrocarbon at 284.8 eV was used as the energy reference to correct for charging. N_2-physisorption experiments were conducted at 77 K using the Autosorb-1-MP automated gas adsorption station from Quantachrome Corporation. Optical absorption measurements were carried out on a Perkin Elmer Lambda 900 UV-vis-NIR spectrophotometer. A substrate made from fused silica and an aluminium mirror served as the reference for transmission and reflection measurements, respectively. The film thickness was determined with an Alpha Step IQ Surface Profiler from KLA Tencor. For crystal structure visualization, the software Crystal Impact Diamond version 3.2h was used.

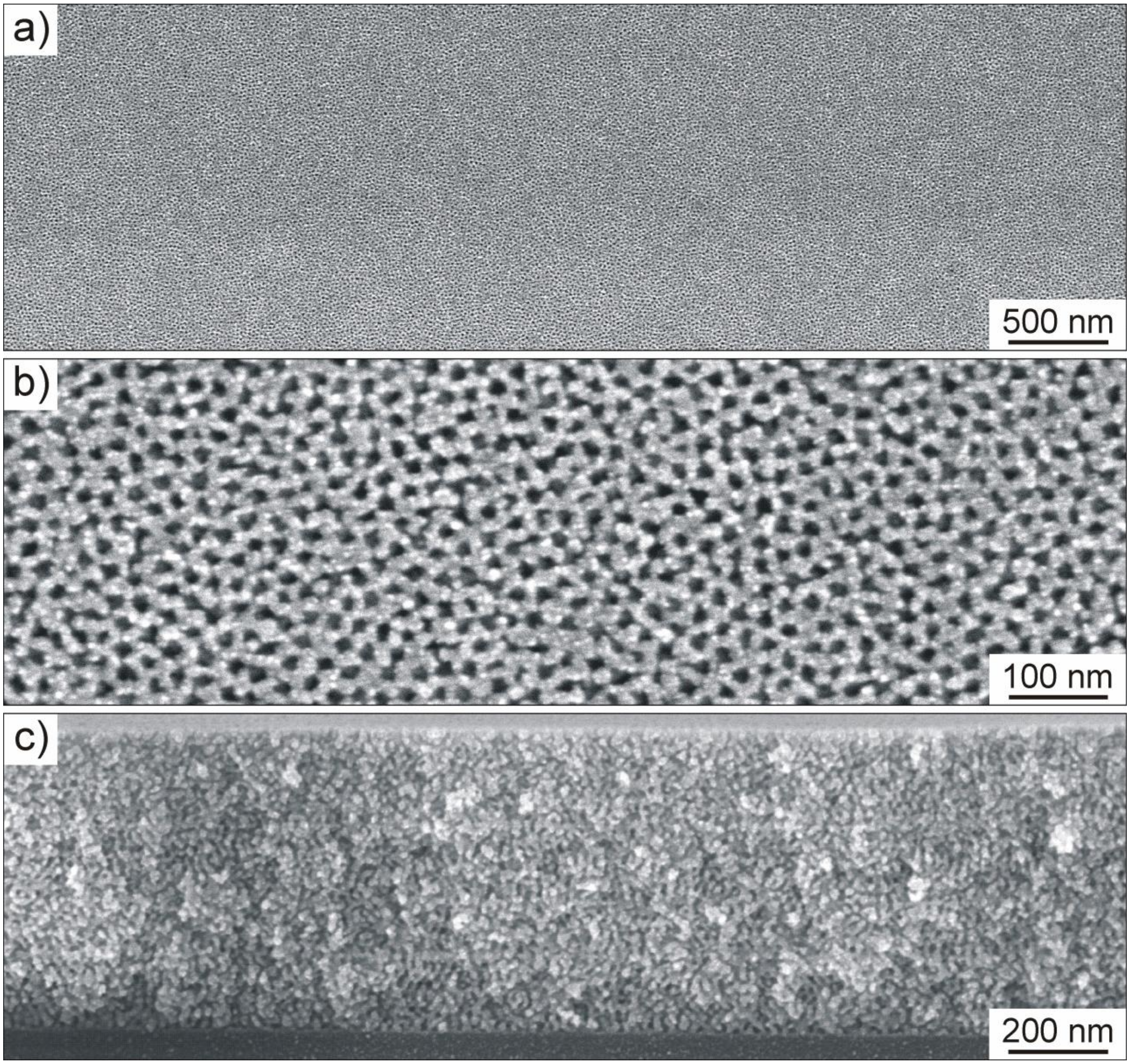

Figure S1. Low- and high-magnification SEM images of KLE-templated *C*-type Er_2O_3 thin films after thermal annealing at 800 °C. (a, b) Top view data showing a distorted cubic network of open pores. Also, it can be seen that the presence of larger structural defects can be ruled out and that the top surface is crack-free on the micrometer level. The latter result suggests that the mesoporous Er_2O_3 thin films prepared in this work can effectively withstand the stresses that develop during thermal treatment. (c) Cross-sectional data showing that the pores persist throughout the bulk of the films.

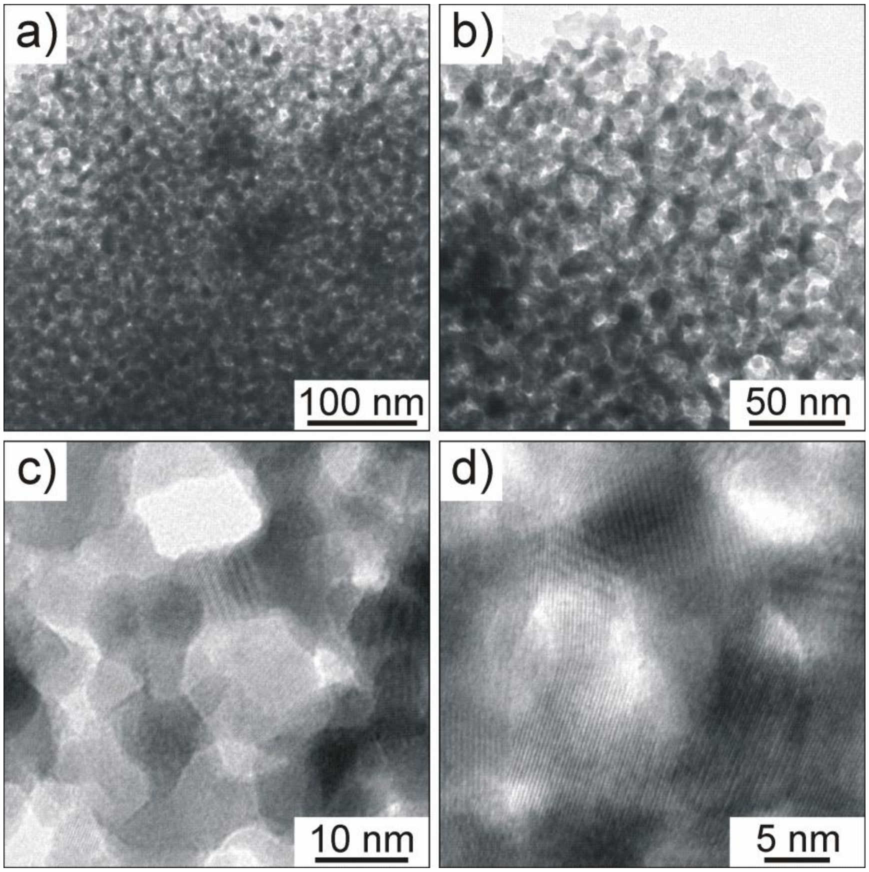

Figure S2. (HR)TEM images of KLE-templated *C*-type Er_2O_3 thin films heated at 800 °C. These data verify both the homogeneity of the 3D pore structure and the nanocrystalline nature of the inorganic walls with randomly oriented, sub-10 nm crystallites.

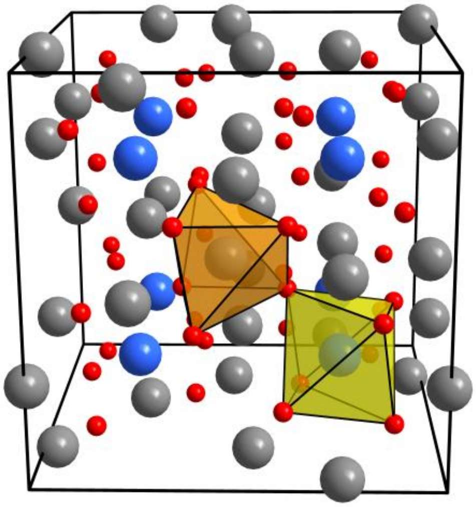

Figure S3. Scheme of the cubic *C*-type Er_2O_3 unit cell. Oxygen atoms occupying the 46*e* sites are shown in red and erbium atoms on both 8*b* and 24*d* sites in blue and gray, respectively. It should be noted that the size of the oxygen atoms has been reduced by a factor of 3.5. As shown in panel (b) of Figure 4 in the manuscript, erbium oxide crystallizes in a purely cubic *C*-type rare-earth sesquioxide structure with space group $Ia\overline{3}-T_h^7$ (a = 10.54 Å). The unit cell contains 32 erbium atoms and 48 oxygen atoms, equivalent to 16 formula units of Er_2O_3. In this fluorite-derived (bixbyite) structure, erbium atoms occupy two crystallographically non-equivalent six-fold positions to oxygen as indicated by the octahedra - eight erbium atoms are located on the *b* sites with high symmetry (S_6) and twenty four on the *d* sites (C_2). In contrast, all of the forty eight oxygen atoms are equivalent and occupy the *e* sites (C_1).

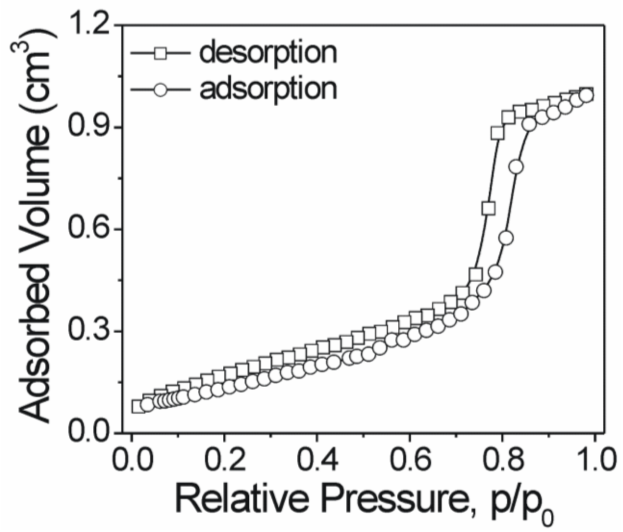

Figure S4. N_2-adsorption/desorption isotherms obtained on 600 nm thick, KLE-templated *C*-type Er_2O_3 films with a total area of 50 cm^2 after thermal annealing at 900 °C. These data provide both a BET surface area of ~180 m^2·cm^{-3} and a total porosity of ~51 %. We estimate the error margin as being ±10 %.

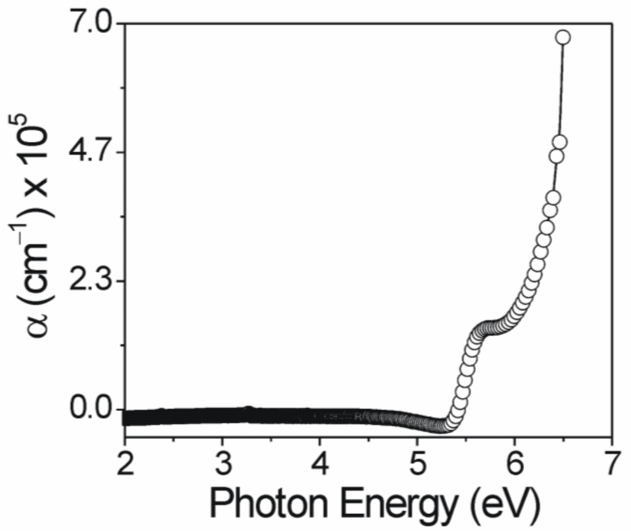

Figure S5. Plot showing the absorption coefficient, *α*, versus photon energy at room temperature for KLE-templated *C*-type Er_2O_3 thin films heated at 800 °C. We find a strong UV peak at approx. 5.35 eV (equivalent to 232 nm light), which arises due to oxygen-metal charge transfer. This transition corresponds to the optical band gap energy, in agreement with literature data.

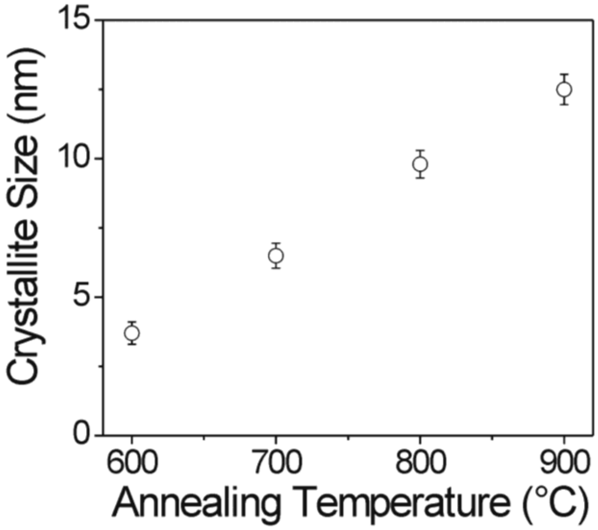

Figure S6. Plot showing the crystallite size from Scherrer analysis versus annealing temperature. Crystalline domain size begins at 3-4 nm at 600 °C and reaches ~13 nm at 900 °C. Interestingly there is an almost perfect linear relation between size and annealing temperatures, which allows for fine-tuning of the nanocrystalline *C*-type domain sizes in the walls of the mesoporous Er_2O_3 thin films.