SUPPLEMENTRARY INFORMATION

Crystalline Nanoporous Metal Oxide Thin Films by post-synthetic Hydrothermal Transformation: SnO_2 and TiO_2

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Methods

Chemicals

Tin tetrachloride [$SnCl_4$], Niobium(V) ethoxide [$Nb(C_2H_5O)_5$] and Titanium(IV) butoxide [$Ti[O(CH_2)_3CH_3]_4$] were purchased from Aldrich. Niobium(V) chloride [$NbCl_5$] was purchased from Riedel-de Haen. Triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer, Pluronic F127 [$(HO(CH_2CH_2O)_{106}$-$(CH_2CH(CH_3)O)_{70}$-$(CH_2CH_2O)_{106}H$] was purchased from Sigma, while absolute ethanol and concentrated HCl (12 mol/l, 37 wt%) were from VWR company. All of the chemicals were used as received without any purification.

Preparation of Solutions.

The solutions for the formation of mesoporous metal oxide thin films were prepared by the following procedure:

The preparation of Sn-sol.

1 g of $SnCl_4$ was added to a solution of 0.4836 g F127 in 7.0463 g ethanol, then1.92 ml concentrated hydrochloric acid (12 mol/l HCl) was subsequently added to obtain finally a clear solution. The Sn-sol was stirred at room temperature overnight; afterwards it was stable for weeks. The final molar ratio of the Sn-sol was 1:(0.007-0.008):(40-50):(2-6):(17-50) = $SnCl_4$:F127:EtOH:HCl:H_2O.

The preparation of Nb-sol.

0.572 g of $Nb(C_2H_5O)_5$ or 0.485 g $NbCl_5$ was added to a solution of 0.4836 g F127 in 7.0463 g ethanol, then1.92 ml concentrated hydrochloric acid (12 mol/l HCl) was subsequently added to obtain finally a clear solution. The Nb-sol was stirred at room temperature overnight; afterwards it was stable for weeks. The final molar ratio of the Nb-sol was 1:(0.015-0.017):(85-107):(4.3-12.8):(36.3-107) = $Nb(C_2H_5O)_5$ or $NbCl_5$:F127:EtOH:HCl: H_2O.

The preparation of Ti-sol.

0.9 g of $Ti[O(CH_2)_3CH_3]_4$ was added to a solution of 0.4836 g F127 in 7.0463 g ethanol, then1.92 ml concentrated hydrochloric acid (12 mol/l HCl) was subsequently added to obtain finally a clear solution. The Ti-sol was stirred at room temperature overnight; afterwards it was stable for weeks. The final molar ratio of the Ti-sol was 1:(0.01-0.0116):(58-72):(2.9-8.7):(24.65-72.5) = $Ti[O(CH_2)_3CH_3]_4$:F127:EtOH:HCl:H_2O.

Preparation of mesoporous thin films.

The thin films were prepared on glass and silicon substrates of ca. 2×2 cm^2. The cleaning included washing with an alkaline/soap solution, rinsing with distilled water and ultrasonic treatment in ethanol. Dust was removed directly before the final coating by spinning ethanol for a minute. 100 µl of the synthesis solution were spin-coated at 4000 rpm for half minute on the glass or silicon substrates at 10 % relative humidity (RH). The low humidity was achieved by splitting dry nitrogen from a gas bottle in two paths. One was directed through a glass frit placed in distilled water. The final gas stream was pressed from the bottom into the spin coater and the humidity was adjusted by the gas flows of both streams. Every time after placing a substrate in the spin coater the coating was performed after a stable value was reached. The fresh films were dried at 60 °C for one day; afterwards they were subjected to a water vapor atmosphere at 100 °C for four days at 90 % RH. After the psHT, a thermal treatment at progressively higher temperature with a general increase (1 °C/min) in temperature was employed.

Characterization.

X-ray diffraction patterns of the thin films were taken on an XDS-2000 diffractometer in θ-θ geometry (Scintag Inc.) using Cu-Kα radiation (1 °/min data acquisition; 0.02 ° step size). Transmission electron microscopy was performed on a TITAN 80-300 operating at 300 kV; film parts were scratched from the substrate and collected on an amorphous holey carbon film on a copper grid. Cross-sections were prepared by dimple-grinding and ion-polishing. Raman spectra were recorded on a Jobin Yvon Horiba HR800 UV Raman microscope using a HeNe laser emitting at 632.8 nm. X-ray photoelectron spectra of Ti2p and O1s were obtained with a Kratos Axis Ultra DLD instrument.

Nitrogen physisorption was carried out on a NOVA 4000e (Quantachrome Instruments) at 77 K on samples scratched from several identical thin films. Samples were outgassed at 150 °C in vacuum overnight before the measurement. Surface area calculations were made using the Brunauer-Emmett-Teller (BET) equation in the range of p p_0^{-1}=0.05 to 0.25. Pore size distributions were determined using the DFT-method (Kernel: NLDFT equilibrium model, cylindrical pores, N_2 on silica).Ellipsometric porosimetry measurements were carried out on a Woollam VASE M2000-D ellipsometer equipped with a controlled-humidity chamber at different partial pressures at a measurement angle of 75°. The recording of isotherms was performed using homemade Labview-controlled gas mixer. Digital mass flow controllers ensured the accurate dosing of the carrier gas nitrogen and the liquid isopropanol or toluene, which was vaporized in a controlled evaporation and mixing element. Partial pressures were calculated using the van der Waals equation. Determination of porosity characteristics was performed using the Kelvin equation adapted for isopropanol adsorption measurements.

Figure S1 XRD of the mesostructured titania after psHT and the mesoporous titania after calcination.

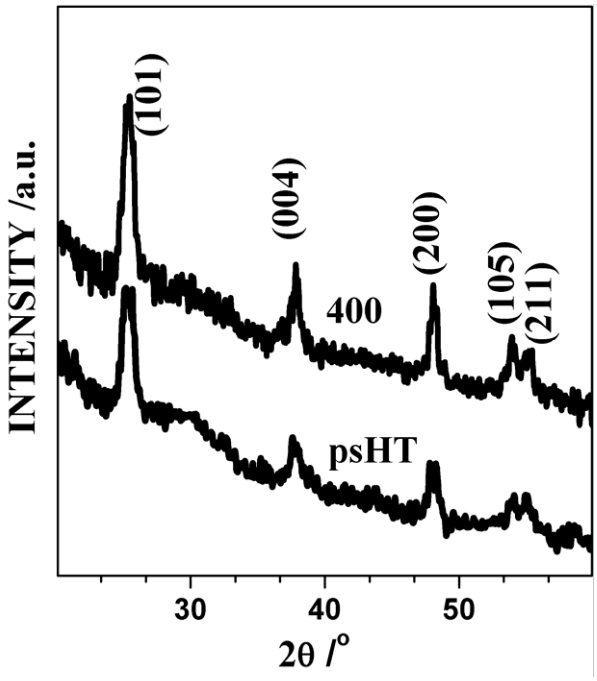

Figure S2 XPS spectra of the mesoporous titanium dioxide thin film calcined at 400 °C. (A) shows that Ti_{2p} appears as a spin-orbit double at ca. 458.84 eV and ca. 464.47 eV. (B)Two O1s peaks appear after deconvolution, which are attributed to lattice oxygen (O_L,530.4 eV), and surface hydroxyl oxygen (O_{-OH}, 532eV).

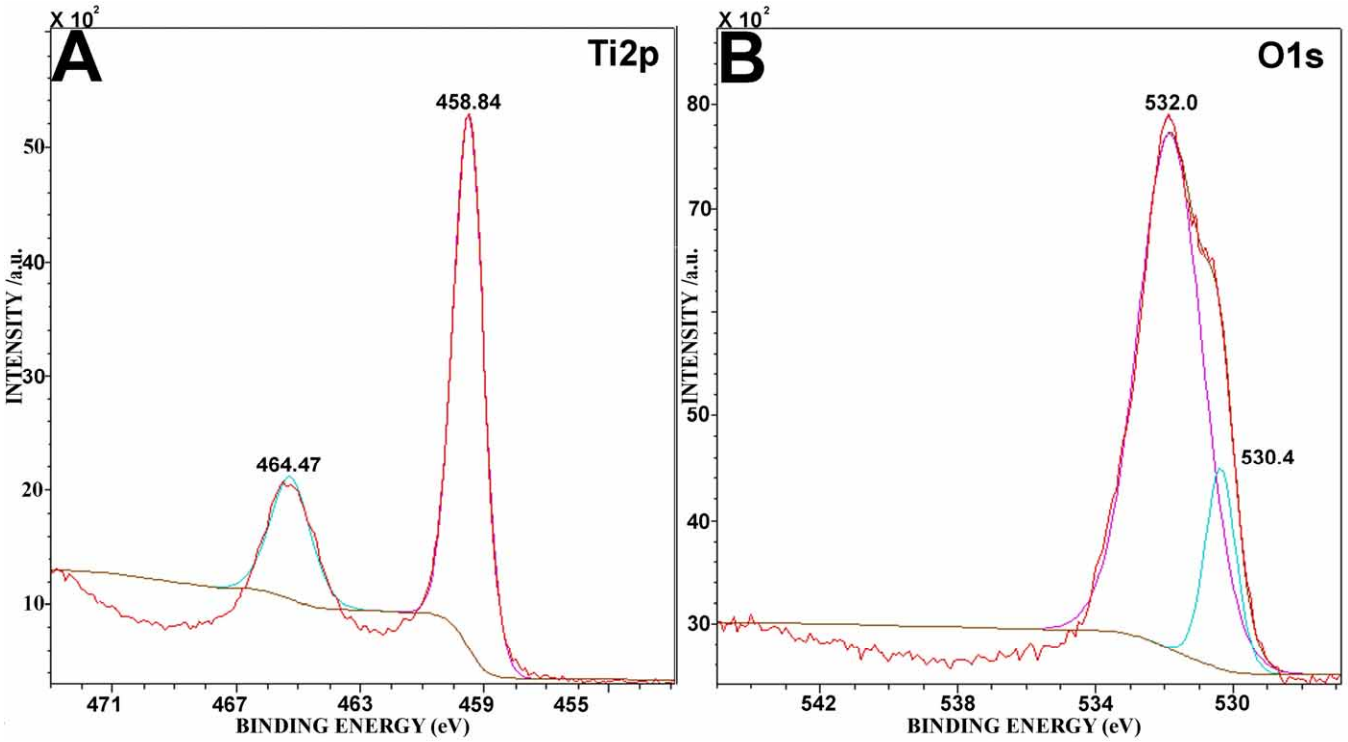

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Figure S3. N_2 adsorption/desorption isotherm and corresponding pore-size distribution (inset) for scratched off material from mesoporous Nb_2O_5 thin films (A), TiO_2 thin films (B), and SnO_2 thin films (C) calcined at 400 °C.

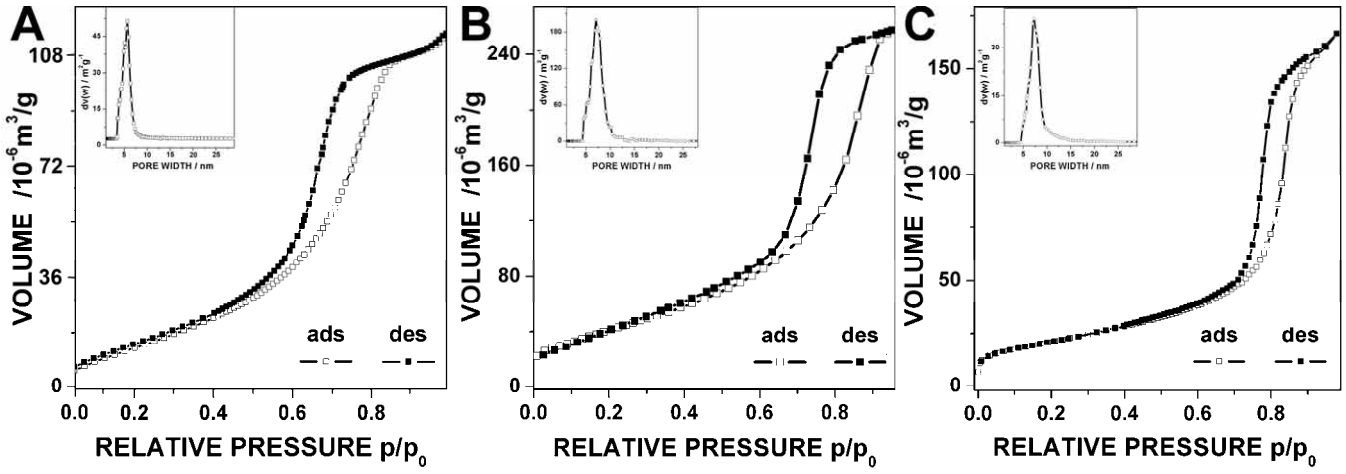

Figure S4. Pore size distribution of niobium oxide thin film (A), titanium dioxide thin film (B) and tin dioxide thin film (C), all calcined at 400 °C, using the desorption branch of adsorption-desorption isotherms of the EP measurements.

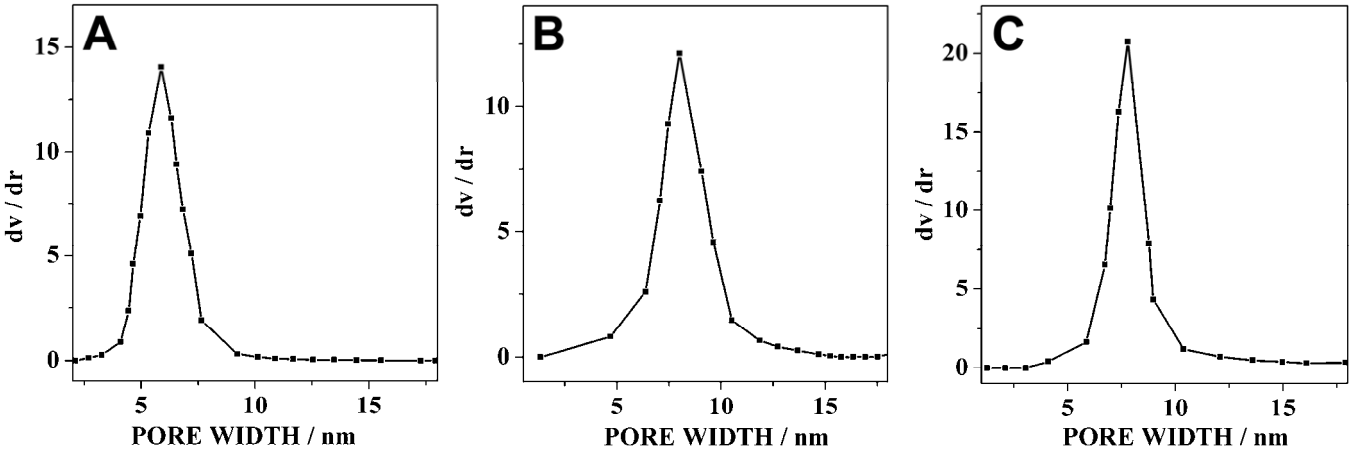

Figure S5. shows the excellent transparency of niobium oxide thin film (A), titanium dioxide thin film (B), tin dioxide thin film (C) calcined at 400 °C and empty glass slide (D).