

# Assembly of Antimony-Doped Tin Oxide Nanocrystals into conducting Macroscopic Aerogel Monoliths

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## Electronic Supplementary Information

### Experimental

Antimony(III) acetate (99.99 %), tin(IV) chloride (99.99% metals basis), toluene (anhydrous, 99.8 %), benzyl alcohol (puriss., 99 – 100.5% GC), acetone ( $\geq 99.99$  %) and chloroform ( $\geq 99.8$  %) were purchased from Sigma-Aldrich. Liquid carbon dioxide was provided by PanGas AG, Switzerland. All chemicals were used as received without further purification.

#### Preparation of ATO nanoparticles

The synthesis of antimony doped ( $\text{Sb}/(\text{Sb}+\text{Sn}) = 10$  at.%) tin oxide nanoparticles was performed according to a procedure reported by Müller *et al.*,<sup>1</sup> which was later adapted to microwave-assisted method by Niederberger *et al.*<sup>2</sup> The reaction mixture was prepared in a glove box with argon atmosphere. 1.35 mmol (403 mg) of antimony(III) acetate were dissolved in 10 mL of toluene and stirred until completely dissolved. 12.3 mmol (1.44 mL) of tin(IV) chloride and 30 mL of benzyl alcohol were added to the solution outside the glove box. Subsequently, 20 mL of this clear solution was transferred to a 35 mL glass vessel sealed with a Teflon cap. The reaction mixture was heated in a microwave reactor (CEM Discover, 2.45 GHz) at 150 °C for 9 minutes. Finally, the brown precipitate was extracted by centrifugation and washed three times with acetone.

### ATO dispersion, gelling and supercritical drying

First, 400 mg of washed, but still wet ATO nanoparticles were stirred in 1 mL of deionized H<sub>2</sub>O resulting in a light brown, turbid dispersion. Subsequently, to remove excess acetone, the solution was placed in a round-bottom glass flask and a weak vacuum was applied for 30 min under slow stirring. The gelling was performed by transferring the ATO dispersion into a Teflon cup and by heating the suspension in a saturated water atmosphere inside a sealed jar at 90 °C for 1 h (Supplementary Figure S1). Finally, the Teflon cups were removed and the gels immersed in aqueous solutions for the exchange of the pore liquid to acetone. This was performed in 10 vol% steps for 12 h each, until the entire pore liquid contained 100 % acetone, where it was held for at least 24 h. Then, the acetone containing gel was critically dried in a Leica Critical Point Dryer 030. The result was a disc shaped monolithic aerogel measuring 0.3 x 1.5 cm.

### Heat treatment

The dried aerogels were annealed inside an alumina based crucible in a Nabertherm P 330 furnace at 400 °C (7 h ramp time), 475 °C (8.25 h ramp time) and 550 °C (9.5 h ramp time) for 1 – 300 minutes, followed by slow cooling to room temperature inside the oven (> 5 hours).

### Characterization

For the analysis of residual organics attenuated total reflectance infrared (ATR-IR) spectra of the aerogels were recorded in the range of 375 – 4000 cm<sup>-1</sup> wavenumbers with a Bruker ALPHA FT-IR spectrophotometer. Furthermore, a thermogravimetric analysis (TGA, Mettler Toledo SDTA851e) was performed on supercritically dried aerogels in the range of 25 °C – 900 °C at a rate of 1 °C min<sup>-1</sup>. Additionally, elemental analyses were carried out on a device of LECO.

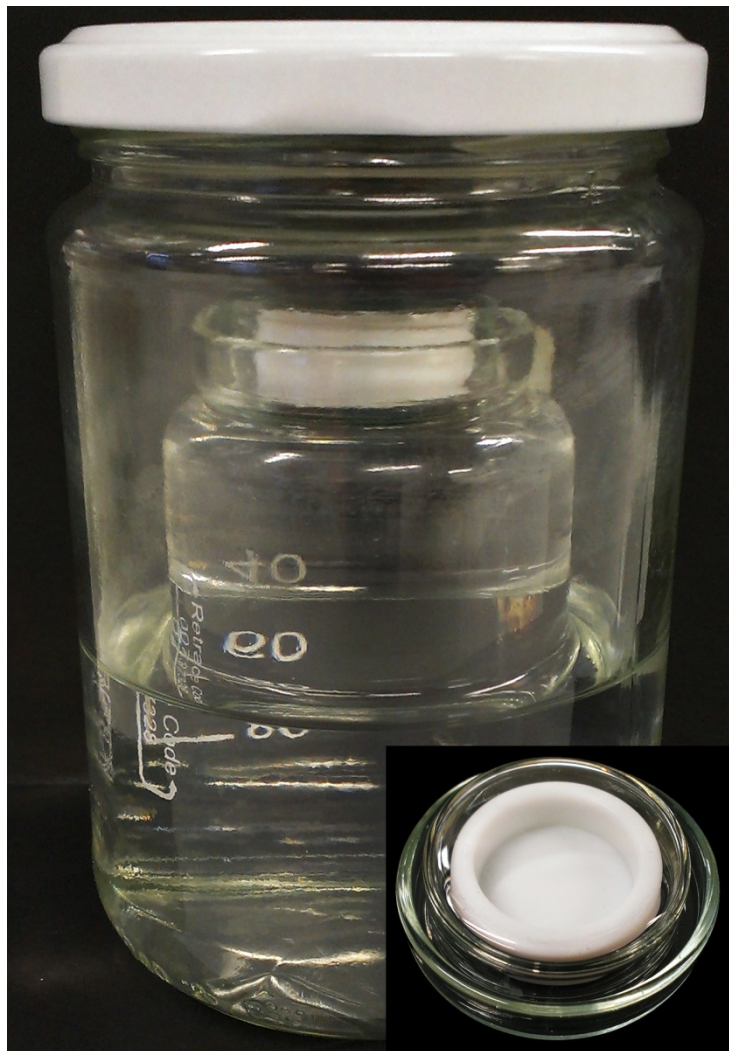
Powder X-ray diffraction was measured on a PANalytical Empyrean equipped with a PIXcel 1D detector and a Cu K<sub>α</sub> X-ray tube. By using the Scherrer equation on the (110) peak broadening, the average crystal size could be calculated.

The microstructure was investigated by scanning electron microscopy (SEM) on a FEI Magellan 400 and a Hitachi SU-70. The samples were placed on a polished aluminium sample holder and silver paste was used to fix the aerogel sample. High resolution transmission electron microscopy (HRTEM) was carried out on a JEOL JEM-2200FS microscope operated at 200 kV. The samples for TEM characterization were dispersed in chloroform and transferred onto a carbon coated copper grid on a filter paper and subsequently dried in air at room temperature.

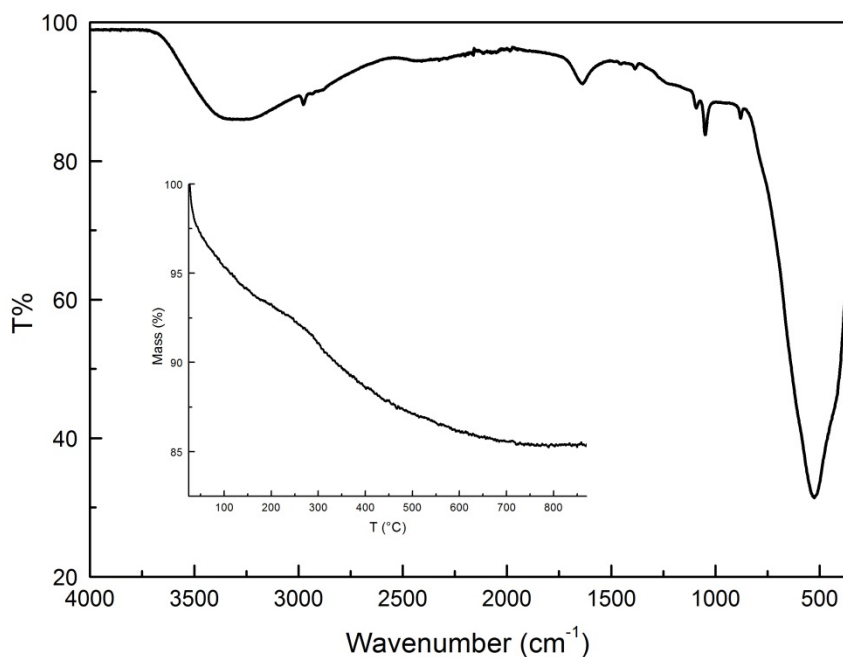
For the surface area analysis, the samples were outgassed at 100 °C for at least 15 h and nitrogen gas sorption measurements were carried out on a Quantachrome Autosorb iQ at 77 K. The surface area was determined via the Brunauer-Emmet-Teller (BET) method and the pore size and pore volume were determined by a density functional theory (DFT) analysis using a Non Local DFT (NLDFT) calculation model for nitrogen at 77 K based on silica cylindrical pores.<sup>3</sup>

The conductivity measurements were carried out on all ATO aerogels with a Keithley 237 high voltage source measure unit. The two point electrodes were placed with a weight of 1 g at a distance of 2 mm to each other on the sample. 1 V was applied as source between the electrodes and the current was measured. The resistance could then be calculated *via* Ohm's law.

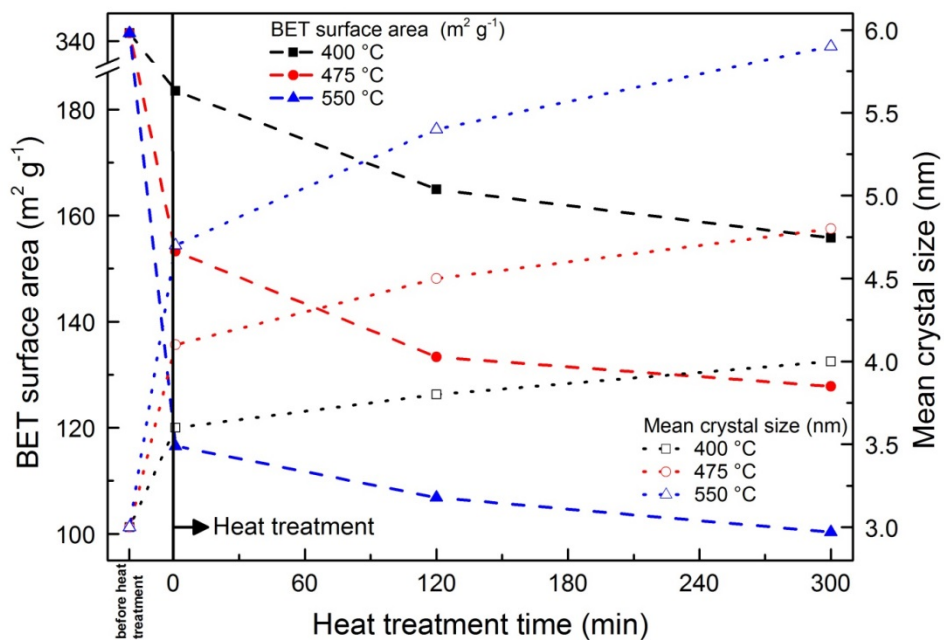
## Supplementary Figures



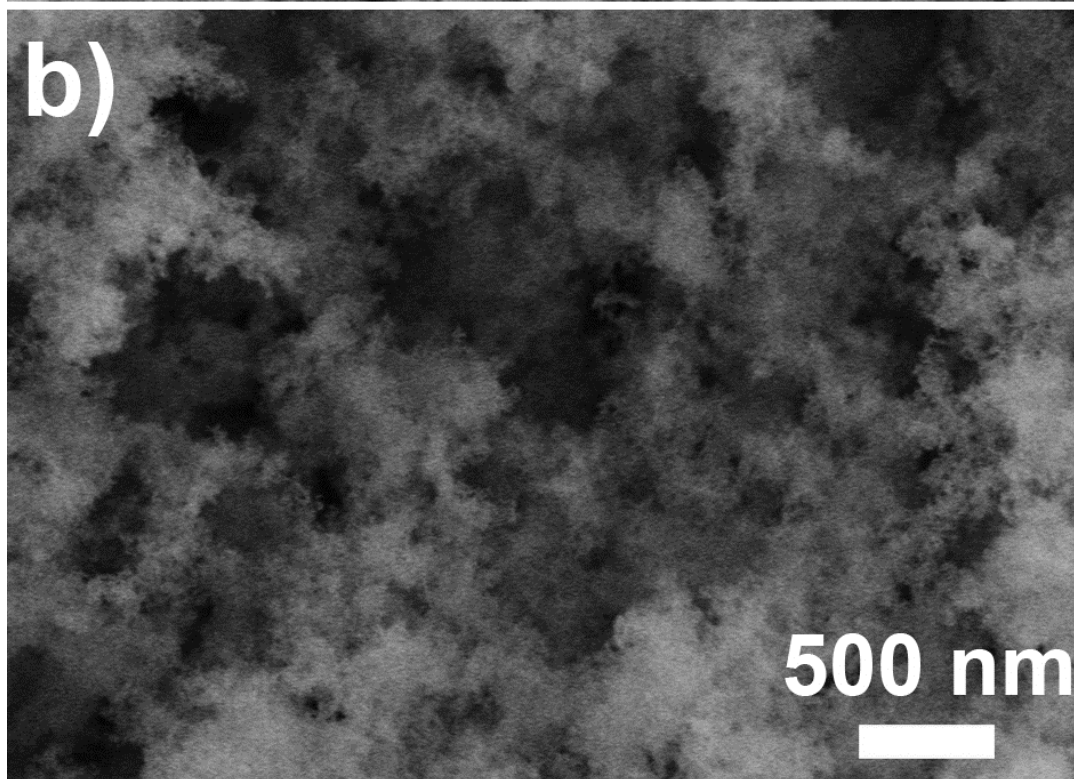
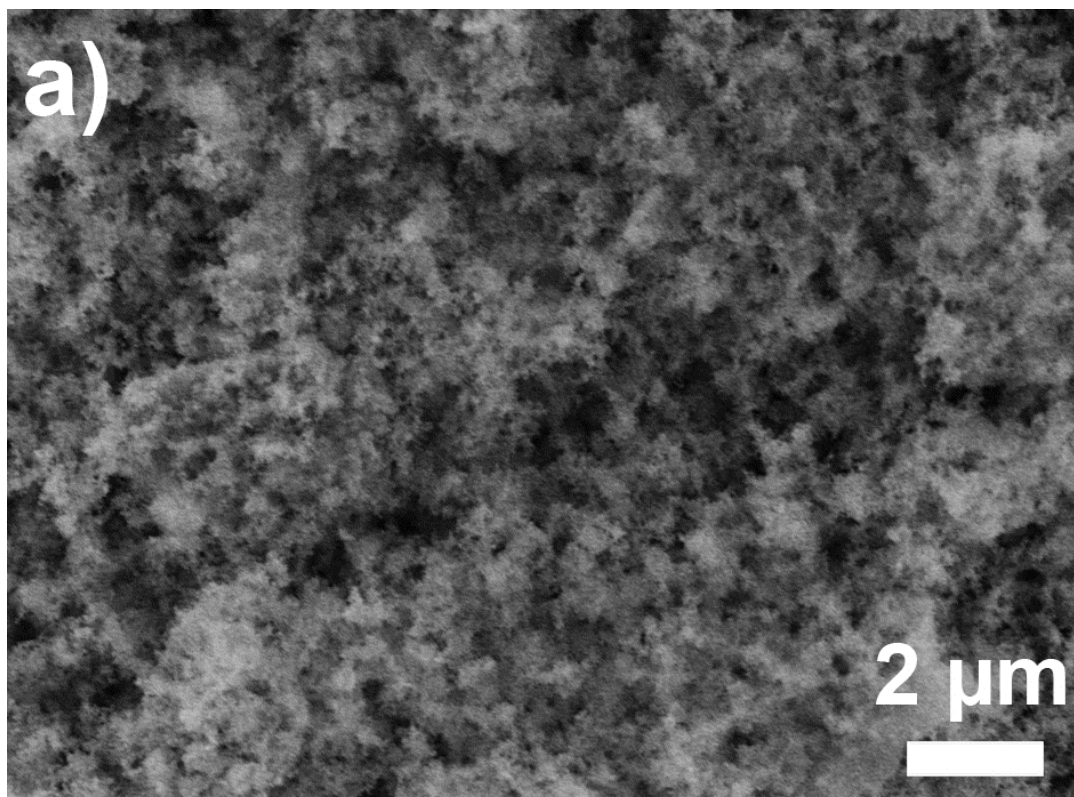
**Supplementary Figure S1** Setup for a saturated water atmosphere inside a sealed glass vessel for the heat treatment. The inset shows a Teflon cup covered by a Petri dish.



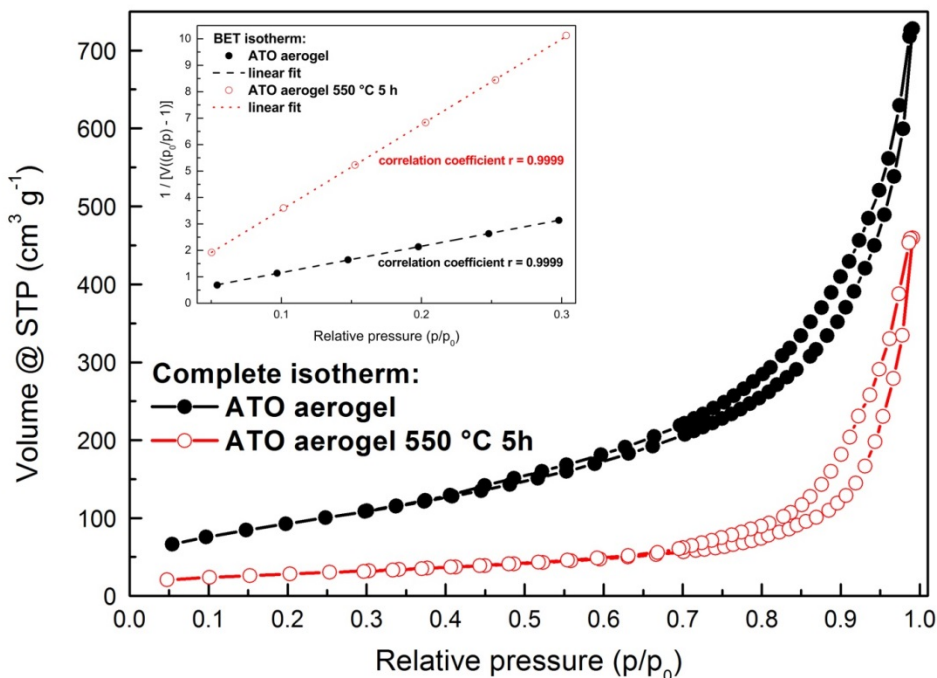
**Supplementary Figure S2** FT-IR spectrum of the as-synthesized ATO aerogel. The inset shows the thermogravimetric curve (TGA) of the as-synthesized ATO aerogel.



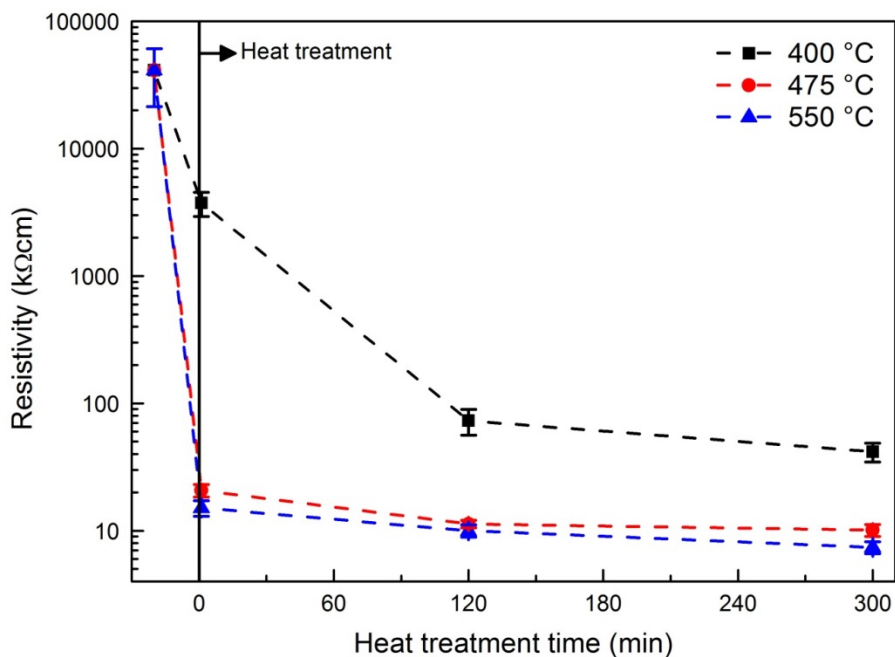
**Supplementary Figure S3** BET surface area and mean crystal size for ATO aerogels before and after heat treatment as a function of temperature and heat treatment time. Black squares stand for a heat treatment temperature of 400 °C, red dots for 475 °C and blue triangles for 550 °C. Solid symbols represent BET surface values, whereas open symbols refer to the calculated mean crystal sizes.



**Supplementary Figure S4** SEM images of an ATO aerogel after supercritical drying. **a)** At low magnification the homogenous and open-porous percolating network constructed of nanoparticles is visualized and **b)** at high magnification even pores within the fine primary structures measuring just a few nanometers in size are shown.



**Supplementary Figure S5** Complete adsorption-desorption isotherm for an ATO aerogel before and after heat treatment at 550 °C for 5 h. Inset: Corresponding BET isotherms and linear fits reveal a specific surface area of 343 m<sup>2</sup> g<sup>-1</sup> and 100 m<sup>2</sup> g<sup>-1</sup>, respectively.



**Supplementary Figure S6** Measured conductivity values of ATO aerogels before and after heat treatment as a function of temperature and heat treatment time. Black squares stand for a heat treatment temperature of 400 °C, red dots for 475 °C and blue triangles for 550 °C.

## References:

- (1) Müller, V., *et al.*, *Chem. Mater.* **2009**, 21 (21), 5229-5236.
- (2) Luo, L., *et al.*, *Chem. Mater.* **2013**, 25 (24), 4901-4907.
- (3) Landers, J., *et al.*, *Colloids Surf., A* **2013**, 437, 3-32.