

Supporting Information

Full Experimental Details

Sodium stannate trihydrate (95 %), potassium stannate trihydrate (99.9 %), potassium hexahydroxoantimonate (V) (Fluka, 99%), nitric acid (>65 %), acetone (p.a), tetrachloroauric acid trihydrate (99.9 %), chloroplatinic acid (>37.5 % Pt) and sodium borohydride (>96%) were purchased from Sigma-Aldrich. Acetic acid (p.a) was received from Normapur and trisodium citrate (99%) from Merck. Deionized water (MilliQ, 18.2 MΩcm) was used to prepare aqueous solutions, diluting acids and washing samples.

Preparation of SnO₂ particle sol and gelation

To a freshly prepared solution of 0.033 M sodium hexahydroxostannate(IV) in water 1.5 equivalents (eq.) of 2 M nitric acid were quickly added at room temperature while stirring. The solution became white and turbid immediately, but the turbidity vanished within 10 minutes when stirred constantly to form a clear, colorless sol.

The sol was stirred for at least one hour after the first addition of nitric acid. The gelation can be induced by addition of more acid to a total amount of at least 2 eq. H⁺ per hexahydroxostannate. Typically 3.5 eq. nitric or acetic acid were added to a total of 5 eq. H⁺ per hexahydroxostannate. The addition of acid is done while stirring and the stirrer is stopped after 5 seconds to both ensure complete mixing and to prevent damages to the forming hydrogel by the stirrer. The sol also can be destabilized to form a gel by addition of the same volume ethanol.

Antimony doped tin oxide (ATO) gels

For the preparation of ATO gels potassium hexahydroxoantimonate(V) was dissolved in hot deionized water. The hexahydroxoantimonate solution was cooled down and potassium hexahydroxostannate(IV) is added to achieve a molar fraction of 2.5 % to 10 % Sb/Sn. Because sodium hexahydroxoantimonate(V) precipitates, potassium hexahydroxostannate(IV) was used instead of the sodium salt to obtain ATO gels. Sol formation was done like for the pure tin oxides by adding 1.5 eq. of nitric acid. After 1 h the gelation is induced by further addition of 3.5 eq. nitric acid.

After supercritical drying a fraction of each ATO sample was calcined in a muffle furnace in air. The temperature was ramped to 550 °C with 2 K/min. After holding this temperature for 2 h the oven was naturally cooled down.

Noble metal particle loaded tin oxide gels

The procedure reported by Brown et al. was used to synthesize small citrate stabilized gold particles.²⁶ For the preparation of 15 mg Au particles 0.075 mmol gold(III) chloride trihydrate were dissolved in 250 mL deionized water. To this stirred solution 1.16 mL sodium citrate solution (5 wt%) were added. One minute later 2.9 mL of a fresh prepared ice cold solution of 0.13 mmol sodium borohydride and 0.115 mmol sodium citrate was injected

quickly. The solution turned deep red immediately. The Au particles have a diameter of 4-5 nm and an absorption maximum at 504 nm.

The method by Bigall et al. was used to synthesize citrate stabilized platinum particles.²⁵ For 15 mg Pt nanoparticles 0.075 mmol hexachloroplatinic(IV) acid were dissolved in 350 mL boiling water and 1.62 mL sodium citrate solution (5 wt%). A freshly prepared ice cold solution of 0.077 mmol sodium borohydride and 0.16 mmol sodium citrate in 3.85 mL water was rapidly injected. The solution turned dark brown within 5 seconds. The solution was kept boiling for another 10 minutes and quenched with ice water. The Pt particles have a diameter of 3-5 nm.

The noble metal nanoparticles solutions can directly be used to form hybrid Au/SnO₂ or Pt/SnO₂ gels without any additional treatment. To obtain a gel with a loading of 5 wt% metal particles a solution containing 15 mg metal nanoparticles is mixed with a tin oxide sol prepared from 2 mmol sodium hexahydroxostannate and 3 mmol nitric acid and gelation is induced by adding further 7 mmol nitric acid while stirring. With Au particles a deep red or with Pt particles a dark grey gel sedimented, respectively. The supernatant solution was clear and colorless indicating a complete incorporation of the nanoparticles into the gel.

Washing, solvent exchange and supercritical drying

The hydrogels were aged over night before washing with deionized water 5 times over a course of 3 days. The gels were transferred to extraction thimbles, where the solvent was exchanged against acetone. The thimbles were transferred to a Quorum Technologies E3100 Critical Point dryer. The acetone was exchanged with liquid carbon dioxide by flushing several times over the course of 2 days at 12 °C. Supercritical drying was performed by sealing the autoclave, heating to 40 °C and slowly releasing the carbon dioxide.

The syntheses yield fine non monolithic gels of white color in the case of pure and Sb doped tin oxide aerogels or deep red or dark grey color for noble metal particle loaded tin oxide aerogels.

Also two xerogels of 5 wt.-% Au/SnO₂ were prepared by ambient pressure drying at elevated temperatures. One sample was dried from water after washing, the other sample was dried from hexane. Therefore the solvent was first exchanged to ethanol and then to hexane.

Characterization

Dynamic light scattering

DLS measurements were performed using Malvern Instruments Zetasizer Nano ZS in a quartz cuvette. The measurement settings for the LASER and attenuator were automatically optimized by the device. Each measurement lasts 50 s and was done three times. For tin oxide a refractive index of 1.93 and for the solvent the viscosity and refractive index of pure water were used. Particle sols prepared from solutions of 0.033, 0.0667 and

0.133 mol/l sodium hexahydroxostannate $\text{Na}_5\text{Sn}(\text{OH})_6$ with 0.5, 1.0, 1.5 and 1.9 equivalents of HNO_3 per stannate ion were measured.

Nitrogen physisorption

Nitrogen physisorption isotherms were recorded with a Quantachrome Nova3000e Surface Area and Pore Size Analyzer with nitrogen at 77 K. Prior to measurement samples were degassed for 2 hours at 100 °C in vacuum. The specific surface area was calculated using the BET equation (5 data points from 0.05 to 0.2 p/p_0). The pore size distribution is calculated with the BJH model from the desorption branch.

Powder X-Ray Diffraction

For Powder X-Ray Diffraction aerogels were redispersed in acetone using ultrasound and dropcasted onto an oriented silicon single crystal slab. X-Ray diffractograms were acquired with a Bruker Phaser D2 in reflection mode with nickel filtered Cu K_α radiation ($\lambda = 0.15418 \text{ nm}$) equipped with a Lynxeye multipoint detector. The diffractograms were recorded from $15^\circ - 100^\circ 2\theta$ in 0.02° steps with 4 s per step.

TEM imaging

For TEM imaging aerogels were dispersed in acetone assisted by ultrasound. The suspension was dropcasted onto a copper grid with Carbon/Formvar film (Plano S162) and removed after 5 seconds by soaking with KimTech precision wipes.

Brightfield TEM images were acquired with FEI Tecnai T20, equipped with LaB_6 cathode operating with accelerating voltage of 200 kV.

SEM Imaging

Scanning electron microscopy was conducted with Hitachi SU-8020 microscope. The Samples were fixed on sticky carbon pads and excess sample was blown off with pressurized air.

For EDX measurements the aerogel was dispersed in acetone with ultrasound and the suspension was dropcasted onto a silicon wafer.

Electrical conductivity

Electrical conductivity measurements with 20 mg calcined aerogel powder pressed between two copper electrodes in a pressure cell similar to the one used by Ozouf and Beauger.⁸ The area of copper electrodes is 0.785 cm^2 . The press was loaded with a weight of 13 kg, resulting in a pressure of approximately 160 N/cm^2 . By a Gamry Instrumens Reference 600 Potentiostat voltages of -200 to 200 mV were applied and the resulting current

was measured. The conductance was calculated from the slope of the i-U diagram. The thickness of 20 mg the pressed powder were estimated to be 0.195 mm as 200 mg aerogel powder pressed with the same pressure result in a 1.95 mm thick pellet.

X-Ray photoelectron spectroscopy

All XPS studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with a monochromatic Al K α ($h\nu = 1486.6$ eV) X-ray source of 300 W at 15 kV. The kinetic energy of photoelectrons was determined with hemispheric analyzer set to pass energy of 160 eV for wide-scan spectra and 20 eV for high-resolution spectra. During all measurements, electrostatic charging of the sample was avoided by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same value that was necessary to set the C 1s peak to 285.00 eV.

Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Spectrum background was subtracted according to Shirley. The high-resolution spectra were deconvoluted by means of the Kratos spectra deconvolution software. Free parameters of component peaks were their binding energy (BE), height, full width at half maximum and the Gaussian-Lorentzian ratio.

Catalytic CO Oxidation

Catalytic Carbon monoxide oxidation tests were performed in a fixed bed tubular reactor (inner diameter 6 mm). For one test 50 mg of tin oxide aerogel loaded with 5 wt% Au particles were used. The CO and CO₂ concentrations were monitored with two NDIR-sensors smartModul^{PREMIUM} (Pewatron). The temperature inside the catalyst bed was measured with a thermocouple inserted in a glass capillary. The sample was exposed to a gas flow of 9800 ppm CO, 0,1 l/h O₂ in a total flow of 5.26 l/h (balance was nitrogen). The GHSV is 105200 mL*g⁻¹*h⁻¹.

The aerogel sample was tested as prepared after supercritical drying at room temperature and with oven temperatures of 50, 80, 110, 150 and 200 °C holding each temperature step for at least 25 min. The temperature inside the catalyst bed can be higher at high conversions due to exothermic CO oxidation.

After the test during the heat up phase the gas was switched to 0.1 l/h O₂ in 5.16 l/h N₂ and temperature raised to 300 °C for one hour. After this activation treatment the samples were cooled down to room temperature the gas mixture switched back to CO stream and the samples were with same temperature stages again.

The CO conversion was calculated based on the CO detector signal averaged over the last 5 minutes of each temperature step.

For comparison also the two 5 % Au/SnO₂ xerogels were prepared and tested for CO Oxidation. To compensate the height of the catalyst bed, as the xerogel has much smaller volume the xerogel was ground in mortar and mixed with 50 mg of pure tin oxide aerogel.