Processing of Cr doped SrTiO$_3$ nanoparticles into high surface area aerogels and thin films

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Experimental details

Chemicals

Strontium (metallic dendritic pieces, purified by distillation, 99.9 % trace metals basis), titanium(IV) isopropoxide (99.999 % metals basis), 2-[2-(2-methoxyethoxy) ethoxy] acetic acid (MEEAA, technical grade), benzyl alcohol (anhydrous, 99.8 %), ethanol (absolute), n-hexane (CHROMASOLV®, for HPLC ≥99.5 %) were purchased from Sigma-Aldrich. Chromium(III) acetylacetonate (97 %) was purchased from Fluka. Liquid carbon dioxide (≥99 %), argon (99.999 %), nitrogen (99,999 %) and helium (99,999 %) were provided by PanGas AG, Switzerland. All chemicals were used as received without further purification.
Preparation of nanoparticles

The synthesis of Cr doped SrTiO₃ nanoparticles was performed according to a modified protocol by Niederberger et al. The reaction mixture was prepared in a humidity- and oxygen-free glove box with argon atmosphere. 11.4 mmol (1 g) of metallic strontium were dissolved in 100 mL of benzyl alcohol at 75 °C and stirred for 72 h until completely dissolved. Subsequently, the molar equivalent of titanium(IV) isopropoxide (3.375 mL) was added to the solution. For doping with chromium (SrTi₁₋ₓCrₓO₃), x = 0.3, 2, 5, 10 %), the corresponding amount of chromium (III) acetylacetonate was added to the reaction solution. The homogeneous mixture was then transferred to four 40 mL glass liners, inserted into 45 mL Teflon-lined stainless steel autoclaves (Parr acid digestion bombs) and heated in a furnace (Memmert UFE 400) at 200 °C for 48 h. Finally, the precipitate was extracted by centrifugation and washed three times with absolute ethanol.

Dispersion, gelling and dip coating

In order to produce a stable dispersion of particles, a procedure by Schmid et al. was adapted to functionalize the SrTi₁₋ₓCrₓO₃ nanoparticles with MEEAA, which we previously used for functionalizing BaTiO₃ nanoparticles. First, 200 mg of washed, wet SrTiO₃ nanoparticles were stirred in 5 mL of a 0.3 M MEEAA solution in ethanol for 3 h at room temperature. Subsequently, to remove the unbound excess of MEEAA, hexane was added to the solution in a volumetric ratio of >5:1. The functionalized nanoparticles were separated through centrifugation and re-dispersed in 1 mL of ethanol.
The gelling procedure was initiated by adding deionized water to the SrTi$_{1-x}$Cr$_x$O$_3$ dispersion in a volumetric ratio of 3:1. This mixture was then transferred to 5 mL syringes cut open and placed in a saturated ethanol atmosphere in an oven at 70 °C for 30 minutes to induce gelation. The gels were immediately covered with liquid to prevent drying and cracking, followed by solvent exchange to pure acetone in 10 vol. % steps, each lasting ≥ 12 h. To preserve the microstructure, the gels were supercritically dried in a Leica Critical Point Dryer 030 or in a Tousimis 931 GL resulting in macroscopic aerogel monoliths.

Thin films were prepared on fused silica substrates cleaned with acetone and ultra-sonication and deposited by repeated dip-coating (NIMA) from a 5 % Cr doped SrTiO$_3$ dispersion under ambient conditions. The immersion and withdrawal speed was set to 60 mm/min and 30 dips were performed. After deposition, the films were heat-treated in air at 600 °C for 2 h with a ramp speed of 1 °C min$^{-1}$, followed by naturally cooling to room temperature inside the furnace.

**Characterization**

Powder X-ray diffraction (XRD) was measured on a PANalytical Empyrean equipped with a Cu K$_\alpha$ X-ray tube operated at 45 kV and 40 mA and a PIXcel 1D detector. Fixed slits optics were used in order to meet the constant volume criterium. Refinement of unit cell parameters was performed using the FullProfSuite software package.$^{[4,5]}$ The background was defined by linear interpolation of a set of background points which were obtained using the HighScore software from PANalytical. The peak shape function used to model the data was the Thompson-Cox-Hastings
pseudo-Voigt function.\textsuperscript{[6]} By using the Scherrer equation on the (110) reflection, mean crystallite sizes were calculated by using the effect of peak broadening.

For the microstructural analysis, scanning electron microscopy (SEM) was performed on a Hitachi SU-70 or on a Leo 1530 SEM Gemini, both operated at 5 kV. Samples were placed on a polished aluminium sample holder and silver paste was used to fixate and contact the aerogels. Thin films were attached to carbon films and sputtered with 3 nm Pt on a Safematic sputter coater CCU-010. High resolution transmission electron microscopy (HRTEM) was carried out on a JEOL JEM-2200FS microscope operated at 200 kV. EDX measurements were carried out on a FEI Talos F200X microscope operated at 200 kV in STEM mode. The aerogel samples for TEM characterization were dispersed in chloroform and transferred onto a carbon coated copper grid placed on a filter paper and ambient dried.

The surface adsorbed organics were analyzed by attenuated total reflectance infrared (ATR-IR) spectra, which were recorded in the range of 375 – 4000 cm\(^{-1}\) on a Bruker ALPHA FT-IR spectrophotometer. Carbon elemental analysis of the samples were measured on a LECO device. Prior to gas sorption analyses with nitrogen at 77 K, the samples were outgassed at 100 °C for at least 24 h on a Quantachrome Autosorb iQ. The surface area was determined via the Brunauer-Emmet-Teller (BET) method and the pore size was determined by a density functional theory (DFT) analysis using a Non Local DFT (NLDFT) calculation model for nitrogen at 77 K on silica cylindrical pores.\textsuperscript{[7]}

Powder UV/vis spectra were obtained on a JASCO V-770 spectrophotometer equipped with an ILN-725 integrating sphere with background subtraction.
Figure S1 XRD data measured using a wavelength of 1.5418 Å and Rietveld refined data for SrTi$_{0.9}$Cr$_{0.1}$O$_3$ and SrTiO$_3$. 
Figure S2 Diffraction peak position of the (110) reflection for SrTi$_{1-x}$Cr$_x$O$_3$ nanoparticles in the range of $2\theta = 30.5 – 34^\circ$.

Figure S3 ATR-FTIR spectra of 10 % Cr doped SrTiO$_3$ nanoparticles after synthesis and after functionalization with MEEAA.
Figure S4 Transmission electron micrograph overview of a 10 % Cr doped SrTiO₃ aerogel.
Figure S5 EDX spectrum of 10 % Cr doped SrTiO₃ confirming the presence of the dopant.

Figure S6 HAADF image of 10 % Cr doped SrTiO₃ and corresponding Sr and Cr elemental mapping.
**Figure S7** DFT pore size distribution for the undoped (black squares) and 10 % Cr doped (red circles) SrTiO$_3$ aerogel.

**Table S1** Unit cell parameters for different Cr doping levels of SrTiO$_3$ as obtained by Rietveld refinement.

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References