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A fast route to modified tin oxide aerogels using hydroxostannate precursors

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Nanostructured tin oxide materials with a high specific surface area and porosity are promising for applications such as electrocatalysis, lithium ion batteries or sensors. Here, we present a facile strategy for the synthesis of tin oxide aerogels using inexpensive hexahydroxostannate as tin precursor. This easy and scalable method yields tin oxide aerogels with a high specific surface area and wide pore size distribution. The method can be modified by adding hexahydroxoantimonate to obtain antimony doped tin oxide aerogels that show an electrical conductivity after annealing. A cogelation with other preformed nanoparticles (e.g. Au, Pt) leads to mixed gels. Both modifications do not have a large impact on the porous properties of the obtained aerogels. Tin oxide materials prepared via this route can be tailored to a specific application by versatile modification possibilities.

Introduction

Tin(IV) oxide is a wide-bandgap semiconductor and has been investigated for many applications such as anode material for Li ion batteries,^{1,2} gas sensors,³ dye sensitized solar cells⁴ and different fields of catalysis, photocatalysis^{5,6} and electrocatalysis.^{7–9} To obtain good performance in these applications it is crucial to provide a large specific surface area to enhance exchange reactions. For this purpose nanostructured materials are used. A pore system is important to enable diffusion of Li ions, analyte molecules or reactants through the material. Aerogels combine both aspects, they have a high surface area and a wide pore size distribution that allows for a fast transport.

Tin oxide can be modified in specific ways to increase its versatility for certain applications. For example, it can be doped with antimony to obtain electrically conductive antimony doped tin oxide (ATO) for electronic or electrocatalytic applications. Metal nanoparticles can be loaded onto the material to optimize its sensitivity, response time and selectivity of sensor materials or provide active centers in catalysts.

There are several approaches reported to synthesize tin oxide aerogels. Wu et al. described an all inorganic route, where the spontaneous formation of a tin oxide gel is induced by increasing the pH value caused by diluting a solution of tin(IV) chloride in a water/ethanol mixture.¹⁰ Most other published methods require organic reactants. Like many other metal oxides, tin oxide gels can be formed by the hydrolysis of tin alkoxides.¹¹ By adding antimony alkoxide to this hydrolyzation route conductive antimony doped tin oxide aerogels can be obtained.⁸ Furthermore, the ATO gels can be loaded with palladium particles with a post preparative treatment to obtain a potential fuel cell catalyst.¹² Harreld et al. synthesized aerogels via a non-hydrolytic approach by the condensation of tin alkoxides and tin chlorides.¹³ Baumann et al. presented a facile method to synthesize tin oxide aerogels from inexpensive tin(IV) chloride, but they used carcinogenic and highly volatile propene oxide.¹⁴ This method was modified by Correa-Baena by adding an antimony precursor to obtain conductive ATO aerogels.^{15,16} The route by Rechberger et al. to conductive ATO aerogels includes several steps.¹⁷ First, they prepared nanoparticles in organic solvents assisted by microwave radiation. A highly concentrated aqueous suspension of these particles can be gelled by a heat treatment..

However, to date there is no report on a route leading to modified tin oxide aerogels that do not require expensive or dangerous reactants and that can be performed with low effort. Using inorganic reactants and water as the solvent is desirable, because of low cost and less impact on the environment. Tin chlorides are inexpensive and soluble precursors for an aqueous approach, but adsorbed halides from the precursor would have a negative influence on the sintering behavior of metal oxides during a thermal treatment.^{18–20}

In this study we present a very facile, all-inorganic route to high surface area tin oxide aerogels. The tin precursor used in this halide-free method are sodium or potassium salts of the hexahydroxostannate(IV) anion. It is known, that solutions of hexahydroxostannate(IV) form gel like precipitates if two equivalents of acid per equivalent tin are added.²¹ But so far, these hydrogels have not been supercritically dried to obtain tin oxide aerogels.

Results and Discussion

Formation of tin oxide sol

Adding a weak coordinating acid such as nitric or acetic acid to an aqueous solution of hexahydroxostannate results in a turbid solution. When less than 2 equivalents (eq.) are added, the solution becomes clear again after some minutes. If more than 2 eq. acid are added, the turbidity does not vanish and a hydrogel sediments. The turbidity indicates that there is a formation of particles and large aggregates. The vanishing of the turbidity in the case of less than 2 eq. H^+ added indicates the dissolution of these aggregates. The resulting particle sol is stable for weeks even in high concentrations of up to 1 wt%.

The dynamic light scattering (DLS) of the sol measured at least one hour after addition of nitric acid shows small particles with an average diameter of 3.2 nm, the distribution is broad with a standard deviation (σ) of 1 nm (Figure 1).

Moreover, the dependence of the particle size on the stannate concentration and equivalents of nitric acid was investigated. The mean diameters, determined by DLS, are shown in boxplots in Figure 1. The mean diameters range from 2.8 to 4.1 nm. The σ of the individual size distributions vary from 0.8 to 1.2 nm. A high stannate concentration of 0.133 mol/L (2 wt.% if fully transformed to SnO_2) leads to a sol with larger particles. The minimum average particle size of 3 nm is observed for a number of 1.5 eq. nitric acid. A low amount of 0.5 eq. or a large amount of 1.9 eq. nitric acid, which is close to the point where gelling starts, leads to larger particles of 3.6 and 3.3 nm, respectively.

Gel formation

The sol used for further studies is obtained by addition of 1.5 eq. of nitric acid. It can be destabilized to form a voluminous and turbid hydrogel by a second addition of acid to a total of more than 2 eq. H^+ per stannate ion. The duration of the gelation by a second addition of acid depends on the type and amount of acid and can further be controlled by temperature. As it can be seen in Table 1, the gel formation always occurs almost immediately if the pH during gelation is in the range from 2-3 either by addition of weak acetic acid or low excess of nitric acid. If a large excess of strong nitric acid is added, resulting in pH value below 1, the duration of gel formation is expanded to several minutes. Only in this case the duration can be significantly influenced by temperature.

Table 1: Gelation times using different amounts of nitric or acetic acid at different temperatures.

Acid	Total number of H^+ eq.	Resulting pH	Temperature	Gelation time*
Nitric Acid HNO_3	2.5	2.3	RT	10 s
		0.7	RT	30-45 min
	5		0 °C	4-6h
			70 °C	30 s
Acetic Acid HOAc	2.5	3	RT	< 5s
		2.8	RT	< 5s
	5		0 °C	10 s
			70 °C	< 5s

* Approximated duration until maximum turbidity and starting of flocculation or sedimentation of the hydrogel

The dependence of gelation times on pH can be explained by the colloidal stability of the charge stabilized tin oxide particles. Zeta potential measurements on ATO particle dispersions by Li et al. show that the zeta potential and colloidal stability is minimal in the pH range from 2-3 and increases for pH values lower than 2.²² Besides, the particle sol can be destabilized to form a gel by addition of organic solvents like acetone or ethanol. In this case the gel formation takes place within seconds. In contrast to the hydrogels formed by acid addition, these solvogels are compact and opaquely white.

For the ease of preparation a gel formation with an excess of nitric acid at room temperature is preferred. The gelation time is relatively short but allows complete mixing without damaging the forming gel structure by stirring. The presented route is a fast and convenient method to obtain tin oxide aerogels. Hexahydroxostannates are inexpensive tin precursors and only water as a solvent and diluted acids as low hazardous reagents are needed. For supercritical drying (SCD) the exchange with acetone and carbon dioxide is necessary. The method can easily yield material in large scale, just limited by the supercritical drying process.

Characterization of pure tin oxide gels

Figure 2 shows the powder X-ray diffractograms (XRD) of gels formed by addition of nitric acid and acetone in comparison. Both patterns exhibit only reflexes of cassiterite type SnO_2 . This shows that tin(IV) oxide particles are formed after the first addition of acid and that these do not change if gelation is induced by a second addition of acid. The very strong reflex broadening indicates very small particles or a poor crystallinity.

The nitrogen physisorption isotherm for the obtained aerogels is typical for aerogels (Figure 3, top). According to IUPAC classification, it is a type II isotherm with multilayer adsorption and no plateau at high relative pressures, which is a characteristic of samples containing macropores.²³ The hysteresis indicates capillary condensation in the mesopores. The specific surface area (SSA) of aerogels prepared by addition of acid at room temperature is in the range of 340-375 m^2/g , which is close to the best reported values of 383 m^2/g for tin oxide aerogels obtained via the epoxide method.¹⁴ The SSA of aerogels prepared by the addition of acid at 0 °C or 70 °C is lower and ranges from 267-330 m^2/g . Gels obtained by the addition of ethanol to a tin oxide sol have much lower SSA of 110 m^2/g . The tin oxide aerogels display the typical wide pore size distribution, with a maximum around 10 nm (Figure 3, bottom).

Scanning and transmission electron microscopy (SEM and TEM) was used to characterize the morphology of the gels. SEM investigations reveal a sponge-like structure with large variety of pore sizes (Figure 4 a). From the TEM images in Figure 4 b and c it can be seen that the gel formed by the addition of acid is a fine network of small primary particles of 3-4 nm in diameter. The diameter of the primary particles in the gel matches very well with the nanoparticle diameter obtained from DLS measurements of the initial sol. Figure 4 d shows the structure of an aerogel formed via the destabilization of a tin oxide sol by applying ethanol. The primary particles form large aggregates that are connected to a network. The compact aggregates exhibit a small internal surface area, confirmed by nitrogen physisorption measurements.

Conductive ATO aerogels

The stannate route to obtain tin oxide can easily be modified by adding hexahydroxoantimonate(V) to the hexahydroxostannate solution prior to the first addition of acid. The duration of the gelation upon the second addition of acid is shortened with increasing amount of antimony to ten seconds at room temperature when the Sb content is 10 at%. Please note that the addition of acid to a solution of hexahydroxoantimonate without hexahydroxostannate leads to the formation of a compact precipitate but not a hydrogel.

After supercritical drying the resulting ATO aerogels appear completely white. Upon a subsequent annealing at 550 °C in air the ATO gels turn blue. This indicates an incorporation of Sb(V) ions in the tin oxide lattice, which leads to the formation of oxygen vacancies. The resulting degenerated n-type semiconductor material has a plasmon absorption onset in the orange to red part of the visible spectrum.²⁴ Hence, the blue color is more intense for samples containing more Sb.

The atomic ratio of Sb to Sn was studied by energy dispersive X-ray (EDX) analysis for the samples with precursor ratios of 5 and 10 %, respectively. The result of the analysis was a Sb/Sn ratio of 4.5 ± 0.4 at% and 10.1 ± 0.6 at%, respectively. Accordingly, the Sb from the hexahydroxoantimonate precursor is completely incorporated in the resulting gels.

The conductivity of calcined ATO gels was characterized in a pressure cell similar to the one deployed by Ozouf and Beauger.⁸ The measured specific conductivities are listed in 2: Table 2.

Table 2: Specific electric conductivity of ATO aerogel samples calcined at 550 °C

Sb content (at%)	0	2.5	5	7.5	10
Specific conductivity (S/cm)	$1.4 \cdot 10^{-5}$ *	0.017	0.053	0.13	0.14

* non-ohmic behavior, conductance calculated from current measured at voltage of 100 mV.

The SSA of the ATO gels after supercritical drying and after calcination is shown in Figure 5. The SSA of the tin oxide aerogels after supercritical drying is only slightly decreased by the addition of antimony, but they are still larger than 300 m^2/g . After calcination at 550 °C the aerogels retain a SSA of approximately 100 m^2/g . Furthermore, samples with higher antimony content exhibit larger SSAs.

Table 3 shows the specific conductivity and SSA of the ATO aerogel with 10 at% Sb obtained via the stannate route in comparison to ATO gels reported in the literature. The ATO gel from the stannate route reaches the same conductivity as samples prepared by Ozouf and Beauger or Rechberger *et al.*, who needed harsher calcination temperatures and a UV radiation treatment for 30 h prior to calcination in the latter to obtain good conductivity, respectively. Rechberger *et al.* reported on ATO aerogels, that actually samples with 5 at.% Sb showed better conductivity, but the UV treatment was only done with samples containing 10 at.% Sb.. The ATO aerogels from the stannate route exhibit the largest SSA, due to the mild temperatures and large SSA before the calcination

Table 3: Specific Conductance and SSA of ATO aerogels from this work compared to reported values from the literature.

Reference	Sb content (precursors) (mol%)	Treatment / Calcination	Specific conductivity (S/cm)	SSA (m ² /g)
Stannate route	10	550 °C/2h	0.14	130
Ozouf and Beauger ⁸	10	600 °C/6h	0.15	87
Rechberger <i>et al.</i> ¹⁷	10	UV+500°C/2h	0.027	117
Correa-Baena <i>et al.</i> ¹⁶		UV+650°C/2h	0.15	90
	15	800 °C/6h	0.071	
	20			38

The XRD pattern of the calcined ATO samples in Figure 6 only shows reflexes of cassiterite SnO₂. In contrast to the calcined ATO aerogels prepared by Ozouf and Beauger no significant shift for the positions of the reflections is observed.⁸ Caused by the thermal treatment, the crystallites fuse to larger particles, which results in narrower reflexes than observed for the aerogel right after supercritical drying. The FWHM of the reflections increases with the Sb doping level. For the (1 1 0)-reflection it changes from 1.60° for the calcined pure tin oxide gel to 2.07° for the sample containing 10 at% Sb. This indicates that the crystallite size is smaller for samples that contain more antimony, which explains the higher SSA.

The effect of the antimony content on crystallite size and SSA is in agreement with results of Rechberger *et al.* and Correa-Baena *et. al.*, who also found that the crystallite size is smaller and the retained SSA of calcined aerogels is larger for samples with higher antimony content.^{16,17}

Incorporation of noble metal particles by cogelation

Citrate stabilized noble metal particles were synthesized via aqueous routes using sodium borohydride as a strong reducing agent.^{25,26} These yield small spherical gold particles with a diameter of 4-5 nm and platinum particles with a diameter of 3-4 nm, respectively. The sols of the metal particles can be directly mixed with the tin oxide particle sol without any treatment like washing, exchange or removal of the stabilizer, keeping this method very simple. When a noble metal nanoparticle solution is mixed with a stannate solution, the colloidal stability is decreased due to the high pH value and ionic strength. Nevertheless the noble metal particles are not destabilized upon mixing with the tin oxide sol as the ionic strength and pH value of the stannate solution are decreased to moderate values by the acid addition to form the tin oxide particles.

The second addition of acid destabilizes tin oxide and noble metal particles simultaneously leading to the gel formation. As the TEM picture in Figure 7 shows, the excess of tin oxide particles prevents the formation of aggregates of metal particles leading to a homogenous dispersion of noble metal particles on the tin oxide gel, even with a noble metal loading of 10 wt%.

The noble metal contents were determined for Au 5.4±0.6 wt% and for Pt 5.6±0.3 wt% and 10.9±1.1 wt% Pt, respectively, by EDX analysis. This matches the targeted compositions of 5 wt% and 10 wt%, respectively.

The SSA of the mixed aerogel is only slightly decreased by the addition of sodium citrate or citrate stabilized noble metal particles, as the values in Table 4: SSA of mixed noble metal/tin oxide aerogels. show.

Table 4: SSA of mixed noble metal/tin oxide aerogels.

Sample	Pure SnO ₂	SnO ₂ + citrate	5 wt% Au	5 wt% Pt	10 wt% Pt
SSA (m ² /g)	342	310	335	320	302

The XRD pattern of the aerogel loaded with platinum particles after SCD in Figure 8 shows additional reflections at 39.8° and 46.2° that correspond to the (1 1 1) and (2 0 0) lattice planes of platinum, respectively. The reflexes are more pronounced for the sample with the higher loading of 10 wt%. The peaks are broadened due to the small size of platinum particles (similar for Au/SnO₂, not shown here).

CO Oxidation

A tin oxide aerogel and two xerogels containing 5 wt% Au particles were tested in catalytic CO oxidation. As the conversion plot in Figure 9 shows, the initial activity of the aerogel and the xerogel dried from hexane during the heat up phase is lower than that of the xerogel. Most likely, this behavior can be explained by organic residues and CO₂ from the supercritical drying process. These have to be removed from the aerogel or the xerogel (hexane) by heating first. At 200 °C, both, aerogel and xerogel (water) show high CO conversion of 95 %, the xerogel (hexane) only reaches 75 % conversion. After activation at 300 °C in O₂/N₂ stream the activity is further increased, resulting in nearly full conversion >97 % at 200 °C for the aerogel and xerogel (water). The xerogel (hexane) shows conversion of 96 % but significantly increased its activity compared to 200 °C before the activation. The actual performance of the catalyst is rated by the conversion at low temperature after the activation. The xerogel (water) shows the best results, with still 77 % CO conversion at 50 °C. The aerogel and the xerogel (hexane) show similar, but lower conversions of 68 % and 67 %, respectively, at the same temperature stage. It seems that the better retention of the pore structure by supercritical drying or drying from hexane with low surface tension does not have a positive influence on the catalytic performance in this case. The CO molecule is rather small and the diffusion to the active site is not the rate limiting step in this reaction. Unlike the xerogel (water) the aerogel and the xerogel (hexane) were in contact with organic solvent before drying. Therefore we it is assumed that the contact with organic solvents or the residues adsorbed on the surface after drying caused a degradation of the gold surface. Unfortunately, there is no way to determine the specific Au surface area by TEM imaging, because even if the average diameter of the Au particles is known, the fraction of the particle surface covered by contact to the tin oxide support remains unknown.

The catalytic performance of the Au/SnO₂ gels does not compete to 2 nm small Au particles supported on TiO₂ or Fe₂O₃ obtained by impregnation or coprecipitation route. Those catalysts reach full conversion even at low temperatures.²⁷ The performance of the aerogel catalyst may be improved by using smaller Au particles for cogelation, but the synthesis requires stronger ligands such as CTAB or organic media. Before cogelation the necessary ligand exchange or phase transfer without agglomeration of very small Au particles is challenging. Strong adsorbing amine or even thiol ligands may also block catalytic sites.

This work shows the use of mixed aerogels obtained by cogelation of preformed particles. By separate colloidal synthesis it is possible to form alloyed particles or particles with distinct facets. Using these in a cogelation like the one presented here allows the preparation of catalysts tailored to specific reaction that hardly can be obtained by classical coprecipitation or impregnation routes. Furthermore, it also may be used for tin oxide based sensor materials whose behavior and selectivity is enhanced by metal particles.

Conclusions

Tin oxide aerogels were synthesized by a facile, all-inorganic route starting with hexahydroxostannate precursors. The gels exhibit a sponge like morphology and high specific surface areas up to 375 m²/g.

The synthesis route can be modified by adding hexahydroxoantimonate to obtain antimony doped aerogels, which show electrical conductivity after calcination in air at 550 °C. Samples containing 7.5 and 10 at% Sb exhibit the best conductivity and retain a specific surface area of up to 130 m²/g, which is the highest value for ATO aerogel samples calcined at this temperature.

With this method it is also possible to obtain mixed gels by cogelation. In this, the gelation of the tin oxide sol is induced after mixing it with a sol of other nanoparticles, which was exemplary shown for gold and platinum nanoparticles. The particles are evenly distributed over the gel without agglomeration. The good dispersion of the Au nanoparticles is shown by catalytic tests of the CO oxidation, which is sensitive to the particle size.

To conclude, this synthesis method is very facile as it can be done in beakers at room temperature and avoids expensive or dangerous reagents. It can be easily modified to obtain conductive ATO aerogels or gels loaded with other nanoparticles.

Future work should center on applications that benefit from the large specific surface area and the transport properties caused by the wide pore size distribution of the tin oxide aerogel, such as catalysis or sensors.

Experimental

This Section contains only a brief description of the actual tin oxide aerogel synthesis. For details about characterization and test series see the Electronic Supporting Information.

In order to obtain tin oxide sol 1.5 mmol nitric acid were added to a freshly prepared solution of 1 mmol sodium or potassium hexahydroxostannate in 40 mL deionized water under vigorous stirring. The solution turns turbid but

clears again after some minutes. The sol is stirred for one more hour. The sol can be destabilized to a solvigel by the addition of an organic solvent (ethanol) or a further addition of acid to a total amount of more than 2 eq. H^+ per stannate ion. The gels are washed several times with water and the solvent exchanged to acetone. Supercritical drying was performed after the exchange of the acetone against liquid CO_2 in an autoclave and heating the closed autoclave to 40 °C. The CO_2 becomes supercritical and is slowly released.

To obtain ATO aerogels 2.5 to 10 % of the potassium hexahydroxostannate are replaced by potassium hexahydroxoantimonate(V) prior to sol synthesis. While calcining ATO aerogels at 550 °C in muffle furnace the gels turn blue.

Citrate stabilized Au or Pt particles are synthesized following the route of Brown et al.²⁶ or Bigall et al., respectively.²⁵ The noble metal particle sols are mixed with the tin oxide sol without any treatment and cogelation is induced by the addition of 3.5 mmol nitric acid per mmol hexahydroxostannate. For the 5 % Au/ SnO_2 system also xerogels from water and hexane as solvent via conventional drying were produced and their catalytic performance in CO oxidation was tested.

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