

Scandium oxide nanoparticles produced from sol–gel chemistry

David Grosso*^a and Paul A. Sermon^b

^aLaboratoire Chimie de la Matière Condensée, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France. E-mail: grosso@ccr.jussieu.fr

^bDepartment of Chemistry, School of Physical Science, University of Surrey, Guilford, UK GU2 5XH

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A new method to produce scandium oxide nanoparticles with dimensions <80 nm is reported. This method could be of great interest for homogeneous incorporation of scandium oxide in specific materials, and in the production of thin Sc₂O₃ films. Colloidal particles of oxo–hydroxo scandium were synthesised by the sol–gel method. The particle morphology was characterised by TEM analysis. The particles so formed were lozenge shaped platelets (*ca.* 66 × 37 × 4.5 nm) and were highly stable in suspension in alcoholic solution. The xerogel material was produced by slowly evaporating the solvent from the sol. Its thermal stability, structure and composition were deduced from XRD, TGA–DSC, N₂-BET isotherms, ¹³C{¹H} NMR CP MAS and FTIR investigations. The particle morphology was retained upon calcination at 773 K, and the bulk xerogel exhibited a mesoporous structure with a surface area of 180 m² g⁻¹. Sc₂O₃ porous xerogel optical coatings were produced on fused silica substrates by dip coating. As shown by UV transmission experiments, these films exhibited a high transparency in the wavelength range 200–1000 nm, and refractive indices up to 1.84 at 350 nm when calcined at 773 K.

Introduction

In the past, scandium sol–gel chemistry has not been well developed and scandium oxide has only been considered for specific applications such as a dopant in garnet lasers,¹ a stabiliser for zirconia, or a densifier in silicon nitride.^{2,3} Its presence can also be found in mixed nickel–copper oxides to produce materials that are NO₂ sensitive.⁴ Catalytic applications have been studied in terms of propan-2-ol decomposition and CO oxidation on surfaces of porous Sc₂O₃ bulk materials synthesised *via* precipitation in aqueous medium.^{5,6} More recently, the potential application of high-power pulsed UV lasers in inertial confinement fusion has stimulated the study and the development of new materials with high refractive index, high transparency at the emitted radiation, and good thermal stability. These can be used as components for mirrors, shields, protective layers and polarizers. Scandium oxide is potentially suitable as a material for such applications because of its high bulk refractive index ($n_H = 2.0$ at $\lambda = 300$ nm), its high band gap (5.7 eV, corresponding to an UV cut-off of 215 nm), and its high melting point (2753 K).⁷ For multilayer UV-mirrors, scandia coatings, produced by chemical vapour deposition, have already shown high reflective properties and higher laser damage resistance than any other high index material deposited by such physical methods.⁸ Unfortunately, the latter technique produces dense optical films that exhibit poor mechanical resistance.⁹ High density materials are required for highly reflective films. On the other hand, when irradiated at high energy, a too high density of the film induces a low thermal relaxation, and therefore a low mechanical stability. By contrast, highly porous coatings exhibit lower degradation induced by thermal dilatation because they tend to be more responsive to energy relaxation throughout the network. High refractive index porous films are already used as UV optical components, and are usually made of deposited nanoparticles of ZrO₂ or HfO₂ produced *via* sol–gel chemistry. The colloidal oxide particles are *softly* deposited *via* dip or spin coating, leading to porous films with better mechanical properties than CVD deposited films. In addition, liquid-

deposition methods offer advantages in terms of low cost and ability to coat large and irregular shaped substrates, with a good control on the thickness and structure.¹⁰

A simple method to produce highly stable colloidal particles of scandium oxide by sol–gel chemistry in an alcoholic medium is reported here. These particles are highly stable *lozenge* shaped platelets suspended in methoxyethanol. They would be of great interest for homogeneous incorporation of fine particles of scandium oxide in the materials described above. Homogeneous thin films (30–100 nm thick) are produced by dip coating fused silica substrates. The optical properties of bare and thermally treated (773 K) coatings are briefly explored by UV spectroscopy.

Experimental

Preparation of scandia sol

ScOOH-based platelet-lozenge shaped particles were produced from Sc(acac)₃ (acac = acetylacetonate (pentane-2,4-dionate)) (π -KEM). The precursor was dissolved in 2-methoxyethanol (MOE) (Aldrich) in which a methoxyethanoic solution containing a ratio (*r*) of deionised H₂O to Sc^{III} of 4 (pH = 7.5) was slowly added (the final Sc^{III} concentration was adjusted to 0.03 mol dm⁻³). MOE is very hygroscopic, and absorbed water from the atmosphere is often sufficient to initiate hydrolysis of the precursor. Before being aged for two weeks, the solution was refluxed until the yellow colour, corresponding to solvated Sc(acac)₃, vanished and a light bluish aspect, corresponding to the presence of the suspended particles, simultaneously appeared. The final sol was centrifuged in order to remove larger aggregates. After being sealed and aged for four months, the sol developed a flocculate accompanied by a sudden increase of the viscosity (*i.e.* $\eta = 1.55$ cP between 1 and 100 days ageing, $\eta = 1.90$ cP after 123 days ageing). A transparent gel could be obtained *via* very slow evaporation of *ca.* 70% of the MOE solvent at room temperature and pressure.

Preparation of coatings

Thin films were produced by dip coating on optically polished fused-silica disks of dimensions 5×45 mm. Surfaces were first cleaned with HNO_3 , before being washed with H_2O and dried with anhydrous ethanol and propan-1-ol. In order to produce thin films with optical thickness $H = 88.5$ nm (*i.e.* $H = hn = \lambda_o/4$, where H is the optical thickness, h the physical thickness, n the refractive index and λ_o the wavelength of maximal reflection), the withdrawal rate and the number of dips were adjusted to 0.30 cm s^{-1} and seven dips respectively. Before characterisation, and with the aim of eliminating multiple reflection effects, one of the coated sides was removed using $\text{HNO}_3\text{-H}_2\text{O-EtOH-PrOH}$. FTIR, ^{13}C CP MAS NMR, and TGA analyses showed the presence of acac groups, suggesting that hydrolysis was not complete. Such acac groups, remaining bound to the particles, induce an intrinsic absorption at $\lambda_{\text{max}} = 312$ nm (due to $\pi\pi^*$ or $n\pi^*$ electronic transitions of delocalised electrons),¹¹ reducing the optical performance of the film at 351 nm. In order to purify the coating from these organic species and to densify the structure, films were calcined at 773 K for 5 h in air.

Methods of characterisation

After deposition on carbon-coated copper grids, the dimensions of the scandium-based particles were measured from micrographs, taken with a transmission electron microscope (JEOL 2000fx TEM). The composition of the particles were previously determined by EDAX. The thickness of the particles were deduced from the measurement of the shadow dimension, obtained by vapour deposition of gold (incident angle of deposition = 60°) on the TEM grid supporting the particles. With the aim of verifying the particle morphology and structure after calcination at 773 K, the bulk material was redispersed in propan-1-ol and reanalysed by TEM.

The xerogel was obtained by solvent evaporation, before being ground, washed with ethanol, centrifuged and dried in vacuum at 373 K. The as prepared powder material was analysed using FTIR spectroscopy (Nicolet, Magma-IR550) using KBr discs containing 5% of sample by weight, and by ^{13}C NMR CP MAS spectroscopy on a Bruker MSL 400 MHz apparatus with the following conditions: rotor spin = 4000 Hz, $T_{90} (^1\text{H}) = 6 \mu\text{s}$, contact time $T_c = 2$ ms, and recycling delay = 5 s. N_2 -BET analyses was performed with 0.200 g of sample with a Micromeritics ASAP 2010 apparatus after outgassing *in situ* at 573 K. As a result of the high price of our precursor, BET values were calculated from only one measurement, and uncertainties are thus not quoted. TGA-DSC measurements were performed with 20 mg of sample, under O_2 , and at a heating rate of 5°C min^{-1} on a DuPont 2000 apparatus. X-Ray diffraction was also applied to finely ground pure samples, using a Cu-K α X-ray source, employing scan steps of 0.01° and an integration time of 60 s using a PW1710 apparatus.

Optical properties of coatings were deduced from UV transmission spectra (Perkin Elmer UV-NIR lambda 9). Refractive indexes were evaluated from the reflection coefficient at a quarter wavelength optical thickness, neglecting absorption and scattering factors. The refractive index (n_{fs}) of the fused silica substrate was taken as 1.474 at $\lambda_o = 351$ nm.

Results

Characterisation of ScOOH-based particles

EDAX obtained for ScOOH-based particles deposited on carbon coated copper grids indicated the characteristic energy dispersive peak of Sc at 4.05 keV. Particles were homogeneous and presented an anisotropic lozenge-platelet shape with average dimensions of 66 ± 8 nm length and 37 ± 5 nm width as shown in Fig. 1(a). After shadowing the particles with a thin

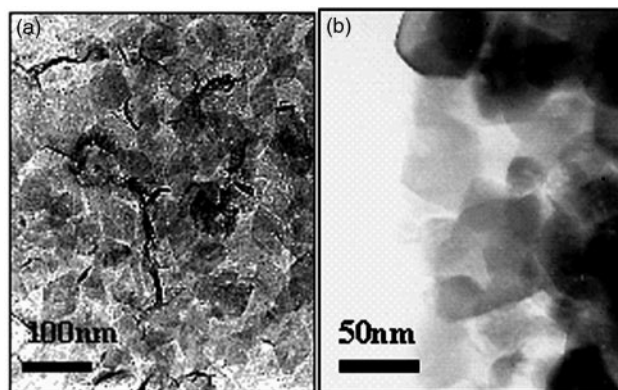


Fig. 1 TEM micrographs of (a) ScOOH-based particles (1 cm = 93 nm, $\times 58000$) and (b) Sc_2O_3 particles obtained by calcination at 773 K (1 cm = 48 nm; $\times 87000$).

layer of vapour deposited gold, the ScOOH-based particle average thickness was evaluated as 4.5 ± 0.5 nm according to TEM. The orientation of the shadowed particles with the plane, their potential overlapping and the fact that electron bombardment may affect their molecular structure, led us to assume that this measurement is only a close approximation of the real thickness.

Characterisation of the scandium oxy-hydroxide xerogel

FTIR spectra of the precursor, the dried xerogel, and the calcined materials are shown in Fig. 2. FTIR spectra of $\text{Sc}(\text{acac})_3$ exhibited $\nu(\text{Sc-O})$ bands at 439 and 650 cm^{-1} in addition to bands at 1580 and 1530 cm^{-1} corresponding to $\nu(\text{C-O})$ and $\nu(\text{C=C})$. Such bands are characteristic of the bidentate chelation of Sc^{III} by acac. After refluxing $\text{Sc}(\text{acac})_3$ in the presence of H_2O and MOE, characteristic bands of ScOOH were formed (*i.e.* $\nu(\text{OH})$ at 3400 cm^{-1} , $\nu(\text{O-H})$ at 469 and 607 cm^{-1}).¹² Both the $\nu(\text{C=C})$ and $\nu(\text{C-O})$ absorptions at 1530 and 1580 cm^{-1} , respectively, were still present but were less intense, suggesting that hydrolysis condensation occurred but that some acac was not exchanged and remained complexed to Sc^{III} . Low intensity bands at 1120 and 1074 cm^{-1} were attributed to $\nu(\text{C-C})$ and $\nu(\text{C-O})$ from methoxyethanoate groups, as a result of the exchange of some acac groups with

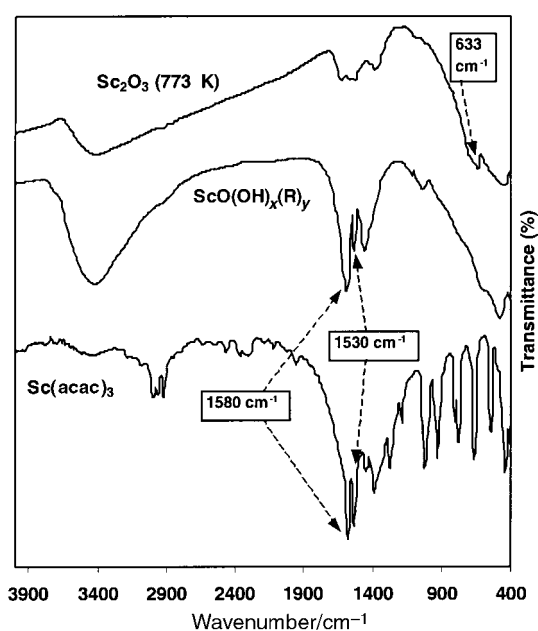


Fig. 2 FTIR spectra of the $\text{Sc}(\text{acac})_3$ precursor, the ScOOH-based xerogel ($R = \text{MOE}$ or acac) and Sc_2O_3 obtained by calcination at 773 K.

solvent molecules. Hence, the particles are composed of ScOOH units, but also contain acac and methoxyethanoate groups. The characteristic absorption of symmetric and antisymmetric stretching of RCO_2^- was not observed, suggesting that acetate groups, or ester byproducts, were not formed during the reaction. A sharp absorption band corresponding to $\nu(\text{Sc}-\text{O})$ at 633 cm^{-1} from Sc_2O_3 was visible only after calcining the compound at 773 K.

^{13}C NMR CP MAS spectroscopy was performed on the $\text{Sc}(\text{acac})_3$ precursor and on the washed and dried xerogel. In the spectrum of $\text{Sc}(\text{acac})_3$ (Fig. 3), two types of $-\text{CH}=\text{}$ groups are present (103.3 and 102.2 ppm) with relative integral ratios of 1:2, suggesting that two different configurations of complexing acac exist in the precursor. The same observation is seen for the CH_3 signals at 27.8 and 29.4 ppm. The presence of four C–O peaks at four different chemical shifts (188.8, 191.1, 191.7 and 196.3 ppm) confirms this observation, since the carbonyl groups are inequivalent in the chelating acac. The spectrum recorded for the ScOOH-based xerogel exhibits broader peaks ($\Delta v_{1/2} = 250\text{ Hz}$ for the xerogel *cf.* 55 Hz in the precursor spectrum), showing a larger distribution of chemical shifts. The ScOOH-based material also shows the presence of acac and methoxyethanoate groups as previously detected by FTIR. Bands at 24.5 and 26.5 ppm are attributed to CH_3 from chelating acac while the resonance at 103 ppm is assigned to $-\text{CH}=\text{}$ from acac in its enolic form. In addition, the presence of two chemical shifts for the C–O groups (192 and 182 ppm) suggests that the acac units contained in the particles are chelating, but may have several configurations. Carbon atoms from the methoxyethanoate groups are observed at 76.5 ppm ($\text{Sc}-\text{O}-\text{CH}_2$), 72.6 ppm ($\text{Sc}-\text{OCH}_2\text{CH}_2$), and 58.7 ppm (OCH_3). Therefore, organics contained in the washed xerogel powder are partly retained bidentate acac in enolic form and partly retained alkoxide from exchange with solvent. A low intensity resonance at 163 ppm could not be attributed. The determination of the relative quantity of acac and MOE could not be deduced from the integrals as the CP method is not quantitative.

Thermogravimetric analysis showed that the xerogel contained 13 wt% of physically adsorbed H_2O and MOE, and

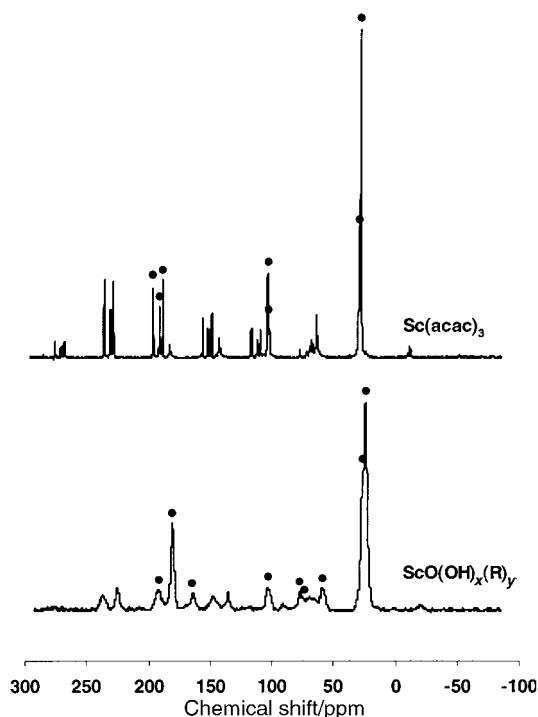


Fig. 3 ^{13}C CP MAS NMR spectra of the $\text{Sc}(\text{acac})_3$ precursor and the ScOOH-based xerogel ($\text{R} = \text{MOE}$ or acac).

27 wt% of bound organic groups (calculated from the dried xerogel weight) (Fig. 4). DSC analyses recorded endothermic activities from 353 to 393 K, related to desorption of water and MOE. Exotherms were present between 473 and 793 K in air, suggesting that the thermal decomposition of organics occurred in this temperature range (the exothermic peak at 525 K is attributed to MOE and those between 573 and 700 K to acac). The dehydration of ScOOH to Sc_2O_3 usually takes place at *ca.* 673 K (as reported for thermal treatment of $\text{Sc}(\text{OH})_3$ formed in aqueous medium¹³), and therefore cannot be observed as this overlapped with the loss of organic species.

The X-ray diffraction pattern in Fig. 5 was recorded for finely ground and dried ScOOH-based powder. It exhibits weak and broad Bragg peaks, characteristic of small and/or distorted crystalline particles which could not be properly indexed. However the larger inter-planar distance as calculated from the first diffraction peak is 11.6 Å. ScOOH is referenced in the literature with a $\gamma\text{-FeOOH}$ type lamellar orthorhombic structure which would be consistent with the anisotropic

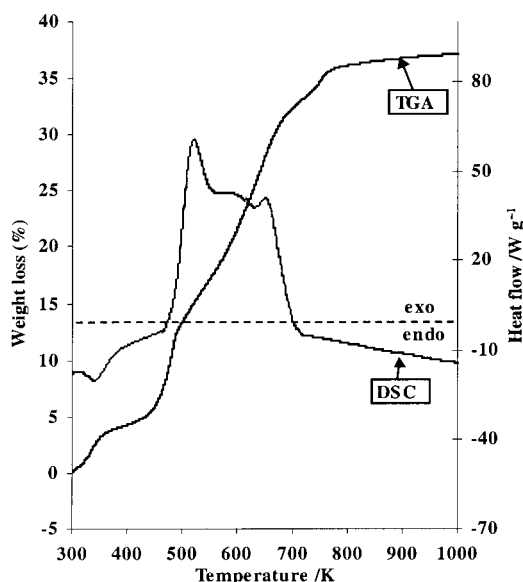


Fig. 4 TGA–DSC plots of the ScOOH-based xerogel.

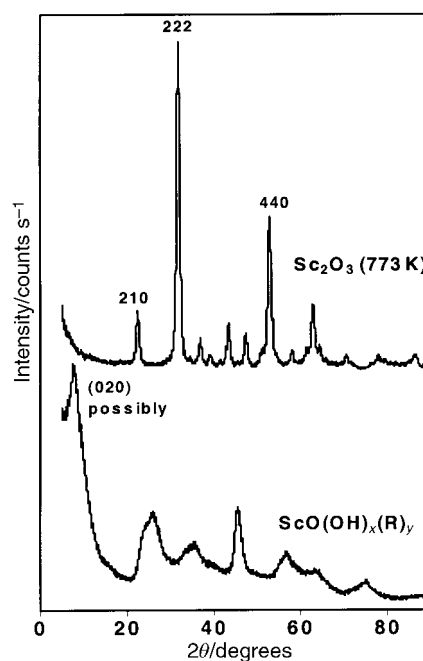


Fig. 5 Powder XRD spectra of the ScOOH-based xerogel ($\text{R} = \text{MOE}$ or acac), and Sc_2O_3 obtained by calcination at 773 K.

lozenge plate-like shape of our particles.¹⁴ After calcination at 773 K, the XRD pattern was characteristic of cubic Sc_2O_3 ($a=9.85 \text{ \AA}$) with exact relative peak intensities ($d(211)=4.02 \text{ \AA}$, $d(222)=2.84 \text{ \AA}$, etc.).¹⁵ The TEM micrograph of Fig. 1(b) shows Sc_2O_3 particles obtained after calcination at 773 K, redispersion in propan-1-ol and deposition on the TEM grid. The particles still retained their lozenge shape and size, suggesting that the transformation occurring during heat treatment did not affect the particle morphology. Hence, the final particles are cubic, and were formed *via* a topotactic transformation, characteristic of oxy-hydroxide lamellar compounds upon heat treatment.¹⁴ As a result, the initial structure of the particles are consistent with a $\gamma\text{-ScOOH}$ double layer structure with acac and MOE organic groups bound to some scandium atoms. According to the 27 wt% loss recorded by TGA (Fig. 4), less than a third of the scandium atoms are combined with organic ligands.

The N_2 adsorption-desorption isotherm recorded for the xerogel calcined at 773 K was of type IV with a capillary condensation hysteresis loop, suggesting that the structure is mesoporous (Fig. 6). The total BET surface area was estimated as $130 \text{ m}^2 \text{ g}^{-1}$, while the Langmuir surface area was calculated to be $180 \text{ m}^2 \text{ g}^{-1}$. The desorption cumulative pore volume (V_p) of pores was estimated as $0.14 \text{ cm}^3 \text{ g}^{-1}$, and the desorption average pore diameter d_p was 3.6 nm. Therefore the particles organised themselves into a mesoporous structure with small enough pores to prevent scattering of UV radiation. The low volume of pores indicates that the material is sufficiently dense to show a high refractive index. Materials calcined at 773 K show a high surface area that might be utilized for applications in catalysis.

Coating characterization

The UV-VIS transmission spectrum scandia-based films deposited on fused silica substrates is shown in Fig. 7. The background was previously recorded with two bare fused silica substrates disposed at normal incidence to the reference and analyzing beams. The optical properties and physical thickness deduced from these spectra are given in Table 1. The refractive indices were evaluated in terms of $1 - (T + A + S) = R = [(n^2 - n_{\text{FS}} n_{\text{air}})^2 / (n^2 + n_{\text{FS}} n_{\text{air}})^2]$ at a quarter wavelength optical thickness (*i.e.* $H = (\lambda_0/4)$), neglecting the absorption and scattering factors (*i.e.* $A=0$ and $S=0$).¹⁶ λ_0 is the wavelength of the minimum transmission corresponding to the first harmonic of the quarter-wave film, T is percentage of transmission at λ_0 , H is the optical thickness obtained from $H = nh = (\lambda_0/4)$, where h is the physical thickness of the film and n and n_{FS} are the refractive indices of the coating and the fused silica substrate at λ_0 respectively. The low absorption band,

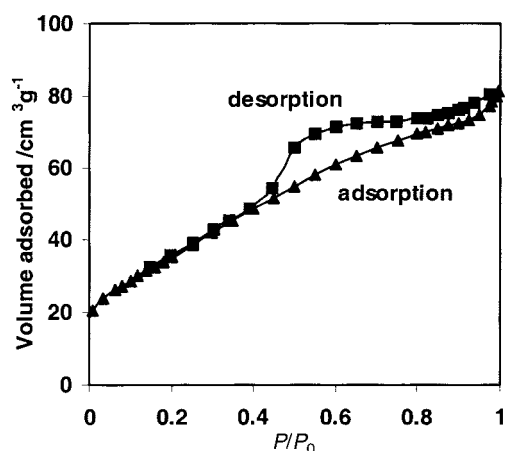


Fig. 6 N_2 adsorption-desorption isotherm at 77.5 K obtained for Sc_2O_3 obtained by calcination at 773 K.

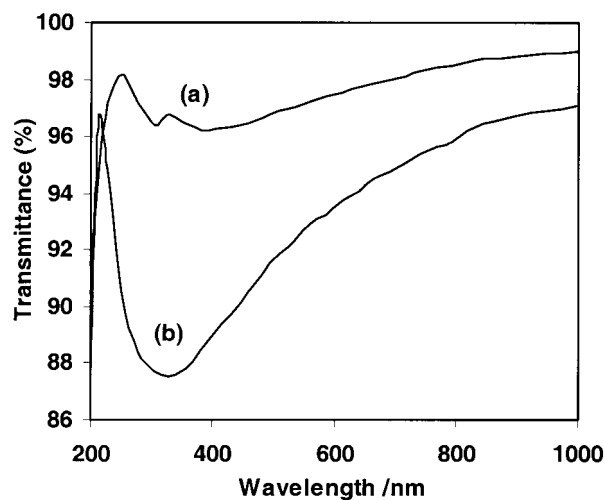


Fig. 7 UV transmittance of a single side coated substrate with (a) untreated ScOOH -based particles and (b) Sc_2O_3 particles obtained by calcination at 773 K.

present for the untreated film at $\lambda_{\text{max}}=312 \text{ nm}$, corresponds to electronic transitions of acac species remaining in the xerogel film. This absorption disappeared once the coating was thermally treated at 773 K, suggesting successful removal of this organic compound by thermal decomposition. The refractive indices were calculated to be 1.60 ± 0.01 for the untreated film and 1.84 ± 0.01 for the calcined film, the calcination being accompanied by a corresponding decreasing of the film thickness (h) due to densification of the layer ($h=60 \text{ nm}$ for as-prepared films and $h=45 \text{ nm}$ for calcined films). Thicker films calcined at 773 K show a transparency of $>99.5\%$ at wavelengths $>300 \text{ nm}$.

Discussion

Sc^{3+} generally adopts an octahedral symmetry, and three acac ligands fulfil this criterion leading to the stable $\text{Sc}(\text{acac})^{3+}$ complex and high temperatures reached at the MOE refluxing point (398 K), were required to initiate decomposition. Substitution of the first acac ligand by OH or $\text{OCH}_2\text{CH}_2\text{OCH}_3$ groups can then take place, accompanied by a decrease of the coordination number of Sc^{III} from six to five. Precondensation probably occurs by olation, owing to the incomplete coordination sphere of the initial intermediates. Chains composed of $\text{Sc}(\text{OH})_2(\text{R})$ units ($\text{R} = \text{acac}$ or MOE), attached by two bridging hydroxo bridges, may be formed and the polycondensation process can be continued *via* olation and oxolation between fully coordinated chains and non-fully coordinated oligomeric intermediates, leading to oxy-hydroxy-scandium based sheets with some acac and MOE groups attached to scandium atoms. The organic groups are proposed to be bound to apices of the octahedral units on each face of the double oxy-hydroxide sheets, blocking these sites and slowing potential condensation in this direction. The relative rates of oxolation-olation reactions, and the steric hindrance created by the presence of organic groups in addition to their poor leaving properties, lead to the formation of anisotropic particles with homogeneous lozenge-platelet shapes. The X-ray-diffraction pattern of the ScOOH -based particles exhibits Bragg peaks that could not be indexed satisfactorily. However, the particles contained reticular regions that diffracted to some extent, suggesting that they were not amorphous, which is consistent with their anisotropic shape. FTIR showed the characteristic vibration bands of the ScOOH lamellar structure. Upon calcination at 773 K, the particles undergo a transformation to cubic Sc_2O_3 , showing behavior commonly observed for lamellar oxy-hydroxide compounds such as $\gamma\text{-AlOOH}$ or $\gamma\text{-FeOOH}$ (*i.e.* a

Table 1 Optical properties of as prepared ScOOH-based coatings and Sc₂O₃ obtained by calcination

Treatment of scandia films	λ_0/nm	T (%)	H/nm	n_{FS}	n^a	h/nm
None	380	96.2	95	1.472	1.60	60
773 K in air for 5 h	330	87.6	82	1.479	1.84	45

^aUncertainty ± 0.01 .

topotactic transformation). The larger inter-planar distance, calculated from the first diffraction peak obtained for pure γ -ScOOH, is reported to be $d(020)=6.5 \text{ \AA}$.¹⁴ For our particles, the larger recorded distance of 11.6 \AA is almost double this value, suggesting that organic moieties may be located at the surface of the platelets, and also intercalated between the double oxy-hydroxide layers. Such a presence will lead to a variation of the lattice parameters with respect to the pure ScOOH structure. If 11.6 \AA is assumed to be $d(020)$, the lattice parameter b ($=23.2 \text{ \AA}$) is 10.2 \AA larger than the corresponding value (13.01 \AA) observed in the pure ScOOH structure. An inter-planar spacing difference of 5.1 \AA would be consistent with the presence of MOE and/or acac groups intercalated between the double oxy-hydroxide scandium sheets. However, as less than a third of the scandium atoms is combined with a MOE or an acac groups, a non-homogeneous distribution of the organic ligands is expected in the structure, leading to a variety of interplanar distances causing low resolution of the Bragg peaks. No information concerning the ratio of acac to MOE, or of the ratio of intercalated and surface bound acac or MOE could be obtained. As the thickness (e) of the calcined cubic Sc₂O₃ particles could not be obtained by a direct measurement, an approximate value of this dimension was calculated knowing the density of cubic Sc₂O₃ ($d=8.4 \text{ g cm}^{-3}$), the two other dimensions of the platelets ($L=66 \pm 10 \text{ \AA}$ and $l=37 \pm 5 \text{ \AA}$), the surface area of the material ($A=130-180 \text{ m}^2 \text{ g}^{-1}$), and assuming the surface area corresponds to the sum of the surface area of each particle taken separately. The thickness e given by the relation $e=2Ll/[AdLl-4(L^2+l^2)^{1/2}]$, has a value of $1.7 \pm 0.5 \text{ nm}$. Comparing this thickness with the thickness of the non-calcined particles ($e=4.5 \pm 0.5 \text{ nm}$), the thickness reduction is consistent with the hypothesis for the initial structure of the particles, *i.e.* that the organic ligands may be combined with scandium atoms on the surface of the platelets and also within the inter-sheet spacing. Similar lozenge shapes have been produced by sol-gel polycondensation to form $\text{Y}(\text{OH})_3$,¹⁷ and by thermohydrolysis of chelated oxo-hydroxy-iron precursors.¹⁸ The advantage of such flat scandia lozenge particles lies in their potential horizontal organization on a surface when deposited from a liquid phase. Therefore, thin films produced by dip-coating with the present material are expected to be relatively dense.

Conclusions

Results obtained from TEM investigation on the sol suggested that ScOOH-based particles were lozenge platelets with average dimensions $66 \times 37 \times 4.5 \text{ nm}$. Calcining the particles induces a topotactic transformation to cubic Sc₂O₃ with a contraction of the particle thickness to 1.7 nm owing to dehydration and loss of organic ligands. These particles are stable and could be used for homogeneous incorporation of scandium oxide in composite materials. In the present work, they were successfully used for the production of homogeneous optical coatings of high refractive index. Once calcined at

773 K, the cubic Sc₂O₃ coating exhibited a good transparency to UV radiation and a refractive index of 1.84. This refractive index is lower than that of bulk Sc₂O₃ (2.0 at 350 nm), suggesting a porosity of 16%. It is difficult to relate this value to the porosity obtained *via* N₂-BET measurements since films deposited by dip-coating are usually denser than the bulk material.¹⁹ The porous scandia coatings described here are composed of discrete particles and may accept higher mechanical deformation (lower interfacial stresses and high thermal relaxation) than denser CVD deposited Sc₂O₃ films. This improvement can be added to the lower cost involved using a liquid deposition method, and also the possibility of producing highly pure films by using highly purified the sol-gel precursors. Full characterisation of such scandia-based xerogel films will be published separately.

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