Tailoring the phase of Li–Al–O nanoparticles by nonaqueous sol–gel chemistry

Mattia Alberto Lucchini¹ · Elena Tervoort¹ · Mohamed Tarik² · Markus Niederberger¹

Received: 23 January 2017 / Accepted: 10 March 2017 / Published online: 3 April 2017
© Springer Science+Business Media New York 2017

Abstract A facile nonaqueous sol–gel synthesis for Li–Al–O nanoparticles with tunable stoichiometry and phase purity has been developed. Adjusting the reaction conditions, γ - Al_2O_3 , α - Al_2O_3 , LiAl_5O_8 , β - LiAlO_2 , and γ - LiAlO_2 nanoparticles can be synthesized. For the first time, the synthesis of phase-pure nanoscaled β - LiAlO_2 is obtained at low temperature. All the products were characterized by X-ray powder diffraction, Fourier-transformed infrared, small-angle X-ray scattering, transmission electron microscopy/scanning electron microscopy, nitrogen sorption and elemental analysis. The extensive characterization points out some main features for the products: phase purity, nanoscale size, high surface area, good thermal stability, and good dispersion in ethanol. These properties are rarely combined in a single product, making the proposed protocol an important tool for the future applications of Li–Al–O nanoparticles in the field of catalysis and absorptive materials.

Graphical Abstract Nonaqueous sol–gel chemistry: an easy and versatile protocol for compositionally tuneable, phase-pure, and high surface area Li–Al–O nanoparticles.

Keywords Nonaqueous sol–gel · Alumina · Lithium aluminate · Nanoparticles

Electronic supplementary material The online version of this article (doi:10.1007/s10971-017-4360-9) contains supplementary material, which is available to authorized users.

✉ Mattia Alberto Lucchini
mattia.lucchini@mat.ethz.ch

¹ Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, Zürich 8093, Switzerland

² General Energy Research Department, Paul Scherrer Institut, Villigen PSI, Villigen 5303, Switzerland

1 Introduction

Lithium-aluminium oxide nanoparticles (NPs) are fundamental components in many technological applications [1]. The possibility to use these materials as catalyst support [2–5], luminescent [6–9], ion-conductive [10, 11], and adsorptive materials [12–14] and in polymer nanocomposites [15–17] has been demonstrated. In the ternary Li–Al–O system, four phases of interest can be identified, namely, Al_2O_3 , LiAl_5O_8 , lithium aluminate (LiAlO_2), and Li_5AlO_4 [18]. Up to now, many protocols have been proposed for the synthesis of these compounds as nano-sized powders: sol–gel [18–20], chemical vapor deposition [21, 22], hydrothermal [23, 24], solid-state reaction [25, 26], combustion method [27, 28], self-flux synthesis [29], high energy ball milling [30], and homogeneous precipitation [31].

In spite of the many protocols available, the possibility to obtain nano-sized, phase-pure products at low temperature still represents a major challenge for most of the Li–Al–O phases. Indeed, the majority of the protocols lead to amorphous [9, 19, 31], hydrated [24, 32], or mixed-phase products [2, 29] requiring high-temperature synthesis conditions or additional annealing steps to obtain the desired final products. These additional processes have direct influence on the properties of the samples and a truly nano-sized product is usually not anymore available. In this respect, the development of a general approach for the synthesis of Li–Al–O NPs is highly desirable.

An additional difficulty arises from the numerous metastable structures available for each phase. For pure aluminium oxide, α - Al_2O_3 is the thermodynamically stable phase, where the oxygen sublattice is hexagonal-close-packed and aluminium cations occupy 2/3 of the octahedral sites [33]. In addition to the stable α -phase, many metastable phases (transition alumina, such as χ - Al_2O_3 , η - Al_2O_3 , δ - Al_2O_3 , κ - Al_2O_3 , θ - Al_2O_3 , γ - Al_2O_3 , and ρ - Al_2O_3) are reported to crystallize at lower temperature. These metastable phases are irreversibly converted in the stable α -phase upon annealing at high temperature [15, 34]. The presence of transition phases in the product strongly depends on the synthesis protocol and thermal treatment of the sample.

LiAlO_2 can crystallize in three different crystalline phases, namely, hexagonal α - LiAlO_2 , orthorhombic β - LiAlO_2 , and tetragonal γ - LiAlO_2 [35]. Among these, the α and β phases are known to be stable at low temperature and to convert into the high-temperature γ -phase upon annealing [36]. The conversion temperature α , $\beta \rightarrow \gamma$ depends on the synthesis parameters and lies between 400 and 1000 °C [36]. α - LiAlO_2 and γ - LiAlO_2 are the main component for ceramic matrixes in molten carbonate fuel cells due to their low solubility in the electrolyte and relatively good stability at high temperature and operating conditions [37–39]. β - LiAlO_2 phase is less investigated due to the difficulties in the synthesis of a phase-pure product and to the limited temperature range of stability.

LiAl_5O_8 is reported to exist in two crystalline phases, a low-temperature primitive cubic (ordered) and a high temperature spinel form (disordered) [40], whose catalytic activity and luminescent properties are reported to be significantly different [2].

Regarding the great variety of stoichiometry and phases available in the Li–Al–O system, it is evident that the possibility to develop a reliable protocol for the synthesis of a phase-pure product with small crystal size and high surface area is a crucial step for the application of these materials. In this regard, a nonaqueous sol–gel route represents an appealing option.

In the last 20 years, nonaqueous sol–gel chemistry proved to be an extremely powerful tool for the synthesis of

single crystalline nano-sized powder of metal oxides [41]. The main advantage of this approach is the precise control over composition, dimension and crystallinity of the product, combined with the possibility to easily disperse the final product both in aqueous and organic solvents. This strategy has been already adopted for the synthesis of crystalline γ - Al_2O_3 [42] and alkaline earth aluminate NPs [43]. We developed a nonaqueous sol–gel protocol for the synthesis of Li–Al–O NPs with tuneable stoichiometry. In particular, phase-pure γ - Al_2O_3 , α - Al_2O_3 , LiAl_5O_8 , β - LiAlO_2 , and γ - LiAlO_2 NPs were successfully synthesized. All the products are characterized by phase purity, good crystallinity, small crystal size, and high surface area, and are easily dispersible at high concentration in ethanol-based solvents. Considering the versatility of the proposed protocol and the appealing properties of the synthesized particles, we expect our synthesis to open up new possibilities for the application of Li–Al–O NPs, especially in the fields of catalysis, solid ionic conductors, luminescent materials, and particle-based aerogels.

2 Experimental

2.1 Materials

Aluminium acetylacetonate (Aldrich 99%), benzyl amine (Fluka $\geq 99\%$), lithium chloride (anhydrous, Sigma Aldrich $\geq 99\%$) were stored under Ar atmosphere. Ethanol, acetone, and hexane were purchased from Sigma-Aldrich and used as received.

2.2 Synthesis of Li–Al–O NPs

Aluminium acetylacetonate (2.5 g) was first dissolved in benzyl amine (100 ml) together with the proper amount of lithium chloride (Table 1) inside an Ar-filled glovebox. The solution was then transferred into a steel autoclave (200 ml Parr acid digestion bombs), and carefully sealed. The autoclave was kept in a furnace at 200 °C for 12 h. The resulting suspensions were centrifuged, the precipitates thoroughly washed with ethanol and acetone, and subsequently dried in air at 60 °C. If needed, the washed powders can be easily dispersed and stored in ethanol as dispersion with concentration as high as 40 mg/ml without observable sedimentation over weeks (Fig. S1).

2.3 Characterization

X-ray powder diffraction (XRD) patterns were recorded using a PANalytical diffractometer (Empyrean, Cu K_α radiation). Crystallite radius (r_{XRD}) was estimated from the Scherrer equation (after correction for instrumental

Table 1 Summary of synthesis parameters and analytical results (ICP-MS, XRD, SAXS, and BET)

Phase	Starting sample	Annealing temperature	ICP-MS Li:Al	XRD r_{XRD} [nm]	SAXS			BET	
					$r_{\text{SAXS, av}}$ [nm]	$r_{\text{SAXS, fr}}$ [nm]	RSD%	SSA [m ² g ⁻¹]	r_{BET} [nm]
γ -Al ₂ O ₃	LiAl_0	— ^a	0:1	1.5	2.4	1.8	62	423.7	1.9
α -Al ₂ O ₃		1100 °C	0:1	41.0	42.1	44.2	34	9.8	77.1
LiAl ₅ O ₈	LiAl_0.2	900 °C	—	4.5	5.2	4.5	32	111.8	7.4
β -LiAlO ₂	LiAl_10	— ^a	1:1	5.0	8.9	2.0	72	193.9	5.7
γ -LiAlO ₂		800 °C	1:1	11.3	17.1	16.2	39	56.2	20.4

r_{XRD} crystallite radius calculated with Eq. 1, r_{SAXS} crystallite radius calculated from SAXS measurements, SSA specific surface area, r_{BET} crystallite radius calculated with Eq. 2

^a Sample as prepared

broadening):

$$r_{\text{XRD}} = \frac{K\lambda}{2\beta \cos \theta}, \quad (1)$$

where K is a dimensionless shape factor (a value of 0.89 was used), λ is the X-ray wavelength, and β and θ are the full width at half maximum and the angle at the maximum intensity of the considered diffraction peak, respectively. An instrumental broadening of 0.1 degree was considered.

Nitrogen sorption experiments were carried out on a Quantachrome Autosorb-iQ-C-XR at 77 K, with nitrogen (99.999%) and helium (99.999%) provided by PanGas AG, Switzerland. Before the measurement, the samples were outgassed in vacuum at 100 °C for 24 h. Crystallite radius was calculated from the measured surface area (r_{BET}), assuming spherical particles, from the following equation [44]:

$$r_{\text{BET}} = \frac{3}{\rho \text{ SSA}}, \quad (2)$$

where SSA is the specific surface area calculated by the multipoint Brunauer–Emmett–Teller (BET) method (desorption branch), ρ is the solid density, and 3 is a geometrical factor.

Scanning electron microscopy (SEM) analyses have been performed on a LEO 1530 Gemini instrument working at 5 kV. For the sample preparation, a small amount of powder was dispersed in iso-propanol and after sonication few drops of the dispersion were deposited on Si substrate. After deposition, the samples were sputtered with 3 nm of Pt.

Transmission electron microscopy (TEM) analysis of the products were performed on X-FEG FEI Talos, operating at 200 kV coupled with Super X energy-dispersive X-ray spectrometer. The samples were prepared dispersing dry powder in iso-propanol. After sonication, few drops of the colloidal dispersion were deposited on a copper-grid support with perforated carbon foil.

Fourier-transformed infrared spectroscopy (FT-IR) measurements were performed on a Bruker Alpha instrument in attenuated total reflectance geometry.

Elemental analysis was carried out by an inductively coupled plasma mass spectrometer (ICP-MS) (Agilent 7700×). The samples were first digested in 3 ml HNO₃ (65%) and 3 ml HCl (30%). A second digestion run was performed after adding 0.5 ml HF (50%) to completely dissolve the thermally treated samples. All the samples were diluted in a 1% HNO₃ solution with a total dilution factor between 1×10^6 and 3×10^6 . Li and Al standard solutions with concentrations between 0 and 100 ng/ml were prepared and used for calibration.

3 Results and discussion

NPs in the Li–Al–O system were synthesized using LiCl as additive in the reaction between aluminium acetylacetonate and benzyl amine. Lithium chloride was chosen since it does not react with benzyl amine under the selected reaction conditions. The phase of the final product was successfully tuned, changing the starting molar ratio of Li:Al in the synthesis mixture. This ratio, X, is used in the text to identify the samples, named as LiAl_X. In the following, the results are divided according to the stoichiometry of the final product. For each product, the dimension of the particles was evaluated by using small-angle X-ray scattering (SAXS), XRD, gas sorption, and electron microscopy (EM) analysis. The combination of different techniques is fundamental to obtain reliable, complete, and representative information. Indeed, XRD peaks broadening is sensitive to crystal dimensions, but just crystalline structures are detected and big crystallites are usually overestimated. On the other side, SAXS allows to detect amorphous structures, but the shape of the particles has to be known to perform the data interpretation. This information can be obtained from

Fig. 1 XRD patterns (a) and FT-IR spectra (b) of samples LiAl_0 at room temperature, annealed at 900 °C and at 1100 °C for 2 h. TEM image (c) of sample LiAl_0 as prepared, together with a magnification (inset). SEM image (d) of the sample annealed at 1100 °C

EM even if just a small portion of the sample is usually considered in the analysis. Finally, the SSA of the sample can be converted to an equivalent radius, but also in this case morphological information are required.

3.1 γ -Al₂O₃ and α -Al₂O₃

In agreement with a previous report [42], the nonaqueous sol-gel reaction of aluminium acetylacetonate in benzyl amine (sample LiAl_0) results in pure Al₂O₃ NPs with γ -phase at room temperature.

A complete characterization of the product and its evolution at high temperature were not investigated in the previous report, and therefore are included in the present work. The evolution of the crystal phase as function of the annealing temperature was followed by XRD and FT-IR analysis and the results are shown in Fig. 1a and b, respectively.

The as-prepared powder retains γ -phase until 900 °C without any detectable impurities. In this temperature range, no pronounced differences in the broadening of the peaks can be observed, suggesting small variation in the crystals

size and good thermal stability. The conversion to α -phase starts at 1000 °C and it completes at 1100 °C, in agreement with other reports on γ -Al₂O₃ particles [19, 45, 46].

The phase transition $\gamma \rightarrow \alpha$ can be easily followed also by IR spectroscopy focusing in the region between 400 and 1200 cm⁻¹. The IR spectrum of γ -Al₂O₃ NPs is characterized by broad absorptions between 400 and 1200 cm⁻¹ related to multiple vibrations of AlO₄ tetrahedra and AlO₆ octahedra [33, 47]. More features arise after the transition to α -phase. In this case, the spectrum is characterized by strong bands at 490, 561, and 635 cm⁻¹, which are identified to be characteristic for α -Al₂O₃ [19, 33, 45, 48, 49]. The evolution of the spectra suggests a direct transition $\gamma \rightarrow \alpha$ for the synthesized system without the intermediate formation of another transition phase, normally observed in cases where boehmite is the as-prepared product [34]. The direct conversion of γ to α alumina is advantageous because it increases the range of stability of the γ -phase and it reduces the particle growth usually related to phase transformations [45, 50].

The crystal size of the sample was analyzed by means of SAXS. SAXS is a powerful tool for measuring particle

dimensions in the nanometer range based on electron density and it has been successfully adopted to investigate numerous organic and inorganic materials [51]. Average radius ($r_{\text{SAXS, av}}$), most frequent radius ($r_{\text{SAXS, fr}}$), and relative standard deviation (RSD%) obtained from the data analysis are reported in Table 1.

For the as-prepared sample, a $r_{\text{SAXS, av}}$ of about 2 nm was observed. This value is qualitatively in agreement with the XRD results since the pronounced broadening can be related to small crystallite sizes ($d < 5$ nm). A semi-quantitative comparison between the two techniques can be performed converting the XRD broadening of the peaks in an average radius of the crystallites by the Scherrer equation (Eq. 1). Even if this formula was demonstrated to be often inadequate, it remains a valid tool to qualitatively compare dimensional data [52]. The obtained values are reported in Table 1. By comparing r_{SAXS} and r_{XRD} , a good agreement can be observed for the as-prepared LiAl₀ sample.

After the conversion to α -Al₂O₃, a strong increase in particle dimensions can be expected from the sharp peaks referred to the α -phase. Converting the broadening to average crystal radius (Eq. 1), a value of 41 nm is obtained. This increase in dimension was confirmed by SAXS measurement where a $r_{\text{SAXS, av}}$ of 42 nm was obtained.

SSA and equivalent BET radius calculated from Eq. 2 (r_{BET}) are reported in Table 1. For the as-prepared sample, a SSA of 424 m² g⁻¹ (corresponding to an r_{BET} of 1.9 nm) was observed. This value is outstandingly high for dry powder and represents the highest values available in the literature for crystalline γ -Al₂O₃ NPs [24, 45, 46, 53]. The high surface area can be related to the extremely small dimension of the primary particles and the formation of only loose agglomerates during the drying process. Furthermore, the good agreement between r_{BET} and r_{XRD} suggests the formation of loose agglomerates with open porosity. After conversion to α -Al₂O₃, the SSA is reduced to 10 m² g⁻¹, corresponding to an average r_{BET} of 77 nm.

TEM analysis performed on as-prepared LiAl₀ showed the presence of small partially crystalline particles (Fig. 1c). This evidence is in good agreement with the results from XRD, SAXS, and BET where the presence of small particles with high SSA was envisioned. The good thermal stability of the particles can be observed upon annealing the powder at 900 °C for 2 h. As suggested from the limited peak sharpening, the particles increase only slightly their dimensions, reaching an average diameter of about 5 nm (see TEM image in Fig. S2).

The conversion to α -phase carries a dramatic increase in the crystallite dimension as suggested by the sharp XRD peaks and low SSA. In Fig. 1d, a SEM image of the sample annealed at 1100 °C confirms the presence of big particles ($d > 100$ nm) as main components, even if smaller units are

still detectable. The increase in crystal size explains the decrease in SSA. Similar behavior was observed by Li et al. [19], where 15-nm γ -Al₂O₃ NPs remain fairly unchanged upon thermal treatment until the conversion to α -Al₂O₃ (1000 °C), where a rapid growth up to 200 nm is observed.

The concentration of Li in γ -Al₂O₃ and α -Al₂O₃ was measured by ICP-MS investigation and the results are reported in Table 1. As expected from the absence of LiCl in the reagent mixture, no Li has been detected in the products.

3.2 LiAl₅O₈

Phase-pure LiAl₅O₈ NPs were synthesized with a molar ratio of Li:Al of 1:5 (sample LiAl_{0.2}). In Fig. 2, XRD patterns (a) and FT-IR spectra (b) of sample LiAl_{0.2} annealed at different temperatures are reported.

The as-prepared sample shows diffraction peaks typical for γ -Al₂O₃ and this does not significantly change upon annealing at 800 °C. Cubic LiAl₅O₈ phase appears after treatment at 900 °C and it remains the only phase in the system until about 1200 °C. Above this temperature, α -Al₂O₃ starts to be present as secondary phase and it remains the only component upon annealing at 1500 °C (Fig. S3). The transition LiAl₅O₈→ α -Al₂O₃ can be ascribed to the evaporation of Li₂O at high temperature [40].

FT-IR spectroscopy helps to further investigate the transition γ -Al₂O₃→LiAl₅O₈. Even if the spectrum of as-prepared powders suggests phase-pure γ -Al₂O₃, a mild heating to 600 °C brings new vibrational features not related to pure alumina phase and which are retained until about 800 °C. The assignment of these bands is not straightforward, but they could originate from partially disordered mixed AlO₄-LiO₄ structures. The observation of these bands is particularly important since the possibility to distinguish two samples, equivalent under XRD investigation, brings important information on the surface features and catalytic activity of the sample.

After annealing at 900 °C, numerous stronger absorption bands are observed in the region 400–1200 cm⁻¹. In agreement with the literature, these bands are characteristic for LiAl₅O₈ phase [40, 47, 54]. The assignment of these vibrations to particular groups is extremely difficult. According to Kutty et al. [40], LiO₄, LiO₆, AlO₄, and AlO₆ groups simultaneously participate in the absorption bands. Tarte [47] made a more detailed investigation of the assignment of the bands but mostly Li–O/Al–O mixed vibrations were considered responsible for the absorptions.

Nitrogen adsorption on as-prepared LiAl_{0.2} suggests particles of ~2 nm and SSA of ~400 m² g⁻¹. These values are close to those obtained for the as-prepared sample LiAl₀.

Fig. 2 XRD patterns (a) and FT-IR spectra (b) of sample LiAl_{0.2} at room temperature and annealed 2 h at 800 and 900 °C. In c, a TEM image of sample LiAl_{0.2} annealed 2 h at 900 °C is shown

After annealing at 900 °C (conversion to LiAl₅O₈) an average radius of 4.5 nm was calculated from the XRD broadening. This value is confirmed by the TEM image reported in Fig. 2c, where crystalline NPs with average radius around 4 nm are observed. Similar average radius is obtained by SAXS measurements (r_{SAXS} 5.2 nm).

The high temperature treatment required for the conversion to LiAl₅O₈ necessarily brings a decrease in SSA. Phase-pure LiAl₅O₈ NPs can be obtained with a SSA as high as 112 m² g⁻¹ (Table 1). This is one of the highest values reported in the literature for LiAl₅O₈ [2, 36, 55]. Using Eq. 2, the SSA is converted to an equivalent particles radius of 7.4 nm. Similarly to sample LiAl₀, the good agreement between r_{SAXS} , r_{XRD} , and r_{BET} can be related to the formation of loose and porous agglomerates, which retain almost the theoretical maximum surface area of the single nanoscaled components. This possibility is confirmed by Fig. 2c, where numerous pores between the particles can

be observed. It is worth underlining that the possibility to retain nanoscale dimensions after annealing is a major advantage of the proposed nonaqueous sol-gel protocol. This can be directly related to the direct synthesis of small crystalline particles, whose tendency to sinter at high temperature is generally lower than the one of other amorphous or hydrated products reported in the literature.

The molar ratio Li:Al in the as-prepared LiAl_{0.2} sample was found to be 1:7. After conversion to LiAl₅O₈, a reliable measurement was not anymore possible due to the incomplete digestion of the sample.

3.3 β-LiAlO₂ and γ-LiAlO₂

Increasing the concentration of LiCl in the synthesis mixture, LiAlO₂ particles can be synthesized. Phase-pure β-LiAlO₂ NPs are obtained with a molar ratio Li:Al of 10:1 (sample LiAl₁₀). The synthesis of β-LiAlO₂ NPs at room

Fig. 3 XRD patterns (a) and FT-IR spectra (b) of samples LiAl₁₀ at room temperature and annealed at 600 and 800 °C for 2 h. In the lower part, TEM of sample LiAl₁₀ as prepared (c) and annealed at 800 °C (d)

temperature is unexpected since this metastable phase is usually obtained after annealing the low-temperature phase α -LiAlO₂ to 400 °C [36]. To the best of our knowledge, this is the first report on the low-temperature synthesis of phase-pure β -LiAlO₂ NPs. This possibility opens a new opportunity for the application of this material, whose potential is usually not investigated due to the difficult synthesis protocol.

In Fig. 3, the XRD patterns (a) of sample LiAl₁₀ annealed at different temperatures are reported together with the corresponding FT-IR spectra (b). LiAlO₂ in the β -phase is stable until 600 °C. Above this temperature, the thermal treatment causes the phase conversion to γ -LiAlO₂ that remains the only phase in the system upon annealing at 800 °C. Treating the powders above 1000 °C brings to the appearance of LiAl₅O₈ as secondary phase (Fig. S4). The evolution toward phases with lower lithium content is related to the evaporation of Li₂O and it finally leads to the complete conversion to α -Al₂O₃ [40].

Figure 3b shows the FT-IR spectra of sample LiAl₁₀ annealed at different temperature. The transition β -LiAlO₂ → γ -LiAlO₂ can be observed via IR spectroscopy despite the

two phases present similar intense bands at 790, 650, 540, and 447 cm⁻¹. The bands at 790 and 650 cm⁻¹ can be related to the stretching frequencies of AlO₄ tetrahedra, while the bands at 540 and 447 cm⁻¹ refer to a mixture of frequencies in the AlO₄-LiO₄ lattice [47, 55, 56].

TEM pictures of β -LiAlO₂ and γ -LiAlO₂ are shown in Fig. 3c and d, respectively. β -phase NPs are characterized by crystalline particles with broad size distribution between 3 and 15 nm. These values are confirmed by SAXS measurements, where a similar dimensional range with broad distribution is suggested (Table 1). SSA of pure β -LiAlO₂ was found to be higher than 190 m² g⁻¹. This value is in agreement with the presence of crystallites with average r_{BET} of 5.7 nm.

After annealing at 800 °C, β -LiAlO₂ was converted to γ -LiAlO₂. As shown from TEM image in Fig. 3d, crystalline particles with average size around 35 nm are observed in the sample. Same information can be obtained from XRD and SAXS measurements (Table 1). The increase in dimension was related to a decrease in SSA that however was observed to be higher than 55 m² g⁻¹. This value is in line, if not higher, with the SSA values reported in the literature for γ -

LiAlO₂ [36, 38, 57, 58]. Nevertheless, a major advantage has to be pointed out for the proposed method. The possibility to start from small β -LiAlO₂ NPs allows to retain nano-size dimension even after annealing. Indeed, even if similar values of SSA are reported in the literature, the reported particles are usually porous agglomerates with dimension well above 1 μ m [58]. This has direct impact on the possibility to process the products and to use the powder in real micro-sized devices.

The molar ratio Li:Al for both LiAlO₂ phases was found to be 1:1, in agreement with the phase suggested by XRD and FT-IR measurements.

4 Conclusions

In this paper, we propose a versatile nonaqueous sol–gel protocol for the synthesis of alumina and LiAlO₂ NPs with tuneable stoichiometry and phase. In particular, γ -Al₂O₃, α -Al₂O₃, LiAl₅O₈, β -LiAlO₂, and γ -LiAlO₂ NPs can be synthesized tuning the reaction parameters. All the products are characterized by nanoscale size, good crystallinity, phase purity, high surface area, thermal stability, and easy dispersion in ethanol. Contrary to most of the reports available in the literature, alumina and LiAlO₂ are obtained in crystalline form directly after the synthesis. The good crystallinity of the as-prepared products, together with the small crystal dimensions and the thermal stability, allows to retain size in the nanoscale even after annealing at high temperature.

The easiness and versatility of the protocol, combined with the appealing properties of the products, are expected to open new application fields for Li–Al–O NPs where phase purity and nanoscale dimensions are strictly required.

Acknowledgements The authors gratefully thank ETH Zürich for financial support. We also acknowledge the Scientific Center for Optical and Electron Microscopy (ScopeM) of ETH Zürich for providing the facilities.

Conflict of interest The authors declare that they have no conflict of interest.

References

- Baudín C (2014) 2.02—processing of alumina and corresponding composites A2. In: Sarin VK (ed.) Comprehensive hard materials. Elsevier, Oxford, p 31–72
- Ge Y et al. (2012) Influence of crystalline phase of Li–Al–O oxides on the activity of Wacker-type catalysts in dimethyl carbonate synthesis. *Front Chem Sci Eng* 6(4):415–422
- Trueba M, Trasatti SP (2005) γ -Alumina as a support for catalysts: a review of fundamental aspects. *Eur J Inorg Chem* 2005 (17):3393–3403
- Knözinger H, Ratnasamy P (1978) Catalytic aluminas: surface models and characterization of surface sites. *Cat Rev* 17(1):31–70
- Morterra C, Magnacca G (1996) A case study: surface chemistry and surface structure of catalytic aluminas, as studied by vibrational spectroscopy of adsorbed species. *Cat Today* 27 (3–4):497–532
- Wu X et al. (2012) Ultrathin amorphous alumina nanoparticles with quantum-confined oxygen-vacancy-induced blue photoluminescence as fluorescent biological labels. *J Phys Chem C* 116 (3):2356–2362
- Anjiki A, Uchino T (2012) Visible photoluminescence from photoinduced molecular species in nanometer-sized oxides: crystalline Al₂O₃ and amorphous SiO₂ nanoparticles. *J Phys Chem C* 116(29):15747–15755
- Liu S et al. (2006) Ultraviolet irradiation-induced photoluminescence degradation in γ -alumina nanoparticles. *Appl Phys Lett* 89(5):051911
- Yu ZQ, Li C, Zhang N (2002) Size dependence of the luminescence spectra of nanocrystal alumina. *J Lumin* 99 (1):29–34
- Islam MM, Bredow T (2015) Interstitial lithium diffusion pathways in γ -LiAlO₂: a computational study. *J Phys Chem Lett* 6 (22):4622–4626
- Indris S et al. (2012) Li ion dynamics in a LiAlO₂ single crystal studied by 7Li NMR spectroscopy and conductivity measurements. *J Phys Chem C* 116(27):14243–14247
- Lata S, Samadder SR (2016) Removal of arsenic from water using nano adsorbents and challenges: a review. *J Environ Manage* 166:387–406
- Ghaemi N (2016) A new approach to copper ion removal from water by polymeric nanocomposite membrane embedded with γ -alumina nanoparticles. *Appl Surf Sci* 364:221–228
- Kasprzyk-Hordern B (2004) Chemistry of alumina, reactions in aqueous solution and its application in water treatment. *Adv Colloid Interface Sci* 110(1–2):19–48
- Mallakpour S, Khadem E (2015) Recent development in the synthesis of polymer nanocomposites based on nano-alumina. *Prog Polym Sci* 51:74–93
- Amaro AM et al. (2016) Effect of irregular shaped nanoalumina on the enhancement of mechanical properties of epoxy resin nanocomposites using DDM as hardener. *Compos Part B Eng* 84:17–24
- Alzarrag FA et al. (2015) The use of different alumina fillers for improvement of the mechanical properties of hybrid PMMA composites. *Mater Des* 86:575–581
- Aoyama M et al. (2013) Synthesis and characterization of lithium aluminate red phosphors. *J Lumin* 135:211–215
- Li J et al. (2006) Low temperature synthesis of ultrafine α -Al₂O₃ powder by a simple aqueous sol–gel process. *Ceram Int* 32 (5):587–591
- Nguefack M et al. (2003) Preparation of alumina through a sol-gel process. Synthesis, characterization, thermal evolution and model of intermediate boehmite. *Phys Chem Chem Phys* 5 (19):4279–4289
- Chi C et al. (2016) Oriented growth and electrical property of LiAl₅O₈ film by laser chemical vapor deposition. *J Ceram Soc Jpn* 124(1):111–115
- Chou MMC et al. (2009) A novel method to synthesize a large area of single crystalline LiAl₅O₈ nanorods. *Cryst Growth Des* 10 (1):191–194
- Ghanizadeh S et al. (2014) Synthesis of nano α -alumina powders using hydrothermal and precipitation routes: a comparative study. *Ceram Int* 40(1, Part B):1311–1319
- Noguchi T et al. (2008) Rapid synthesis of γ -Al₂O₃ nanoparticles in supercritical water by continuous hydrothermal flow reaction system. *J Supercrit Fluids* 46(2):129–136

25. Ol'ga NK, Vadim PT (2013) Synthesis of Li_5AlO_4 involving a repulping mixing in a Li_2CO_3 saturated solution. *J Phys Conf Ser* 416(1):012009
26. Teresa Flores-Martínez M, Pfeiffer H (2015) CO_2 chemisorption and cyclability analyses in $\alpha\text{-Li}_5\text{AlO}_4$: effects of Na_2CO_3 and K_2CO_3 addition. *Greenh Gases* 5(6):802–811
27. Pitale SS et al. (2011) Cathodoluminescent properties and surface characterization of bluish-white $\text{LiAl}_5\text{O}_8\text{:Tb}$ phosphor. *J Appl Phys* 109(1):013105
28. Laishram K, Mann R, Malhan N (2012) A novel microwave combustion approach for single step synthesis of $\alpha\text{-Al}_2\text{O}_3$ nanopowders. *Ceram Int* 38(2):1703–1706
29. Hashimoto S et al. (2009) Self-flux synthesis and photoluminescent properties of LiAl_5O_8 . *Mater Res Bull* 44(1):70–73
30. Razali WAW et al. (2014) Large-scale production and characterization of biocompatible colloidal nanoalumina. *Langmuir* 30(50):15091–15101
31. Su X, Chen S, Zhou Z (2012) Synthesis and characterization of monodisperse porous $\alpha\text{-Al}_2\text{O}_3$ nanoparticles. *Appl Surf Sci* 258(15):5712–5715
32. Lock N et al. (2009) In situ high-energy synchrotron radiation study of boehmite formation, growth, and phase transformation to alumina in sub- and supercritical water. *Chemistry* 15(48):13381–13390
33. Boumaza A et al. (2009) Transition alumina phases induced by heat treatment of boehmite: an X-ray diffraction and infrared spectroscopy study. *J Solid State Chem* 182(5):1171–1176
34. Zhou RS, Snyder RL (1991) Structures and transformation mechanisms of the η , γ and θ transition aluminas. *Acta Crystallogr Sect B* 47(5):617–630
35. Dronskowski R (1993) Reactivity and acidity of Li in lithium aluminum oxide (LiAlO_2) phases. *Inorg Chem* 32(1):1–9
36. Khomane RB, Agrawal A, Kulkarni BD (2007) Synthesis and characterization of lithium aluminate nanoparticles. *Mater Lett* 61(23–24):4540–4544
37. Kim J-E et al. (2009) Using aluminum and Li_2CO_3 particles to reinforce the $\alpha\text{-LiAlO}_2$ matrix for molten carbonate fuel cells. *Int J Hydrogen Energy* 34(22):9227–9232
38. Choi HJ et al. (2009) Cost-effective synthesis of $\alpha\text{-LiAlO}_2$ powders for molten carbonate fuel cell matrices. *Fuel Cells* 9(5):605–612
39. Kim SD et al. (2005) Phase and microstructure stabilities of LiAlO_2 in molten Li/Na carbonate for molten carbonate fuel cells. *J Power Sources* 143(1–2):24–29
40. Kutty TRN, Nayak M (1998) Cationic distribution and its influence on the luminescent properties of Fe^{3+} -doped LiAl_5O_8 prepared by wet chemical methods. *J Alloys Compd* 269(1–2):75–87
41. Niederberger, M. and Pinna, N, Metal oxide nanoparticles in organic solvents. In: Engineering materials and processes. 2009: Springer: London.
42. Zhou S, Antonietti M, Niederberger M (2007) Low-temperature synthesis of γ -alumina nanocrystals from aluminum acetylacetonate in nonaqueous media. *Small* 3(5):763–767
43. Karmaoui M et al. (2009) A general nonaqueous route to crystalline alkaline earth aluminate nanostructures. *Nanoscale* 1(3):360–365
44. Gregg SJ, Sing KSW (1982) Adsorption, surface area and porosity. Academic Press, London, p 313
45. Sun Z-X et al. (2008) Effects of calcination temperature on the pore size and wall crystalline structure of mesoporous alumina. *J Colloid Interface Sci* 319(1):247–251
46. Kim S-W, Iwamoto S, Inoue M (2010) Surface and pore structure of alumina derived from xerogel/aerogel. *J Porous Mater* 17(3):377–385
47. Tarte P (1967) Infra-red spectra of inorganic aluminates and characteristic vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra. *Spectrochim Acta A* 23(7):2127–2143
48. Shek CH et al. (1997) Transformation evolution and infrared absorption spectra of amorphous and crystalline nano- Al_2O_3 powders. *Nanostruct Mater* 8(5):605–610
49. Barker AS (1963) Infrared lattice vibrations and dielectric dispersion in corundum. *Phys Rev* 132(4):1474–1481
50. Wu X et al. (2016) Novel $\text{Al}_2\text{O}_3\text{-SiO}_2$ composite aerogels with high specific surface area at elevated temperatures with different alumina/silica molar ratios prepared by a non-alkoxide sol-gel method. *RSC Advances* 6(7):5611–5620
51. Li T, Senesi AJ, Lee B (2016) Small-angle X-ray scattering for nanoparticle research. *Chem Rev* 116(18):11128–11180
52. Lucchini MA et al. (2014) Continuous synthesis of nickel nanopowders: characterization, process optimization, and catalytic properties. *Appl Catal B Environ* 156:404–415
53. Seo JG et al. (2008) Effect of calcination temperature of mesoporous alumina xerogel (AX) supports on hydrogen production by steam reforming of liquefied natural gas (LNG) over Ni/AX catalysts. *Int J Hydrogen Energy* 33(24):7427–7434
54. Singh V et al. (2008) EPR and luminescence properties of combustion synthesized $\text{LiAl}_5\text{O}_8\text{:Mn}$ phosphors. *Mater Chem Phys* 110(1):43–51
55. Ribeiro RA, Silva GG, Mohallem NDS (2001) The influences of heat treatment on the structural properties of lithium aluminates. *J Phys Chem Solids* 62(5):857–864
56. Gessner W, Müller D (1983) Zur Koordination des Aluminiums im $\beta\text{-LiAlO}_2$. *Zeitschrift für anorganische und allgemeine Chemie* 505(10):195–200
57. Jiménez-Becerril J, García-Sosa I (2011) Synthesis of lithium aluminate by thermal decomposition of a lithium dawsonite-type precursor. *J Ceram Process Res* 11:5
58. Heo SJ et al. (2016) Stability of lithium aluminate in reducing and oxidizing atmospheres at 700 degrees C. *Int J Hydrogen Energy* 41(41):18884–18892.