Surfactant-free hydrothermal synthesis of lithium aluminate microbricks and nanorods from aluminium oxide nanoparticles†

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β-$LiAlO_2$ microbricks and rectangular nanorods have been successfully synthesized from Al_2O_3 nanoparticles by a simple hydrothermal process without any surfactant or template, by simply changing the Li/Al molar ratio.

Over the past decade, one-dimensional (1-D) nanosized building blocks such as nanorods, nanowires, nanotubes and nanobelts have attracted immense interest because of their distinctive geometries, novel physical and chemical properties, and potential applications in nanodevices.[1] One-dimensional nanostructures can be fabricated by template-directed growth methods by using carbon nanotubes[2] or porous alumina templates,[3] the vapor–liquid–solid (VLS) mechanism,[4] and the vapor–solid (VS) mechanism.[5] Liquid-phase synthesis could be performed at milder conditions, yet it requires surfactants as soft templates that have to be removed afterward by combustion. Thus, a serious challenge that scientists and engineers have to face to unfold the full potential of applications and prospects of nanotechnology is the development of sustainable large-scale manufacturing techniques for time and cost-effective production.

Lithium aluminate ($LiAlO_2$) is a potential candidate for an electrolyte matrix of molten carbonate fuel cell (MCFC) and a tritium breeding blanket of fusion reactor due to its chemical and thermal stability. For these applications, long rod-shaped or fibrous lithium aluminate forming a fine porous structure is especially desirable.[6,7] Most previous approaches to the preparation of lithium aluminate employed high temperatures and expensive precursors.[8]

We have recently reported the controlled fabrication of α-$LiAlO_2$ and γ-$LiAlO_2$ nanotubes *via* a surfactant-templated hydrothermal methods.[9] Here, we report for the first time a surfactant-free hydrothermal synthesis of β-$LiAlO_2$ microbricks and rectangular nanorods from Al_2O_3 nanoparticles. Because we use very mild conditions and all inorganic low-cost raw materials, scale-up of this procedure for large-scale production should be very easy.

Detailed experimental and characterization procedure is given in the Supporting Information.† In brief, LiOH (98+% Aldrich) and Al_2O_3 nanopowder (Aldrich) with sizes of *ca.* 20–150 nm, were stirred together with 36 mL distilled water for 1 h (Li/Al = 3 and 15). Then the mixture was put into hydrothermal reaction in a Teflon coated reactor at a constant temperature (150 °C) without disturbing for 3 days. The as-obtained white product was separated by centrifugation, washed with distilled water to remove excess LiOH and then dried in an oven at 100 °C overnight.

Representative scanning electron microscope (SEM) images of the reaction product are shown in the Fig. 1 and in the Supporting Information.† As shown in Fig. 1a, a typical SEM image of the product obtained by the hydrothermal reaction with Li/Al = 3 clearly reveals a brick-like morphology. Further, the high magnification SEM image shown in Fig. 1b clarifies that this brick-like morphology has an orthorhombic structure with two edges of 8.45 μm and 8.81 μm respectively, and length of 25 μm; hence they could be called "microbricks". Similarly, the image in Fig. 1c of β-$LiAlO_2$ nanorods prepared by the same hydrothermal reaction with Li/Al = 15 shows a rod like morphology. Yet, the cross-section of the nanorods is not circular but rectangular as shown in Fig. 1d.

These nanorods also have an orthorhombic structure with two edges of 40 nm and 60 nm respectively and lengths of 1–2 μm, and thus could be called "rectangular nanorods". The uniformity in morphology and size is impressive for both samples as demonstrated by SEM images in the Supporting Information (Fig. S1–S2)†. X-ray diffraction patterns in Fig. 1e show that both microbricks (pattern a) and rectangular nanorods (pattern b) are composed of highly crystalline orthorhombic β-$LiAlO_2$ structures. The unit cell parameters for both samples have been determined to be a = 5.3 Å, b = 6.3 Å and c = 4.9 Å, which are also in agreement with the corresponding bulk β-$LiAlO_2$ (space group symmetry $Pna2_1$ (33), JCPDS 33-0785) with the structure shown in Fig. 1f.

From the TEM image in Fig. 2a, it is evident that the nanorods are of fairly uniform lengths of 1–2 μm and diameters of 40–200 nm. Inset Fig. 2a shows the side view of a tip of a nanorod which confirms the orthorhombic nature of the rod. In order to study the lattice structure and to judge the growth direction of β-$LiAlO_2$ rectangular nanorods, a HRTEM experiment was carried out. On the basis of the calculation of the lattice spacing and an analysis of its orientation, it was found that the nanorods grew perpendicular to [110] as seen in Fig. 2b. Inset Fig. 2b shows the corresponding selected area electron diffraction (SAED) pattern.

To investigate the structural information about the environment of the Al nuclei in the samples, we carried out ^{27}Al MAS NMR. Müller *et al.*[10] studied NMR spectra for all the three (α, β, γ) polymorphs of $LiAlO_2$ and concluded that the Al in the β-$LiAlO_2$ was tetrahedrally coordinated confirming an orthorhombic

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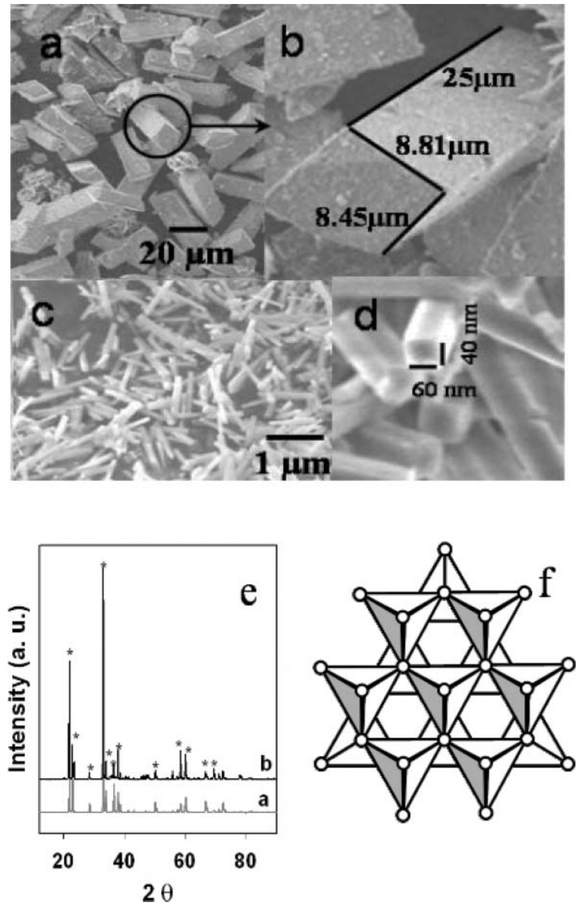

Fig. 1 a) SEM image of β-$LiAlO_2$ microbricks obtained by the hydrothermal treatment of Al_2O_3 nanoparticles with LiOH (Li/Al = 3). b) High magnification image of a microbrick clearly shows that the bricks have orthorhombic structure with edges of 8.45 and 8.81 µm, and a length of 25 µm. c) SEM image of β-$LiAlO_2$ nanorods obtained by the hydrothermal treatment of Al_2O_3 nanoparticles with LiOH (Li/Al = 15). d) High magnification image of the nanorods shows that nanorods also have orthorhombic morphology with edges of 40 nm and 60 nm. e) Typical XRD patterns of β-$LiAlO_2$ microbricks (pattern a) and rectangular nanorods (pattern b). f) A plane view of the arrangement of the tetrahedrals in the structure of β-$LiAlO_2$. The oxygen atoms are located at the vertices of the vertices-linked tetrahedral. The Al and Li atoms are omitted from this structure for simplicity.

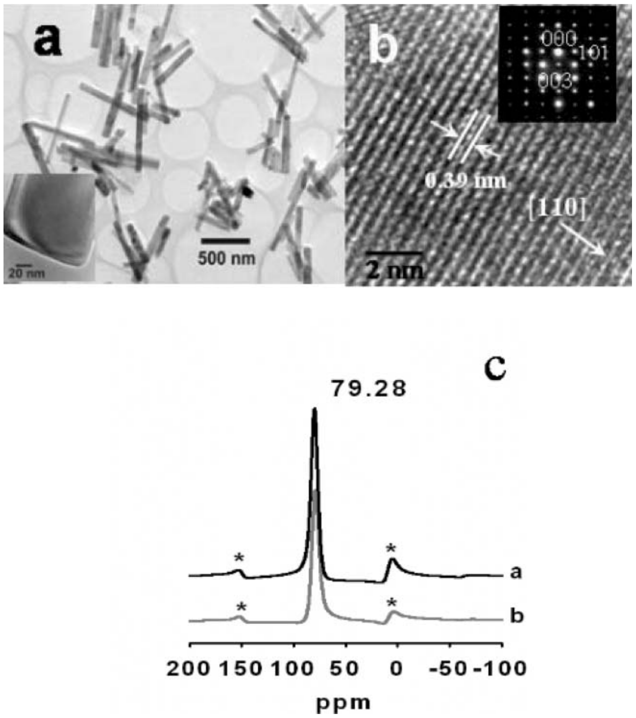

Fig. 2 a) The TEM image of as-obtained nanorods; inset shows the high-magnification image of a tip of a nanorod (bar scale 20 nm). b) The HR-TEM image of a tip of $LiAlO_2$ nanorod showing clear lattice fringes in the direction of [110]; inset is the SAED pattern of the $LiAlO_2$ nanorod. c) ^{27}Al MAS NMR shows the chemical shifts at 79.28 ppm (relative to AlO_4) which confirms the tetrahedral coordination of the aluminium in $LiAlO_2$ microbricks (a) and $LiAlO_2$ rectangular nanorods (b) (* indicates spinning sidebands).

structure for β-$LiAlO_2$. In our ^{27}Al MAS NMR study of $LiAlO_2$-microbricks and $LiAlO_2$-rectangular nanorods we observed essentially the same tetrahedrally coordinated Al. The chemical shift at 79.28 ppm (relative to AlO_4) in Fig. 2c, unambiguously reflects tetrahedral coordination of Al in β-$LiAlO_2$ which confirms an orthorhombic structure for both products. As we do not observe any chemical shift due to octahedrally coordinated Al nuclei in the samples, they must have an orthorhombic structure and not a monoclinic structure as reported for β-$LiAlO_2$ by Chang *et al.*[11]

Although the detailed study of the growth mechanism of the nanorods is in progress, it is clear that the growth of the nanorods is not template-directed or surfactant-assisted, because no additional template or surfactants were introduced into the reaction. As the basic structural unit cell is orthorhombic, our microbricks and nanorods are also orthorhombic. We believe that, the microbricks and rectangular nanorods are formed with the same mechanistic pathway mainly by a dissolution–recrystallization process followed by Ostwald ripening. Thus, Al_2O_3 nanoparticles would be spontaneously dissolved into solution due to a relatively higher free energy compared to nanorods under hydrothermal conditions. At the same time, the growth units in the solution would diffuse onto higher energy surface of the growing nanorods. The larger nanorods would grow at the cost of the small particles.

The influence of chemical potential on the shape evolution of nanocrystals have been elucidated by Peng *et al.*[12,13] who found that, in the case of one-dimensional nanostructure growth, it would be advantageous to have a higher chemical potential. This is mainly determined by the pH value of the adopted reaction system. For example, Wang *et al.*[14] reported the synthesis of lanthanide hydroxide single-crystal nanowires from lanthanide oxide, dissolved in a concentrated nitric acid and reprecipitated by KOH. They observed a significant effect of pH, as pH = 6–7 gave sheets, pH = 9 produced nanowires, and pH = 14 also gave nanowires but with a decreased aspect ratio. In our $LiAlO_2$ study we essentially observed the same effect of OH^- ion concentration, as Li/Al = 3 gave microbricks and Li/Al = 15 gave nanorods under the same reaction conditions. In case of lithium aluminate nanorods synthesis, we used excess LiOH, which would produce more OH^- ions and hence higher chemical potential, which is preferred for the growth of nanorods. As the nanorods and microbricks are two different morphologies by the same reaction,

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one should consider that the excess of OH^- ions covers the surface fully, and reduces the surface energy. Then the growth in radial direction is hindered leading to 1-D growth. But in the case of microbricks, as this excess of OH^- ions is absent, the surface is only partially covered with OH^- ions, hence the crystal grows further in both radial as well as axial directions leading to a low aspect ratio of the microbrick structure. Furthermore, upon heating at 950 °C for 12 h, the β-$LiAlO_2$ nanorods are converted to γ-$LiAlO_2$ nanorods. Yet, the majority of them (>90%) still maintained their morphology, although a few nanorods have been broken to form small nanorods (length *ca.* 500 nm, see XRD, SEM in Supporting Information).† This demonstrates that the nanorods possess thermal stability in maintaining the morphology.

In summary, the present study has demonstrated that β-$LiAlO_2$ microbricks and rectangular nanorods can be successfully synthesized from Al_2O_3 nanoparticles by simple hydrothermal process without any surfactant or template. A critical effect of Li/Al ratio was clearly demonstrated on the morphology of the products, as Li/Al = 3 gives microbricks, whereas Li/Al = 15 gives rectangular nanorods. The obtained microbricks had an orthorhombic structure with edges in the range of 8–9 μm and lengths of 25–27 μm. Similarly, nanorods also had an orthorhombic structure with edges in the range of 40–200 nm and lengths of 1–2 μm. The nanorods maintained their initial morphology under heat treatment at 950 °C for 12 h, although their phase had turned to γ-$LiAlO_2$.

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