Bundles of self-assembled boehmite nanostrips from a surfactant free hydrothermal route

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Abstract

Boehmite nanostrips with average diameter and crystallite sizes of about 19.5 nm and 4.5 nm were prepared through a surfactant free approach and were characterized with XRD, TEM and DTA/TG analyses. Nanostrips self-assembled to form bundles due to lateral surface adsorptions. The effect of Cl^- ions on enhancement of one-dimensional growth of boehmite nanostructures was investigated. The thermal analysis showed that chlorides reduced the formation temperature of α-Al_2O_3 phase.
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1. Introduction

During the last decade, one-dimensional (1D) nanostructures have attracted many researchers due to their weird properties and applications in nanoscience and nanotechnology [1,2]. Among extensive literature on the formation of 1D nanostructure compounds, alumina nanostructure phases (i.e. boehmite, γ- and α-Al_2O_3) have been reported in various morphologies such as nanotubes [3–5], nanowires [6], nanorods [7,8], nanofibers [9,10], lace-like nanoribbons [11] and plate-like nanostructures [12]. Although the thermodynamically stable α-Al_2O_3 phase can be obtained through a sequence of topotactic [13] and reconstructive [14] transformations (i.e. boehmite $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ [15]), the morphology remains unchanged and the final products have the same shape as the initial phases [16]. Therefore, boehmite nanostructures with novel morphologies are relevant precursors for obtaining α-Al_2O_3 nanoarchitectures. Here, bundles of boehmite nanostrips were prepared through a facile surfactant free hydrothermal route and were shown to transform to the α-phase at a lower temperature than what conventionally was reported in the literature (i.e. >1050 °C [17]).

One of the important challenges in thermal transformations of alumina ceramics systems has been attributed to the reduction of the formation temperature of α-Al_2O_3 phase in order to impede the grain growth occurrence during high temperature calcination processes [18]. Nucleation aids such as alumina (α-Al_2O_3) seeds [18], α-Fe_2O_3 [19], V_2O_5 [20] and fluorides [21,22] were reported to have significant influence on reducing the α-Al_2O_3 phase formation temperature. Also, it was indicated that the fluoride ions enhanced the directional growth of the alumina nanostructures [12]. Although several researchers have investigated the effect of chlorides on physicochemical [23], fibrils particle sizes [24] and hydrothermal preparation of boehmite nanostructures [25], no distinct investigation has been attributed to the effect of chloride ions on formation of one-dimensional alumina nanostructures and the α-Al_2O_3 phase transformation temperature. Therefore, the following surfactant free hydrothermal process was developed to investigate the oriented attachment [2,26] of nanocrystals which culminated in obtaining the 1D boehmite nanostructures under the influence of Cl^- ions. The thermal behavior of the obtained nanostructures was also characterized to determine the effect of chloride ions on α-Al_2O_3 formation temperature.

2. Experimental

All the raw materials were purchased from Merck, Darmstadt, Germany and used as received without further purification. In a typical experiment, 0.36 g $AlCl_3 \cdot 6H_2O$ powder was dissolved into 10 ml ethanol under vigorous stirring at room temperature. The mixture was fluxed until a homogenous solution

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was obtained. Then 40 ml deionized water was added slowly to the solution and the mixture was refluxed for 2 h. The resultant colorless solution was put into a Teflon-lined stainless steel autoclave with autogenous pressure control at 200 °C for 24 h. Then the autoclave was cooled down to the room temperature, naturally. A gelatinous precipitate was obtained which was then centrifuged, washed with deionized water and dried in an oven at 70 °C for 24 h. The crystalline phase of the obtained powder was characterized with X-ray diffraction analysis (XRD, Philips X'Pert diffractometer) between the Bragg's diffraction angle range of 5–70° and the pattern was plotted after α_2-stripping. The morphologies and nanostructures were determined with a 200 keV transmission electron microscope (TEM) equipped with a field emission gun (FEG-STEM, Philips CM200). Also, differential thermal analysis (DTA/TG, STA1640) was performed with a heating rate of 5 °C/min from room temperature up to 1200 °C to evaluate the transformation temperatures and thermal behavior of the obtained product.

3. Results and discussions

X-ray diffraction results illustrated that the obtained product was composed of pure boehmite phase with orthorhombic crystal structure, Amam space group (63) and cell constants of about $a = 3.7$ Å, $b = 12.22$ Å and $c = 2.66$ Å. The XRD peaks were well matched with γ-AlOOH reported in the JCPDS File No. 21-1307. The average crystallite size of the obtained boehmite powder was calculated through Scherrer formula ($d = 0.9\lambda/B\cos\theta$, where d, λ, B and θ are average crystallite size, Cu Kα wavelength (0.1541 nm), full width at half maximum intensity (FWHM) of (0 2 0) peak in radians and Bragg's diffraction angle, respectively) to be about 4.5 nm (Fig. 1).

The transmission electron microscopy (TEM) observations reveal the boehmite nanostrips with average diameter of ~19.5 nm and average length of about 300 nm (Fig. 2a–c). The selected area electron diffraction (SAED) pattern of the nanostrips shown inset of Fig. 2a, illustrated the dotted reflections of (1 3 1) and (0 2 2) crystallographic planes and a pale ring pattern attributed to the (2 0 2) plane of boehmite orthorhombic crystal structure, indicating the polycrystalline and nanocrystalline nature of the obtained boehmite nanostrips. The strip-like morphology of the nanostructures is clearly obvious in Fig. 2b, which indicates two individual nanostrips with mesoporous structures. As Fig. 2c exhibits, bundles of nanostrips have formed due to the lateral self-assembly of several individual nanostrips, possibly as the result of the presence of hydrogen bonds between
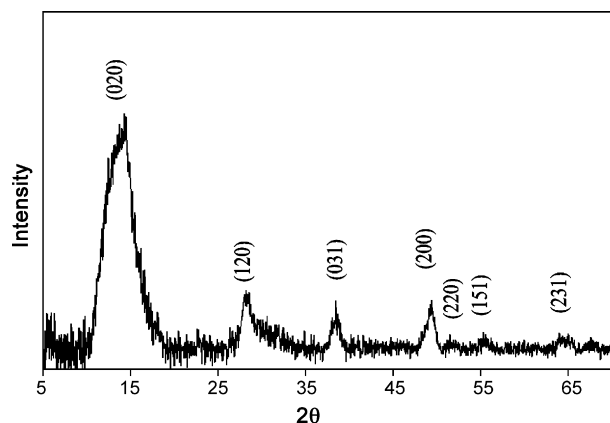
the adjacent single nanostrips through the following suggested mechanism.

The initial dissolution of the raw material in the alcoholic solution led to the reduction of the hydroxylation rate of precursor and inhibition of crystallites growth. Therefore, in this investigation the $AlCl_3 \cdot 6H_2O$ powder was dissolved into ethanol to inhibit the fast growth of the crystallites after subsequent water addition. The following reaction is expected for the formation of Al-alcoholic complex clusters:

$$AlCl_3 \cdot 6H_2O + 148C_2H_5OH$$
$$\rightarrow Al(OC_2H_5)_3 \cdot 145C_2H_5OH + 6H_2O + 3HCl \quad (1)$$
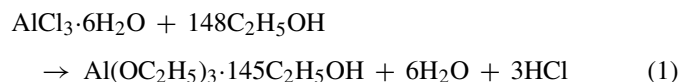
Subsequent water addition culminated in occurrence of hydroxylation process on the surface of the obtained complex clusters and formation of $Al(OH)_3$ colloidal crystallites:

$$Al(OC_2H_5)_3 \cdot 145C_2H_5OH + 3H_2O$$
$$\rightarrow Al(OH)_3 + 148C_2H_5OH \quad (2)$$
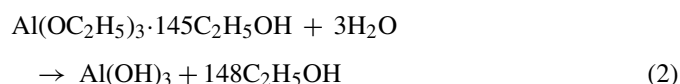
Because of the presence of hydroxyl groups on the surface of aluminum trihydroxide colloids, an ion exchange would occur between surface OH groups and Cl^- ions in the solution. These Cl^--capped $Al(OH)_3$ clusters form directionally due to the oriented attachment mechanism [2,26] and the influence of Cl^- ions in promoting the directional growth (Fig. 3). In hydrothermal conditions these one-dimensional $Al(OH)_3$ clusters, transformed to boehmite (AlOOH) nanostrips.

It has been shown previously that fluoride ions can enhance the directional growth and form 1D nanostructures [12], due to the formation of an AlOF intermediate compound [12,22]. In order to further assess the above mechanism and demonstrate the effect of Cl^- ions in promoting the one-dimensional growth, a same experiment was carried out utilizing $Al(NO_3)_3 \cdot 9H_2O$ as the starting material. In this case the following reactions can occur:

$$Al(NO_3)_3 \cdot 9H_2O + 148C_2H_5OH$$
$$\rightarrow Al(OC_2H_5)_3 \cdot 145C_2H_5OH + 9H_2O + 3HNO_3 \quad (3)$$
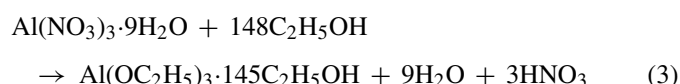
In contrast to the previously mentioned experiment, it is clear that the ionic species in this case is NO_3^-. TEM investigations (Fig. 4) elucidated the formation of nanoparticles, indicating that Cl^- ions have an effective influence on 1D growth of boehmite in the previous case.

In the boehmite lattice, oxygen ions are arranged in a distorted octahedral configuration around aluminum and organized in parallel layers linked by hydrogen bonds [27]. Therefore, the individual boehmite nanostrips self-assemble laterally due to the surface hydrogen bonds and form bundles of boehmite nanostrips as indicated in Figs. 2c and 3. Ma et al. [7] have indicated that the formation of arrays of boehmite nanorods was due to the effect of sodium dodecyl benzene sulfonate (SDBS) surfactant. In this investigation, such bundles of nanostrips were formed without the influence of any surfactant.

The thermal behavior of the obtained boehmite nanostructures were characterized through DTA/TG investigations. The differential thermal analysis (DTA) and thermogravimetric (TG)

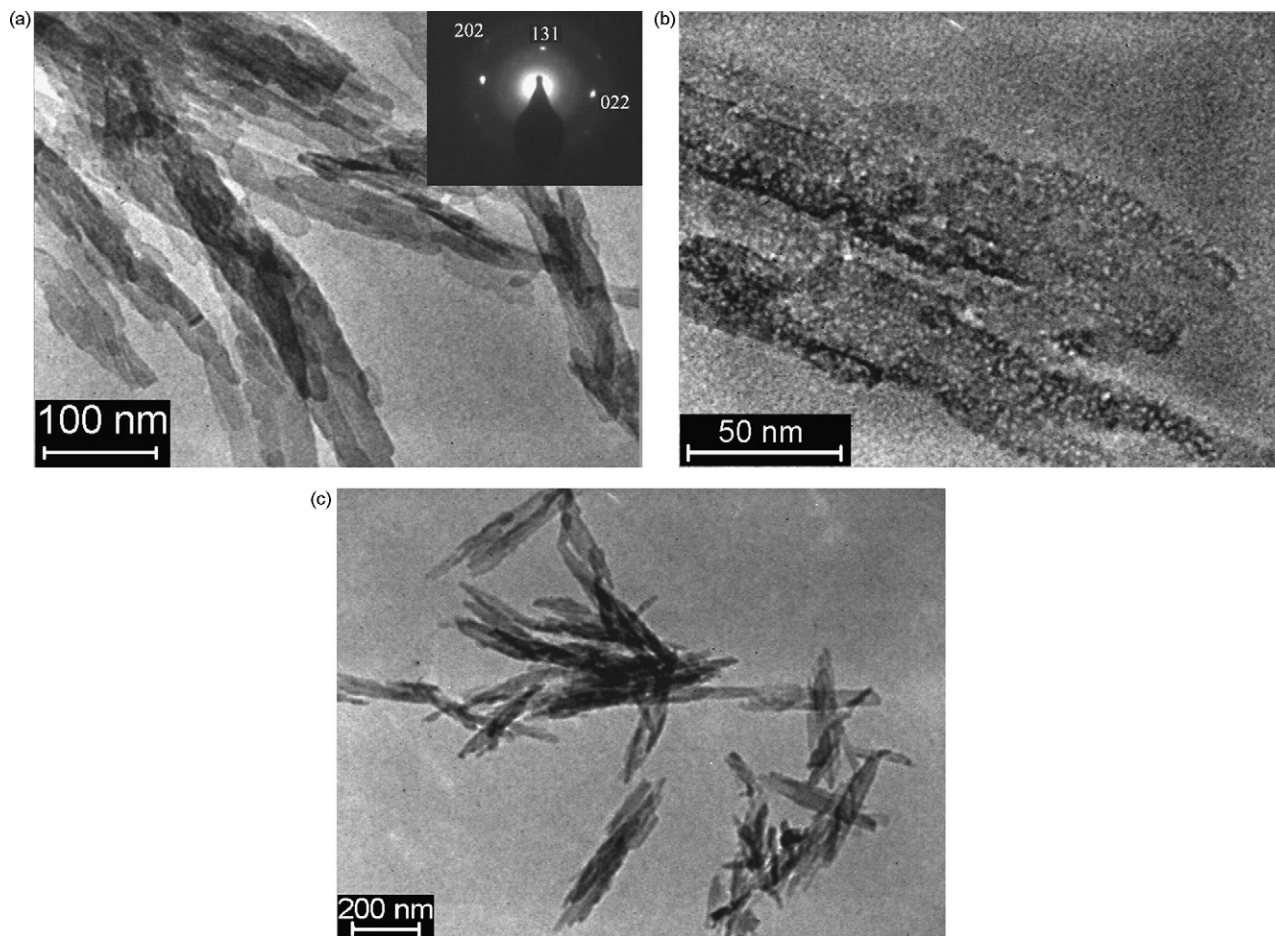

Fig. 1. XRD pattern of the obtained product.

Fig. 2. TEM images of the obtained (a) boehmite nanostrips (inset is the diffraction pattern), (b) two individual nanostrips and (c) bundles of nanostrips.

curves are exhibited in Fig. 5. Four distinguishable areas can be recognized in the curves due to the thermal transformations occurred on the boehmite powder. The total weight loss and transformation temperatures related to each stage are elucidated in Table 1. Stage A is related to the evaporation of physically and chemically absorbed water with a slight endothermic peak around 350 °C, while stage B is attributed to the endothermic transformation of boehmite to transition γ-Al_2O_3 phase at about 470 °C with a total weight loss of 11.27%. The exothermic peak around 535 °C at stage C is due to elimination of volatiles. Stage D with the least weight loss, is an important part in determining the thermal behavior of the obtained powders since the α-Al_2O_3 phase formation occurred at around 945 °C which is a low temperature in comparison with the data pre-

sented in the literature. The α-Al_2O_3 formation temperature in nanoscale systems was reported to occur in the temperatures more than ~1000 °C [14,17]. Various researchers have investigated the effect of additives in reducing the temperature of the mentioned phase transformation [18–20]. Among them, fluorides were reported to reduce the transformation temperature to a high extent [12,21,22]. However, there is no distinct result in the
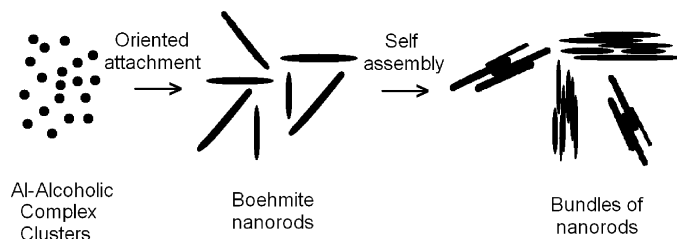

Fig. 4. TEM image of boehmite nanoparticle obtained through utilization of $Al(NO_3)_3 \cdot 9H_2O$ as the precursor.

Fig. 3. Schematic representation of the proposed formation mechanism of the boehmite nanostrips and bundles of nanostrips.

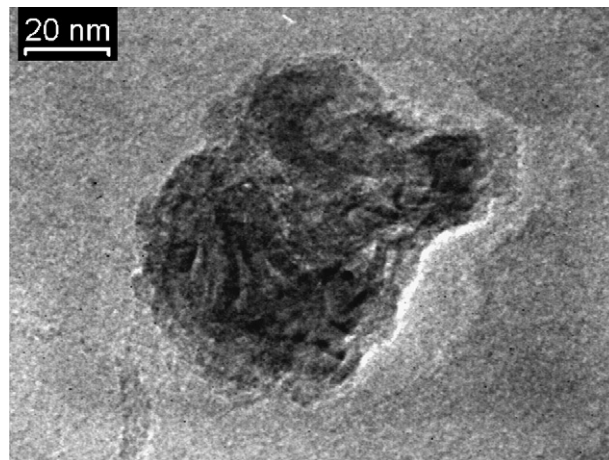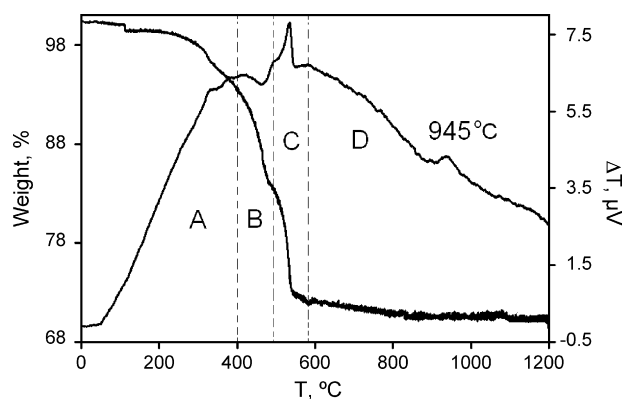Fig. 5. DTA/TG curves related to the thermal analysis of the obtained boehmite nanostrips.

Table 1
Total weight loss and transformation temperature of the obtained nanostrips during each step of thermal analysis

	Total weight loss (%)	Transformation temperature (°C)
A	6.44	350
B	11.27	470
C	13.55	535
D	2.35	945

literature concerning the influence of chlorides in decreasing the α-Al$_2$O$_3$ formation temperature. Here, it is proposed that such reduction in the formation temperature of thermodynamically stable α-alumina phase is attributed to the effect of preliminary mentioned Cl$^-$ ions capped on the surface of boehmite nanostrips and formation of an intermediate AlOCl compound similar to the previous results of the usage of fluorides as the additives [21,22]. Probably the same as AlOF [21,28], AlOCl can accelerate the mass transportation from transition alumina to α-alumina. These results demonstrate that chloride ions have the same influence as fluorides on enhancement of the directional growth and reducing the phase transformation temperature of the alumina phases, however its precise influence needs further investigations.

4. Conclusion

Boehmite nanostrips with average diameter of about 19.5 nm and crystallite size of 4.5 nm were prepared through a surfactant free hydrothermal route from a low cost raw material (i.e. AlCl$_3$·6H$_2$O). Self-assembled bundles were formed from differ-

ent numbers of nanostrips due to lateral hydrogen interactions. The suggested formation mechanism which proposed the formation of nanostrips as a result of Cl$^-$ ions in enhancement of oriented attachment mechanism was confirmed by relevant data. Differential thermal analysis of the obtained product showed a reduction in α-Al$_2$O$_3$ phase formation temperature. Totally, it was shown that chloride ions can enhance the directional growth and decrease the phase transformation temperature in the obtained product.

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