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ORIGINAL ARTICLE

Boehmite (AlOOH) nanostrips and their growth mechanism

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Abstract Crystalline nanostrips of AlOOH have been prepared at 240 °C through a fast route. Powder X-ray diffraction studies reveal that the as-prepared nanostrips are highly crystalline in nature and by morphological investigations using FESEM, it was revealed that the strips have average length of 210 nm and width of 60 ± 20 nm. A plausible theory is proposed which reveals the growth mechanism of nanostrips.

Keywords AlOOH · Soft synthesis · Nanostrips · Formation mechanism

Introduction

Boehmite (AlOOH) nanostructures are of immense significance for use in advanced catalysts, absorbents, composite materials and ceramics [1–3]. Numerous studies on Boehmite have been undertaken recently and considerable efforts have been directed towards the preparation of nanostructures of Boehmite having different morphologies such as nanopowder [4], rods and flakes [5], nanotubes [6] and well-crystallized 1-D nanostructures by employing various techniques [7]. We have previously reported a procedure for Al_2O_3 nanorods and nanoflakes without surfactants and additives [8, 9]. For decades, researchers consistently have been developing efficient synthetic routes to well-defined nanostructures. Experimental investigations reveal the growth parameters like surface energy, growth rate, reaction temperature and time to be critical in determining the behavior of nanostructures. In our view point, the facile, inexpensive and mass preparation of Boehmite (AlOOH) nanostructures still remains blank. Herein, we report the preparation of crystalline AlOOH nanostrips using soft method in which de-ionized water was used as solvent as well as source of oxygen. The method is based on a reaction without using any catalysts or harmful chemicals. This process is unique for its simplicity, high efficiency and its potential to be operated at large scale. In addition, to supplement the mechanism behind growth, a mathematical model has been proposed for the first time.

Experimental

Materials and synthesis

Pure aluminum AR grade (Ranbaxy) with diameter of about 10 μm was used as starting material. In the experiment, 5 mg of aluminum metal powder and 30 ml of de-ionized water have been well sonicated in a glass vial for around 10 min. After sonication, the reaction mixture was transferred to teflon-lined stainless steel chamber of 100 ml capacity and has been kept at 240 °C in an oven for 3 h. After the desired time, the system was allowed to cool naturally. The reaction mixture was centrifuged to reclaim the precipitated sample and washed several times with DI water. The final product was air dried for few hours.

Characterization of samples

The morphology of the product was carried out using field emission scanning electron microscope (FEI SEM, NNL

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200, Japan). Phase structure and the purity of the as-prepared sample were characterized by powder X-ray diffraction (XRD) taken on a Philips (X'Pert PRO PW-3710) diffractometer with 2θ ranging from 10°–80°, using Cu Kα ($\lambda = 0.15141$ nm) radiation operated at 40 kV and 30 mA.

Results and discussion

Structural studies

The XRD pattern of the as-prepared sample, synthesized at 240 °C is shown in Fig. 1. The diffraction pattern reveals the well-defined peaks corresponding to orientation of the (020), (120), (031), (200) and (002) planes. The most intense diffraction peak is (020) lattice plane according to standard pattern [12]. Diffraction peaks of AlOOH with lattice parameters a = 4.76 Å and c = 12.99 Å (corresponding to JCPDS No. 46-1212) are identified unambiguously. The relative broad peaks suggest high crystallinity of the samples. The result is quite different from the traditional process in which only amorphous phase can be obtained from the precipitates derived by sol–gel process before calcinations and further higher temperature heat treatment is normally required to induce crystallization. Thus, this method, the soft option of hydrothermal treatment may be regarded as an alternative to calcinations for promoting the crystallization.

Morphology examinations

The as-prepared sample was directly transferred to FESEM chamber for examination. Figure 2a low–resolution and Fig. 2b high-resolution FESEM images of nanostrips obtained by the reaction of aluminum metal powder with DI water at 240 °C for 3 h.

The FESEM images confirm that the nanostrips are grown in a very high density. It was observed that the grown product has a shape of nanostrips with an average length of 210 nm and a width of 60 ± 20 with an average width of 72 nm as shown in Fig. 3.

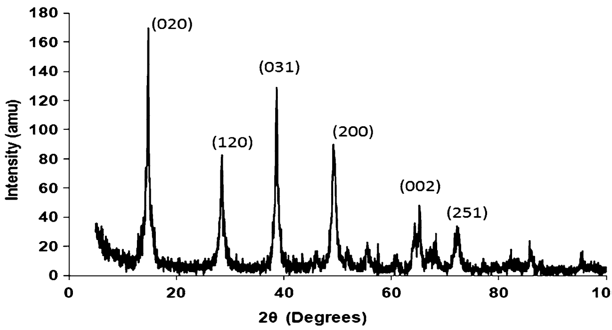

Fig. 1 XRD pattern of as-prepared sample

The nanostrips crystallized were composed of aluminum and oxygen only and the unit cells are very close to orthorhombic structure [10, 11].

Formation mechanism

The formation of AlOOH nanostructures from the reagents of aluminum and water can be explained by the following facile reaction:

$$2\text{Al} + 6\text{H}_2\text{O} \overset{\Delta}{\rightarrow} 2\text{Al(OH)}_3 + 3\text{H}_2(\text{gas}) \quad (1)$$

$$2\text{Al(OH)}_3 \rightarrow 2\text{AlOOH} + 2\text{H}_2\text{O} \quad (2)$$

Now, our primary emphasis is to analyze the formation of Boehmite nanostructures for that we would use tensor notations and Green's functions [14]. As the conditions are inert, the effect due to impurities can be neglected and the mixture can be treated as a binary mixture of aluminum particles and de-ionized water. Firstly, on heating this mixture at a temperature of 240 °C for 3 h leads to the formation of homogenous mixture of aluminum particles and DI water. Secondly, in this mixture, the aluminum crystals are broken down to nanosize under high pressure. Thirdly, due to difference in concentration and temperature there arise concentration and temperature gradients leading to convection, due to which a cell structure occurs which remains even after drying DI water [14, 15]. Now, for a ternary mixture, we have

$$\rho = \rho_0[1 + B_cC + B_c'C' + B_tT] \quad (3)$$

where C' is the concentration of impurities. Since the conditions are inert we have $C' = 0$ and hence for a binary mixture we can write

$$\rho = \rho_0[1 + B_cC + B_tT] \quad (4)$$

where ρ is the density of homogenous mixture of almunium particles and de-ionized water (which depends on both the temperature of this mixture and concentration of aluminum particles in de-ionized water), $B_c = \alpha_c\Delta C$, $B_t = \alpha_t\Delta T$ and α_c and α_t are the solute and thermal expansion coefficients, To write momentum balance equation, we first define $Dv_i = \partial_t v_i + v^j\partial_j v_i$ (with $\partial^i v_i = 0$, i.e., divergence-less vector field), called substantial derivative, which represents the time rate of change of a physical quantity subjected to space- and time-dependant velocity fluid in continuum mechanics. Now, momentum balance equation can be written as:

$$\rho_0 Dv_i = -\partial_i p + \mu\partial^2 v_i - \rho g\lambda_i. \quad (5)$$

where μ is a constant viscosity and other symbols have their usual meanings. we also require equations $DT =$

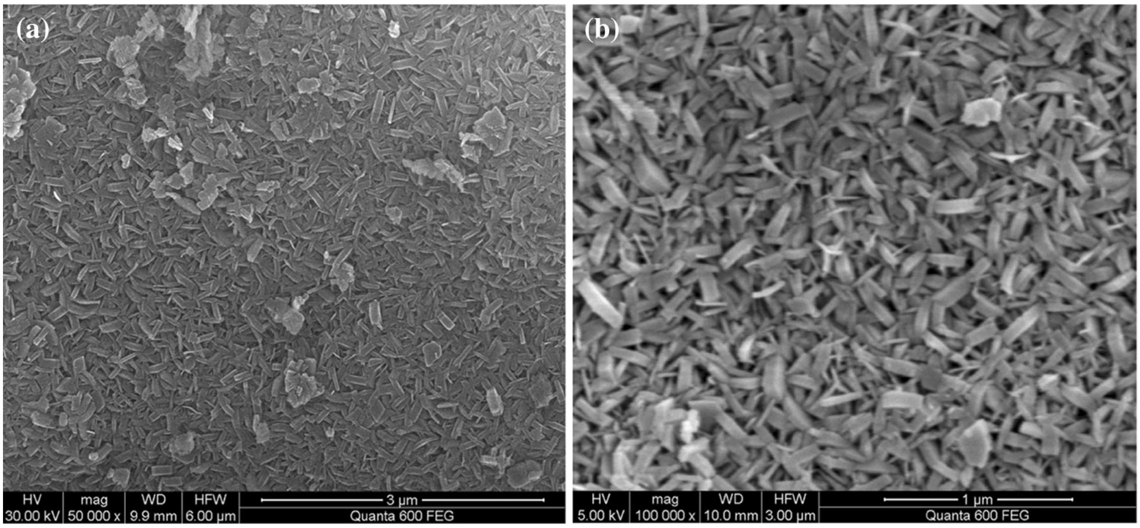

Fig. 2 Typical **a** low- and **b** high-resolution images of nanostrips obtained by the reaction of aluminum powder with water at 240 °C for 3 h

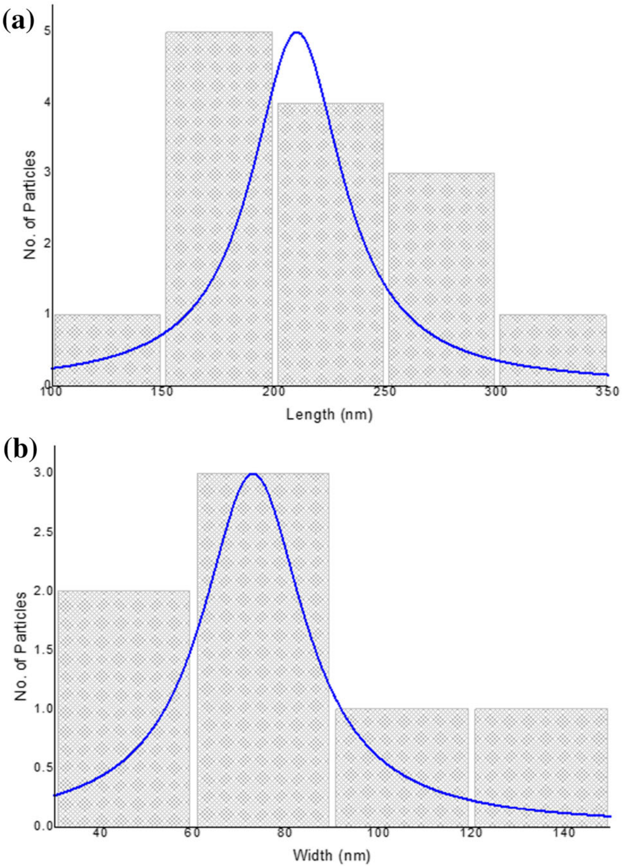

Fig. 3 Histograms showing **a** average length of nanostrips, **b** average width of nanostrips

$\kappa\partial^2 T$ and $DC = d_{11}\partial^2 C$, where d_{11} is the aluminum diffusion coefficient and κ is the thermal diffusivity of the fluid.

Using transformation $x^i \to lx^i, \partial_i \to l^{-1}\partial_i, v_i \to kl^{-1}v_i$, $t \to l^2k^{-1}t$, and $p \to p\mu kl^{-2} + \rho_0 g(l - \lambda^i r_i)$, satisfying the condition $\partial^i v_i = 0$, results in non-dimensional momentum conservation and continuity equations as under:

$$\begin{aligned} &Pr^{-1}Dv_i = -\partial_i p + \partial^2 v_i + R_c C\lambda_i + R_t T\lambda_i, \\ &DC = Le_{11}^{-1}\partial^2 C, \\ &DT = \partial^2 T, \end{aligned} \tag{6}$$

where $Pr = k\rho_0\mu^{-1}$ is the Prandtl number, $R_c = \mu^{-1}k^{-1}B_c\rho_0 g l^3$ is the concentration Rayleigh number, $R_t = \mu^{-1}k^{-1}B_t\rho_0 g l^3$ is the temperature Rayleigh number, and $Le_{11} = kd_{11}^{-1}$ are the Lewis numbers.

Now, using the boundary conditions $\lambda^i v_i = 0$, $\lambda^i\Lambda^j\partial_i v_j = 0$, where $\Lambda^i\lambda_i = 0$, and $C(0) = T(0) = 1$, $C(1) = T(1) = 0, p(1) = 0, \lambda_i = (0,0,1)$ and $r_i = (x,y,z)$, and adding small perturbations to steady-state solutions and defining $D_b^a = a^{-1}\partial_t - b^{-1}\partial^2$, we get

$$\begin{aligned} &D_1^{Pr}u_i + \partial_i\phi - (R_c\theta_c + R_t\theta_t)\lambda_i = 0, \\ &D_{Le11}^1\theta_c - \lambda^i u_i = 0, \\ &D_1^1\theta_t - \lambda^i u_i = 0. \end{aligned} \tag{7}$$

Now,

$$Ea^i = \partial^i\partial^p a_p - \partial^2 a^i. \tag{8}$$

where E is the operator taking twice a curl of any vector field a^i and as we know the gradient of a scalar field vanishes when its curl is taken twice. Further, $E\partial^i\phi = 0$, as u_i is divergence-less, and $\lambda^i(E\lambda_i\phi) = \lambda^i\partial_i\lambda^i\partial_j\phi - \partial^2\phi = \tilde{\partial}^2\phi$. Now, acting by E, contracting by λ_i, using Green's function and applying the boundary conditions (derivatives of $\lambda^i\partial_i$ vanishes on $\lambda^i u_i$) we arrive at

$$D_1^1 D_{Le}^1 D_1^{Pr} \partial^2 \lambda^i u_i = R_c \tilde{\partial}^2 D_1^1 \lambda^i u_i + R_t \tilde{\partial}^2 D_{Le}^1 \lambda^i u_i(r'). \tag{9}$$

and its solution

$$\lambda^i u_i = A \sin n\pi \exp[i(k_x x + k_y y) + \sigma t], \tag{10}$$

Thus, we have

$$C(k_n, k, \sigma) = 0, \tag{11}$$

where

$$\begin{aligned} C(k_n, k, \sigma) = {} & (\sigma + k_n^2 Le^{-1})(Pr^{-1}\sigma + k_n^2)(\sigma + k_n^2)k_n^2 \\ & - (\sigma + k_n^2 Le^{-1})k^2 R_t - (\sigma + k_n^2)k^2 R_c. \end{aligned} \tag{12}$$

By substituting $\sigma = 0$, the critical behavior under temperature dependance is given by

$$C(k_m, k, 0) = 0, \tag{13}$$

where

$$C(k_n, k, 0) = k_n^6 k^{-2} Le^{-1} - Le^{-1} R_t - R_c. \tag{14}$$

Now, the effective Rayleigh number is

$$R = R_t + Le R_c \tag{15}$$

Hence, $R = k_n^6 k^{-2}$. For lowest value $n = 1$, the instability starts at

$$\frac{\partial R}{\partial k^2} = 0. \tag{16}$$

which gives $k^2 = \pi^2/2$, and the value of R will be $R = 657.5$. Thus, by maintaining the rate of evaporation to an extent wherein $R > 657.5$, the formation of nanostructures takes place.

Conclusion

Highly crystalline nanostrips of Boehmite (AlOOH) have been prepared by a fast, an inexpensive and environmentally benign technique. The mechanism for the formation of nanostructures is briefly described in accordance with decomposition of metal with water giving out hydrogen. The formation mechanism has been explained by a mathematical model and it would be quite interesting to apply this technique in other metal and metal oxide nanostructures.

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