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Short communication

Synthesis of alumina nanofibers by a mercury-mediated method

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Abstract

Alumina nanofibers were successfully synthesized in mercury media at room temperature. Structure and morphology of the nanofibers were characterized by TEM, EDX, FESEM, XRD, TG, DTA and N_2 adsorption–desorption. The results show that the as-grown alumina nanofibers are amorphous, and have diameters of 5–15 nm and lengths up to several micrometers. After calcinated at 850 °C for 2 h, the amorphous alumina nanofibers convert to γ-Al_2O_3 nanofibers. The mechanism for the growth of alumina nanofibers was discussed and a model representing the growth process was presented. During the process, mercury will be produced by metathesis reaction of $HgCl_2$ and Al, Al atoms continuously dissolve into mercury and diffuse to amalgam/air interface, and then Al atoms react with oxygen and water in air, finally alumina nanofibers can be formed.

Keywords: A. Calcination; B. X-ray methods; D. Al_2O_3; Fibers

1. Introduction

Since the discovery of carbon nanotubes [1], one-dimensional (1D) nanomaterials have been receiving much attention because of their uniquely electronic, mechanical and chemical properties and potential applications as important components and interconnects in nanodevices [2,3]. As a kind of important structural ceramic materials, alumina have applications in absorbent, catalyst carrier and reinforce of ceramic composites for its high strength, corrosion resistance, chemical stableness, low thermal conductivity, and good electrical insulation [4,5]. Recently, the synthesis of 1D alumina nanomaterials has attracted more attention. Up to date, the most common synthetic strategy of 1D alumina nanomaterials is based on templating of surfactant micelle. Kuang et al. [6] reported that the tubular form of crystalline boehmite AlOOH was fabricated using $AlCl_3{\cdot}6H_2O$ as the alumina precursor in the presence of cationic surfactant. Zhu et al. [7] synthesized alumina with a fiber morphology and large porosity using aluminum hydrate with nonionic poly(ethylene oxide) (PEO) surfactant. Lee et al. [8] used aluminum alkoxide as precursor in the presence of a cationic surfactant and controlled the amount of water under hydrothermal conditions to synthesize alumina nanofibers.

However, the use of surfactant will introduce heterogeneous impurities that limit the applications of alumina due to trace surfactant absorption. Herein, we report a facile mercury-mediated synthetic pathway to the large-scale synthesis of alumina nanofibers in the absence of surfactants.

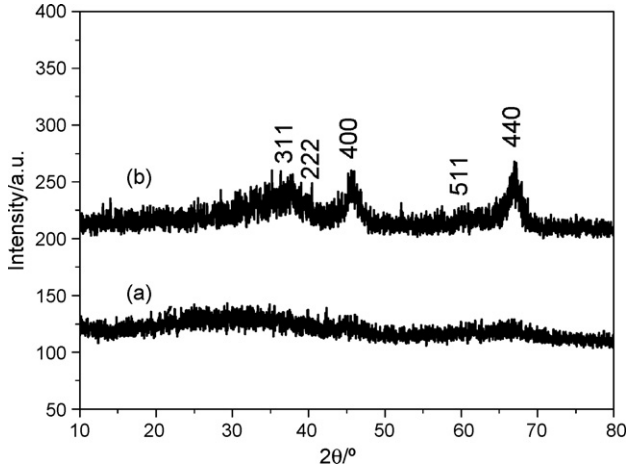

Fig. 1. XRD patterns of (a) as-grown products and (b) products calcined at 850 °C for 2 h.

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2. Experimental

The purity of Al strip is 99.5%. $HgCl_2$ is analytic pure. All the reagents were used without further purification. A typical preparation procedure of alumina nanofibers was as follows: 0.5 g $HgCl_2$ was dissolved into 100 ml distilled water. Al strip was immersed in $HgCl_2$ solution for 5 min at room temperature, then moved from the solution and exposed in air. After a period of time, the white alumina powders could be observed on the surface of Al strip. The as-grown products were heated to 850 °C in air at a heating rate of 3 °C/min, and then were calcined at 850 °C for 2 h.

The products were ultrasonically dispersed in acetone and dropped onto a carbon-coated copper grid for transmission electron microscopy (TEM, JEM-2010F, JEOL) measurement, equipped with an energy-dispersive X-ray (EDX) system. The morphology of Al strip with as-grown products was checked by field emission scanning electron microscopy (FESEM, SIRION200), also equipped with the system of energy-dispersive spectroscopy (EDS) analysis. X-ray diffraction (XRD) was recorded on a BRUKER-AXS X-ray powder diffractometer with Cu Kα radiation (λ = 0.154178 nm) in the range of $10^\circ < 2\theta < 80^\circ$ at a scanning speed of 1°/min. TG and DTA were performed on a TG 2050 thermogravimetric analysis (TGA) from room temperature to 800 °C and a DTA 1600 differential themal analysis (DTA) from room temperature to 1200 °C at a heating rate of 10 °C/min in air. The N_2 absorption–desorption isotherm at liquid nitrogen

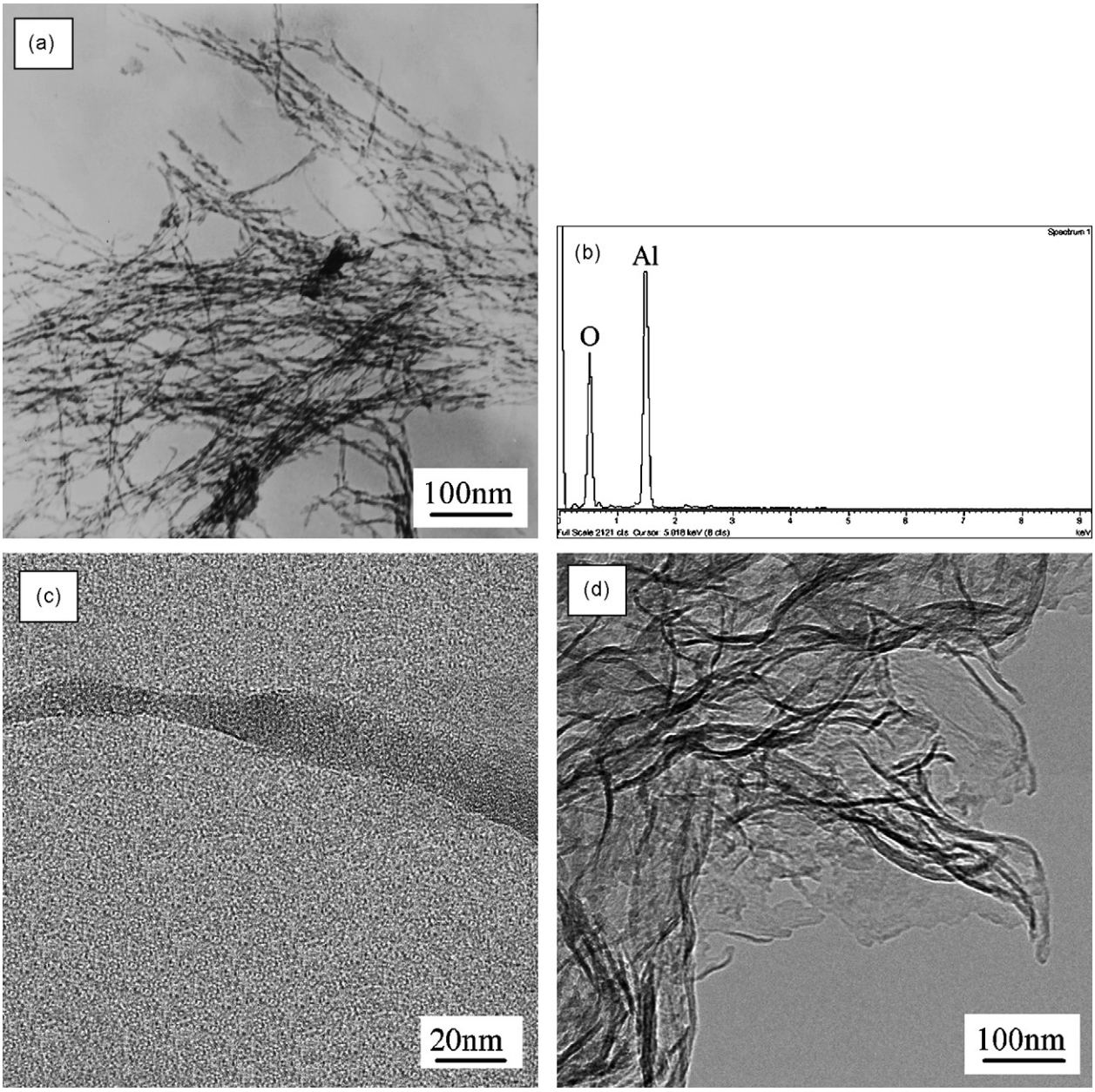

Fig. 2. (a) TEM images of as-grown products, (b) EDX spectrum of alumina nanofibers, (c) TEM images of an individual alumina nanofiber, and (c) TEM images of γ-Al_2O_3 nanofibers.

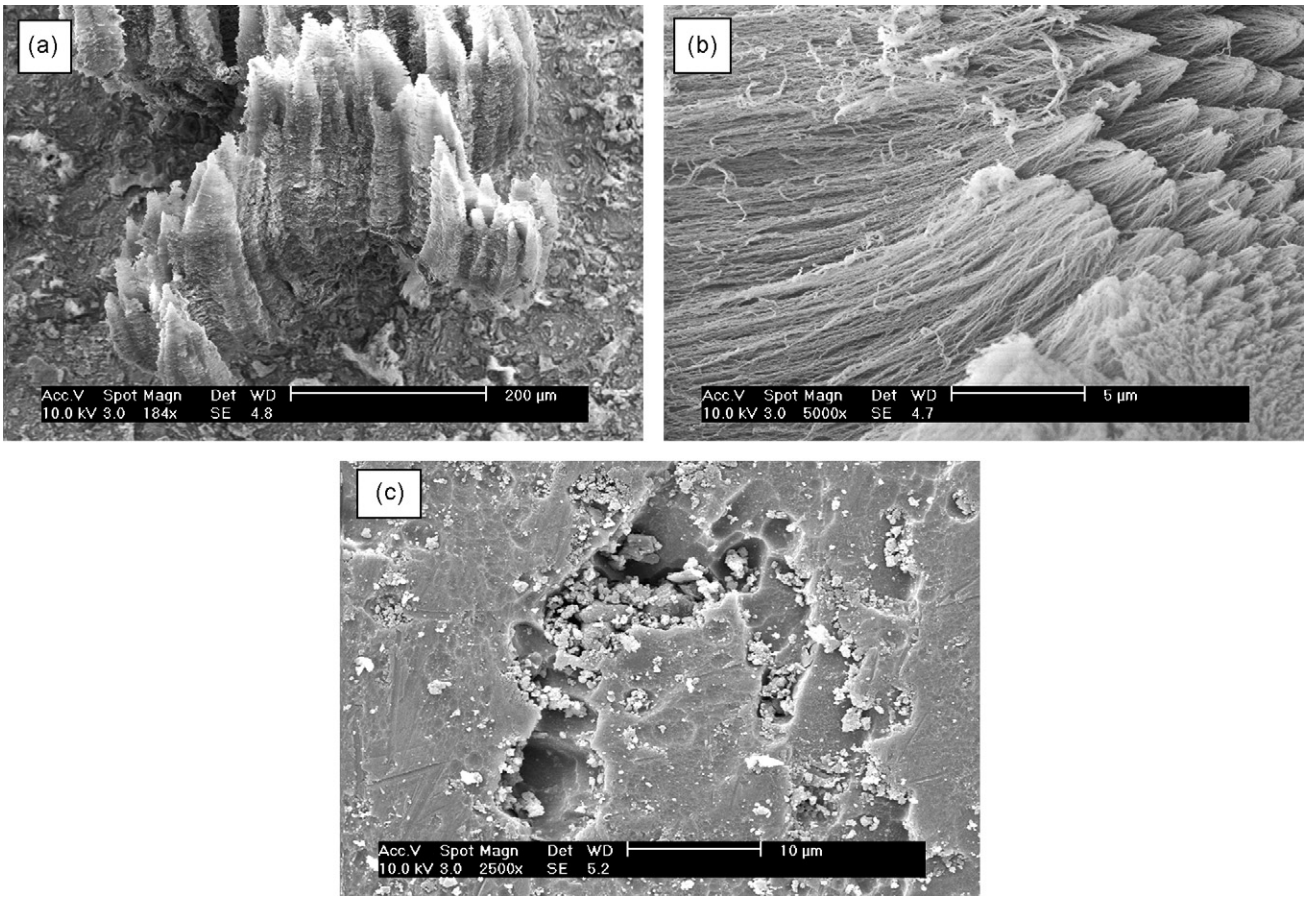

Fig. 3. FESEM images of (a) Al strip with as-grown products on its surface, (b) side face of the as-grown products, and (c) surface of Al strip, with as-grown products removed.

temperature (78 K) were measured by ASAP2010 static volumetric absorption analyzer.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of as-grown and calcined products. The diffraction patterns of the as-grown products indicate that amorphous alumina is obtained (Fig. 1a). After calcined at 850 °C for 2 h, the amorphous alumina transfer to γ-Al_2O_3 (Fig. 1b). The peaks at 37.6°, 39.5°, 45.86°, 60.89° and 67.03° are assigned to (3 1 1), (2 2 2), (4 0 0), (5 1 1) and (4 4 0) reflections of γ-Al_2O_3 (JCPDS Card 10-0425). No peaks from impurities are observed.

Fig. 2a shows TEM image of the as-grown products. The nanofibers are typically about 5–15 nm in diameter for the most of the nanofibers. Fig. 2b shows the EDX spectrum taken for the alumina nanofibers of Fig. 2a. Only the O- and Al-related peaks are present in the EDX spectrum. A magnified image of single nanofiber is shown in Fig. 2c, indicates that the alumina nanofiber is not uniform in diameter, their diameter is about 5–15 nm. After calcined at 850 °C for 2 h, the amorphous alumina nanofibers convert to γ-Al_2O_3 and their fibrous morphology was retained (Fig. 2d).

In order to investigate the formation process of alumina nanofibers, the immersing time of Al strip was shorten to 5 s, the concentration of $HgCl_2$ solution decrease to 0.1%, and FESEM was used to examine the morphology of the Al strip with as-grown products on its surface. The low-magnification FESEM image of Al strip with as-grown products indicates that the products with stalactite morphology vertically grow from the surface of Al strip (Fig. 3a). The high-magnification FESEM image of side face of the stalactite-like products reveals that the as-grown products are constructed by almost paralleled fibrous materials with various lengths up to several micrometers (Fig. 3b). After the as-grown products were removed, there are some holes on the surface of Al strip (Fig. 3c). It is clear that the alumina nanofibers grow from these holes and consume a lot of bulk Al.

According to above investigation, it is reasonable to regard that the growth mechanism of alumina nanofibers is similar to voluminous oxidation of Al by continuous dissolution in a wetting mercury film [9]. The reactions and equilibriums in the process are shown as follows:

$$2Al + 3HgCl_2 = 3Hg + 2AlCl_3 \quad (1)$$

$$4Al + 3O_2 + 2nH_2O = 2Al_2O_3 \cdot nH_2O \quad (2)$$

Although the natural alumina film offers some protection for bulk Al, it contains surface defects [10]. It is difficult for liquid mercury to penetrate into the metal underneath because of its surface tension. However, $HgCl_2$ solution can penetrate (Fig. 4a), react with the bulk Al, and mercury will form by

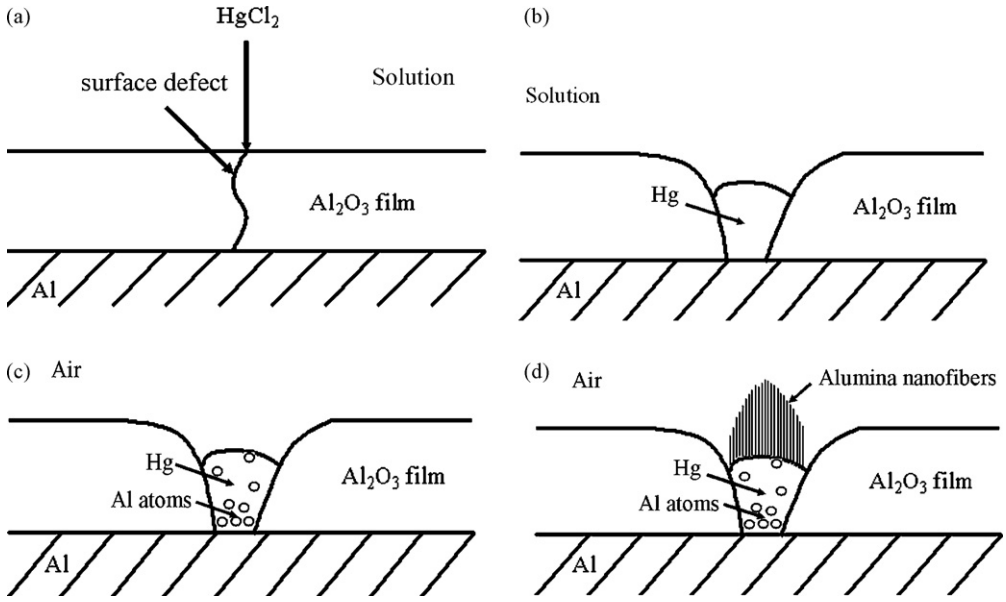

Fig. 4. Schematic representation of the formation process of alumina nanofibers. (a) The penetration of $HgCl_2$ solution, (b) the formation of Hg, (c) the diffusion of Al atoms, and (d) the formation of alumina nanofibers.

metathesis reaction (Fig. 4b). Because protective alumina film is removed, Al atoms continuously dissolve into mercury and form amalgam. After Al strip is moved from $HgCl_2$ solution and exposed in air, Al atoms diffuse from the amalgamated layer near bulk Al to the amalgam/air interface (Fig. 4c), and react with oxygen and water in air (Fig. 4d). Alumina particles assemble by preferred orientation to form nanofibers [11]. As the Al atoms are depleted, more bulk Al dissolves into the mercury and the process continue until mercury volatilize completely.

The heat treatment process of the as-grown products was analyzed by TG and DTA; the results were shown in Fig. 5. It is found that in the range of $t < 600\ ^\circ C$, a weight loss of 40% can be attributed to desorption of adsorbed water and dehydration of alumina hydrate. The exothermic peaks at 835 °C in DTA curve is assigned to a phase transformation of the as-grown amorphous alumina converting to γ-Al_2O_3.

The specific surface area of the obtained alumina nanofibers were studied by N_2 adsorption–desorption. Fig. 6 shows the N_2 absorption and desorption isotherms for alumina nanofibers prepared by Al with purity of 99.5% and 99.99%, respectively. These two absorption and desorption isotherms look rather similar, and display type IV isotherms with type H3 hysteresis loops, which are often associated with the formation of aggregates with slit-shaped pores [12]. According to the above TEM results, it can be concluded that the H3 hysteresis loops in Fig. 6 are corresponding to the filling of mesopores produced by aggregates of alumina nanofibers. The BET specific surface area of the alumina nanofibers prepared by Al with purity of 99.5% and 99.99% are about 164.9 m^2/g and 205.2 m^2/g, respectively. It can be proposed that with increasing purity of Al, the oxidation of Al will accelerate, the supersaturation of alumina in mercury media will increase, and that result in the smaller diameter and bigger specific surface area of the alumina nanofibers.

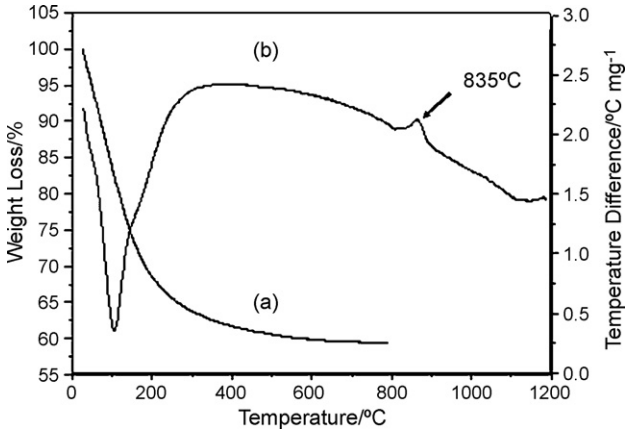

Fig. 5. TG-DTA curves of as-grown alumina nanofibers.

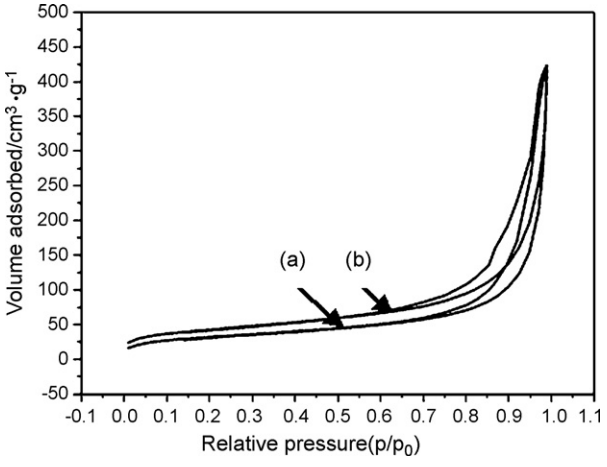

Fig. 6. Adsorption–desorption isotherms of alumina nanofibers.

4. Conclusion

Mercury will form by metathesis reaction and serve as media for oxidation of Al. The as-grown alumina nanofibers are amorphous, and have diameters about 5–15 nm and lengths up to several micrometers. After calcined at 850 °C for 2 h, the amorphous alumina nanofibers converted to γ-Al_2O_3 nanofibers. The increasing purity of Al will give rise to the smaller diameter and bigger specific surface area of the alumina nanofibers.

Acknowledgments

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