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Short communication

Growth kinetics of nanograins in Co_3O_4 fibers

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Abstract

The growth kinetics of nanograins in Co_3O_4 nanofibers has been investigated. Individual fibers were made up of nanograins. The nanograins were observed to coalesce and grow at the expense of the smaller ones, similar to the phenomenon observed in the sintering process of bulk ceramics. The activation energy and the growth kinetics of nanograins were estimated, showing the dominant growth mechanism of nanograins to be likely related to a lattice diffusion process.

Keywords: Co_3O_4; Nanofibers; Gowth kinetics; Electrospinning

1. Introduction

Co_3O_4 has been extensively studied due to its valuable physical and chemical properties. It can be considered as electrode materials in various applications including lithium ion batteries [1–3], electrochromic devices [4] and supercapacitors [5]. In addition, Co_3O_4 is used in solid-state gas sensors [6], heterogeneous catalysis [7] and energy storage [8]. Various nanostructures of Co_3O_4 such as nanopowders [9], nanowires [10] and nanofibers [11] have been prepared by using different synthesis methods.

Electrospinning has been widely used to synthesize nanofibers of a variety of oxide materials because it is a simple, inexpensive and highly reproducible process [12–14]. In recent years, some research groups have succeeded in synthesizing Co_3O_4 nanofibers by electrospinning and their properties were investigated in relation to the preparation conditions and procedures [15]. However, the role of calcination temperature and its duration on the morphology and growth behavior of Co_3O_4 nanograins existing in individual nanofibers has not been addressed yet. This study may provide us a better insight in understanding the use of Co_3O_4 fibers in surface-related applications including gas sensors and catalysis in which the control of surface area of fibers is of importance. In this work, Co_3O_4 fibers were synthesized by electrospinning. The growth kinetics of nanograins in the fibers was investigated.

2. Experimental

For the synthesis of Co_3O_4 fibers by electrospinning, polyvinyl alcohol (PVA) with a molecular weight of 80,000 and cobalt(II) acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$) were used as the precursor materials. A typical experimental procedure for preparing the electrospinning solution is as follows. First, an aqueous 9.5 wt% PVA solution was prepared by dissolving PVA beads in distilled water with constant stirring for 4 h at 70 °C. A 6.66 wt% cobalt(II) acetate solution was added to the PVA solution with constant stirring for 6 h at 70 °C. This produced the formation of a viscous mixed solution of cobalt(II) acetate and PVA.

The solution was loaded into a glass syringe, equipped with a 21-gauge stainless steel needle. The distance between the tip of the syringe needle and the collector of the Al plate was fixed at 20 cm. A positive voltage of 15 kV was applied to the needle while the metal collector was grounded. At the same time, a negative voltage of 10 kV was applied to the metal collector to accelerate the electrospinning process. The feeding rate of the solution was controlled at a constant rate of 0.05 mL/h. The as-spun nanofibers were distributed uniformly over Si wafers. The as-spun fibers were calcined at various temperatures and durations in an oxygen atmosphere using a tube-type furnace to obtain fibers of a pure Co_3O_4 phase and to investigate the grain growth kinetics of nanograins.

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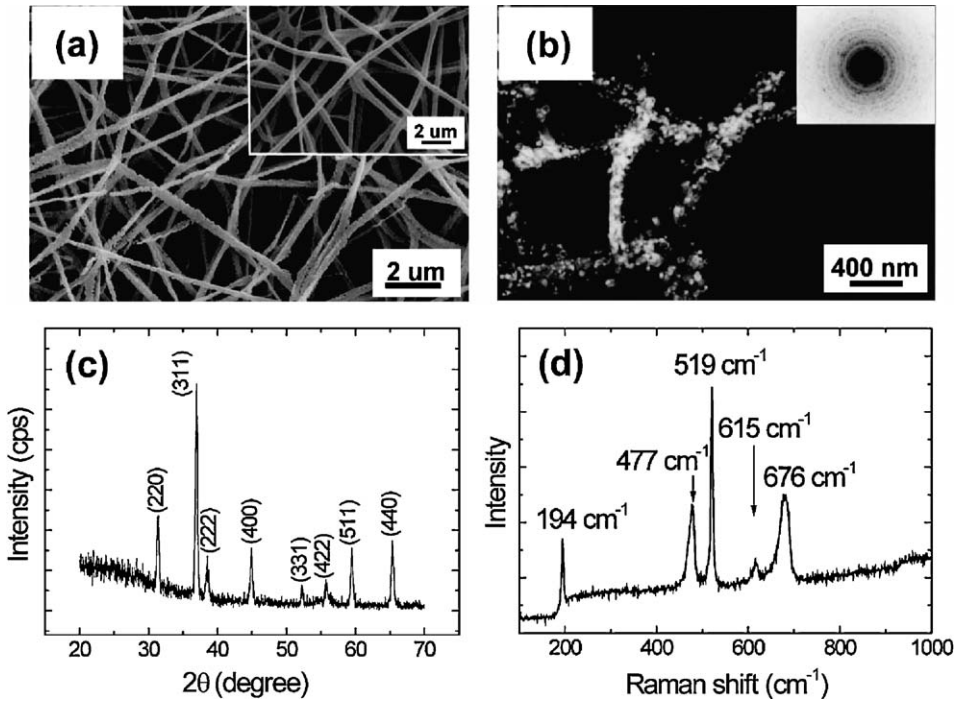

Fig. 1. Results of Co_3O_4 fibers synthesized by electrospinning and subsequent calcination at 600 °C for 6 h; (a) typical FE-SEM image. The inset shows the morphology of as-spun fibers. (b) Bright-field TEM image. The inset shows a selected area electron diffraction pattern of a single Co_3O_4 fiber. (c) X-ray θ–2θ diffraction pattern. (d) Raman spectrum.

The microstructure and phase of the synthesized fibers were examined by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy, respectively. The grain size was measured using an intercept method. The basic steps to this procedure are as follows. One or more straight lines of known length (L) were placed along the fiber length direction. The total number of intercepts (P) was counted. If $P < 20$, additional lines were used on other fibers. The average grain size was estimated from L/P. More than 20 grains were

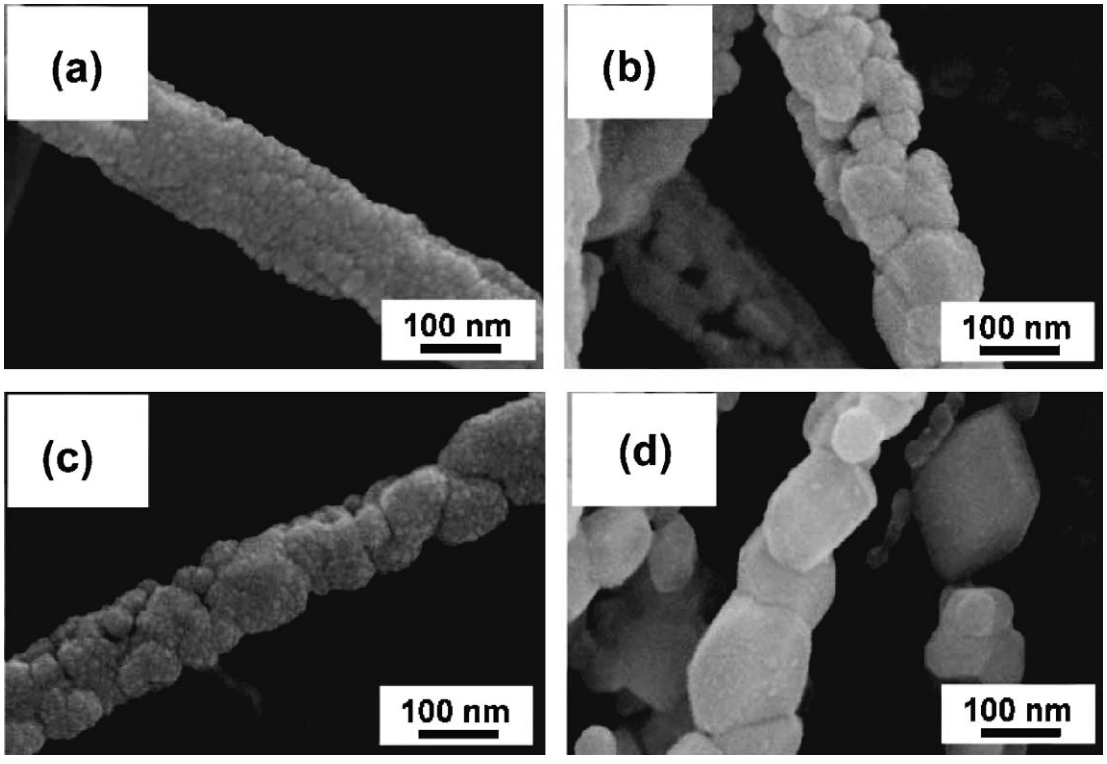

Fig. 2. FE-SEM images of Co_3O_4 fibers calcined at various temperatures for 6 h in an O_2 atmosphere; (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C.

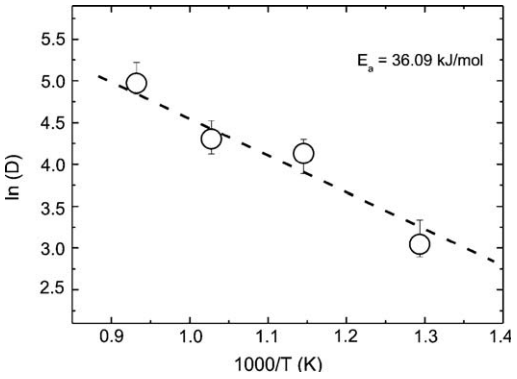

Fig. 3. Plot of ln(D) versus 1/T.

counted for each average grain size. The maximum and minimum intercept distances were used in describing the error bar in each data point.

3. Results and discussion

Fig. 1(a) shows a typical FE-SEM image of Co_3O_4 fibers synthesized by electrospinning and subsequent calcination at 600 °C for 6 h. The inset figure shows the morphology of as-spun fibers. The as-spun fibers must be a mixture of PVA and cobalt(II) acetate with a certain amount of water. They showed an average diameter of ~330 nm and were distributed randomly but uniformly over the Si substrates. After the calcination treatment at 600 °C for 6 h, the diameter of the fibers shrank as small as ~240 nm due to the removal of polymer and solvent as well. The microstructure of the fibers was further investigated by TEM and one of the results is shown in Fig. 1(b). As shown, the individual fibers consist of nanograins of ~60 nm in diameter. The inset shows a selected area electron diffraction pattern obtained from a single fiber. The ring pattern highlights the polycrystalline nature of the individual Co_3O_4 fibers. According to the results of XRD (not presented here), the as-spun fibers showed no crystalline phase, as predicted. However, the calcined fibers show a well crystallized phase (see Fig. 1(c)). The X-ray diffraction pattern reveals the formation of a pure Co_3O_4 phase. Raman spectroscopy was used to again confirm the phase after the calcination treatment, and the result is displayed in Fig. 1(d). This Raman spectrum is typical for pure, polycrystalline Co_3O_4 [16]. As shown, there are five Raman-active modes at 194 cm^{-1}, 477 cm^{-1}, 519 cm^{-1}, 615 cm^{-1} and 676 cm^{-1}, which can be assigned, respectively to F_{2g}, E_g, F_{2g}, F_{2g}, and A_{1g} phonon mode.

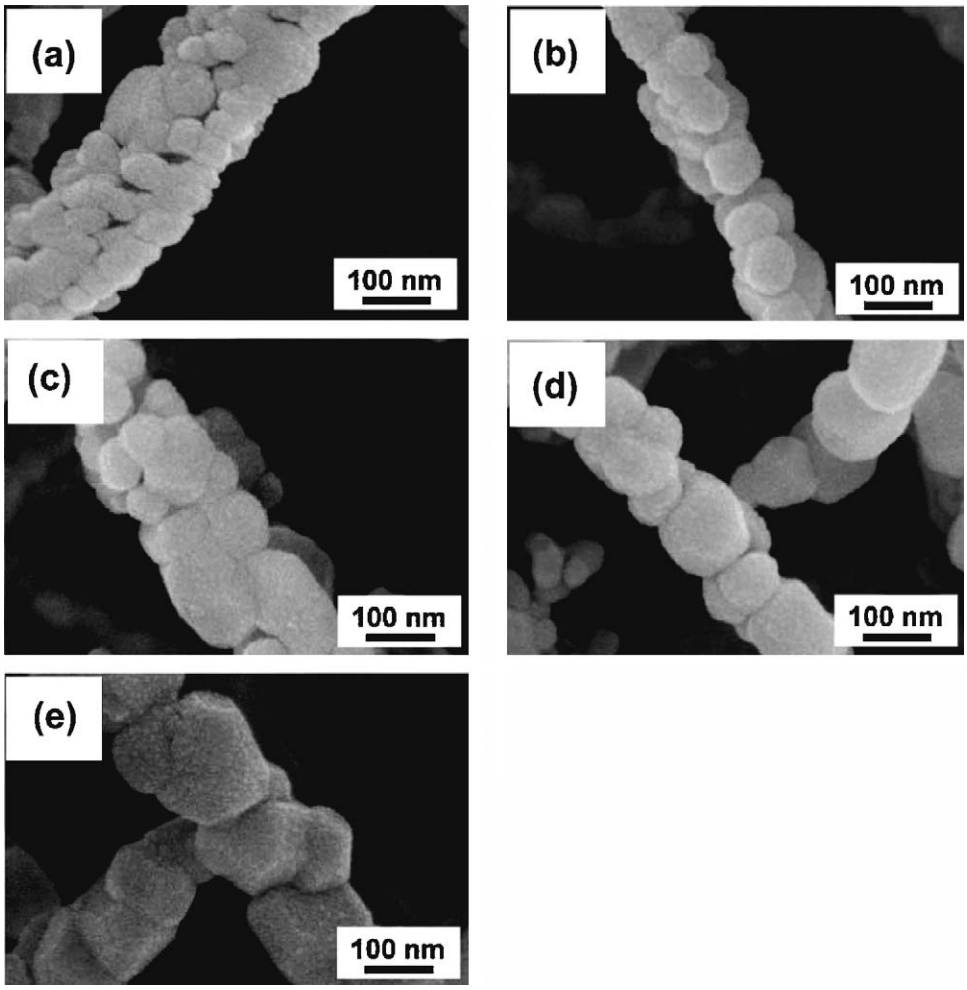

Fig. 4. FE-SEM images of Co_3O_4 fibers calcined at 700 °C in an O_2 atmosphere for various calcination times; (a) 2 h, (b) 6 h, (c) 12 h, (d) 24 h and (e) 48 h.

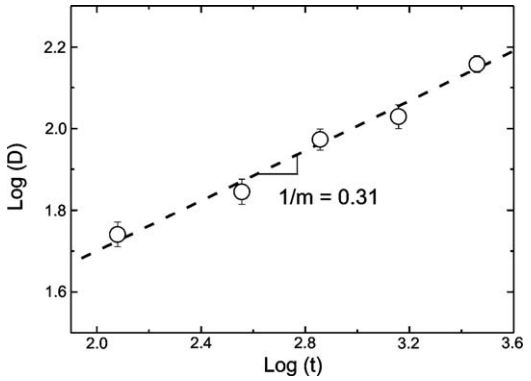

Fig. 5. Plot of log(D) versus log(t).

Fig. 2 shows FE-SEM images obtained from Co_3O_4 fibers after calcination at various temperatures for 6 h in O_2. It should be noted here that as the calcination temperature increases, the growth of nanograins existing in individual fibers is evident, although there appears some distribution in the grain size. The activation energy of the growth process may be obtained by the well-known Arrhenius equation, $D = A\exp(-E_a/RT)$. Here D is the average grain size, A is the pre-exponential factor, E_a is the activation energy for atomic diffusion around the grain boundary, R is the gas constant, and T is temperature in Kelvin. Fig. 3 shows the plot of ln(D) as a function of $1/T$ in Kelvin. E_a was estimated to be 36.09 kJ/mol from the slope, which is nearly the same as the value of 37 ± 7 kJ/mol obtained from the coarsening of nanometer Co_3O_4 powders [17]. According to Ref. [17], however, the activation energy for the growth of micrometer Co_3O_4 powders was 113 ± 8 kJ/mol. The much lower activation energy for the growth of nanograins in electrospinning-synthesized Co_3O_4 fibers is likely to come from the chemical potential of the atoms in nanosized grains to be much higher, thereby being more active in growth.

The grain growth behavior at a fixed temperature can empirically be described as $D_m - D_0^m = K_t$ [18]. Here D is the average grain size, D_0 is the average size at $t = 0$, and K is a constant. The grain growth exponent m is often found to be between 2 and 4 depending on the mechanism of grain growth. The equation can be expressed in the form of $\log(D) = 1/m \log(K) + 1/m \log(t)$, when D_0 can be neglected assuming $D \gg D_0$. Therefore, the slope in the log(D) versus log(t) plot gives us the value of exponent m. In order to estimate m, the fibers were calcined for various times at a fixed temperature. Fig. 4 shows the microstructures of Co_3O_4 fibers calcined at 700 °C in O_2 ambient at various calcination times. As evident, the nanograins gradually increase in size with calcination time. Fig. 5 shows the log(D) versus log(t) plot, showing that the grain growth exponent m is 3.23. The estimated m value supports that the grain growth of nanograins observed in individual fibers possibly occurs through lattice diffusion in a pore control scheme [18].

4. Conclusions

Co_3O_4 fibers were synthesized by electrospinning. The synthesized Co_3O_4 fibers were polycrystalline and consisted of nanograins. Higher calcination temperatures or longer calcination times resulted in the coalescence and growth of nanograins, similar to the phenomenon usually observed in the sintering process of powders or bulk ceramics. The activation energy for the growth of nanograins was estimated to be 36.09 kJ/mol and the dominant grain growth mechanism has been suggested to be possibly related to a lattice diffusion process.

Acknowledgment

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