

## Synthesis and Characterization of Aluminum Oxide Submicro-Rings

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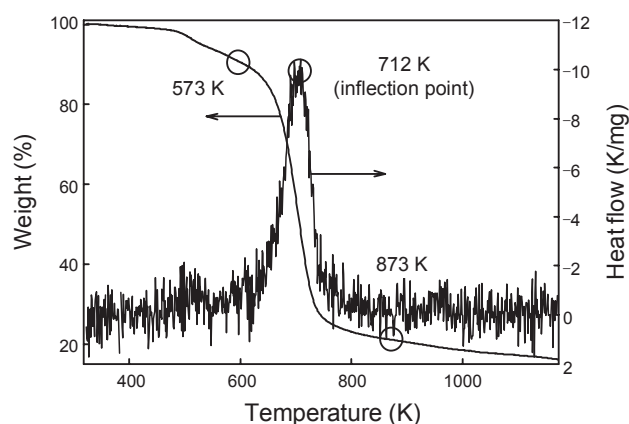
**Key Words:** Submicro-rings, Aluminum oxide, X-ray photoelectron spectroscopy, Electrospinning

Aluminum oxides including alumina ( $\text{Al}_2\text{O}_3$ ) and boehmite ( $\text{AlOOH}$ ) get large attention because those are widely used in many applications, for example, adsorbents for removal of HF and water,<sup>1,2</sup> fabrication of porous ceramics,<sup>3,4</sup> and composite materials for organic/inorganic hybrid coatings.<sup>5,6</sup> A new class of nano- and submicro-sized wire, tube, mats, and belts made to attract a very large research interest in the last few years.<sup>7-12</sup> In this note, we report the physical and chemical properties of aluminum oxide submicro-rings (AO-SMRs) obtained by using electrospinning technique.

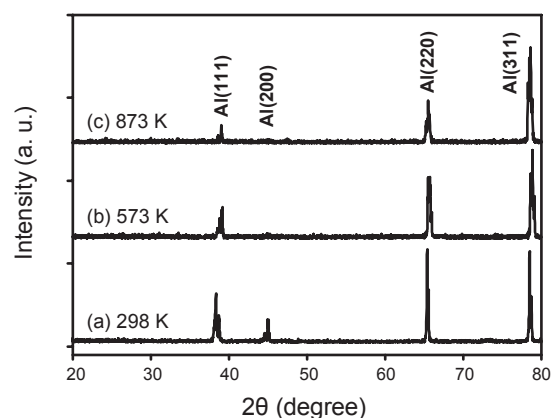
The AO-SMRs were synthesized from aluminum acetate and polyvinylpyrrolidone (PVP) solutions by applying simple electrospinning technique. The PVP ( $(\text{C}_6\text{H}_9\text{NO})_n$ , MW  $\sim 1,300,000$ ) solution was prepared by dissolving 0.62 g PVP in 10 mL ethanol (99.9%) stirring for 2 hrs at room temperature. The aluminum acetate solution was made by dissolving 5 g of aluminum acetate ( $\text{C}_2\text{H}_5\text{AlO}_4$ , MW 140.65) in 5.0 mL distilled water and 6.3 mL ethanol then stirred for 5 hrs at room temperature. All chemicals were purchased from Sigma Aldrich and used as received. The aluminum acetate solution was mixed with PVP solution at 1:1 volume ratio and stirred at room temperature for 5 hrs. The electrospinning solution was obtained after stirring the diluted 7 mL of mixed solution with 2 mL of ethanol for 30 min. The viscosity of the electrospinning solution was checked with a viscometer (A&D; SV-10), and the average viscosity of the solution was  $17 \pm 2$  cP at 295.8 K. The electrospinning solution was transferred to a plastic syringe (5.0 mL) with a needle of 21 gauge. The syringe was mounted on a syringe pump (KDScientific) and an electrically grounded drum collector was covered with aluminum foil. The revolution of the collector was fixed at  $100 \pm 1$  revolutions per minute. Electric fields (Nano NC) of 0.96 and 1.04 kV/cm were applied between the needle and the collector then dense SMR composites were collected on the aluminum foil. We checked the viscosity dependence on the SMR fabrication. When the viscosity of the solution was lower than the SMR collection condition ( $17 \pm 2$  cP), neither SMRs nor fibers were collected since the solution was too sparse. Only fibers were collected without mixing with SMRs over 67 cP of the viscosity because the solution was too dense to electrospin as a ring.

In order to check the decomposition temperature of the SMR composite, thermo gravimetric analysis (TGA) and differential thermo analysis (DTA) were conducted (Figure 1). Dehydration of SMR composite was mainly has occurred until 573 K. Most PVP and hydrocarbons in the SMR composite were decomposed

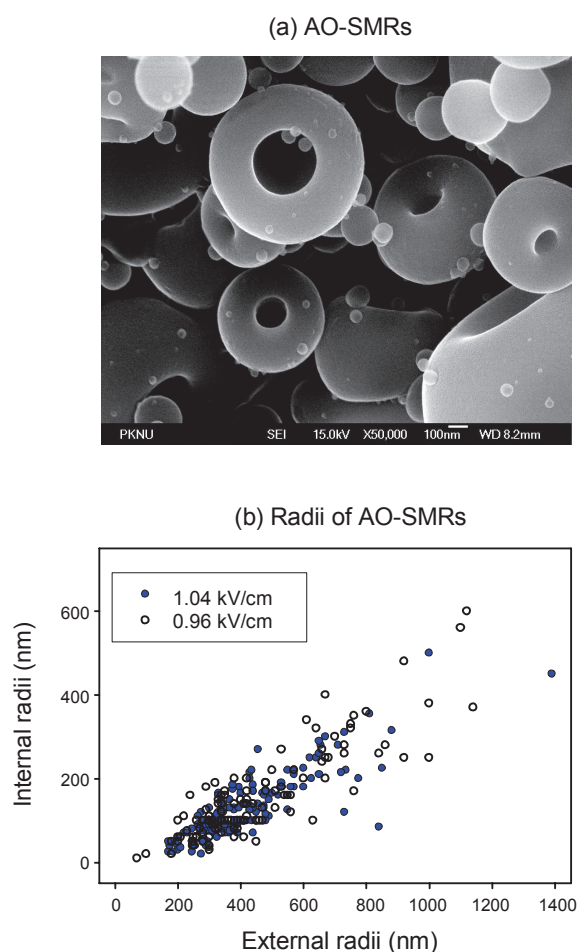
at about 873 K.<sup>13</sup> The obtained SMR composite was calcined to obtain AO-SMRs at two different temperatures named 573 and 873 K. X-ray diffraction (XRD, PHILIPS (Netherlands), X'Pert-MPD System) was performed to identify the crystallinity of the AO-SMRs in glancing mode. XRD study (Figure 2) revealed that only metallic aluminum was formed in crystalline phase and the crystallinity of aluminum oxide was not detected. This implies that aluminum oxide was formed as amorphous phase. As the calcination temperature increased, the crystallinity of Al decreased by a change of the oxidation state of aluminum from metallic to oxide.



**Figure 1.** TGA-DTA spectra of aluminum acetate/PVP composite SMRs.



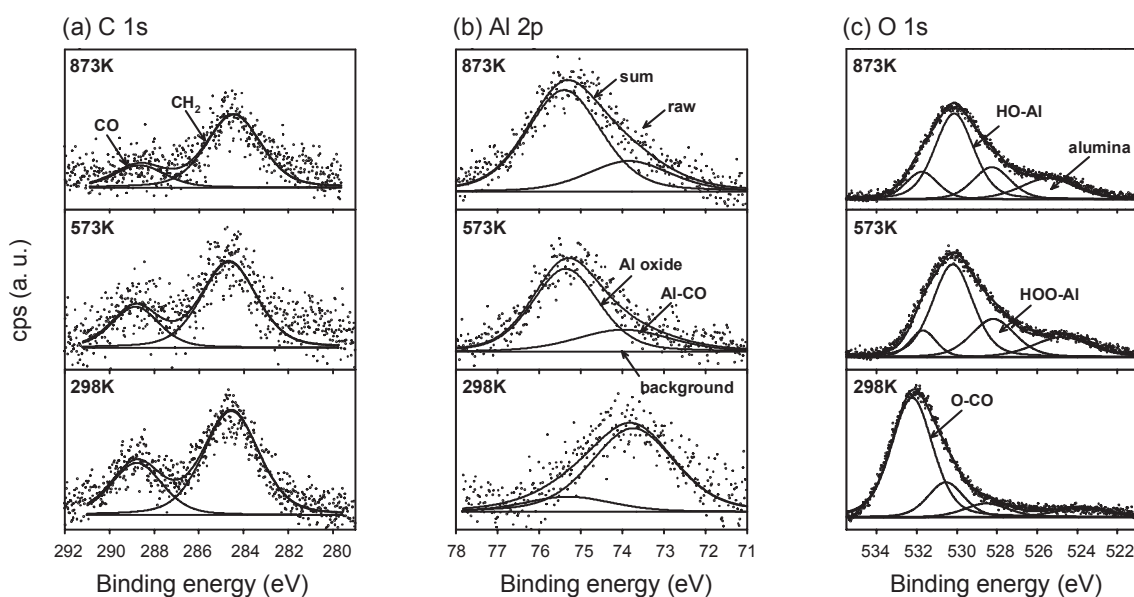
**Figure 2.** X-ray diffraction patterns of aluminum acetate/PVP composite SMRs obtained at 1.04 kV/cm of electric field.



**Figure 3.** (a) Scanning electron microscopy image of AO-SMRs obtained at 1.04 kV/cm of electric field, (b) Radii distribution of AO-SMRs synthesized at  $1.00 \pm 0.04$  kV/cm.

The representative scanning electron microscopy (JEOL, JSM-6700F) image of AO-SMRs obtained at  $1.00 \pm 0.04$  kV/cm of electric field and the radii distribution of AO-SMRs are shown in Figure 3. As shown in Figure 3 (a), the symmetric AO-SMRs were successfully synthesized from aluminum acetate/PVP electrospinning solution. The radii of AO-SMRs were analyzed by using Motic Images Plus 2.0 mL program. The internal and external radii of SMRs are dominantly distributed 50 ~ 200 and 200 ~ 600 nm, respectively. When the electric field between the needle and a drum collector was changed from 0.96 to 1.04 kV/cm, the radii distribution was almost independent with the applied electric fields (Figure 3 (b)). The external and internal radii of the AO-SMRs lied in submicro meter range. In order to control the radii of AO-SMRs precisely, further study is required. X-ray photoelectron spectroscopy (XPS, MultiLAB 2000) was performed for investigation of chemical nature of the AO-SMRs. The detailed experimental parameters applied in this work are described elsewhere.<sup>14</sup> The deconvoluted high resolution XP spectra of AO-SMRs in the binding ranges of C 1s, Al 2p, and O 1s are shown in Figures 4 (a-c), respectively. When the calcination temperature was increased from 293 to 873 K, the intensities of C 1s for carbonyl and aliphatic were decreased by decomposition of hydrocarbon. The ratio of the Al oxide species ( $\text{Al}_2\text{O}_3$ ,  $\text{AlOOH}$ ,  $\text{Al}(\text{OH})_3$ ) increased while the amount of the Al species bound with the carbonyl in PVP decreased as a function of calcination temperature shown in Figure 4 (b). In addition, by increasing the calcination temperature, the oxygen species in Al oxide increased while that in carbonyl decreased (Figure 4 (c)). When the electrospun aluminum acetate/PVP composite SMRs were calcined at 873 K, the hydrocarbons were decomposed and desorbed from the SMR composite. Also the oxygen in the acetate and PVP oxidized metallic aluminum to aluminum oxides in high temperature calcinations.

In conclusion AO-SMRs were successfully fabricated by



**Figure 4.** Deconvoluted high resolution X-ray photoelectron spectra of AO-SMRs obtained at 1.04 kV/cm of electric field in the binding energy regions of (a) C 1s, (b) Al 2p, and (c) O 1s.

applying electrospinning on aluminum acetate/PVP composite solution. The crystallinity of the SMRs was only detected in metallic Al while Al oxides were formed as amorphous phase. As the calcination temperature increased, the metallic Al oxidized to amorphous aluminum oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{AlOOH}$ ,  $\text{Al}(\text{OH})_3$ ). The investigation of chemical nature of AO-SMRs by XPS revealed that aluminum oxides formed during calcination of aluminum acetate/PVP SMR composite. For better control of the size of AO-SMRs, further study is required.

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