

Method for fabricating polymethylmethacrylate micro-nanotube arrays based on spin-coating method and PAA templates

Wei-min Kang^{1,2}, Zhi-xia Jia¹, Hao Liu^{1,2}, Bo-wen Cheng^{1,2}

¹School of Textiles, Tianjin Polytechnic University, Tianjin 300387, People's Republic of China

²Key Laboratory of Advanced Textile Composite Materials, Ministry of Education of China, Tianjin 300387, People's Republic of China
E-mail: liuhao@tjpu.edu.cn

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A novel and low-cost method for fabricating poly(methyl methacrylate) micronanotube arrays (PMMA-MNAs) using a porous anodic aluminium (PAA) template and spin-coating method was presented. PMMA-MNAs with different length micronanotubes were fabricated by changing the temperature of electric heating drying oven and heating time, then characterised by field-emission scanning electron microscope. Experimental results showed that the poly(methyl methacrylate) (PMMA) liquid membrane was obtained by means of spin coating at the spin velocity of 4000 r/min, and can further grow into PMMA-MNAs using an all-through-pore PAA film as template at a certain temperature. The length of PMMA-MNAs increased nonlinearly with the increasing of the oven temperature and trended to a stable value (about 6.51 μm) at 150°C for 1.5 h. Flexible PMMA-MNAs with characteristics of hollow structure will have wide application prospects in catalyst carrier, high precise sensor, drug sustained release and so on. The presented experimental results could facilitate understanding the growth mechanism of polymer nanotube arrays.

1. Introduction: One-dimensional (1D) polymer nanomaterials have received increasing attention due to their excellent properties and potential applications such as optoelectronic devices, sensitive sensors, biotechnology engineering and drug sustained release [1–4]. Among 1D nanomaterials, tubular-structured materials have shown unique chemical and physical properties because of their outer as well as inner surfaces having the ‘wall’ of nanometre thick [5]. Recently, many methods have been found to fabricate the nanotubular materials, such as electrospinning, hydrothermal, template [6–8] and so on. The template method is one of the most common methods to prepare nanotubes [9, 10]. Compared with other templates, porous anodic aluminium (PAA) formed by a two-step anodisation is widely used because of its unique characteristics, well-controlled pore sizes, pore-to-pore distance and pore length [11, 12]. In addition, PAA templates can be removed easily after the fabrication of the nanomaterials using an etching solution such as an acid or an alkali [13]. Although there have been a number of reports on synthesising strategies of the nanotubular structures, such as electrochemical deposition [14], sol-gel synthesis [15], oxidation [16] biomimetic mineralisation [17], the method of spin coating was few described.

In this Letter, poly(methyl methacrylate) nanotube arrays (PMMA-NAs) were fabricated by combining method of spin coating and PAA template. The all-through-pore PAA films were obtained by adjusting pore widening process. The effects of temperature and heating time on the length of PMMA-NA were investigated. PMMA-NA can be utilised as a catalyst carrier, high precise sensor [18], and helpful for the preparation of the flexible materials and other large specific surface area.

2. Methods: High purity aluminium (99.999%) foils were used as the starting material. The aluminium foils were degreased in acetone, rinsed in distilled water and then removed the natural oxide layer in 1 mol/l NaOH solution. Subsequently, the foils were electrochemically polished in a 4:1 volume mixture of ethanol and perchloric acid. The PAA films were formed by a two-step anodisation carried out in 0.03 M oxalic acid mixture with 1 wt% phosphoric acid solution under potential value (U) of 190 V. The first step of anodisation was conducted at 0–1°C for

4.5 h. After that oxide films were removed by chemical etching in a mixture solution of 6 wt% H_3PO_4 and 18 g/l CrO_3 at 60°C for 6 h. The second step of anodisation was conducted at the same experimental conditions as used in the first step except the anodisation time was 2 h. During anodisation, the electrolyte was stirred at a moderate speed. Prior to pore widening which was carried out in 5 wt% H_3PO_4 solution at 30°C for 2, 3, 3.15 and 3.5 h, the remaining aluminium substrate was removed by a wet-chemically etching step with a mixture solution of 3.4 g CuCl_2 and 37 wt% HCl. After that, the obtained PAA template with all-through-pore was covered onto the spin-coated film, which was a spin-coated with 15, 20, 25 and 30 wt% poly(methyl methacrylate) (PMMA)/dimethylformamide (DMF) solution on the surface of slide glass at the spin velocity of 4000 r/min for 30 s. Subsequently, the heat process was carried out in the electric heating drying oven to form micronanotubes at different temperatures for 1.5 h and at 150°C for different interval times. Finally, the PAA template was removed by immersing in 5 wt% H_3PO_4 solution, thus the PMMA micronanotube arrays (PMMA-MNAs) were obtained. Fig. 1 shows the experimental flowchart for preparing PMMA-MNAs. The morphology of the formed PMMA-MNAs was examined with a HITACHI S-4800 FESEM. Image analyses (length of the micronanotubes) were done by the Image-Pro Plus (IPP) software.

3. Results and discussion

3.1. Effect of the pore widening time of PAA: To obtain the optimum all-through-pore PAA films, PAA was dipped in 5 wt% H_3PO_4 solution for pore widening, and the pore widening time was set to 2.5, 3, 3.15 and 3.5 h. Fig. 2 shows the surface and bottom FESEM images of PAA films. When the pore widening time was short, the barrier layer of PAA film was not removed (Fig. 2a₁). With the increasing of the pore widening time, through pores were fabricated (Fig. 2b₁) and their diameters approached those of pores which were on the surface of PAA (Figs. 2c₁ and c₂). However, some pores were destroyed when the pore widening time was 3.5 h. Therefore, 3.15 h was chosen as the optimal pore widening time.

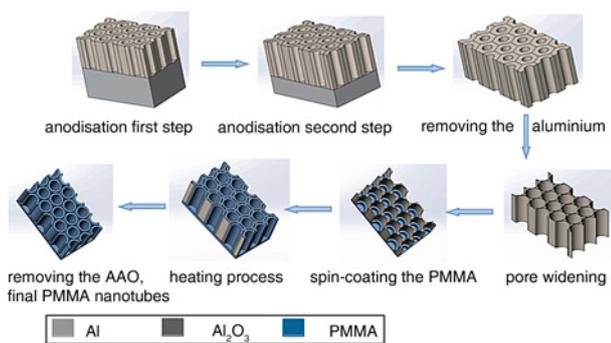


Fig. 1 Fabrication procedure of PMMA-MNAs

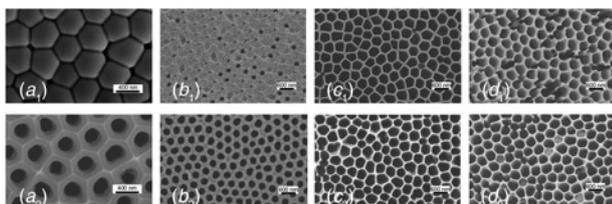


Fig. 2 Bottom and top FESEM images of PAA with different pore widening times: 2.5 h (a₁, a₂), 3 h (b₁, b₂), 3.15 h (c₁, c₂) and 3.5 h (d₁, d₂)

3.2. Effect of PMMA/DMF solution concentration on the structure of microranotubes: A series of PMMA/DMF solution with different concentrations had been applied for the sake of obtaining optimal structure of microranotubes. Fig. 3 shows the sectional FESEM images of microranotubes. When the concentration was 15 wt%, the microranotubes were adhesive and thin (Fig. 3a). With the increasing of PMMA/DMF solution concentration, microranotubes were obviously smoother and straighter (Fig. 3b). However, microranotubes were adhere closer when the concentration was 25 wt% or 30 wt% (Figs. 3c and d). Therefore, 20 wt% was chosen as the optimal concentration of PMMA/DMF solution.

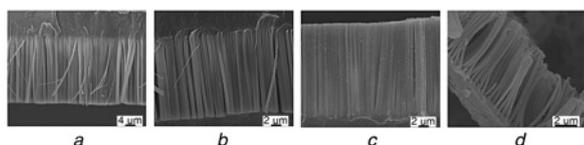


Fig. 3 Sectional FESEM images of microranotubes with diverse PMMA/DMF solution concentration

- a 15 wt%
- b 20 wt%
- c 25 wt%
- d 30 wt%

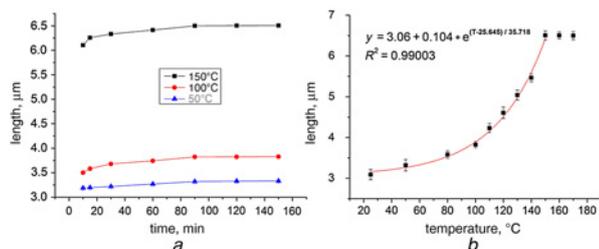


Fig. 4 The relationship between the temperature and length, as well as time and length
a Length of PMMA-MNAs against heating temperature at 50, 100 and 150°C
b Length of PMMA-MNAs against heating time for 2 h

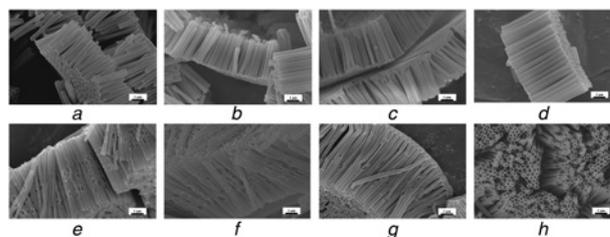


Fig. 5 FESEM images of different lengths of PMMA microranotubes at diverse oven heating temperature

- a 25°C
- b 80°C
- c 100°C
- d 140°C
- e 150°C
- f 160°C
- g 170°C
- h Top view of PMMA-MNAs

3.3. Effect of oven heating time on the length of microranotubes: To investigate the correlation between the length of PMMA-MNAs and the oven processing time, several heating interval times such as 10, 15, 30, 60, 90, 120 and 150 min were selected for preparing the PMMA-MNAs. IPP software was utilised for measuring the length of microranotubes in SEM images. Fig. 4a shows that the extension of heating time was beneficial to the increase of PMMA-MNA length in the initial stage. However, the length of microranotubes was almost no change as the heating time was more than 90 min. It is worth noting that the length of microranotubes was significantly affected by the temperature of electric heating drying oven.

3.4. Effect of the temperature of electric heating oven on the length of PMMA-MNAs: To investigate the effect of oven temperature, PMMA-MNAs were fabricated at different temperatures for 90 min, which were room temperature (25°C), 50, 80, 100, 110, 120, 130, 140, 150, 160 and 170°C, FESEM images were shown in Figs. 5a–h. From the top view of PMMA-MNAs (Fig. 5h), the hollow structure of PMMA-MNAs could be observed clearly. The relationship between the length of microranotubes and the temperature was shown in Fig. 4b. According to the FESEM images in Figs. 4b and 5, it was clearly visible that the length of the microranotubes array increased exponentially with the oven temperature.

The capillary force of PAA contributes to the formation of PMMA micro-nanotubes. The molecular mobility increased because of the decrease of viscosity which is the result of temperature increase. In addition, high temperature resulted in low surface tension. Therefore, the grow rate of the microranotubes increased with rising temperature. However, when the temperature of the oven was over 150°C, the length of hollow microranotubes array trended to a stable value due to the limitation of the original height of PAA template. Thus, the length of the fabricated hollow microranotubes can be easily controlled by controlling the thickness of PAA films.

4. Conclusions: In this Letter, the PMMA-MNAs were successfully fabricated by spin-coating method. The relationship between the length of PMMA-MNAs and oven processing time was similar to the correlation between the length of microranotubes and heating temperature. The length of microranotubes nonlinearly increasing with the increasing temperature before it reached the maximum at 150°C. It was found that the spin coating was a novel and low-cost method to fabricate microranotubular materials with controllable length.

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6 References

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