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Growth Mechanism and Optimized Parameters to Synthesize Nafion-115 Nanowire Arrays with Anodic Aluminium Oxide Membranes as Templates *

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Nafion-115 nanowire arrays are synthesized with an extrusion method using AAO membranes as templates. It is indicated that the vacuum treating of AAO templates before surface decoration plays an important role in obtaining high filling rate of the Nafion-115 nanowires in the AAO templates, while the concentration of Nafion-115 DMSO solutions does not affect the filling rate greatly. The optimized parameters to synthesize the Nafion-115 nanowire arrays are studied. The filling rate of the Nafion-115 nanowires in the AAO templates synthesized with the optimized parameters is about 95%. The growth mechanism of Nafion-115 nanowires is discussed to qualitatively explain the experimental results.

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One-dimensional (1D) nanostructures have attracted much attention due to their peculiar structures, properties and applications in the last decade.[1−12] In recent years, organic nanowires have been widely studied due to their unique properties such as optical properties,[13] electronic transport[14,15] and good processing performance.[16] Nafion is one of the most common commercial organic materials used in proton exchange membrane fuel cells (PEMFCs), and is a registered trade mark by DuPont de Nemours (USA). The properties and applications of different types of Nafion membranes have been intensively investigated since hydrogen energy is considered as one of the most important new energy sources in the near future. Thus, Nafion nanowire arrays have potential applications for nanoscale or microscale PEMFCs which may be used as the power source of nanodevices or microdevices. We have presented a method to synthesize Nafion-115 nanowire arrays with surface decorated anodic aluminium oxide (AAO) as templates[17] and discussed the mechanism of surface decoration systematically.[18] However, the optimized parameters of synthesis process were not shown in the previous reports.[17,18] In this Letter, two important parameters of the synthesis process are investigated. It is indicated that the vacuum treating of AAO templates before surface decoration plays an important role to obtain high filling rate of the Nafion-115 nanowires in the AAO templates, while the concentration of Nafion-115 dimethylsulfoxide (DMSO) solutions does not affect the filling rate of the Nafion-115 nanowires in the AAO templates greatly. The results are practicable to synthesize organic nanowire arrays with AAO as temples.

The Nafion-115 membranes were purchased from DuPont Company (USA). The DMSO reagent to dissolve the Nafion-115 was purchased from Beijing Chemical Reagent Corporation, China. The Nafion-115 DMSO solutions were prepared as follows: (a) A piece of Nafion-115 membrane was cut into small pieces of about 2 mm^2. (b) The small pieces of Nafion-115 membranes were washed in 10% H_2O_2 at 303 K for 2 h to remove organic contamination on the surfaces. Then they were rinsed in distilled water several times quickly. (c) The Nafion-115 pieces were immersed in 10% sulfuric acid at 303 K for 24 h to remove metallic contamination. Subsequently, they were washed with distilled water. (d) The as-prepared small pieces of Nafion-115 were dissolved in DMSO by refluxing at about 450 K under N_2 ambience for about 24 h to form 0.5 wt%, 1.0 wt% and 2.0 wt% DMSO solutions, respectively.[19]

The AAO templates used in our experiments were fabricated by a method of two-step oxidization,[19] with an average pore diameter of about 85 nm and a thickness of 30 μm. First, a clean and dry AAO template with pore diameter about 85 nm was pumped for 30 min to reduce the air pressure in the AAO pores to about 133 Pa. Then 1% sodium dodecyl sulfate (SDS) solution was added while the pump was running. After the AAO template was totally immersed in the 1% SDS solution, the pump was closed and the air pressure returned to normal level. The as-prepared AAO template was immersed in the 1% SDS solution for 8 h. Subsequently, it was washed with distilled water quickly to remove the remnant SDS solution on the AAO surface, and then dried. A check experiment without the vacuum treating process was also carried

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out.

The 0.5 wt%, 1.0 wt% and 2.0 wt% Nafion-115 DMSO solutions were extruded into the pores of the as-prepared AAO membrane under a mechanical pump pressure (0.1 MPa) to synthesize the Nafion-115 nanowire arrays, respectively. Details of the extrude process can be found in our previous paper.[18]

The 5 mol/L NaOH solution was used to etch the surface of AAO templates at room temperature to reveal the top of the Nafion-115 nanowires. The typical morphology of the as-synthesized Nafion-115 nanowire arrays is shown in Fig. 1. A top view of AAO template in Fig. 1(a) shows that most of the AAO template pores are filled with Nafion-115 nanowires whose diameters are about 85 nm. A cross-sectional view of AAO template in Fig. 1(b) clearly shows that the Nafion-115 nanowires have fully filled the AAO pores in the radial direction. After the etching of AAO pore walls, some Nafion-115 nanowires were free. Hence, some nanowires, which moved when the AAO templates were washed and dried, were not well aligned in the cross-sectional scanning electron microscope (SEM) images. The Nafion-115 nanowire arrays synthesized as above are well aligned due to the confinement of AAO template.

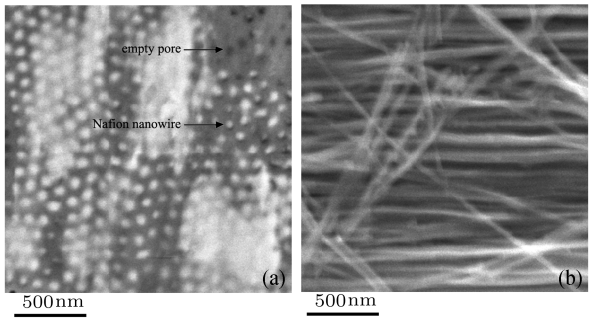

Fig. 1. SEM images the as-synthesized Nafion-115 nanowires in AAO pores: (a) top view, (b) cross-sectional view.

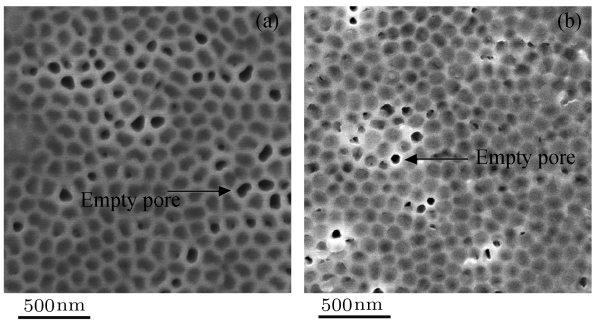

Fig. 2. SEM images showing the filling rates of the Nafion-115 nanowires in the AAO templates prepared: (a) without vacuum treating process, (b) with vacuum treating process.

Figure 2 shows the typical effect of vacuum treating before surface decoration of AAO templates on the filling rate. The filling rates of Nafion-115 nanowires in the AAO templates were measured from at least 20 areas. As shown in Fig. 2(a), the filling rate of Nafion-115 nanowires in the AAO template is about 80% without vacuum treating process. However, the filling rate rises to about 95% in the sample with vacuum treating process as shown in Fig. 2(b). When the 1% SDS solution was used to surface decorate the AAO template without vacuum treating process, some air would be trapped in the AAO pores due to the high air pressure (about 0.1 MPa). However, the residual air pressure (about 133 Pa) in AAO pores was much lower than the atmospheric pressure after the vacuum treating of AAO template. Hence, the 1% SDS solution could better infiltrate the surface of AAO templates, which led to the synthesis of better surface decorated AAO temples with more AAO pore wall surfaces covered by the sulfonic groups. The average surface charge density on the AAO pore wall surface in the vacuum-treated AAO templates is higher than that in the AAO templates without vacuum treating. Thus, the filling rate of Nafion-115 nanowires in the AAO templates increases after the vacuum treating process.

Table 1. Filing rate of the Nafion-115 nanowires in the AAO templates synthesized by different concentrations of Nafion-115 DMSO solutions.

Cases	Concentration	Filling rate
I	0.5 wt%	$\sim$ 90%
II	1.0 wt%	$\sim$ 95%
III	2.0 wt%	$\sim$ 90%

The typical effects of the concentration of Nafion-115 DMSO solutions on filling rate are shown in Fig. 3. For the three cases which are assigned as cases I, II and III, the filling rates of the Nafion-115 nanowires in AAO templates are listed in Table 1. It can be seen from Fig. 3 and Table 1 that the concentration of Nafion-115 DMSO solutions does not affect the filling rate greatly. In the synthesis process of Nafion-115 nanowires, the extrude experiment will not finish until the velocity of extrusion of Nafion-115 DMSO solution though the AAO template becomes extremely low. Hence, the filling rate of Nafion-115 nanowires in the AAO template will tend to reaching a maximum no matter what the concentration of Nafion-115 DMSO solutions is. If the concentration of Nafion-115 DMSO solutions is too low (¡0.5 wt%), the extrusion process will be carried out for too many times. If the concentration of Nafion-115 DMSO solutions is too high, the surface of AAO templates may be covered by a layer of Nafion-115 polymers. Thus, the optimized concentration of Nafion-115 DMSO solutions to synthesize Nafion-115 nanowire arrays is about 1.0 wt%.

During the extrude process, the electrostatic

force acts on a typical Nafion-115 molecule is about 10^{-8} N.[18] The electrostatic force in our case is an attractive force because the Nafion-115 molecules are positive while the AAO pore wall surface is negative. Thus, the Nafion-115 molecules in the Nafion-115 DMSO solution will stack on the AAO pore wall surface and form Nafion-115 nanowires after the extrude process. The vacuum treating before surface decoration of AAO templates can greatly reduce the residual air pressure in AAO pores, which leads to the synthesis of better surface decorated AAO temples with more AAO pore wall surface covered by the sulfonic groups. The higher average surface charge density on the AAO pore wall surface results in greater electrostatic force acts on the Nafion-115 molecules. Hence, the vacuum treating of AAO templates before surface decoration plays an important role to obtain high filling rate of the Nafion-115 nanowires in the AAO templates.

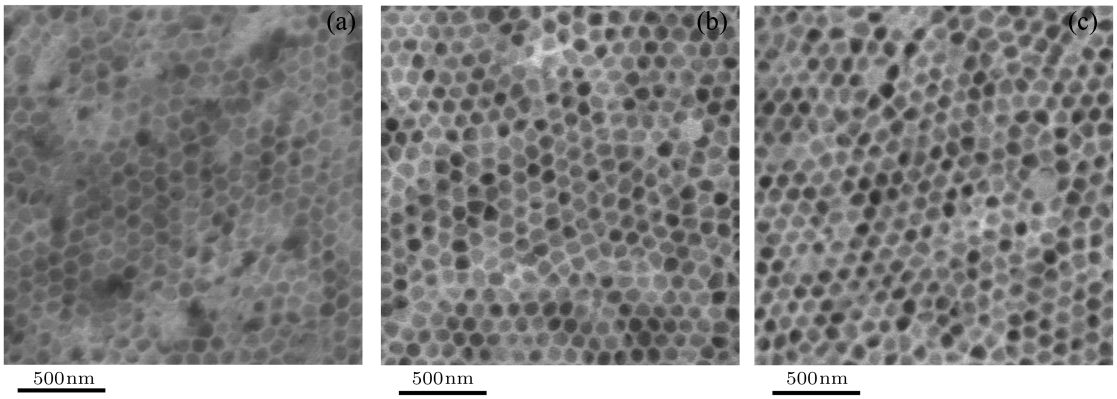

Fig. 3. SEM images showing the filling rates of the Nafion-115 nanowires in the AAO templates prepared by using different concentration of Nafion-115 DMSO solutions: (a) 0.5 wt% Nafion-115 DMSO solution, (b) 1.0 wt% Nafion-115 DMSO solution, (c) 2.0 wt% Nafion-115 DMSO solution.

The proton conductivity of Nafion-115 nanowires was systemically studied in our other work.[20] The proton conductivity of Nafion-115 nanowires decreases sharply when the diameter of Nafion-115 nanowires increases. The relationship of the measured proton conductivity σ_{H^+} in units of $S{\cdot}nm^{-1}$ versus the diameter d in units of μm is $\log(\sigma_{H^+}) = -2.2\log(d) - 2.74$.

In summary, Nafion-115 nanowire arrays have been synthesized with an extrusion method using AAO membranes as templates. The vacuum treating of AAO templates before surface decoration plays an important role in obtaining high filling rate of the Nafion-115 nanowires in the AAO templates, while the concentration of Nafion-115 DMSO solutions does not affect the filling rate greatly. The optimized synthesis process and corresponding parameters are shown. First, a clean and dry AAO template is pumped for 30 min. Then it is immersed in 1% SDS solution for 8 h. Subsequently, it is washed with distilled water quickly to remove the remnant SDS solution on the AAO surface, and then dried. A 1.0 wt% Nafion-115 DMSO solution is used to extruded into the pores of the as-prepared AAO template under a mechanical pump pressure (0.1 MPa) until the velocity of extrusion of the Nafion-115 DMSO solution though the AAO membrane becomes extremely low. The filling rate of the Nafion-115 nanowires in the AAO templates synthesized with the optimized process and parameters is about 95%. The electrostatic force acts on the Nafion-115 molecules is the key factor to synthesize Nafion-115 nanowires. The Nafion-115 molecules will stack on the AAO pore wall surfaces under the attractive electrostatic force and form Nafion-115 nanowires after several times of extrusion.

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