Synthesis and characterization of Nafion®-115 nanowire arrays

2005 Nanotechnology 16 2242

(http://iopscience.iop.org/0957-4484/16/10/045)

INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology **16** (2005) 2242–2244 doi:10.1088/0957-4484/16/10/045

Synthesis and characterization of Nafion®-115 nanowire arrays

Lu Zhang[1,3], **Caofeng Pan**[1,3], **Jing Zhu**[1,4] **and Cheng Wang**[2]

[1] Electron Microscopy Laboratory, School of Materials Science and Technology, Tsinghua University, Beijing 100084, People's Republic of China
[2] Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, People's Republic of China

E-mail: jzhu@mail.tsinghua.edu.cn

Received 29 June 2005
Published 16 August 2005
Online at stacks.iop.org/Nano/16/2242

Abstract
Aligned Nafion®-115 nanowire arrays have been synthesized by an extrusion method with anodic aluminium oxide (AAO) membranes templates in this work. A surface modification was carried out to improve the hydrophobicity of the AAO pore surface. The as-synthesized nanowires are about 85 nm in diameter and several to over ten micrometres in length. Near-IR Raman and IR spectrum studies show that the polymer nanowires are composed of pure Nafion®-115 only.

1. Introduction

Since the discovery of carbon nanotubes in 1991 [1], a large quantity of 1D nanomaterials with different components and varied structures have been reported, such as carbon nanotubes [1], semiconductor nanowires [2], semiconductor nanobelts [3], metal nanorods [4], heterojunction nanowires [5–7] and composite nanostructures [8]. In the meantime, many successful methods have been developed for synthesizing 1D nanomaterials, such as arc-discharge [1, 9], chemical vapour deposition (CVD) [3], laser ablation [2], electrochemical deposition [10], sol–gel [11], template-assisted growth [12] and combinations of the methods mentioned above [5, 8]. However, compared with the fabrication of inorganic 1D nanomaterials, the preparation of organic 1D nanomaterials remains poorly studied, and less successful examples have been reported [13–16]. Nafion® is the most common commercial material used in proton exchange membrane fuel cells (PEMFC). In this work, a method for synthesizing Nafion®-115 nanowire arrays, which are promising as regards application in PEMFC, has been developed.

[3] Contributed equally to this work.
[4] Author to whom any correspondence should be addressed.

2. Experimental section

2.1. The preparation of Nafion®-115 DMSO solution

Some small pieces of Nafion®-115 membranes (0.110 g) were dissolved in 100 ml dimethylsulfoxide (DMSO) by refluxing at 450 K under N_2 ambience for about 40 h to form a 0.1 wt% DMSO solution.

2.2. The fabrication and decoration of AAO membranes

The anodic aluminium oxide (AAO) membranes used as the templates were fabricated by a two-step oxidization method in an aqueous solution of 4 wt% oxalic acid at 273 K [17]. The remaining aluminium at the back of AAO membranes was dissolved in a solution of $CuCl_2$–HCl. The as-prepared AAO membranes were etched in 5 wt% phosphoric acid for 70 min at 303 K to remove the barrier layer and widen the pores to about 85 nm in diameter.

A surface modification was carried out to improve the hydrophobicity of the AAO pore surface. A clean and dry AAO membrane with pore diameters of about 85 nm was immersed in 1% sodium dodecylsulfonate (SDS) aqueous solution for 8 h after being pumped for 1 h. Subsequently, it was washed with distilled water quickly to remove the remnant SDS solution on the AAO membrane surface, then dried. The decoration of AAO membranes proved very helpful for synthesizing the Nafion®-115 nanowire arrays in the following work.

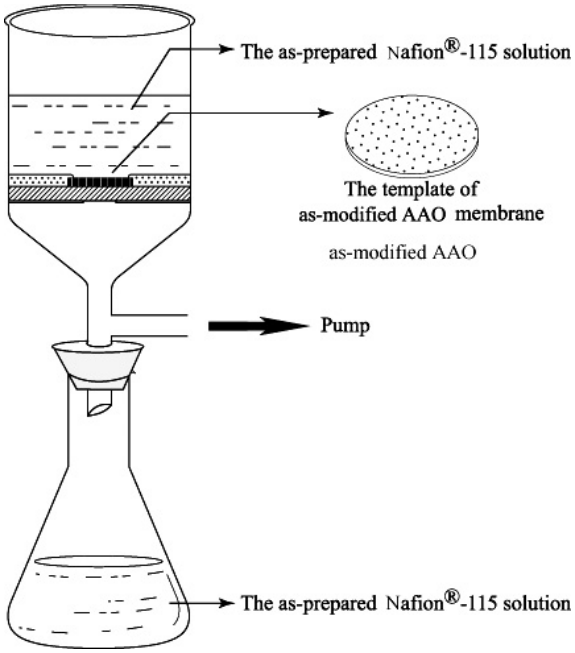

Figure 1. Schematic illustration of the extrusion process for fabricating Nafion®-115 nanowire arrays.

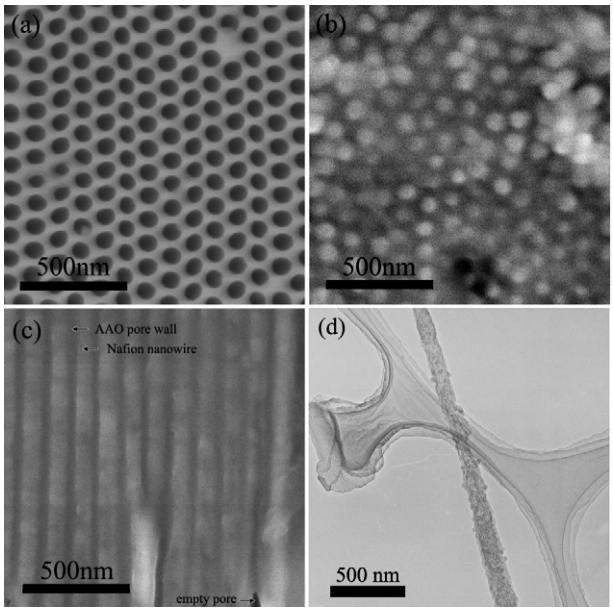

Figure 2. SEM images of: (a) the original surface of AAO membrane used in the extrusion process; (b) the top view of the as-synthesized Nafion®-115 nanowire arrays in the AAO pores; (c) the cross-sectional view of the as-synthesized Nafion®-115 nanowire arrays in the AAO pores; (d) an isolated Nafion®-115 nanowire.

2.3. The synthesis of the Nafion®-115 nanowire arrays

The apparatus set-up for fabricating the Nafion®-115 nanowire array is illustrated in figure 1. The 0.1 wt% Nafion®-115 DMSO solution was extruded into the pores of the AAO membrane under the mechanical pump pressure (0.1 MPa) to form the Nafion®-115 nanowire array. The details of the formation process are shown as below:

(A) Place a piece of as-modified AAO membrane into the funnel and then pour the Nafion®-115 DMSO solution onto the AAO membrane.
(B) Extrude the as-prepared Nafion®-115 DMSO solution into the pores of the AAO membrane under the mechanical pump pressure (0.1 MPa).
(C) Rinse the sample surface with ethanol and distilled water in turn several times quickly and then dry it.
(D) Repeat steps B and C several times until the velocity of extrusion of the Nafion®-115 DMSO solution through the AAO membrane becomes extremely low.
(E) With the aforementioned steps done, the Nafion®-115 nanowire arrays form in the pores of the AAO membrane.

2.4. Characterization of the Nafion®-115 nanowire arrays

Scanning electron microscopic (SEM) images were obtained with a JEOL JSM-6301F microscope. To examine the as-synthesized Nafion®-115 nanowire arrays with SEM, a 5 M NaOH solution was used to etch the AAO surface at room temperature to reveal the top of the Nafion®-115 nanowire arrays. Further etching (removing all the AAO template) was applied to prepare the samples for near-IR Raman and IR spectra tests. Transmission electron microscopic (TEM) images were obtained with a JEOL 200CX microscope.

The near-IR Raman and IR spectra were recorded to characterize the components of the as-synthesized nanowires. Near-IR Raman spectra were recorded using a Renishaw RM2000 microscopic confocal Raman spectrometer (785 nm). The power of illumination used was about 4.7 mW. To prepare the near-IR Raman test sample, some AAO templates with Nafion®-115 nanowire arrays in the pores were etched in 5 M NaOH solution to remove all the template. The as-etched nanowire arrays were first rinsed with distilled water, then dispersed in distilled water. The solution containing Nafion®-115 nanowires was dropped onto a clean slide and dried to form a Nafion®-115 nanowire film for the near-IR Raman test. IR absorption spectra were recorded using a Perkin-Elmer spectrum GX FTIR system with an accessory for attenuated total reflection (ATR). To prepare the IR test sample, a Nafion®-115 nanowire film was prepared as described above first. The resulting film was mixed with KI powders before being pressed to form optical clear pellets.

3. Results and discussion

The SEM images (figure 2) indicate that most AAO pores are filled with nanowires whose lengths are in the range of several to over ten micrometres, and the diameters are about 85 nm confined by the AAO pore diameter. From a top view of the AAO (figure 2(b)), the heads of nanowires can be found to protrude out of the AAO pores after etching the AAO surface. Some empty pores can also be found (dark contrast) in figure 2(b), which is probably due to the DMSO solution loss during the washing process. A cross-sectional view of the AAO template in figure 2(c) clearly shows that the nanowires (bright contrast) have fully filled the AAO pores (grey contrast) in the

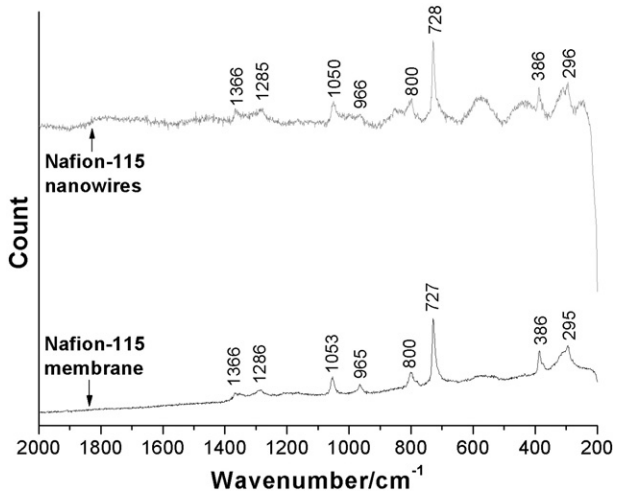

Figure 3. Raman spectra of the original Nafion®-115 membrane and the as-synthesized Nafion®-115 nanowire arrays.

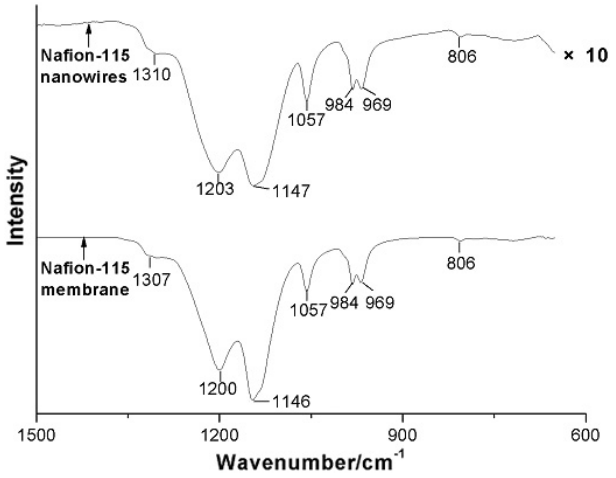

Figure 4. IR spectra of both original Nafion®-115 membrane and as-synthesized nanowires.

radial direction, and their lengths vary from several to over ten micrometres. Due to the confinement of the AAO template, the Nafion®-115 nanowire arrays are well aligned. An isolated Nafion®-115 nanowire is presented in figure 2(d), which is about 90 nm in diameter. All the Nafion®-115 nanowires in figures 2(b)–(d) are similar in diameter.

The Raman spectra of both the original Nafion®-115 membrane and the as-prepared nanowires are compared with each other in figure 3. The background in the Raman spectra of the nanowire sample has been subtracted to reduce the effect of fluorescence. The two spectra are consistent with each other over the whole range of working wavenumber, which demonstrates that the present as-synthesized nanowires are pure Nafion®-115 nanowire arrays. The broadening of the peaks in the nanowire sample may be related to the disorder of the chaotically piled-up Nafion®-115 nanowires, which was induced by the process of sample preparation [18].

Due to the low amount of Nafion®-115 nanowire arrays in the pellets for IR tests, the noise is larger in the IR spectra of nanowire samples. Hence, a smoothing disposal is applied to the spectra of nanowire samples to reveal the true signal. Figure 4 compares the IR spectra of the original Nafion®-115 membrane with that of the as-synthesized nanowires. The IR results also demonstrate that the as-synthesized nanowires are indeed composed of Nafion®-115 polymer.

4. Conclusions

Aligned Nafion®-115 nanowire arrays have been synthesized by an extrusion method with AAO membrane templates. To improve the hydrophobicity of the AAO pore surface, a surface modification was carried out, which has been proved helpful to the extrusion process. The as-synthesized nanowires are quite similar in diameter, with several to over ten micrometres in length. The synthesis process is simple and efficient.

Acknowledgments

This work was financially supported by National 973 Project of China, Chinese National Natural Science Foundation, and the National Centre for Nanoscience and Technology of China.

References

[1] Iijima S 1991 *Nature* **354** 56–8
[2] Morales A M and Lieber C M 1998 *Science* **279** 208–11
[3] Pan Z W, Dai Z R and Wang Z L 2001 *Science* **291** 1947–9
[4] Busbee B D, Obare S O and Murphy C J 2003 *Adv. Mater.* **15** 414–6
[5] Luo J, Zhang L, Zhang Y J and Zhu J 2002 *Adv. Mater.* **14** 1413–4
[6] Luo J, Zhang L and Zhu J 2003 *Adv. Mater.* **15** 579–81
[7] Luo J, Huang Z P, Zhao Y G, Zhang L and Zhu J 2004 *Adv. Mater.* **16** 1512–5
[8] Xu Q, Zhang L and Zhu J 2003 *J. Phys. Chem.* B **107** 8294–6
[9] Colber D T *et al* 1994 *Science* **266** 1218–22
[10] Peng Y, Zhang H L, Pan S L and Li H L 2000 *J. Appl. Phys.* **87** 7405–8
[11] Lei Y, Zhang L D, Meng G W, Li G H, Zhang X Y, Liang C H, Chen W and Wang S X 2001 *Appl. Phys. Lett.* **78** 1125–7
[12] Davydov D N, Sattari P A, AlMawlawi D, Osika A, Haslett T L and Moskovits M 1999 *J. Appl. Phys.* **86** 3983–7
[13] Kageyama K, Tamazawa J and Aida T 1999 *Science* **285** 2113–5
[14] Liu H B *et al* 2003 *J. Am. Chem. Soc.* **125** 10794–5
[15] Feng L, Li S H, Li H J, Zhai J, Song Y L, Jiang L and Zhu D B 2002 *Angew. Chem. Int. Edn Engl.* **41** 1221–3
[16] Qiu H J, Zhai J, Li S H and Wan M 2003 *Adv. Funct. Mater.* **13** 925–8
[17] Zhang X and Zhu J 2003 The optimized parameters of the preparation of anodic aluminum oxide membranes *Thesis for Bachelor's Degree* Tsinghua University (in Chinese edition)
[18] Gruger A, Régis A, Schmatko T and Colomban P 2001 *Vib. Spectrosc.* **26** 215–25