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## Synthesis, Characterization and Properties of Nanostructured Materials by Template-Directed Method

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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NANOSTRUCTURED  
MATERIALS BY TEMPLATE-DIRECTED METHOD

A Thesis

Submitted to the Graduate Faculty of the  
University of New Orleans  
in partial fulfillment of the  
requirements for the degree of

Master of Science  
in  
The Department of Chemistry

by

Liu Ran  
B.E. Jilin University, 2002

August 2004

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## Table of Contents

Abstract.....	iv
Chapter 1 Introduction .....	1
1.1 Introduction to Nanomaterials .....	1
1.2 Template-based Methods .....	1
1.3 Templates.....	2
1.3.1 Commercially Available Anodic Alumina Membrane .....	3
1.3.2 Anodic Alumina Membrane made in the lab.....	5
1.4 Electrochemical Deposition Method.....	6
Chapter 2 Nanowires and Nanotubes.....	9
2.1 Introduction One Dimensional Nanomaterials .....	9
2.2 Experimental Section .....	9
2.2.1 Materials and Equipment .....	9
2.2.2 Fabrication of Metal Nanowires in the AAO membrane.....	10
2.2.3 Characterization .....	16
2.3 Results and Discussion .....	17
2.3.1 Chronopotentiogram for Electrodeposition .....	17
2.3.2 Microscope Characterizations.....	17
2.3.3 Aggregation of the nanowires observed by Optical Microscope.....	21
2.4 Conclusion .....	24
Chapter 3 Superlattice Nanowires Made by Polymer Free Method .....	25
3.1 Introduction.....	25
3.2 Experimental Section .....	26
3.2.1 Materials and equipment.....	26
3.2.2 Equipment for polymer-free method .....	26
3.2.3 Electrochemical Deposition of Striped Nanowires into the AAO membrane	28
3.2.4 Post-treatment of the sample.....	28
3.2.5 Microscope Characterization .....	29
3.2.6 Alignment under magnetic field .....	29
3.3 Results and Discussion .....	30
3.3.1 SEM images .....	30
3.3.2 Field-Emission SEM images.....	31
3.3.4 Magnetic alignment .....	32
3.4 Conclusion .....	33
Reference .....	34
Vita.....	35

## **Abstract**

Nanowires and nanotubes with single component such as gold and nickel were fabricated by electrochemical deposition method directed by the Anodic Alumina Membrane (AAO) as a template. A so called “polymer-free” method has been investigated to make striped nanowires with superlattice structure. Various methods have been used to characterize these nanomaterials, including SEM, FESEM TEM, STM and Optical Microscope. The aggregation of the nanowires and their alignment under the magnetic force were observed under the optical microscope.

# Chapter 1

## Introduction

### *1.1 Introduction to Nanomaterials*

Nanostructured materials are materials with a microstructure, the characteristic length scale of which is on the order of typically 1-100 nanometers. The microstructure refers to the chemical composition, the arrangement of the atoms (the atomic structure), and the size of a solid in one, two, or three dimensions. Effects controlling the properties of nanostructured materials include size effects (where critical length scales of physical phenomena become comparable with the characteristic size of the building blocks of the microstructure), changes of the dimensionality of the system, changes of the atomic structure, and alloying of components (e.g., elements) that are not miscible in the solid and/or the molten state.

The synthesis, characterization and processing of nanostructured materials are part of an emerging and rapidly growing field. Research and development in this field emphasizes scientific discoveries in the generation of materials with controlled microstructural characteristics, research on their processing into bulk materials with engineered properties and technological functions, and introduction of new device concepts and manufacturing methods.

### *1.2 Template-Based Method*

Recently, one dimensional (1D) nanostructures such as wires, rods, belts, and tubes have also become the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanoscale devices.<sup>[1]</sup> Template-directed synthesis represents a straightforward route to these 1D nanostructures instead of the numerous chemical methods. In this approach, the template simply serves as a scaffold within (or around) which a different material is generated *in situ* and shaped into nanostructure with its morphology complementary to that of template. It is

generally accepted that template-directed synthesis provides a simple, high-throughput, cost-effective procedure that also allows the complex topology present on the surface of a template to be duplicated in a single step. This method has a number of interesting and useful features. First, it is very general; people have used this method to prepare tubules and fibrils composed of electronically conductive polymers,<sup>[2]</sup> metals,<sup>[3]</sup> semiconductors,<sup>[4]</sup> carbons,<sup>[5]</sup> and other materials. Furthermore, nanostructures with extraordinarily small diameters can be prepared. For example, Wu and Bein have used this method to prepare conductive polymer nanofibrils with diameters of 3nm (30Å).<sup>[6]</sup> It would be difficult to make nanowires with diameter this small using lithographic methods. In addition, because the pores in the membranes used have monodisperse diameters, analogous monodisperse nanostructures are obtained. Finally, the tubular or fibrillar nanostructure synthesized can be freed from the template membrane and collected. Alternatively, an ensemble of nanostructures that protrude from a surface like the bristles of a brush can be obtained. As a major drawback, nanostructures synthesized using template-directed methods are often polycrystalline, and the quantity of structures that can be produced in each run of synthesis is relatively limited.

### ***1.3 Templates***

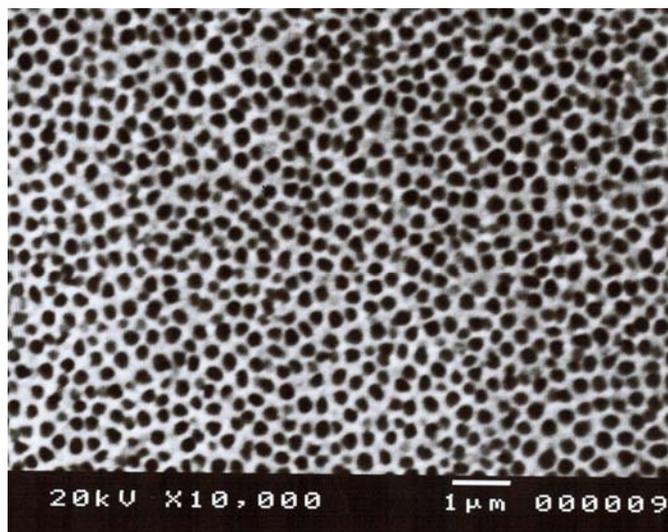
A wealth of templates have been used successfully, with notable examples including step edges present on the surfaces of a solid substrate;<sup>[7]</sup> channels within a porous material;<sup>[8]</sup> mesoscale structures self-assembled from organic surfactants<sup>[9]</sup> or block copolymer;<sup>[10]</sup> biological macromolecules such as DNA strands or rod-shaped viruses;<sup>[11]</sup> and existing nanostructures synthesized using other approaches. Among these templates, porous membranes have become very popular ones. Channels in these membranes can provide templates for the synthesis of 1D nanostructure. This method was pioneered by Martin and several others.<sup>[12]</sup> Two types of porous

membranes are commonly used in such synthesis: polymer films containing track-etched channels and alumina films containing anodically etched pores. Both of them can be obtained commercially from a number of vendors such as Nuclepore, Poretics, and Whatman. For track-etching, a polymer film (6-20 $\mu\text{m}$  thick) is irradiated with heavy ions from nuclear fission to generate damaged spots in the surface of this film. These spots are then amplified through chemical etching to generate uniform, cylindrical pores penetrating the membrane film.<sup>[13]</sup> The pores fabricated using this method are often randomly scattered across the membrane surface; and their orientation may also be tilted by as much as  $34^\circ$  with respect to the surface normal. Porous alumina membranes are often prepared using anodization of aluminum foils in an acidic medium,<sup>[14]</sup> and they usually contain a hexagonally packed 2D array of cylindrical pores with a relatively uniform size. Unlike the polymer membranes fabricated by track-etching, the pores in alumina membranes have little or no tilting with respect to the surface normal and the pore density is also much higher. So it is usually used by our lab to serve as the template.

### *1.3.1 Commercially Available Anodic Aluminum Oxide (AAO) Membrane*

The membranes we have been using in our lab are all purchased from Whatman Company, which are called Anodisc™ Membranes. Anodisc membrane filters consist of an Anopore™ membrane disc, peripherally bonded to an annular polypropylene ring. Anopore is a unique, inorganic membrane, made of aluminium oxide, with a precise non-deformable honeycomb pore structure. Its narrow pore size distribution ensures extremely efficient removal of particles at the rated pore size. Anodisc filters are available in three pore sizes (0.2 $\mu\text{m}$ , 0.1 $\mu\text{m}$  and 0.02 $\mu\text{m}$ ). These membranes are not of high quality because they are mass-produced. First, the actual pore sizes don't agree with ones labeled by the manufacturer. According to SEM image in Figure 1.1, some pore sizes are actually around 300nm if it is labeled as 0.2 $\mu\text{m}$  (200nm). The

membrane has the pore size about 200nm if it is labeled as 0.02 $\mu\text{m}$  (not shown here) pore size. From the SEM image it's obvious to see that the pore sizes are not distributed uniformly. The reason for these defects is because of the difficulties in controlling the experiments parameters in the anodization process.



**Figure 1.1** SEM image of commercial Anodic Alumina membrane labeled with 200nm pore size

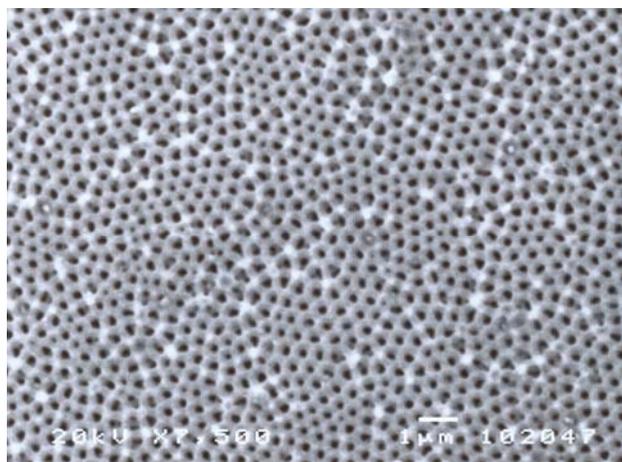
Second, the shape of the pore is not very regular. Other than the ideal round, some pores have shapes like ellipse or even polygon. And instead of hexagonally packed 2D array, the pores are just randomly distributed without any order although their density is high. Figure 1.1 shows these irregularities.

Third, the inside walls of the channels in these membrane are not very smooth, which will increase the roughness of nanowires that are formed inside these channels. And also at the end of these channels, we can find that they become more irregular, some channels may even merge together. This defect will make the nanowires made by these membranes hard to disperse.

Due to a lot of defects of the commercial available AAO membrane, some research groups prepare their own Anodic Alumina Membranes. Such membranes have also been prepared in our group.

### *1.3.2 Anodic Aluminum Oxide (AAO) Membrane made in the lab*

The procedure to prepare the AAO membrane is well known. After the high purity aluminum foil is polished and annealed, it is placed in an acid solution under a positive electric field and converted to AAO membranes during anodization. Their self-organized pore diameters and intra-pore distances can be adjusted by changing the voltage and acid concentration. Anodization time controls the membrane's thickness, which limits the length of nanowires and nanotubes grown in the pores. The researchers have made AAO membranes with pore diameters ranging from 10 to 400 nanometers and with lengths up to 70 micrometers.<sup>[15]</sup> The AAO membrane consists of three distinct layers: aluminum metal, a thin barrier oxide layer, and a relatively thick porous oxide layer, Figure 1.2 shows the SEM results of the AAO membrane made in our lab. The aluminum foil was oxidized in  $\text{H}_3\text{PO}_4$  at  $0^\circ\text{C}$  under the voltage of 195V. From the image, we can see that the pores are distributed more evenly, and the pore sizes are more uniform.



**Figure 1.2** SEM image of Anodic Alumina membrane made in our lab

#### ***1.4 Electrochemical Deposition Method***

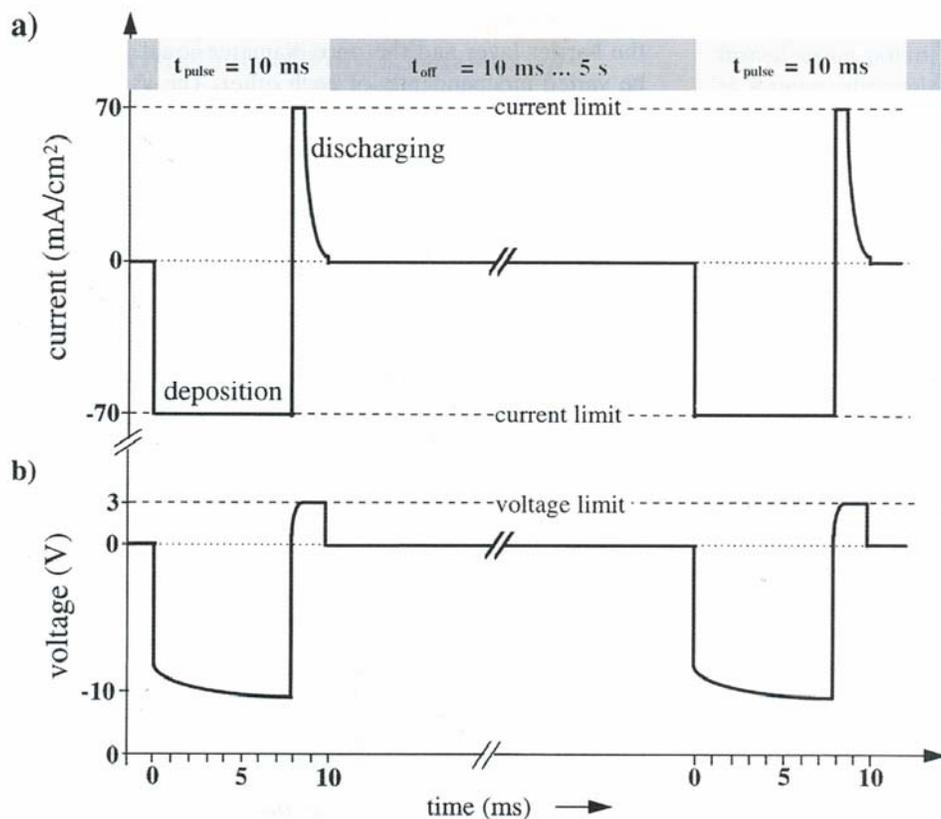
There are several methods to load various materials into the channels of these porous membranes physically or chemically. For example, metals (such as Bi) with relatively low melting points can be directly injected as liquids into pores of the AAO membrane and subsequently solidified into highly crystalline nanowires.<sup>[16]</sup> Most recently, Cao and co-workers also demonstrated the use of electrophoretic deposition to fill the pores of a polymeric or alumina membrane with charged sols generated *in situ* from a sol-gel precursor.<sup>[17]</sup>

Among these methods, electrochemical deposition method is used quite often because of its simplicity. The basic procedure is: first a layer of conductive metal is sputtered onto one side of a piece of membrane and then after the conductive metal side is protected, the membrane can thus be fabricated to an electrode. When this electrode is put into a metal ion containing plating solution and served as cathode, the metal ions can be reduced into metal in the channels, which deposits from the bottom of the channel and grows up to nanowires. There are several advantages of this method. First, it's easy to control the length of the nanowires fabricated inside these the channels because the length of the nanowires are proportional to the deposition time. Second, nanowires with different components can be fabricated by switching the plating solution. In the meanwhile, this method also has some drawbacks. First, the materials that can be loaded into the channels are limited to metals or semiconductors since it requires the conductivity in the electrochemical system. Second, the nanowires synthesized by this method are often polycrystalline. However, single crystals have also been obtained under carefully controlled conditions. For example, Neumann and co-workers have shown pulse electrodeposition could be exploited to selectively grow either single-crystalline or polycrystalline copper nanowires.<sup>[18]</sup>

Several different methods can be used to control the electrochemical deposition. The most commonly used one is Chronopotentionmetry, which means the working current density is constant during the deposition. The advantage of this method is that the lengths of nanowires are easy to be controlled because they are determined by the current density and deposition time. The second one is Chronoamperometry, which means the working potential is fixed during the experiment. It has the merit of selecting the metal to be deposited since different metals will be reduced at different potentials. The drawback of the method is it needs a standard electrode to verify the potential. The third one is the Pulsed Electrodeposition Method. It utilizes the rectifying properties of barrier, which allow the pores of the membrane to be filled uniformly by pulsed sequence.

In Pulsed Electrodeposition Method, the deposition is based on modulated pulse signals in the microsecond range. (Figure 1.3) <sup>[19]</sup> During the relatively long pulse of negative current the metal is deposited on the pore ground. In comparison to the direct current deposition, relatively high current density are applied at the moment of metal deposition, which should increase the number of deposition centers in each pore and also the nuclei formed at higher frequencies are more crystalline. After a short abrupt rise in the negative current pulse, the measured signal of the potential increases a little further, which is due to the charging of the capacitance of deposition interface. After the deposition pulse, a short pulse of positive polarization follows to discharge the capacitance of the barrier layer and to immediately interrupt the electric field at the deposition interface. The delay time  $t_{\text{off}}$ , was varied between 10ms and 5s. During this period the ion concentration recovers. Thus, the concentration of the metal ions is high at the bottom of each pore when the subsequent deposition pulse appears. The delay time,  $t_{\text{off}}$ , improves the homogeneity of the deposition and limits the hydrogen evolution. Overall, it provides an

efficient method to deposit materials like Fe, Co, and NiFe-alloys without removing the barrier layer of the AAO membrane.



**Figure 1.3** Schematic Diagram of the filling of porous alumina structure with nickel by pulsed electrodeposition.

## Chapter 2

### Nanowires and Nanotubes

#### *2.1 Introduction*

Recently, one-dimensional (1D) nanostructures such as wires, tubes have become the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanoscale devices. It is generally accepted that 1D nanostructures provide a good system to investigate the dependence of electrical<sup>[20]</sup> and thermal transport<sup>[21]</sup> or mechanical properties<sup>[22]</sup> on dimensionality and size reduction (or quantum confinement). They are also expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions. In comparison with quantum dots and wells, the advancement of 1D nanostructures has been slow until very recently, as hindered by the difficulties associated with the synthesis and fabrication of these nanostructures with well-controlled dimensions, morphology, phase purity, and chemical composition. As described in Chapter One, electrochemical deposition in an alumina oxide membrane as the template can provide a very effective way to fabricate metal nanowires.

#### *2.2 Experimental Section*

##### *2.2.1 Materials and Equipment*

All solvents and chemicals were of reagent quality and were used as received.

**Membrane:** The Whatman Anodisc<sup>TM</sup> Aluminum Oxide Membrane (AAO) was purchased from VWR Company.

**Plating solution:** The commercial Ni (Nickel Sulfamate RTU,  $\text{Ni}(\text{H}_2\text{NSO}_3)_2$  solution, pH ~ 4.0) and Au (Orotemp 24 RTU,  $\text{KAu}(\text{CN})_2$  solution, containing 8.2 g/liter gold, pH ~ 8.0) electroplating solutions were obtained from Technic Inc.

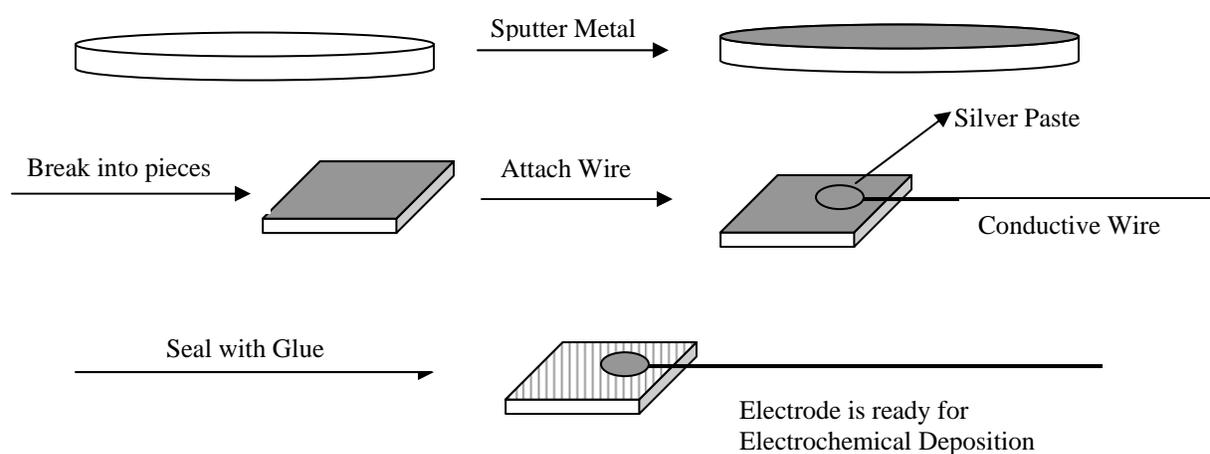
**Chemicals:** Dichloromethane  $\text{CH}_2\text{Cl}_2$  (99.5%, EM Science) NaOH (98%, Sigma)

Glue 3M all purpose glue purchased from Walmart Retail Store

**Equipment:** VMP2 Multi-Channel Potentiostat from Princeton Applied Research

### 2.2.2 Fabrication of Metal Nanowires in the AAO membrane

**Electrode Fabrication:** The whole procedure can be illustrated as the following:



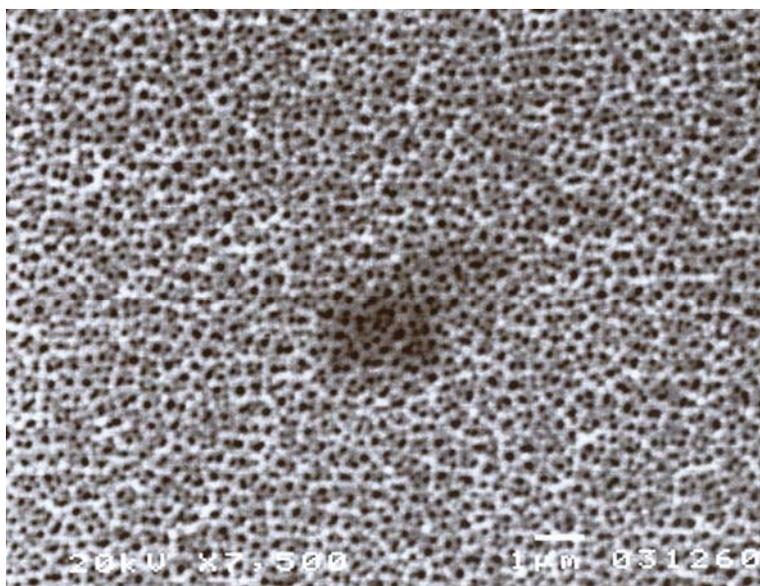
**Figure 2.1** Schematic diagram of making the electrode

*Sputter Metal:* For electrochemical deposition, it requires the membrane to be conductive to serve as the electrode. So the first step is to sputter the metal onto one side of the membrane. There are various metals that can be sputtered onto the membrane depending on the composition of the target. Those most often used by our group are Au-Pd alloy and Ag targets. Au-Pd film is very stable since Au and Pd are all very stable elements. But their stability brings a major drawback, which makes the film difficult to remove since it can not be dissolved even in strong acid like nitric acid. So in order to collect the free standing nanowires, a polish method is used to

remove the Au-Pd film, which can be difficult since it's hard to apply the force uniformly on the brittle membrane when it is polished on the sandpaper.

Ag films solve this problem since they can be dissolved in the dilute nitric acid. Ag can be oxidized in the air but the oxide layer won't affect the conductance very much as long as the membrane is not exposed in air very long after it is deposited.

Another purpose of sputtering metal is to seal the pores of the membrane so the metal can fill the pore completely. However, the sputtered metal actually can not fill the pore because the pore size is relatively big in comparison with the thickness of the metal film. The thickness of the sputtered metal film is proportional to the sputtering time. Our experience told us that at least 800 s sputtering is needed to make the surface of the membrane conductive. And even after 2000 s deposition, we can still find the pores of the membrane are not completely sealed, as shown in Figure 2.2.



**Figure 2.2** SEM image of commercial AAO membrane sputtered by the metal for 2000 s

*Fragmentation of Membrane:* A very sharp blade is needed to cut the membrane into pieces on a very flat surface since the membrane is very brittle. It is preferred that the membrane is cut into pieces with regular shapes since we need to measure the area of the electrode.

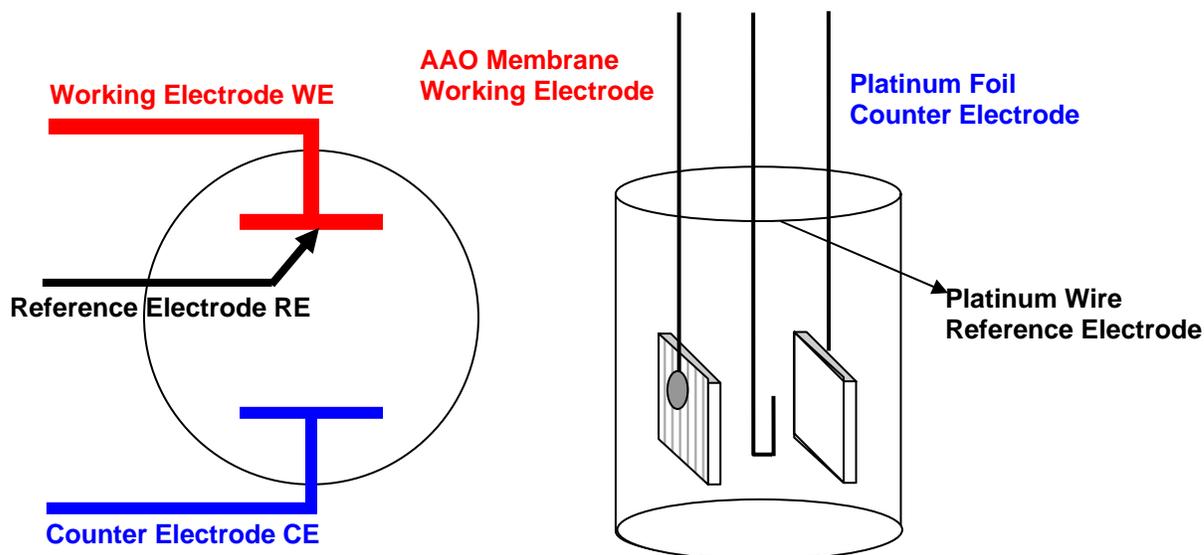
*Attach the wire:* Conductive silver paste is used to attach the wire to the membrane. The density of the silver paste and the amount of the silver paste are two important factors. If the silver paste is too dense, it will be hard to fill the gap between the wire and the membrane. On the other hand, too diluted silver paste will not only weakens the strength of the attachment but also spread out onto the membrane, penetrate the pores and clog them. Usually acetone is used to adjust the density of the silver paste. In terms of the amount of the silver paste, it should be sufficient to maintain the strength of the attachment of the wire to the membrane. But too much glue will also spread out over the membrane and clog the pores.

*Sealing with Glue:* Sealing the membrane with glue has two functions. First, it can cover the surface of the sputtered metal to make it insulated. Otherwise the plating solution will be reduced on the sputtered metal side since it has less resistance to deposit metal onto the conductive side than to deposit it into the pores. Second, it will seal the incomplete space of the pores that are left after the sputtering so that the plating solution will not pass through the pores and get reduced on the other side. The density of the glue is very important in this step since the glue will enter the unsealed pores. Dense glue will not enter the pores too much, while diluted glue will enter the pores. And after it dries, glue nanowires will be formed which can help forming the long nanotubes, which will be discussed later.

### **Electrochemical deposition:**

Before the electrochemical deposition, we need to measure the area of the electrode because we need this parameter to determine the current strength to maintain the current density. The

electrochemical deposition process is carried out in a standard electrochemical cell which is composed of three electrodes as shown in Figure 2.3. The working electrode is the membrane itself, and the counter electrode is made of Pt foil. The reference electrode is simply a piece of bended Pt wire. The reason to choose Pt as the electrodes is due to the stableness of Pt.



**Figure 2.3** Schematic Diagram of Electrochemical Cell

The next step is to calculate the current for the deposition. The current is determined by the current density and electrode area as the following equation:

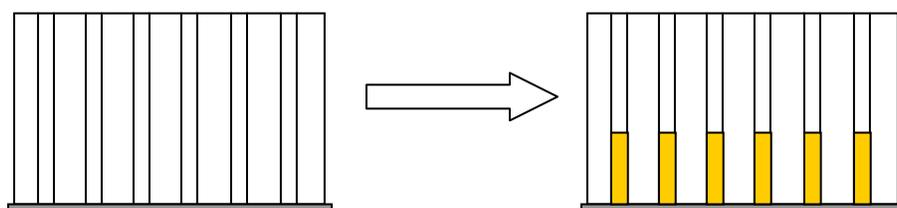
$$\text{Current (I)} = \text{Current Density (I}_{\text{density}}) * \text{Electrode Area(S)}$$

We can calculate the current if we know the surface area of the electrode and the current density that are kept as constant. The current density is usually measured in the unit of  $\text{mA}/\text{cm}^2$ . The most often used current density according to the literature is  $0.5 \text{ mA}/\text{cm}^2$ . However, our experience told us that this current density is not very suitable for this process because the qualities of the nanowires deposited under this current density are not very good. The reason is that the metal can not fill the channels completely under higher current density. So the current

density we choose is only  $0.1 \text{ mA/cm}^2$ , which will guarantee that the nanowires can have smooth surface.

After we setup the current of the potential equipment, we can start to deposit the metal into the pores. This process should be kept undisturbed. The nanowires will grow in the pores at the rate which is determined by the plating solution as well as the current density. Nickel is deposited into the channels first since it can remove the imperfectness at the end of the channels.

(Figure 2.4)



**Figure 2.4** Schematic diagram of depositing Ni into the channels of the membrane

### **Post-treatment of the samples:**

After the electrochemical deposition is finished, we need to process the electrode in order to characterize the nanowires or measure their properties and collect the nanowires for future use.

There are several methods that we can use to treat the electrodes after the deposition is finished. It depends on what kind of assembly of the nanowires we need.

*Nanowires Arrays:* If we need to get nanowires arrays standing on a substrate, we can just simply remove the membrane by 2M NaOH or KOH for half hour since the membrane is composed of  $\text{Al}_2\text{O}_3$  which can be dissolved in the basic solution. After soaked in the basic solution, we need to clean the nanowires by rinsing them with distilled water for several times. Otherwise the alumina left on the nanowires will be absorbed onto them since these nanomaterials have high surface area. This will bring difficulties when the nanowires are

observed under SEM because the alumina coated on the nanowires will make the SEM images look fuzzy.

*Freestanding Nanowires:* If we need to collect these nanowires as freestanding ones, we have to remove the sputtered metal which serve as the substrate and hold these nanowires. Before removing the sputtered metal, we need to remove the glue that seals the membrane. Usually we use  $\text{CH}_2\text{Cl}_2$  to dissolve the glue since it's a very good organic solvent. This step is very tricky since the glue is an adhesive mixture of polymer. When the glue meets  $\text{CH}_2\text{Cl}_2$ , it will become diluted glue and enter into the channels of the membrane, which will attach to the nanowires after the membrane is removed. Due to its adhesive property, once it has stuck to nanowires it will be very hard to clean. So in order to avoid the glue enter into the channel, we need to soak the electrode in  $\text{CH}_2\text{Cl}_2$  for very long time (at least one week is needed, and fresh  $\text{CH}_2\text{Cl}_2$  should be changed everyday). The glue inside the channels will diffuse out but the process is really slow.

After the glue is cleaned the electrode is polished to remove the sputtered metal if it's composed of Au-Pd. And we use nitric acid (4M) to dissolve the sputtered metal if it's silver.

Put the sample into NaOH and the sample soon becomes soft and thin. Now if we shake it with hand, we can find they break into pieces and become little fragments. In the meanwhile, the solution becomes cloudy. After this, we sonicate the sample for a few seconds; we can find the solution become homogeneous colloid with the metal color immediately.

Transfer the nanowire solution into a centrifuge test tube and centrifuge it at 1000-2000 rpm for 2-3 mins. It is not necessary to centrifuge these nanowire solution for a long time at higher spin rate because the nanowires have relatively larger dimensions, which will make the nanowires come down to the bottom of the test tube very soon even without any centrifugation. After the centrifugation, we use pipette to remove the supernatant and the nanowires are now

collected at the bottom of the test tube. We add several milliliters of distilled water into the test tube and redisperse these nanowires. Repeat this process for 5-6 times until the nanowires are clean. Add  $C_2H_5OH$  to the test tube and disperse the nanowires into it for future use.

### *2.2.3 Characterization*

#### **Scanning Electron Microscopy Characterization:**

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis were performed on a JEOL JSM 5410 SEM. The nanowire arrays were affixed to conductive carbon tape and loaded on specimen mounts for SEM. The nanowires solution can be dropped onto the SEM sample holder directly and after the solution is evaporated, nanowires will be left on the surface of the specimen mounts.

#### **Transmission Electron Microscopy Characterization**

Transmission electron micrographs (TEM) and electron diffraction patterns were obtained by using a JEOL 2010 TEM operating at 200 kV. The samples were prepared by mounting small pieces of mesh on TEM copper grid and directly loaded in TEM for observation.

#### **Optical Images:**

Optical images with 400 times magnification were obtained by Fluorescence Microscope (Olympus IX-70). A high performance charge-coupled device (CCD) camera (Rupert Scientific, model 256HB) with a  $512 \times 512$  pixel array is used for digital fluorescence imaging of the samples.

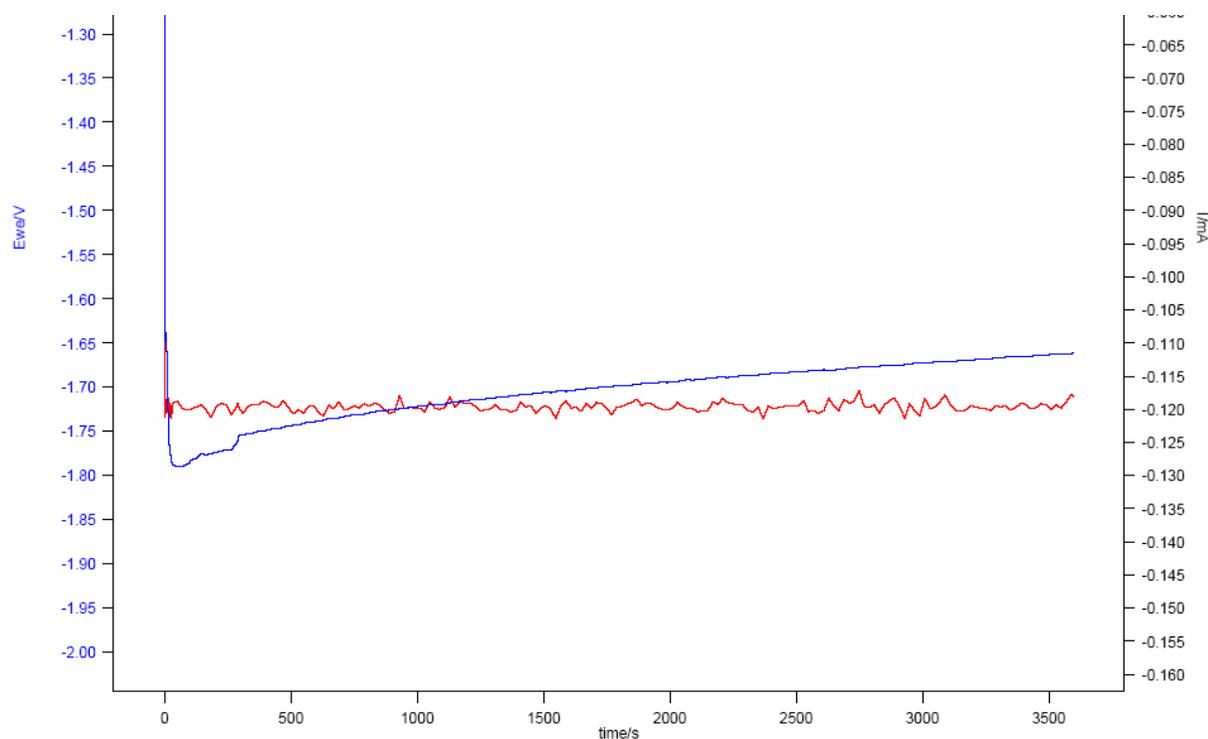
#### **Scanning Tunneling Microscope (STM) Characterization:**

STM was performed on Multimode Scanning Probe Microscope (SPM) which is controlled by NanoScope<sup>®</sup> IIIa controller.

## 2.3 Results and Discussion:

### 2.3.1 Chronopotentiogram for Electrodeposition

Figure 2.5 is a typical chronopotentiogram for the electrodeposition of gold into AAO membrane with about 300 nm diameter pore size at applied constant current density of 0.10 mA/cm<sup>2</sup>. The potential-time curve shows a slight overpotential at the first stage of electrodeposition, and then eventually the potential reaches a steady state. The stable plating potential indicates homogeneous growth of gold within the AAO membrane, thus the length of Au deposited can be controlled by varying the plating time.

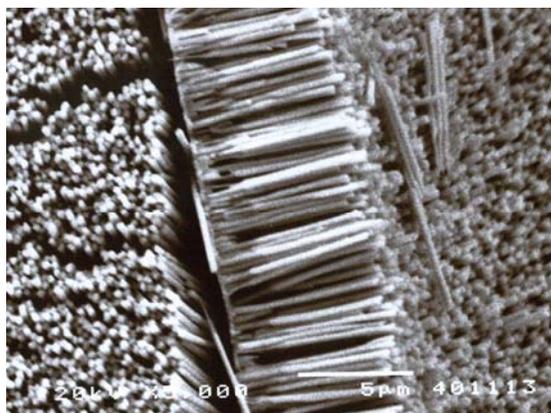


**Figure 2.5** Chronopotentiogram for the electrodeposition of gold into AAO membrane

### 2.3.2 Microscope Characterizations

Figure 2.6 shows typical gold nanowires array on the Au-Pd substrate. Nickel was deposited into

the channels at current density  $0.2\text{mA}/\text{cm}^2$  for 40mins. Then the channels were filled by gold at current density of  $0.1\text{mA}/\text{cm}^2$  for 9 hours. The darker parts in the images are nickel and brighter parts are gold.



**Figure 2.6** Gold nanowires array on the substrate after the membrane is removed by NaOH

Figure 2.7 (a), (b) shows dispersed gold nanowires. Ni was deposited into the channels at  $I_{\text{density}} = 0.2\text{mA}/\text{cm}^2$  for 30 mins. Then the channels were filled by gold at  $I_{\text{density}} = 0.1\text{mA}/\text{cm}^2$  for 8 hours.



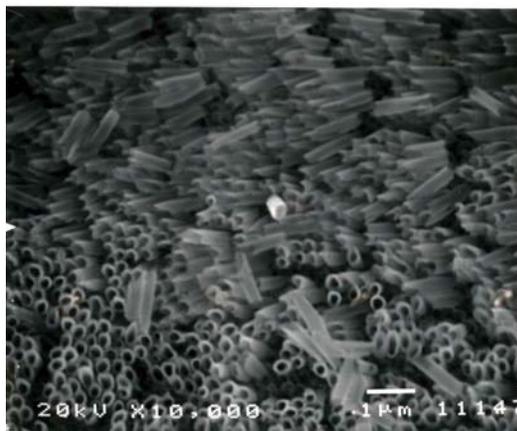
**Figure 2.7(a)** SEM image of free standing gold nanowires.



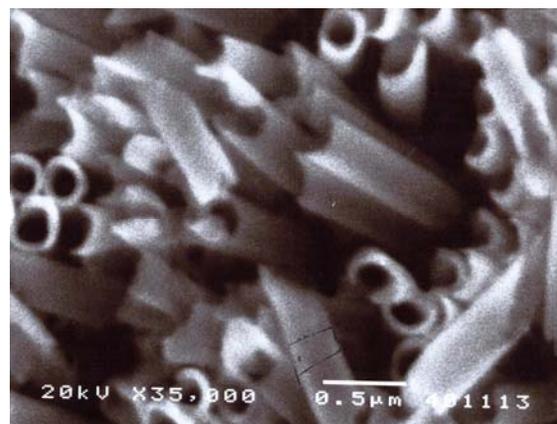
**Figure 2.7(b)** SEM image of higher magnification of gold nanowires

Figure 2.8(a), (b) shows nickel nanotubes formed in the porous membrane with the assistance

of glue. Nickel was deposited into the channels for 2h at current density of  $0.1\text{mA}/\text{cm}^2$ . According to higher magnification SEM image, the external diameters and internal diameters of these nanotubes are around  $300\text{nm}$  and  $200\text{nm}$ , respectively. The wall thickness of these nanotubes is around  $50\text{nm}$ .

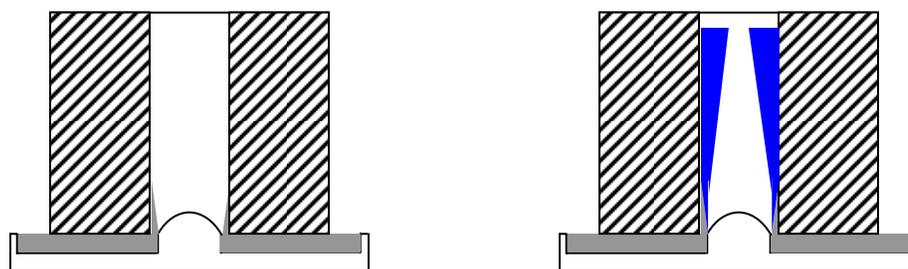


**Figure 2.8(a)** SEM image of Ni nanotubes formed in the AAO membrane



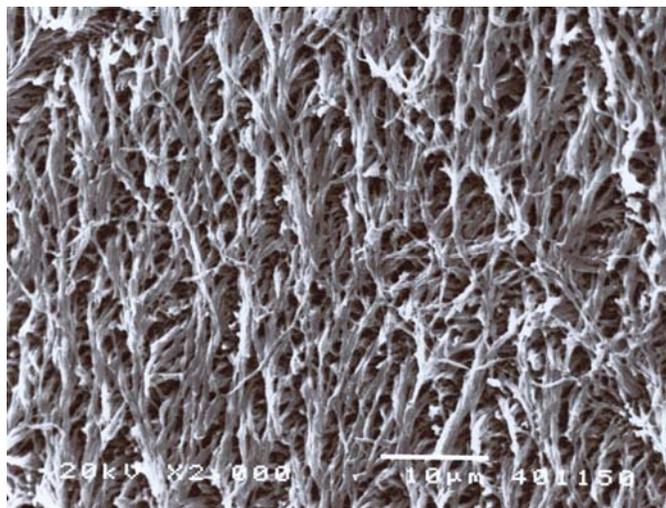
**Figure 2.8(b)** Higher magnification of SEM image of Ni nanotubes formed in the AAO membrane

Because the sputtered metal can't seal the pores completely, the conductive part exposed to the plating solution will be a circle-like shape after sealed by the glue. At the same time, the glue will enter into the unsealed pores. If the glue is dense and not used too much, the glue will form a "hill" at the bottom of the pore. (Figure 2.9) When the electrochemical deposition is carried out under this condition, the nanotubes will grow inside the pores by the direction of the sputtered metal circle. But eventually the nanotubes will seal themselves after several hours of deposition at current density of  $0.1\text{mA}/\text{cm}^2$ .



**Figure 2.9** Schematic Diagram of forming glue wires in the channels

If the glue is diluted and larger amount is used, it will flow into the pores, after drying, glue nanowires will form inside the channel, Figure 2.10 the SEM image of glue nanowires. Very long metal nanotubes can be formed inside the channel by the direction of these glue nanowires.



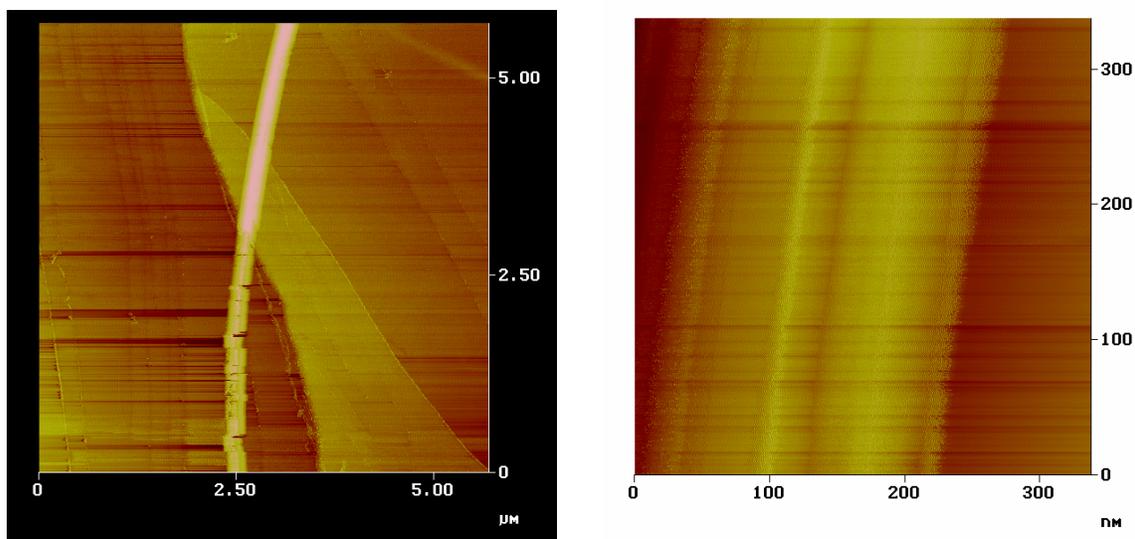
**Figure 2.10** Glue nanowires formed in the AAO membrane

Figure 2.11 is TEM image of the nanowire made by pulsed electrochemical deposition method at current density  $20\text{mA}/\text{cm}^2$ , the pulse time is  $0.01\text{s}$  with 4000 cycles while the rest time is  $2\text{s}$  each time. Because there is no nickel seal, the end of the nanowire forms a branch structure, reflecting the irregular channel at the bottom of the membrane.



**Figure 2.11** TEM image of the gold nanowire fabricated by pulsed electrochemical method

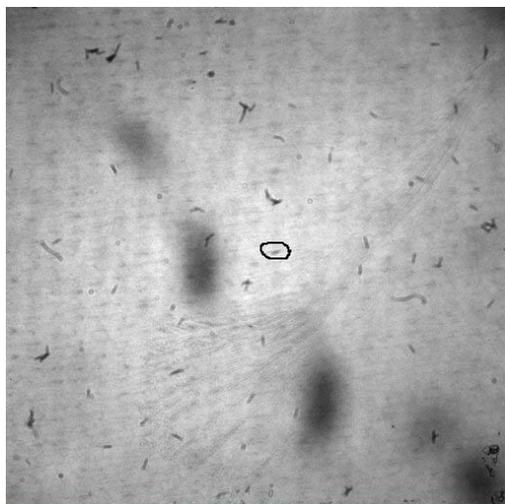
Figure 2.12 (a), (b) show STM results of the nanowires fabricated in the AAO membrane labeled with 20 nm pore size. Thus the nanowires have pore size of around 200 nm. And STM results show the pore sizes are consistent with what are expected. Figure 2.12(a) shows lower magnification of a single nanowire, which breaks into small parts and leave their position due to the sweep of the STM tip. Figure 2.12(b) is the higher magnification image of this nanowire.



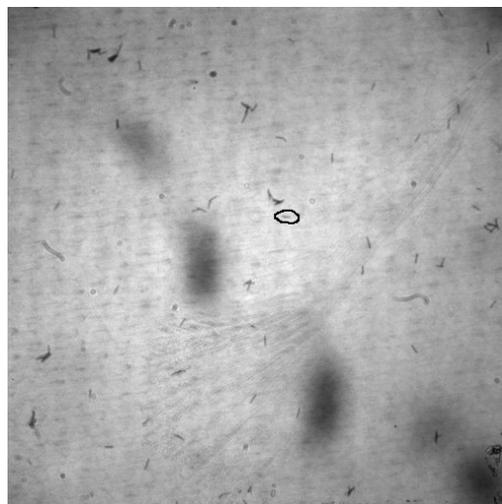
**Figure 2.12 (a) (b)** STM results of a single gold nanowire. Lower and higher magnification respectively

### 2.3.3 Aggregation of the nanowires observed by Optical Microscope

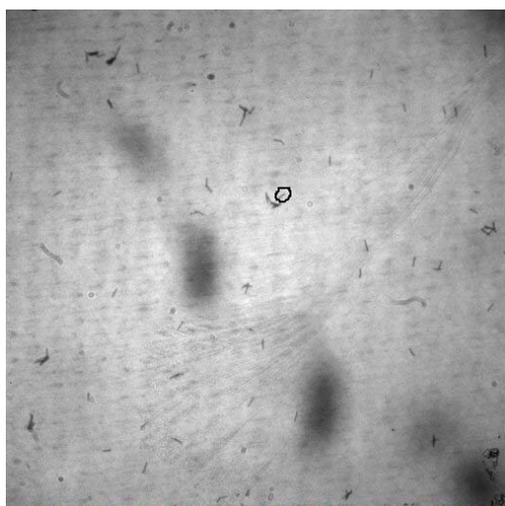
Nanomaterials can have a tendency to aggregate because they tend to lower their energy by decreasing their surface area after aggregation. Under the optical microscope, we can see the nanowires are “swimming” randomly, which is so-called Brownian motion. Eventually, we can observe that the nanowires aggregate into bundles. Figure 2.12 (a)-(l) show the aggregation process by monitoring one single nanowire. From a series of optical images, we can see that this single nanowire labeled with a circle flows toward a nanowire bundle and finally joins it into a bigger bundle. Once it has merged itself into bundle, the nanowire doesn’t move any more, it “disappears” in Figure 2.12 (k), (l) after it joins into the bundle.



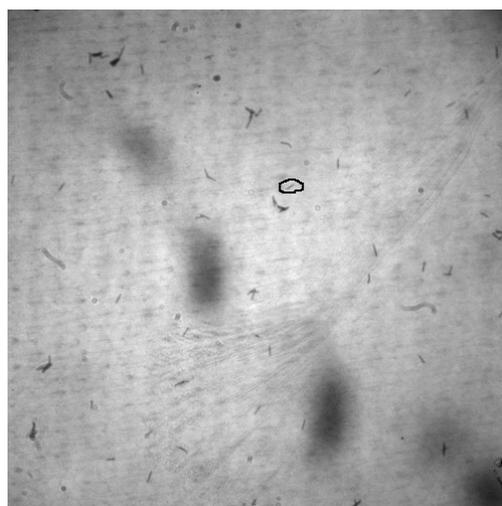
(a)



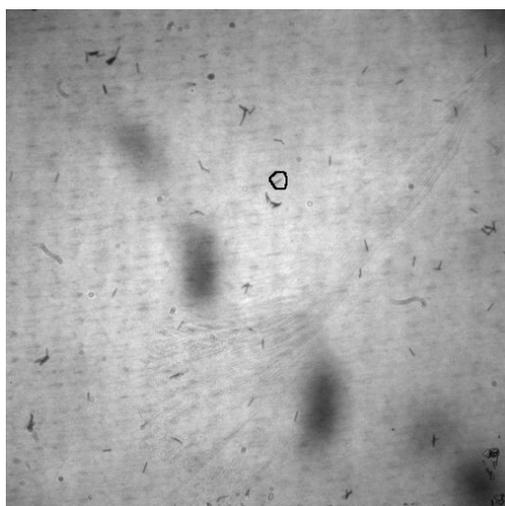
(b)



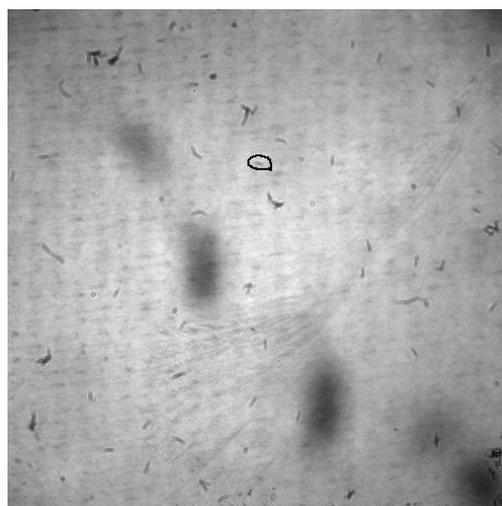
(c)



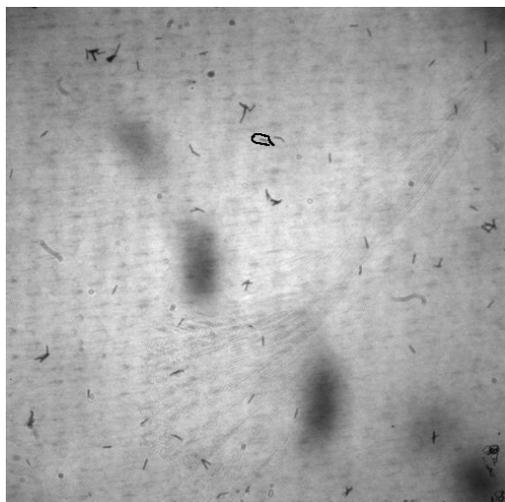
(d)



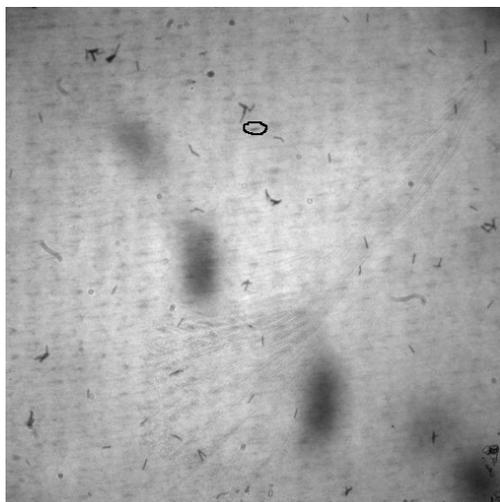
(e)



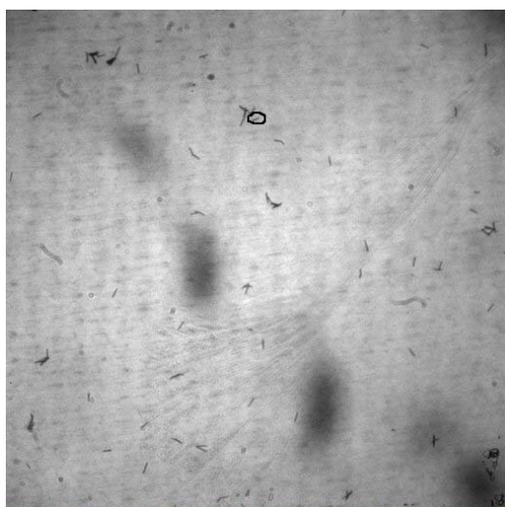
(f)



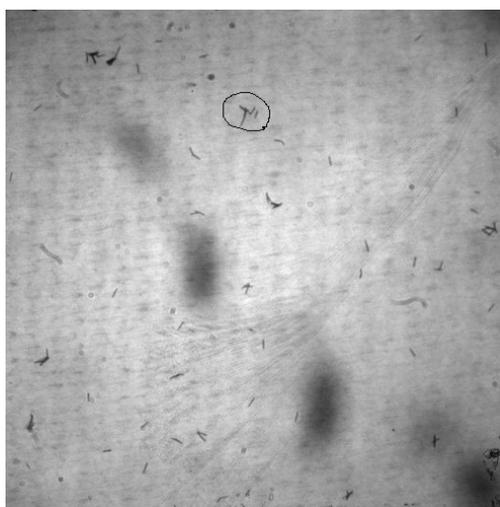
(g)



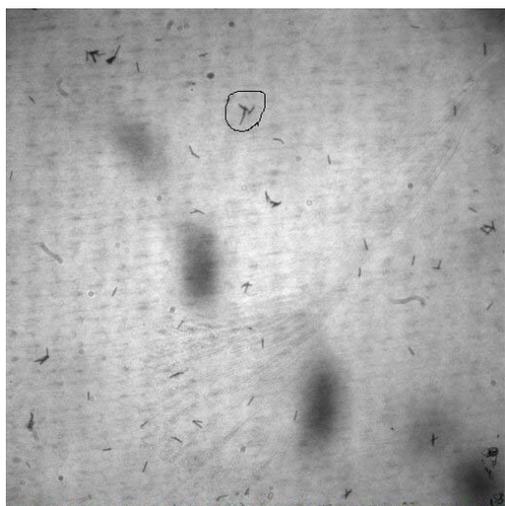
(h)



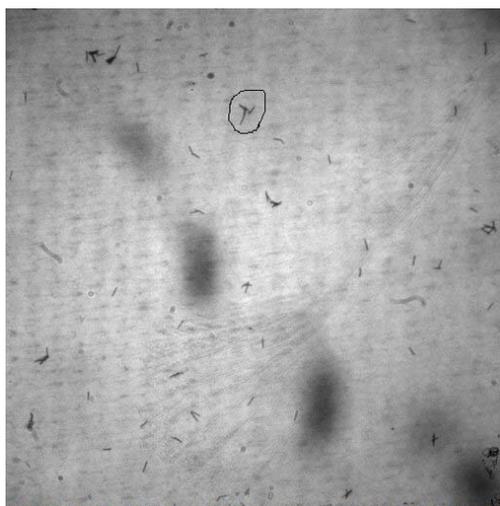
(i)



(j)



(k)



(l)

## ***2.4 Conclusions***

Gold nanowires and nickel nanotubes were successfully fabricated in the AAO membrane. Nanowires arrays as well as free-standing nanowires were obtained after post-treatment of the sample. SEM, TEM were used to characterize these nanostructured materials. The mechanism of forming nickel nanotubes was studied. Their behavior in solution was observed by optical microscope, including the Brownian motion and their aggregation.

## Chapter 3

### Striped Nanowires Made by Polymer Free Method

#### 3.1 Introduction

By sequentially depositing different metals into the nanopores, multisegments or striped metal nanowires can be fabricated.<sup>[23]</sup> These nanowires are also described as a superlattice structure. Electrochemical deposition methods are very suitable to fabricate these striped metal nanowires. The length of each segment can be controlled by the charge passed in each plating step and the sequence of the multiple segments is determined by sequence of the plating steps. One potential application of these striped nanowires is as building blocks for nanoscale electronic device since these metal nanowires are still highly conductive compared to the bulk metal if the length of nanowire does not dramatically affect the resistivity of the wires. However, nanowire electrical characteristics can be markedly altered by incorporation of other materials; for example, Au-CdSe-Au wires exhibit photoconductivity.<sup>[24]</sup> Despite the sub-wavelength diameter of these striped nanowires, the reflectivity of individual segments 300nm in diameter and 1-3  $\mu\text{m}$  in length closely matches that expected for the corresponding bulk metals.<sup>[25]</sup> Thus, the striping pattern of the nanowires makes these particles very attractive for information storage, analogous to barcodes in the macroscopic world. Under the magnetic field, nanowires with Ni component can be aligned, which will help to assemble individual nanowires. Due to the different chemical reactivities of the “stripe” metals, these strips can be modified with appropriate molecules. For example, Au binds strongly to thiols and Pt has high affinity to isocyanides. Using this strategy, nanowires could assemble deterministically into cross- or T-shaped pairs, or into more complex shapes.<sup>[26]</sup> It is also possible to use specific interactions between selectively functionalized segments of these nanowires to direct the assembly of nanowire dimers and oligomers, to prepare

two-dimensional assemblies between nanowire and substrate, and to prepare three-dimensional colloidal crystals from nanowire-shaped objects.<sup>[27]</sup>

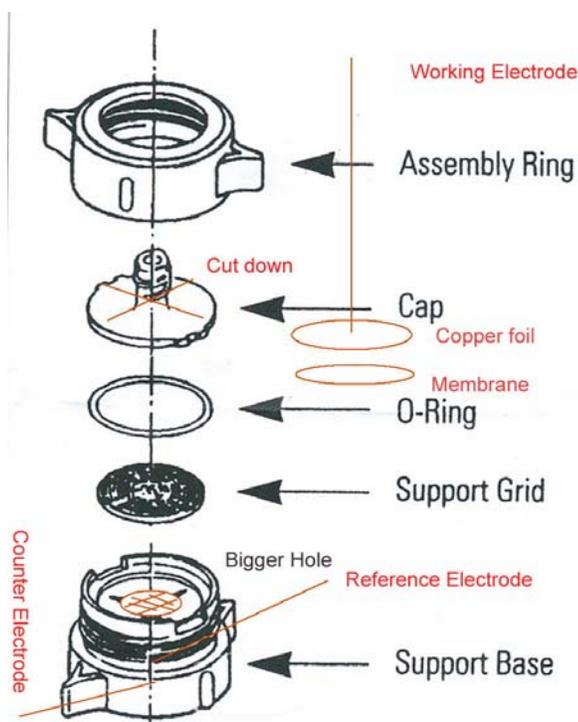
Due to the difficulties in removing the glue when treating the sample, it was necessary to find another way to alternate route. A polymer-free method described in this paper provides a very practical method to fabricate nanowires with stripes. It shortens the period of the experiment and allows a large scale of nanowires with stripes to be successfully made.

### 3.2 Experimental Section:

#### 3.2.1 Materials and equipment

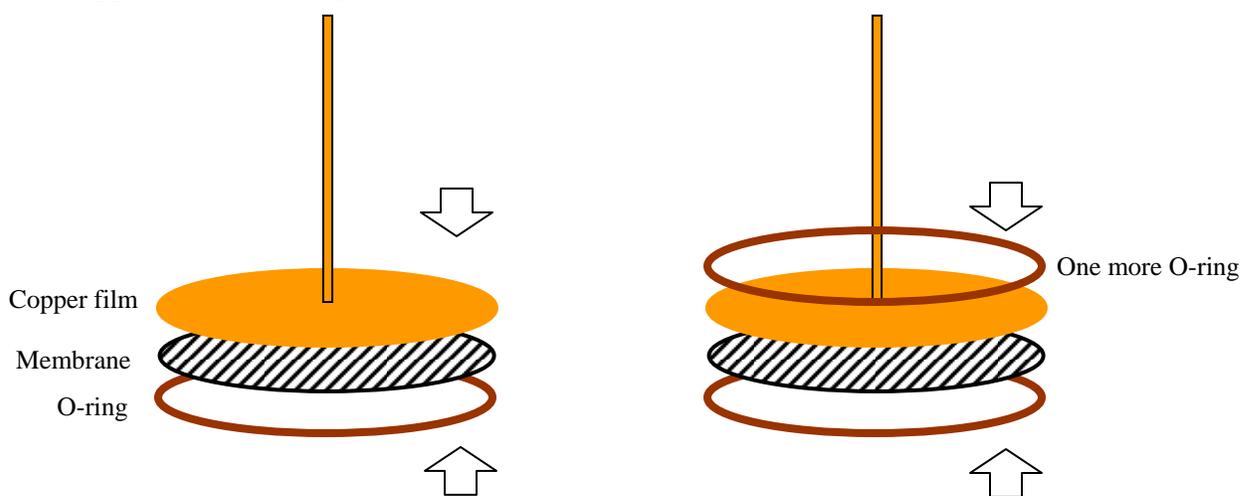
All the chemicals and equipments are the as same as what described in Section 2.2.1 in chapter 2. The filter holder is purchased from VWR which can fit AAO membranes that have diameters of 25mm.

#### 3.2.2 Equipment for polymer-free method



**Figure 3.1** Equipment for polymer-free method to make nanowires

Shown in Figure 3.1, the equipment is actually made from a modified filter holder. The plastic outlet on the cap is cut so that the filter can be put on flat table. And a big hole is made at the bottom of the support base in order to let the plating solution contact the membrane adequately. Two holes were drilled on the wall of the support base symmetrically. One hole is for putting the reference electrode in, one is for counter electrode. The support grid is not used in this system because it will prevent the solution from contacting the membrane. The membrane is sputtered with Ag film. And the conductive side is clamped to a copper film by the filter. A conductive wire was soldered on the copper film to serve as working electrode. An O-ring is used in this system to guarantee the seal between the membrane and the copper film. However, the effect of this seal is not very ideal, initially there was plating solution coming between the membrane and the copper film, which resulted in metal depositing onto the conductive side of the membrane. Thus modification was made to this system, which is to add one more O-ring between the cap and the copper film as the Figure 3.2 shows:



**Figure 3.2** Schematic Diagram of membrane assembly in polymer-free method

The membrane is clamped carefully between the copper film and the support base by the force applied by the screwing the filter tightly.

As an advantage, the surface area of the membrane is fixed in this system because only membrane with diameter of 25mm can fit into this filter. The inside diameter of the membrane determines the electrode area that will be exposed to the plating solution.

### *3.2.3 Electrochemical Deposition of Striped Nanowires into the AAO membrane*

By switching the plating solution, striped nanowires can be fabricated into the channels of the membrane. First, nickel is deposited into the channels to seal the pores as well as fill the bottom of the channel with imperfect structures. Since Ni can be dissolved in the acid, so it can be easily removed even though it's deposited on the other side of the membrane. At the current density  $0.1\text{mA}/\text{cm}^2$ , at least 24 hours are needed to seal the pores and remove the imperfections of the channels in the membrane. Otherwise gold wires will link to each other since some channels at the bottom of the membrane merge together. This will bring difficulties to separate these nanowires after the membrane is removed.

Gold is deposited into the pores in relatively shorter time. We can calculate the deposition time of the gold by measuring the length of the nanowires and their deposition time since they are proportional. Deposition at current density of  $0.2\text{mA}/\text{cm}^2$  for 26 minutes is needed if gold segment length is 300nm according to our calculation. We can label this gold as Au-1.

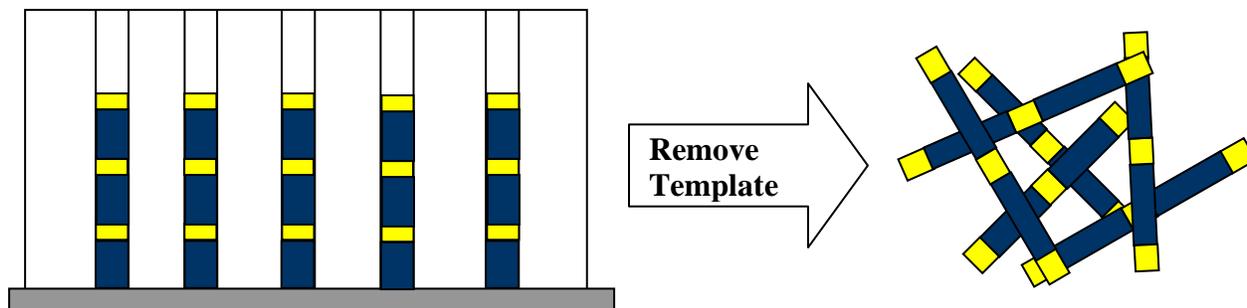
Consequently, relatively longer nickel segments are deposited at current density of  $0.3\text{mA}/\text{cm}^2$  for 4hrs and labeled as Ni-1.

Repeat these steps for another 2 times, thus Au-2, Ni-2, Au-3 can be loaded into these channels.

### *3.2.4 Post-treatment of the sample*

After the deposition is finished, the sample was soaked in nitric acid for about 30 seconds to remove the sputtered silver on the back of the membrane. Then 2M KOH or NaOH was used to

remove membrane, the free standing nanowires were obtained after sonication. An adequate amount of basic solution must be added to dissolve the AAO membrane, otherwise the alumina oxide will react with NaOH to form a white flocculant, which will absorb onto the nanowires and making SEM observation difficult. The nanowires were rinsed with distilled water for several times and finally dispersed in C<sub>2</sub>H<sub>5</sub>OH.



**Figure 3.3** Schematic diagram of post-treatment of striped nanowires

### *3.2.5 Microscope Characterization:*

SEM, TEM, Optical Microscope were used to characterized these striped nanowires similarly as described in Chapter 2 Section 2.2.3

In order to obtain the detailed surface morphology of these striped nanowires, LEO 1530VP Variable Pressure Field-Emission Microscope is used to characterize these nanowires.

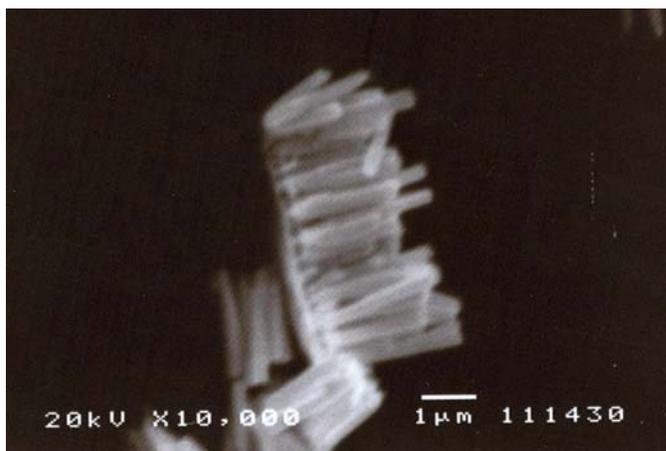
### *3.2.6 Alignment under magnetic field*

The solution of striped nanowires was dropped on the glass slide and observed under the optical microscope. Initially magnetic stirring bar is used to align these nanowires, but due to the weakness of the magnetic strength of stirring bar, the nanowires failed to be aligned. Finally a piece of very strong permanent magnet was applied and aligns these striped nanowires.

### 3.3 Results and Discussion

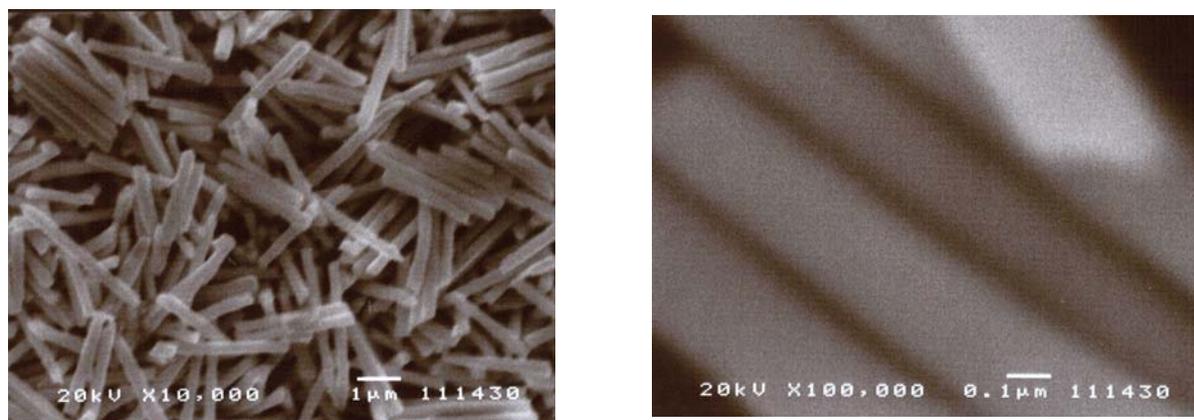
#### 3.3.1 SEM images

Figure 3.4 shows some gold nanowires synthesized by this polymer free method. Here nanowires were still immobilized on the substrate because the plating solution leaking between the membrane and the copper and metal was deposited on the back contact side of the membrane. Not enough deposition of nickel may also cause this problem.



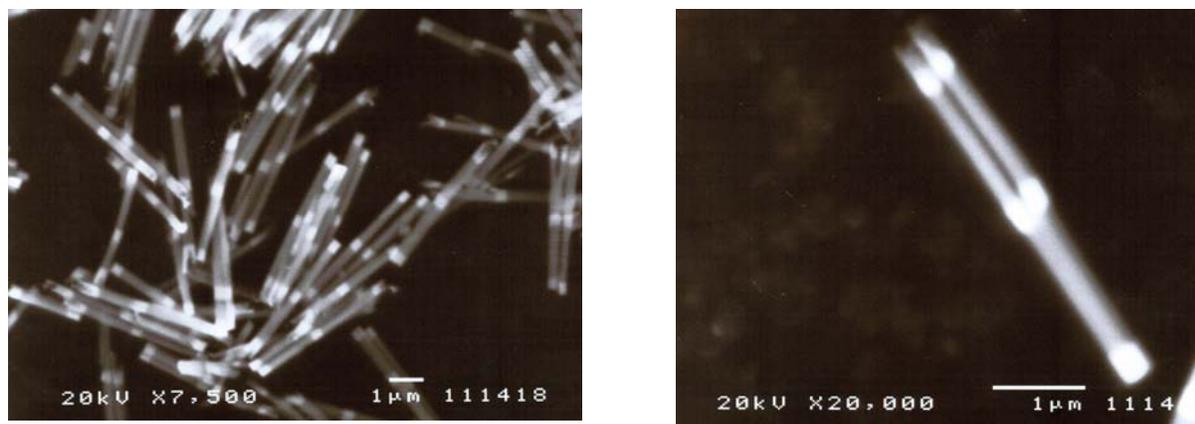
**Figure 3.4** Initial result of gold nanowires fabricated by the polymer-free method

Some improvements are made when the Ni deposition time is elongated. From Figure 3.5 (a), (b), we can still find that the nanowires' surface roughness which maybe caused by the incomplete seal.



**Figure 3.5 (a),(b)** Gold nanowires synthesized by polymer-free method after Ni deposition time is elongated

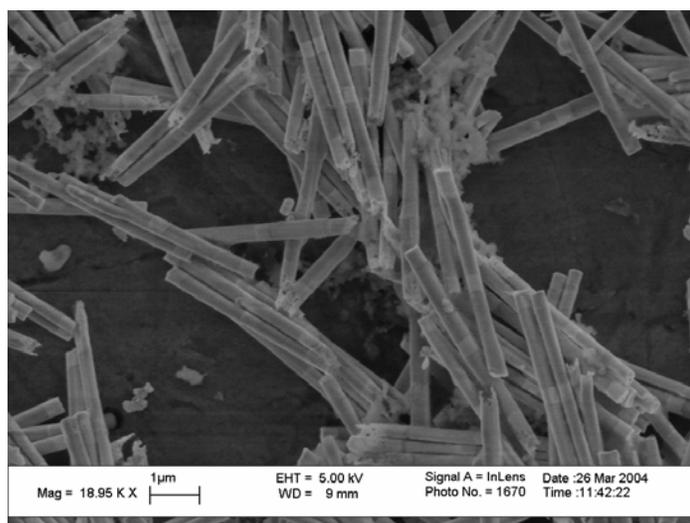
After one more O-ring is added, the qualities of the striped nanowires are enhanced due to much better seal between the membrane and the copper film, as shown in Figure 3.6 (a), (b).



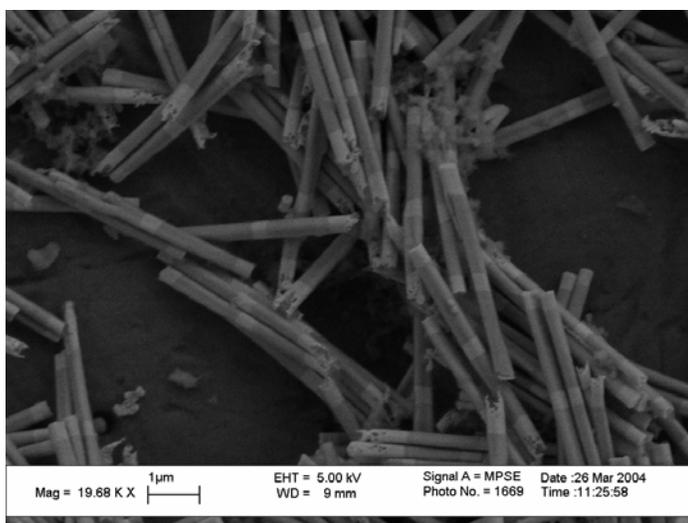
**Figure 3.6 (a), (b)** Striped nanowires obtained after better seal by adding one more O-ring

### 3.3.2 Field-Emission SEM images

Figure 3.7(a), (b) show the Field-Emission SEM images of the striped nanowires. This microscope has two modes which are InLens and MPSE respectively. The InLens mode has the capability of obtaining high resolution image under high vacuum, while the MPSE mode has the advantage of acquiring three-dimensional information of the object. Thus the mixed signal of InLens and MPSE is used to take both of the two advantages.



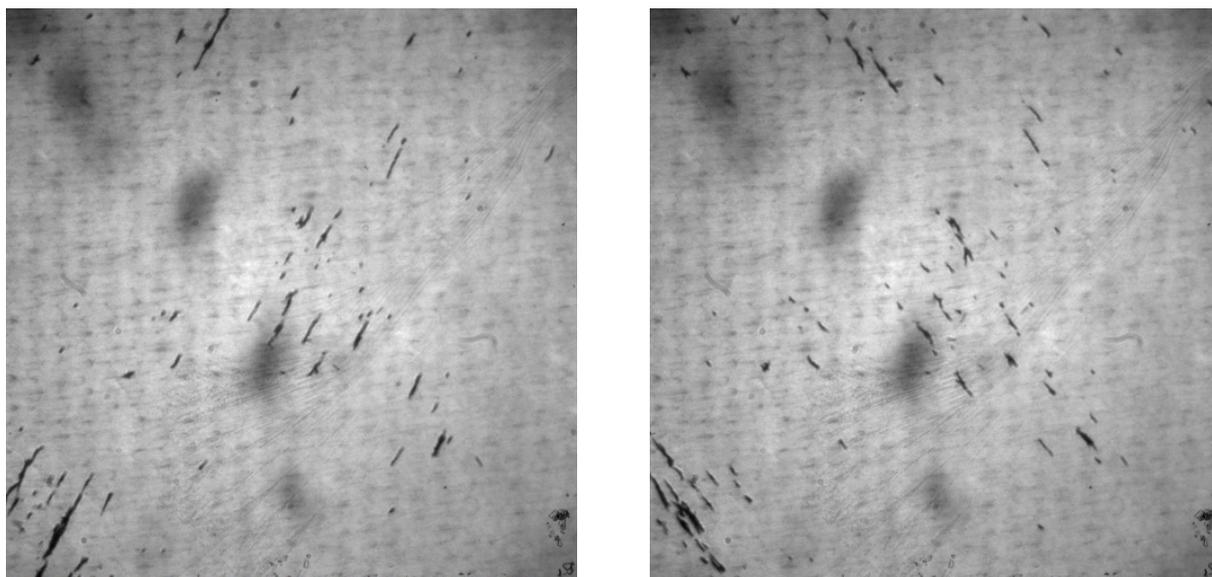
**Figure 3.7 (a)** FESEM image obtained by the mixed signal of InLens and MPSE



**Figure 3.7 (b)** FESEM image obtained by the signal of MPSE

### *3.3.4 Magnetic alignment*

Figure 3.8 (a),(b) show the alignment of these stripe nanowires



**Figure 3.8 (a), (b)** Magnetic Alignment of striped nanowires under magnetic force

### **3.4 Conclusions**

Striped nanowires with Au-Ni-Au-Ni-Au segments were successfully fabricated in AAO membrane clamped in the membrane filter without any assistance of glue. SEM was used to characterize these nanowires. Detailed morphology of the nanowires was obtained by Field-Emission SEM. Under strong magnetic force, these striped nanowires were successfully aligned and observed by an optical microscope.

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## **Vita**

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