Synthesis of polyaniline nanotube arrays through template dipping method

SUN CHUANYU*, WANG YU
Department of Materials Chemistry, Yinuo Institution, Changchun, 130033, China

The quasi- 1D polyaniline nanotube (PANINT) arrays have been fabricated by a very simple method of "template dipping" based on highly ordered porous anodic alumina (PAA) membrane. It was known that the nanotubes were hollow and the outer diameters were about 230nm which was similar to the channel size of the template by the scanning electron microscopy (SEM). The PANINT arrays were ordered, they have an uniform diameter, and paralleled each other. It has been indicated that the macromolecule chains remain the structures of which was in the solution by the UV- Vis spectra.

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1. Introduction

Since 1991, Iijma [1] from Japanese company NEC used the arc discharge method discovering carbon nanotubes in the cathode sediment incidentally, using various methods to prepare a one-dimensional / quasi-one-dimensional structure materials has become focus of nanomaterials research in recent years. There are many methods to prepare one dimension / quasi-one-dimensional nanostructure materials, such as arc discharge method, catalytic pyrolysis, laser ablation, evaporation condensation method from physical method and also chemical vapor deposition, electrochemical method, polymerization method, sol-gel method from chemical method. Although these methods have been used to synthesize a variety structure and properties of nanomaterials, there are still some problems such as difficult to control the particle size and shape, particle disordered arrangement and the preparation of harsh conditions and other short comings.

Among various synthesis routes for monodisperse nanowires with a high aspect ratio (diameter of nanowires/their length), the nanoporous alumina template-assisted method is of great interest due to its easy and inexpensive manufacturing process.

In recent years, with the deepening of nanomaterials research,a method called template synthe sis has drawn increasing attention [2~8]. The template synthesis of nanostructures is an integrated strategy for the synthesis of a physical, chemical and other methods, to make people have more degrees of freedom in design, fabrication and assembling a variety of nanostructured materials and their array system. It occupies an important position and broad application prospects in nanostructure science. There are many templates for the synthesis of nanomaterials, such as polycarbonate template, template carbon nanotubes and porous anodic alumina (PAA) template. Due to the PAA template has the advantages of high porosity, high temperature, good insulation, uniform pore size distribution; pore size, hole depth by the preparation conditions to facilitate regulation and the preparation of nanotubes or nanowires separated easily from the hole, it has become a research focus of the template method. PAA template wetting polymer melt solution or polymer solution to prepare polymer nanotubes is a very simple and universal method [9]. It can be used to prepare the tubular structures of several tens of nanometers to the micron level. The Steinhart [10] put the polymer on the surface of the PAA template, and then heated to the glass transition temperature of the polymer. Polymer is then liquefied into the PAA holes. In a few minutes to 30 minutes of time, the liquid polymer will form a wetting layer in the holes of the template. And then annealed in a vacuum environment, we can prepare polymer nanotubes with tube wall thickness of 20 ~ 50 nm, and length up to 100μm. Steihart etc [10,11] successfully prepared polystyrene, polytetrafluoroethylene, poly (methyl methacrylate) nanotubes with template wetting method. Liu et al [12] prepared carbon nanotubes using PAA templates with "dip-and-dry" method. The diameter of carbon nanotubes is about 220 ~ 310 nm, about 60μm in length, consistent with the PAA template size used before. This experiment uses a very simple way - the template impregnation, use NMP solution of polyaniline as the mother liquor, to prepare the polyaniline nanotubes (PANINTs) array.

2. Experimental

2.1 Main instruments and reagents

JSM-6700F scanning electron microscope (SEM), Japan, JEOL;

U-4100 UV-Vis spectrometer, Japan, High-Technologies Corporation;

ZKO72 type vacuum oven, Shanghai Experimental Instrument Factory Co., Ltd.

Porous anodic alumina (PAA) template: UK, Whatman;

Intrinsic polyaniline (EB / PANI), Changchun Institute of Applied Chemistry;

N-methyl pyrrolidone (NMP), Beijing Yili Fine Chemicals Co., Ltd., analytical grade.

2.2 Experimental procedures

2.2.1 The preparation of PANI saturated solution

Accurately take 1.0000g polyaniline, and add it to the 100mL round bottom flask. Then add 100mL of N-methyl pyrrolidone, with magnetic stirring. Slowly heated in an oil bath to 60 ° C and thermal insulation for 6h, standing, filtration and filtrate alternate reserved.

2.2.2 Preparation of PANINTs / PAA composite membrane

Take a template with pore size of about 200 nm, rinse with deionized water and then ultrasound about 30 min; Rinse with ethanol, ultrasound 30 min; Cleaning with acetone, ultrasound 30 min. After removing evaporated to dryness for reserve.

Impregnated in the NMP solution of polyaniline, after removing to dry it in the infrared lamp. And then impregnate and dryseveral times, put the samples in the infrared lamp for fully dry.

2.2.3 Preparation of the PANINTs

The above proceeds PANINTs / PAA composite membrane is glued to the copper conductive adhesive, remove the PAA template in the 3 mol / L NaOH solution then we can get PANINTs array.

3. Results and discussion

3.1 SEM structural characterization

The scanning electron micrograph of blank PAA template surface and cross section are as shown in Fig. 1 (A) and (B):

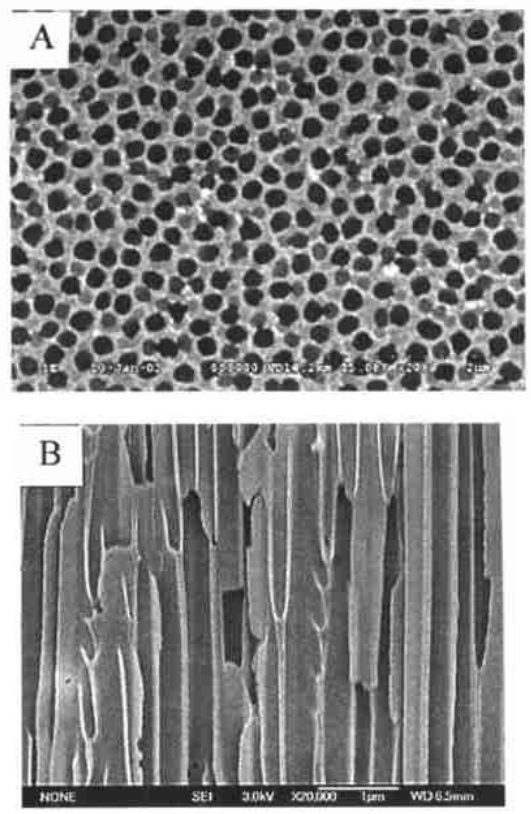

Fig. 1. SEM images of (A) : surface and (B) : cross section of PAA membrane.

It can be seen from the figure, the average hole of the PAA template is 200±30nm. The size of the hole is basically uniform. Nano-holes perpendicular to the surface of the PAA template and parallel to each other. However, some holes have defects.

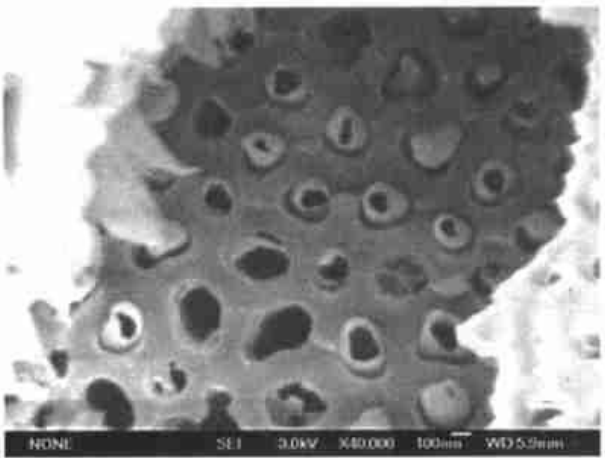

Fig. 2. SEM image of PANINTs/ PAA composite membrane.

Fig. 2 is the the scanning electron micrographs of the surface of PANlNTs / PAA composite membrane after removing polyaniline overlay. We can see from the figure that the PANINTs / PAA composite membrane surface is covered with a layer of polyaniline film. Remove the surface of the PANI layer, we can see the nanotubes in PAA holes. Polyaniline nanotubes are hollow tubular structures, the aperture of the tube diameter and the PAA template is basically the same, about 230 nm; wall thickness of 50 ~ 60nm; Tube diameter about 110 ~ 130nm. In addition, part of the hole is empty, may be due to the template surface blockage or caused by the removal of surface polyaniline layer.

When NMP solution of polyaniline in contact with the PAA template, first contact with the template surface. As the template be wetting by the solution, the solution will enter the PAA holes under the capillary force of the siphon, to spread along the hole wall. As solvent evaporation in the dry process will make polyaniline cohesion, forming of the nanotube structure with upper and lower surfaces through. Excess polyaniline will form PANI film in the template surface (as Fig. 2, left and right sides of polyaniline layer).

After using NaOH solution to remove the PAA template, scanning electron micrograph is shown in Fig. 3. Fig. 3 (A) is a scanning electron micrograph of a large area of polyaniline nanotubes array, (B) is high maganification micrograph of PANI nanotube arrays of (A). From the figure we can see: Polyaniline nanotubes are neatly arranged, uniform in length and parallel to each other. Outer diameter of nanotube is about 230nm, basically the same with the holes of PAA template. Nanotube wall is smooth and complete, with no damage and crack.

Template impregnation method can be seen as polyaniline solution's assembly process under the capillary force. Interface effects play a very important role in this process. In the initial stages of infiltration, a thin layer of film covers the pore walls of the PAA template. This is because the cohesive driving forces to completely fill the holes to be compared with adhesive forces are very weak[10]. With the extension of the infiltration time and wetting fluid volume increases, film gradually thickens. If the volume and concentration of the infiltrating fluid is large enough, it is entirely possible to get a solid polyaniline nanowires.

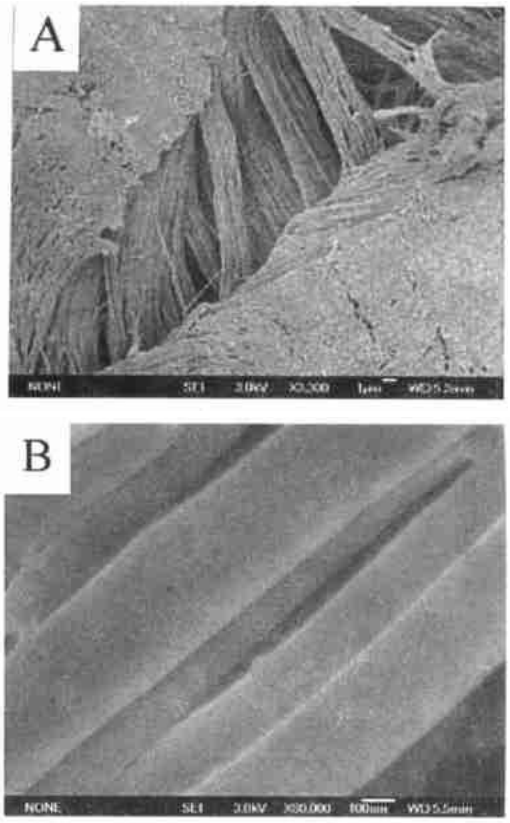

Fig. 3. SEM images of (A): large area PANINTs arrays and (B) : high maganification of (A).

3. 2 The UV- visible absorption spectroscopy

Fig. 4 is the UV-visible spectra of NMP solution of polyaniline, the intrinsic polyaniline films and PANINTs / PAA composite membrane.

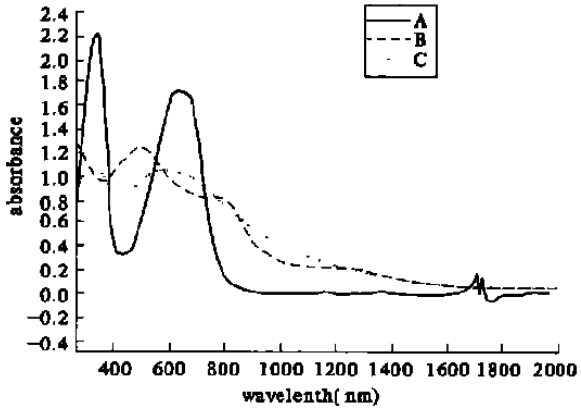

Fig. 4. UV_Vis spectra of (A) : NMP solution of PANI;(B) PANI film and (C) : PANINTs/ PAA composite membrane.

From Fig. 4, in UV - visible absorption spectra of (C) by PANINTs / PAA composite membrane, we can see the transition absorption peak of benzene ring total yoke chain at 320 nm and transition absorption peak between energy levels of π_Q and π_B at 580 nm. Compared with (A): NMP solution of PANI and (B): PANI film, π-π^* transition absorption peak of conjugated chain in benzene ring in the intrinsic polyaniline moves from 270 nm of membrane to 320 nm of nanotube, then to 324 nm of the NMP solution; the absorption peak of 493 nm in the polyaniline film also changes to 580 nm in the nanotube, then to 634 nm in the NMP solution. This shows from the polyaniline film to PANINTs, then to the NMP solution of polyaniline, polymer chain changes from the curl configuration to become expanded, to make π conjugate increases. This illustrates as confinement effect of PAA in the PANINTs structure, leading to the contraction curl of polymer chain in polyaniline is restricted, and retaining part of the stretched configuration in solution so that the degree of polymer chain in the PANINTs straight chain increases. PANINTs in 580 nm at the absorption peak is obviously wide than Polyaniline Film in 493 nm at the absorption peak, it can fully describe the commencement of the polymer chain in PANINTs more fully than film.

4. Conclusions

We can use the PAA templates to prepare PANINTs array through impregnation. The method is simple, cheap and easy to get the instruments and medicines. The shape and size of the nanotubes can be used through the template to be regulated. This method can also be used to prepare a nanotube array of other polymer materials, but we should pay attention to whether the interface effect of the solution and the porous template(Hydrophilic or hydrophobic) matches each other.

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*Corresponding author: chuanyuvip@tom.com