Available online at www.sciencedirect.com
SCIENCE DIRECT®
Synthetic Metals 153 (2005) 337–340
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Morphological and electrical characteristics of polyaniline nanofibers

Roch Chan Yu King [a], Frédérick Roussel [b,*]

[a] University of Science and Arts of Oklahoma, Chickasha, OK 73018, USA
[b] Laboratoire de Thermophysique de la Matière Condensée, UMR CNRS 8024, ULCO, MREI, 59140 Dunkerque, France

Abstract

Polyaniline nanofibers with an average diameter of <100nm were synthesized from two different polymerization processes. They were fabricated either a) via a template-free procedure at the interface of a heterogeneous (biphasic) medium composed of an organic solvent (toluene or CCl_4) containing the monomer (aniline) and an aqueous layer containing the oxidizing agent (ammonium peroxydisulfate, APS) and camphorsulfonic acid (HCSA) as the dopant or b) in a homogeneous (monophasic) medium in which nanofiber growth is promoted by the presence of a small amount (<1% by wt.) of single-walled carbon nanotubes as an added polymerization "seed" template. UV/Vis spectra of the nanofibers were obtained from pressed pellets or solution-cast thin films on glass slides confirming the conducting (doped) state of polyaniline. The electrical properties of the as-synthesized nanofibers (press pellets) were obtained via the conventional four-probe technique. Linear voltage-current (V-I) characteristics were recorded providing an estimated value of the electrical conductivity. The morphology and average diameter of the obtained nanofibers were investigated by Scanning Electron Microscopy (SEM).

Keywords: Polyaniline and derivatives, Interface preparation, Scanning transmission electron microscopy, UV-Vis-NIR absorption

1. Introduction

Polyaniline nanofibers are the subject of intensive studies due to their promising use in nanotechnology (e.g. nanoelectronic circuitry, nanosensors etc...). Unlike the traditional, non-fibrillar (granular) polyanilines synthesized via conventional chemical or electrochemical methods, the fibrillar-conducting counterparts have a unique attribute in that they exhibit large surface areas. Therefore, they should provide enhanced performance (e.g. improved kinetics) in applications where a high surface contact area is needed between the nanostructures and its environment. Compared to other conducting polymers, polyanilines can be easily switched (reversibly) from an insulating to a conducting state via either protonic acid doping or base dedoping processes (Figure 1). Traditional methods of nanofibers syntheses include the use of solid templates such as zeolites [1], controlled pore-sized membranes [2] or soluble templates such as surfactants [3] or polymers [4]. In this work, polyaniline nanofibers were prepared via either a) template-free procedures [5-7] at the interface of a heterogeneous (biphasic) medium composed of an organic solvent (toluene or CCl_4) containing the monomer (aniline) and an aqueous layer containing the oxidizing agent (ammonium peroxydisulfate, APS) and camphorsulfonic acid (HCSA) as the dopant or b) in a homogeneous (monophasic) medium in which nanofiber growth is promoted by the presence of a small amount (<1% by wt.) of single-walled carbon nanotubes as the polymerization "seed" template [8]. The electrical and morphological properties of the nanofibers, prepared with variable amounts of reagents (monomer, dopant and oxidizing agent) were obtained via the conventional 4-probe technique and SEM, respectively. The UV/Vis spectra were recorded either from pressed pellets or from solution-cast thin films on glass slides.

2. Experimental

2.1 Nanofiber synthesis

All chemicals were of analytical grade and used as received (Aldrich, Saint Quentin Fallavier, France).

* Corresponding author. Tel: +33-3-2865-8255; fax: +33-3-2865-8241;
E-mail: frederick.roussel@univ-littoral.fr

0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2005.07.268

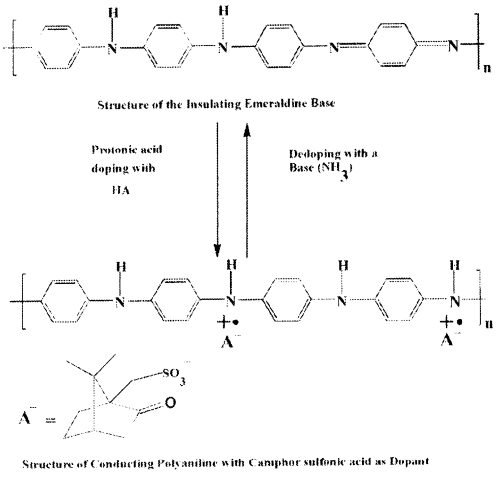

Fig. 1: Protonic acid doping or base dedoping processes of polyaniline.

-Procedure A [5]: a 3.55 mmol amount of aniline was dissolved in 50 ml CCl_4. Ammonium peroxydisulfate (APS) 1.58 mmol and camphorsulfonic acid (HCSA) 4.66 mmol were dissolved in 50 ml water. The aniline/APS ratio was about (3:1). The water solution was then pipetted slowly on top of the organic solution over a 8 min period. The reaction flask was left undisturbed at room temperature for 3 minutes after which time a very thin bluish-green layer appeared at the interface. The polymerization was allowed to proceed overnight (18h). An aliquot of the water layer (~5 ml) was placed in a dialysis tube with a 12000-14000 MW cutoff (Fisher Scientific, France). The by-products are removed by dialysis against deionized water until the water bath pH reaches a value of ~4.5. Samples from the dialysis tube were taken, laid on glass slides and dried overnight under vacuum in a dessicator at room temperature.

-Procedure B [9]: a 5.48 mmol amount of aniline was dissolved in 50 ml toluene. Ammonium peroxydisulfate (APS) 1.26 mmol and camphorsulfonic acid (HCSA) 0.5 mol were dissolved in 50 ml water. The aniline/APS ratio was about (4:1). A second experiment was performed with a ratio of (1:1). Along the sides of the beaker containing the aqueous solution, the organic phase was gently added. The resulting two-phase system was left undisturbed for 18h. The reaction mixture was suction filtered and the dark green precipitate washed repeatedly with water and acetone. The resulting precipitate was redoped in aq. 1.0M HCSA solution, suction filtered and washed with acetone to remove excess dopant. The resulting nanofibers were vacuum dried at room temperature overnight.

-Procedure C: A suspension of 2.8 mg of purified-single walled carbon nanotubes (1.2-1.5 nm diameter) in water/Triton X-100 was added to a stirred solution of 1.50M HCl (60 ml) containing aniline (790mg, 8.50mmol). The resulting mixture was stirred for 10 min after which time a solution of sodium metavanadate (220mg; 1.62 mmol) in 40 ml of 1.50M HCl was added. Stirring was continued for another 18h. A sample of this mixture was taken, washed with de-ionized water and vacuum dried for SEM analysis. Another sample was taken and dialyzed overnight until a neutral pH was obtained at which point the initial green (doped state) fibers turned blue (dedoped state). The dedoped fibers were then redoped with 1.5M HCl for 5h after which time a sample was retrieved, vacuumed dried and analyzed via SEM.

2.2 Characterization

The electrical properties of polyaniline nanofiber pellets were studied by a conventional four probe method [10]. A Lake Shore 120CS DC current source and a Chauvin-Arnoux CA 5240G numeric multimeter were used for the experimental setup. The UV/Vis spectra were recorded on a Perkin Elmer Lambda 2S spectrophotometer. Scanning Electron Microscopy studies were carried out on a LEO 438VP microscope operating at 15 kV.

3. Results and Discussion

3.1 Electrical and optical properties.

Using the four-probe method, the electrical properties of Pani(HCSA) nanofibers prepared according to Procedure A with a ratio of aniline/APS (3:1) and Procedure B with a ratio of aniline/APS (4:1) and (1:1), respectively, were investigated affording the electrical conductivity σ and sheet resistivity Rs. All samples exhibit a highly linear (V-I) curve shape confirming Ohmic behavior. Experimental data are gathered in Table 1.

Table 1
Conductivity (σ) and sheet resistivity (Rs) values of Pani(HCSA) films; d is the average thickness of the conducting layer as estimated by using a microcaliper Mitutoyo (Japan); ϕ is the diameter range of Pani(HCSA) nanofibers as deduced from SEM measurements.

	d (μm)	σ (S/cm)	Rs(Ω/sq.)	ϕ (nm)
Procedure A (3:1)	10	0.01	100000	38-76
Procedure B (4:1)	200	1.6	31	67-87
Procedure B (1:1)	130	0.5	154	-
Procedure C	85	3.9	32	35-90

Nanofibers obtained from procedure A have a much lower conductivity compared to those prepared according to Procedure B. This behavior can be explained by a partial dedoping process that took place during the dialysis. It is interesting to note that Procedure B provided fibers with a better conductivity when the ratio of aniline/APS was (4:1). This result is in agreement with the usual conductivity (1-10 S/cm) of Pani synthesized under a conventional method. In the case of a (1:1) ratio the lower conductivity obtained probably arises from an overoxidized state [9]. Surprisingly, this (4:1) versus (1:1)