Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Synthetic Metals 153 (2005) 313–316
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Fabrication and Applications of Conducting Polymer Nanotube, Nanowire, Nanohole, and Double Wall Nanotube

J. Joo [a,*], B. H. Kim[a], D. H. Park[a], H. S. Kim[a], D. S. Seo[a], J. H. Shim[a], S. J. Lee[a], K. S. Ryu[b], K. Kim[c], J. -I. Jin[c], T. J. Lee[d], and C. J. Lee[d]

[a] *Department of Physics, Korea University, Seoul 136-701, Korea*
[b] *Electronics & Telecommunications Research Institute, Daejeon 305-350, Korea*
[c] *Department of Chemistry, Center for Eletro- & Photo-Responsive Molecules, Korea University, Seoul 136-701, Korea*
[d] *Department of Nanotechnology, Hanyang University, Seoul 133-791, Korea*

Abstract

We fabricated nanotubes, nanowires, and double wall nanotubes (DWNTs) of (semi) conducting poly (3,4-ethylenedioxythiophene) (PEDOT), poly (*p*-phenylenevinylene) (PPV), and polypyrrole (PPy) through electrochemical polymerization or chemical vapor deposition method by using Al_2O_3 nanoporous template. The formation of the nanotubes, nanowires, and DWNTs was confirmed by SEM and TEM images. The formation of tube or wire, the length, and the thickness of wall of the nanotubes were controlled through various synthetic conditions, such as polymerization time and applied current (or voltage). Inorganic ferromagnetic Ni or organic light emitting PPV materials was synthesized outside or inside the conducting polymer nanotube as the form of DWNT. Two PL peaks were observed for carbonized PPV/light emitting PPV DWNTs. We fabricated nanoholes on the surface of conducting PEDOT-PSS [poly (4-styrenesulfornate)] films through high-energy ion irradiation. For electrical and optical properties of the nano-systems, *I-V* characteristics curves and UV/Vis absorbance spectra were measured. The UV/Vis absorbance spectrum of PPy nanowires varied with the dissolving solvent of template. The applications of the nanotubes, nanowires, and nanoholes of conducting polymers to electrode of capacitor and to nanotip emitters of field emission (FE) are presented.

Keywords: Conducting polymer; nanotube; nanowire; double wall nanotube; nanohole; nanotip.

1. Introduction

π-Conjugated organic materials have been applied to nanoscale devices or microelectronics with the development of Si based nanotechnology [1,2]. Nanoscale π-conjugated organic molecules and polymers can be used for biosensors, electrochemical devices, single electron transistors, nanotips of field emission display (FED), etc [3-5]. Recently, the giant magneto-resistance of the hybrid spin-valve consisted with inorganic ferromagnetic materials and organic Alq_3 molecule was reported [6]. Researchers have focused on synthesis and applications of nanoscale organic molecules and polymers. Nanoporous template method has been studied for the synthesis of organic nanomaterials [7,8], which has advantages such as low cost, control of intrinsic properties and size, and mass production.

In this study, we report the synthesis of π-conjugated PPy, PEDOT, PPV nanotubes and nanowires, and their double wall nanotubes (DWNTs), through electrochemical polymerization or chemical vapor deposition (CVD) method by using Al_2O_3 nanoporous template [9]. We observed that the intrinsic properties and physical dimensions of the systems were controlled by synthetic conditions. We demonstrate that the nano-systems can be applied to nanotip emitters of FED. We also fabricated nanoholes on the surface of

* Corresponding author: Tel: +82-2-3290-3103; fax: +82-2-927-3292; E-mail: jjoo@korea.ac.kr.

0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2005.07.221

conducting PEDOT-PSS films through high-energy ion irradiation.

2. Experimental

Conducting or semiconducting PPy and PEDOT nanotubes and nanowires were synthesized through electrochemical polymerization method using Al_2O_3 nanoporous template, which was purchased from Whatman Co. Pyrrole and EDOT monomers (≥ 98% purified samples) were purchased from Aldrich. For dopant and solvent in electrolyte, we used tetrabutylammonium hexafluorophosphate ($TBAPF_6$) or dodecylbenzenesulfonic acid (DBSA) as dopant and distilled water or acetonitrile as solvent. We used HF or NaOH solution for dissolving Al_2O_3 template after polymerization. It should be noted that NaOH solution has the effect of de-doping. For the PPV DWNTs, pristine PPV material was synthesized inside carbonized PPV nanotubes by using the CVD method [10]. The carbonization of initial PPV nanotube was performed in furnace at 750 °C. For the Ni/PPy DWNTs, ferromagnetic Ni nanotubes were synthesized outside PPy-$TBAPF_6$ nanotubes through electrochemical method in solution with $NiSO_4$-$6H_2O$, $NiCl_2$-$6H_2O$, and H_3BO_3. The free-standing film of PEDOT-PSS was cast by using commercial Baytron P. High-energy (3 MeV) Cl^{2+} ions with 5×10^{15} ions/cm^2 dose were irradiated onto the PEDOT surface through Al_2O_3 template as mask, and the nanoholes were homogeneously formed.

The structure and formation of π-conjugated polymer nanotubes and nanowires were investigated by using UV/Vis absorbance spectra (HP 8453), SEM (JEOL JSM-5200), and TEM (JEOL 1200EX) experiments. For electrical properties of nano-systems, *I-V* characteristic curves were measured. The pattern of electrode was prepared by photolithography. Temperature dependence of *I-V* characteristics was performed by using a CTI- Cryogenics closed cycle refrigerator system. For applications of conducting polymer nanotubes and nanowires, we fabricated the cell of FE. The FE cell consisted of ITO for anode and the nanotube or nanowire layer for cathode. The distance between anode and nanomaterials was ~150 μm, and the cell was kept in vacuum under 10^{-6} Torr. For capacitance, electrochemical cell consisted of electrode of the PEDOT-PSS films with and without nanoholes, a separator of porous olefin film, and 1M Et_4NBF_4 in acetronirile.

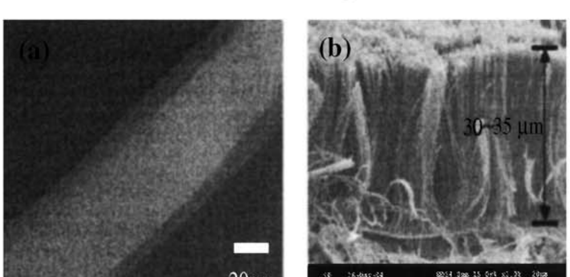

Fig. 1 (a) TEM photograph of PEDOT-DBSA nanotube and (b) SEM photograph of PEDOT-DBSA nanowires, with diameters of 100 nm.

3. Results and Discussion

3.1 Structural and optical properties

Figures 1 (a) and (b) show the TEM and SEM photographs of the PEDOT-DBSA nanotube and nanowires, with diameters of 100 nm. The thickness of the nanotube was ~10 nm. The synthesized nanotubes have an open end at the top, with the filled end at bottom (Au evaporated part) in nanowires. As the polymerization time and applied current increased from 10 min to 30 min and from 10 mA to 30 mA, respectively, the inside of the tubes filled and formed in the wire.

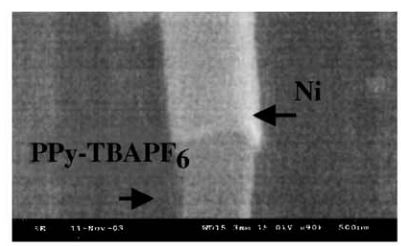

Fig. 2 SEM photograph of the PPy-$TBAPF_6$ and the Ni double wall nanotubes.

Figure 2 presents the SEM image of DWNT of the conducting PPy-$TBAPF_6$ nanotube (inside) and the ferromagnetic Ni nanotube (outside). The thickness of the Ni nanotubes was ~30 nm. The formation of the Ni nanotube was also confirmed through energy dispersive X-ray spectrometry (EDX) experiments. The hybrid DWNTs of the π-conjugated polymer with the ferromagnetic Ni materials can be used for the devices in spintronics as spin-valve [6].

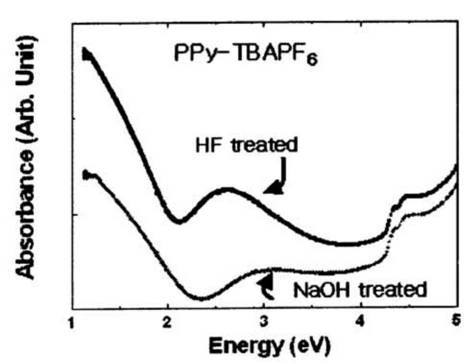

Fig. 3 Comparison of UV/Vis absorbance spectra of HF or NaOH treated PPy-$TBAPF_6$ nanowires.