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Synthesis, characteristics, and field emission of doped and de-doped polypyrrole, polyaniline, poly(3,4-ethylenedioxythiophene) nanotubes and nanowires

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Abstract

Doped and de-doped nanotubes and nanowires of polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene) were synthesized by the electrochemical polymerization method, using Al_2O_3 nanoporous templates. The electrical and optical properties of the nanotubes and nanowires were controlled through various synthetic conditions, such as doping level, dopant, and template-dissolving solvents. The diameters and wall thicknesses of the nanotubes were 100–200 nm and 10–30 nm, respectively. To determine the electrical and optical properties of the nano-systems, I–V characteristic curves with gate bias, dc conductivity, and UV–vis spectra were measured. We observed that the nano-systems were transformed from a conducting state to a semiconducting (or insulating) state through the process of de-doping using the template-dissolving solvents. Possible applications of these nanotubes and nanowires in the construction of nanotip emitters in field emission displays and polymer-based transistors are presented.

Keywords: Conducting polymer; Nanotube; Nanowire; Transistor; Field emission

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1. Introduction

π-Conjugated polymers (or conducting polymers) have been intensively studied in the fields of fundamental and applied researches, because of their one-dimensional intrinsic properties and their potential for commercial applications [1]. They have relatively high conductivity, are light in weight, inexpensive, flexible, air-stable, etc. The π-conjugated polymers, most notably polypyrrole (PPy), polythiophene (PT), polyaniline (PAN), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(*p*-phenylenevinylene) (PPV) have been synthesized, in free-standing film and bulky powder form, through the electrochemical or chemical polymerization methods [2]. They have been used to construct organic light emitting diodes (OLED) [3], organic field effect transistors (OFET) [4], electromagnetic interference (EMI) shielding [5], anti-static coatings [6], and capacitors [7].

With the development of Si-based nanotechnology, π-conjugated organic materials have been applied to many nanoscale devices and microelectronic devices [8,9]. Nanoscale π-conjugated organic molecules and polymers can be used for biosensors [10], electrochemical devices, single-electron transistors [11], nanotips in field emission displays (FED) [12], etc.

Research has currently been focused on the synthesis, characteristics, and applications of nanoscale organic molecules and polymers, such as polyacetylene, PPy, poly(3-hexylthiophene), etc. [13,14]. The nanoporous template method has been established for the synthesis of organic nanomaterials, as it has many advantages [15,16]. These advantages include low cost, control of electrical or optical properties and of dimension, mass production, etc. [17].

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In this study, we report the synthesis, characteristics, and field emitting applications of doped and de-doped PPy, PAN, and PEDOT nanotubes and nanowires, prepared by electrochemical polymerization method [18,19]. The nano-systems were transformed from a conducting state to a semiconducting (or insulating) state through the process of de-doping, with the treatment of NaOH as a solvent. We observed that physical dimensions such as diameter, length, and wall thickness of the nano-systems were controlled by polymerization time and applied current. The dc conductivity, *I–V* characteristic curves, and optical properties of the nano-systems were measured, and they varied with sample size, doping level, dopant, and template-dissolving solvent. We demonstrate that the doped nano-systems can be applied to nanotip emitters in FEDs and active nanomaterials in polymer-based transistors.

2. Experimental

π-Conjugated PPy, PAN, and PEDOT nanotubes and nanowires were synthesized by the electrochemical polymerization method, using Al_2O_3 nanoporous template (diameter = 100–200 nm). Templates with 200 nm diameters were purchased from Whatman Co. Nanoporous templates with 100 nm diameters were fabricated in the author's lab by the anodizing technique, using Al [20]. Pyrrole, aniline, and EDOT monomers (≥98% purified samples) were purchased from Aldrich. For dopants and solvents in electrolyte, we used tetrabutylammonium-hexafluorophosphate ($TBAPF_6$), perchloric acid ($HClO_4$), camphorsulfonic acid (CSA), or dodecylbenzenesulfonic acid (DBSA) as the dopant and distilled water, *N*-methyl-2-pyrrolidinone (NMP), or acetonitrile as the solvent. The Au was thermally evaporated on one side of the nanoporous template, and attached to the stainless steel working electrode. For PPy-$TBAPF_6$ nanotubes, we used $TBAPF_6$ as the dopant [pyrrole:$TBAPF_6$ (or CSA) = 5:1 in molar ratio] and an applied current of 2–3 mA for 1 min. For PPy nanowires, we used the same dopant, doping level, and current, but polymerization time was longer, about 15–40 min. For PAN nanotubes or nanowires, we used $HClO_4$ as the dopant (aniline:$HClO_4$ = 1:3 in molar ratio) and an applied voltage of 1.4 V for 60 min. We used DBSA as the dopant for PEDOT nanotubes and nanowires (EDOT:DBSA = 3:1 in molar ratio). We used HF or NaOH solution to dissolve the Al_2O_3 template after polymerization. It should be noted that NaOH solution has the effects of the de-doping or the counter-ion exchange between the intercalated anion and OH^- in solution [21].

The formation of π-conjugated polymer nanotubes and nanowires was investigated with SEM (JEOL JSM-5200) and TEM (JEOL 1200EX) experiments. The optical properties of the systems were investigated through UV–vis absorbance spectra (HP 8453). In order to determine electrical properties of the nanotubes and nanowires, we measured dc conductivity (σ_{dc}) using the 4-probe technique to eliminate contact resistance, and *I–V* characteristic curves with and without gate bias. The 4-probe patterns and the field effect transistor were prepared through photolithography. For applications of conducting polymer nanotubes and nanowires, we fabricated a field emission (FE) cell. The FE cell consisted of ITO for the anode, and the conducting polymer nanotubes or nanowires for the cathode. The distance between the anode and the nanomaterials was ∼150 μm, and the cell was kept in vacuum, under 10^{-6} Torr [22].

3. Results and discussion

3.1. Structure and optical properties

Fig. 1 shows TEM and SEM photographs of π-conjugated PPy, PAN, and PEDOT nanotubes and nanowires. We observed the formation of nanotubes and nanowires of PPy, PAN, and PEDOT, as shown in Fig. 1. The length of PPy, PAN, and PEDOT nanotubes and nanowires was controlled up to ∼40 μm as shown in Fig. 1(d). The diameter of the nanotubes and nanowires was ∼100 or 200 nm, depending on the diameter of the nanoporous template used. We observed that polymerization was initiated from the wall-side of the Al_2O_3 nanoporous template. It should be noted that the synthesized nanotubes have an open end at the top, with the filled end at bottom (Au evaporated part) in nanowires. As polymerization time increased, the nanotubes filled and formed nanowires, and length increased.

Fig. 2(a) presents the UV–vis absorbance spectra of HF or NaOH treated PPy-$TBAPF_6$ nanowires. De-doping was carried out by using NaOH solution. For HF treated PPy-$TBAPF_6$ nanowire samples, the bipolaron peak was observed at ∼2.6 eV (∼470 nm) due to doping [23]. For the NaOH treated PPy-$TBAPF_6$ nanowire samples, the π–π^* transition peak was weakly observed at ∼3.0 eV (∼400 nm). These results imply that the PPy-$TBAPF_6$ nanowire samples were transformed into a semiconducting (or insulating) state through the de-doping or the counter-anion exchange with treatment of NaOH as the dissolving solvent. Fig. 2(b) compares the UV–vis absorption spectra for NaOH treated PAN-$HClO_4$ nanotubes and the HCl re-doped PAN-$HClO_4$ ones. We observed π–π^* transition peaks at ∼3.5 eV (∼350 nm) for the NaOH treated PAN-$HClO_4$ nanotubes. For the HCl re-doped PAN-$HClO_4$ nanotube samples, the intensity of the polaron peak at ∼2.7 eV (∼450 nm) increased with increasing the doping level, as shown in Fig. 2(b) [24]. We confirmed polymerization from the measured UV–vis spectra. The optical and electrical properties of the nano-systems varied with different template-dissolving solvents, by alterations in the re-doping process.

3.2. Electrical properties

Fig. 3 shows the photograph of the PPy-$TBAPF_6$ nanowire sample on the 4-probe electrodes, made by photolithography.