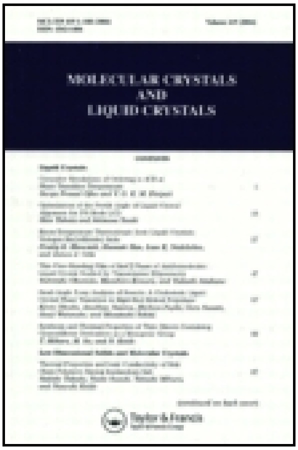

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Electrochemical Polymerization of Polypyrrole Nanotubes and Nanowires in Ionic Liquid

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ELECTROCHEMICAL POLYMERIZATION OF POLYPYRROLE NANOTUBES AND NANOWIRES IN IONIC LIQUID

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Polypyrrole (PPy) nanotubes and nanowires were synthesized through electrochemical polymerization method in nanoporous anodisc aluminum oxide (Al_2O_3) template. The electrolyte consisted of pyrrole monomer, solvent, and ionic liquid dopant such as $BMIMBF_4$(1-butyl-3-methyl imidazolium tetrafluoroborate) or $BMIMPF_6$(1-butyl-3-methyl imidazolium hexafluorophosphate), which is stable in air and moisture. The length and diameter of PPy nanotubes and nanowires were determined by the synthetic conditions such as polymerization time, current, and dopant. The formation of nanotube and nanowire of PPy sample was confirmed by using field emission scanning electron microscope and transmission electron microscope. The UV/Vis and Raman spectra have been investigated for structural properties of the systems. We compare electrical properties of nano size PPy materials with bulky PPy ones prepared in the same chemical conditions.

Keywords: electrochemical polymerization; ionic liquid; nanotube; nanowire; polypyrrole

1. INTRODUCTION

π-Conjugated polypyrrole (PPy) have attracted considerable interest for fundamental and applied researches because of the potential of commercial use [1]. They have relatively high conductivity, light weight, low cost, flexibility, and air stability. The bulk PPy materials had been synthesized through electrochemical or chemical polymerization method [2,3]. The PPy nanotubes and nanowires were synthesized through electrochemical polymerization method by using nanoporous template [4].

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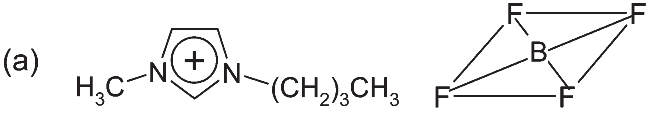
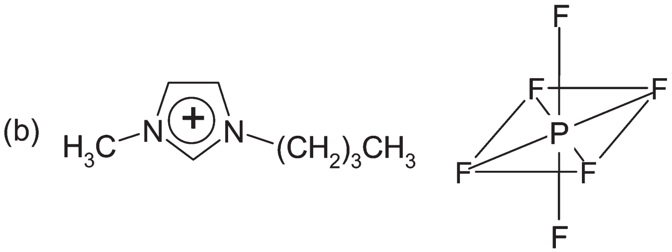
Ionic liquid dopants such as 1-butyl-3-methyl imidazolium tetrafluoroborate ($BMIMBF_4$) and 1-butyl-3-methyl imidazolium hexafluorophosphate ($BMIMPF_6$) are room temperature molten salts and widely recognized as solvents for 'green' organic and polymer synthesis because they exhibit non-flammability and non-volatility [5]. Ionic liquid as electrolyte has advantages such as high-ionic conductivity and wide potential window. Therefore, ionic liquids has been extensively utilized for a variety of electrochemical processes [6]. Furthermore, it was found that $BMIMBF_4$ and $BMIMPF_6$ could be recovered by a simple extraction of the remaining pyrrole monomer from the ionic liquid after use, and then reused without significant loss of reactivity for the polymerization [7]. Figure 1 shows the schematic chemical structure of $BMIMBF_4$ and $BMIMPF_6$ molecules.

In this study, we synthesized PPy nanotubes and nanowires through electrochemical polymerization by using $BMIMBF_4$ and $BMIMPF_6$ ionic liquid as dopant. The diameter of PPy nanomaterials was controlled from ~130 nm to ~230 nm, depending on doping level and applied current. The length of PPy nanomaterials was also controlled from 20 μm to 30 μm through polymerization time. We observed the π–π^* transition peak at ~3.0 eV for the PPy nanonmaterials. The electrical property such as I-V characteristic curve varied with dissolving solutions (HF or NaOH) to remove nanoporous template.



$BMIMBF_4^-$



$BMIMPF_6^-$

FIGURE 1 Schematic chemical structure of $BMIMBF_4$ and $BMIMPF_6$ molecules.

2. EXPERIMENTAL

π-Conjugated PPy nanotubes and nanowires were synthesized through electrochemical polymerization method using Al_2O_3 nanoporous template. Electrolyte consisted of solvent such as acetonitrile and dopant such as $BMIMBF_4$ and $BMIMPF_6$. One side of Al_2O_3 nanoporous template was coated with thermally evaporated Au, and attached on the working electrode of stainless steel by using silicone tape for electrochemical polymerization. We used NaOH or HF solution to remove Al_2O_3 template after polymerization. It is noted that the NaOH solution has the effect of de-doping. The formation of nanotube and nanowire of PPy was confirmed by using field emission scanning electron microscope (SEM, JEOL JSM-5200), transmission electron microscope (TEM, JEOL 1200EX) and Raman scattering (JOBIN YVON T64000) experiments. For structural property of the systems, we measured UV/Vis absorbance spectra (HP 8453).

3. RESULTS AND DISCUSSION

Figures 2(a), (b) and (c) shows TEM and SEM photographs of PPy-$BMIMBF_4$ nanotubes and nanowires. We observed the formation of PPy nanotube as shown in Figures 2(b) and (c). The wall thickness of PPy-$BMIMBF_4$ nanotube was $50 \sim 80$ nm. We synthesized PPy-$BMIMBF_4$ nanotubes and nanowires in various synthetic conditions such as polymerization time, applied current, doping level, and etc. We observed that the length and diameter could be controlled by polymerization time, current, and dopant. For example, the diameter of PPy-$BMIMBF_4$ nanotubes varied from ~130 nm to ~230 nm by applied current and doping level, as shown in Figure 2(d).

Figure 3 presents the UV/Vis absorbance spectra of PPy-$BMIMBF_4$ nanotubes [8]. The re-doping and de-doping of PPy-$BMIMBF_4$ nanotubes had been carried out by using cyclic voltammetry. The oxidation and reduction had been occurred during 10 times or 20 times potential scanning in 0.1 M $BMIMBF_4$ ionic liquid. The π–π^* transition peak was clearly detected at ~3.0 eV for the PPy-$BMIMBF_4$ nanotubes (10 times potential scanning), while that of the nanotubes (20 times potential scanning) was relatively reduced, as shown in Figures 3(a) and (b) [9].

Figure 4 shows Raman spectrum of PPy-$BMIMBF_4$ nanotubes. The nanotubes were treated with 3 M NaOH to remove Al_2O_3 template. The Raman characteristic peaks at 1576 cm^{-1}, 1319 cm^{-1}, and 1044 cm^{-1} correspond to the C=C backbone stretching, the C–C stretching, and the C–H in-plane bending modes, respectively [10]. Based on the results of UV/Vis and

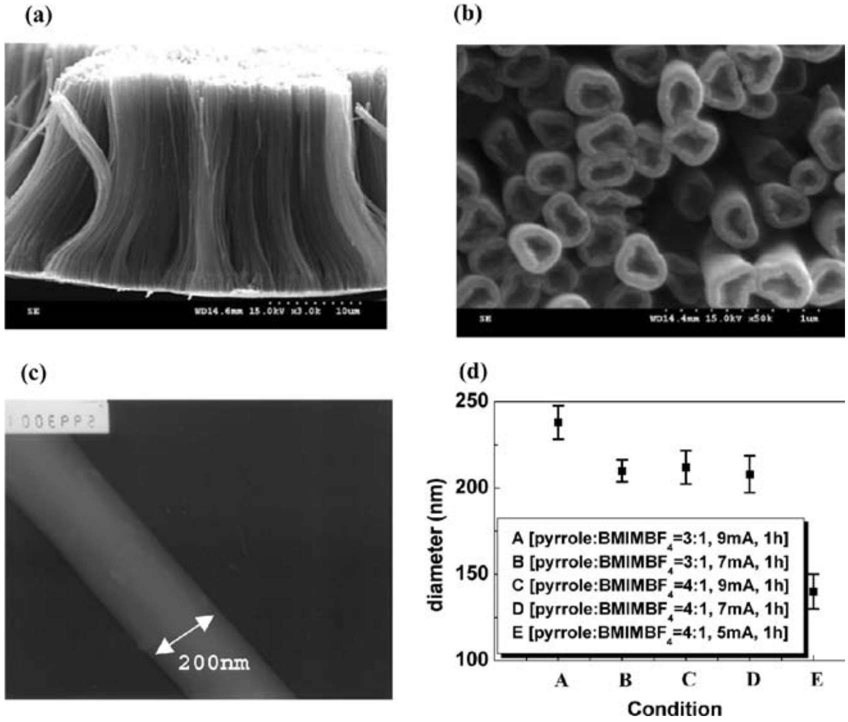
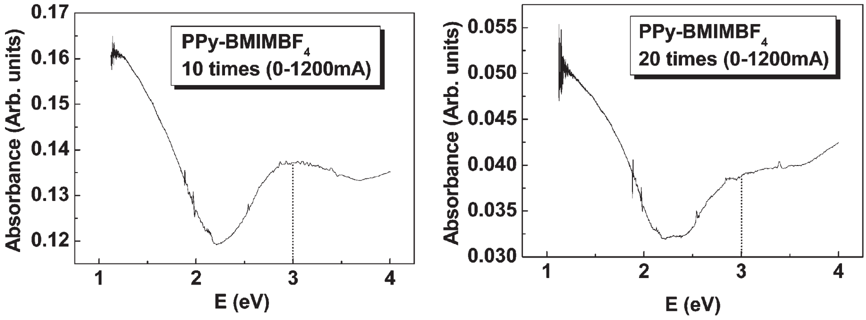


FIGURE 2 (a) Side view and (b) top view of PPy-BMIMBF$_4$ nanotubes obtained from SEM, (c) TEM image of PPy-BMIMBF$_4$ nanotubes, (d) variation of diameter of PPy-BMIMBF$_4$ nanotube depending on various synthetic conditions.



(a) (b)

FIGURE 3 UV/Vis absorbance spectra of PPy-BMIMBF$_4$ nanotube samples; (a) 10 times potential scan and (b) 20 times potential scan.

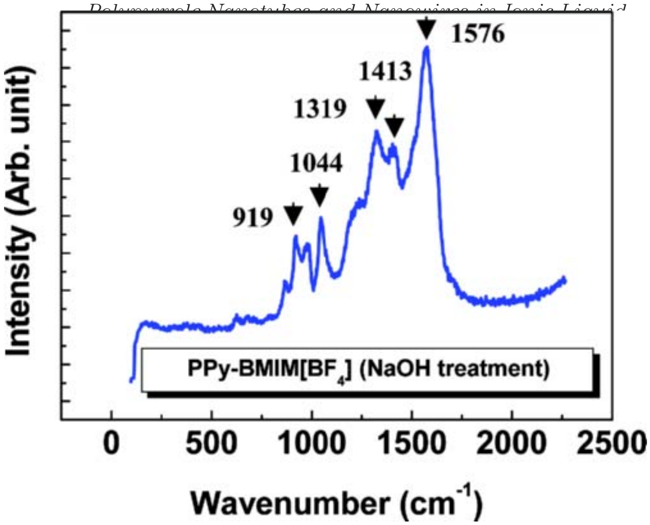
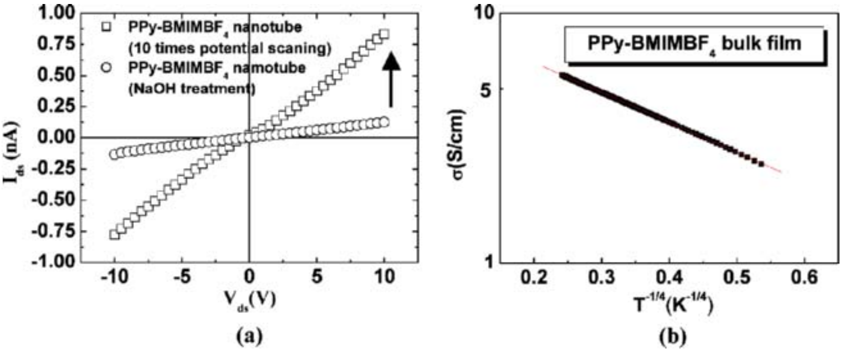


FIGURE 4 Raman spectrum of PPy-BMIMBF$_4$ nanotubes treated with 3 M NaOH solution.

Raman spectra, we confirmed the polymerization of pyrrole with BMIMBF$_4$ dopants.

Figure 5(a) compares the I-V characteristic curves of 10 times potential scanned and NaOH treated one strand of PPy-BMIMBF$_4$ nanotube at room temperature. It is noted that NaOH treated PPy nanotube was de-doped state. The current level of NaOH treated PPy-BMIMBF$_4$ nanotube is much reduced compared to 10 times potential scanned, i.e., re-doped samples.



(a) (b)

FIGURE 5 (a) I-V characteristic curves of 10 times potential scanned and NaOH treated one strand of PPy-BMIMBF$_4$ nanotube, (b) temperature dependent of σ_{dc} of bulk PPy-BMIMBF$_4$ films.

The σ_{dc} of bulk PPy-BMIMBF$_4$ samples prepared in the same synthetic conditions was $\sim 5\,\mathrm{S/cm}$ at room temperature. Temperature dependence σ_{dc} of bulk PPy-BMIMBF$_4$ samples was followed to 3D variable range hopping model as shown in Figure 5(b) [11].

4. CONCLUSION

We synthesized PPy nanotubes and nanowires through electrochemical polymerization method by using Al$_2$O$_3$ nanoporous template and BMIMBF$_4$ or BMIMPF$_6$ ionic liquid. The length and diameter of tube or wire were controlled by polymerization time, applied current, and doping level. From UV/Vis absorbance spectra, we observed the π–π^* transition at $\sim 3.0\,\mathrm{eV}$ for the systems. We confirmed the polymerization of pyrrole from Raman characteristic peaks. Based on the measured I-V curves, the electrical properties varied with dissolving solution to remove nanoporous template.

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