Doped and de-doped polypyrrole nanowires by using a BMIMPF₆ ionic liquid

Hyun Seung Kim, Dong Hyuk Park, Yong Baek Lee, Dae-Chul Kim, Hyun-Jun Kim, Jeongyong Kim, Jinsoo Joo

Abstract
We electrochemically synthesized \( \pi \)-conjugated polypyrrole (PPy) nanowires by using an environmentally stable and recyclable ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), as a dopant, based on an anodic alumina oxide (Al₂O₃) nanoporous template. The de-doped states of the PPy nanowires were obtained from doped PPy nanowires through cyclic voltammetry (CV) using a solution of the catalyst in the BMIMPF₆ ionic liquid. We confirmed the de-doped states of PPy nanowires based on a decrease of the bipolaron peak of the ultraviolet and visible (UV–vis) absorbance spectra. The formation of PPy nanowires was visualized by using scanning electron microscopy and transmission electron microscopy. We studied the optical and structural properties of the doped and de-doped PPy nanowires by UV–vis absorbance and Fourier transform-infrared spectra. Our work included obtaining a laser confocal microscope Raman spectra for a single strand of the PPy nanowires.

Keywords: Polypyrrole; Nanowire; Ionic liquid; Electrochemical polymerization

1. Introduction
\( \pi \)-Conjugated polymer nanomaterials have been extensively studied in several fields of academia and for possible use in industrial applications because of their excellent electrical and optical properties [1,2]. They have been synthesized through electrochemical, chemical, or chemical vapor deposition polymerization methods with or without nanoporous templates [3–6]. Among various synthetic methods of polymer nanomaterials, a template method is relatively simple and effective for fabrication of \( \pi \)-conjugated polymer nanomaterials. Using this method, the shape and dimensions of nanotubes or nanowires can be controlled through synthetic conditions and the diameter of nanopores of the template [7]. However, the control of the doped and de-doped states of the polymer nanosystems has not been thoroughly studied.

\( \pi \)-Conjugated polymer nanomaterials have been applied to biological and chemical sensors, nanotip emitters in field emission displays (FEDs), optoelectronic devices, and electrochromic devices [8–12]. Recent research efforts on \( \pi \)-conjugated polymer nanotubes and nanowires have focused on the electrical or optical properties of the systems as a function of different nanosizes [13–16]. Conducting PPy nanomaterials have received extensive attention because of their environmental stability and potential applications to electrodes, nanotip emitters in FEDs, nanactuators, etc. [17–20]. The control of doping states of PPy nanowires could provide more varied applications to nanodevices.

The synthesis, characteristics, and applications of doped PPy nanotubes and nanowires by using various salt forms of dopants were reported earlier [5,18,19]. In this study, we report on the synthesis and resultant characteristics of doped and de-doped PPy nanowires by using an environmentally stable and recyclable ionic liquid, such as 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), as a dopant [21]. Ionic liquids are a form of molten salt with melting points under 100 °C. These liquids are very stable, highly conductive, and easily recyclable after use, therefore providing many opportunities for green chemistry and commercial applications [22–24]. The de-doped states of the PPy nanowires were electrochemically...
induced from the doped PPy nanowires through cyclic voltammetry (CV) using a solution of the catalyst in the BMIMPf6 ionic liquid. From the ultraviolet and visible (UV–vis) absorbance and Fourier transform-infrared (FT-IR) spectra of the PPy nanowires including the laser confocal microscopy spectra of a single strand of PPy nanowires, we observed variations of the optical and structural characteristics in the doped and de-doped PPy nanowires.

2. Experimental

π-Conjugated PPy nanowires were electrochemically synthesized based on an anodic alumina oxide (Al2O3) nanoporous template with a 200 nm diameter of nanopores at room temperature (RT). The electrolyte for the synthesis consisted of a solvent, a dopant, and a monomer. We purchased the purified pyrrole monomer, which was used without further purification, from Aldrich Inc. A BMIMPf6 ionic liquid was used as a dopant and an acetonitrile (CH3CN) was used as a solvent. The molar ratio of the pyrrole monomer to the BMIMPf6 dopant was 5:1. For the polymerization of the pyrrole, we applied a current density of 1.8 mA/cm2 for 13 min. To remove only the Al2O3 nanoporous template, we used a 2 M HF solution. The remained PPy nanowires were in doped states [18,21]. After then, we performed a de-doping process of the PPy nanowires in an acetonitrile (CH3CN) solution of 0.1 M BMIMPf6 without pyrrole monomers by using CV. The potential range and scan rate for the de-doping process were 0–1.6 V and 25 mV/s, respectively. We observed that a stable reduction process was performed in a solution of the BMIMPf6 ionic liquid. Fig. 1(a) shows the schematic chemical structures of the PPy unit and BMIMPf6.

The formation of PPy nanowires was investigated by using scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, JEM-2000EXII) experiments. The optical and structural properties of doped and de-doped PPy nanowires were investigated by means of UV–vis absorbance (HP 8453) and FT-IR (BOMEN MB-104) spectra. We performed laser confocal microscope (LCM) Raman experiments to study the chemical structure of a single strand of the PPy nanowires. The experimental details for the LCM Raman spectrum were reported earlier [25].

3. Results and discussion

Fig. 1(b) shows a side view of the SEM image of PPy nanowires with a length of ∼25 μm. The PPy nanowires had a uniform and continuous array grown from the Au electrode. We observed that the PPy nanowires had open ends with a diameter of ∼200 nm as shown in the top inset of Fig. 1(b). We noted that the bottom parts (i.e. the Au electrode part) of the Al2O3 nanoporous template were filled with PPy materials in the form of PPy nanowires as shown in the bottom inset of Fig. 1(b).

Fig. 2(a) shows the FT-IR transmittance spectra of the PPy nanowires after the removal of the Al2O3 nanoporous template by using a HF solvent. The peaks at 1442 cm−1 and 1553 cm−1 were the results of the C–N and C–C stretching vibrations, respectively [26]. The peaks at 1035 cm−1 and 1294 cm−1 were assigned to in-plane C–H stretching vibration and in-plane C–H deformation, respectively. The peaks, centered at 962 cm−1 and 1155 cm−1, were assigned to the doping induced peaks. We observed the hydroxyl group peaks at 844 cm−1 and 1085 cm−1. The FT-IR characteristic peaks observed here were almost identical with those of the NaOH-treated PPy nanotubes doped with tetrabutylammonium-hexafluorophosphate (TBAPf6) [19]. These results confirmed the polymerization of pyrrole. Fig. 2(b) compares the FT-IR transmittance spectra of the doped and de-doped PPy nanowires in the wavenumbers in a range from 1400 cm−1 to 1600 cm−1. The ratios of the integrated areas of I1533/I1442 of the FT-IR peaks, centered at 1442 cm−1 and 1533 cm−1, were 1.77 and 2.82 for the doped and de-doped PPy nanowires, respectively. The ratio of the integrated areas I1533/I1442 represents the effective π-conjugation lengths of the PPy nanotubes [13]. The relatively higher area ratio of I1533/I1442 implied the shortening of the π-conjugation length [13]. The results implied that the effective π-conjugation length of the PPy nanowires decreased after the reduction (i.e. de-doping) process.

Fig. 3 compares UV–vis absorbance spectra of the doped and de-doped PPy nanowires. For the doped PPy nanowires, a broad bipolaron peak was observed at ∼462 nm, while the π−π* transition at ∼387 nm disappeared as shown in Fig. 3 [27].
π−π* transition peak of the de-doped PPy nanowires was weakly observed at ∼387 nm [27].

The broad bipolaron peak at ∼462 nm of the doped PPy nanowires considerably decreased after the de-doping process.

Fig. 3. A comparison of UV–vis absorbance spectra of the doped and de-doped PPy nanowires in methanol solution.

Fig. 4. A comparison of laser confocal microscope Raman spectra of a single strand of the doped and de-doped PPy nanowires.

Comparing with the UV–vis absorbance spectrum of the NaOH-treated PPy–TBAPF$_6$ [18], we found that the de-doping process of the PPy nanowires, using the CV in a solution of BMIMPF$_6$ ionic liquid, was more effective. We also observed the relatively higher UV–vis absorbance tail for the doped PPy nanowires above ∼700 nm representing the higher free charge carrier tail.

Fig. 4 compares the LCM Raman spectra of a single strand of the doped and de-doped PPy nanowires. The LCM Raman characteristic peaks at 1580 cm$^{-1}$, 1379 cm$^{-1}$, and 1047 cm$^{-1}$ corresponded to the C=C stretching, the antisymmetrical C–N stretching, and the C–H in plane bending, respectively. The LCM Raman characteristic peaks of the single strand of the PPy nanowires are listed in Table 1 [15]. We confirmed the chemical structure of the PPy material based on the results of the LCM Raman spectra for a single strand of the PPy nanowires. We observed that the LCM Raman intensities of the de-doped PPy single nanowire were relatively enhanced and sharper as a result of the de-doping effect, as shown in Fig. 4. These results

Table 1
Assignments of characteristic peaks of laser confocal microscope Raman spectra for a single strand of doped and de-doped PPy nanowires (NWs)

<table>
<thead>
<tr>
<th>Peak assignments</th>
<th>Raman shift (cm$^{-1}$)</th>
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<tbody>
<tr>
<td></td>
<td>Doped PPy NWs</td>
</tr>
<tr>
<td>Ring deformation associated with bipolaron</td>
<td>916</td>
</tr>
<tr>
<td>Ring deformation associated with polaron</td>
<td>959</td>
</tr>
<tr>
<td>Symmetrical C–H in plane bending associated with polaron</td>
<td>1047</td>
</tr>
<tr>
<td>Symmetrical C–H in plane bending associated with bipolaron</td>
<td>1067</td>
</tr>
<tr>
<td>Antisymmetrical C–H in plane bending</td>
<td>1247</td>
</tr>
<tr>
<td>Antisymmetrical C–N stretching</td>
<td>1379</td>
</tr>
<tr>
<td>C=C stretching</td>
<td>1580</td>
</tr>
</tbody>
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suggest that the de-doping process for the PPy nanowires could be effective when using the CV in the BMIMPF₆ ionic liquid. The de-doping process using the CV in a solution of ionic liquid could be used for other conducting polymer nanomaterials prepared by an electrochemical synthetic method.

4. Summary

We synthesized π-conjugated PPy nanowires through an electrochemical polymerization method by using Al₂O₃ nanoporous templates. The doped and de-doped states of the PPy nanowires were electrochemically controlled through cyclic voltammetry based on a solution of a catalyst in the BMIMPF₆ ionic liquid. The doped and de-doped states of the nanosystems were confirmed by means of UV–vis absorbance, FT-IR spectra, and laser confocal microscope Raman spectra. We observed that the bipolaron peak of the PPy nanowires decreased by means of a de-doping process in the BMIMPF₆ solution, implying a successful reduction process. From the analysis of FT-IR spectra, the effective π-conjugation length of the PPy nanowires could vary with the de-doping process. We observed more clearly Raman characteristic peaks of a single strand of the de-doped PPy nanowires obtained from the laser confocal microscope Raman spectra.

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References