Confocal microscope photoluminescence and electrical characteristics of single poly(3-hexylthiophene) nanowire strand

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The photoluminescence (PL) spectra and images of a single strand of poly(3-hexylthiophene) (P3HT) nanowires with different doping states were compared by means of a laser confocal microscope with a high spatial resolution. The P3HT nanowires were electrochemically synthesized by using an ionic liquid as a dopant. From the ultraviolet and visible absorption spectra, the doping and dedoping effects of the P3HT nanowires through the treatment of organic solvent were investigated. The electrical conductivity of the single strand of the lightly doped P3HT nanowires was estimated to be \( \sim 3.5 \times 10^{-3} \) S/cm, which was higher than that (\( \sim 5.4 \times 10^{-5} \) S/cm) of the dedoped one. From the laser confocal microscope PL experiments, we quantitatively observed more homogeneous and three to eight times brighter light emission from the single strand of the dedoped P3HT nanowires. © 2007 American Institute of Physics. [DOI: 10.1063/1.2824460]

Electrical and optical properties of the \( \pi \)-conjugated polythiophene and its derivatives such as poly(3-hexylthiophene) (P3HT) and poly(3-methylthiophene) have been investigated in the macroscopic scale and have varied with synthetic conditions such as doping level,\(^1\) used dopants,\(^2\) or synthetic temperature\(^3\) as well as the size of the pendant alkyl group.\(^4\) The P3HT has good solubility, allows for easy processing, and has good electroactivity, which contribute to its usefulness for organic based optoelectric devices.\(^5\)–\(^8\)

\( \pi \)-conjugated polymer nanotubes and nanowires can be promising organic nanomaterials for nanotechnology because of easy processing, higher aspect ratio and surface area, and easy control of their chemical and physical properties through synthetic conditions.\(^9\) The structural and electrical characteristics of a single strand of the polymer nanotubes and nanowires have been studied through a scanning electron microscope (SEM), a transmission electron microscope (TEM), and a photo- or e-beam lithography techniques.\(^10\) The nanosize effects of the polymers have been studied in terms of transition of the charge transport mechanism and of variation of morphology.\(^11\) The photoluminescence (PL) for a single strand of the polymer nanowires should be studied in nanometer scale both for fundamental research and applications to nanodevices. In this work, we investigate nanometer scale PL characteristics for the single strand of light emitting P3HT nanowires with different doping states by using a laser confocal microscope (LCM). The LCM PL characteristics and dc conductivity (\( \sigma_{dc} \)) of the single strand of P3HT nanowires varied with doping levels.

The light emitting P3HT nanowires were electrochemically synthesized through an \( \text{Al}_2\text{O}_3 \) nanoporous template with a diameter of nanopores of \( \sim 200 \) nm and thickness of \( \sim 60 \) \( \mu \)m (Whatman International Ltd). The electrolyte consisted of 0.1M 3-hexylthiophene (3HT) monomers, 0.02M 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF\(_6\)) as a dopant,\(^12\) and anhydrous acetonitrile (CH\(_3\)CN) as a solvent.\(^9\) The 3HT monomers and BMIMPF\(_6\) dopants were purchased from Aldrich Inc. and used without further purification. The current density and voltage applied to the electrode for the polymerization were \( \sim 1.4 \) mA/cm\(^2\) and 4.5–5.0 V, respectively. For this study, we applied the bias for 8 min for a desirable synthesis. After polymerization, either 2.0M HF or 2.0M NaOH solvent was used in order to remove the \( \text{Al}_2\text{O}_3 \) template only.

For the SEM and TEM images, we used the JEOL KSM-5200 and 2100 EX systems, respectively. For the ultraviolet and visible (UV/Vis) absorption spectra of P3HT nanowires in chloroform (CH\(_2\)Cl\(_2\)) solution, the HP-8453 system was employed. For the measurement of the current-voltage (\( I-V \)) characteristic curves, the P3HT nanowires homogeneously dispersed in anhydrous ethanol were dropped onto the surface of a photolithography pattern with Au electrodes. We measured the nanometer scale PL images and spectra for the isolated single strand of the P3HT nanowires by using a homemade LCM built around an inverted optical microscope (Axiovert 200, Zeiss GmbH). The incident laser power with excitation wavelength at 488 nm and the acquisition time for each LCM PL spectrum were fixed at 37.5 \( \mu \)W and 1 s, respectively. The detailed method for LCM PL experiments was reported earlier.\(^13\)

A TEM image of the isolated single strand of P3HT nanowires was shown in the inset of Fig. 1. The diameter of the single strand of P3HT nanowires was 150–200 nm. We observed that the P3HT nanowires had open ends at the top parts and were assembled into the form of bundles of P3HT nanowires, as shown in the inset of Fig. 1. Figure 1 compares the normalized UV/Vis absorption spectra of the P3HT nanowire samples treated with HF and NaOH solvents at room temperature (RT). The \( \pi-\pi^* \) transition peaks of the P3HT nanowires treated with HF and NaOH were observed at 404…
and 430 nm, respectively. The $\pi-\pi^*$ transition peak of the HF treated P3HT nanowires was blueshifted by the amount of 26 nm compared with that of the NaOH treated P3HT nanowires. A broad bipolaron peak at 830 nm was observed for the HF treated P3HT nanowires, while that of the NaOH treated P3HT nanowires disappeared due to dedoping effect, shown in Fig. 1. The intensity ratio of the bipolaron peak to the $\pi-\pi^*$ transition peak for the HF treated samples was ~0.02, suggesting the lightly doped states. These observations have originated from the lightly doping or dedoping effect on the P3HT nanowires with the treatment of HF or NaOH solvent, respectively, to remove the $\text{Al}_2\text{O}_3$ template.

The UV/Vis absorption spectra for the P3HT nanowires obtained here were the same as for the bulky P3HT samples reported earlier.

Figure 2 shows the $I-V$ characteristic curves of a single strand of the HF and NaOH treated P3HT nanowires at RT. The top inset of Fig. 2 shows a photograph of the single strand of the P3HT nanowires loading on the two probe Au electrodes. The measured current of the single strand of the HF treated P3HT nanowire linearly increased from ~9.5 to 9.1 nA as the bias increased from ~4.0 to 4.0 V. The current level of the single strand of the NaOH treated P3HT nanowires was ~35 to 40 pA, with an applying bias from ~4.0 to 4.0 V, as shown in the bottom inset of Fig. 2. This current level was ~250 times less than that of the HF treated P3HT single nanowire. Using the slope of the $I-V$ characteristic curves in Fig. 2 and the dimensions (i.e., diameter and length) of the single nanowire strand, the $\sigma_{dc}$ of the single strand of the HF and NaOH treated P3HT nanowires were estimated to be $\sim 3.5 \times 10^{-7}$ and $\sim 5.4 \times 10^{-5}$ S/cm at RT, respectively. It was assumed that there existed contact resistance between the sample and the electrode because of the use of the two probe contact method. The results of the $I-V$ characteristics and $\sigma_{dc}$ support that the HF treated P3HT single nanowire was in relatively higher conducting states than that treated with NaOH solvent. Therefore, we denote the HF and NaOH treated P3HT nanowire samples as the lightly doped and dedoped ones, respectively.

A LCM can be utilized to obtain the quantitative results of a PL spectrum and intensity for an isolated single strand of

![FIG. 1. (Color online) Normalized UV/Vis absorption spectra of the P3HT nanowires treated with HF (■) and NaOH (○) solvents. Inset: A TEM image of the single strand of P3HT nanowire after removing the $\text{Al}_2\text{O}_3$ template by using a HF solvent. Bottom inset: Top view of a SEM image of the P3HT nanowires.](http://apl.aip.org/apl/2007_91_263102_F1.png)

![FIG. 2. $I-V$ characteristic curves of the single strand of the lightly doped, i.e., HF treated (■), and dedoped, i.e., NaOH treated (○), P3HT nanowires. Top inset: Microscope photograph of the single strand of P3HT nanowire, loaded on the Au electrodes. Bottom inset: Magnification of the $I-V$ characteristic curves of the dedoped P3HT single nanowire strand.](http://apl.aip.org/apl/2007_91_263102_F2.png)

![FIG. 3. (Color online) Three-dimensional LCM PL image of (a) the lightly doped, i.e., HF treated P3HT single nanowire strand and (b) the dedoped, i.e., NaOH treated P3HT single nanowire strand. (c) Comparison of LCM PL spectra of the single strand of the lightly doped and dedoped P3HT nanowires.](http://apl.aip.org/apl/2007_91_263102_F3.png)
nanowires or nanotubes. The LCM PL spectrum and image of the single strand of the P3HT nanowires were obtained in the same laser power (37.5 μW). Figures 3(a) and 3(b) show the three-dimensional PL images with a measured voltage of the single strand of lightly doped and dedoped P3HT nanowires, respectively. The measured voltages representing PL intensity for the single strand of the lightly doped and dedoped P3HT nanowires were 0.3–0.4 and 1.2–2.3 V, respectively. These voltages implied that the LCM PL intensity of the dedoped single P3HT nanowire strand was three to eight times higher than that of the lightly doped P3HT ones. For the lightly doped P3HT nanowire, we observed the relatively large fluctuation of the LCM PL intensity at different voltages. The sharp peaks in the PL spectra at 526 and 570 nm were originated from the Raman modes. The integrated area of LCM PL spectrum of the dedoped P3HT nanowire was approximately six times larger than that of the lightly doped P3HT ones. For the lightly doped P3HT nanowire, which might originate from the doping effect by the use of NaOH solvent. For the lightly doped P3HT nanowire, we observed the relatively large fluctuation of the LCM PL intensity at different positions, as shown in Fig. 3(a). Figure 3(c) compares the LCM PL spectra of the single strand of lightly doped and dedoped P3HT nanowires. The LCM PL spectra of the single strand of the nanowires were measured in at least seven different positions on the same isolated nanowire sample and then averaged to obtain the final LCM PL spectra. The main PL peaks of the single strand of the lightly doped and dedoped P3HT nanowires were observed at 551 nm (green light emission) and 593 nm (yellow–green light emission), respectively. The sharp peaks in the PL spectra at 526 and 570 nm were originated from the Raman modes. The integrated area of LCM PL spectrum of the dedoped P3HT nanowire was approximately six times larger than that of the lightly doped P3HT nanowire, which might originate from the dedoping effect by the use of NaOH solvent. For the lightly doped P3HT single nanowire, the PL quenching due to the dopants or PF₆ counterions might exist.

In summary, the light emitting P3HT nanowires were electrochemically synthesized by using BMIMPF₆ ionic liquid as a dopant, based on an Al₂O₃ template. From the UV/Vis absorption spectra, we observed the lightly doped and dedoped states of the P3HT nanowires through the treatment of HF and NaOH solvents, respectively. Based on the I-V characteristic curves, the HF treated P3HT single nanowire was in higher conducting states than that treated with NaOH solvent. We observed that the nanometer scale LCM PL intensity and spectrum of the single strand of P3HT nanowires varied with the doping state. Compared with the lightly doped P3HT single nanowire, the PL intensity of the single strand of the dedoped P3HT nanowires was more homogeneous and three to eight times higher in nanometer scale, which were confirmed through the quantitative comparison of LCM PL spectra.

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