Tuning optical properties of poly(3-hexylthiophene) nanoparticles through hydrothermal processing

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Abstract
Poly(3-hexylthiophene) (P3HT) nanoparticles (NPs) were prepared by a reprecipitation method. Hydrothermal processing applied external pressure to the pristine P3HT NPs at temperatures ranging from 60 to 150 °C. Optical absorption and photoluminescence (PL) spectra for the hydrothermally treated P3HT NPs varied markedly with the processing temperature. With increasing treatment temperature, the absorption peak broadened and the peak position shifted from 510 to 623 nm; moreover, the intensity ratio of the 0–1 to 0–0 emission varied. These changes were caused by interactions between the P3HT main chains and alkyl side groups and conformational modifications induced by the high pressure during the hydrothermal process. The evolution of the optical absorption spectra of the P3HT NPs during the hydrothermal processing was strongly correlated with the variation of PL excitation spectra and with the PL emission spectra of a single NP.

Keywords: poly(3-hexylthiophene), nanoparticles, optical absorption, photoluminescence, hydrothermal process, interchain interaction

1. Introduction
Poly(3-hexylthiophene) (P3HT) materials have been intensively studied for applications in organic optoelectronics because of their high solubility in organic solvents and controllable crystallinity. Considerable effort has been made to improve the intrinsic characteristics of p-type P3HT materials to enable their use in organic field-effect transistors and organic photovoltaic cells (OPVCs) [1–3]. When P3HT was used as the donor material in bulk heterojunction (BHJ) OPVCs, the power conversion efficiency ($\eta$) was about 5% owing to nanoscale phase separation induced by annealing [4]. To increase $\eta$ in BHJ-OPVCs, it is important to clarify the mechanism of exciton generation and dissociation at the interface of p-type P3HT and n-type organic materials [5]. In addition to increase $\eta$, it is necessary that the organic active layers in OPVCs have optical characteristics that allow the efficient absorption of solar energy. Many researchers have reported tandem [6] and hybrid [7] structures with increased absorption efficiency of solar light in a wide spectral range.

The optical characteristics of inorganic and organic nanostructures such as the absorption and photoluminescence (PL) efficiency can be controlled by their size, shape, and crystallinity on the basis of energy bandgap tuning [8]. Various synthetic methods [9], post-treatment [10] and hybridization with hetero-nanomaterials [11] have been studied as means of tuning the optical properties of nanostructures. Hydrothermal processing has been used to synthesize metal oxides such as TiO$_x$ [12] and ZnO$_x$ [13] and to modify the material properties. Zhou et al [14] reported that hydrothermal treatment converted graphene oxide to a stable graphene solution. Jung et al [15] induced the structural transformation of organic copper phthalocyanine nanowires to hollow rectangular nanotubes using hydrothermal processing. Such treatment is promising for tuning the optical characteristics of organic...
semiconducting nanoparticles (NPs) and nanowires for application in OPVs.

In this study, P3HT NPs were fabricated in an aqueous suspension using a recrystallization method [16]. To modify the optical properties, the P3HT NPs were hydrothermally treated in an aqueous suspension, i.e., pressurized in a chamber at various temperatures. The ultraviolet and visible (UV/Vis) absorption spectra changed markedly upon treatment, with the intensity and width of the features depending on the temperature of hydrothermal treatment. These observations agreed with the results for PL in solution, PL excitation (PLE) spectra, and PL from single P3HT NPs measured with a laser confocal microscope. Analysis suggests that the hydrothermal treatment induced conformational modifications and altered the interactions between the P3HT main chains and alkyl side groups, which changed the optical properties of the P3HT NPs.

2. Experimental details

2.1. Fabrication of P3HT NPs

The P3HT NPs were fabricated by a recrystallization method [16]. Regioregular P3HT powder (regioregularity: 90–93%, Mw = 50 k, Sigma-Aldrich Corp) was used without further purification. Twenty milligrams of powder was dissolved in 20 ml of tetrahydrofuran, then 1 ml of the solution was added dropwise to 20 ml of deionized water and stirred vigorously for 10 min. Nanoparticles were formed in the aqueous suspension because of the hydrophobic property of P3HT. Large aggregates were filtered out with a membrane filter (pore diameter 800 nm).

2.2. Hydrothermal process

An autoclave (Parr Instrument Acid Digestion Bombs; 4744 general-purpose bomb) served as the chamber for the hydrothermal process. Pristine P3HT NPs dispersed in deionized water (21 ml) were placed in the Teflon beaker (45 ml) of the chamber, which was heated in an oven to a temperature between 60 and 150 °C for 10 h. This procedure applied external pressure to the P3HT NPs, which we roughly estimated as 15 bar at 100 °C using the data of [17]. Then, the chamber was naturally cooled for 5 h. A homogenous dispersion of nanoparticles was obtained by sonicating the P3HT NP solution for 60 s with a high-power ultrasonicator (Ulsso Hitech Co, ULH 700 s).

2.3. Characterization

The NP surface morphology and size distribution were characterized by scanning electron microscopy (SEM, JEOL-4300) and transmission electron microscopy (TEM, Tecnai 20). UV/Vis and Fourier transform infrared (FTIR) absorption spectra were recorded using Agilent 8453 and Nicolet 380 spectrometers, respectively, and a Hitachi F-7000 instrument was used for PL and PL excitation (PLE) measurements. PL spectra from a single P3HT NP were acquired using a laser confocal microscope (LCM, NanoFocus Inc., Albatross SPM).

3. Results and discussion

Figure 1 and its insets show SEM and TEM images, respectively, of the pristine P3HT NPs and P3HT NPs hydrothermally treated at various temperatures. The labels of the treated samples, HT060, HT090, HT110, HT120, HT130 and HT150, indicate the temperature of the treatment in °C. The diameters of the pristine and HT060 P3HT NPs shown in figures 1(a) and (b) were 77 ± 11 and 88 ± 11 nm, respectively. The shape and degree of aggregation for P3HT NPs treated at temperatures of 110 °C and above were clearly different from those of the pristine and HT060 NPs. Aggregation occurred at elevated temperatures, and the NP diameters in the HT110 and HT150 samples shown in figures 1(c) and (d) were 184 ± 50 and 471 ± 107 nm, respectively.

Figure 2(a) shows the normalized UV/Vis absorption spectra of the pristine and hydrothermally treated P3HT NPs. Absorption peaks are observed at 510, 550 and 610 nm for the pristine P3HT NPs, which coincide with those of spin-coated P3HT films [18]. The energy difference between the absorption peaks at 510 and 550 nm originates from the coupling of the π–π* transition with one C=C stretching phonon [19]. The peak at ~610 nm is associated with an interchain interaction according to the results of a simulation of the absorption and PL spectra [20]. The UV/Vis absorption spectra changed markedly with increasing hydrothermal temperature, as shown in figure 2(a): the peaks shifted to longer wavelengths and their relative intensities changed. The absorption peak at ~510 nm was dominant for pristine, HT060 and HT090 samples. With increasing temperature, the absorption intensity at ~550 nm gradually increased for the HT110, HT120 and HT130 samples, and the 610 nm peak, which corresponds to the 0–0 transition, is the strongest for the HT150 P3HT NPs. A long-wavelength tail also progressively developed with increasing hydrothermal temperature.

To explain the evolution of the UV/Vis absorption spectra, the conformational modification of polymer chains during the hydrothermal processing should be considered. A blue shift in the absorption peaks upon annealing P3HT NPs and films was reported in [16, 21, 22], which was associated with the decrease in the π-conjugation length in the polymer chain, and changes in the peak intensities with annealing were noted in [23, 24]. In contrast, a redshift was observed in this study. When the thiophene rings of P3HT main chains assume a more planar structure, the absorption spectra of the corresponding polymers are redshifted [25]. Therefore, we assign the observed redshift to the planarization of the thiophene rings in polymer chains induced by the external pressure applied during the hydrothermal processing. Hess et al [26] reported the suppression of the blue shift in P3HT films annealed under pressure. The variation of the relative peak intensities in figure 2(a) can be explained in terms of the interchain interaction and aggregation. Clark et al [27] suggested that vibronic bands in the excited states of polythiophene materials can form owing to the interchain interaction during the aggregation, and that the intensity ratio of 0–0 absorption
Figure 1. SEM images of (a) pristine, (b) HT060, (c) HT110 and (d) HT150 P3HT NPs. Insets show TEM images of the corresponding samples.

(∼610 nm) to 0–1 absorption (∼550 nm) reflects the strength of the interchain interaction in the weak excitonic coupling regime. As shown in figure 2(b), the intensity ratio of 0–0 to 0–1 absorption increases with the hydrothermal temperature, indicating the enhancement of the interchain interaction. The intensity ratio of the 0–0 to 0–2 absorption increases and that of the 0–2 to 0–1 absorption decreases with increasing temperature. The latter ratio is related to the Huang–Ray factor, which represents the coupling between the electronic transition and the phonon mode according to the Franck–Condon model [27]. The magnitude of the Huang–Ray factor multiplied by the phonon energy is the average relaxation energy from the upper vibronic state to the lowest vibronic state within an excited electronic state. With increasing hydrothermal temperature, the Huang–Ray factor and relaxation energy decreased, implying the planarization of thiophene rings, as also reflected by the redshift of the absorption peaks. From the analysis of the UV/Vis absorption spectra, we suggest that with increasing hydrothermal temperature, the interchain interaction and the ring planarity in P3HT main chains strengthened owing to the pressure applied during the hydrothermal process.

Figure 3(a) shows the normalized PL spectra of the pristine and hydrothermally treated P3HT NPs in solution. The main PL peak originating from the 0–0 transition appears at about 650 nm together with a shoulder at 710 nm due to the 0–1 transition; this agrees with the spectra of solid-state bulk PL of the P3HT material [20]. The 0–0 (650 nm) and 0–1 (710 nm) peaks originate from the excitonic and aggregated emissions, which result from the crystalline P3HT with interdigitated alkyl side chains and the crystalline P3HT with tilted alkyl side chains, respectively [28]. The hydrothermal processing induced a slight redshift of the PL peaks of the 0–0 and 0–1 emissions for the P3HT NPs from 650 to 653 nm and from 710 to 712 nm, respectively. With increasing process temperature, the PL shoulders at about 710 and 810 nm became more prominent, as shown in figure 3(a), indicating that the external pressure increased the crystallinity of the P3HT NPs with tilted side chains. The relative PL intensity ratio of the 0–1 emission to the 0–0 emission was greatest for the HT110 sample, as shown in the inset of figure 3(a), and the shoulders at 615 and 810 nm also strengthened in the HT110 and HT120 samples.

Figure 3(b) shows the LCM PL spectra for the pristine and hydrothermally treated single P3HT NPs. The spectra were averaged over 20 different dry NPs. The main 0–0 emission peak at 650 nm is similar to that in the spectra of the NP solution. However, the intensity and position of the 0–1 emission peak at 692–708 nm were different for the individual NPs and varied significantly with the hydrothermal temperature. Its dominance increased for the HT060 and HT110 samples, in qualitative agreement with the changes in the UV/Vis absorption spectra. The 0–1 to 0–0 PL intensity ratio was maximum for the HT110 sample, which is consistent with the PL spectra in solution. Similar
results for the MEH-PPV film were reported in [29]. The external pressure in the hydrothermal processing increased the interchain interaction, increasing the degree of tilt of the alkyl side chains and the planarity of thiophene rings, and decreasing the distance of interchain $\pi$-stacking. The solution and LCM PL spectra suggest that the interchain interaction increased (i.e. the interchain distance decreased) as the hydrothermal temperature was increased from 60 to 110 °C; however, severe conformational changes in the P3HT chains may have occurred during the hydrothermal processing at temperatures of 130 °C and above, decreasing the 0–1 emission for the HT150 sample.

Figure 4 and its inset show the normalized excitation spectra for the 653 and 715 nm emissions, respectively. The three PLE peaks at 500, 540 and 600 nm are closely related to the UV/Vis absorption peaks, and the increase in the relative PLE intensity at 600 and 640 nm is similar to that in the UV/Vis absorption spectra (in figure 2(a)). The PLE intensity at 540 nm increased as the hydrothermal temperature was raised from 60 to 120 °C, while it decreased at 130 °C and above as shown in figure 4. The PLE results are qualitatively consistent with the solution and LCM PL spectra.

Figure 5 shows a comparison of the FTIR absorption spectra of the bulk P3HT materials and the pristine and hydrothermally treated P3HT NPs. Characteristic peaks of the bulk P3HT material were observed at 722, 823, 1057,
Table 1. Assignment of the FTIR absorption peaks in the bulk P3HT and P3HT NPs.

| Peak position (cm⁻¹) | Assignment                        | References                      |
|---------------------|-----------------------------------|---------------------------------|
| 667                 | Ring deformation                  | Abdou and Holdcroft [30]        |
| 722                 | Methyl rock mode of hexyl group   | Abdou and Holdcroft, Louarn et al [30, 31] |
| 823                 | C=H bending                       | Abdou and Holdcroft, Louarn et al [30, 31] |
| 1057                | C≡S-O stretching                 | Abdou and Holdcroft, Louarn et al [30, 31] |
| 1377                | Methyl deformation                | Abdou and Holdcroft, Louarn et al [30, 31] |
| 1460                | Symmetric ring stretching mode    | Abdou and Holdcroft, Louarn et al [30, 31] |
| 1510, 1560          | Asymmetric ring stretching mode   | Abdou and Holdcroft, Louarn et al [30, 31] |
| 1633                | C≡C stretching mode               | Abdou and Holdcroft, Louarn et al [30, 31] |
| 1712                | C≡O stretching mode               | Abdou and Holdcroft, Louarn et al [30, 31] |

1377, 1460, 1510, 1560 and 1633 cm⁻¹ [30, 31], which were also present in the pristine and hydrothermally treated P3HT NPs. The peak assignment is summarized in table 1. The FTIR spectra suggest that the polymeric structure of the P3HT NPs was retained after the hydrothermal processing. For the HT110 and HT150 samples, the 667 cm⁻¹ peak related to ring deformation [31] was slightly enhanced and sharpened. For the HT150 sample, the intensity and full width at half maximum of the 1560 cm⁻¹ peak related to the antisymmetric ring stretching mode increased compared with those of the symmetric ring stretching mode at 1460 cm⁻¹. The FTIR spectra suggest that hydrothermal processing at temperatures of 110°C and above deformed the thiophene rings of the polymer chains, making them more antisymmetric.

4. Conclusion

P3HT NPs prepared by a reprecipitation method were hydrothermally processed at various temperatures. The variations in the optical absorption spectra, such as redshift and broadening of the peaks, depended on the treatment temperature. The intensity ratio of the 0–1 to 0–0 emission also varied with the hydrothermal temperature, as revealed by PL, PLE, and LCM PL spectra. These changes are associated with enhanced interchain interaction and ring deformation induced by the high pressure applied during the hydrothermal processing. Therefore, hydrothermal processing is a promising post-treatment for tuning the optical properties of π-conjugated polymeric NPs.

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