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Improved electrical and optical properties of Poly(3,4-ethylenedioxythiophene) via ordered microstructure

Wei Feng^{1,3}, Yu Li¹, Jun Wu¹, Hideki Noda², Akihiko Fujii²,
Masanori Ozaki² and Katsumi Yoshino²

¹ School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

² Department of Electrical Engineering and Information System, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565-0871, Japan

E-mail: weifeng@tju.edu.cn

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Abstract

Poly(3,4-ethylenedioxythiophene) (PEDOT) nanorods (80–150 nm in diameter) and nanospheres were synthesized through a self-assembly method using ferric chloride (FeCl₃) and ammonium persulfate (APS) as oxidants, respectively, and camphorsulfonic acid (CSA) as the dopant. The PEDOT nanorods showed broader absorption bands, higher crystallinity and much higher room-temperature conductivity (approximately 300 S cm⁻¹) than the PEDOT nanospheres. Such obviously distinct properties of these products were considered to be due to the much lower rate of polymerization with FeCl₃ than APS, which made the growth of PEDOT according to the suggested cylinder micelles more moderate and regular; as a result, the morphology of the microstructure changed and the crystallinity, the doping level, the molecular orderliness and the conductivity of PEDOT synthesized under lower rate of polymerization improved intensely at the same time.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Conducting polymers have received considerable attention because of their excellent electronic properties, wide range of conductivity, the fact that they retain their light weight, their mechanical properties, and processing advantages [1]. Poly(3,4-ethylenedioxythiophene) (PEDOT), in addition to its outstanding stability, high electrical conductivity and low redox potential, is unique among the family of conducting polymers in that its small band gap

³ Author to whom any correspondence should be addressed.

confers high optical transparency in the doped state [2–5]. For these reasons, nowadays, it has been widely studied for many potential applications such as modified electrodes, solar cells, electroluminescent devices and sensors [6–9].

One-dimensional (1D) structures such as tubes and rods have attracted much attention recently because of their unique optical, electrical and mechanical properties, which suggest they may have promising applications in electrical and optoelectronic nanodevices [10–12]. The most common way to obtain 1D conducting polymers is template-guide electropolymerization [13–15]. Nowadays, utilizing structured molecules such as surfactants [16] or electrolytes [17] into the chemical polymerization bath to obtain specific morphology of conducting polymers has become another facile way. Some organic dopants, such as camphorsulfonic acid (CSA), β -naphthalene sulfonic acid, and *p*-toluene sulfonic acid, have also been found to be able to form specific emulsions or micelles leading to 1D structures through the self-assembly process [18]. This method is very convenient despite the fact that the size of the product cannot be controlled specifically at this moment.

Recently, 1D PEDOT has been synthesized through electrochemical polymerization in the pores of an aluminium oxide template [14], a hexane/water reverse microemulsion system using sodium bis(2-ethylhexyl) sulfosuccinate cylindrical micells as the template and ferric chloride (FeCl_3) as the oxidant [19, 20], and a microemulsion system using sodium dodecyl sulfate as surfactant and FeCl_3 as oxidant [21]. However, as far as we know, there have been few reports comparing the optical and electrical properties of 1D PEDOT with the traditional grain PEDOT. Therefore, we adopted CSA as the functional dopant in order to synthesize 1D PEDOT. FeCl_3 and ammonium persulfate (APS) were adopted as oxidants. Eventually, 4–10 μm long PEDOT nanorods with diameters in the 80–150 nm range assembling together as large particles were obtained by using FeCl_3 , while traditional PEDOT nanospheres were obtained using APS. Surprisingly, these different structured PEDOT exhibited extremely distinct properties. The different optical and electrical phenomena of these products were characterized and the reasons for them discussed in this study.

2. Experimental details

3,4-ethylenedioxythiophene (EDOT) was purchased from Bayer AG. CSA was obtained from Sigma-Aldrich Company Ltd. The oxidants APS and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from Tianjin Chemical Company. All of the above reagents were of analytical grade and were used as received without further treatment.

5.6 g of CSA was dissolved in de-ionized water and then 0.3 ml of EDOT monomer was added into the solution under gentle magnetic stirring in an ice bath (0–5 °C). The mixture was kept in the ice bath for at least 30 min to ensure that the temperature at the beginning of polymerization was between 0 and 5 °C. Then 5 ml 0.47 M oxidant aqueous solution was added to the solution to start the polymerization. The reaction time was 72 and 24 h with FeCl_3 and APS as oxidants, respectively. The synthesized PEDOT precipitate was obtained through centrifugation and then washed with de-ionized water several times to remove the redundant dopant and oxidant. Finally, the dark-blue product was obtained after being dried in vacuum at 60 °C for 24 h.

The morphology of the resulting PEDOT was measured with a Hitachi S-5000 field scanning electron microscope (SEM) and a Hitachi H-8100T transmission electron microscope (TEM). The samples for the SEM measurements were mounted on aluminium studs using adhesive graphite tape before analysis, while for the TEM measurements the samples were dispersed on reticular copper coated with a carbon support film. Fourier transform infrared (FTIR) spectra in the range of 650–3500 cm^{-1} on PEDOT sample pellets made with KBr

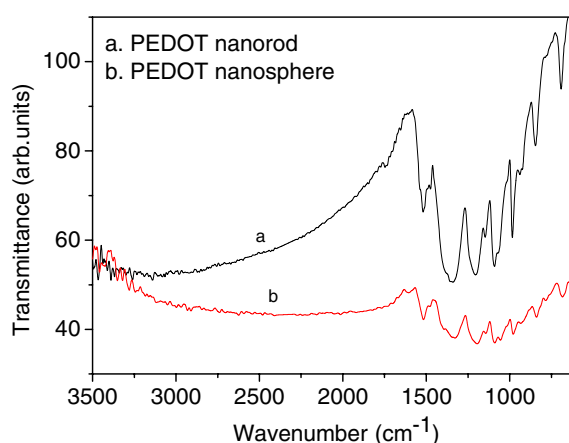


Figure 1. Infrared spectra of the PEDOT nanorods (a) and nanospheres (b).

were measured by means of an infrared spectrophotometer (JASCO corporation, FT/IR-300E). The ultraviolet–visible–near-infrared (UV–vis–NIR) spectra of PEDOT dissolved in dimethyl sulfoxide (DSMO) were recorded from 300 to 1500 nm on the Hitachi UV300 UV–visible spectrophotometer. The fluorescence spectra were obtained on a Hitachi F-4500 spectrometer. A small number of samples were dissolved in 5 ml DSMO solution and the excitation wavelength was selected at 430 nm. The x-ray scattering of the products was carried out on an RINT x-ray diffraction instrument with Cu $K\alpha$ radiation. X-ray diffraction (XRD) measurements using Cu $K\alpha$ radiation were performed with a powder x-ray diffractometer (RINT 1100, Rigaku). The room-temperature conductivity of compressed PEDOT pellets was measured by the four-probe method using a programmable DC voltage/current generator (Advantest R6144 and Keithley 2000). The temperature dependence of conductivity at 140–300 K was measured by a four-probe method using a Keithley 2000 programmable current source and 181 nanovoltmeter.

3. Results and discussion

3.1. FTIR spectra measurement

The same amount by weight of resultant PEDOT synthesized using FeCl_3 or APS respectively was used for FTIR measurement. Typical FTIR spectra are shown in figure 1; they are in good agreement with the previously reported results [19, 22]. The vibrations at 1310 and 1515 cm^{-1} are due to the C–C or C=C stretching of the quinoidal structure of thiophene ring and the ring stretching of thiophene ring, respectively. The peaks originating from the stretching in the alkylendioxy group are observed at 1210, 1173 and 1089 cm^{-1} . The peaks assigned to C–S bond stretching in the thiophene ring are also observed at 987, 815 and 682 cm^{-1} . The weak peak at 1043 cm^{-1} is attributed to the absorption of the $-\text{SO}_3\text{H}$ group which proves that the resulting PEDOT is in the doped state [23]. The presence of the peak at 1680 cm^{-1} in the case of being oxidized by APS indicates the existence of an overoxidized carbonyl group due to the powerful oxidant APS [22]. However, the larger absorption intensity of rod-like PEDOT than sphere-like PEDOT may be brought about by its more regular conjugated structure that facilitates the coupling of electrons and consequently enhances the value of molecular polarization.

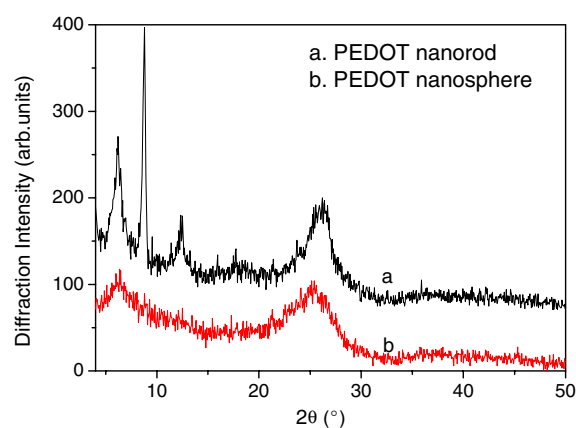


Figure 2. X-ray scattering pattern of PEDOT (a) nanorods and (b) nanospheres.

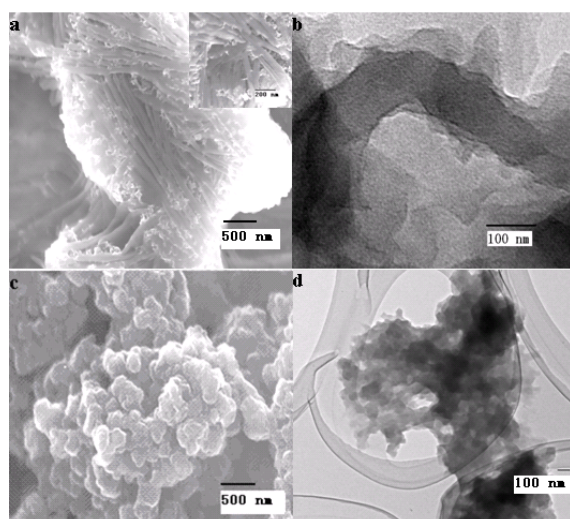


Figure 3. SEM images of the PEDOT nanorods (a) and nanospheres (c) and the TEM images of PEDOT nanorods (b) and nanospheres (d); the inset picture in (a) is the SEM image of PEDOT nanorods under high magnification.

3.2. XRD measurement

Figure 2 shows the XRD patterns of resultant PEDOT oxidized by FeCl_3 and APS respectively. Three broad peaks centred at $2\theta = 6.5^\circ$ (corresponding to the (100) reflection), $2\theta = 12.8^\circ$ (corresponding to the (200) reflection) and $2\theta = 26.8^\circ$ (corresponding to the (020) reflection) and an intense sharp peak at $2\theta = 8.9^\circ$ (corresponding to the (001) reflection) are observed in the PEDOT oxidized by FeCl_3 while just two broad peaks centred at $2\theta = 6.5^\circ$ and $2\theta = 25^\circ$ are observed in the PEDOT oxidized by APS. The reduction in intensity of the peak at 6.5° and the peak at 25° shifting to a lower angle reveal the decrease of the doping level [22]. The novel sharp peak at $2\theta = 8.9^\circ$ is assigned to the repeat unit of the polymer chains [24] which may indicate the improvement of the polymer chain ordering. The more intensive and narrow peaks of PEDOT oxidized by FeCl_3 compared to those oxidized by APS illustrate the enhanced crystallinity under lower rate of polymerization; this phenomenon has also been reported in the polyaniline system [25].

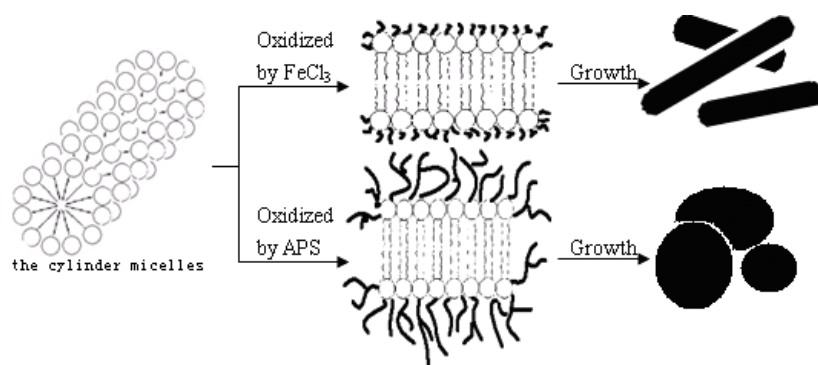


Figure 4. A schematic illustration of the formation of PEDOT nanorods and nanospheres using FeCl_3 and APS respectively. At first, cylinder micelles composed of ACS (hollow circle) and EDOT (straight line) form; after adding different oxidant, the PEDOT grows under different rates of polymerization and finally obtains different morphology.

3.3. Microstructure measurement

The typical micromorphology of the resultant PEDOT is shown in figure 3. From the SEM images shown in figure 3(a), we can see that PEDOT oxidized by FeCl_3 is in a 1D shape with diameters ranging from 80 to 150 nm; these nanorods stack together forming large particles. The TEM image shown in figure 3(b) illustrates that the structure is rod-like. PEDOT oxidized by APS is in traditional sphere-like shapes, with diameters ranging from 100 to 200 nm; these agglomerated with smaller grains with diameters ranging from 60 to 80 nm, as seen in the SEM and TEM images shown in figures 3(c) and (d) respectively. Considering the outstanding hydrophobic property of EDOT (only 2.1 g l^{-1} is soluble in water), sufficient CSA was dissolved in de-ionized water in order to ensure the suggested micelles in other conducting polymers [18], which are composed of doped acid CSA and EDOT and act as a soft templates for the formation of the rod-like structures, can form in the reaction. When the oxidant is FeCl_3 , the growth of PEDOT is tempered and tends to accord with these micelles because of the weak oxidation/reduction potential, and finally rod-like PEDOT is synthesized; when the oxidant is APS, however, the growth of PEDOT is very aggressive and does not accord with the micelles well because of the powerful oxidant competence of APS, and finally aggregated sphere-like PEDOT is synthesized. The suggested mechanisms are shown in figure 4.

3.4. UV-vis-NIR spectra measurement

Figure 5 shows the UV-vis-NIR spectra of PEDOT oxidized by FeCl_3 and APS respectively. The spectrum of dark-blue PEDOT oxidized by FeCl_3 exhibits a broad absorption region starting near 500 nm and having a peak at 910 nm corresponding to the polaron state carriers [26], and is very similar to that of the previously reported fully doped PEDOT [27]. The spectrum of PEDOT oxidized by APS exhibits a peak at 496 nm corresponding to the $\pi-\pi^*$ electronic transition and the peaks at 710 and 750 nm and a shoulder at 893 nm are attributed to the polaron state carriers. A band gap of 1.63 eV can be estimated from the red-edge of this band ($\sim 760 \text{ nm}$). In the region of the polaron carrier, there are several subgaps, and the transition of these subgaps merges to a single one as the doping level increases [27]. Comparing the patterns of the spectra, it can be seen that the doping level of PEDOT oxidized by APS is lower than that of PEDOT oxidized by FeCl_3 , which is in good agreement of the analysis by

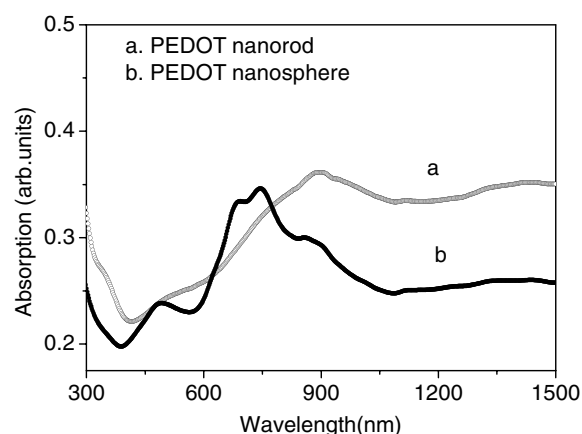


Figure 5. UV-vis-NIR absorption spectra of the PEDOT nanorods (a) and nanospheres (b).

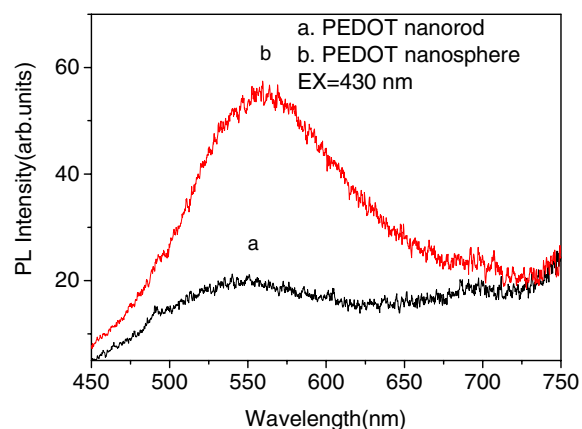


Figure 6. The photoluminescence spectra of the PEDOT nanorods (a) and nanospheres (b).

XRD. Some monomers, not attracted by CSA, are able to participate in the polymerization under rapid rate of reaction. As a result, more ACS is doped in the PEDOT oxidized by FeCl_3 than APS, especially in the aqueous circumstance where EDOT is almost insoluble. Figure 6 shows the photoluminescence (PL) spectra of the different nanostructures of the PEDOT products. These spectra confirm our hypothesis further. When the PEDOT nanospheres were excited by a laser source (430 nm), the emission spectrum showed a strong wide peak centred at 561 nm, while the emission spectrum of PEDOT nanorods excited by the same source displayed a very weakened peak at 535 nm. The quenching of the luminescence intensity is mainly assigned to the higher doping level in PEDOT nanorods because the fluorescence in the conducting polymer is consequently quenched by the doping level increase [28]. These results demonstrate that decreasing the speed of reaction is a facile way to enhance the doping level. The small blue-shift of PEDOT nanorods can be explained by the increase of the conjugated level, because the conjugated level increases with the enhancement of doping level in conducting polymer systems. Moreover, the special 1D transport property in PEDOT nanorods facilitating the movement of electrons, and holes and defects such as the surface states of the samples contribute to the quenching of luminescence in PEDOT nanorods as well.

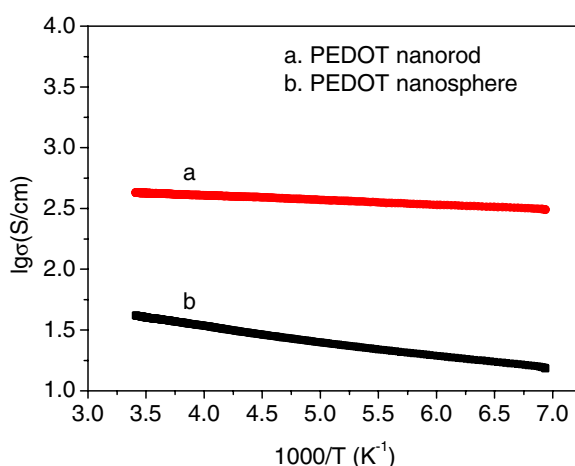


Figure 7. Four-probe measurements of the temperature dependence of the conductivity for PEDOT (a) nanorods doped with CSA using FeCl_3 as an oxidant and (b) nanospheres doped with CSA using APS as an oxidant; these reported values are an average of three measurements.

3.5. Conductivity measurement

Conductivities of the resultant rod-like and sphere-like PEDOT were measured by the four-probe method. The value of room-temperature conductivity of PEDOT oxidized by FeCl_3 is calculated to be about 300 S cm^{-1} , which is excellent and much higher than that of other previous reports [19, 20, 22, 29, 30] by almost one order of magnitude. The value for PEDOT oxidized by APS, however, is just 35 S cm^{-1} . The outstanding conductivity of PEDOT oxidized by FeCl_3 is generated from these factors: the enhanced doping level as we analysed in the XRD, UV-vis-NIR spectra, and PL spectra; the enhanced crystallinity which is helpful for the mobility of electrons; the change of morphology from sphere to rod, because of the unique mechanism of 1D electron transfers inducing the conductivity of a 1D structure such as a fibre or tube to be larger than that of a 3D structure such as a block or sphere [31]; and the process of polymerization which excludes the redundant reagent, e.g. surfactant, in the final product.

The calculated temperature dependence of conductivity of the resulting PEDOT oxidized by different oxidants was measured between 140 and 300 K, and the result is shown in figure 7. It was found that the conductivity of both measured samples decreases with decreasing temperature, which is a typical semiconductor behaviour. The temperature dependence of conductivity (σ) is described by the multitrap and release (MTR) model as follows:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right).$$

Here σ_0 is a constant, E_a is the activation energy of charge carriers, k_B is the Boltzmann constant and T is the temperature in kelvin [32]. The value of E_a of the PEDOT oxidized by FeCl_3 and APS is estimated to be ~ 0.058 and ~ 0.17 meV from the slope of σ versus $1000/T$ in figure 7, respectively. These values are smaller than those of previous reports [33–35], and E_a of rod-like PEDOT is much less than that of sphere-like PEDOT, which is in agreement with the results of the room-temperature conductivity measurement, and also confirms our previous analysis.

4. Conclusion

1D PEDOT nanorods were obtained by using CSA as the functional dopant and FeCl_3 as oxidant through aqueous solution polymerization, while traditional PEDOT nanospheres were obtained when using APS as an oxidant. Dissolving sufficient CSA to exert the effect of

functional dopant and adopting weak oxidant FeCl₃ to reduce the rate of polymerization facilitates the formation of 1D structures of PEDOT. 1D structured PEDOT, in exhibiting high crystallinity, high doping level and especially excellent conductivity, is superior to the traditional morphological form. This method is convenient and environmentally friendly, and this form of PEDOT with high conductivity can be potentially applied in wide areas such as field emission and solar cell devices.

Acknowledgments

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