Facile Optimal Synthesis of Inherently Electroconductive Polythiophene Nanoparticles

Xin-Gui Li,*[a, b] Ji Li,[a] and Mei-Rong Huang*[a, b]

Abstract: Polythiophene (PTh) nanoparticles were successfully synthesized by a simple chemical oxidative polymerization in the presence of a very small amount of cetyltrimethylammonium bromide (CTAB). The polymerization yield, particle size, bulk electrical conductivity, and solubility of the PTh nanoparticles have been optimized by adjusting the CTAB/FeCl₃ oxidant/thiophene monomer ratio, thiophene concentration, polymerization temperature, and reaction time. The structure of the PTh nanoparticles was systematically characterized by IR and UV/Vis spectroscopy, wide-angle X-ray diffraction, laser particle-size analysis, field-emission scanning electron microscopy (SEM), and transmission electron microscopy (TEM). It was found that the number-average diameter ($D_n$) and size polydispersity index (PDI) of the particles decrease significantly from 4.19 µm and 1.21 to 203 nm and 1.056, respectively, with a slightly increasing CTAB concentration. SEM and TEM reveal that the PTh particle size is reduced to 67 and 36 nm, respectively. The conductivity increases on raising the FeCl₃/thiophene ratio or on lowering the CTAB concentration and polymerization temperature. A moderate monomer concentration and polymerization time are very beneficial for achieving highly conducting PTh. The highest conductivity of virgin PTh is $3.1 \times 10^{-4} \, \text{S} \cdot \text{cm}^{-1}$ and can be further elevated to $50 \, \text{S} \cdot \text{cm}^{-1}$ by doping in iodine vapor. Under optimized polymerization conditions, the significant variation of the conductivity of the PTh particles in virgin and doped states was well confirmed by the intensity and wavelength of the UV/Vis spectral band owing to the large π conjugation. The PTh particles demonstrate uncommon characteristics including easy synthesis, low cost of production, large π-conjugated structure, high conductivity, solution processability, and extensive potential for further application.

Keywords: conducting materials · iodine doping · nanoparticles · polythiophenes · semiconductors

Introduction

Polythiophene (PTh) and its derivatives have attracted considerable attention over the past few decades.[1-4] They have been studied for various important applications including corrosion protection, solar cells, sensors, catalyst carriers, supercapacitors, and modified electrodes because of their high conductivity, excellent environmental stability, and unique photovoltaic and electronic properties.[5-10] However, the poor processability of non-substituted PTh, which is insoluble and infusible, badly limits its further extensive application. One of the effective methods to improve the processability is the preparation of PTh nanomaterials, which can be well dispersed in different matrix materials. Up to now, the template synthesis has been the main technique for obtaining nanoscale PTh materials; it can be used to prepare PTh with a regular structure such as nanotubes or nanowires.[11,12] High-performance PTh tubules with diameters of 20 and 200 nm have been synthesized by electropolymerization of thiophene in boron trifluoride diethyl etherate solution in the presence of microporous alumina membranes as the templates.[11] Submicrometer-long PTh wires have also been fabricated in mesoporous silica matrices.[12] However, removal of the template after the formation of the nanosized PTh is difficult and may damage the nanostructure in the process. This might be the biggest flaw of the template method. Gamma irradiation during the polymerization of thiophene can afford nanowire-shaped PTh,[13] but this procedure requires sophisticated equipment. Therefore, it is still...
necessary to find a simple way to obtain PTh nanomaterials. The surfactant method may be a good choice because it has been widely applied to the fabrication of other nanoscale conductive polymers such as polyaniline and polypyrrole in aqueous polymerization media.\textsuperscript{[14,15]} However, very few reports on the chemical oxidative polymerization of thiophene in an aqueous medium are found due to the poor water solubility of thiophene monomer and thus an extremely low yield except for a recent study on an oxidative polymerization of thiophene in aqueous media containing surfactant for the preparation of PTh nanoparticles.\textsuperscript{[16]} Besides, the chemical oxidative polymerization of thiophene in a non-aqueous reaction media containing surfactant for the synthesis of nanosized PTh has not been extensively studied.

In this work, a small amount of vital cetyltrimethylammonium bromide (CTAB) was added into the acetonitrile medium for the chemical oxidative polymerization of thiophene. The polymerization yield, structure, iodine doping, and properties of the nanoparticles were elaborated by IR and UV/Vis spectroscopy, X-ray diffraction, laser particle-size analysis, SEM, and TEM techniques.

**Results and Discussion**

**Synthesis of PTh nanoparticles**

**Potential and temperature of the polymerization solution:** The progress in the polymerization of thiophene was tracked by the open-circuit potential (OCP) and temperature of the reaction solution, as seen in Figure 1. The primary colorless thiophene solution demonstrates an initial OCP of 245 mV versus SCE; the OCP rapidly rose with pouring the oxidant solution into the monomer solution and reached its maximum of 1374 mV after 4.5 min. Following that, a gradual OCP decrease was observed until the OCP remained more or less constant, indicating the end of the polymerization.\textsuperscript{[17]} During the polymerization, the variation of the OCP follows the Nernst equation [Eq. (1)]:

$$OCP = E_0 + \frac{RT}{nF} \ln \left( \frac{C_O}{C_R} \right)$$

in which $E_0$ is the standard electrode potential of the polymerization, $R$ is the gas constant, $T$ is the absolute temperature, $n$ is the number of electrons, $F$ is the Faraday constant, and $C_O$ and $C_R$ are the concentrations of the oxidant and reductant (i.e., monomer), respectively. Obviously, the value of the OCP depends on the oxidant/monomer ratio, that is, the higher the ratio, the larger the OCP value. It seems that the polymerization could be divided into two stages according to the OCP variation in Figure 1. The maximum OCP should be attributed to the sudden and quick addition of the oxidant solution because of the significant increase of $C_O$ but decrease of $C_R$. In the first stage before the OCP maximum, chain initiation and propagation occurred immediately and dramatically upon adding the oxidant. With the OCP variation, the color of the polymerization solution darkened quickly, an indication of the formation of dark polymer precipitates. In the second stage after the OCP maximum, the oxidatively active polymers or intermediates formed in the first stage likely polymerized further with each other or with the residual monomers or oligomers to form a higher molecular-weight polymer, which may be the main reaction in this stage. As the chain propagation repeated between the active polymers/intermediates and the residual monomers/oligomers, a large amount of oxidant was consumed, leading to a further gradual decline of the OCP. The end of polymerization results in a relatively stable $C_O/C_R$ ratio, thus a gradually steady OCP after 480 min.

The variation of the polymerization solution temperature is similar to that of the OCP, indicating an exothermic polymerization, but the exothermicity is not high because the temperature rise is only 1.5°C. It is coincidental that the time of reaching the maximal temperature corresponds to the maximal OCP; this suggests that the maximal rate point of the oxidative polymerization appeared at 4.5 min.

**Polymerization yield:** There are five important synthetic parameters that influence the thiophene polymerization. The effect of the CTAB content on the yield of thiophene polymerization, shown in Figure 2, exhibits a monotonically decreased yield with increasing relative CTAB content. One of the reasons is that the thiophene monomer would be packaged by the CTAB in CH\textsubscript{3}CN, consequently reducing the contact opportunity between monomer and oxidant. Therefore, the more CTAB added, the lower the yield is. It can be seen that the polymerization yield was only 18.6% even if no CTAB was used, implying that the polymerizability of the thiophene is not high under these circumstances.

The effect of the oxidant FeCl\textsubscript{3}/monomer thiophene (O/M) molar ratio on the polymerization yield is shown in...
Figure 3. A nearly linear rise of the polymerization yield from 13.5 to 45.9% appears with an increasing O/M molar ratio from 2:1 to 6:1. A much lower yield at a low O/M ratio should be ascribed to the insufficient oxidant that would rapidly be consumed during the initial stage of the polymerization. Apparently, a higher O/M molar ratio will produce a higher yield, because more oxidant with a constant thiophene content provides a great deal more oxidizing activation centers in the polymerization system and accordingly many more monomers could be oxidized to participate in chain propagation.

A positive correlation between monomer concentration and polymerization yield is also revealed in Figure 4, that is, more monomers resulted in a higher polymerization yield. The yield increased from 24.5 to 60.1% as the monomer concentration rose from 0.05 to 0.25 M under otherwise fixed conditions. It can be explained by the fact that at a higher monomer concentration, the probability of the contact between oxidant and monomer would be larger, and more monomer can participate in chain initiation and propagation at the same time. It should be noted that in a higher thiophene concentration range from 0.1 to 0.25 M, the rising rate of the yield decreases because the amount of chain propagation gradually becomes constant. A similar relationship between furan monomer concentration and polymerization yield has been revealed during the chemical oxidative polymerization of furan with FeCl₃ as oxidant at 15°C.[18]

Figure 5 illustrates the influence of polymerization temperature on the polymerization yield. The temperature clearly has a relatively weak effect on the yield. It is interesting that the yield exhibits a minimum at 40°C, which is something like the dependence of the yield on the polymerization temperature of furan with a minimal yield at 25°C.[18] The polymerization temperature, however, has a great impact on the conductivity of the PTh, which will be discussed in detail later.
The polymerization time, unlike the temperature, has a great influence on the polymerization yield, as shown in Figure 6. As the polymerization time increases from 3 to 24 h, the polymerization yield rises from 34.5 to 53.2%. It seems that the polymerization rate is very fast during the initial polymerization time of 6 h. After that, the polymerization becomes slower and slower because the amount of residual monomers and oxidants that participate in the polymerization becomes less and less as time elapses.

**Structure of PTh nanoparticles**

**IR spectra**: The IR spectra of the four typical PTh samples are shown in Figure 7. The weak bands at 3060 and 2924 cm\(^{-1}\) can be assigned to the C–H stretching vibrations of the thiophene ring.\(^{[5,19]}\) The peaks at 1490 and 1441 cm\(^{-1}\) belong to C=C symmetric stretching vibrations of the thiophene ring. The absorbance at 1329 cm\(^{-1}\) is attributed to C–C stretching vibrations.\(^{[5,20,21]}\) The second strongest band at 1031 cm\(^{-1}\) as well as the 1115 cm\(^{-1}\) band can be attributed to the in-plane C–H aromatic bending vibrations.\(^{[20]}\) The strongest absorbency at 784 cm\(^{-1}\) is ascribed to C–H out-of-plane stretching vibrations, indicating the α-position linkage between the thiophene rings,\(^{[22,23]}\) whereas the absorbanes at 690 and 642 cm\(^{-1}\) are indicative of C–S stretching of the thiophene ring.\(^{[21,22]}\) These characteristic absorbances confirm the formation of PTh with a 2,5-substituted thiophene ring, that is, a real polymer has been obtained although the polymerization conditions affected the structure of the resulting PTh to some extent. It can be observed from Figure 7 that polymerization conditions have an influence on the polymer structure. The band intensities at 1031, 1115, 1205, 1329 and 642 cm\(^{-1}\) decline with increasing polymerization time or polymerization temperature, whereas that at 784 cm\(^{-1}\) remains fixed. The new band at 1676 cm\(^{-1}\) in curve c (Figure 7) may be due to the C=C asymmetric stretching vibration of the thiophene ring.

**UV/Vis spectra**: The UV/Vis spectra of the PTh prepared with different CTAB/thiophene molar ratios are shown in Figure 8. There are two bands in the spectra, the medium band around 300 nm (λ\(_1\)) due to a π–π* transition (i.e., a small π-conjugated structure) of thiophene units and the strong broad band (λ\(_2\)) from 450 to 570 nm due to a π–π* transition (i.e., a large π-conjugated structure) of the PTh backbone.\(^{[24]}\) This suggests that the PTh samples are partly doped based on previous reports that the absorption band of PTh appears at 770 nm in a doped state and 440 nm in an undoped state.\(^{[6,24]}\)

The broad band indicates the coexistence of both long and short effective conjugation structures in the PTh chains.\(^{[24–27]}\) It is worth noting that λ\(_1\) of the monomer appears at 273 nm, which is about 30 nm shorter than λ\(_1\) of the PTh, because the small π conjugation in a single thiophene ring has been converted into large π conjugation upon the oxidative polymerization of the thiophene monomer, accompanied by a redshift.
After an intensity normalization of the relatively stable $\lambda_1$ band due to small $\pi$ conjugation (i.e., intraring electrons) in the thiophene units, the $\lambda_2$ band due to large $\pi$ conjugation is comparable to some extent. The intensity of the $\lambda_2$ band is significantly affected by the CTAB content; that is to say, the higher the CTAB/thiophene molar ratio, the lower intensity and the shorter the wavelength of the $\lambda_2$ band. Note that the thiophene monomer hardly ever exhibits a $\lambda_3$ band. The $\lambda_3$ band with a longer wavelength and higher intensity means that the PTh has a larger amount of longer-conjugated structure. Obviously, CTAB is not beneficial to the preparation of highly $\pi$-conjugated PTh, although CTAB is greatly advantageous to the fabrication of nanosized PTh, as discussed below.

Figure 9 shows the UV/Vis spectra of the PTh particles synthesized with different FeCl$_3$/thiophene molar ratios (a) and thiophene monomer concentrations (b). With an increase in the FeCl$_3$/thiophene ratio, the $\lambda_2$ band monotonically becomes stronger, especially with an increase of the FeCl$_3$/thiophene ratio from 2:1 to 3:1. This is an indication that more oxidant is favorable for the attainment of well $\pi$-conjugated PTh chains, and the optimal FeCl$_3$/thiophene molar ratio might be 6:1. Note that the maximal absorption wavelength of the $\lambda_2$ band is around 530 nm, which suggests that the conjugated length may be almost constant regardless of the variation of the FeCl$_3$/thiophene ratio. It is of interest that with elevating thiophene monomer concentration from 0.05 to 0.25 M, the intensity of the $\lambda_2$ band rises first and then declines, exhibiting a maximum at the monomer concentration of 0.15 M. The weakest $\lambda_2$ band appears at the lowest monomer concentration of 0.05 M, and the $\lambda_2$ band at 0.1 M displays the shortest maximal band wavelength that is about 10 nm shorter than the others. In summary, for the synthesis of PTh with the best conjugated structure the optimal thiophene concentration is 0.15 M.

The UV/Vis spectra of the PTh prepared with different polymerization temperatures and times are displayed in Figure 9c and d. Apparently, the intensity of the $\lambda_2$ band gradually decreases with an increase of the polymerization temperature from 0 to 50°C, with a dramatic intensity decline occurring between 30 and 40°C. This indicates that larger $\pi$-conjugated PTh can be prepared at a lower temperature. The thiophene polymerization at an elevated temperature is instead violent and thus unfavorable for the formation of a highly conjugated structure. A similar relationship between the $\lambda_2$ band intensity and polymerization time has been observed in Figure 9d. We were surprised to find that both the maximal intensity and maximal wavelength of the $\lambda_2$ band simultaneously appear at the polymerization time of 6 h, implying that the PTh formed for 6 h has the largest degree of $\pi$-conjugation, the longest conjugated length, and/or the highest doping level. Notably, the PTh nanoparticles obtained in this study have larger $\lambda_2$, $\lambda_3$ intensity ratios and/or longer $\lambda_2$ wavelengths than PTh and its derivatives prepared by other methods,[5,16,21,28–30] which suggests that the PTh nanoparticles obtained here have a longer $\pi$-conjugation length. It can be concluded that the optimal polymerization time is 6 h for the formation of the PTh with the best conjugated structure.

Wide-angle X-ray diffractograms: The wide-angle X-ray diffractograms of four kinds of PTh samples are shown in Figure 10. All four diffractograms exhibit a broad diffraction peak at the Bragg angle of approximately 24°, which is in accordance with previous reports[21,31,32] and an indication of the existence of an amorphous PTh. Compared with curves a) and b), a new weak diffraction at $2\theta$ = 35.3° appears in curves c) and d), which signifies the residue of a small amount of FeCl$_2$. Perhaps the PTh chains were doped with more FeCl$_2$ because more FeCl$_2$ must interact with the PTh chains at a higher O/M molar ratio of 6:1 regardless of a thorough rinse with water. It is also revealed that the diffraction peak due to FeCl$_2$ is stronger in curve c than in curve d, which implies that the doping level of the PTh obtained during the polymerization time of 6 h is higher, which is consistent with the UV/Vis spectrum and electrical conductivity results.

Size and distribution: Figure 11 displays the number-average diameter ($D_n$) and its distribution index of the PTh particles dispersed in water. The $D_n$ first declines sharply and then slowly with an increasing CTAB/thiophene molar ratio from 0 to 1:5, whereas the polydispersity index (PDI) exhibits a...
minimum (1.056) at a CTAB/thiophene molar ratio of 1:15. The \( D_n \) of the PTh particles is 4.19 \( \mu \)m when no CTAB is used, whereas the \( D_n \) is as small as 203 nm at a CTAB/thiophene molar ratio of 1:5, which indicates a great advantage of adding CTAB for the fabrication of much smaller PTh particles. Newly formed PTh particulates would efficiently be encased by the CTAB, so the second growth on the particulates could effectively be suppressed during the polymerization, leading to a much smaller \( D_n \). Furthermore, the higher the CTAB content, the smaller the PTh particles. However, too much CTAB will unfortunately result in too low a yield (Figure 2). Therefore, the optimal CTAB/thiophene ratio would be 1:5 for the efficient fabrication of fine uniform PTh particles.

Polymerization time is one of the important factors affecting the size of PTh particles, as illustrated in Figure 12. The PTh particles seem to be big (2.41 \( \mu \)m) at 3 h and become even bigger (2.81 \( \mu \)m) at 12 h. After that, the particles become much smaller as the polymerization time elapses, and their \( D_n \) and PDI significantly decrease to 223 nm and 1.22, respectively, at 24 h. That is to say, the maximal \( D_n \) value (2.81 \( \mu \)m) at 12 h can convert into the minimal \( D_n \) value (223 nm) at 24 h. Apparently, a relatively long polymerization time is advantageous for obtaining small and uniform PTh particles. The very small particulates formed at the initial polymerization stage have high surface energy, tending to spontaneously agglomerate into large particles by second growth. It is notable that the large particles could be shattered into much smaller ones by vigorous stirring in the presence of CTAB because the CTAB can prevent the small particles from agglomerating.

**Morphology:** Field-emission SEM images of two PTh samples are shown in Figure 13. It can be observed that all of the PTh samples are almost spherical or ellipsoidal particles with a similar size. Typical diameters of the PTh particles...
prepared with a CTAB/FeCl₃/thiophene molar ratio of 1:60:10 at 0°C for 6 h and CTAB/FeCl₃/thiophene molar ratio of 1:10:5 at 30°C for 24 h are found to be 120 and 67 nm, respectively. The TEM images in Figure 14 suggest that the PTh particles synthesized with CTAB/FeCl₃/thiophene molar ratio of 1:10:5 at 30°C for 24 h have a diameter of around 36–47 nm, which is even smaller than the diameter observed by SEM. The particle size becomes smaller with changing measurement methods from laser particle-size analysis (LPA) to SEM to TEM under different testing conditions. The larger particle size found by using SEM instead of TEM is attributable to the existence of the sputtered gold layer with a thickness of around 15 nm on the PTh particles, signifying that the particle size determined by SEM may be 15 x 2 = 30 nm larger than that by TEM. And the largest particle size by LPA might originate from possible swell of and/or relatively poor dispersion of the PTh particles in water because the particle samples for SEM and TEM are both taken from dispersions in alcohol. It can be concluded that CTAB indeed plays a key role in the preparation of PTh nanoparticles because under vigorous stirring the nanoparticles trapped in CTAB can become well dispersed in the solution. The PTh nanoparticles still remain well dispersed in pure water and alcohol even after removal of the CTAB from the nanoparticles.[30] During thiophene polymerization, CTAB clearly acts as the dispersant instead of the emulsifier in CH₃CN because CTAB could not form regular stable micelles in the two-phase system. This could explain why the particles obtained were not all spherical as in emulsion polymerization. SEM photographs confirm this, and this is also similar to the relevant reports.[20,33] Note that the dry PTh samples could be dispersed well in water, ethanol, and some other solvents upon ultrasonic treatment, but some particles would sink to the bottom of the solution after a few days, indicating that the dispersion stability of PTh particles is not high enough, as discussed below.

**Stability of the PTh particle dispersions:** The stability of the dispersion of purified PTh particles strongly depends upon the particle size. As shown in Figure 15, the 203 nm-size particles after an ultrasonic treatment of 30 min can uniformly and stably disperse in pure water for at least 18 h, whereas the 2.65 μm-size particles after the same ultrasonic treatment cannot stably disperse in pure water. In fact, most of the 2.65 μm-size particles will precipitate soon after the ultrasonic treatment. However, two types of PTh particles after ultrasonic treatment can stably disperse in N-methylpyrroldione (NMP) for a much longer time than in water, possibly due to their better dispersibility and/or solubility in NMP, which have both been further confirmed by a stronger band around 450 nm for 203 nm-size particles and by a much stronger band around 560 nm for 2.65 μm-size particles (shown in Figure 16). Figure 16 indeed indicates that the 203 nm-size particles form a stable nanosized dispersion in water because of their water-insolubility, while the 2.65 μm-size particles form an unstable dispersion in water. The stable and uniform dispersion of the PTh nanoparticles could be attributed to the stabilization of a very small amount of residual CTAB on the particles and/or self-stabilization from the static repulsion between the negative.

**Figure 14.** TEM images of PTh particles prepared at a CTAB/FeCl₃/thiophene molar ratio of 1:10:5 at 30°C for 24 h.

**Figure 15.** Stability of aqueous dispersions of a) the PTh nanoparticles (203 nm) synthesized with a CTAB/FeCl₃/thiophene molar ratio of 1:10:5 at 30°C for 24 h and b) the PTh microparticles (2.65 μm) synthesized with CTAB/FeCl₃/thiophene molar ratio of 1:60:10 at 0°C for 6 h.

**Figure 16.** UV/Vis spectra of aqueous and NMP dispersions of the PTh nanoparticles (203 nm) synthesized with a CTAB/FeCl₃/thiophene molar ratio of 1:10:5 at 30°C for 24 h and the PTh microparticles (2.65 μm) synthesized with CTAB/FeCl₃/thiophene molar ratio of 1:60:10 at 0°C for 6 h.
charges of the nanoparticles and the lone electron pair on the sulfur atom of the thiophene units.

**Properties of the PTh particles**

**Bulk electrical conductivity:** The virgin scarlet PTh particles exhibit relatively low conductivity ranging between $10^{-9}$ and $10^{-4} \text{ S cm}^{-1}$ (see Figures 2–6) because their doping level is very low. The dependence of electrical conductivity on the CTAB content is illustrated in Figure 2. It seems that the conductivity steadily decreases from $2.7 \times 10^{-7}$ to $6.2 \times 10^{-10} \text{ S cm}^{-1}$ when increasing the CTAB/thiophene molar ratio from 0 to 1.5. This reveals that the existence of the CTAB is disadvantageous to the formation of PTh with high molecular weight and/or large $\pi$ conjugation, which is verified by the UV/Vis spectra in Figure 8. Furthermore, the PTh obtained in the presence of CTAB is more difficult to dope with FeCl$_3$; this also reduces the conductivity to some extent. Apparently, the conductivity of PTh is very low even in the absence of any surfactants like CTAB, and thus other polymerization conditions should be carefully optimized.

It can be seen from Figure 3 that the bulk electrical conductivity is significantly influenced by the oxidant concentration. A gradual rise of the conductivity from $5.2 \times 10^{-2}$ to $1.7 \times 10^{-7} \text{ S cm}^{-1}$ was revealed with increasing FeCl$_3$/thiophene molar ratio from 2:1 and 6:1. This is because a higher oxidant concentration can realize a higher doping level and better $\pi$ conjugation, which has been proved by the UV/Vis spectra in Figure 9a. A similar positive relationship between the conductivity of PTh doped by iodine vapor and the FeCl$_3$/thiophene ratio has been observed, and upon iodine doping all the conductivity has remarkably been improved by 5 to 6 orders of magnitude.

Figure 4 shows that the conductivity of PTh rises first and then declines with increasing thiophene concentration from 0.05 to 0.25 m, displaying a maximal conductivity of $8.9 \times 10^{-5} \text{ S cm}^{-1}$ at 0.15 m. This has been validated by the maximal absorbance of the 543 nm band of the PTh formed at 6 h in Figure 9d. The I$_2$-doped PTh possesses a very similar variation of the conductivity with the polymerization time; the conductivity of PTh doped by iodine vapor is higher than 1 S cm$^{-1}$ and the maximum is 50 S cm$^{-1}$. The maximal iodine doping level up to 148.7% is likely responsible for such high conductivity. Clearly, the $\pi$-conjugation length would reach a maximum at 6 h because a polymerization time that is too long would result in overoxidization of the PTh by the residual oxidant.[23,35] In a word, the optimal polymerization time is 6 h for the synthesis of the PTh with the highest conductivity.

Besides I$_2$ vapor, HCl and HClO$_4$ can also be used as dopant to improve the conductivity despite a relatively weak increase in the conductivity, as summarized in Table 1. The iodine vapor method would be the optimal doping method by which the conductivity of the PTh would increase from $3.1 \times 10^{-4}$ to 50 S cm$^{-1}$.[6,36–39]

<table>
<thead>
<tr>
<th>Virgin</th>
<th>1m HCl</th>
<th>Dopant</th>
<th>1m HClO$_4$</th>
<th>I$_2$ vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>color</td>
<td>scarlet</td>
<td>black</td>
<td>black</td>
<td>black</td>
</tr>
<tr>
<td>conductivity [$\text{S cm}^{-1}$]</td>
<td>$3.1 \times 10^{-4}$</td>
<td>$7.5 \times 10^{-4}$</td>
<td>$8.5 \times 10^{-3}$</td>
<td>50</td>
</tr>
<tr>
<td>improvement [%]</td>
<td>–</td>
<td>142</td>
<td>2642</td>
<td>$1.6 \times 10^{7}$</td>
</tr>
</tbody>
</table>

**Solubility:** The PTh particles are insoluble in several organic solvents such as acetone, formic acid, acetic acid, chloroform, 3-methylphenol, and tetrahydrofuran, but partly soluble in polar solvents such as NMP, DMSO, and H$_2$SO$_4$ (98%). The very strong absorbance at 560 nm in Figure 16 is evidence that the PTh microparticles are soluble in NMP to some extent, whereas the insoluble aqueous dispersion of the PTh microparticles exhibits much weaker absorbance. This signifies that the PTh microparticles synthesized in this study have a solution processability like the PTh derivatives.
Similarly, the PTh nanoparticles synthesized in this study also exhibit stronger absorbance at 450 nm in NMP than in water, indicating a potential solution processability in NMP. Besides, the PTh nanoparticles can directly be used to fabricate nanocomposites with controllable properties and functionalities.\[17,35\]

**Conclusion**

Fine PTh nano- and microparticles with narrow size distribution, controllable size, and high electrical conductivity have been successfully synthesized by a facile chemical oxidative polymerization in the presence of a very small amount of CTAB with FeCl\(_3\) and CH\(_3\)CN as oxidant and medium, respectively. The PTh particles prepared at a CTAB/FeCl\(_3\)/thiophene molar ratio of 1:60:10 with a thiophene concentration of 0.15 M at 0°C for 6 h exhibit the maximal conductivity of 3.1 \times 10^4 S/cm that is remarkably enhanced to 50 S/cm upon simple doping by iodine vapor, together with a moderate polymerization yield of 46.6%. The conductivity of the PTh particles exhibits nearly the same trend as the intensity and wavelength of the UV/Vis spectral band due to the large \(\pi\) conjugation with optimized polymerization conditions. The soluble PTh particles synthesized in this study possess an uncommon combination of several characteristics including ease of synthesis, low cost, high and controllable conductivity, and potential processability. It would not be long before these PTh particles would find more extensive practical potential.

**Experimental Section**

**Materials:** Thiophene, FeCl\(_3\), acetonitrile (CH\(_3\)CN), cetyltrimethylammonium bromide (CTAB), and other reagents were chemically pure and used as received.

**Synthesis of PTh nanoparticles:** CTAB (0.4 mmol, 0.158 g) was mixed with CH\(_3\)CN (10 mL) in a reaction vessel. Thiophene (4 mmol, 0.32 mL) dissolved in a solution of CH\(_3\)CN (10 mL) was added to the CTAB solution and stirred in a water bath for 30 min at 30°C. Subsequently, the solution of anhydrous FeCl\(_3\) (8 mmol, 1.297 g) in a solution of CH\(_3\)CN (20 mL) was added dropwise into the transparent thiophene solution. The color of the mixture at once changed from colorless to black, and the mixture was consistently stirred for 24 h. Then the mixture was centrifuged and was further purified with ethanol and water several times until the top-layer liquid in the centrifuge tube was colorless. During this purifying procedure, the color of the PTh precipitate changed from greenish black to dark red because a reduction from ethanol can change the PTh state from oxidized to reduced.\[12\] Finally, the virgin PTh powder was dried in air at 60°C for 48 h. The resultant polymer in its virgin state was converted into its doped state by treating the polymer particles in a solution of HClO\(_4\) or HCl for 24 h, or in iodine vapor for 72 h. The doped PTh samples obtained are all black. The nominal polymerization of the thiophene is described in Scheme 1.

**Iodine doping procedure:** Iodine vapor was used to dope PTh particles in a closed vessel containing iodine particles (100 mg) and PTh powder (15 mg) at a constant temperature of 60°C under atmospheric pressure for 72 h. Note that the PTh powder does not make direct contact with the iodine particles. The I\(_2\) doping level was measured by weight gain of the final doped PTh powder.

**Instruments:** The polymerization process was tracked by an open-circuit potential (OCP) technique using a saturated calomel electrode (SCE) as a reference electrode and a Pt electrode as a working electrode. IR reflection–absorption spectra of the PTh particles were recorded on a Nicolet Magna 550 FTIR spectrometer at 2 cm\(^{-1}\) resolution. UV/Vis spectra of the PTh particles in NMP were determined by using a double beam UV/Vis spectrophotometer in a wavelength range of 200–900 nm at a scanning rate of 400 nm min\(^{-1}\). The wide-angle X-ray diffraction analysis was performed using a D/Max 2550 model X-ray diffractometer over a 20 range from 5 to 70°. The size and distribution of the PTh particles in water were analyzed using a Beckman Coulter LS230 laser particle-size analyzer. Particle morphology was observed using field-emission SEM (Quanta 200FEF; FEI Company Eindhoven, The Netherlands) and TEM (Hitachi H900). The bulk electrical conductivity of an approximately 0.5-mm-thick pressed disk of PTh particles was measured using a two-probe method with a useful area of 0.785 cm\(^2\) at room temperature. The polymerization yield was calculated as shown in Equation (2):

\[
\text{Yield} = \frac{\text{weight of the virgin PTh particles obtained}}{\left(\frac{82 \times \text{thiophene mole number added}}{100}\right)} \times 100\% \quad (2)
\]

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