# Synthesis and Characterization of Poly(3,4-ethylenedioxythiophene) Nanoparticles Obtained Through Ultrasonic Irradiation

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**ABSTRACT:** Poly(3,4-ethylenedioxythiophene) (PEDOT) nanoparticles with a size of 50–100 nm were prepared by the oxidation polymerization of the monomer 3,4-ethylenedioxythiophene (EDOT) under ultrasonic irradiation. The structure and morphology of PEDOT, as well as the electrical conductivity were characterized. Compared with the conventional stirring method, the PEDOT nanoparticles prepared by ultrasonic irradiation have a smaller particle size and are more uniform and spherical due to the dispersion, emulsifying and disruption effects of ultrasound. The yield of PEDOT by ultrasonic irradiation can reach ∼ 50%, and the conductivity of PEDOT is high up to 11 S/cm. A decrease in particle size due to the ultrasonication can lead to more effective doping and enhanced conductivity. The reaction time, temperature and ultrasound power output have significant effects on the field and electrical conductivity of PEDOT. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2146–2152, 2010

**Key words:** poly(3,4-ethylenedioxythiophene); nanoparticles; ultrasound; conductive polymer

## INTRODUCTION

Poly(3,4-ethylenedioxythiophene) is one of the most successful conducting polymers and has attracted more attention because of its excellent environment stability, low oxidation potential, low band gap, as well as its good and stable electrochromic behavior from blue to transparent in neutral and oxidized states, respectively.[1] The synthesis of PEDOT has two different types of polymerization reactions: oxidative chemical polymerization and electrochemical polymerization. The traditional methods resulted in large aggregated PEDOT particles with a wide size distribution of the spherical particles, relatively low conductivity and field.[2] Oh and Im[3] prepared PEDOT particles in micellar solution using sodium dodecylbenzene sulfonic acid (DBSA) as a surfactant and $FeCl_3/Na_2S_2O_8$ as an oxidant in aqueous media. However, PEDOT particles were poorly defined and showed a tendency to form aggregates. Louwet et al.[4] reported that the synthesis of stable PEDOT dispersions in water with the help of polystyrene-sulfonic acid, but the morphology of PEDOT was not disclosed.

Ultrasound can lead to new chemical reaction and improve the reaction rate, thus opens up a new chemistry i.e. sonochemistry.[5] Suslick et al.[6] reported the sonochemical preparation of metallic nanoparticles. Previously, we reported that the aggregates of nano silica can be broken apart and redispersed in the aqueous medium, and thus the long-term stable polymer/nano silica composite latex can be prepared through ultrasonicially initiated *in situ* emulsion polymerization.[7,8] We also employed ultrasonic irradiation to prepare the electrical conductive polyaniline nanoparticles,[9] polyaniline/$TiO_2$,[10] polyaniline/$SiO_2$ nanocomposite.[11] Especially, the high intensity ultrasound not only can accelerate the heterogeneous liquid–liquid chemical reaction, but also can break the aggregation and reduce the particle size due to its dispersion, crushing, stirring, emulsifying, and activation effect, and thus has a better control on the morphology of particles.

In this study, ultrasonic irradiation was introduced to prepare the advanced conducting PEDOT nanoparticles. Ultrasonic irradiation not only can reduce the PEDOT particle size, but also can promote more effective doping, and enhance the polymerization rate and polymer field. The structure and morphology of PEDOT nanoparticles were characterized and the effects of ultrasonic time, reaction temperature and ultrasound power output on the field and electrical conductivity of PEDOT were studied.

## EXPERIMENTAL

### Materials

3,4-Ethylenedioxythiophene (EDOT) (98%) was purchased from Suzhou Industrial Park Yacoo Chemical Reagent Co., Iron(III) chloride (99%) was purchased from Shanghai Aibi Chemistry Preparation Co., and Dodecylbenzene sulfonic acid (DBSA) from Tokyo Kasei. The reagents were used as-received without further purification.

### Apparatus

The reaction apparatus was described in the previous article.[7] The ultrasonic irradiation instrument is VC-1500 (Sonic & Material Co., Newtown, CT), and has the following characters: standard titanium horn of diameter 22 mm, adjustable power out, replaceable flat stainless steel tip. The glass reactor was self-designed and made in house.

### Preparation of poly(3,4-ethylenedioxythiophene) particles through ultrasonic irradiation

Poly(3,4-ethylenedioxythiophene) (PEDOT) were prepared using dodecylbenzene sulfonic acid (DBSA) as a surfactant and doping agent, Iron(III) chloride ($FeCl_3$) as an oxidant. The PEDOT particles were prepared according to the following steps. Firstly, 0.044 M DBSA micelle solution was prepared by dissolving a certain amount of DBSA in 100 mL of deionized water in a 250 mL round flasket. Secondly, monomer EDOT was added to the DBSA micelle solution and the mixture was stirred for 1 h. Thirdly, the monomer EDOT aqueous solution and 10 mL $FeCl_3$ aqueous solution (1.165 mol/L) were introduced the reaction vessel, and then the cooling water was circulated. Fourthly, ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly into the mixture emulsion system. After the reaction started, the reaction temperature increased from 15 to 30°C in 3 min. After 1 h irradiation, the reaction was stopped. Finally, the products were collected by filtration and then were introduced into a 250 mL Soxhlet flask. The Soxhlet extraction was carried out for 48 h with distilled water and methanol, respectively, and then the products were dried under vacuum at 60°C for 24 h. A small amount of the samples were redispersed in methanol by ultrasonication for 10 min to observe the particle morphology.

### Preparation of poly(3,4-ethylenedioxythiophene) particles through conventional stirring

As a control experiment, the PEDOT particles were prepared through conventional stirring by using the same formulation and process as those in the ultrasonic irradiation.

### Characterization

The PEDOT yield at different reaction time was determined gravimetrically:

$$\text{Yield } (\%) = \frac{W_p}{W_m} \times 100\%$$

where $W_p$ is the weight of the obtained PEDOT and $W_m$ is the weight of the monomer EDOT introduced.

An Inspect F SEM instrument (FEI company, USA) was utilized to observe the morphologies of PEDOT particles. Samples were dispersed in methanol by ultrasonication for 10 min, dried on cover glasses and sputter-coated with gold before observation. The particle size distribution was measured by laser diffraction particle size analyzer (LDPSA) (Mastersizer 2000, Malvern Instruments) by using ethyl alcohol as the solvent. X-ray diffraction patterns (XRD) for PEDOT particle samples were conducted on a DX-1000 X-ray diffractometer with Nickel filtered CuKα radiation (λ = 1.54178 Å) operating at 40 kV. The analysis was performed at the diffraction angle 2Θ from 2 to 60° at a speed of 0.06°/s. Fourier transform infrared (FTIR) spectra of the samples in KBr pellets were recorded on a Nicolet 560 FTIR spectrometer. The spectra were collected from 4000 to 400 $cm^{-1}$, with a 4 $cm^{-1}$ resolution over 20 scans. The thermogravimetric analysis (TGA) curves were recorded on a TA Q600 instrument thermal analyzer with a heating rate of 10°C/min in the range of 50–800°C under nitrogen gas atmosphere. The electrical conductivity measurements were conducted on a SDY-4 four-probe instrument (Guangzhou Semi-conductive Materials Institute, China) on the pressed pellets of PEDOT particles.

## RESULTS AND DISCUSSION

### Morphology of PEDOT particles

Ultrasound cavitation can produce immense shock wave and rapid microstream, so it has the dispersing, pulverizing, emulsifying function, and can be used to produce smaller and uniform latex particles.[12] In addition, ultrasound can be used to control the formation of ordered structure.[13,14] For the easily aggregated PEDOT particles, ultrasound has more special effect on the dispersion and size reduction.

The particle size and size distribution of PEDOT particles were determined by laser diffraction method. Figure 1 shows the size and size distribution
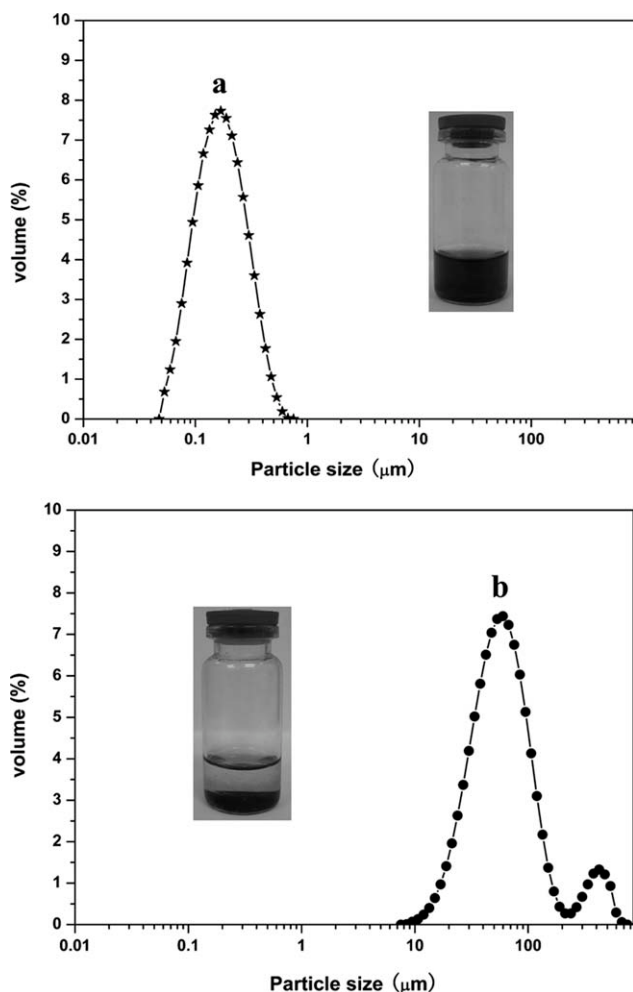
**Figure 1** Size and size distribution of the PEDOT particles in the colloid dispersions obtained through (a) ultrasonic irradiation and (b) conventional stirring. The insets are the digital pictures of the PEDOT colloid dispersions obtained by two methods.

of the PEDOT particles in the colloid dispersions (pH $\sim$ 1.7) prepared through ultrasonic irradiation and conventional stirring. As shown in Figure 1(a), the mean size of PEDOT particles obtained by ultrasonic irradiation is $\sim$ 0.18 μm, and the size distribution is unimodal. However, for conventional stirring, the particle size distribution is bimodal and relatively wide, and the mean size of PEDOT particles corresponding to the two peaks is $\sim$ 49 and $\sim$ 420 μm, respectively. Clearly, the size of the PEDOT particles obtained through ultrasonic irradiation is much smaller than conventional stirring. The digital pictures of PEDOT colloid dispersions obtained through two methods were shown in Figure 1. The color of colloid dispersions (a) is deeper than the color of colloid dispersions (b), which means a better dispersion and colloidal stability for ultrasonic method. It supports that ultrasonic irradiation can produce much smaller particles than conventional stirring.

SEM was used to observe the size and morphology of particles. Figure 2 shows the SEM images of the PEDOT particles obtained through two methods. The diameter of the PEDOT particles prepared through ultrasonic irradiation is 50–100 nm and the morphology is relatively uniform spherical [Fig. 2(a,b)]. The diameter of particles observed by SEM is smaller than that obtained from laser diffraction method. The reason may be that the particles are in the dried state during SEM observation. For conventional stirring, the diameter of the particles become much larger and the particles are aggregated in the colloid dispersions with an irregular shape [Fig. 2(c,d)], which is consistent with the data obtained from laser diffraction determination.

The chemical oxidation polymerization of EDOT occurs in a micellar solution of anionic surfactant DBSA. In this case, DBSA micelles may be the main loci of polymerization, just as the traditional emulsion polymerization initiated by chemical initiator due to a higher concentration of DBSA ($\sim$ 4.4 × 10$^{-2}$ mol/l) above the critical micelle concentration, which is $\sim$ 2 × 10$^{-3}$ mol/L.[15] The hydrophobic monomer EDOT is preferentially adsolubilized into the hydrophobic core of the micelle, then the oxidant penetrated into the micelle, and initiate the oxidation polymerization of monomer inside the micelle. Due to the low pH value ($\sim$ 1.7) in the PEDOT/DBSA colloid dispersions and high ionic strength (higher $FeCl_3$ concentration), the colloid is not stable, and thus will lead to an irregular PEDOT morphology and large aggregates if using conventional stirring. However, ultrasound can produce a new dynamic balance between collision and breaking of particle due to its thermal and solvodynamic shear effects associated with the acoustic cavitation phenomenon in solution,[5] leading to a better control on the morphology of particle and size reduction of particles.

## Structure characterization

### FTIR analysis

Figure 3 shows the FTIR spectra of monomer EDOT, the PEDOT prepared through conventional stirring and ultrasonic irradiation. Compared with Figure 3(a), the characteristic peaks of EDOT disappeared in the FTIR spectra of the PEDOT samples [Fig. 3(b,c)]. The characteristic band of PEDOT at 1336 cm$^{-1}$ is attributed to C—C or C=C stretching of quinoidal structure of thiophene ring, which also indicates the PEDOT sample is in a doped state. The peak at 1519 cm$^{-1}$ is attributed to the ring stretching of thiophene ring. The peaks at 1186, 1139, and 1080 cm$^{-1}$ are attributed to C—O—C bond stretching mode; and the peak at 977, 833, and 682 cm$^{-1}$ are attributed to the vibration absorption of C—S bond
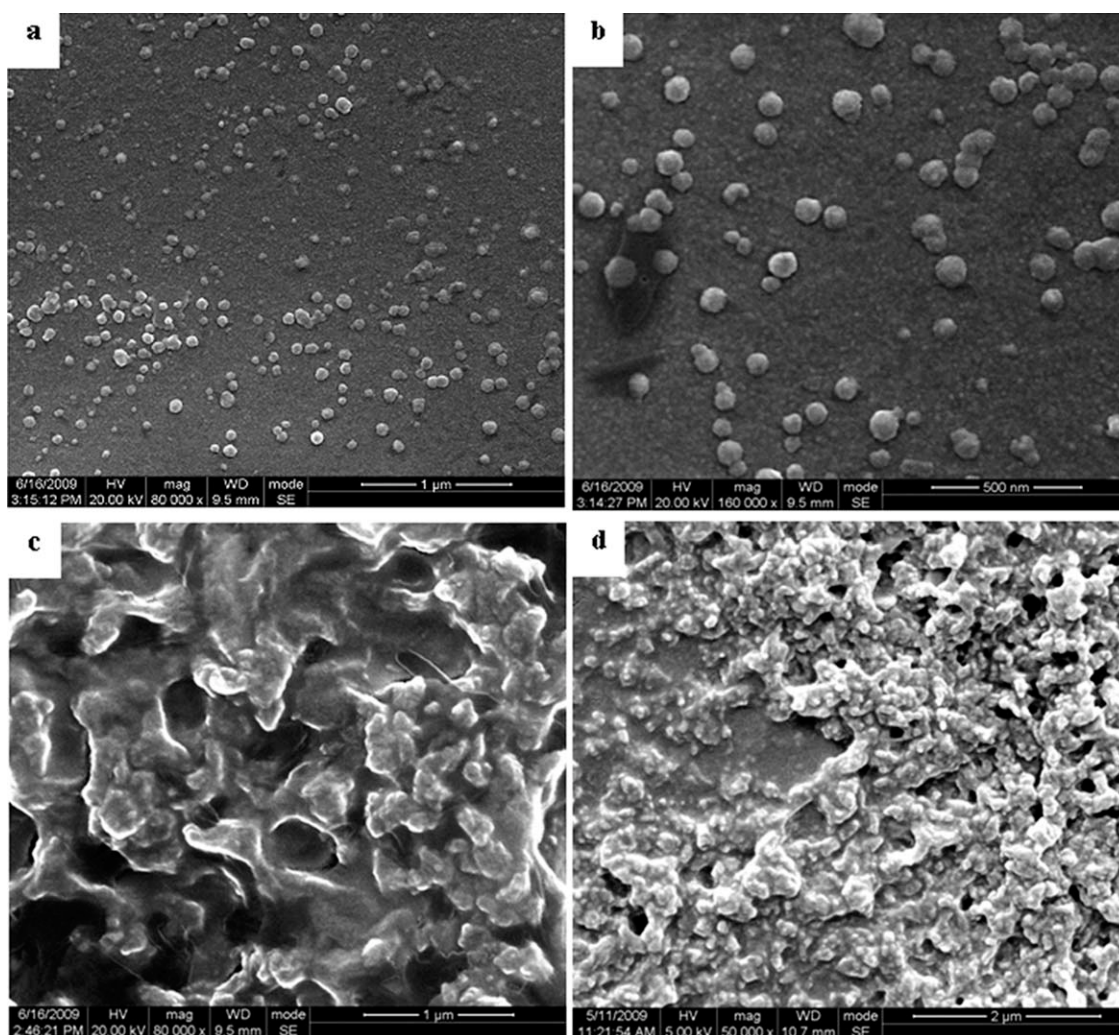
**Figure 2** SEM images of PEDOT particles prepared through ultrasonic irradiation (a,b) and conventional stirring (c,d).

in the thiophene ring. The peaks at 2800 to 3000 $cm^{-1}$ are partially ascribed to the aliphatic C—H stretching mode of the long alkyl tail of DBSA.[16] If taking the peak at 1629 $cm^{-1}$ as a internal standard, it can be noted that the peak intensity of aliphatic C—H stretching mode at 2800 to 3000 $cm^{-1}$ for the PEDOT sample obtained by ultrasonic irradiation [Fig. 3(c)] is higher than that by conventional stirring [Fig. 3(b)]. This result indicates that ultrasound can enhance the doping efficiency of DBSA in the PEDOT.
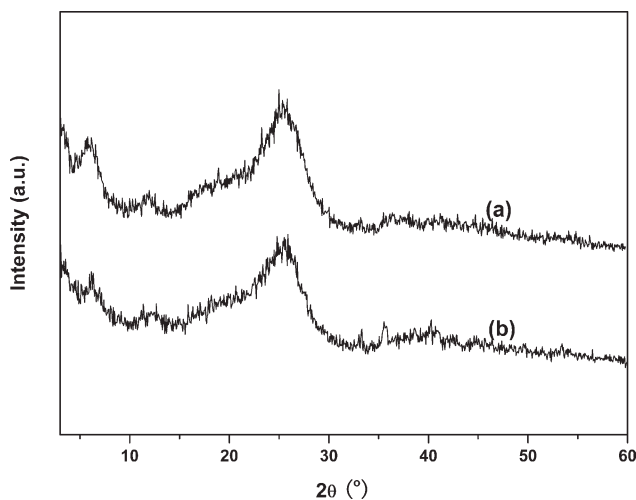
X-ray diffraction analysis

XRD patterns of PEDOT particles are shown in Figure 4. For both PEDOT samples prepared through ultrasonic irradiation and conventional stirring, the diffraction patterns are similar and the diffraction peaks were observed at the diffraction angle $2\Theta \approx$ 6.5, 12.8, and 26.2°, which are attributed to crystalline the plane (100), (200), (020) of PEDOT, respectively.[17–20] The results suggest both PEDOT samples

are semicrystalline. However, the PEDOT sample obtained through ultrasonic irradiation showed a slight higher diffraction intensity of the crystalline plane (100) at $2\Theta \approx 6.5°$ than that obtained through conventional stirring as shown in Figure 4(a,b), which indicates a more ordered structure of PEDOT.
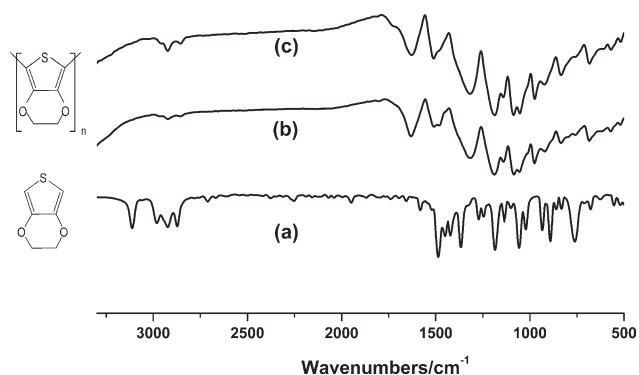


**Figure 3** FTIR spectra of the monomer EDOT (a) and PEDOT obtained through conventional stirring (b) and ultrasonic irradiation (c).

**Figure 4** X-ray diffraction patterns of the PEDOT obtained through (a) ultrasonic irradiation and (b) conventional stirring.

The enhanced doping level of DBSA under ultrasonication should account for this. PEDOT doped with DBSA can form a layer structure, which gives a intense peak in X-ray diffraction patterns at the low angle of $2\Theta \approx 6.5°$, and an increase in the doping level can strengthen this peak.[18–20]

### Thermogravimetric analysis

The TGA curves are shown in Figure 5. It shows that prepared PEDOT is stable up to 200°C. The thermal degradation started from 200°C, and major decomposition occurs in the temperature region between 300 and 450°C. The thermal degradation behavior is similar for both samples obtained through (a) ultrasonic irradiation and (b) conventional stirring. A similar TGA result of PEDOT prepared by anodic oxidation polymerization was previously reported by Choi et al.[2]
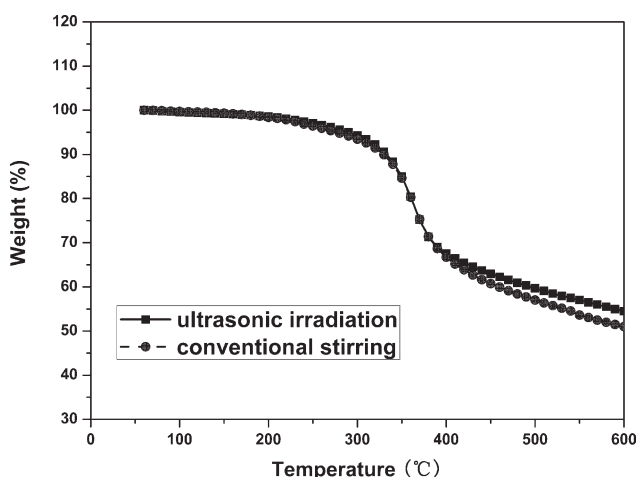


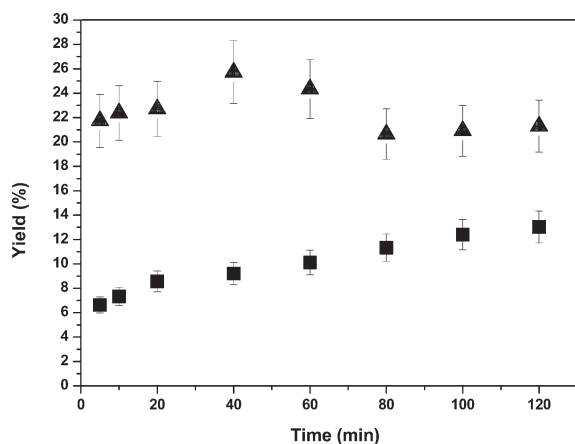**Figure 5** TGA curves of the PEDOT obtained through ultrasonic irradiation and conventional stirring.
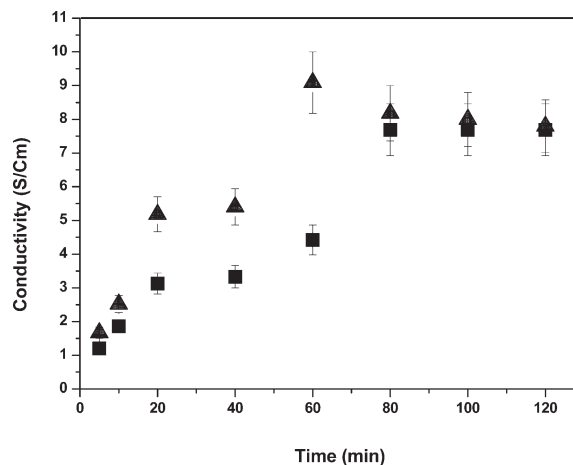
**Figure 6** Variation of the conductivity of PEDOT particles obtained through ▲ ultrasonic irradiation (temperature: 30°C, power output: 900 W) and ■ conventional stirring (temperature: 30°C) with the reaction time.

### Electrical conductivity and polymerization yield

#### Effect of time

The effects of ultrasound and conventional stirring on the conductivity of PEDOT particles were studied. The results were shown in Figure 6. Ultrasonic irradiation contributes to a slight increase in conductivity compared with conventional stirring. The reason is possibly that ultrasound contributes to produce more uniform spherical and smaller nanoparticles and to improve the doping degree of DBSA in PEDOT. The conductivity of the samples obtained by ultrasonic irradiation first increases, and then slightly decreases with the reaction time. The increase in the conductivity with time is related to the increase in the polymer field. The slight drop at longer time is possibly due to the degradation effects of ultrasonic irradiation.[5,21] On the other hand, the conductivity of the PEDOT particles obtained by conventional stirring increased with increasing the reaction time. When the reaction time reached 80 min, the conductivity of the samples nearly kept constant.

The variations of the PEDOT yield with the reaction time are shown in Figure 7. Ultrasonic irradiation contributes to the increase in PEDOT yield compared with conventional stirring. Under the ultrasonic irradiation, the conversion of EDOT reached ∼ 22% in 5 min, and then kept nearly constant. As a contrast, under the conventional stirring, the conversion of EDOT reached only ∼ 12% in 120 min. As mentioned above, ultrasonic cavitation can generate very high local temperature and pressure, a very rigorous environment for chemical reaction. Ultrasound can accelerate the diffusion and collision probability of monomer and reaction species, and

**Figure 7** Variation of PEDOT yield obtained through ▲ ultrasonic irradiation (temperature: 30°C, power output: 900 W) and ■ conventional stirring (temperature: 30°C) with the reaction time.

further enhance the polymerization rate of monomer EDOT.

### Effect of temperature

Figure 8 shows the effect of the reaction temperature on the conductivity and yield of PEDOT. The results showed that with increasing the reaction temperature, the PEDOT yield obtained by ultrasonic irradiation increased. Because an increase in the temperature will lead to enhance the diffusion coefficient of monomers in the aqueous media. The conductivity of PEDOT particles also increased with increasing the temperature in the low temperature range. When the reaction temperature is above 30°C, the conductivity of the PEDOT particles has no considerable change. The reason may be that the doping efficiency of DBSA in PEDOT reach constant at such temperature.[2]
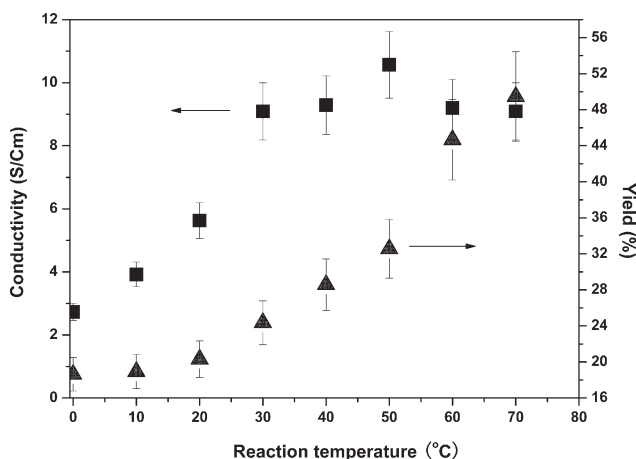


**Figure 8** Effect of temperature on the conductivity of the PEDOT particles obtained through ultrasonic irradiation (left) and PEDOT yield (right) (power output: 900 W, reaction time: 1 h).
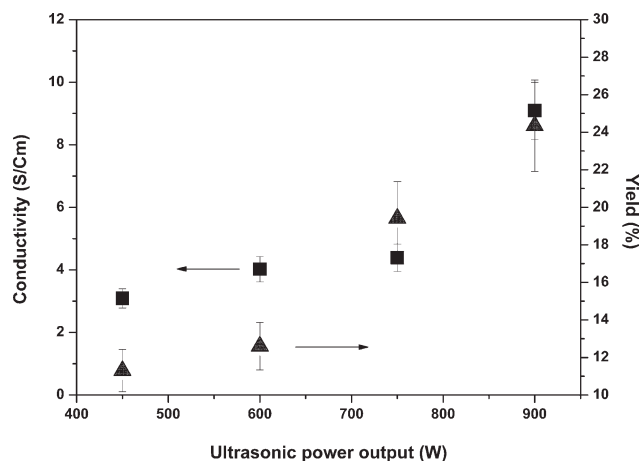


**Figure 9** Effect of ultrasonic power output on the conductivity of the PEDOT particles obtained through ultrasonic irradiation (left) and PEDOT yield (right) (temperature: 30°C, reaction time: 1 h).

### Effect of power output

For ultrasonically assisted polymerization, an important parameter affecting the formation of the PEDOT particles is the ultrasound power output. The polymerization of the EDOT was carried out using ultrasonic power output of 450, 600, 750, 900 W. Figure 9 shows the conductivity and yield of PEDOT obtained at different power output. With increasing power output, the conductivity as well as the yield of the samples increased with the power output. This should be attributed to the stronger sonochemical effects of ultrasonic irradiation at higher power output.

## CONCLUSIONS

Ultrasonic irradiation was successfully introduced to prepare the electrical conductive PEDOT nanoparticles. The PEDOT nanoparticles prepared by ultrasonic irradiation are uniform and spherical, and the particle size is in the range of 50–100 nm with narrow particle size distribution. Because of the multiple influences of the dispersion, emulsifying and disrupting effects, ultrasonic irradiation not only has a better control on the morphology of PEDOT particles compared to conventional stirring, but also enhances the polymerization rate of EDOT and the electrical conductivity of PEDOT particles. The electrical conductivity of prepared PEDOT is high up to 11 S/cm and the yield can reach ∼ 50%. This opens up a new approach to synthesize the PEDOT ultrafine particles.

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