

# Polypyrrole nanoparticles and dye absorption properties

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## **Abstract**

Polypyrrole (PPy) nanoparticles were prepared by using microemulsion polymerization processes at 3°C. Particle characterization was performed by using FTIR, elementary analysis, UV-VIS spectra and SEM. The size of the nano particles varied from about 50-100 nm to 100-200 nm with the change in concentration of surfactant from 0.8M to 0.44M. Polypyrrole nanoparticles were dedoped by a 10% NaOH solution, followed by a redoping process using a nuclear fast red kernechtrot dye, which has a sulfonate group. Dedoping changed the optical absorption properties of the nanoparticles.

*Keywords:* Polypyrrole; Nanoparticles; Absorption; Surfactant.

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## 1. Introduction:

Recently, nano-structured particles have received considerable attention as they have many potential applications in catalysis, chromatography, controlled release of drugs and pigment applications [1-2]. Due to small particle sizes, in the range of 10-100 nm, nanoparticles have large surface area for reactions and highly porous in sol form [3].

Conducting polymer nanoparticles, having a wide range of electrical properties, can be used in composites or films for applications in batteries, molecular electronics, conducting paints and photo-voltaic cells [4]. Polypyrrole (PPy) is one of the important conducting polymers with high electrical conductivity, good stability in air, and has been used in the preparation of nanoparticles with some degree of success. Synthesis of Fe<sub>2</sub>O<sub>3</sub> encapsulated polypyrrole nanoparticles [5] and colloidal dispersions of PPy using ultra-fine SiO<sub>2</sub> and SnO<sub>2</sub> in aqueous environment [6] have been reported.

In the preparation of polymer nanoparticles, polymerization reactions are often carried out in a microemulsion environment (microemulsion polymerization). At relatively low temperatures, the mobility of surfactant is restricted, reducing the inner volume of micelles, which encapsulate the monomer and the oxidant. Reduced micelle volume results in reduced nanoparticle size. Microemulsion polymerization method allows particles to transfer into spherical aggregates through the surfactant template. Some research groups have reported the preparation of conducting polymer nanoparticles by using microemulsion polymerization processes and reported particle sizes in the range of 50 to 200nm [7]. There are two reasons for using the surfactants in the polymerization. One is the creation of a micro reactor vessel, where monomer is restricted in a localised environment formed by encapsulation by the surfactant and the other reason is to improve the physical properties of polymers such as conductivity, stability, solubility in organic solvents, and processibility [8].

It is important to be able to remove the dopant anion from the conducting polymer matrix to improve the dye absorption of the conducting nanoparticles. For polypyrrole, it is difficult to remove the acidic dopant from the polymer matrix because of the

affinity of the dopant anion to the polypyrrole chain and inaccessibility of the dopant molecules in the polymer matrix. However, if the particle size is reduced to nano level the dedoping of polypyrrole could be easier due to increased surface to volume ratio. Dedoping of polypyrrole in the nano scale has not been reported.

In this paper, we report the preparation of the polypyrrole (PPy) nanoparticles by using microemulsion polymerization. Nanoparticles were functionalized by an acid dye using dedoping followed by a redoping process.

## **2. Experimental**

### *2.1 Materials*

Pyrrole (AR), ferric chloride (AR), dodecyltrimethyl-ammonium bromide (DTAB) and nuclear fast red kernechtrot ( $C_{14}H_8NNaO_7S$ ) were obtained from Aldrich and were used as received.

### *2.2 Instruments*

FTIR and UV-Visible spectra were obtained from a Bruker Vertex 70, FTIR spectrometer, and Cary 3 UV-Visible spectrophotometer, respectively. Nanoparticles were observed under LEO1530(FEG) Scanning Electron Microscope (SEM).

### *2.3 Polypyrrole nanoparticle preparation*

Equal amounts of pyrrole were added to solutions containing different amounts of dodecyltrimethyl-ammonium bromide (DTAB) as surfactant and ferric chloride as oxidant. Both 0.44M and 0.8M of dodecyltrimethyl ammonium bromide (DTAB) were added into 40ml of deionized water at 3 C in two different experiments. 1.0g (14.9mmol) of pyrrole was added dropwise and stirred at 3 C for 2 hours. Then 9.25g (34.3mmol) of ferric chloride was added into the solution. The polymerization reaction was subjected to high speed stirring for 3 hours. The solid product was obtained by separating the reaction solution in a separation funnel, and methanol was

added into the funnel to wash out the surfactant and residual ferric chloride. The black powder was dried in a vacuum oven at room temperature. Elemental analysis results were C (51.83%), H (3.44%), and N (16.56%). The ratio is very similar to the composition of pure polypyrrole. The conductivity of nanoparticle pellets was measured by using a four point probe.

#### *2.4 Dedoping and redoping the polypyrrole nanoparticles*

The nanoparticles were dedoped by dispersing them into a 10% NaOH solution. In order to achieve the maximum dedoping yield, an additional amount of about 20 ml NaOH solution was added to 1 mg of nanoparticles. The dedoping process is conducted at room temperature over night. Then, the dedoped particles were separated by using a funnel. Nanoparticles were repeatedly rinsed by distilled water followed by drying in vacuum oven at room temperature.

The dedoped nanoparticles were dispersed in a dye solution with a concentration of  $1.49 \times 10^{-2}$  mmol/l. The red dye colour disappeared quickly upon mixing. The nanoparticles were separated and dried by using the same method.

Elemental analysis results for PPy nanoparticles by 10% NaOH treatment were C (51.57%), H (3.07%) and N (14.24%). The ratio is very similar to the composition of pure polypyrrole.

### **3. Results and discussions**

#### *3.1. PPy nanoparticle size and morphology*

The surfactant (DTAB) was stirred in the deionized water to form a uniform solution. The monomer (pyrrole) was dripped into the solution while stirring. When the oxidant (ferric chloride) was added into the solution, the solution changed colour from yellow to green and finally to black. With low surfactant concentrations of less than 0.2M the nanoparticles had poor dispersion and formed agglomerates.

Conversely, when surfactant concentration was higher than 0.8 M, there was no yield of PPy nanoparticles.

When nanoparticles were prepared by using 0.44 M DTAB, the particle size was about 100-200nm with a spherical morphology (Fig. 1). When the concentration of surfactant was increased and the reaction temperature was decreased, the particle size diminished and the shape became elongated rather than round (Fig. 2). The size of PPy nanoparticles prepared from 0.8 M DTAB surfactant at 3 C was around 50-100 nm. This result indicated that the particle size and morphology depend on the concentration of the surfactant. Polypyrrole nanoparticles are formed in micelles, which encapsulate the pyrrole monomer and the ferric chloride. Thermodynamically stable micelles are formed at high surfactant water ratios. High concentration of surfactant in the microemulsion polymerization process leads to smaller micelle dimensions and hence smaller PPy particle size. A synthesis temperature of 3°C was preferred rather than room temperature as lower reaction temperatures result in smaller micelles, which restrained the growth of PPy particles and gave rise to smaller nanoparticles.

Fig. 1. PPy nanoparticles. Particle size: 100-200 nm.

Fig. 2. PPy nanoparticles. Particle size: 50-100 nm.

The histogram seen in Figure 3 shows a lower particle size distribution for the sample obtained by using surfactant/pyrrole ratio of 0.80 at 3°C. The average particle size is 67 nm, with the distribution ranging from a minimum of 7.5 nm to a maximum of 127.5 nm.

Fig. 3. Size distribution of PPy nanoparticles.

Table 1 lists the average size of PPy nanoparticles at different temperature and surfactant concentrations. By carefully selecting the experimental conditions, the particle size can be decreased further. For example, when the lower synthesis temperature (3°C) and a high surfactant concentration were accompanied by a high speed stirring, an average particle size of 10-15 nm was achievable (Fig. 4).

Table 1. The particle size and physical properties of the nanoparticles from different preparation conditions.

Fig. 4. Further reduction in the particle size of PPy nanoparticles.

### **3.2. FTIR transmission spectra**

The FTIR transmission spectra of the dedoped PPy nanoparticle powders in KBr showed characteristic polypyrrole peaks at 1545, 1458 and 788  $\text{cm}^{-1}$  for ring stretching, conjugated C-N stretching, and C-H wagging vibrations, respectively. When the PPy nanoparticles were reacted with NaOH, the FTIR spectrum showed characteristic peaks similar to untreated particles. This indicates that NaOH treatment does not affect the polypyrrole structure.

Elemental analysis results confirmed that about 2.7% chloride was removed after treatment with NaOH. Although NaOH is a strong base, it can not remove all the acid ions in the polypyrrole matrix, since polypyrrole is hydrophobic and has a dense matrix structure.

### 3.3. UV-VIS and absorption ability

When 1mg ( $1.49 \times 10^{-2}$  mmol) of the nanoparticles were added into the dilute dye solution (10ml,  $1.25 \times 10^{-4}$ M), the red colour rapidly disappeared. UV visible absorption in Figure 5 shows that the concentration of the dye decreased after adding the PPy nanoparticles in the solution. The UV-VIS spectra of the nanoparticles confirmed that a small dye peak appeared at 475-550 nm after the PPy particles were immersed into the dye solution (Fig.5).

Fig. 5. UV visible absorption spectra of PPy nanoparticles without NaOH treatment.

After NaOH treatment, the PPy nanoparticles showed stronger absorption (Fig.6). This suggests that removal of  $\text{Cl}^-$  from PPy nanoparticles increased the dye uptake of the polymer. From the optical absorption coefficient of the dye, we can estimate the quantity of dye uptake by the nanoparticles. The absorption capabilities of the nanoparticles to the dye are listed in Table 1. It is clear that the absorption ability of the NaOH treated nanoparticles is about 1.4 times larger than the untreated nanoparticles. In other words, absorption properties of PPy nanoparticles increased about 40% after being treated in NaOH solution. Conductivity also increased about 20% after dye redoping.

Fig.6. UV visible absorption spectra of PPy nano particles after 10% NaOH treatment.

### 3.4. Conductivity of polypyrrole nanoparticles

Conductivity of PPy nanoparticles reduced slightly from 0.077 to 0.06 S/cm after 10% NaOH treatment. This is attributed to partial removal of  $\text{Cl}^-$  from the surface of PPy nanoparticles by NaOH (dedoping). The  $\text{Cl}^-$  ion acts as a dopant and hence

improves the conductivity of the polymer. Partial removal of the dopant anion increases the electrical resistivity of the particles. The reduction of Cl<sup>-</sup> concentration upon dedoping can be clearly observed from the elemental analysis, which showed that weight percent of Cl<sup>-</sup> before NaOH treatment was about 15.2 whereas after NaOH treatment was about 12.5.

The red dye solution (C<sub>14</sub>H<sub>8</sub>NNaO<sub>7</sub>S ) was used to redope the nanoparticle. As the red dye has a -SO<sub>3</sub><sup>-</sup> group, it was able to function as a dopant anion and improve the conductivity of PPy nanoparticles. PPy nanoparticles were added to a highly concentrated solution of the red dye over night, resulting in a 20% increase in the electrical conductivity. The dye was used to replace the chloride ion and redoping the particles by dye molecules, which have sulfonic anion groups resulted in improvement of conductivity. The use of such functional dyes in this process will modify optical absorption spectra of the PPy and introduce additional functions such as UV resistance and photo induced electron transport properties. Dye induced charge transfer would reduce the band gap. In this work a dye with sulfonate group was specially selected to improve the electrical and UV stability of PPy nanoparticles. Future work will focus on utilisation of this method to functionalize the conducting polymer nanoparticles.



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## **Figure and Table Captions**

Figure 1. PPy nanoparticles. Particle size: 100-200 nm.

Figure 2. PPy nanoparticles. Particle size: 50-100 nm.

Figure 3. Size distribution of PPy nanoparticles.

Figure 4. Further reduction in the particle size of PPy nanoparticles.

Figure 5. UV visible absorption spectra of PPy nanoparticles without NaOH treatment.

Fig.6. UV visible absorption spectra of PPy nano particles after 10% NaOH treatment.

Table 1. The particle size and physical properties of the nanoparticles from different preparation conditions.

## Figures and Tables

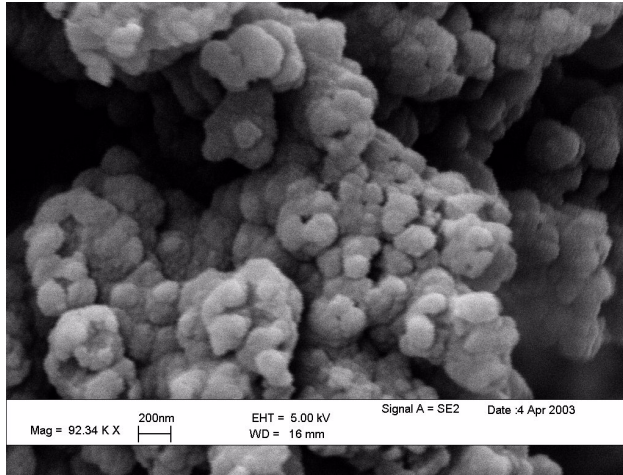


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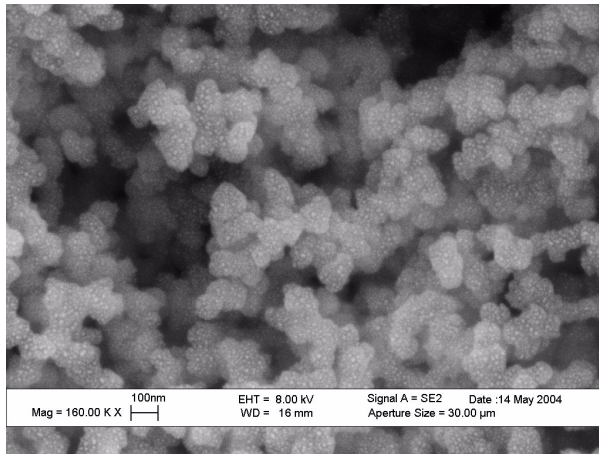


Figure 2. PPy nanoparticles. Particle size: 50-100 nm.

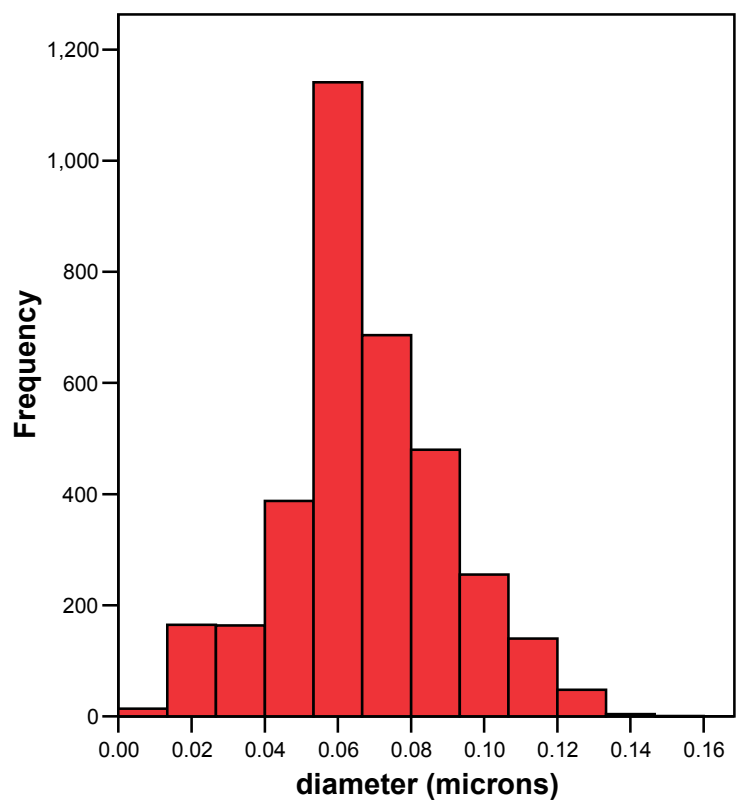


Figure 3. Size distribution of PPy nanoparticles

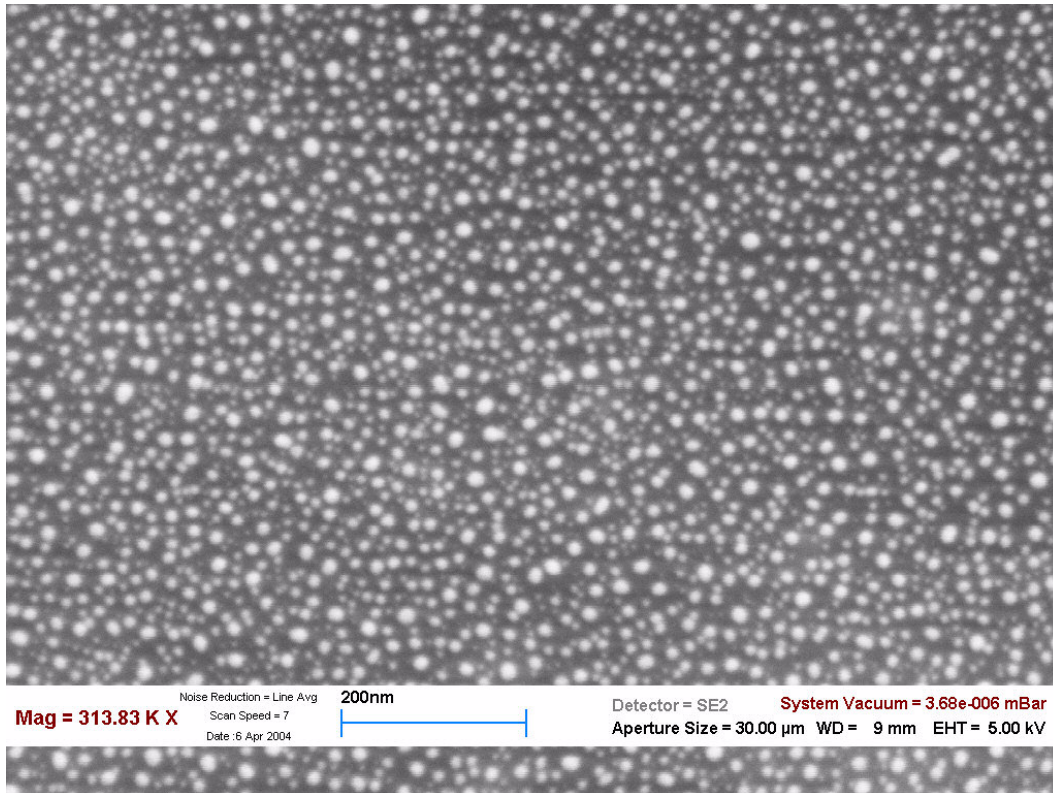


Figure 4. Further reduction in the particle size of PPy nanoparticles.

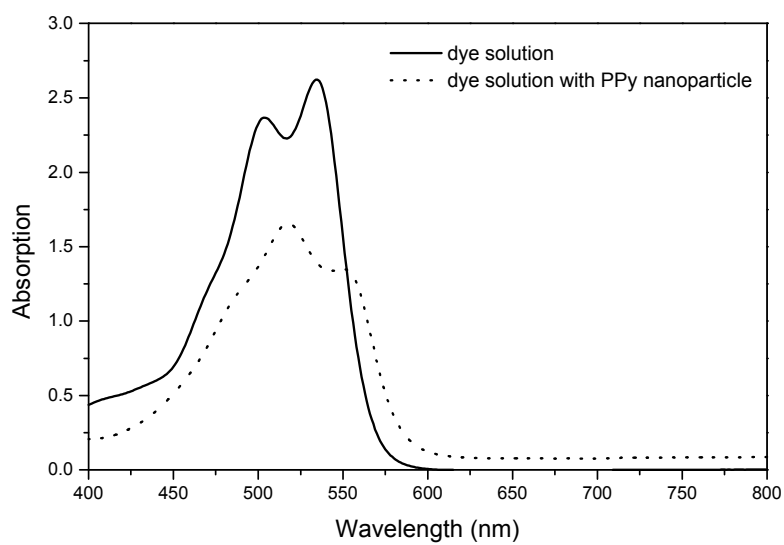


Figure 5. UV visible absorption spectra of PPy nanoparticles without NaOH treatment.



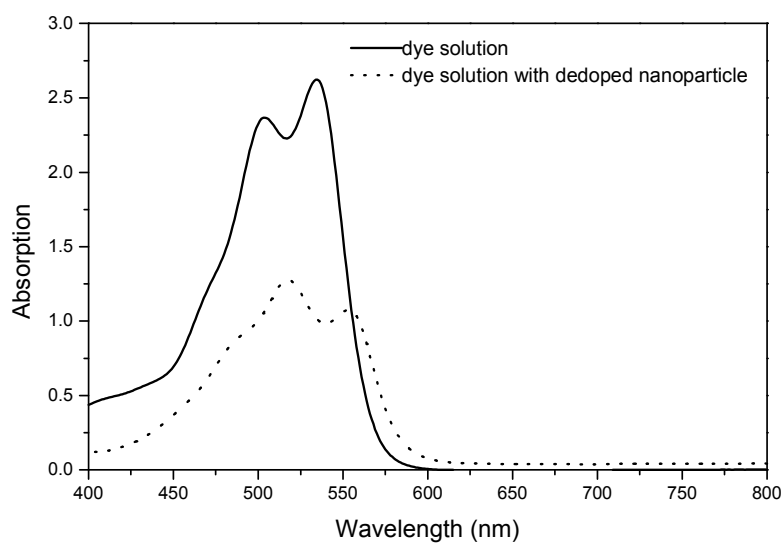


Fig.6. UV visible absorption spectra of PPy nano particles after 10% NaOH treatment.

Table 1. The particle size and physical properties of the nanoparticles from different preparation conditions.

Surfactant/ pyrrole	T(°C)	Average Particle size (nm)	Std Dev	Absorption (mg/mg)	Conductivity (S/cm)
0.44	Room temp	149	38.10	46.7	0.077
0.44	3	119	42.6	46.7	0.077
0.80	3	67	22.5	46.7	0.077