Fabrication and Characterization of Polypyrrole Nanoparticles for Supercapacitor Electrode Materials

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Abstract: In the present work Polypyrrole nanoparticles are synthesized by oxidative polymerization method in the presence of aqueous nitric acid(HNO₃) as solvent and ferric chloride (FeCl₃) as oxidizing agent. During polymerization process the solvent and oxidizing agents played a crucial role in modifying the nanostructures of polypyrrole (PPy). Scanning electron microscopy (SEM) revealed the uniform globule morphology and narrow size distribution of produced PPy particles in acid medium. Combined effect of solvent and oxidant are advantageous for the production of PPy nanoparticles (PPyNPs) with a yield of 90%. Four point probe method and strong UV-Visible band confirm high electrical conductivity of PPy due to a large π-conjugation in the polymer structure. The nature and composition of PPyNPs were confirmed by X-ray diffraction (XRD) spectrometer and Fourier transform infrared spectroscopy (FTIR). Electrochemical properties were confirmed by cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) spectra. CV and GCD spectra illustrate the excellent electrochemical properties of PPyNPs which show higher specific capacitance of 398 F g⁻¹ at 100 mAg⁻¹ current density. It has wide applications in electronic and electrochromic devices, sensors, membrane separation, corrosion protection, chromatographic stationary phase, rechargeable batteries, drug delivery, supercapacitors, lightweight batteries and microwave shielding etc.

Keywords: Polypyrrole; Cyclic voltammetry; Galvanostatic charge discharge; FTIR spectroscopy; Nanoparticles.

1. Introduction
In recent years, conducting polymers a specific class of polymers, viz. polyaniline, polypyrrole, polythiophene, are an attractive class of versatile materials. Among this conducting polymers, polypyrrole (PPy) is a promising polymer for many applications [1] such as supercapacitors[2], solar cells [3], biosensor [4], electrode bater [5], gas sensors [6], micro actuators[7], electrochromic devices [8], electromagnetic shielding devices [9], anticorrosion coatings [10], light emitting diodes (LED) [11], etc. because of their higher electrical conductivity, high charge densities, high doping-rate during charge-discharge process, color changes associated with their oxidation state, variable electro-magnetic parameters and lower cost(compared to noble metal oxides), facile synthesis through electrochemical and...
chemical processing, good environmental stability and tunable electrical and optical properties, than many other conducting polymers [12-15]. Polypyrrole nanoparticles have been manufactured by electrochemical and chemical methods in the presence of numerous solvents such as water, chloroform, methanol, ethanol, aqueous HNO₃, HCl, acetonitrile, tetrahydrofuran, benzene and ethylene glycol with numerous oxidizing agents like (FeCl₃), hydrogen peroxide, ammonium persulfate (APS), ferric nitrate, etc. [16-18]. However, synthesis of polymers by electrochemical process is a complex process that affects the yield of PPy through numerous factors such as the concentration and existence of monomer-electrolyte, solvent, pH, temperature, electrode, cell conditions and applied potential. Therefore, optimizing all these parameters in one experiment is difficult, but chemical polymerization method does not require any specialized instrument and is applicable for producing these polymers in large quantities. It is rather a fast process for high yield synthesis of polypyrrole [19-20]. Recently, nano sized conductive polymers such as nanorods, nanotubes, nanofibers and nanowires are being paid attention due to their high surface area and small size, leading to superior application for optoelectronic nano-devices [21]. Thus, in the present investigation, a systematic study has been carried out to observe the structure morphology, conductivity and electrochemical properties of polypyrrole thin films synthesized by using the chemical oxidative polymerization method.

2. Experimental

2.1. Materials

Pyrrole monomer, Sodium dodecyl sulfate (SDS), N-methyl-2-pyrrolidone (NMP) and poly tetrafluoroethylene (PTFE) were purchased from Sigma Aldrich. The commercially available pyrrole was purified by a simple distillation process to obtain a colorless pure liquid. Ferric chloride (FeCl₃) purchased from Loba chemie, Mumbai, India and Nitric was purchased from and Merck limited, Mumbai, India were used as received.

2.2. Synthesis of PPy nanoparticles

A basic and widely used technique for the synthesis of polypyrrole nanoparticles is as follows: first, the mixture of pyrrole monomer (2.5 mM) and SDS (0.412 g) was added to a 75 mL HNO₃ (0.35 M) aqueous solution in an ice bath at 0°C. The oxidant solution was prepared by mixing FeCl₃ (5 mM) in 25 ml aqueous HNO₃ (0.35 M) and subsequently added drop wise to the above solution kept in the ice bath. The reaction mixture was placed in the ice bath maintained at 0°C for 24 h with continuous stirring. Eventually, the PPy nanoparticles (PPyNPs) produced were isolated by filtration and washed away with excess of de-ionized water. The reaction mixture was centrifuged four or five times after the reaction until the solution was colorless.

2.3. Fabrication of PPyNPs enrobed glassy carbon electrode

A GCE was polished to a mirror with 0.3 and 0.05 μm polishing paper and alumina pastes before modification. The electrode was then ultrasonically rinsed in ethanol and sequentially deionized water. The electrode materials were prepared by mixing 85% of the PPyNPs, 10% of activated charcoal and 5% of poly tetrafluoroethylene (PTFE) as binder in few drops of NMP then the obtain slurry (5μL) were lowered with a microsyringe on the surface of glassy carbon electrode (GCE) and allowed to dried at 70°C in the oven for 20 minutes. The electrode was placed closed firmly over a small bottle during the process, thus gradually evaporating water and producing more consistent films. The resulting electrodes have been cleaned with water and prepared for further tested at room temperature. The cyclic voltameter and galvanostatic charge discharge characterization of the electrode was carried out in the presence of 1.0 M sulfuric acid electrolyte.
2.4. Characterization
The structure and morphology of PPyNPs was analyzed by scanning electron microscope (ZEISS EVO-50 SEM machine) operating at an accelerating voltage of 20kV. Fourier transform infrared spectra of prepared sample were taken by an Agilent Technologies Cary 630 FTIR spectrophotometer. XRD data of PPy powders were obtained from X-ray diffractometer (PANalytical XPERT –PRO). The conductivity of the PPyNPs were measured by four-probe conductivity meter (Model: CCS-01 programmable current source and a DMV-001 microvoltmeter supplied by SES Instrument Pvt. Ltd. India). Electrochemical measurements were performed on Metrohm Autolab (MULTI AUTOLAB M204) using three electrode assemblies consisting of a platinum plate being used as counter electrodes, a standard calomel electrode (SCE) being used as a reference electrode and PPyNPs enrobed glassy carbon electrode (PPy-GCE) being used as a working electrode. The electrochemical output of the working electrode was evaluated by using CV and GCD tests performed between 0.0V to 0.8V in 1M H₂SO₄ electrolytic solution.

3. Result and Discussions
3.1. Morphological analysis
The scanning electron micrographs (Fig.1 (a) & (b)) of the PPyNPs show their globular structure. It can be clearly seen from the SEM micrographs that the spherical PPy nanoparticles are of <150 nm size and are almost uniform in structure and distribution [22].

Figure 1. (a) & (b) SEM images of PPy nanoparticles at different magnification

3.2. FTIR analysis
The FTIR spectrum of PPy nanoparticles (Fig. 2) showed charge carries bipolaron bands at 928 and 1210 cm⁻¹ indicating that the PPy formed is in the oxidized state [23]. The strong peaks between 1500 to 1400 cm⁻¹ are assigned to fundamental vibration of pyrrole ring [24-25]. The peak 3445 cm⁻¹ is assigned to N-H stretching vibration from pyrrole [26].
3.3. XRD analysis
XRD diffractogram (Fig.3) of the PPy nanoparticles showed a broad peak centered at 2θ value around 26 confirming amorphous nature of PPyNPs[25-26].

Figure 3. XRD spectra of PPy nanoparticles.
3.4. Conductivity studies
The conductivity of PPy nanoparticles as high as 39 S/cm has been obtained which is due to the formation of nano sized particles because of the presence of sodium dodecyl sulfate (SDS) which act as an anionic surfactant. In the present study, the conductivity of PPyNPs is much higher than that of other reported method [27].

3.5. Electrochemical studies
The electrochemical properties of the PPy nanoparticles were examined by cyclic voltammetry and galvanostatic charge discharge spectroscopy. The CV spectra of PPy-GC electrode at different scan rates are shown in Fig.4a. With the increase in the scan rates, current density was also increased. The shape of the curve is elliptical, which shows its involvement of high current. Fig. 4(b) displays the GCD curves of the PPy enrobed GC electrode. The specific capacitance of PPy-GC electrode was measured by galvanostatic charge discharge spectra using the equation (1)

\[ C_s = \frac{I \times \Delta t}{m \times \Delta V} \]

Where \( \Delta t \) represents discharge time, \( \Delta V \) is discharge voltage, \( I \) represent current and \( m \) is mass of electrode material.

The specific capacitance of PPy-GC electrode at 100mAg\(^{-1}\) current density is about 398 F g\(^{-1}\) which confirms the good electrochemical performance of PPy nanoparticles.

![Figure 4](image-url)

**Figure 4.** (a) Cyclic voltammetry (CV) spectra of PPy nanoparticles with different scan rate; (b) Galvanostatic charge discharge (GCD) spectra of PPy nanoparticles at 100mAg\(^{-1}\) current density in 1M H\(_2\)SO\(_4\) electrolyte.

4. Conclusions
The polypyrrole was synthesized using oxidative chemical polymerization method in the presence of FeCl\(_3\) as oxidizing agent. The PPy films had a uniform spherical morphology which was confirmed from SEM. The composition and amorphous nature of the PPy nanoparticles are confirmed by FTIR and XRD techniques. CV and GCD spectra illustrate the excellent electrochemical properties of PPy nanoparticles which show higher specific capacitance of 398 F g\(^{-1}\) at 100mAg\(^{-1}\) current density. The proposed work has
been applied successfully in electronic and electrochemical devices because of higher electrical conductivity of PPyNPs.

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