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A facile method to synthesize polypyrrole nanoparticles in the presence of natural organic phosphate



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ABSTRACT

The conductive polymers with unique nanostructures have attracted intense interest due to their potential application. Here the well-defined polypyrrole nanoparticles were facile fabricated via the facile chemical oxidative polymerization of pyrrole with high feeding ratio of phytic acid. Phytic acid is a renewable resource and a natural carbohydrate compound with a vast number of phosphate groups from plant which was used as the template and dopant for the nanostructured conductive polymer for the first time. The samples exhibit the well-defined nanoparticles observed by scanning electron microscope (SEM) and atomic force microscope (AFM). The PPy nanoparticles were achieved and outstanding electrical conductivity as high as 5263 S m^{-1} was obtained with the feeding mass ratio of phytic acid: pyrrole=3:7. Furthermore, the polypyrrole nanoparticles were characterized with Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), and electrical conductivity techniques.

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1. Introduction

During the last decade, the focus on the use of intrinsically conductive polymers (ICPs) in organic electronic devices has led to the development of a totally new class of smart materials [1–3]. Electronic devices working at high operating frequencies, such as fast computers and cellular phones, require materials that combine good dielectric properties with both excellent mechanical strength and ease of processing [4,5]. Polypyrrole (PPy) is one of the most widely investigated conductive polymers because of its remarkable thermal and environmental stability and good electrical conductivity, which is favorable for various applications such as batteries [6], solar cells [7], supercapacitors [8], actuators [9], sensors and shielding of electromagnetic interferences [10], etc. However, some potential applications have not yet to be exploited because of its insolubility and poor processability. In order to overcome these disadvantages, various approaches, such as preparing PPy with size in nanometer scales [11], doping PPy base with a functionalized protonic acid [12], have been developed. By far, many PPy nanoparticles dispersed in solutions have been prepared by polymerization of pyrrole in water in the presence of steric dopants such as poly(vinyl alcohol), polyvinylpyrrolidone,

sodium poly(styrene sulfonate), which impede agglomeration of the PPy nanoparticles [13–17]. The size and stability of PPy nanoparticles are influenced by the structure, molecular weight and concentration of the dopants. However, there are only a few reports about PPy doped with phosphoric acid derivative and they exhibit conductivity below 10 S m^{-1} [18,19].

Phytic acid ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$, also called “inositol hexaphosphate”, IP_6 —for short) is an organic macromolecule consisting of 24 oxygen atoms, 12 hydroxyl groups, and 6 phosphate carboxyl groups. IP_6 is mostly found in legume seed, cereal grains, nuts, and beans [20,21] and which widely used as cleansing agent, water treatment agent, food additives and cosmetic additive, has been proved that it is non-toxic to human and “green” to environment [22]. The strong antioxidant and non-toxic properties of phytic acid also make this compound distinctive and resourceful for using as a food preservative. Phytic acid is usually added to fruits and vegetables to prevent spoilage of these products. In U.S. sodium phytate was recognized as GRAS substance and has been applied as a preservative for baked goods since 1997 [23]. The development and utilization of phytic acid, as a green project, has a vast prospect. It is reported that PPy films were deposited on copper from phytic acid solution via electropolymerization for corrosion protection of copper. Although this film offered corrosion resistance, it was not suitable for mass production, and not suitable to use as filler to anticorrosion coatings. To the best of our knowledge, there has been no report about the chemical oxidative

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polymerization of pyrrole with phytic acid as template and dopant, and the effect of phytic acid on the formation and properties of the PPy nanoparticles by far.

In this paper, high conductive PPy nanoparticles with conductivity hitting 5263 S m^{-1} have been developed with IP₆ as the dopant. The as-prepared nanoparticles were characterized by FTIR, TGA, SEM and AFM techniques. The preparation conditions were optimized to obtain the highest electrical conductivity with well-controlled nanoparticles morphologies. In addition, the growth mechanism of PPy nanoparticles in the presence of phytic acid was proposed.

2. Materials and methods

2.1. Materials

Pyrrole monomer (Acros Organics) dehydrated with calcium hydride for 24 h was distilled under reduced pressure before use. Phytic acid (70%), ammonium peroxydisulfate (APS, 99.9%), and absolute alcohol were supplied by Aladdin Chemical Reagent Co., Ltd., China. The double-distilled water was used throughout.

2.2. Preparation of PPy-IP₆ nanoparticles

A typical procedure for the preparation PPy nanoparticles is given for samples. Different amount of IP₆ was added to 100 ml of double distilled water in a 250 ml round-bottom flask and stirring until dissolved. Freshly distilled pyrrole (1.0 ml, 144 mmol) was added to the above solution, and the mixture was stirred for 45 min in ice-cold conditions to obtain a pale brown solution mixture. APS (0.9 g, 15 mmol) in 10 ml of double distilled water was added drop by drop to the above solution, and stirring was continued for 10 h under ice-cold conditions and a nitrogen atmosphere. The resulting precipitates were washed with deionized water and ethanol. Finally, the product was dried in vacuum at 60 °C for 24 h to obtain the desired PPy-IP₆ nanoparticles as a dark powder. The conditions of the polymerizations are given in Table 1.

2.3. Experimental techniques

The Fourier transform infrared (FTIR) measurements (Impact 400, Nicolet, Waltham, MA) were carried out with the KBr pellet method. Thermogravimetric analysis (TGA) was obtained with a TA Instrument Q500 thermogravimetric analyzer at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from 25 to 700 °C under a nitrogen atmosphere. The morphologies of the PPy-IP₆ samples were observed using scanning electron microscopy (SEM) (XL-20, Philips Corporation, Netherland). The PPy aqueous dispersions characterized with scanning probe microscope (AFM) (NT-MDT, Russia). The electrical conductivities of the PPy powders were measured using SDY-4 Four-Point Probe Meter (Guangzhou Semiconductor Material

Table 1
The conditions of the polymerizations investigated in this work.

Sample	Py (ml)	IP ₆ (mg)	Theoretic PPy content (%)	Yield (%)	Conductivity (S m^{-1})
S-1	1	50.9	95	83.2	532
S-2	1	107.4	90	77.1	3051
S-3	1	241.8	80	70.8	5263
S-4	1	414.4	70	64.5	2472

$$\text{Yield} = M_{\text{PPy-IP}_6} / (M_{\text{Py}} + M_{\text{IP}_6}) \times 100\%$$

Where $M_{\text{PPy-IP}_6}$ referred to mass of precipitate, M_{Py} the mass of pyrrole monomer, M_{IP_6} the mass of IP₆.

Academe) at ambient temperature employing the method on a pressed pellet according to the formula:

$$\sigma = 1/\rho = V/I = F_{(D/S)} \times F_{(W/S)} \times W \times F_{sp}$$

where σ referred to electrical conductivity, V is the voltage, I is the current, D is the diameter of the pellets, W is the thickness of the pellets, S is the average space between of the probes, $F_{(D/S)}$ is the amendatory coefficient of the diameter of the pellets, $F_{(W/S)}$ is the amendatory coefficient of the thickness of the pellets, and F_{sp} is the amendatory coefficient of the space between of the probes. The pellets were obtained by subjecting the powder sample to a pressure of 30 MPa. The reproducibility of the result was checked by measuring the electrical conductivity three times for each pellet. The temperature dependence of conductivity was determined by WDJ-1 Temperature Change Resistance Measuring Instrument (Institute of Chemistry the Chinese Academy of Sciences) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from 25 to 150 °C.

3. Results and discussion

3.1. Spectral analysis

The FTIR spectra of PPy-IP₆ samples are presented in Fig. 1. For the samples, the peaks at 1533 and 1464 cm^{-1} are associated with the C–C and C–N stretching vibration in the pyrrole ring. Additionally, the strong peak near 872 cm^{-1} presents the doping state of PPy, and the broad band at 1030 and 1300 cm^{-1} demonstrates the C–H and C–N in-plane deformation vibration and stretching vibrations, respectively. All results demonstrate almost the same peak positions of the main IR bands which are associated with the structure of the PPy [24–27]. Meanwhile, it is indicated that PPy has been doped with IP₆. We observed that the intensity of the 3400 and 974 cm^{-1} absorption band of –OH was increased with increasing IP₆ feeding ratio. Similar behaviors were also found the 974 cm^{-1} absorption band, which was attributed to the P–OH. More hydroxyl groups become accessible that helps to form the uniform PPy particles, and the result is confirmed in the section of morphological analyses.

3.2. Morphological analyses

The morphologies of the nanomaterials were recorded using SEM microscopy and AFM microscope. The SEM images of PPy-IP₆ sample at higher magnification reveal the presence of globular particles as shown in Fig. 2. The particle size of the PPy-IP₆ powders changed smaller from submicrometer to tens nanometers

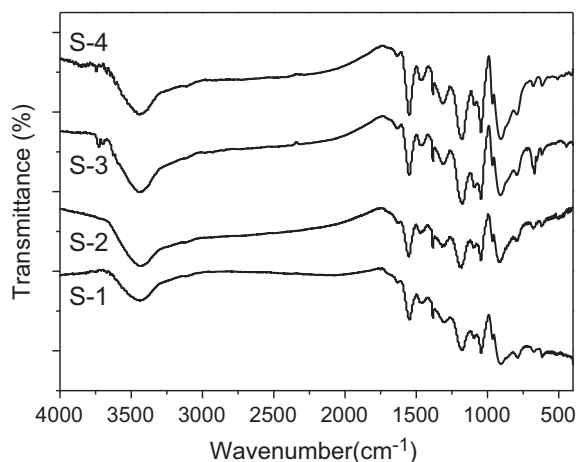


Fig. 1. The FTIR spectra of PPy-IP₆ samples.

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