

Preparation and Characterization of Functional Polypyrrole Particles

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Introduction: Conductive polypyrrole (PPy), because of its chemical and environmental stability, biocompatibility, electrical conductivity and ionic exchange property, has gained significant interest for its potential applications in fuel cells, biosensors, drug delivery and biomaterials [1]. Pyrrole as a monomer has various derivatives based on which functional PPy can be synthesized. While such functional PPy often has compromised electrical conductivity, its functional groups can be attached to biomolecules to greatly increase its capacity to interact with biological systems. Our objective is to synthesize PPy particles having the capability to covalently link with biomolecules such as proteins, peptides and nucleic acids, via surface functional groups on PPy. In this study, two types of functional PPy derivatives were synthesized and a facile emulsion polymerization was employed to prepare the functional PPy particles.

Materials and methods: 1-(2-carboxyethyl)pyrrole (Py-COOH) and N-(3-aminopropyl)pyrrole (Py-NH₂) were synthesized according to the procedures described by Azioune [2] and Abu-Rabeah [3]. The chemical structures of these two pyrrole derivatives were confirmed with Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). PPy-COOH and PPy-NH₂ were synthesized by water-in-oil (chloroform) (3:7) emulsion polymerization using dodecylbenzenesulfonic acid sodium (DBS) as emulsifier, FeCl₃ as oxidant and chlorine anions (Cl⁻) as dopant. The products were characterized with FTIR and X-ray photoelectron spectroscopy (XPS).

Results: Both carboxyl and amino groups were separately introduced to pyrrole via simple hydrolysis and reduction reactions using LiAlH₄ and 1-(2-cyanoethyl)pyrrole according to the literatures [2,3]. The molecular structure of Py-COOH and Py-NH₂ was confirmed according to FTIR and NMR analyses. As showed in Figure 1, it is clear that the FTIR absorption spectrum of Py-COOH recorded carboxyl C=O stretch at 1709 cm⁻¹. There are also strong and sharp absorptions at 3290 cm⁻¹ and 3375 cm⁻¹ corresponding to the NH₂ groups in Py-NH₂. The results of ¹H NMR and ¹³C NMR (Fig.2) analyses offered a further confirmation of the structures.

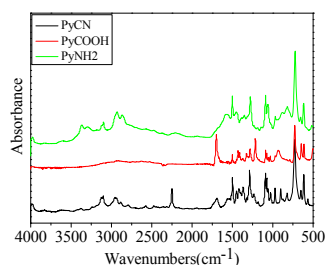


Figure 1. FTIR spectra of functional monomers Py-CN, Py-COOH, and Py-NH₂

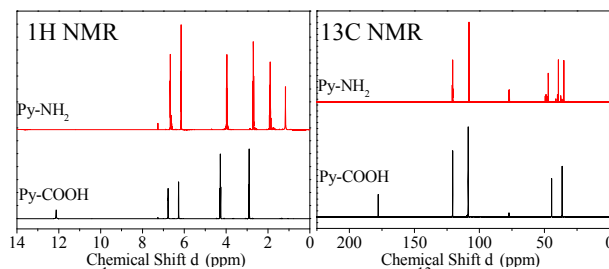


Figure 2. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) results of the functional pyrrole monomers.

The FTIR spectra of PPy and PPy-COOH showed the characteristic peaks of PPy-COOH at 1700 cm⁻¹ due to O=C=O, and peaks at 1184 cm⁻¹ and 1385 cm⁻¹ assigned to C-N stretching. Figure 3 shows the XPS results. The survey scan of XPS spectrum of PPy-COOH showed remarkably increased oxygen content in comparison with that of the pure PPy (25.5% for PPy-COOH vs. 10.3% for pure PPy), resulting from the abundant of COOH groups. With further analysis of the high resolution spectra of carbons (C_{1s}), a distinct peak appeared at the high binding energy side of the C_{1s}, which is characteristic of OC=O. XPS spectra also revealed the presence of Cl⁻ as dopant and appreciable amount of ferric ion probably detained by the strong electrostatic interaction with COO⁻.

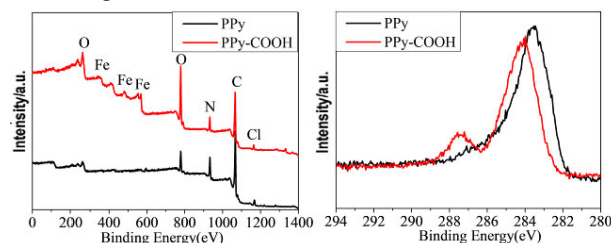


Figure 3. Full XPS spectrum and C_{1s} core level spectrum of PPy and PPy-COOH

Conclusions: Two types of pyrrole derivative monomers were synthesized via simple chemical reactions. By use of emulsion polymerization, PPy-COOH particles with appreciable quantities of carboxyl groups on the particle surface were prepared. The presence of ferric ions indicates the difficulty to completely remove all oxidant residuals. The functional and conductive PPy particles will be used to immobilize biomolecules and introduce electrical interaction through those molecules.

References:

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- [2] Ammar A, et al. *Lungmuir.* 2004;20:3350-3356
- [3] Khalil AR, et al. *Biomacromolecules.* 2005;6:3313-3318