Synthesis and Characterization of Functionalized Polypyrrole Particles

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Introduction:

Polypyrrole (PPy) has raised significant interest for its potential applications in fuel cells, biosensors, drug delivery and biomaterials, because of its electrical conductivity, chemical and environmental stability, biocompatibility, and ionic exchange property [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 to biomolecules such as proteins, peptides and nucleic acids, via surface functional groups on PPy. In this study, two types of functional pyrrole derivatives were synthesized and a facile emulsion polymerization was employed to prepare the functional PPy particles.

Materials and Methods:

1-(2-carboxyethyl)pyrrole (PPy-COOH) and N-(3-aminopropyl)pyrrole (PPy-NH_2) 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). Their respective copolymers with pyrrole, with different percentages of functional monomers, were synthesized through water-in-oil (chloroform) (3:7) emulsion polymerization using dodecylbenzenesulfoinc acid sodium (DBS) as emulsifier, $FeCl_3$ 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 $LiAlH_4$ and 1-(2-cyanoethyl)pyrrole according to the literatures [2,3]. The NMR (Fig. 1) and FTIR (Fig. 2) spectra confirmed the molecular structure of Py-COOH and Py-NH_2.

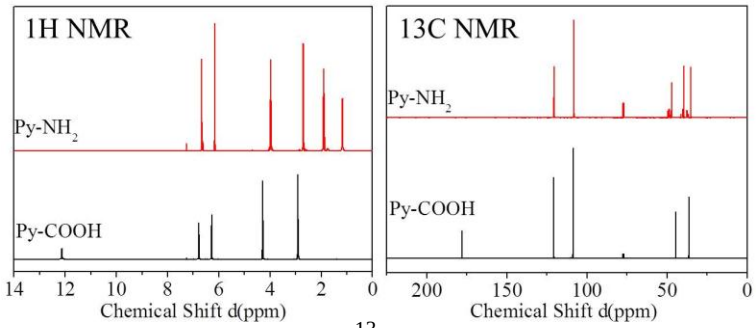

Figure 1. ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) results of the functional pyrrole monomers

Py-NH_2: ^1H NMR δ ($CDCl_3$): 1.17(s, 2H, NH_2), 1.91 (m, 2H, CH_2-2), 2.72 (t, 2H, CH_2-1), 3.97 (t, 2H, CH_2-3), 6.14 (d, 2H, CH-β), 6.66 (d, 2H, CH-α);^{13}C NMRδ ($CDCl_3$): 35.1 (CH_2-2), 39.4 (CH_2-1), 47.1(CH_2-3), 108.1(CH-β), 120.6(CH-α).

Py-COOH: ^1H NMR δ ($CDCl_3$): 2.90 (t, 2H, CH_2-1), 4.28 (t, 2H, CH_2-2), 6.27 (d, 2H, CH-β), 6.78 (d, 2H, CH-α), 12.13(s, H, COOH);^{13}C NMR δ ($CDCl_3$): 36.4 (CH_2-1), 44.5(CH_2-2), 108.7 (CH-β), 120.7(CH-α) , 177.6(COOH).

The results of FTIR analysis offered a further confirmation of the structures. As showed in Figure

2A, 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 NH_2 groups in Py-NH_2.

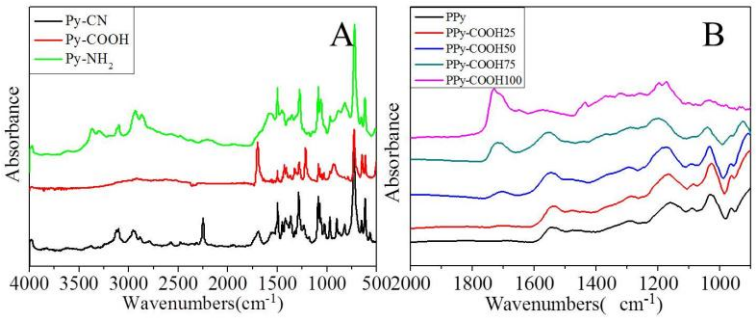

Figure 2. FTIR spectra of functional monomers (A):Py-CN, Py-COOH, and Py-NH2 ; polymers(B): PPy, PPy-COOH25(Py/Py-COOH=25/75), PPy-COOH50(Py/Py-COOH=50/50), PPy-COOH75(Py/Py-COOH=75/25), PPy-COOH100(Py/Py-COOH=0/100).

The FTIR spectra of polymers (Fig. 2B) showed the characteristic peaks at 1700 cm^{-1} due to O-C=O， and peaks at 1184 cm^{-1} and 1385 cm^{-1} assigned to C-N stretching. With the increase in Py-COOH component, the intensity of the absorption derived from C=O increases significantly. Figure 3 shows the XPS results. The survey scans of the XPS spectra 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 COOH groups. With the further analysis of the high resolution spectra of carbons (C_{1s}), a distinct peak appeared at the high binding energy side of the CCC, which is characteristic of OC=O. With the molar ratio of Py-COOH changing from 0 to 100%, the peak area at 288.9 eV also increased proportionally, which confirms the results of FTIR.

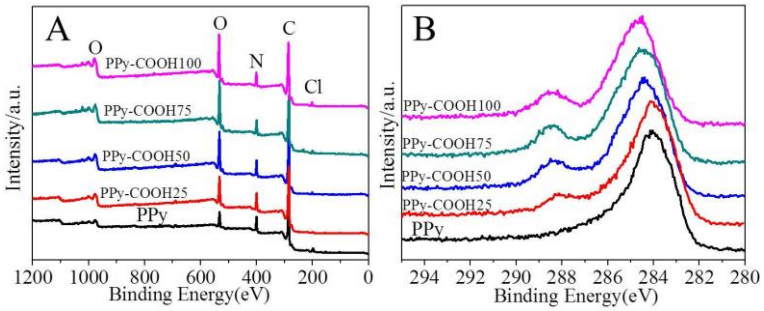

Figure 3. Full XPS spectrum and C_{1S} core level spectrum of PPy and PPy-COOH

Discussion:

Two types of pyrrole derivative monomers were synthesized via simple chemical reactions. Through emulsion polymerization, PPy-COOH particles with different quantities of carboxyl groups on the particle surface were prepared. Depending on the electrical conductivity and chemical reactivity of the copolymers, the optimal feeding ratio of the functional monomers will be further studied. The functional and conductive PPy particles will be used to immobilize biomolecules and to investigate the interactions between electrical field and the biomolecules.

References:

[1] Wei S, et al. Macromol. Chem. Phys. 2009;210:1379-1386
[2] Ammar A, et al. Lungmuir. 2004;20:3350-3356
[3] Khalil AR, et al. Biomacromolecules. 2005;6:3313-3318