Synthesis electroactive polyurea with aniline-pentamer-based in the main chain and its application in electrochemical sensor

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ABSTRACT

The electrochemical oxidation of ascorbic acid (vitamin C, AA) on the surface of carbon paste electrode (CPE) modified with electroactive polyurea (EPU) was studied by using cyclic voltammetry. EPU, with aniline-pentamer-based in the main chain, was synthesized from oligoaniline and p-phenylenediamine by oxidative coupling polymerization. The well-defined molecular structure of the oligoaniline was confirmed by LC-Mass, ^{1}H NMR and FTIR spectroscopy. The in situ chemical oxidation of the reduced form of soluble, EPU in N-methyl-2-pyrrolidone was monitored by UV–visible absorption spectra. Moreover, the electroactivity of the EPU was evaluated by performing electrochemical cyclic voltammetry studies. A linear relationship between the concentration of AA added and the change of peak current obtained, as shown by the linear calibration curve of the amperometric response of the CPE modified with EPU sensor to the concentration of AA ($R^2 = 0.996$, $n = 10$). The limit of detection for the EPU-CPE was estimated 6.1 μM at signal/noise of 3.

1. Introduction

Conducting polymers have been classified as a new class of materials in the past decades and attracted extensive research activities due to it exhibited broad spectrum of potential commercial applications in electronic, optical, and biological research fields [1,2]. Among these types of polymers, polyaniline (PANI) has been considered one of the most promising electrode materials due to its facile synthesis, environmental stability, unique electronic properties, and simple acid–base doping/dedoping chemistry [3]. PANIs have lately drawn intensive attention from polymer scientists, physicists, and material scientists because of their widespread technological applications e.g., including chemical sensors [4,5], gas-separation membranes [6], supercapacitors [7,8], and artificial muscles [9]. However, PANIs synthesized by conventional methods have low solubility in common solvents [10], and it is difficult to obtain them with structures defined precisely in terms of the oxidation state and the level of chemical doping.

Recently, electroactive polymers incorporated with aniline oligomers have attracted research attention because of their superior properties such as good solubility, mechanical strength and the ability to form films [11,12]. Several kinds of polymers with

conjugated oligoaniline in the main chains were prepared by Zhang et al. [13–16] through polycondensation or oxidative coupling polymerization. The fabricated copolymers not only contain well-defined conjugated segments, but also provide an opportunity to present a better understanding about the structure–property relationships and the conducting mechanism of conjugated polymers; knowledge which is limited by the complexity of their molecular structure and their poor solubility in organic solvents. Wei et al. and Chen et al. incorporated aniline oligomers into polylactide and obtained copolymers that showed good electroactive, biodegradability, and processing properties [17,18]. Wang and co-workers also prepared electroactive polymers containing aniline oligomer in the main chain and the side chain, which exhibited electrochemical properties, electrochromic behaviors and fluorescent sensing properties [19–23]. In our group, electroactive polymers have been well studied as electrochromic materials [24,25], anticorrosion coatings [26–28], and photoresponsive materials [29,30]. To the best of our knowledge, the practical applications of electroactive polymers used as electrochemical sensors have seldom been reported. In this study, we synthesized electroactive polyurea (EPU) through simple oxidative coupling polymerization and used it to modify the carbon paste electrode (CPE) as an electrochemical sensor. The electroactive properties enable EPU to have a potential to apply in the advanced sensors for detecting minimal amounts of chemical species such as the ascorbic acid (vitamin C, AA). AA is known for its anti-oxidant properties in foods and

drinks. It is also important in several human metabolic processes involving oxidation and reduction. Therefore, the detection of AA is important in pharmaceutical, clinical and food industries. Several techniques have been reported for the determination of AA, including spectroscopic, chromatographic, enzymatic and electroanalytical methods [31–34]. Among them, electrochemical methods are considered one of the best potential approaches because of their high sensitivity and simplicity. Here, we used AA as a model to test the practical applications of the EPU-CPE sensor. A linear relationship between the concentration of AA added and the change of peak current obtained, as shown by the linear calibration curve of the amperometric response of the sensor to the concentration of AA ($R^2 = 0.996$, $n = 10$).

2. Experimental

2.1. Materials and instrumentation

N-Phenyl-p-phenylenediamine (NPPD, 98%, Aldrich), hexamethylene diisocyanate (HDI, 98%, Alfa), 1,4-phenylenediamine (99%, Aldrich), ammonium persulfate (APS, 98%, Merck), dichloromethane (99.5%, Merck), N-methyl-2-pyrrolidone (NMP, 99%, Merck), hydrochloric acid (37%, Riedel-deHaën), ammonium hydroxide (30%, Riedel-deHaën) were used as received without further purification. All of the chemicals were of reagent grade unless otherwise stated. Mass spectra were obtained on a Bruker Daltonics IT mass spectrometer model Esquire 2000 (Leipzig, Germany) with an Agilent ESI source (model G1607-6001). The chemical structure of the oligoaniline and the EPU were determined by ^{1}H NMR spectroscopy on a Bruker 400 spectrometer, using deuterated dimethyl sulfoxide (DMSO) as the solvent. Fourier transform infrared spectra were collected using an FTIR spectrometer (JASCO FTIR-4100) at room temperature. UV–visible absorption spectra were collected using a UV–visible spectrometer (JASCO V-650). Electroactive experiments were performed on VoltaLab 40 (PGZ 301) analytical voltameter using a conventional three-electrode system.

2.2. Synthesis of EPU

2.2.1. Synthesis of monomer of electroactive oligoaniline

A total of 1.68 g (10 mmol) of HDI was dissolved in 10 mL of tetrahydrofuran (THF) and then introduced dropwise over 30 min into a stirred solution of 3.68 g (20 mmol) of NPPD dissolved in 10 mL of THF. The solution was magnetically stirred for 3 h and subsequently poured into 500 mL of distilled water to precipitate the electroactive oligoaniline. The as-prepared oligoaniline was then filtered, washed with excess amount of distilled water and dichloromethane several times, and finally dried under dynamic vacuum at room temperature for 24 h. The as-prepared oligoaniline was obtained in a yield of ca. 90%. ^{1}H NMR (d$_6$-DMSO): $\delta = 8.17$ (s, 2H, due to H5), $\delta = 7.84$ (s, 2H, due to H8), $\delta = 7.25$–7.23 (d, 4H, due to H6), $\delta = 7.15$–7.11 (t, 4H, due to H10), $\delta = 6.96$–6.90 (t, 8H, due to H7, H9), $\delta = 6.70$–6.66 (t, 2H, due to H11), $\delta = 6.02$–5.99 (t, 2H, due to H4), $\delta = 3.07$–3.02 (d, 4H, due to H3), $\delta = 1.41$–1.29 (8H, due to H1, H2)), as shown in Fig. 1(a). Ion trap-MS: m/z calculated for $C_{32}H_{36}N_6O_2 = 536.7$. Found 535.0 (M − H)$^-$, as shown in Fig. 1(b). The as-prepared oligoaniline characterization is given as follows (Fig. 2(a)): FTIR (KBr, cm^{-1}): 3333 (s, υ_{NH}), 2932 (w, saturated hydrocarbon), 1631 (vs, $\upsilon_{C=O}$), 1560 (vs, $\upsilon_{C=C}$ of quinoid rings), 1511 (s, $\upsilon_{C=C}$ of benzenoid rings).

2.2.2. Synthesis of EPU

EPU was prepared by simultaneously dissolving 2.68 g (5 mmol) of oligoaniline and 0.54 g (5 mmol) of 1,4-phenylenediamine into 26 mL of a stirring solution that contained 20 mL of NMP, 3 mL of
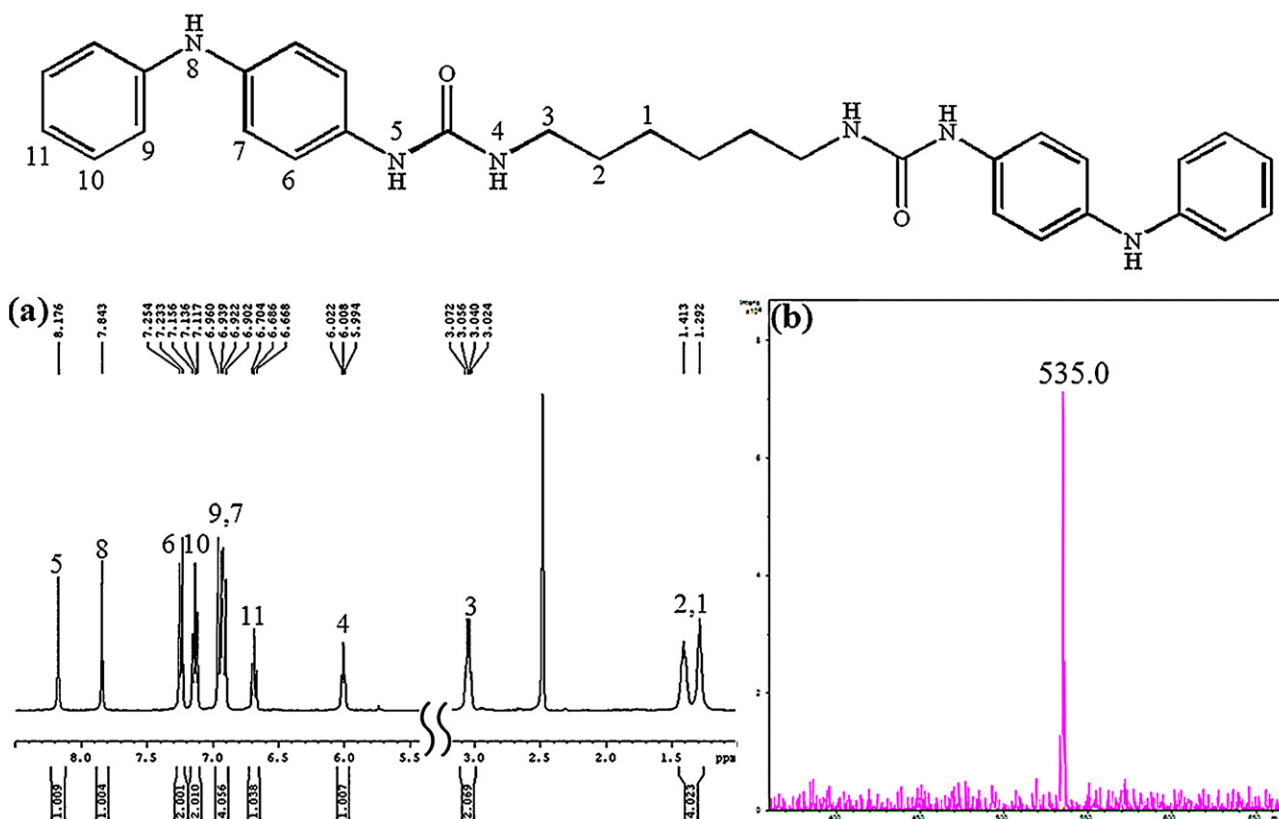

Fig. 1. (a) ^{1}H NMR and (b) LC-mass of oligoaniline.