



Synthesis and characterization of organo-soluble aniline oligomer-based electroactive doped with gold nanoparticles, and application to electrochemical sensing of ascorbic acid



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ABSTRACT

Organo-soluble aniline oligomer-based electroactive polyimide (EPI) doped with gold nanoparticles (GNPs) applied in sensing ascorbic acid (AA) was presented. Conjugated aniline trimer (AT3) and aniline tetramer (AT4) were synthesized and characterized via ¹H NMR, FTIR, and MS spectroscopic studies. Subsequently, the organo-soluble electroactive polyimide (EPI) was prepared by chemical imidization of electroactive poly(amic acid) (EPAA), followed by characterization through FTIR and GPC analyses. Moreover, formation of reduced gold nanoparticles (GNPs) upon the surface of EPI was confirmed by XRD, SEM-EDS, TEM and ICP-OES. Based on CV studies, the redox capability of as-prepared materials was found to show a decreasing trend of EPI-4G > EPI-4 > EPI-3. The as-prepared EPI-4G modified carbon paste electrode (CPE) turned out best in sensing AA at lower oxidative potential with good sensitivity, relative low detection limit, broad linear dynamic range and best selectivity for a tertiary mixture of ascorbic acid (AA)/dopamine (DA)/uric acid (UA) compared to the other tested electrodes.

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1. Introduction

Ascorbic acid (AA), commonly known as vitamin C, is a required nutrient due to its anti-oxidant properties, thus often exists in large amounts in many foods and drinks. AA is also important in many human metabolic processes because of its redox property. This vitamin plays an essential role in biological, and is usually used to treat and prevent common colds and complex diseases [1] such as infertility, cancer, AIDS and mental illness. Thus, designing a facile and fast method to detect AA with a high selectivity and sensitivity is significant for application in food, cosmetics, pharmaceutical, and medical fields. Many techniques have been used in sensing AA, such as spectroscopic [2], chromatographic [3], enzymatic [4] and electroanalytical [5] methods. Among them, electrochemical methods are the best potential approaches because of their simplicity and high sensitivity toward AA. Therefore, the requirement for

materials having higher redox property is essential to fulfill the improvement in electrochemical sensor applications.

In recent years, there are many encouraging developments towards commercialization of electroactive polymers applied in electroluminescent devices, corrosion resistant coatings, electrostatic dissipation coatings, and electrochemical sensors [6–14]. However, one major problem associated with the large-scale commercial application is the limited processability of electroactive polymers. For example, polyaniline solution in N-methyl-2-pyrrolidinone (NMP) often leads to the formation of gels. Also, unsubstituted polythiophene and polypyrrole are not soluble in common organic solvents.

To overcome these problems, many researchers focused on the synthesis of electroactive oligomers of well-defined structures in the past decades. For example, Wei et al. reported the synthesis and characterization of amine-terminated aniline trimer (ACAT) [15]. Zhang et al. explored the synthesis of aniline tetramer and pentamer and study their redox properties [16]. Also, the polymeric derivatives for the aniline oligomers of well-defined structures have also evoked great research interests in academic studies and industrial applications. For example, Yeh et al. reported the

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preparation and diverse applications of ACAT-based electroactive epoxy [17], polyimide [18], polyamide [19], polyurethane [20] and polyurea [21], etc. Among the aniline oligomer-derivative polymers, electroactive polyimide attracted extensive research interests due to the integration of high mechanical strength of polyimide and reversible redox/doping properties of conducting polymers. For example, Yeh et al. demonstrated that the mechanical strength of electroactive polyimide containing ACAT fragments was found significantly higher than that of conventional polyimide membrane [22]. However, published research reports in terms of aniline oligomer-based electroactive polyimide was usually prepared from thermal imidization. Research works related to organo-soluble aniline oligomer-based electroactive polyimide have seldom been mentioned.

On the other hand, several nanoparticles, including metals, oxides, and semi-conducting nanoparticles have been used to develop electrochemical sensor. For example, gold/silver nanoparticles, or silver-silica hybrid nanostructures used as sensor substrates have been explored by several laboratories [23–25]. Among these nanomaterials used as components in electrochemical sensors, gold nanoparticles (GNPs) have received intense interests because they exhibit several intriguing properties [26,27]. GNPs, with diameter of 1–100 nm, exhibit high surface energy and surface-to-volume ratio that offer a stable immobilization of huge amount of biomolecules maintaining their bioactivity. Moreover, GNPs permit fast and direct electron transfer between many electroactive species and electrode materials.

In this study, comparative studies of sensing AA with electroactive polyimide containing different chain length of conjugated diamines was presented. Moreover, the gold nanoparticle was reduced upon surface of electroactive polyimide to get the sensing of AA at lower oxidative potential with good sensitivity, relative low detection limit and broader linear dynamic range. First, the aniline trimer (AT3) and aniline tetramer (AT4) was synthesized by oxidative coupling reaction, followed by characterization by ^1H NMR, FTIR and Mass spectroscopy. Subsequently, organo-soluble EPI-4 and EPI-3 was prepared by reacting AT3 and AT4 with dianhydride to give electroactive poly(amic acid) (EPAA), followed by performing chemical imidization to convert EPAA into EPI. The as-prepared organo-soluble EPI was then characterized by ^1H NMR, FTIR and GPC. Moreover, the EPI-4 was immersed in 19 mL of 0.1 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution for 6 h. The formation of reduced GNPs on the surface of EPI-4 was further confirmed by the XRD pattern, SEM-EDS, TEM and ICP-OES. Redox behavior of as-prepared electroactive materials can be observed by electrochemical CV studies and UV-visible absorption spectroscopy. The electrochemical sensor for sensitivity studies of AA sensing constructed by CPE modified with EPI-4G, EPI-4, EPI-3 and bare CPE was performed and compared. The selectivity studies of electrochemical sensor of CPE modified with EPI-4G, EPI-4, EPI-3, and bare CPE was also investigated by differential pulse voltammetric studies (DPV) towards a tertiary mixture of AA/UA/DA.

2. Experimental section

2.1. Chemicals and instrumentations

Aniline (Sigma-Aldrich, 99.5%) was distilled prior to use. 4,4'-diamino-diphenylamine sulfate hydrate (TCI, 97%), *N*-phenyl-1,4-phenylene diamine (Sigma-Aldrich, 98%), 4,4'-(4,4'-isopropylidene-diphenoxy)bis(phthalic anhydride) (Sechem, >99%), hydrazine (Alfa Aesar, 98%), and ammonium persulfate (APS, Sigma, 98%) were used as received without further purification. Acetic anhydride (J. T. Baker, > 99%), pyridine (J. T. Baker, > 99%), dimethyl formamide (DMF, J. T. Baker, 99%), *N,N*-dimethylacetamide (DMAC,

Macron, 99%), *N*-methyl-2-pyrrolidone (NMP, Macron, 99%), dimethyl sulfoxide (DMSO, Macron, 99%), tetrahydrofuran (THF, Macron, 99%), chloroform (CHCl_3 , Macron, 99%), L-ascorbic acid (AA, Sigma-Aldrich, 99%) were used as received without further purification. Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$; Alfa Aesar, 99.99%), hydrochloric acid (HCl; Riedel-deHaën, 37%), ammonium solution (NH_4OH , Riedel-dehaën, 25%), and methanol (MeOH, Riedel-dehaën, 99.8%) were used as received. All reagents were reagent grade unless otherwise stated.

^1H NMR investigations were run on a Bruker 300 spectrometer, referenced to internal standard of tetramethylsilane (TMS). DMSO was used as solvent. Fourier-transformation infrared (FTIR) spectroscopic analysis was performed using an FTIR spectrometer (JASCO FT/IR-4100) at room temperature. Mass spectra were obtained using a Bruker Daltonics IT mass spectrometer model Esquire 2000 (Leipzig, German) with an Agilent ESI source (model G1607 – 6001). Weight-average and number-average molecular weights of EPI-3 and EPI-4 were determined on a Waters GPC-150CV (USA) equipped with a differential refractometer detector and a Styragel HT column using NMP as eluent and monodisperse polystyrenes as calibration standards.

Microstructures of EPI-4G membranes were imaged with a JEOL-200FX TEM (Japan). Samples for TEM study were cut into thin film with 60–90 nm thickness by a diamond knife. Electrochemical experiments were performed on a VoltaLab 50 (PST050) analytical voltammeter using a conventional three-electrode system. Electrochemical experiments were performed in a cell containing 20.0 mL phosphate buffer solution (PBS, 0.1 M, PH = 7) at room temperature, using a coiled platinum wire as the auxiliary electrode, a glass cell consisting of Ag/AgCl (3 M NaCl) as the reference electrode, and EPI- (EPI-3, EPI-4 and EPI-4G) modified carbon-paste electrode (CPE) as the working electrode.

2.2. Synthesis of aniline oligomers

2.2.1. Synthesis of aniline trimer (AT3)

To synthesize AT3, aniline (1.48 g, 0.016 mol) and 4,4'-diaminodiphenylamine sulfate (4.73 g, 0.016 mol) were dissolved in HCl aqueous solution (1.0 N, 150 mL) containing 15 g of NaCl. A solution of ammonium persulfate (3.6 g, 0.016 mol) in HCl aqueous solution (1.0 N, 25 mL) was added at a rate of approximately 60 drops min^{-1} to the previously described solution maintained at operational temperature of 5 °C using a dropping funnel. The reaction mixture was stirred for 1 h at 5 °C. The resulting precipitate was collected through filtration, followed by washing with large amounts of HCl aqueous solution (1.0 N, 400 mL). Then, the filtrate was washed with NH_4OH solution (1.0 N, 100 mL) and followed by washing with copious amount of distilled water. Thus, a blue powder was further dried in dynamic vacuum oven at an operational temperature of 50 °C for 24 h. The crude product of AT3 was obtained as blue powder with a yield of ~40% [28].

2.2.2. Synthesis of aniline tetramer (AT4)

To prepare AT4, diphenylamine 1.84 g (0.01 mol) and 4,4'-diaminodiphenylamine sulfate (2.1 g, 0.01 mol) were dissolved in a ternary solvent system (100 mL of DMF, 20 mL of distilled water and 15 mL of HCl 1.0 N, 135 mL). A solution of ammonium persulfate (2.28 g, 0.01 mol) in HCl aqueous solution (1.0 N, 25 mL) was added at a rate of approximately 60 drops min^{-1} to the previously described solution at 0 °C using a dropping funnel. The reaction mixture was stirred for 1 h at 0 °C. It was then transferred into a 1000 mL of beaker containing 700 mL of distilled water to precipitate the product. The precipitate was collected by vacuum filtration through a Buchner funnel and washed by 400 mL of 1.0 N HCl, followed by washing with 100 mL of 1.2 N ammonium hydroxide

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