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Development and characterization of a flexible electrochromic device based on polyaniline and enzymatically synthesized poly (gallic acid)

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ABSTRACT

An effective polyaniline-based electrochromic device was successfully achieved using the enzyme-mediated poly (gallic acid) as a polyaniline polymerization template. Poly (gallic acid) proved non-toxic upon the conducted cytotoxicity assays. Thermogravimetric analysis of the novel polyaniline-poly (gallic acid) complex displayed a remarkable increase in thermal stability compared to polyaniline-HCl doped, polyaniline-poly (styrene sulfonate), polyaniline-poly (isobutylene-alt-maleic anhydride) complexes. Polyaniline-poly (gallic acid) water dispersion was readily processed by spray-coating on indium tin oxide-poly (ethylene terephthalate) sheet. These novel electrode was employed as an electroactive layer in flexible electrochromic device with propylene carbonate-poly (methyl methacrylate)-$LiClO_4$ polymer electrolyte. The transmittance of the electrochromic device at 650 nm in a wide voltage range varied from 59% (−0.87 V) to 37.1% (+0.33 V) giving an optical contrast of 22% and a life up to 700 cycles.

1. Introduction

The production of flexible devices from polymers with adequate electrical conductivity and redox properties has been widely investigated during the past decades for applications in electrochromic devices (ECD)s, polymeric light emitting diodes, photovoltaic cells, sensors, actuators or field effect transistors [1–4].

The polyaniline (PANI) capacity to switch between different electrochemical oxidation states, which directly influence their absorption of the spectra, has attracted increasing attention for the ECDs production [5–7]. Sydorov et al. reported in 2013 an interesting work in spectroelectrochemical properties of ECDs produced by complementary architectures of PANI and poly (3-methylthiophene). These authors described their materials as more cost-effective than other conducting polymers used for ECDs production [7]. Nonetheless, the processability of conductive PANI is challenging due to its poor solubility in many solvents due to the intermolecular bonds between the amino and imino groups of adjacent chains [8]. Therefore, several efforts have been conducted to address this issue. The approaches involve the modification of the benzene ring or NH moiety with different functional groups, such as $-CH_3$, $-OCH_3$, $-SO_3$, the grafting of alkyl side chains or the introduction of acidic polymers or acid polyelectrolytes negatively charged as templates [9]. Regarding the latter, several polyacids have been reported, such as poly (styrene sulfonic acid) (PSS) [10].

We recently reported the environmentally friendly synthesis of a novel polyphenolic acid with a controlled molecular structure by

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the enzyme-mediated oxidative polymerization of the naturally abundant gallic acid (GA) in aqueous media [11]. The resulting poly (gallic acid) (PGAL) was a semiconductor with high water solubility. The PGAL has been demonstrated non-toxic in the present work and it has been used as template for effective dispersion of synthesized PANI. The resulting PANI-PGAL complex has been chemically and electrochemically characterized and it presents higher thermal stability compared to PANI-PSS, HCl-doped PANI and PANI-polymethylmetacrilate (PANI-PMA) complexes. The novel PANI-PGAL complex has been used in a flexible electrochromic device displaying an optical contrast up to 22% at 650 nm and endures up to 700 cycles at cell voltages between −0.87 V and +0.33 V (vs $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$).

2. Experimental section

2.1. Materials

Laccase from *Trametes versicolor* (LTV) lyophilized free enzyme (stored at −20 °C) was supplied by Fluka (USA). GA (reagent grade) and 2-azino-bis-(3-etilenbenzotiazolina-6-sulfonate) (ABTS) were purchased from Sigma-Aldrich (USA). Enzyme specific activity was determined by mixing ABTS (0.56 mM) solution (900 μL) with sodium acetate (0.1 M; pH 5.0) to 100 μL of LTV solution (0.05 mg/mL). Oxidation of ABTS was monitored spectrophotometrically by the increase in the absorbance at 420 nm (ξ_{420}, $3.6 \times 10^4\,M^{-1}\,cm^{-1}$). Enzymatic activity unit (U) was defined as the amount of protein necessary to oxidize 1 μmol of ABTS per minute. Specific activity of LTV used in this study was 6.82 U/mg protein. Ethanol (technical grade) was obtained from Química Barsa SA de CV (Mexico). Aniline, ammonium persulfate (APS), poly(sodium-4-styrenesulfonate) (PSS) with M_W of 76,000 g/mol and poly (isobutylene-alt-maleic anhydride) (PAM) (M_W 6000 g/mol) were supplied by Sigma-Aldrich (Mexico). Indium tin oxide coated polyethylene terephthalate (PET-ITO) (60 Ω/sq surface resistivity), $LiClO_4$, propylene carbonate (PC) and poly(methyl methacrylate) (PMMA) with $M_w = 120{,}000$ g/mol were supplied by Sigma-Aldrich (Mexico).

2.2. C**itoxocity assay for PGAL**

PGAL solutions with different concentrations (0–200 μg/mL) were exposed to cell cultures MFC-7 (breast adenocarcinoma from human, Sigma-Aldrich), HCT15 (colon from human, Sigma-Aldrich) and HeLa Cell (epitheloid cervix carcinoma, Sigma-Aldrich) for cytotoxic assays in RPMI medium at 37 °C and 5% CO_2. Sulphorrodamine B was monitored at 564 nm to assess *in vitro* cytotoxic effect by comparing the amount of dye attached to the membrane protein treated *versus* to the non-treated one.

2.3. Enzymatic synthesis of PGAL

PGAL was synthesized and characterized according to the method reported by López et al. [11]. In a typical experiment; 250 mL of acetate buffer (pH 5, 0.25 M), 8.5 g of GA and 20 mL of NaOH (2 M) were added in an amber round bottom 500 mL flask. Reaction was initiated by the addition of 256 U of LTV and was stirred with a constant air supply to kept 1.5 mg/L of molecular oxygen dissolved in the mixture as monitored in a Applisens O_2 sensor (Aplikkon, USA) at 25 °C for 24 h. Then, product was precipitated in 1/10 cold ethanol (v/v), filtered and dried under vacuum to give a black powder in 90% yield and M_n of 7000 g/mol.

2.4. Polymerization of anilines in the presence of PGAL, PSS and PAM templates

In a typical reaction for production of PANI-PGAL complex, 0.03 mol PGAL, calculated considering the molecular weight of the monomer, was added to 0.067 mol of aniline in 310 mL of HCl (0.25 M) placed in a 1 L container at 25 °C and mixed using a four blade propeller at 1500 rpm (aniline:PGAL ratio of 1:0.45 mol:mol). Then, APS (0.067 mol) in 48 mL of water was added dropwise for 1 h and stirred under nitrogen inert atmosphere for 3 h. For PANI-PAM complex, 20 g of PAM (0.07 mol) was dissolved in 235 mL of HCl (0.82 M) and of 6.7 g of aniline (0.07 mol). APS (0.07 mol) solution in 50 mL of water was gradually added during 15 min. Then, the mixture was stirred (1500 rpm) under inert atmosphere for 3 h at 25 °C. For PANI-PSS complex, 16.6 g of PSS (0.07 mol) was dissolved in 260 mL of HCl (0.84 M) and 6.7 g of aniline (0.07 mol). Next, 16 g of APS (0.07 mol) solution in 50 mL of water was gradually added during 15 min. The reaction contents were stirred (1500 rpm) under inert atmosphere for 3 h at 25 °C. All products were collected by filtration, washed with deionized water and dried under vacuum *prior* to use.

2.5. Synthesis of HCl-doped PANI

Aniline (0.1 mol) was dissolved in 100 mL of HCl (1 M) in a round-bottomed flask cooled at 4 °C under mechanical stirring (1500 rpm). Then, 51.5 mL of APS (2.4 M) aqueous solution was added dropwise to the reaction mixture for 1 h until 0.12 mol of APS had been added. Reaction contents were stirred under inert atmosphere for 8 h at 4 °C. PANI-doped HCl product was collected by filtration, washed with HCl (1M) and dried under vacuum.

2.6. Characterization of products

Molecular weight distribution of PGAL was measured by size exclusion chromatography (SEC) using an Agilent 1200 series liquid chromatographer equipped with a refractive index detector and two Waters (USA) ultrahydrogel 500 (7.8 × 300 mm) columns in serie calibrated with polyethylene glycol standards (Varian, USA). Samples were eluted with deionized water with LiCl (0.1 M) using 0.8 mL/min flow rate. Samples were dissolved in the mobile phase and filtered (0.45 μm) *prior* to injection into the chromatographer. Infrared (FT-IR) spectra were acquired with a Perkin Elmer Spectrum GX FT-IR System in KBr pellets. UV–vis spectra were measured in a Thermo Scientific Genesys 10S spectrophotometer (cuvette 3 cm^3 at 0.02 w/v%). Samples were dispersed in deionized water at pH 2. Blank water curves were subtracted from each spectrum. Thermogravimetric (TGA) analysis of PGAL and PANI complexes was conducted in a Perkin Elmer Pyris I TGA under inert nitrogen atmosphere with 20–850 °C sweep at 20 °C/min rate. Initial sweep of volatiles (25–100 °C) was carried out by triplicate before each sample measurement. Stability in water dispersions of PANI complexes were performed in test tubes of 1.4 cm inner diameter and 14.8 cm height at 25 °C. 20 mL of aqueous suspension for each PANI complex (3 wt%) were introduced into the tubes and stirred for 5 min. The time at which 50% of the dispersion was aggregated (the height of the supernatant equals the height of the sediment) was recorded as t(50). Scanning Electron Microscopy (SEM) micrographs were obtained in a JEOL JSM–5900LV microscope (Japan). Samples of synthetized PANI complexes were spray-coated on a clear acetate sheet and dried at 60 °C *prior* to analyses in the microscope.