



Disposable electrochromic polyaniline sensor based on a redox response using a conventional camera: A first approach to handheld analysis



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ABSTRACT

We present a disposable optical sensor for Ascorbic Acid (AA). It uses a polyaniline based electrochromic sensing film that undergoes a color change when exposed to solutions of ascorbic acid at pH 3.0. The color is monitored by a conventional digital camera working with the hue (H) color coordinate. The electrochromic film was deposited on an Indium Tin Oxide (ITO) electrode by cyclic voltammetry and then characterized by atomic force microscopy, electrochemical and spectroscopic techniques. An estimation of the initial rate of H , as $\Delta H/\Delta t$, is used as the analytical parameter and resulted in the following logarithmic relationship: $\Delta H/\Delta t = 0.029 \log[AA] + 0.14$, with a limit of detection of 17 μM . The relative standard deviation when using the same membrane 5 times was 7.4% for the blank, and 2.6% (for $n = 3$) on exposure to ascorbic acid in 160 μM concentration. The sensor is disposable and its applicability to pharmaceutical analysis was demonstrated. This configuration can be extended for future handheld configurations.

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1. Introduction

Direct sensing schemes using chemical sensors cannot be applied if the analyte or analytes do not show adequate intrinsic analytical properties. In that case, reagent-mediated sensing is used in a huge variety of schemes and materials [1,2].

An interesting group of materials using optical sensing are those that show electrochromism, a reversible optical change in a material induced by an electron-transfer (redox) process or sufficient electrochemical voltage [3]. Examples of electrochromic materials include metal oxide films (tungsten oxide), viologens (4,4'-bipyridylum salts), conjugated conducting polymers (polymeric thiophenes and pyrroles), and metal coordination complexes (transition-metal polypyridyl complexes) [4]. Electrochromic materials can be classified in different ways; one of the most simple consist on consider the solubility of each redox state that is categorized in three types [5]. Type I, such as methyl viologen, numerous metal complexes and organic redox indicators, is soluble in both reduced and oxidized states. Type II includes materials that are soluble in one redox state but form a solid film on the surface of an electrode following electron transfer. Examples are reversible electrodeposition of metals and heptyl viologen [4]. In type III

electrochromic materials, both or all redox states are solid, such as WO_3 or conjugated conducting polymers.

Conjugated conducting polymers are very sensitive to the microenvironment within the polymer matrix due to the delocalization of π -bonded electrons over the polymeric backbone [6]. Many of these materials are electrochromic as thin films. Conducting polymers can be transformed from an electrically insulating state to conducting materials through several doping techniques such as: (1) chemical doping by charge transfer groups, (2) electrochemical doping, (3) doping by acid–base chemistry, (4) photodoping and (5) doping by charge injection [7]. Among them, polyaniline (PANI) is the most interesting because of its ease of synthesis, low-cost monomer, tunable properties, and better stability compared to other conducting polymers [8]. PANI film has been used as the active layer in electrochromic devices since it can reversibly change colors upon electrochemical doping and de-doping treatments [9] and also for modifying functional material by inkjet-printing [10].

The unsubstituted PANI presents problems of insolubility and infusibility; the emeraldine base is soluble in some polar organic solvents, but it is an insulator, whereas emeraldine salts are conductive but usually insoluble and non-processable. To improve the solubility and induce fusibility of this polymer required for any application, various procedures have been adopted ranging from doping with functionalized protonic acids to copolymerization or the incorporation of polar functional groups [7].

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PANI films show multiple color changes depending on their redox state: (a) leucoemeraldine, the fully reduced form that is colorless and electrically insulating, (b) pernigraniline, the fully oxidized form, violet in color and also electrically insulating, and (c) emeraldine, a half oxidized and stable intermediate green color that has significant electrical conductivity [11].

The color of PANI depends on their absorption characteristics, appearing around 320 nm, 400 nm and 850 nm. The band at 320 nm, attributed to the band gap, is the principal one in reduced PANI leucoemeraldine, in addition to a small band around 850 nm. With the oxidation of PANI, the 320 nm band steadily decreases, growing a new band at about 400 nm, and the 850 nm band increases and shifts to 750 nm. These bands are attributed to the polarons and bipolarons associated with the formation of the quinoid units due to the oxidation of the amine to imine groups [12].

The use of PANI for optical sensing refers mainly to pH determination and pH related analytes because the degree of oxidation of the polymer depends on the pH [13]. Thus, films of chemically polymerized PANI are proposed to optically measure the pH between 2 and 12 in the NIR [14] or in the visible region [15,16]. Another approach consists of the immobilization of PANI onto the core of a silica optical fiber, measuring the intensity of the NIR evanescent field for pH between 3 and 12 [17]. The immobilization of PANI coating microfluidic channels is also studied for pH measurement via absorbance and color by means of a digital camera, which makes it possible to detect pH gradients using an imaging technique [18]. The modification of cellulosic paper with PANI nanoparticles has been carried out for the determination of acidic analytes such as HCl both in solution and gas, measuring the color by means of a scanner [19]. In a similar way, covering PANI films with a layer of silicone permits the determination of analytes in solution such as acetic acid and ammonia [15]. An optical gas sensing device for ammonia was developed using a LED–photodiode setup and a PANI layer deposited on glass [20] or on poly(methyl methacrylate) and polystyrene blend films [21]. A copolymer of aniline and anthranilic acid was used as the support for the immobilization of urease allowing the spectrophotometric determination of urea [22]. Another strategy is the use of PANI type polymers containing boronic acid side groups capable of recognizing saccharides such as fructose by inducing spectral changes [23]. The ability of some fiber/net membranes containing PANI to trigger a series of redox and doping reactions including complex formation with metal ions is the basis of a naked-eye procedure for Cu(II) identification and quantification based on RGB coordinates calculated from reflectance spectra [24].

The use of PANI for ascorbic acid determination has been carried out using different strategies in the literature, with electrochemical being the most common. The preparation of modified electrodes by electrodeposition of gold on polyaniline films prepared on titanium was employed for the electrooxidation of AA [25]. Another modified electrode based on a film that contains immobilized laccase with a cysteine self-assembled monolayer coated with functionalized quantum dots is capable of retaining its activity to oxidize AA [26]. Polyaniline is used to modify electrodes improving the electrochemical properties, especially with screen-printed carbon electrodes [10] or with doped agents such as dodecylbenzene sulfonic acid by drop-casting technique [27]. One interesting option is the use of polyaniline film as a molecularly imprinted polymer where AA was used as a template molecule for electrode fabrication [28].

Additionally, PANI films have been used for the spectrophotometric determination of redox analytes such as hydrogen peroxide by chemical polymerization of aniline in the microwells of microtiterplate and glucose by enzyme immobilization [29]. Bossi et al. use coated microplates based on monitoring the changes in optical

absorption of the PANI film resulting from the reduction process from AA [30].

The aim of this study is to develop a disposable optical sensor for ascorbic acid based on monitoring the color changes of an oxidized PANI film with a conventional digital camera. The film is prepared by electrochemical doping on an ITO electrode, which achieves precise control of the doping level and higher precision in the preparation than with the usual chemical doping discussed above. We describe the use of the HSV hue-oriented color space, whose initials indicates Hue, Saturation and Value, that represents the color information by using one single parameter, the *H* coordinate (hue). The *H* coordinate is a qualitative signal independent from reagent concentration and the optical path, meaning that it will not be affected by differences in thickness or the lack of membrane homogeneity, or the reagent concentration between batches of sensors, which reduces the precision of measurements [31].

2. Experimental section

2.1. Chemicals

Saline buffer was prepared in 0.2 M sodium chloride (Panreac Química S.L, Barcelona, Spain. <http://www.panreac.es/>) and 0.5 M sodium dihydrogen phosphate (Panreac), adjusted to pH 3.0 by adding HCl (35%, Panreac). Aniline solution, grade 99%, was obtained from Sigma–Aldrich (Sigma–Aldrich Química S.A., Madrid, Spain, <https://www.sigmaaldrich.com/spain.html>). Ascorbic Acid 99% (AA) was purchased by Sigma–Aldrich. Different standard solutions of AA were prepared by weighing and solution in buffer. Acetone and acetic acid were obtained by Panreac. A 0.2 M solution of aniline (Sigma) was prepared in 0.5 M sulfuric acid (95%, Panreac). Reverse-osmosis type quality water (Milli-Q Plus185 from Millipore, Molsheim, France) was used throughout.

2.2. Apparatus and software

The potentiostat Autolab PGSTAT 128 N (Metrohm Autolab B.V., Utrecht, The Netherlands) with conventional electrochemical cell has been used for electrochemical studies containing: platinum counter electrode, Ag/AgCl reference electrode and ITO coated glass (15–25 Ω /sq surface resistivity) or ITO coated plastic working electrode (60 Ω /sq surface resistivity) both obtained by Sigma. We used ITO coated glass in all the optimization study in order to reuse the electrodes after an acid washing process. The ITO coated plastic offer only a single use and cheap sensor. An electrochemical quartz crystal microbalance (EQCM) module made it possible to perform a mass change per unit area by recording the change in resonant frequency of a quartz crystal oscillator where 6 MHz EQCM Crystal Au/TiO₂ was used.

For the spectroelectrochemical measurement, a PalmSens handheld potentiostat/galvanostat (B.V., Utrecht, The Netherlands) with ultraviolet–visible diode array spectrophotometer HP 8453 (Nortwalk, CT, USA) with Chemstation software package was used. A Canon PowerShot G12 photographic camera was used for *H* parameter acquisition (Fig. 1). Micro-Raman Spectrometer Dispersive JASCO NRS-5100 with Spectrum Manager Software (2011) was used for Raman spectroscopic data. The conditions for Raman spectra were an exposure time of 15 s and a laser wavelength of 785.11 nm, scanning from 350 cm^{-1} to 1750 cm^{-1} with a laser intensity of 0.2 mW with 12 accumulations. Atomic Force Microscopy (AFM) measurement was carried out with a Multimode Nanoscope IIIa from Digital Instruments (Veeco Metrology Group, Santa Barbara, CA, USA); other instruments consisted of a Crison digital pH-meter (Crison Instruments, Barcelona, Spain) with combined glass-saturated calomel electrode.

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