Journal of Molecular Liquids xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Fabrication of an electrochemical sensor based on nanostructured polyaniline doped with tungstophosphoric acid for simultaneous determination of low concentrations of norepinephrine, acetaminophen and folic acid

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A R T I C L E I N F O

Article history:
Received 16 October 2012
Received in revised form 6 November 2012
Accepted 12 November 2012
Available online xxxx

Keywords:
Electrochemical sensor
Polyaniline
Nanostructure
Norepinephrine
Acetaminophen
Folic acid

A B S T R A C T

Nanostructured polyaniline (PANI) doped with tungstophosphoric acid (TPA) was prepared; its structure was confirmed by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). An electrochemical sensor was fabricated in a simple way by modification of carbon paste electrode with this nanostructured material (CPE-PANI/TPA). Because of the catalytic activity of TPA and the unique properties of PANI, this sensor was used for catalytic determination of norepinephrine (NE), acetaminophen (AC) and folic acid (FA), individually and simultaneously. Cyclic voltammetry experiments showed that the oxidation potential of these substances shifted to negative values and their oxidation current increased sharply by use of this sensor rather than by use of bare carbon paste electrode. Linear dynamic ranges and detection limits were obtained respectively as 8.0×10^{-8}–2.0×10^{-3} M and 5.0×10^{-8} M for NE, 9.0×10^{-7}–1.9×10^{-3} M and 2.0×10^{-7} M for AC and 2.0×10^{-6}–2.1×10^{-3} M and 3.0×10^{-7} M for FA by differential pulse voltammetry. The proposed electrochemical sensor was used for the determination of these substances in pharmaceutical and blood serum samples.

1. Introduction

Norepinephrine (NE) is an important catecholamine neurotransmitter and is secreted by the adrenal medulla. It is released as a metabotropic neurotransmitter from nerve endings in the sympathetic nervous system and some areas of the cerebral cortex. Many diseases are related to changes of its concentration [1]. Thus the quantitative determination of NE in biological fluids for medical control and in pharmaceutical formulations for quality control analysis is important. Besides various methods such as spectrophotometry [2], capillary electrophoresis [3], gas chromatography [4] and high-performance liquid chromatography [5]; electrochemical methods have also been employed for detection of NE [6–9].

Acetaminophen (AC) is the most extensively employed drug as pain reliever and fever reducer. However, overdoses of AC cause liver and kidney damage and may lead to death [10,11]. Several methods have been used for the determination of AC including spectrophotometry [12], chromatographic methods [13] and electroanalysis by modified electrodes [14–18].

Folic acid (FA, also known as vitamin M and folacin or folate) is a widely distributed water-soluble vitamin [19]. FA deficiency causes failure to make the purines and thymine required for DNA synthesis [20]. FA is a potential agent for cancer prevention by free radical scavenging and antioxidant activity [21]. Numerous methods for the measurement of FA are available, such as capillary electrophoresis [22] and high-performance liquid chromatography [23]. Also electrochemical methods have been used for this purpose [24,25,18].

AC administration increases brain serotonin levels [26] and serotonin is known to play a role in NE release in the brain [27]. Also, FA works primarily in the brain and nervous system and is necessary for the synthesis of NE and serotonin in the nervous system. Also, some substances like nonsteriodal anti-inflammatory drugs such as AC can inhibit FA from being absorbed or used by the body. Likewise, when taken for long periods of time, AC can also increase the need for FA [28]. Therefore simultaneous determination of NE, AC and FA is important.

Different electrochemical techniques including voltammetric [29–31] and potentiometric [32–43] techniques have many advantages in pharmaceutical and environmental analyses [44,45]. Carbon paste electrodes (CPEs) have wide applications. Besides the advantages such as low cost, easy preparation and simple surface renewal process, the possibility of incorporation of different substances during the paste preparation allows the fabrication of different modified electrodes (MEs) with desired composition [46,47]. Various materials have been used to fabricate MEs which can enhance the electron transfer rate and reduce the overpotential of the oxidation of substrates [48–50]. MEs have an ability to catalyze the electrode process by selective interaction of the compound on the surface of the electrode with the target analyte at the electrode interface. These

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http://dx.doi.org/10.1016/j.molliq.2012.11.008

Please cite this article as: M. Mazloum-Ardakani, et al., , Journal of Molecular Liquids (2012), http://dx.doi.org/10.1016/j.molliq.2012.11.008

electrodes considerably enhance the selectivity in electroanalytical determinations [51].

Application of nanomaterials in various fields of science and technology has been extensively developed due to the unique properties of these materials [52]. The nanostructured materials with large specific surface area could provide a good platform for catalysis [53], separation [54], sorption [55], sensing [56], fuel cells [57], DNA sensors [58] and fabrication of modified electrodes and electrochemical sensors [59–64]. On the other hand, conducting polymers (e.g. polyaniline, PANI) are of great scientific and technological importance because of their unique electrical, electronic, magnetic and optical properties [65,66]. With the recent development in nanoscience and nanotechnology, conducting polymer nanostructures received an ever increasing attention [67].

Heteropolyacids (HPAs) are used as homogeneous and heterogeneous catalysts for oxidation and acid catalyzed reactions due to their unique physicochemical properties [68]. In recent years, HPAs have considerable interest as multifunctional material and have been widely used in analytical chemistry, biochemistry and medicine [69]. Among various classes of HPAs, Keggin dodecatungstophosphoric acid (TPA) with the chemical formula of $H_3PW_{12}O_{40}$, has received considerable attention due to its high acidity and ease of preparation [70]. To increase the surface area of catalysts, HPA has been supported by different materials. The inclusion of TPA in a polymer matrix to enhance catalytic activity and sensitivity due to the increase of surface area is shown [71].

In this paper because of the catalytic activity of TPA and the unique properties of PANI, TPA was doped in PANI (PANI/TPA). After verification of the PANI/TPA nanostructure, a carbon paste electrode was modified with it (CPE-PANI/TPA) and this electrode was used for catalytic determination of NE, AC and FA, individually and simultaneously.

2. Experimental

2.1. Apparatus and chemicals

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, Netherlands). All experiments were carried out in a three electrode cell including CPE-PANI/TPA, Ag/AgCl (KCl 3.0 M, Azar electrode, Iran) and a Pt wire (Azar electrode, Iran) as working, reference and counter electrodes, respectively. All solutions were freshly prepared with double-distilled water. NE, AC, FA and all other reagents were of analytical grade from Merck (Darmstadt, Germany). The graphite fine powder and paraffin oil (DC 350, 0.88 g cm^{-3}), both from Merck (Darmstadt, Germany), were used as received. Phosphate buffers were prepared from orthophosphoric acid (Merck Darmstadt, Germany) and its salts and pH values were measured using a Metrohm 691 pH meter.

2.2. Preparation of nanostructured polyaniline doped with TPA

2.2.1. Synthesis of the polyaniline

Polyaniline salt from hydrochloric acid was prepared by aqueous polymerization pathway according to a reported procedure in the literature. PANI base was obtained by undoping of the obtained salt. In a typical experiment, 6 ml of freshly distilled aniline was added to 35 ml of 1.7 M HCL in a 500 ml round bottom flask. The solution was kept under constant stirring at (0–5) °C. To this solution 13.68 g of sodium persulfate in 250 ml of water was added drop-wise for 60 min. The solution was allowed to warm up to room temperature and the reaction was allowed to continue for 4 h. The precipitated PANI-hydrochloride salt was filtered and washed with 250 ml distilled water followed by 50 ml methanol. The PANI powder was dried at 120 °C for 1 h. The PANI salt from hydrochloric acid (5 g), synthesized previously, was stirred in 25 wt.% aqueous ammonia solution (100 ml) for 24 h at room temperature. The PANI base powder was filtered, washed with water (100 ml) followed by acetone (50 ml), and dried at 120 °C for 1 h.

2.2.2. Preparation of polyaniline doped with TPA

To a suspension of PANI (500 mg) in CH_3CN (50 ml) in a 100 ml round bottom flask, TPA (250 mg) was added with stirring. The mixture was stirred for 24 h. The solid was filtered, washed with 200 ml water and 50 ml acetone and dried at 120 °C for 1 h. The PANI/TPA with 18% of TPA was obtained.

2.3. Preparation of the CPE-PANI/TPA electrochemical sensor

The PANI/TPA modified carbon paste electrodes were prepared by mixing 0.1 g of PANI/TPA, 0.9 g of graphite powder and an appropriate amount of paraffin oil with a mortar and pestle until a uniform paste was obtained. The paste was then packed into the end of a glass tube (3.4 mm i.d. and 10 cm long). The electrical contact was provided by inserting a copper wire into the carbon paste. This electrode was used as electrochemical sensor. The unmodified carbon paste electrode was prepared in the same way without adding PANI/TPA.

3. Results and discussion

3.1. Characterization of nanostructured polyaniline doped with TPA

Polyaniline (PANI) doped with TPA (18 wt.% loading amount of TPA) was prepared with an appropriate portion of heteropoly acid. The doped polymer was analyzed by FT-IR in order to confirm the presence of a Keggin anion of TPA on the polymer. The Keggin ion structure is well known, and consists of a PO_4 tetrahedron surrounded by four W_3O_{13} groups formed by edge-sharing octahedral. These groups, are connected to each other by corner-sharing oxygen atoms. This structure is responsible for the bonds of Keggin ions between 1200 and 700 cm^{-1} in the FT-IR spectrum.

The FT-IR spectra of PANI, TPA and 18 wt.% PANI/TPA are shown in Fig. 1A. The vibrational bonds observed for the polyaniline base are reasonably explained on the basis of the normal modes of aniline and benzene. In curve a, the characteristic peak at about 1597 cm^{-1} arises from the stretching vibration of the $N{=}Q{=}N$ ring. The peak at about 1496 cm^{-1} is attributed to the stretching vibration of the $N-B-N$ ring (where B refers to the benzenoid ring and Q refers to the quinoid ring). The bands near 1294 cm^{-1} and 820 cm^{-1} can be assigned to C–N stretching of the secondary aromatic amine and an aromatic C–H out-of-plane bending vibration, respectively [72].

As shown in curve b of Fig. 1A, the IR spectrum will change after polyaniline is doped with heteropoly acid. When comparing with the PANI base, the band at 1597 cm^{-1} (arising from the quinoid diimine unit) and the band at 1496 cm^{-1} (arising from C–C aromatic ring stretching of the benzenoid diimine unit) in PANI/TPA are shifted to lower wave numbers of 1583 and 1492 cm^{-1} respectively. These results confirm the doping of PANI and are in agreement with other reports [72,73]. Moreover, in doped polyaniline, characteristic peaks of TPA confirm the presence of Keggin anions on the polymer. As shown in curve c of Fig. 1A, pure TPA, exhibited the typical IR bands at 1081, 982, 888 and 793 cm^{-1} associated to the Keggin ions [74,75]. In the IR spectra of PANI/TPA with 18% loading (curve b of Fig. 1A), the bands of TPA appear around 887, 983 and 1081 cm^{-1}, while the band at 793 overlapped with the C–N stretching of PANI at 820 cm^{-1}. These results confirm that TPA on the PANI still retains the Keggin structure.

A scanning electron microscopy (SEM) of PANI/TPA is shown in Fig. 1B. The SEM image shows that this structure was formed as some individual nanoparticles and also some agglomerated nanoparticles.

Please cite this article as: M. Mazloum-Ardakani, et al., , Journal of Molecular Liquids (2012), http://dx.doi.org/10.1016/j.molliq.2012.11.008