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Carbon nanotubes versus polyaniline nanoparticles; which transducer offers more opportunities for designing a stable solid contact ion-selective electrode

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ABSTRACT

Sensors that exploit the unique properties of nanomaterials establish the most rapidly growing sensor research area. Remarkable achievements in nanotechnology and ion selective electrodes (ISEs) lead to explore a wide variety of approaches that develop completely calibration-free ISEs. This work offers construction and comparative evaluation of the performance characteristics of multiwall-carbon nanotubes (CNTs) and polyaniline nanoparticles (PANI) as ion-to-electron transducers between an ionophore-doped PVC membrane and glassy carbon electrodes. With respect to the previously published reports, the current comparison was performed side by side under similar experimental conditions and hence the advantages and shortcomings of each transducer nanoparticles were directly highlighted in light of ISE figures of merit. Apparently, the inclusion of CNTs and PANI nanoparticles added more stability to the electrical signal due to their excellent electronic and chemical properties. Moreover, the fast ion-to-electron transduction allows obtaining short response times and the hydrophobic behavior avoids the formation of water layers at the electrode/membrane interface. These results enabled the production of a series of SC-ISEs with improved piece-to-piece reproducibility where the potential was stable over 60 and 45 days with drift of 0.8 mV h^{-1} and 0.7 mV h^{-1} for CNT and PANI based sensors, respectively. The electrodes were utilized for determination of buspirone as a model pharmaceutical drug.

1. Introduction

Nanoparticles have attracted a growing interest in the development and fabrication of stable solid contact ion selective electrodes (SC-ISEs) for several applications. It is well known that the sensor materials are the key components that can be used in assembling high performance electrochemical sensing platforms to determine target analytes [1].

Recently, research that combines between nanotechnology and ISEs leads to explore a wide variety of approaches that develop completely calibration-free ISEs [1,2]. Conducting polymers nanoparticles [3,4], redox-active self-assembled monolayers (SAMs) on gold nanoclusters [5] and carbon nanotubes [6] are different possible solutions pursued to prepare sensors with outstanding potential stability and identical calibration curves.

Carbon nanotubes have remarkable structural, electrical and thermal properties since being discovered by Iijima in 1991 [7]. CNTs are simply deposited over various surfaces, which makes them ideal for SC-ISEs. They have been used as ion-to-electron transducing layer in ISEs [6,8] in addition of being incorporated in the fabrication of biosensors [9,10].

Alternatively, conducting polymer of polyaniline nanoparticles (PANI) can be prepared either electrically or chemically. PANI as an ion to electron transducer was used in many SC-ISEs [3]. Recently, nanostructured (nano-particles/-rods/-wires) conducting polyaniline with unusual physical and chemical properties has attracted great research interests because it exhibits enhanced performance. Stable dispersions of PANI nanoparticles in both aqueous and organic solvents were also recently prepared [4,11,12].

The goal of this work was to evaluate the long term stability and piece-to-piece reproducibility of solid contact ISE with two different ion to electron transducers, namely; CNT and PANI. The fabricated electrodes were tested and investigated for determination of buspirone as a model pharmaceutical drug, Fig. 1. To the best of our knowledge, this report is one from the on-going efforts on evaluating the behavior of PANI and CNT based SC-ISEs as an ion-to-electron layer for determination of a pharmaceutical compound [13–16].

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were of analytical reagent grade, and water was bi-distilled. Polyvinyl chloride (PVC), calix-6-arene

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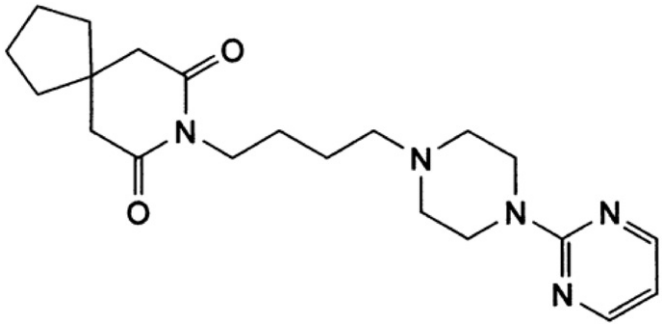

Fig. 1. Chemical structure of buspirone.

(CX6) and multi wall carbon nanotube powder (MWCNT) were obtained from Fluka (Steinheim, Germany). 2-Nitrophenyl octyl ether (NPOE), sodium dodecylsulfate (SDS), aniline and tetra phenyl borate were purchased from Aldrich (Steinheim, Germany). Tetrahydrofuran (THF) and xylene were obtained from BDH (Poole, England). Ammonium persulfate (APS) was obtained from E. Merck (Darmestadt, Germany).

Buspirone (BU) reference standard was kindly supplied by Smithkline Beecham Glaxo, Egypt. Its purity was found to be 100.11 ± 0.55% according to official USP method [17]. Buspar® tablets (15 mg BU per tablets) were manufactured by Smithkline Beecham Glaxo, Egypt batch no. N102909. Dapoxetine was kindly supplied by SEDICO (South Egypt for Drug Industries Co.), Egypt.

2.2. Preparation of CNT and conducting PANI dispersions

A chemical polymerization procedure was used for preparation of PANI nanoparticle dispersion [4]. For CNT, 0.2% wt. MWCNT powdered in a miller and dispersed in 10 mL 1% SDS solution as described by Rius and coworkers [18]. The dispersion was homogenized using a tip sonicator for 30 min.

2.3. Fabrication of membrane sensors

For CNT, a spray-gun containing the dispersion was placed at 30 cm from the top of the electrode. To achieve a homogenous deposition, the MWCNT dispersion was sprayed for 2 s, dried by hot air blower, thoroughly washed with water and dried with the hot air-blower again. A volume of 30 μL of a THF solution containing the components of the outer BU-selective membrane was added to cover the CNT layer.

For PANI, the SC layers were prepared by drop casting 10 μL of PANI dispersion (10% in xylene) on GC electrode. The solvent was allowed to evaporate for 24 h before adding 30 μL of a THF solution containing the components of the outer BU-selective membrane to cover the PANI layer.

For comparison, blank BU-ISE was prepared without ion to electron transducers layer by applying the ion-selective membrane directly on the GC electrode.

The entire outer membranes of the three sensors were then allowed to evaporate overnight and then the solid contact electrodes were conditioned in 10^{-4} mol L^{-1} BU solution. The conventional BU-selective membrane solution had the following composition: 33.50% PVC, 65.71% NPOE, 0.16% NaTPB and 0.63% CX6 in 6 mL of THF.

2.4. Potentiometric measurements

Potentiometric measurements were carried out using an Ag/AgCl double-junction type external reference electrode (Thermo Scientific Orion 900200, MA, USA; 3.0 M KCl saturated with AgCl as an inner filling solution and 10% KNO_3 as bridge electrolyte) and Jenway digital ion analyzer model 3330 (Essex, UK). A Jenway pH glass electrode (Essex, UK) was used for pH adjustments. Calibrations of BU were determined by a stepwise dilution of buffered BU solutions with pure pH buffer (10 mM phosphate buffer pH 7.0) and continuous EMF measurements. Unbiased selectivity coefficients were determined with the separate solution method [19]; reported logarithmic values are averages for three electrodes. Glassy carbon working electrode, part number: CHI104, was purchased from CH Instruments, Inc., (TX, USA).

2.5. Determination of pharmaceutical formulation

A mass of Buspar® powdered tablets equivalent to 21.10 mg BU was transferred into 100-mL volumetric flask and filled to the mark with phosphate buffer of pH 7.0 to prepare a 10^{-3} mol L^{-1} solution of BU. The potentiometric measurements were performed using the proposed sensors in conjunction with the Ag/AgCl reference electrode, and the potential readings were used to estimate the corresponding drug concentration from the calibration plots.

3. Results and discussion

The aim of this work was to compare the performance of SC-ISEs based on different ion to electron transducers. A series of ion-selective electrodes with improved piece-to-piece reproducibility were prepared by utilizing CNT dispersion and the PANI nanoparticles as ion-to-electron transducers in SC-ISEs.

Carbon nanotubes have a notable charge-transfer capability between heterogeneous phases and can be easily deposited over solid-contact electrodes [6]. From a comparative point of view, the environmental stability and the processability make PANI nanoparticles an attractive candidate for application as an intermediate layer of SC-ISEs. The stability of potentiometric signal via incorporation of nanostructured moieties is attributed to the large contact area between the ion-selective membrane and the electronically conducting nanostructured material which generates a large double-layer capacitance that stabilizes the potential [20].

It was recently demonstrated that both materials can be described as an asymmetric capacitor where one side is formed by electrons (holes) in the carbon nanotube wall or along the conjugated polymer chain, in PANI nanoparticles, and the other side is formed by cations (anions) in the ion-selective membrane. Transduction mechanism in CNT can be attributed to a high double layer capacitance whereas in the case of PANI, it is anticipated to be due to the faradaic process (redox capacitance) involving reversible oxidation (doping) of the conjugated polymer chains with simultaneous insertion/expulsion of charge-compensating ions. Thus, it can be assumed that in the case of fast ion and electron transfer and transport processes, both types of mechanisms give rise to similar capacitive behavior [6].

3.1. Performance characteristics of CNT and PANI nanoparticle-based SC-ISEs

In spite of extensive research in the SC-ISE area, it appears that obtaining SC-ISEs with reproducible standard potentials is still a significant challenge [21]. In this study, initial experiments to compare the influence of CNT and PANI on the short/long term stability and detection limit of the SC electrodes were performed. The response for BU using CNT-based SC-ISE (sensor 1), PANI-based SC-ISE (sensor 2) and blank SC-ISE (sensor 3) was compared.

The electrochemical performance characteristics of the three proposed sensors are systematically evaluated according to the IUPAC standards [22,23] and illustrated in Table 1. Typical calibration plots are shown in Fig. 2. The average slopes of the calibration plots are 56.6, 58.3 and 50.6 mV/concentration decade for sensors 1, 2 and 3, respectively. Table 1 shows that sensor 2 can detect BU in very dilute solutions down to 3.16×10^{-7} mol L^{-1}, which is approximately one order of magnitude lower than that of sensor 1 and one and half order of magnitude lower than that of sensor 3. The reason behind the lower detection limit of both sensors 1 and 2 may be attributed to the absence of the inner water film in which primary ions may accumulate during