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Electrical and sensing properties of partially benzylated β-cyclodextrin: Effect of benzyl chain length

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Abstract

Thin films of two partially benzylated β-CDs (β-cyclodextrins) were used to functionalize ITO (indium tin oxide) and Si/SiO_2 substrates which were deposited by spin coating technique, to fabricate respectively a diode device and an EIS (electrolyte–insulator–semiconductor) sensor. We have studied electrical properties of ITO/β-CDs $(Bz)_{n=5,10}$/Al diodes by means of current–voltage measurement and impedance spectroscopy. The application of these new modified β-CD $(Bz)_{n=5,10}$ in the field of chemical sensors has been studied. Electrochemical capacitance measurements with EIS structures were made to test and calibrate physico-chemical sensors with regards to their sensitivity and selectivity. The sensing properties of these partial benzylated β-CD films towards Pb^{2+} in aqueous solution for sensor application were tested.

A significant effect of the average of benzylation degree on both electrical and sensing properties has been investigated.

Keywords: Benzylated β-CD; Ion sensors; EIS structure; Space charge limited current (SCLC); Equivalent circuit

1. Introduction

Molecular host-guest recognition systems [1–6] such as calixarenes and cyclodextrins have been applied successfully to chemical sensors due to their good physical and chemical stability, compatibility with large field applications and lead to low cost devices. Particularly, cyclodextrins (CDs) have emerged as an ideal candidate for this pursuit due to its well-defined molecular cavity and its ability to accommodate a variety of guest molecules [7]. Nevertheless, the strong solubility of CDs in water makes their use difficult in the development of chemical sensors working in aqueous media. In our group, different immobilization methods have been used to overcome this problem: β-CDs molecules were fixed to silica insulator surfaces; either by chemically grafting polymethyl-hydrosiloxanes (PMHS) chains as a coupling agent [8] or by physically incorporating CDs in plasticized poly (vinyl chloride) (PVC) [9]. In previous work, we have tested chemically modified β-CDs by grafting five benzyl groups and used them as sensitive membranes for Pb^{2+} detection [10].

In this work, the first section is devoted to the study of the electrical properties of ITO/β-CDs $(Bz)_{n=5,10}$/Al diodes in order to have an insight into the transport mechanisms and to investigate the solid interface present in these diodes. We have shown a space charge limited current and a better conductivity for the longer benzyls chains. The interfaces are modelled by an electrical equivalent circuit.

In the second section, we discuss the effect of the average of benzylation on sensing properties of the membranes in correlation with electrical properties of the sandwich structures.

2. Experimental

2.1. Materials

The β-CD derivative used in this work to functionalize ITO (indium tin oxide) and EIS (electrolyte–insulator–semiconductor) devices, has been synthesized by a partially

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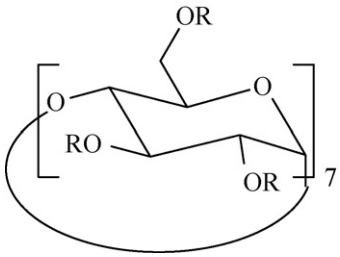

Fig. 1. Design of β-CD(Bz)$_{n=5,10}$, where R = H or R = Bz: $CH_2(C_6H_5)$.

benzylation of β-cyclodextrin as described in previous work [10]. We obtain two average of benzylation degree $n = 5$ and 10 (noted as following: β-CDs $(Bz)_5$ and β-CDs $(Bz)_{10}$ as seen in Fig. 1), by the variation of different proportions of reactors.

2.2. Diode fabrication

Thin films were obtained by spin-coating 10^{-2} M of β-CDs(Bz)$_{n=5,10}$ chloroform solutions on ITO glass substrates which were precleaned by successive ultrasonic treatment for 20 min in acetone and methanol followed by drying with nitrogen gas [11] (ITO-thickness 100 nm, sheet resistance 20 Ω/cm^2). The obtained uniform film has been left to dry in an oven at atmospheric pressure at 80 °C for 30 min. ITO thin films have been used, due to their good efficiency as hole injecting material into organic thin film. The aluminium top electrode used as cathode, was deposited on β-CDs $(Bz)_{n=5,10}$ thin film by thermal evaporation through appropriately shadow masks in high vacuum conditions (10^{-6} Torr).

2.3. Sensor fabrication

A silicon silica wafer (Si/SiO_2) was obtained from the Institute of Microtechnology of the University of Neuchatel (Switzerland). The samples were [1 0 0] p-type silicon wafers with thermally grown silica insulating layer (60 nm thickness) and a gold layer, which ensured the electrical contact on the backside of silicon. The silica insulator surface has been treated by hot sulfochromic mixture in order to remove the carbonaceous impurities and to increase the number of free silanol sites by opening siloxane bonds [12–15]. After this treatment, the substrates have been rinsed thoroughly with ultra pure water in order to remove any weakly bonded physisorbed species. A solution of β-CD (Bz) molecules in chloroform was spread out on the substrate.

The spinning rate of the samples was about 2400 rpm. The obtained film has been left to dry in an oven at atmospheric pressure at 80 °C for 30 mn. The thickness was estimated by the AFM (atomic-force microscopy) scratching technique to be about 20 nm.

2.4. Instrumentation

The current–voltage characteristics of the ITO/β-CDs $(Bz)_{n=5,10}$/Al devices were measured from an applied bias of −5 to 5 V by using a Keithley 236 source measure unit. The

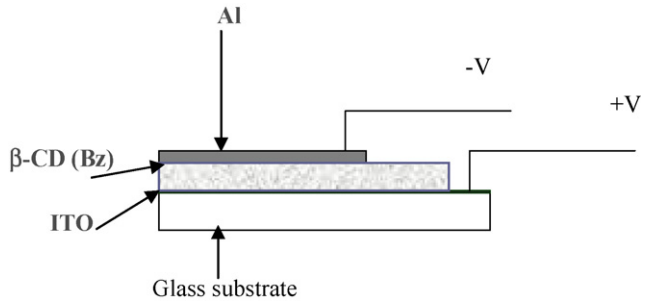

Fig. 2. ITO/β-CD(Bz)/Al diode heterostructure.

diode structure studied is a metal/polymer/metal consisting of indium tin oxide as positive contact and an Aluminium electrode as the negative contact as shown in Fig. 2.

In dynamic measurement, the excitation potential is given by:

$$V = V_0 + V_{\text{mod}} \cos(\omega t) \quad (1)$$

with V_0 is the dc bias and V_{mod} is the oscillation level and $\omega/2\pi$ is the frequency. In our case, the measurements were performed in the following conditions $V_0 = 0$ V and V_{mod} of 50 mV over a frequency range of 500 Hz–13 MHz using a computer controlled HP 4192A LF. All electrical measurements were performed in dark and at room temperature.

The EIS structures, represented in Fig. 3, were characterized by capacitance voltage measurements (C–V) method [16]. All measurements were performed in an electrochemical cell with three electrodes: the working electrode, a Pt counter electrode and saturated calomel reference electrode (SCE). A variable dc bias (V) and a constant superimposed alternative signal were applied to the working electrode using an impedance analyzer Voltalab 4 (radiometer analytical) controlled by a computer. The alternative signal amplitude was 10 mV at 10 KHz frequency were applied to the working electrode. The C–V measurements are based on the determination of the electrochemical impedance for different polarization of the cell. The flat band potential V_{FB}, varies with the ionic concentration in the cell when charges are adsorbed at the insulator surface. The sensitivity or the response of the sensor is determined by the value of the slope of the curve ΔV_{FB} as a function of the ion concentration. This variation follows the Nernstian law within a limited concentration range.

In order to avoid any intervention of electrolyte ions in the ionic equilibrium at the sensitive interface and thus any inter-

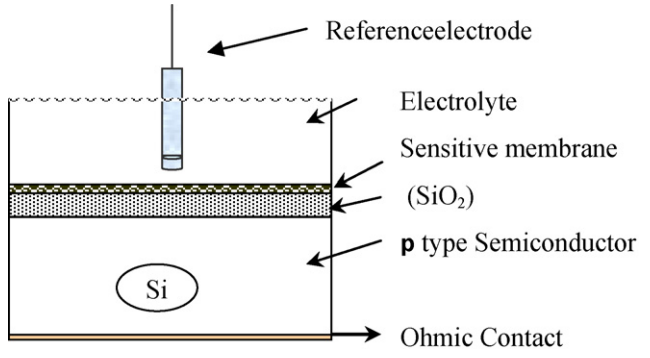

Fig. 3. Schematic of an EIS structure.