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Impedimetric sensing of cesium ion based on a thiacalix[4]arene self-assembled gold electrode

Mojtaba Shamsipur [a,*], Mehdi Asgari [b,*], Mohammad Ghannadi Maragheh [b], Dominique Matt [c]

[a] Department of Chemistry, Razi University, Kermanshah, Iran
[b] NFCS, NSTRI, Tehran, Iran
[c] Université Louis Pasteur, Laboratoire de Chimie Inorganique Moléculaire, F-67008 Strasbourg Cedex, France

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ABSTRACT

The self-assembly of cis-P,P′-dibromo{5,17-dibromo-11,23-bis(diphenylthiophosphine)-25,26,27,28-tetrapropoxycalix[4]arene} (thiacalix[4]arene) containing two sulfur groups in lower rim on gold surfaces is investigated. The thiacalix[4]arene/gold interface is investigated by means of atomic force microscopy (AFM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The AFM imaging shows the formation of a high density of small pits, a deep gold layer, and a typical feature of self-assembled organosulfur monolayers on gold. CV measurements performed in the presence of $[Fe(CN)_6]^{4-/3-}$ redox couple indicating the passivation of metal electrode, which results in a reduction of redox current after the layer formation. The EIS data were approximated using constant phase element model. The EIS was also used to investigate the selectivity properties of thiacalix[4]arene self-assembled gold electrodes by measuring R_{ct} and total impedance increase in the presence of different salt solutions. It was found that thiacalix[4]arene self-assembled gold electrodes are able to compel cesium ions. The results show good selectivity for cesium ions and a decrease in its detection limit (1.15×10^{-9} M).

1. Introduction

During the past 20 years, calixarenes have received much attention as the basis for the design of molecular receptors with selective binding properties for either ions or natural molecules [1,2]. Such applications in sensors and electrodes [3,4] continued to be popular. Also, calixarenes as the third generation supramolecules have drawn special regards among synthetic chemists due to their various binding properties. It is established that the selectivity and efficiency of metal ion binding of calixarene ionophores depend on the nature of binding groups attached, on the size of the calixarene skeleton, and in particular for calix[4]arene derivatives, on the conformation of the macrocycle. Reviews demonstrate the sensing applications of these intriguing molecules [4,5]. Calix[4]arenes with ester groups are known to act as a selective ionophore especially for Na^+ ion [6]. Properly functionalized calixarenes exhibit excellent ion-binding property due to their rigid three-dimensional cavities for the selective inclusion of inorganic ions or organic cations in aprotic solvents [7,8]. In addition to their physical pore size, electrochemical activity of calix[4]arenes is endowed by simple derivatization with quinone and thus enables the voltammetric analysis of hard metal ions in nonaqueous media.

In the last decade, new technology requirements for materials led to the development of new methods to bind organic compounds to the surface of metals. Organic compounds which bind covalently to either conductor or insulator surfaces can form thin ordered films called self-assemble monolayers (SAMs). The delicate control of surface parameters, ease of preparation, and ability to couple all this with the use of electrodes under the monolayer have spurred many investigations into applying SAMs on gold to a wide variety of scientific and technological areas; these include corrosion protection, surface wetting, construction of bio- and chemical sensors, construction of colloidal nanostructure (linked cluster networks), biological immobilization of DNA, proteins and cells, fabrication of nano-devices, together with controlling the alignment and orientation of liquid crystals, growth and deposition of polymer films to name some of the huge volume of the applied reports. SAMs have been functionalized with a wide range of novel surface moieties including fullerenes [9], hexasaccharides [10], cyclodextrins [11], and calixarenes [12,13]. Other materials besides gold, have been found to adsorb thiol containing compounds, among which

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* Corresponding authors. Tel.: +98 21 88221117; fax: +98 21 88221116.
E-mail address: mehdiasgari2002@yahoo.com (M. Asgari).

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are other metals such as silver, copper, and even liquid mercury [14], or semiconductors such as GaAs(1 0 0) [15,16].

Electrochemical impedance spectroscopy (EIS) is a rapidly developing electrochemical technique for the investigation of bulk and an interfacial electrical property of any kind of solid or liquid material connected to or is part of an appropriate electrochemical transducer [17]. Any intrinsic property of a material or a specific process affecting the interfacial properties of an electrochemical system can potentially be studied by EIS [18,19]. Thus, EIS is well-suited tool to monitor different stages necessary for biosensor fabrication, its characterization, and detection and recognition of the immobilized molecule and its ligand interaction. EIS can also be utilized as an analytical tool for the measurement of electric property changes of the sensor in the presence of increasing concentrations of the analyte. Several papers have been published based on the use of the impedance transduction on enzyme-based biosensors [20,21], immunosensors [22–24], DNA hybridization [25,26], and cellular growing behavior [27], indicating a sophisticated technique for use in sensing systems.

In the present work, the preparation and characterization of a new gold electrode modified with the self-assembly of thiacalix[4]arene are reported, and electroanalytical applications of the modified electrode for measurement of Cs^+ with accent on the EIS abilities are presented.

2. Experimental

2.1. Chemicals and synthesis

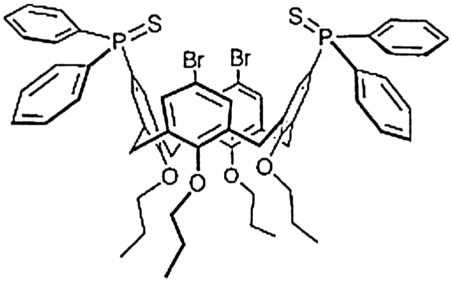
Salts, KCl (Merck, Germany), K_4 Fe $(CN)_6$ (Merck, Germany) and cesium nitrate (Merck, Germany) were of analytical grade and used as received. The calix[4]arene was synthesized in Dominique Matt's laboratory (Scheme 1) [28]. The aqueous solutions were prepared using ultra pure water. Chloroform (Merck, Germany) was utilized for preparation of solutions in self-assembly step.

2.2. Preparation of working electrode

Gold electrode was employed as a substrate for working electrode. This was polished on aqueous alumina suspension and washed with distilled water and then the gold surface was cleaned in an ultrasonic bath for 10 min in acetone and then dried under argon flow. The dried electrode was dipped for 5 min in "piranha solution". After cleaning, the gold electrode was immediately immersed in a 2 mM thiacalix[4]arene chloroform solution for 24 h at room temperature in a closed door vessel. After formation of the self-assembled monolayer, the gold electrode was rinsed with chloroform and dried under argon flow.

2.3. Electrochemical impedance spectroscopy

For electrochemical impedance spectroscopy, a three-electrode cell was utilized, with the self-assembled gold electrode as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as reference electrode. The EIS analyses were performed using an Autolab30(2) potentiostat/galvanostat equipped with FRA analyzer in the frequency range of 0.01 Hz–100 kHz, using a modulation potential of 10 mV.



Scheme 1. Structure of used calix[4]arene.

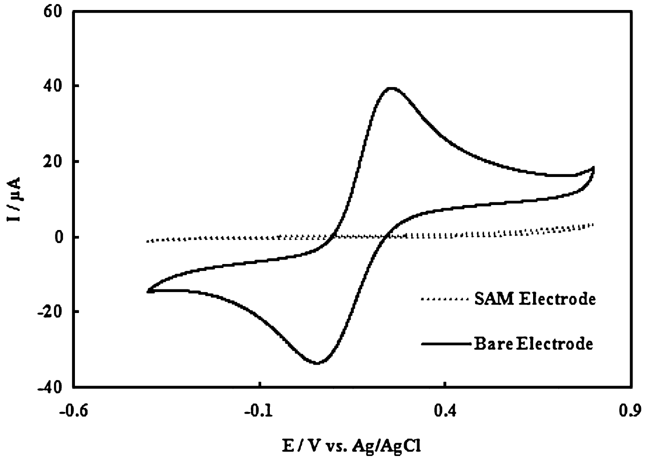


Fig. 1. Cyclic voltammograms of bare gold electrode and thiacalix[4]arene self-assembled gold electrode in 5 mM $K_4Fe(CN)_6$ + 5 mM $K_3Fe(CN)_6$, 0.1 M PBS solution (pH = 7) with Scan rate of 50 mV s^{-1}.

To avoid any interference from the electrolyte ions with the ions to be analyzed, ammonium acetate was used as electrolyte, as reported elsewhere [29]. As the calixarene cage is hydrophobic and the NH_4^+ ion is hydrophilic, the latter cannot enter into the cavity of the calixarene. Moreover, the pH of electrolyte allows preservation of the intermolecular hydrogen bonds between the hydroxyl groups which are responsible for the calixarene conformation [30].

2.4. AFM analysis

The atomic force microscopy (AFM, DS95-50 DME Denmark) was used to analyze the topography of the gold surfaces before and after self-assembly. Images were acquired in contact mode and the measurements were performed in air at 20 °C, by means of micro-levers, fabricated from low stress silicon nitride with a spring constant of ca. 0.03 N/m and length of 220 µm and a tip radius of 10–30 nm. The scan rate was typically 1 Hz/s.

3. Results and discussion

3.1. Electrochemical characterization of self-assembled monolayer

Assembly process and blocking behavior of the gold electrode surface were studied by $K_4Fe(CN)_6$ redox reaction. Although a complete characterization of SAMs depends largely on the use of XPS, ellipsometry, contact angle measurements, etc. [31], electrochemical techniques such as cyclic voltammetry [32] can be used effectively to understand the packing density and pinholes distribution in SAM monolayers. It is well known that a self-assembled monolayers can form a lipophilic barrier for electron transfer across the interface of electrode surface and hydrophilic probes in solution. CV experiments at the monolayer covered electrodes can measure diffusion-limited current which depends on the presence of pinholes in the monolayer [33]. The kinetics of the redox probe is presented by the efficiency of the monolayer in blocking redox reactions, as expressed by peak-to-peak separation [34].

Fig. 1 shows the CVs of self-assembled gold electrode for coupling sensing elements in 5 mM $K_4Fe(CN)_6$ and 0.1 M PBS solution of pH 7. A progressive increase in peak-to-peak separation values can