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Characterization of gold-thiol-8-hydroxyquinoline self-assembled monolayers for selective recognition of aluminum ion using voltammetry and electrochemical impedance spectroscopy

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HIGHLIGHTS

- Recognizing Al(III) on Au functionalized with *p*-((8-hydroxyquinoline)azo) benzenethiol.
- Impedance spectroscopy in conjunction with voltammetry is used for signal transduction.
- Advantages include wide response range, high selectivity and stability, and ease of fabrication.
- The sensor is successfully examined for determination of Al(III) in blood serum samples.

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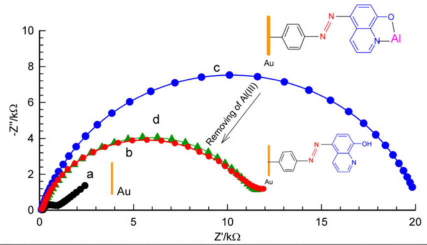
GRAPHICAL ABSTRACT



(a) Bare Au, (b) Au-SHQ, (c) Au-SHQ-Al(III), and (d) recovered Au-SHQ.

ABSTRACT

Gold electrode surface is modified via covalent attachment of a synthesized thiol functionalized with 8-hydroxyquinoline, *p*-((8-hydroxyquinoline)azo) benzenethiol (SHQ), for the first time. The behavior of the nanostructured electrode surface (Au–SHQ) is characterized by electrochemical techniques including cyclic and differential pulse voltammetry (CV and DPV), and electrochemical impedance spectroscopy (EIS). The modified surface is stable in a wide range of potentials and pHs. A surface pK_a of 6.0 ± 0.1 is obtained for Au–SHQ electrode using surface acid/base titration curves constructed by CV and EIS measurements as a function of pH. These results helped to determine the charge state of the surface as a function of pH. The gold modified electrode surface showed good affinity for sensing the Al(III) ion at pH 5.5. The sensing process is based on (i) accumulation and complex formation between Al(III) from the solution phase and 8HQ function on the Au electrode surface (recognition step) and (ii) monitoring the impedance of the Au–SHQ–Al(III) complex against redox reaction rate of parabenzoquinone (PBQ) (signal transduction step). The PBQ is found to be a more suitable probe for this purpose, after testing several others. Thus, the sensor was tested for quantitative determination of Al(III) from the solution phase. At the optimized conditions, a linear response, from 1.0×10^{-11} to 1.2×10^{-5} M Al(III) in semi-logarithmic scale, with a detection limit of 8.32×10^{-12} M and mean relative standard deviation of 3.2% for $n = 3$ at 1.0×10^{-7} M Al(III) is obtained. Possible interferences from coexisting cations and anions are also studied. The results show that many ions do not interfere significantly with the sensor response for Al(III). Validity of the method and applicability of the sensor are successfully tested by determination of Al(III) in human blood serum samples.

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1. Introduction

Aluminum ion, Al(III), a widely dispersed element on the earth, has not been attributed any essential role by nature in living

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processes. On the contrary, it is a well-established neurotoxin and is assumed to be linked with various neurodegenerative diseases related to the proteins, DNA, enzymes, especially, Alzheimer and Parkinson's. The Al(III) ion can contribute to the oxidative damage of biological membranes [1–3]. The toxicity of Al(III) toward fishes, algae and plants is also well documented [4]. Thus, it is important to develop new analytical methods for the determination of Al(III) in water, foods, and biological fluids like blood. Determination of Al (III) concentrations in blood, either serum or plasma, is of major clinical importance [5]. For example, for patients with impaired renal function, the Al(III) concentration in serum can be 100-fold greater than in individuals with normal renal function [6].

Analytical techniques reported for Al(III) determination are mainly based on extraction followed by atomic absorption [7] and emission [8] spectroscopy, spectrophotometry [9], electrochemiluminescence [10], and electrochemical methods [11]. The electrochemical methods benefit from their simplicity, lower price, and better analytical performance. Besides, the compact and lightweight electrochemical instruments allow the analysis being easily performed in the field and readily automated [12]. In particular, the methods developed based on chemical modification of the electrode surface [13] are interesting. Usually, quantitative electroanalysis of the metal ions, accumulated by complexation onto the surface of the chemically modified electrodes, can be followed by stripping voltammetric (SV) analysis directly for electroactive metal ions, or indirectly by using electroactive ligands for electroinactive metal ions.

Direct quantitative determination of Al(III) by stripping voltammetry is difficult, because it is reduced at potential of -1.75 V vs. Ag/AgCl, which is close to the hydrogen evolution potential. Thus, indirect determination of Al(III) based on adsorptive stripping voltammetry of a thin film of some electroactive ligands adsorbed on hanging mercury drop or mercury film electrode has been developed [14]. Due to intrinsic drawbacks of mercury electrodes, such as toxicity and instability, great efforts have been made to develop mercury-free solid modified electrodes [15]. For example, determination of Al(III) by potentiometric ion-selective electrodes [16], and voltammetry at the carbon electrodes modified by using dopamine [17], alizarin [18], and 8-hydroxyquinoline (8HQ) [19] have been reported.

The 8HQ is a versatile ligand which has been used in analytical as well as in synthetic coordination chemistry. This molecular unit is an ideal building block for different purposes such as metallosupramolecular assembly [20]. A series of 8HQ analogues have shown potential application for treatment of the neurodegenerative diseases [21], probably by removing metal ions like Cu(II), Zn (II), Al(III), and Fe(III) from their complex structures. The 8HQ and its derivatives have so far been immobilized on various surfaces and used for kinetic purposes or analytical applications, e.g., determination of Al(III) (Supplementary Data, Table S1).

Recently, we have constructed several of the gold-thiol self-assembled monolayers (SAMs) functionalized with various organic and biological moieties and tested them for electrochemical determination of different metal ions (Supplementary Data, Table S2). In particular, we have developed a new strategy for determination of Fe(III) [22,23], which has potential applications for other metal ions. In addition, despite the interesting behavior of SAMs, no previous report has been published regarding application of these types of modified electrodes for quantitative determination of Al(III).

The possibility to use this strategy [22,23] for determination of Al(III) is briefly introduced here. The complexed form of Fe(III) with deferrioxamine (DFO) on gold (Au–MPA–DFO–Fe(III)) is (i) active with a well-defined redox wave around 0.00 V vs. SCE, and (ii) inactive without any redox reaction wave in positive potential regions. Thus, we found two potential regions for determination of Fe(III): (i) around 0.00 V where no redox probe is needed (thus called active mode) and less accurate data is obtained, and (ii) around +0.200 V where a redox probe is used (thus called inactive mode) and more accurate data is obtained [24].

The situation for Al(III) is different. Since the active mode of Al (III) is not accessible in the applicable potential window in aqueous solutions, we have developed a method for determination of Al(III) based on being inactive.

Accordingly, we have fabricated a new gold-thiol SAM electrode functionalized with 8HQ group, and used it as a sensor for accumulation and quantitative determination of Al(III) from solution phase. The modified electrode has shown a good affinity towards the Al(III). Finally, the experimental data, demonstrating successful application of the sensor for selective determination of Al(III) in real (human blood serum) samples are presented and discussed.

The sensing process is based on (i) accumulation and complex formation between Al(III) from solution phase and 8HQ group from the Au–SHQ electrode surface (recognition step) where SHQ denote the synthesized thiol, *p*-((8-hydroxyquinoline)azo) benzenethiol (SHQ), and (ii) monitoring the impedance of Au–SHQ–Al (III) complex against redox reaction rate of parabenzoquinone (PBQ) electrochemically (signal transduction step). The PBQ is used as a more suitable probe for this purpose, after testing several others like FcMeOH, $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_6]^{3+}$. Any reversible redox reaction, being sensitive to the surface changes and modifications, may be used for this purpose. Electrochemical impedance spectroscopy (EIS) in conjunction with differential pulse voltammetry (DPV) is used for characterization of the sensor and transduction of the analytical signals. The EIS technique benefits of several unique advantages, and has been used by us (see Supplementary Data, Table S2) and others [24,25] for quantitative chemical analysis.

2. Experimental

2.1. Materials and reagents

$Al(NO_3)_3 \cdot 9H_2O$ (99.999%), 8-hydroxyquinoline (8HQ), 4-aminothiophenol (4-ATP), trichloroacetic acid (TCA), hexaammineruthenium(III) chloride ($[Ru(NH_3)_6]Cl_3$), parabenzoquinone (PBQ), ferrocenemethanol (FcMeOH) and other chemicals were of analytical grade purchased from commercial sources (Merck® or Sigma–Aldrich®) and used as supplied, without further purification. All the solutions were prepared with double-distilled water. Phosphate buffer and acetate buffer saline (PBS and ABS) solutions were prepared in desired pHs by using 0.1 M NaH_2PO_4/Na_2HPO_4 or 0.05 M acetic acid/sodium acetate, respectively. Supporting electrolyte for buffers in all electrochemical measurements was 0.1 M $NaClO_4$. The pH of the solution was adjusted using corresponding acids or 0.1 M NaOH solutions. The working solutions of Al(III) were prepared in ABS solution (pH 5.0) from 0.10 M Al(III) stock solution. This solution was prepared by dissolving required amount of $Al(NO_3)_3 \cdot 9H_2O$ in 0.01 M nitric acid. Serum samples of healthy human volunteer blood donations were obtained from Esfahan blood transfusion organization (EBTO, Isfahan, Iran).

Functionalization of Au with 8HQ was performed by ex-situ synthesis of the related 8HQ functional thiol, and then, transferring it onto the Au surface. Synthesis of functional thiol *p*-((8-hydroxyquinoline)azo) benzenethiol, abbreviated as SHQ (Fig. 1), was performed according to the literature [26] and approved by FTIR and NMR measurements (Supplementary Data, Figs. S1 and S2).

2.2. Apparatus

All electrochemical measurements were performed by using Potentiostat/Galvanostat AUTOLAB 30 (Eco Chemie, Utrecht, The

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