



Simple and rapid mercury ion selective electrode based on 1-undecanethiol assembled Au substrate and its recognition mechanism



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ARTICLE INFO

Article history:

Received 15 August 2016

Received in revised form 2 October 2016

Accepted 8 November 2016

Available online 12 November 2016

Keywords:

Mercury ion

1-Undecanethiol

Self-assembled monolayer

Recognition mechanism

Density functional theory

ABSTRACT

A simple and rapid mercury ion selective electrode based on 1-undecanethiol (1-UDT) assembled Au substrate (Au/1-UDT) has been well constructed. 1-UDT was for the purpose of generating self-assembled monolayer on gold surface to recognize Hg^{2+} in aqueous solution, which had a working concentration range of 1.0×10^{-8} – 1.0×10^{-4} mol L^{-1} , with a Nernst response slope of 28.83 ± 0.4 mV/ $-\text{pC}$, a detection limit of 4.5×10^{-9} mol L^{-1} , and a good selectivity over the other tested cations. Also, the Au/1-UDT possessed good reproducibility, stability, and short response time. The recovery obtained for the determination of mercury ion in practical tremella samples was in the range of 99.8–103.4%. Combined electrochemical analysis and X-ray photoelectron spectroscopy (XPS) with quantum chemical computation, the probable recognition mechanism of the electrode for selective recognition of Hg^{2+} has been investigated. The covalent bond formed between mercury and sulfur is stronger than the one between gold and sulfur and thus prevents the adsorption of 1-UDT molecules on the gold surface. The quantum chemical computation with density functional theory further demonstrates that the strong interaction between the mercury atom and the sulfur atom on the gold surface leads to the gold sulfur bond ruptured and the gold mercury metallophilic interaction.

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1. Introduction

In recent decades, the environmental and food-borne problems caused by rapid and intensive industrialization and urbanization have been receiving tremendous attention all over the world. Among these problems, heavy-metal-related pollution has become a tremendously serious problem in many countries [1–5]. Mercury (Hg), as it is known, is a kind of heavy metals having toxicity. Trace amount of Hg can generate strong toxicity, destroy the cell metabolism and basic functions, and damage the liver function and lead to kidney failure [6,7]. Its determination at low concentration level is necessary for supporting living organisms, including humans [7,8]. Currently, the general detection methods for mercury ions included spectrophotometry [9], atomic absorption/emission spectroscopy (AAS/AES) [10,11], inductively coupled

plasma mass spectrometry (ICP-MS) [12], surface-enhanced Raman scattering (SERS) spectroscopy [13], and fluorescence spectrometry [14], etc. Despite the high sensitivity and accuracy, these methods often possessed some disadvantages for the determination of Hg^{2+} , for example, the complication of the sample preparation and the high cost of the equipment. Developing an inexpensive, simple, rapid and sensitive analytical method for the determination of Hg^{2+} is highly required.

Ion selective electrode (ISE) method is an important branch of electrochemical analysis for detecting mercury ion. It is a kind of convenient and potential analysis that treats an ion selective electrode as an indicating electrode. Because of simple preparation procedure, rapid detection speed, good selectivity and low detection limit, ISEs have been widely used in various areas such as food, environment, medicine, agriculture, and life science, etc [15,16]. As a quick analysis tool, the key of ion selective electrode is the preparation of carrier membrane for different targets [17–19]. And some organic compounds such as polyvinylpyridine [20], Schiff base [21], calixarene derivative [22] have been successfully used as active materials for mercury ion detection. However, these electrodes often possessed some disadvantages for the determination of Hg^{2+} , such as relatively narrow concentration range, poor stability

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and selectivity. Therefore, the preparation of mercury ion selective electrode with good selectivity and low detection limit is highly required. A lot of compounds containing N, O and S atom have been proved to have strong affinity with heavy metal ions [23–29], and some compounds containing sulfur atoms have been successfully used as active carrier for mercury ion selective electrode [19,30,31]. On the other hand, only little information is available on the recognition mechanism of quantum chemistry for mercury ion, which means that any new mechanistic information derivable from such interactions is yet to be fully realized. The advance in density functional theory (DFT)-based quantum chemical computations has made this powerful tool increasingly available for theoretical investigation of the thiol self-assembled films on gold electrode for recognition of metal ions such as Hg^{2+} .

This work is part of an on-going program devoted to the study about the adsorption of thiol molecules on gold electrodes for recognizing mercury ions. Our current attempt at elucidating the mechanisms of mercury ion – 1-undecanethiol (Hg^{2+} – 1-UDT) interactions on gold surface involves assessment of the ion selective electrode performance. In this paper the experimental approaches and DFT computations have been performed to investigate the recognition mechanism between Hg^{2+} and 1-UDT on gold surface in aqueous solution. The motivation for the computational study is not so much to explain specific data for each system, but rather to give a confirmatory result in which to understand the relative interaction behavior between Hg^{2+} and 1-UDT on gold surface.

2. Experimental and computational details

2.1. Chemicals

The compound of 1-undecanethiol (1-UDT, $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$, MW = 188.37) was purchased from the Sigma Aldrich company (USA), and its structure is shown in Fig. 1. Trihydroxymethyl aminomethane (Tris), ethanol, concentrated sulfuric acid, hydrochloric acid, potassium ferricyanide ($[\text{K}_3\text{Fe}(\text{CN})_6]$) and potassium ferrocyanide ($[\text{K}_4\text{Fe}(\text{CN})_6]$), HgCl_2 , and Na_2SO_4 were obtained from Changsha Yufeng Chemicals Co. (China), which were of analytical reagent grade and used without further purification. The deionized water with specific resistance of $\geq 18.3 \text{ M}\Omega \cdot \text{cm}$ was obtained from a NanoPure Infinity Ultrapure water system (Barnstead/ThermoFisher Corp., Dubuque, IA, USA), which was used throughout all the experiments.

2.2. Electrode preparation

Gold disk electrode (3 mm, Shanghai Xianren Instrument Co., LTD, China) was firstly polished using a series of alumina powders (0.3, 0.1 and 0.05 μm), and then sonicated in deionized water/EtOH/deionized water for 10 min in sequence. Immediately before modification, the cleaned electrode was thoroughly rinsed with the deionized water. Then the cleaned gold electrode was immersed in 0.1 mol L^{-1} 1-UDT solution for 48 h at room temperature, that the deposition solution was prepared using ethanol as a solvent medium. Finally, the modified electrode was employed to detect mercuric ion under weakly acidic conditions.

2.3. Computational details

All theoretical computations were performed within the framework of density functional theory (DFT) using the Materials Studio; MS Modeling 6.0 software (Accelrys Inc., USA). The 1-UDT molecule

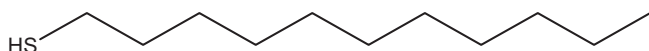


Fig. 1. Structure of 1-UDT molecule.

structure and the Au surface were modeled by means of the DFT electronic structure program CASTEP using a Mulliken population analysis as well as a Hirshfeld numerical integration procedure [32–34]. Using the DNP basis set and the Perdew Wang (PW) local correlation density functional, the electronic parameters for the simulation included restricted spin polarization.

Calculations were carried out in a simulation box ($4.19 \text{ \AA} \times 2.96 \text{ \AA} \times 10.96 \text{ \AA}$) to model a representative part of the interface, devoid of arbitrary boundary effects. The box was comprised of the Au slab, cleaved along the (110) plane and a vacuum layer of 20 \AA height. The geometry of the bottom layer of the slab was constrained to the bulk positions whereas other degrees of freedom were relaxed before optimizing the Au (110) surface, which was subsequently enlarged into a supercell. 1-UDT molecules were adsorbed on one side of the slab. The molecular geometry structures of the 1-UDT in this study are shown in Fig. 2a. Temperature was fixed at 298 K. Optimized structures of 1-UDT and the Au surface were used for the energy calculations. Interactions between 1-UDT, Hg^{2+} and the Au (110) surface were carried out in the simulation box ($4.19 \text{ \AA} \times 2.96 \text{ \AA} \times 30.01 \text{ \AA}$) with periodic boundary conditions. The Au (110) was first built and relaxed by minimizing its energy via molecular mechanics using the molecular simulation program (Fig. 2b). The surface area was increased with a vacuum slab of thickness of 20 \AA . The CASTEP was used to study the chemical reaction mechanism of 1-UDT and Hg^{2+} onto the Au (110) surface. The structure optimizations and corresponding total energy calculations of the most stable geometries were based on the generalized-gradient approximation (GGA) function with the Perdew–Burke–Ernzerhof correction [35]. For core electrons in the lowest lying atomic orbitals, the DFT semicore potential was implemented for relativistic effects [36]. The CASTEP electronic options were adjusted as follows: Monkhorst–Pack k-point mesh parameters were set to Gamma; self consistent field procedures were carried out with a convergence criterion of 10^{-5} , using direct inversion in an iterative subspace (DIIS) and orbital occupancy smearing parameter of 0.005 Ha to speed up SCF convergence [37].

We have neglected solvent and charge effects in all our simulations and performed the calculations at the metal/vacuum interface. Although this is clearly an oversimplification of the factual situation, it is adequate to qualitatively illustrate the differences in the adsorption reaction behavior of both molecules and provide sufficient insight to rationalize our experimental findings.

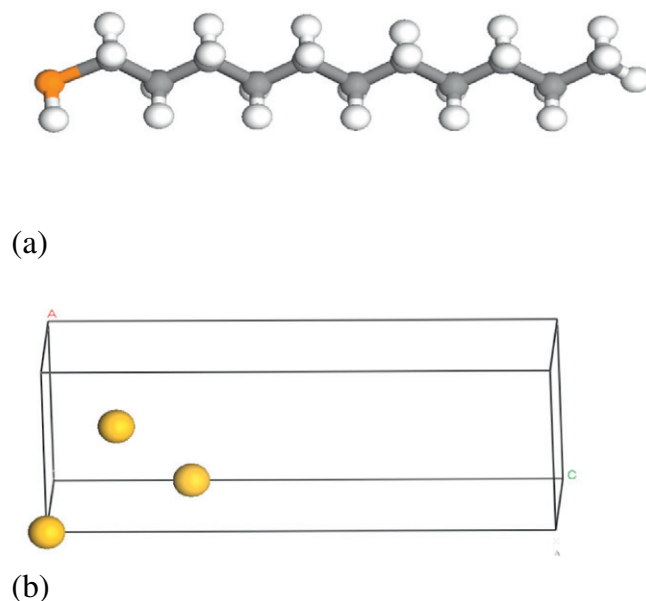


Fig. 2. Geometry structures of 1-UDT molecule (a) and Au (110) surface (b).

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