



Using nanoparticle aggregation to give an ultrasensitive amperometric metal ion sensor

J. Justin Gooding*, Jarred Shein, Leo M.H. Lai

School of Chemistry, The University of New South Wales, Sydney 2052, Australia

ARTICLE INFO

Article history:

Received 8 July 2009

Received in revised form 19 August 2009

Accepted 21 August 2009

Available online 28 August 2009

Keywords:

Gold nanoparticles

Copper detection

Self-assembled monolayers

Electrochemical sensors

ABSTRACT

Herein we show an electrochemical sensor for the detection of copper ions that has a limit of detection below 1 pM. This extraordinarily low limit of detection is achieved in two ways. The first is to use SAM modified electrodes to give low background current where electron transfer to the underlying polycrystalline electrode is achieved through gold nanoparticles attached to the terminus of the SAM. The gold nanoparticles are modified with cysteine to allow copper accumulation. The second way the low detection limits are achieved is by the addition of cysteine-modified nanoparticles to the sample solution, as well as the SAM modified electrode. The complexation of copper with the nanoparticles in solution causes them to aggregate with these aggregates accumulating on the electrode. Thus a higher percentage of copper in the solution is collected at the electrode giving the enhanced detection limits.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

One of the major foci of sensor research is to reduce the detection limit of the final device. This in itself is an important goal but this cannot be achieved by increasing the sensitivity of the detector alone. Equally important considerations are the background signal and the response time. Limiting the background clearly becomes progressively more important as analyte concentration decreases so that the analytical signal is discernable. The issue of response time is really an issue of the analyte actually finding the sensing surface. In the vast majority of devices, the sensing surface is located in a defined position in space, at the surface of the transducer that is either a flat surface or more recently a nanostructured surface. With very low concentrations of analyte it may take an inordinate amount of time for the analyte to actually find the sensing surface. The slow response time is a consequence of the time taken for a species to diffuse through a planar sheet which has a squared dependency on the thickness of that sheet [1]. Optical sensors have provided a solution to this problem by creating an intimate mixture between the sample and the sensors. This can be achieved either by dispersing the sensor throughout the sample using nanoparticle [2,3] or by dispersing the sample throughout the sensor using nanoporous sensing materials [4–6]. Such strategies have the twin benefit of reducing the diffusional pathlengths and potentially collecting a larger proportion of the analyte in the sample. In electrochemical systems, such strategies are less viable. Dispersed

nanoparticles as amperometric sensors is naturally not possible with electrochemical systems as each nanoparticle would require a wire to be attached to allow amperometry to occur. Mesoporous electrodes have been fabricated but the large electrode surface areas that result can result in high background capacitances and hence high background signals.

The purpose of this paper is to introduce a sensing system that combines functionalised nanoparticle modified electrodes and functionalised nanoparticles in solution as an approach to give low background modified electrodes that interact intimately with the sample for analysis. The idea is based on an observation by us [7,8] and others [9–17] that attaching nanoparticles or nanotubes onto the ends of otherwise passivating SAMs opens up conducting channels through which electron transfer can proceed as though the SAM is not even present. The mechanism of this phenomenon is currently of active investigation by us [8] and the Fermin group [14–17]. Regardless of the mechanism it does provide a simple strategy by which nanoelectrode arrays can be fabricated with low background capacitances and a simple strategy to fabricate blocked electrochemical sensors analogous to the nanowire concept we developed previously [18,19]. This is achieved by modifying an electrode with a SAM of 11-amino-1-undecanethiol that passivates the electrode from positively charged redox active species in solution. The amine on the distal end of the SAM are used to bind gold nanoparticles which are subsequently modified with cysteine as a selective ligand for Cu^{2+} as we have shown previously [20]. Dispersed into the sample solution are more cysteine-modified gold nanoparticles. We have shown that each Cu^{2+} is complexed by 2 cysteine molecules [20] and hence addition of Cu^{2+} to the sample will cause the nanoparticles to aggregate [13]. Here

* Corresponding author. Tel.: +61 2 9385 5384; fax: +61 2 9385 6141.
E-mail address: Justin.gooding@unsw.edu.au (J.J. Gooding).

we show that these aggregates bind to the electrode surface to give an ultrasensitive Cu^{2+} sensor with a limit of detection below 1 pM.

2. Experimental section

2.1. Chemicals

Ruthenium [III] hexamine chloride (98% purity) and 11-amino-1-undecanethiol, hydrochloride (AUT) was purchased from Aldrich (Sydney, Australia). *L*-cysteine hydrochloride (98% purity), potassium chloride (99% purity) and hydrogen tetrachloroaurate [III] were from Sigma (Sydney, Australia). Copper(II) nitrate (98% purity) and tri-sodium citrate (99% purity) were from Ajax Chemical Co. (Sydney, Australia) while ammonium acetate (96% purity) was purchased from May and Baker (Sydney, Australia). All the aqueous solutions were prepared in Milli-Q water (18 M cm, Millipore, Sydney, Australia).

Gold nanoparticles were synthesized using a 1 mM solution of HAuCl_4 (0.17 g) in Milli-Q water that was boiled prior to adding sodium citrate with constant stirring. A colour change started to occur 10 s after the addition of the citrate solution according to the method of Frens [21]. The resulting aquasol had a concentration of ~ 17 nM and a diameter of 12.3 ± 0.5 nm as determined by SEM.

2.2. Instruments and measurements

The electrochemical characterisation techniques of cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed in a conventional three-electrode cell with gold working electrode (CHI 101), an Ag|AgCl reference (CH Instruments Inc. Texas, USA) and a home made platinum flag as a counter electrode. CV was carried out using an Autolab (MEP Instruments, Sydney, Australia) potentiostats. SWV analysis was performed using the BAS 100B Electrochemical Analyser (Bioanalytical System Inc., Lafayette,

USA). Scanning electron microscopy was conducted using a Hitachi S-900 SEM (Berkshire, England).

2.3. Preparation of modified electrodes

Gold working electrodes were cleaned by polishing with $1.0 \mu\text{m}$ alumina, followed by 0.3 and $0.05 \mu\text{m}$ alumina slurry on microcloth pads (from Buehler, Lake Bluff, IL, USA) and then by electrochemical cleaning by cycling between -300 mV and $+1500$ mV in 50 mM H_2SO_4 at a scan rate of 150 mV s^{-1} . To form SAMs 1 mM solutions of 11-amino-1-undecanethiol (AUT) were prepared in a 99% pure, distilled ethanol solvent. The gold electrodes were left in the respective solutions for 48 h at room temperature.

The SAM modified gold electrodes were further modified with a gold nanoparticles, to give the constructs shown in Fig. 1, by placing the electrodes in the gold colloid solution for 8 h. The same procedure was performed on gold foils to enable the surfaces to be imaged using SEM. To modify the surface bound gold colloids with cysteine for copper detection the electrode was placed in a solution of 0.1 mM *L*-cysteine in Milli-Q water for 2 h. To modify solution dispersed gold nanoparticles with cysteine the same 0.1 mM *L*-cysteine in Milli-Q water solution was used.

2.4. Detection of copper

A 0.05 M ammonium acetate buffer solution (pH 7.0) was used for both the accumulation of copper and electrochemical measurements. Copper ions accumulated at the modified gold electrodes at open circuit potential for 10 min without stirring in the 0.05 M ammonium acetate buffer solution containing copper nitrate. Accumulation of copper ions was also carried out with a 17 nM cysteine-modified nanoparticle in solution for 10 min to enable

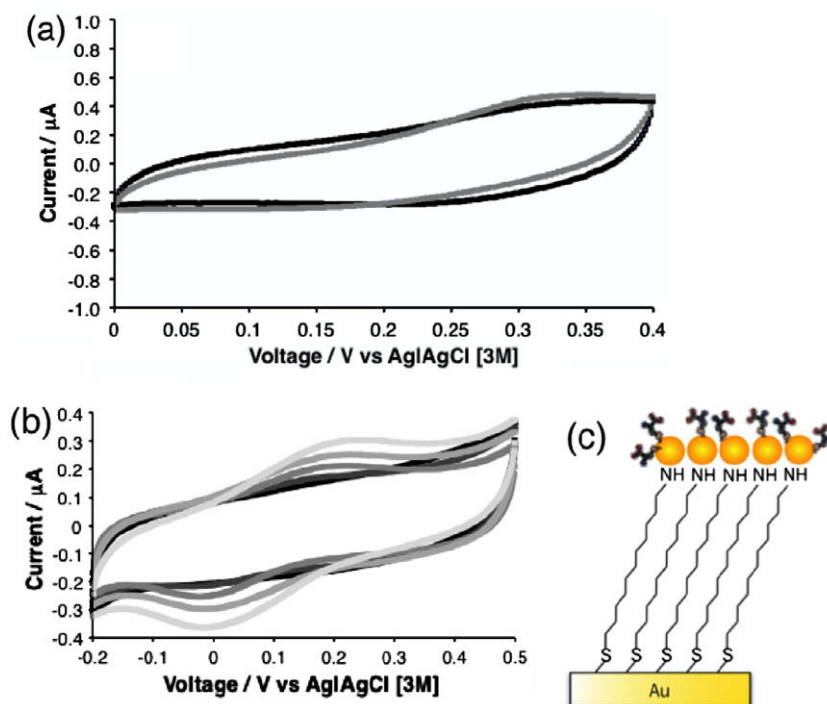


Fig. 1. (a) CV of non-modified nanoparticle exposed to 1 mM copper solution; before copper exposure (black) and after copper exposure (grey). (b) Cyclic voltammogram (CV) of *L*-cysteine modified nanoparticle electrodes with varying amounts of copper; from the darkest to the lightest, 0 nM, 1 nM, 100 nM, 100 mM and 1 mM. (c) Schematic of the modified nanoparticle electrode construct with an aminoundecylthiol base layer and topped with *L*-cysteine-modified nanoparticles.

Download English Version:

<https://daneshyari.com/en/article/181104>

Download Persian Version:

<https://daneshyari.com/article/181104>

[Daneshyari.com](https://daneshyari.com)