Sensors and Actuators B 195 (2014) 223–229

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Gold electrodes from recordable CDs for the sensitive, semi-quantitative detection of commercial silver nanoparticles in seawater media

E.J.E. Stuart[a], K. Tschulik[a], D. Lowinsohn[a,b], J.T. Cullen[c], R.G. Compton[a,*]

[a] Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom
[b] Department of Chemistry, Instituto de Ciencias Exatas, Universidade Federal De Juiz de Fora, 36036-330 Juiz de Fora, MG, Brazil
[c] School of Earth and Ocean Sciences, University of Victoria, Victoria, BC, Canada V8W 3V6

ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form 7 January 2014
Accepted 11 January 2014
Available online 20 January 2014

Keywords:
Silver nanoparticles
CDtrodes
Seawater
Commercial nanoparticles

ABSTRACT

We report the use of homemade disposable gold electrodes fabricated from commercial recordable CDs for the detection and quantification of silver nanoparticles from a consumer product in a seawater sample. The "CDtrode" is immersed in a seawater sample containing silver nanoparticles for a certain amount of time during which the silver nanoparticles adsorb onto the CDtrode surface under open circuit conditions. The CDtrode is then transferred to an aqueous electrolyte and oxidative stripping is used to determine the amount of silver nanoparticles that have become stuck to the electrode surface. Depending on immersion time and silver nanoparticle concentration, up to a full monolayer coverage of silver nanoparticles on the CDtrode surface has been achieved.

1. Introduction

The detection of nanoparticles (NPs) that have been released into the aquatic environment is a major challenge facing environmental scientists [1]. One type of man-made nanoparticle that researchers are determined to detect in natural waters are silver nanoparticles (AgNPs); this is due to their extensive incorporation into everyday products (e.g. medical dressings, sportswear and household appliances [2–4]) resulting in inevitable environmental release as well as their essentially unknown impact on the environment [5–8].

A solution to this analytical challenge is to use a simple electrochemical technique where a "sticky" electrode is introduced into a AgNP suspension and left for a certain amount of time during which the NPs will stick to the electrode surface under open circuit conditions [9]. Any immobilised NPs are then oxidatively stripped off the electrode allowing quantification of the AgNPs not only on the electrode surface but also, with suitable calibration, in the solution of interest.

Proof-of-concept studies simulating the environmental detection of AgNPs have validated the application of this sticking and stripping technique for the real-time detection of AgNPs using disposable "sticky" carbon electrodes in real seawater media [9,10].

The use of disposable electrodes is important for ensuring low cost field-based sampling and is ideal for long-term experiments where electrodes might need to be suspended in seawater for up to several days in order to ensure a sufficient signal can be gained for quantification due to the reportedly low concentrations of NPs present in natural waters [11]. Previous studies testing the suitability of disposable electrodes for this application have used commercially available screen printed carbon electrodes that have been modified with cysteine to achieve a "sticky" surface reporting a maximum surface coverage of AgNPs on the electrode surface of less than 1% [10]. Note that the "sticky" electrodes provide a qualitative indication of the presence or absence of nanoparticles and also allow the approximate detection of concentration levels with order of magnitude estimates usually being adequate in this area of detection.

A simple method to produce home-made disposable gold electrodes was first reported by Angnes et al. [12] who proposed using recordable compact discs (CDs) to achieve extremely versatile, commonly available "one way use" gold electrodes at low cost that behave almost identical to commercial gold macroelectrodes. The potential of these CDtrodes was soon recognised by the scientific community and they have since been used to study self-assembled monolayers [13], quantify mercury in both natural waters [14] and fish samples [15], in the determination of selenium [16] and in the production of microfluidic devices [17]. Recently, Xiong et al. [18] reported a simple method for the construction of CDtrodes based on the thermal lamination construction technique proposed by Neudeck et al. [19]. Thorough testing of the laminated CDtrodes

* Corresponding author.
E-mail address: richard.compton@chem.ox.ac.uk (R.G. Compton).

0925-4005/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2014.01.040

revealed their ability to generate accurate and reproducible results for commonly used systems in both aqueous solutions and ionic liquids [18].

Howard [1] has suggested that the challenge of detecting NPs in the aquatic environment is the lack of existence of analytical techniques capable of measuring dispersed NPs in a liquid phase as opposed to dissolved species. Hitherto laminated CDtrodes have only been used to study the electrochemistry of dissolved species [18]. Herein we propose their application to the detection of AgNPs from a consumer product in seawater media via the sticking and transfer stripping method described above and summarised in Fig. 1. The aim is to use unmodified CDtrodes for the semi-quantitative analysis of AgNPs giving the user an estimation of AgNP concentration to within an order of magnitude and improve upon the maximum surface coverage values reported in previous work for AgNP sticking at an electrode surface. We report that the extent of AgNP adhesion observed at laminated gold CDtrodes in this study can reach full monolayer coverage on the electrode surface circumventing the need for the use of "sticky" electrodes as in [9,10]. We emphasise that this work is semi-quantitative due to the high variability associated with AgNP sticking at the Au CDtrodes, these typically large errors are a generic feature of nanoelectrochemistry caused by the increased sensitivity of nanoparticles to any adsorbed species present on the electrode surface thereby reducing the area available for nanoparticle sticking.

2. Experimental

2.1. Materials and set-up

Unless stated otherwise all chemicals were purchased from Sigma–Aldrich. All solutions were made up using ultrapure water with resistivity not less than 18.2 MΩ cm at 25 °C (Millipore). The AgNPs used in this study are from a commercially available colloidal silver cleaning spray product (Higher Nature Ltd., East Sussex, UK) with a AgNP concentration of 47 pM. The AgNP concentration was determined by depositing 2 μL of the spray on the surface of a glassy carbon macroelectrode (r = 1.5 mm), drying the electrode under N_2 and oxidatively stripping off the dropcasted AgNPs in 0.1 M $NaClO_4$, the concentration was then calculated from the charge of the anodic peak observed taking into consideration the size of the NPs (r = 11 nm, determined via Anodic Particle Coulometry and Nanoparticle Tracking Analysis [20]), the one electron oxidation of each Ag atom, as well as the density and molar mass of Ag. Seawater samples were collected from Saanich Inlet, Victoria, Canada using 5 L Niskin bottles (General Oceanics, FL, USA) fixed to a stainless steel hydrowire and transferred to the laboratory in trace metal clean low density polyethylene bottles (250 mL) where they were stored at 4 °C.

For the electrochemical set-up, a μAutolab II potentiostat was used with a three electrode configuration: a Ag/AgCl reference electrode (potential vs. SHE = 0.222 V, 3 M KCl, eDAQ, Red Box Direct Ltd., Ireland), a carbon rod counter electrode and a Au CDtrode (r = 1 mm) or Au micro (r = 4.2 μm, IJ Cambria Scientific Ltd., Llanelli, UK) working electrode.

2.2. Fabrication of CDtrodes

The CD etching process is summarised in Fig. 2. The gold CD (MAM White Inkjet Gold Archive Disc) was first introduced into a bath of 0.6 M NaOH for a minimum of 20 min to fully remove the white inkjet printable surface. After rinsing with water and leaving to air-dry the CD was placed into a bath of conc. HNO_3 as in [12]. It takes approximately 3 min for the polymer film to start to peel away from the gold surface; a water jet can then be used to fully remove the film before drying the newly exposed gold surface with nitrogen.

Scissors were used to cut the CD to the desired electrode size (8 mm × 8 mm) and an electrical connection to the CD piece was achieved with adhesive copper tape (Farnell element 14, Leeds, UK). A hole (r = 1 mm) was punched in one page of a laminating film before positioning the CDtrode between the two pages of film ensuring that the gold was exposed through the punched hole. The laminating film was then passed through the laminator (Ativa AT-100A4) three times to ensure a sufficient seal. For experiments requiring the CDtrode to be in solution for long periods of time (>25 h) nail polish (Sabrina Cosmetics, Germany) was applied to the edges of the CDtrode to reinforce the laminated seal.

2.3. AgNP sticking in seawater at gold CDtrodes

An aliquot of AgNP nanoparticles (6 mL) was added to 12 mL seawater so that the concentration of AgNPs was 15.6 pM. The AgNP–seawater mixture was then sonicated for 5 min to ensure a homogeneous dispersion of NPs in solution. CDtrodes were placed in the AgNP–seawater solution for the desired sticking time. Glassware used for NP sticking experiments was thoroughly cleaned with aqua regia (3:1, hydrochloric acid:nitric acid) between experiments. Sticking experiments were also performed with varying AgNP concentrations in the range of 1.1–15.6 pM for a fixed sticking time of 1 h.

2.4. Stripping of AgNPs adhered to gold CDtrodes

Upon completion of the desired sticking duration the CDtrodes were carefully transferred from the AgNP–seawater solution to 0.1 M $NaClO_4$. Either linear sweep voltammetry or cyclic voltammetry was then employed at a scan rate of 20 mV s^{-1} in 0.1 M $NaClO_4$ to oxidatively strip off the nanoparticles that had become immobilised on the CDtrode surface.

2.5. Reduction of $K_3Fe(CN)_6$ at gold CDtrodes

A solution of 1 mM $K_3Fe(CN)_6$/0.1 M KCl was degassed with N_2 for 15 min before studying the voltammetry of the $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ redox couple using Au CDtrodes at a scan rate of 50 mV s^{-1}.

2.6. AgNP sticking and stripping at a gold microelectrode

A gold microelectrode (r = 4.2 μm) was suspended in a chloride free and chloride contaminated suspension of laboratory synthesised citrate-capped AgNPs (r = 11 nm) for 3 h. Details of the AgNP synthesis can be found in [21], determination of AgNP size was performed via Nanoparticle Tracking Analysis [22] and the concentration was determined as described in Section 2.1 for the AgNP spray. Cyclic voltammetry was then used to study the oxidation of AgNPs in a chloride free and chloride contaminated sample at a scan rate of 20 mV s^{-1}. For the chloride free experiment, the gold microelectrode (r = 4.2 μm) was suspended in the stock solution of AgNPs (60 pM) before transferring to a 0.1 M solution of TraceSELECT® Ultra nitric acid for stripping against Hg/Hg_2SO_4 reference electrode (potential vs. SHE = 0.615 V, IJ Cambria Scientific Ltd., Llanelli, UK). A suspension of AgNPs (3.6 pM) in 0.1 M $NaClO_4$ solution containing ≤0.003% chloride anions was used to investigate AgNP sticking and stripping in the presence of chloride ions, the leaking of chloride ions from the Ag/AgCl reference electrode used could also contribute to the chloride contamination. Between experiments, the gold microelectrode was polished with alumina (1.0, 0.3 and 0.05 μm) on soft lapping pads (micro cloth PSA, Buehler) and electrochemically cleaned by voltammetric cycling in 0.1 M H_2SO_4 at a