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An antifouling electrode based on electrode–organic layer–nanoparticle constructs: Electrodeposited organic layers *versus* self-assembled monolayers

Safura Taufik¹, Abbas Barfidokht, Muhammad Tanzirul Alam, Cheng Jiang, Stephen G. Parker, J. Justin Gooding*

School of Chemistry, Australian Centre for NanoMedicine ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, The University of New South Wales, Sydney, NSW 2052, Australia

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ABSTRACT

Electrodes modified with organic layers and nanoparticles are promising tools for analytical devices. A major challenge however is how to make electrodes that resist the nonspecific protein adsorption from biological media? Herein, we report gold electrode–organic layer–gold nanoparticle constructs as a platform for electrochemical biosensing. This study focuses on the fabrication of antifouling electrodes with the organic layers formed by two different approaches; self-assembled monolayer (SAM) procedure and electrochemical reduction of aryl diazonium salts, followed by the attachment of gold nanoparticle (AuNP) to allow the electrochemistry to proceed. The results show that the electrodes modified with ethylene oxide-based SAM enable a better antifouling behaviour with less adsorption of human serum albumin (HSA) as compared to the electrodes modified with ethylene oxide-based aryl diazonium-derived layer. Furthermore, findings suggest such distinction could be due to the surface packing and/or conformation of organic film on Au electrodes.

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1. Introduction

Electrochemical biosensors are becoming essential tools for a wide range of applications such as medical, industrial and environmental monitoring [1–4]. The development of sensing interface for this purpose, mainly for clinical diagnosis, is a big challenge because such devices are typically exposed to biological fluids. Biological fluids typically contain a large number of proteins and cells which can non-specifically adsorb to the interface and deleteriously alter the performance of the sensor. Thus, engineering the surface of the electrode in order to improve the ability of interface to resist nonspecific adsorption of proteins is of vital importance. In this regard, we have recently reviewed elsewhere the strategies developed to date that allow electrochemical biosensors to operate in biological fluids [5].

Chemical modification of surfaces with poly(ethylene oxide) (PEO), also commonly known as poly(ethylene glycol) (PEG), provides coatings with excellent resistance to the surface being fouled with proteins and cells [6]. Steric repulsion and water barrier effects resulting from the structuring of water in the environment surrounding ethylene oxide chains have often been proposed to explain protein resistance to surfaces [7,8]. Different strategies for

immobilisation of PEG molecules onto surfaces have been reported and generally it involves coupling of ethylene oxide units to functional groups that have an affinity for the target surface [9–11]. The most commonly used is PEG or oligo(ethylene glycol) (OEG) terminated alkanethiol molecules from which self-assembled monolayers (SAMs) on gold surface can be formed. These SAMs form well-defined densely-packed structures on gold [12]. The first work on OEG-SAMs was introduced by Prime and Whitesides [13] in 1991 that describe the interaction of proteins with organic surfaces of alkanethiols with different terminals. They have suggested that alkanethiolate SAMs terminated with ethylene oxides are more effective in resisting protein adsorption than SAMs terminated with other groups not containing the ethylene oxide units. Following that, numerous studies on OEG-SAMs have been done to further investigate and understanding the molecular mechanism of ethylene oxides in protein resistance [8,13–17].

Another method to modify surfaces with organic layers is *via* electrodeposition from aryl diazonium salts [18,19]. It has been demonstrated by Liu and co-workers [20] that organic thin films that are formed using aryl diazonium salts on gold electrode have greater stability as compared to gold-thiol chemistry, under conditions such as applying repeated cycling, sonication and over time storage. The attachment of OEG molecules on gold electrodes based on the electrodeposition of aryl diazonium salts has been reported previously [21, 22] and it has made a comparison on the antifouling behaviour of the surfaces compared to those immobilised by SAMs. In these studies they showed that the OEG layers reduced nonspecific adsorption of

* Corresponding author.

E-mail address: Justin.gooding@unsw.edu.au (J.J. Gooding).

¹ Permanent address: Department of Chemistry, Centre for Defence Foundation Studies, National Defence University of Malaysia, Sungai Besi Camp, 57000 Kuala Lumpur, Malaysia.

proteins to surface even though the OEG-aryl-diazonium derived layer had inferior protein resistance compared to OEG-SAMs on gold [22,23].

A limitation with the modification of surfaces using ethylene oxides in relation to electrochemistry is that, formation of dense packed layers which limit nonspecific protein adsorption would also hinder electron transfer across the organic layer to the electrode surface. This modification introduces antifouling properties to the electrodes but at the same time the modified surfaces are no longer of use for electrochemistry. We have explored a number of solutions to this issue [21,24–27], and the first example was by incorporating OEG layers as molecular wires, through which electron transfer could proceed to the electrode [26]. In this way, the electrochemistry was allowed to occur through the wires on the antifouling electrodes. This method was used for fabrication of amperometric immunosensors for the detection of glycosylated haemoglobin (HbA1c) in serum [28] and antibiotic in milk [29]. Later on, the molecular wire was replaced with nanoparticle (NP) assemblies in order to improve the developed technology towards a more stable and sensitive immunosensor [27,30,31].

The strategy to use NP was based on an electrode-insulator-NP construct where it has been demonstrated that gold nanoparticles (AuNPs) attached on the passivated organic layer lead to electron transfer as efficient as on the bare electrode [32–37]. The explanation on efficient electron transfer at electrode-insulator-NP is provided by Chazalviel and Allongue [38], reported that tunnelling the electron at a sandwich structure of metal-insulator-metal NPs is by far easier (about 12 orders of magnitude) than tunnelling the electron between metal and redox species in solution. This is attributed to a higher density of states (DOS) of the metal NPs as compared to the dilute redox species in solution. At the metal NP surface, as with many bare metal electrodes, electrons only have to tunnel through a thin solvent layer which does not appreciably impact the measured kinetics [39]. Apart from the efficient kinetic observed at electrode-insulator-NP constructs, the NP, in this case AuNP, can also be served as a platform to assemble the rest of the immunosensor in an analogous manner to the molecule wire. In the work presented by Liu and co-workers [30] they have developed an amperometric immunosensor based on the immobilisation of AuNPs on aryl diazonium-derived OEG layer modified for the detection of HbA1c. The sensing interface was fabricated by electrochemical reduction of aminophenyl diazonium salt formed from *p*-phenylenediamine, followed by the attachment of AuNP on amine groups. In order to prevent nonspecific adsorption, OEG with carboxylic acid terminal group (OEG-COOH) was covalently attached on the free amine groups available on the diazonium-derived layer. It was reported that the amperometric immunosensor could be used for the detection of HbA1c in human whole blood [30].

The purpose of this work is to develop a more efficient way of preparing antifouling surfaces using electrode-organic layer-NP constructs. For this purpose, the organic layer is formed by self-assembly and the results are compared to the electrodeposition approach reported by Liu and co-workers [30] (see Scheme 1 for the two surface constructs). These two interfaces will be referred to as Au-EO-AuNP for the electrode where the intervening organic layer is an alkanethiol SAM (Scheme 1a) and Au-Ph-AuNP/OEG where the interface is prepared as in Scheme 1b. Characterisation of the developed interfaces was conducted using cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and fluorescence microscopy.

2. Experimental methods

2.1. Reagents and materials

Hexa(ethylene glycol) dithiol, *p*-phenylenediamine, potassium hexacyanoferrate(III), potassium hexacyanoferrate(II), albumin from human serum (HSA), bovine serum albumin-fluorescein

isothiocyanate (FITC-BSA), potassium phosphate monobasic, sodium phosphate dibasic (98% purity), sodium chloride, and 1,3-dicyclohexylcarbodiimide (DCC) were purchased from Sigma-Aldrich (Sydney, Australia). Hydrogen tetrachloroaurate(III) and trisodium citrate (purity of 99%) from Sigma (Sydney, Australia) were used to synthesise gold nanoparticles (AuNP). Sulphuric acid (98%), hydrochloric acid (32%), sodium nitrite, sodium hydroxide and potassium chloride were obtained from Ajax Finechem Pty. Ltd. (Taren Point, Australia). 2,5,8,11,14,17-hexaoxanonadecan-19-oic acid (OEG₅-COOH) was purchased from Biomatrik Inc. (Zhejiang, China). All reagents were used as received and aqueous solutions were prepared in Milli Q water (18 MΩ cm, Millipore, Sydney, Australia).

2.1.1. Materials

Polycrystalline gold electrodes were purchased as 1 mm-diameter discs from eDAQ Pty. Ltd. (Australia) and used for all electrochemical measurements. Gold-coated polyester films were purchased from Materia Inc. (California, USA) and used for X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and fluorescence microscopy studies.

2.2. Electrode preparation

Gold electrodes were polished with 1.0, 0.3 and 0.05 μm alumina slurries made from dry Buehler alumina and Milli-Q water on microcloth pads (Buehler, Lake Bluff, IL). The polished gold electrodes were rinsed thoroughly with Milli-Q water, and were dried under the flow of nitrogen gas. Electrochemical pre-treatment was performed after polishing by 25 successive scans between gold redox potential (−0.1 V to +1.5 V vs. Ag|AgCl|3 M KCl) in 0.05 M H₂SO₄ aqueous solution at 100 mV s^{−1}. After that, the electrodes were rinsed with Milli-Q water and dried under the stream of N₂ gas.

Gold-coated polyester films were cleaned by immersing for about 5 min in ethanol, followed by rinsing with copious amount of Milli-Q water and blow-dried under the flow of nitrogen.

2.3. Electrode modification

The fabrication strategy for the sensing interface based on the formation of self-assembled monolayer (SAM) on the gold electrode is presented in Scheme 1a. Gold electrodes are first modified by incubation in 10 mM of hexa(ethylene oxide) dithiol in ethanolic solution for 5 h in the dark at room temperature to form the monolayer of hexa(ethylene oxide) dithiol modified gold (Au-EO) surface. Subsequently, AuNPs are covalently attached on the monolayer by incubation in gold colloidal solution for 2.5 h at room temperature forming the Au-EO-AuNP surface. The fabricated interface is referred to Surface 1.

As shown in Scheme 1b, surface modifications based on aminophenyl diazonium derived layer, AuNP and OEG-COOH were reported previously, but on glassy carbon electrode [27]. In the current work, the same fabrication procedures were deployed for modification of gold surfaces. Briefly, 4-aminophenyl modified gold surface (Au-PhNH₂) was fabricated by electrochemical reduction of aminophenyl diazonium cations. It was generated from *p*-phenylenediamine dissolved in aqueous HCl in the presence of NaNO₂ as reported previously [40–42]. Cyclic voltammogram of the electrochemical reduction is shown and discussed in detail in the Supporting Information (see Fig. S1). The amine-terminated layers were then converted to diazonium groups for the attachment of AuNP. It was achieved by incubating the surface in NaNO₂ and HCl to form 4-phenyl diazonium chloride modified surface followed by scanning the potential of modified surface between 0.5 to −0.5 V in AuNP solution to form AuNP-phenyl modified gold (Au-Ph-AuNP) surface. It was mentioned previously that only about 10% amines were converted to

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