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Research paper

Light-activated electrochemistry without surface-bound redox species

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ABSTRACT

Semiconducting electrodes that are in depletion, can support appreciable electron transfer only when illuminated. This phenomenon has been implemented on silicon electrodes passivated by a protective organic self-assembled monolayer (SAM) to confine electrochemistry to microscale regions on an unstructured electrode surface by shining light only on those regions. This method, referred to as light-activated electrochemistry (LAE), has so far only been studied using electrodes with surface-bound redox mediators that are either covalently or electrostatically attached to a SAM-modified silicon electrode. In the current report, we extend LAE to redox species in solution using gold nanoparticles (AuNPs) attached to the SAM-modified silicon electrodes. Cyclic voltammetry showed that faradaic electron transfer to redox species in solution can be switched on/off using light. Furthermore, the modified silicon electrodes were stable to more than 650 redox cycles, even when scanning to anodic potentials, with negligible oxide growth and no noticeable change in the voltammograms. Using a variety of redox species in solution, it was shown that with n^{-}-Si-SAM-AuNP electrodes negligible current was observed in the dark but appreciable faradaic electrochemistry was observed upon illumination. It was also shown that to ensure electron transfer proceeded *via* the AuNPs only, nonspecific adsorption of the redox species to the monolayer surface needed to be avoided.

1. Introduction

Light-activated electrochemistry (LAE) is a technique where electrochemistry can be spatially resolved using a light pointer on a flat unstructured silicon electrode modified with an organic self-assembled monolayer (SAM) with only one ohmic contact [1]. LAE is distinguished from other photoelectrochemical methods for 1) being able to undertake localised faradaic reactions compared to addressable potentiometric methods, 2) it takes advantage of the industrially-available low band gap Si (100) as the photoelectrode, and 3) the photo electrode is stabilized for a significant number of redox cycles using an organic SAM. With this method, high density electrode arrays without the constraint of connecting wires and bonding pads are possible. In other words, an unpatterned monolithic surface can be turned into an electrode array without any predetermined architecture, simply by sequentially shining light on different regions of the surface [2]. The prerequisites for this method to work are 1) the silicon electrode must be protected from oxidative corrosion using a self-assembled monolayer, 2) the electrode must be in depletion such that there is no appreciable faradaic electrochemistry in the dark but faradaic processes are observed upon illumination and 3) for appreciable electron transfer upon illumination there must be strong electronic coupling between the redox species and the underlying electrode through the organic monolayer on the electrode surface [2].

As a result of the above criteria for LAE, thus far, LAE has been studied almost exclusively with covalently attached redox species where an organic SAM derived from 1,8-nonadiyne passivates the Si electrode against electron transfer and oxidation [3,4], and a redox mediator like ferrocene [2,5] or anthraquinone [6] is covalently attached to the alkyne end. Due to the difference between the mediator redox potential and the semiconductor Fermi level, a redistribution of the charge carriers inside the semiconductor takes place leading to bending of the energy bands and formation of a rectifying junction which is a prerequisite for photoelectrochemistry and LAE [7]. When using electrodes with the mentioned configuration, a second redox species in the solution can be reduced or oxidised, depending on the oxidation state and formal potential of the attached redox mediator. The one exception was a study by Wu et al. where redox species were in

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solution, with no redox species covalently attached to the SAM, but strong electronic coupling and appreciable electron transfer was shown to be due to some of the redox species electrostatically adsorbing to the SAM [8].

The limitation of having surface bound redox species is that the redox potential of the surface bound redox species must be matched to each particular redox species in solution. To expand the scope of LAE so one surface can be used to directly oxidise or reduce many different dissolved species, metallic nanoparticles attached to the monolayer modified surface could be employed [9–11]. There have been numerous reports on using gold nanoparticles (AuNPs) as electrochemical switches and electron transfer mediators on SAM-modified metallic electrodes [12–21] and Si [22]. What has been shown in a theoretical paper by Chazalviel and Allongue to explain the experimental observations is the exchange current density between the underlying electrode and the AuNPs is so high that the potential applied to the underlying electrode is essentially transferred through the monolayer to the nanoparticle. In other words, these electrode-SAM-AuNP constructs are a way to form electronic connections to nanoparticles on an otherwise passivated surface [21]. In a more recent study by Khalid and El Helou et al. [23] semiconductor quantum dots were employed to fabricate Au-SAM-QD electrodes and then using a light pointer, electrochemical reactions were confined to desired locations on the electrode. The question arises therefore that can AuNPs attached to the end of a SAM-modified silicon electrode be used in LAE?

The electrochemical instability together with photoelectrochemical behaviour in some cases have been taken advantage of for local photoelectrochemical etching of semiconductors [24,25] while some have exploited photoelectrochemical properties to locally electrodeposit metals on silicon [26,27]. Whereas, to make practical use of LAE, the base Si needs to be stable in terms of electronic properties. One major cause of instability of Si-based electrodes is the gradual formation and growth of Si oxide in aqueous solutions, leading to decay in electron transfer from Si to the redox species. Bard and Wrighton during the late 70 s and early 80 s extensively studied Si-based photoelectrochemical cells for energy harvesting applications [28,29]. Nonetheless, lack of stability due to oxidation of the base Si was the key impediment in large-scale exploitation and commercialization of these systems. The same still applies to today's use of Si electrodes for faradaic electrochemical applications. A report by Ciampi et al., however, showed stable Si(100) electrodes, for more than 1000 cyclic voltammetry (CV) cycles with the attached ferrocene [3]. However, a recent report [30] showed that AuNPs catalyze the oxidation of highly-doped *p*-type Si when attached to the SAM passivated silicon, leading to a fast decay in electrochemical response of the electrode. Therefore, the stability of poorly-doped Si-SAM-AuNP when performing LAE is a significant issue for such constructs to become practical.

In addition to the stability, non-specific adsorption of the dissolved species to the electrode surface is integral to the design of the electrochemical system and interpretation of the results. One source of non-specific adsorption and electrode/probe interaction is electrostatics [31], particularly when amine-AuNP bond, which has an electrostatic nature, is used for the immobilization of the AuNPs [32]. Therefore, studying the Si-SAM-AuNP construct in redox probes with different charges to understand the behaviour of the system is necessary.

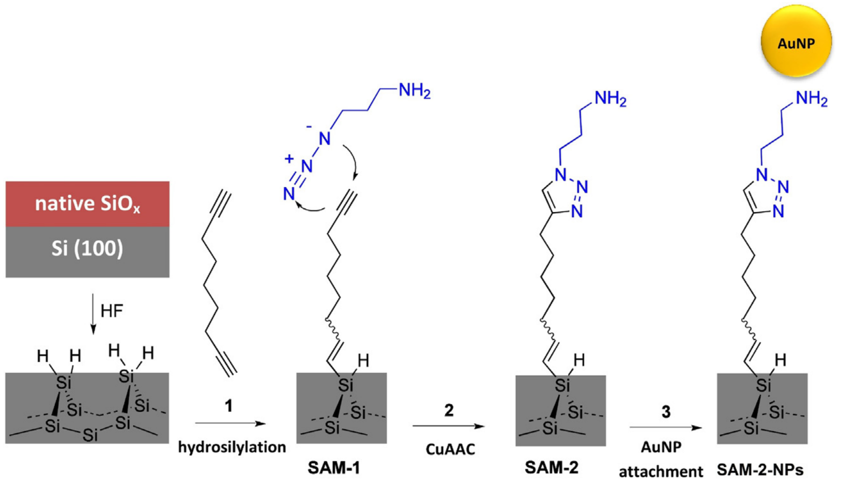
The purpose of this paper is to answer the question, can AuNPs attached to amine-terminated poorly-doped Si-SAM electrodes be used for practical LAE of dissolved redox species as opposed to attached to the surface? To fully answer that question requires the stability of the fabricated electrodes to be evaluated, with the results compared to the similar system of highly-doped Si, as well as a range of redox species to be assessed to determine the scope of this new capability.

2. Experimental procedure

2.1. Materials

All solvents were distilled prior to use. Milli-Q water (>18 MΩ cm) was used for surface cleaning procedures and to prepare solutions. Solutions used for silicon cleaning and etching were prepared from semiconductor-grade 30% H_2O_2 (Sigma-Aldrich, Sydney, Australia), 98% H_2SO_4 (Sigma-Aldrich, Germany) and 50% hydrofluoric acid (Ajax Finechem, Australia). Silicon wafers ((100) ± 0.5° p^+-type, boron-doped 0.001-0.003 Ω.cm and (100) ± 0.5° n^--type, phosphorous-doped, 8–12 Ω.cm) were purchased from Siltronix. 1,8-Nonadiyne (Sigma-Aldrich, Sydney, Australia was used as received in the thermal hydrosilylation of the hydrogen-terminated wafers.

For electrochemical measurements, four redox species were used. These were hexammineruthenium (III) chloride ($Ru(NH_3)_6{}^{3+}$) (Sigma-Aldrich, Sydney, Australia), ferrocene methanol (FcMeOH) (Alfa Aesar, Sydney, Australia), potassium hexacyanoferrate(III)



Scheme 1. Surface preparation steps including (1) native oxide removal in HF followed by hydrosilylation in degassed 1,8-nonadiyne, (2) clicking the azido propylamine by copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC), and (3) attaching the AuNPs by incubation in 480 pM AuNP dispersion for 3 hours.