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Silicon-SAM-AuNP electrodes: electrochemical “switching” and stability

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Abstract

The immobilization of gold nanoparticles (AuNPs) on functionalized electrodes has been shown to be an effective way for switching on the electrochemistry at an otherwise passivated surface. Herein, attachment of AuNPs onto the industrially-available p^+ -Si(100) electrodes was studied by means of cyclic voltammetry and X-ray photoelectron spectroscopy. The hydrosilylation of p^+ -Si(100) with 1,8-nonadiyne followed by the “click” of azido propylamine onto the alkyne end, protected the p^+ -Si(100) against oxidation and prevented the electron transfer from dissolved $\text{Ru}(\text{NH}_3)_6^{3+}$. Upon attachment of AuNPs, however, electron transfer was initially restored. The performance of the p^+ -Si-SAM-AuNP electrode was found to decay with repeated voltammetric cycling due to the formation of SiO_x underneath the self-assembled monolayer (SAM). These results suggest that p^+ -Si-SAM-AuNP electrodes can be used in electrochemical devices for single use applications but are not suitable for long-term use.

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Introduction

Microfabrication techniques and raw material processing developed by the microelectronics industry have paved the path for the application of silicon in other areas of science and engineering, including photoelectrochemistry [1-3]. The challenge in using silicon for electrochemical applications, however, is the oxidation of the material in aqueous media, which leads to the formation of a barrier against electron transfer. Recently, well-established surface modification routes using self-assembled monolayers (SAMs) formed from the hydrosilylation reaction of alkenes and alkynes have opened up opportunities to exploit the properties of silicon in aqueous solutions [4-10]. The covalent nature of the Si-C bond and the dense packing of these SAMs make possible the formation of an effective passivating monolayer against oxidation, while being thin enough to allow electron tunnelling. This tunnelling does not occur directly from the electrode through the SAM to the redox species in the solution unless a mediating redox species like ferrocene is grafted to the SAM or an excessively high potential window is employed, which in the latter case causes the oxidation of base Si [11]. In this regard, successful efforts have been made to modify oxide-free Si(111) [12, 13] with attached ferrocene [14, 15]. Si(111), compared to Si(100), showed superior oxidation resistance after modification by SAMs until the report by Ciampi et al [16]. In that report, alkyne-terminated Si(100) electrodes with grafted ferrocene were shown to remain stable, with no detectable oxide, even after 1000 electrochemical cycles. This finding was important as Si(100) is the dominant orientation of Si wafers in the microelectronics industry.

The previously mentioned ferrocene-terminated electrodes could be used to drive a mediated redox reaction by the ferrocene/ferricenium reaction [17, 18]. However, use of these electrodes in this manner is limited to potentials where ferrocene can serve as a mediator. To tackle this, instead of a redox mediator, a conductor like gold or platinum in the form of nanoparticles can be attached to the SAM. Accordingly, Shein et al. [19] and Bradbury et al. [20] showed the capability of gold nanoparticles (AuNPs) on SAM-modified gold electrodes to act as sites for electron tunnelling from the underlying electrode, through the SAM to the dissolved redox species. Later, this system known as electrode-SAM-nanoparticle constructs was reported on Si(100) electrodes modified with an alkenylthiol SAM followed by attachment of gold nanoparticles by Le Saux et al. [21]. They observed that the electron transfer from Si to $\text{Fe}(\text{CN})_6^{3-}$ ions in the electrolyte switched on upon attachment of AuNPs.

In addition to their switching capability, AuNPs are interesting in other manners too: they can be further functionalized, they show unique optoelectronic properties, they possess excellent biocompatibility, and their size can be tuned based on the biological analyte [22-24]. This has led to numerous studies on the electrochemical behaviour of electrode-organic monolayer-nanoparticle constructs [25, 26], most of which were undertaken using base electrodes made of gold [19, 20, 27-30] and in some cases glassy carbon [31, 32] as well as theoretical predictions of their behaviour [33]. All of this, when combined with the properties of the base Si, make Si-SAM-AuNP constructs promising electrode materials for electrochemical sensors.

In this paper, the alkyne-terminated highly-doped Si electrodes are modified with AuNPs by using an amine linker and the electrochemical behaviour of the electrodes before and after AuNP attachment are studied by cyclic voltammetry (CV). The purpose is to explore whether the exquisite stability achieved with alkyne terminated monolayers on silicon electrodes can be translated to electrode-

SAM-nanoparticle constructs. As a result, the stability of the fabricated Si-SAM-AuNP construct in terms of oxide formation and CV peak shape change is addressed.

Experimental procedure

Materials: All solvents were distilled prior to use. For surface cleaning and all aqueous solution preparation, Milli-Q water ($>18\text{ M}\Omega\text{ cm}$) was used. For Si processing, solutions were prepared from semiconductor grade reagents including 30% H_2O_2 (40287, Sigma-Aldrich, Sydney, Australia), 98% H_2SO_4 (40306, Sigma-Aldrich, Germany), and 50% hydrofluoric acid (258, Ajax Finechem, Australia). Silicon wafers ($100 \pm 0.5^\circ$ p^+ -type boron-doped $0.001\text{--}0.003\ \Omega\cdot\text{cm}$ as the electrode material were purchased from Siltronix. At this doping level the wafers are considered degenerately doped (10^{20} cm^{-3}) giving them behaviour akin to a metal. The rest of the materials used were 1,8-nonadiyne (161306, Sigma-Aldrich, Sydney, Australia), 3-bromopropylamine hydrobromide (B79803, Sigma-Aldrich, Sydney, Australia) sodium azide (S2002, Sigma-Aldrich, USA), sodium citrate tribasic dihydrate (S4641, Sigma-Aldrich, Sydney, Australia), gold(III) chloride trihydrate (520918, Sigma-Aldrich, Sydney, Australia).

For electrochemical measurements, hexamineruthenium (III) chloride (252005, Sigma-Aldrich, Sydney, Australia) was used as the redox probe. To form a non-rectifying ohmic contact between the Si and the copper plate, gallium-indium eutectic (12478, Alfa Aesar, USA) was applied using a silica paper.

To obtain a 0.2 mM colloidal dispersion of 30 nm AuNPs, the method of Frens [34] was used. For the synthesis of azidopropylamine, to a stirring aqueous solution of 1.5 M 3-bromopropylamine hydrobromide at 100°C , 25 mL of 3.2 M sodium azide solution was abruptly added and heated under reflux for 24 h at 100°C . The organic phase was then extracted using diethyl ether and vacuum-dried ($^1\text{H NMR}$: (300 MHz, D_2O) δ 1.90 (quin, 2H), 2.92 (t, 2H), 3.48 (t, 2H)).

Surface preparation: Hydrosilylation of Si has been reported in detail elsewhere [16]. In short, after cleaning with Piranha solution, the native oxide on Si was removed by acid treatment in 2.5% HF, followed by hydrosilylation in degassed 1,8-nonadiyne at 165°C for three hours. In order to attach the azido propylamine to the surface, to a reaction tube containing the Si sample, 15 mM of azido propylamine (2:1 isopropanol:water), 0.5 mol% copper sulphate pentahydrate relative to the azide and 50 mol% sodium ascorbate relative to the azide were added and left in dark for 45 minutes without excluding the air from the reaction. Next, the sample was thoroughly washed with EtOH, Milli-Q water, 0.5 M HCl, and dried with a stream of Ar. The final step in the surface preparation was incubating the amine-terminated surface in the AuNP colloidal dispersion for 3 hours, followed by a rinse with Milli-Q water and storing under Ar.

Electrochemical studies: Electrochemistry was performed using a CHI660D potentiostat, CH Instruments, Texas, USA, operating with the CHI Software version 11.13. The three-electrode setup comprised of a Teflon cell, Pt mesh counter electrode, Ag/AgCl in 3M KCl reference electrode, and the fabricated silicon as the working electrode. The exposed area of the electrode through the Viton gasket was 0.342 cm^2 which was taken into account for the current density measurements. Solutions were degassed for a minimum of 10 minutes prior to studies by bubbling high purity argon through

the solution using a gas dispersion tube and maintaining a blanket of the inert atmosphere on the solution during the experiment.

Characterization:

X-ray photoelectron spectroscopy (XPS) experiments were performed on an ESCALAB 220iXL (Thermo Scientific) with a mono- chromatic Al KR X-rays (1486.6 eV) and Scanning electron microscopy (SEM) was performed using a FEI Nova NanoSEM 450 FE-SEM equipped with a Schottky field emission gun.

Results and discussion

Figure 1a shows the scheme of the surface preparation. Success of the steps in the surface modification procedure was confirmed using high-resolution XPS and SEM. The hydrosilylation and click steps were verified by N1s and C1s narrow scans (not shown here) with the click efficiency of approximately 60%. Figure 1b shows the Si narrow scan after the click reaction with barely detectable amounts of Si oxide, based on the peak located at about 102.5 eV. However, after deposition of AuNPs, a detectable amount of oxide, calculated to be approximately 5.60 atomic percent, was observed (Figure 1c), which is just above the detection limit of the XPS. As the surface preparation comprises three steps, compared to similar works reporting no detectable oxide after the third step [35], this oxide formation is attributed to attachment of AuNPs onto the surface acting as a catalyst for SiO_x formation. It is unlikely that the AuNPs deform the SAM and open oxygen penetration pathways referring to the previous reports, [29, 33]. Figure 1d evidently shows the Au 4f doublet after the incubation of the electrode in 0.2 M AuNPs dispersion, indicating the successful attachment of AuNPs. Further analysis by the SEM in Figure 1e indicated the AuNPs cover 14.3% of the electrode surface. The mean centre-to-centre distance between the NPs is 58 nm, number of particles per unit area is 252 μm^{-2} , and the mean diameter of the NPs is 21.8 nm. Reported values have a 5% measurement uncertainty. The inset is the cross-section of the electrode, showing the AuNPs losing their spherical shape upon attachment to the surface and spreading over the electrode to form hemispheres due the strong interaction between the amine and the AuNP.

Cyclic voltammograms of the modified electrodes before and after addition of the AuNPs are shown in Figure 2a. Prior to addition of the AuNPs, the amine-terminated surface showed a featureless voltammogram with no discernible faradaic process, showing the SAM effectively blocked access of the Ru(NH₃)₆³⁺ to the silicon electrode surface in terms of electron transfer. Upon addition of the AuNPs, strong faradaic peaks appeared, showing the electrochemistry proceeded between the Si electrode and the Ru(NH₃)₆³⁺ due to efficient electron transfer from the silicon electrode to the AuNPs as predicted by the theory of Chazalviel and Allongue [33]. Assuming that the AuNPs do not come into contact with the underlying Si [29], the electron transfer is predominantly due to the electron tunnelling across the monolayer as the nanoparticles provide the platform for electron transfer from the Si to the redox species [36]. The peak current was observed to be linear with the square root of the scan rate, indicating it is a diffusion controlled process with a rate constant of heterogeneous electron transfer, determined using the Nicholson method [37] of $0.12 \pm 0.01 \text{ cm s}^{-1}$ at scan rates below 500 mV s⁻¹. Importantly, to observe this “switching on” of the electrochemistry upon addition of nanoparticles, the redox species must have the same charge as the distal end of the SAM. For example, if negatively charged Fe(CN)₆³⁻ was employed then we have shown previously

that it will electrostatically bond with the SAM and there will be sufficient electronic coupling for appreciable electron transfer to proceed even in the absence of nanoparticles.

The stability of the fabricated electrode during several hundred CV cycles was assessed based on the separation between the anodic and cathodic peaks (ΔE_p). For this purpose, the electrode was tested for more than 650 consecutive CV cycles. The results for every 50 cycles in Figure 2b show a continuous increase in ΔE_p . For the first 30 cycles, there is barely a discernible change, but from cycle 30 to 400 this change is fast both in terms of current and ΔE_p . Then it slows down after 400 cycles and appears as almost indistinctive peaks beyond 650 cycles. The degradation, as verified by XPS on the same sample in Figure 2c, is due to the formation of a uniform Si oxide film calculated to be 18.92 atm.%, which compared to the value of 5.60% before the stability test, has increased more than 3 times. Although previous reports [16] showed ferrocene-terminated Si(100) electrodes with superior oxide formation resistance, the system studied here is not as stable, showing that the surfaces can only be used for less than 30 electrochemical cycles before the spread of the oxide on the silicon surface deleteriously affect the electrochemistry. One might attribute the decay to the nanoparticles detaching from the surface. However, SEM results on the same sample in Figure 2d after the stability test shows the presence of the nanoparticles with almost the same frequency ($239 \pm 9 \mu\text{m}^{-2}$) on the surface. There is, however, some tentative evidence from the SEM (Figure 1e inset) of deformation of the nanoparticles that could then imply there may be some access of the gold to the silicon causing the oxidation. We are now investigating if this is the case.

Conclusion

The work here demonstrates the ability of AuNPs to act as a very effective switch for electrochemical devices made using Si-based electrodes. Besides acting as a switch, AuNPs enable us to fabricate Si-based electrodes capable of driving electrochemical reactions with the redox species in the electrolyte, as opposed to attached to the surface. This concept could be made even more promising by using poorly-doped Si base electrodes in order to enable the experimentalist to perform localized electrochemistry with a light pointer. Furthermore, AuNPs can be functionalized to act as a binding medium for a variety of analytes, making this construct a promising electrode material for electrochemical sensor arrays. The life span of the electrodes, however, is not meant for long-term applications due to AuNP-induced oxidation of Si, but suitable for single use sensing processes.

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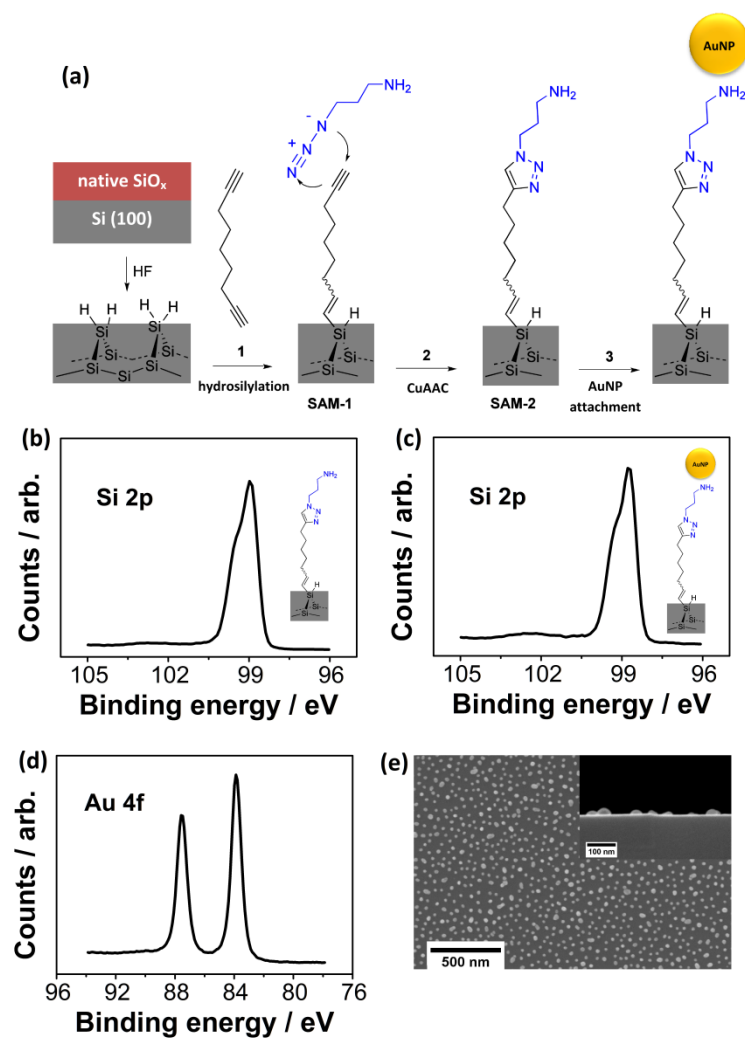


Figure 1- a) Schematic representation of the surface preparation, b) XPS Si 2p narrow scan after the click step with a small amount of detectable oxide, c) Si 2p narrow scan after attachment of AuNPs with a more prominent SiO_x -related peak, d) Au 4f narrow scan of the amine-terminated electrode after incubation in AuNP dispersion and e) SEM micrograph of the surface showing a plethora of monodispersed AuNPs on the surface. The inset is a cross-section of the electrode showing the nanoparticles form a hemisphere as they attach to the amine.

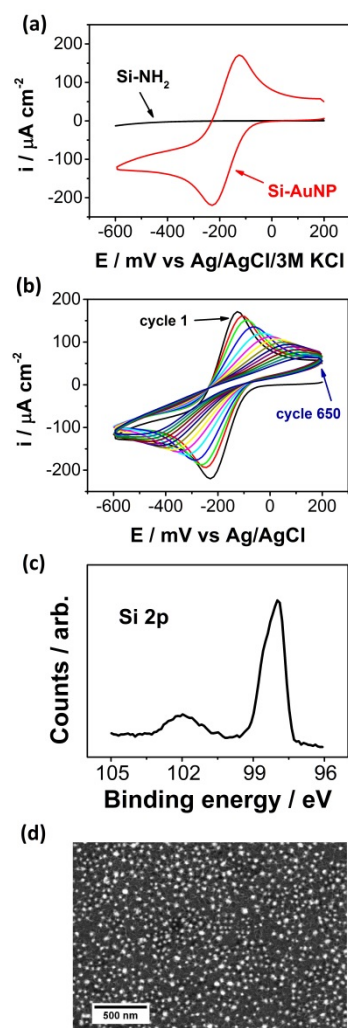


Figure 2- a) Cyclic voltammogram of the amine-terminated (black) and AuNP-terminated (red) p^+ -Si surfaces in 100mM KCl + 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ at 100 mVs^{-1} , b) CV of the AuNP-terminated p^+ -Si surfaces for every 50 cycles up to 650 cycles in the same conditions as (a), c) XPS narrow scan of Si 2p showing a noticeable oxide peak at around 102.5 eV, and d) SEM image of the surface after more than 650 electrochemical cycles showing the same frequency of AuNPs as before the experiment.

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