Electrochemical surface nanopatterning by selective reductive desorption from mixed metal surfaces

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ABSTRACT

We report on a novel strategy to the functionalisation of electrode surfaces based on the preparation and patterning of mixed metal electrodes using metal selective electrodesorption of a sacrificial alkanethiol. Plain palladium (Pd) and plain polycrystalline gold (poly-Au) electrodes were used initially to determine metal specific potential windows within which electrodesorption of the short alkanethiol mercaptoethanol could be achieved. We found that stripping of mercaptoethanol from gold was achieved at potentials lower than $-0.800\,V$, whilst stripping from palladium was achieved at more positive potentials i.e. around $-0.650\,V$. Mixed metal electrodes were prepared by electroplating for short period of times palladium onto poly-Au electrodes. The resulting surfaces were characterised electrochemically in $1\,M\,H_2SO_4$ and clearly exhibited reduction peaks for both gold and palladium oxide formation. The mixed metal electrodes were coated with mercaptoethanol, which was further selectively removed from Pd by cyclic voltammetry in NaOH in the Pd-specific potential window. The presence of bare Pd domains revealed following electrodesorption was confirmed by subsequently adsorbing the electroactive alkanethiol 6-ferrocenylhexanethiol onto the freshly revealed Pd. Cyclic voltamogramms exhibited sharp redox peaks that could only be attributed to the successful immobilisation of 6-ferrocenylhexanethiol onto fresh Pd domains. Control surfaces, i.e. MCE fully coated Pd/Poly-Au electrode, exposed to 6-ferrocenylhexanethiol did not exhibit significant voltammetric features, attesting to the efficient patterning of the mixed metal electrode by employing metal specific reductive desorption of short alkanethiols. The possibility to pattern electrode surfaces in such way will find application in the field of diagnostics, and also in heterogeneous catalysis where Pd–Au alloys have received an increased interest in the recent years.

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1. Introduction

Fine chemical structuring of electrode surfaces is typically achieved by the formation of self-assembled monolayers (SAM) of alkanethiols [1–4] or alkanesilanes [5,6] of varying chemical functionality. Chemical and biochemical diagnostics have largely benefited from the latest advances made in the field and bi-functional surfaces have now become a pre-requisite to favour the recognition of a targeted compound and enhance recognition efficiency [7,8] while excluding a range of undesired interferents from interacting with the surface [9,10]. Chemisorption from a mixture of alkanethiols in solution and the resulting self-assembled monolayer is reported as a practical approach for the realisation of such surfaces where ordering and distribution of the functional chemical head groups at the surface is controlled by the ratio of one component to the other and consequently by the ther-modynamic equilibrium existing between the two species at the liquid–solid interface [11,12]. Although practical and facile to implement, such an approach inherently suffers from a lack of control over the surface arrangement, lack of stability and consequently large surface-to-surface irreproducibility [13,14].

On the other hand, direct physical surface patterning of sensor surfaces could remedy issues associated with the tight control required over these processes. By tuning either surface morphology (e.g. polycrystallinity, nanoelectrode bundles [15–18]) or composition during fabrication (e.g. mixed metal, alloy electrodes [19–21]), one can expect to reliably introduce mixed functionality at surfaces based on the inherent characteristics of the base transducer. As such, the quality of functionalisation (i.e. homogeneity of distribution and spacing of functional head groups) and therefore sensor-to-sensor repeatability could be greatly improved.

Of particular interest, the use of mixed metal surface could be employed to disperse functionality on surfaces based on the surface distribution of the metals. By carefully selecting the metals based on their catalytic and electrochemical characteristics, patterning based on the selective reductive desorption of short alkanethiols from one metal preferably than from another can be envisaged.

The developed approach could be exploited for the construction of reproducible biosensor surfaces, particularly DNA sensors, where the state of the art in formation of mixed self-assembled monolayers is based on the chemisorption of alkanethiols. However, this is a thermodynamically driven process where small changes in, for example, length of chemisorption, concentration of alkanethiols used, temperature etc., can have a large effect on the make up of the mixed self-assembled monolayer formed and has a large impact on reproducibility, for example in DNA sensors, where a mixed SAM of DNA probe and short chain alkanethiol is frequently used. The approach reported here details the formation of self-assembled monolayers that can be controlled by the substrate material used. Thus, highly reproducibly patterned surfaces can be produced, and the mixed SAMs formed on these surfaces (for example forming a mixed SAM of a short chain alkanethiol, which could be selectively desorbed from Pd, and a DNA probe adsorbed), would be much more reproducible that those obtained via thermodynamically driven approaches, leading to more reproducible DNA detection using biosensors fabricated using this approach.

Here we report on a novel strategy to the functionalisation of electrode surfaces based on the exploitation of the electrochemical properties of bi-metallic electrode of palladium (Pd) and gold (Au) to prepare mixed-functionality sensor surfaces. After initially finding that we could selectively desorb the short alkanethiol mercaptoethanol (MCE) from Au electrodes and from Pd electrodes via electrochemical reduction using metal specific potential windows, we realised we could use Au/Pd electrodes to control the lateral distribution of chemical functionalities at the surface. Although our prime interest in the development of such surfaces lies in their application in the field of medical diagnostics for DNA sensing, the realisation of functional Pd/Au electrode is also attractive for heterogeneous catalysis where Pd/Au alloys have seen an increased interest in the recent years [20,22–24].

2. Experimental

2.1. Materials

Palladium dichloride (PdCl$_2$, 99.9%, Aldrich), sodium perchlorate (NaClO$_4$, 98%, Sigma), sulphuric acid (H$_2$SO$_4$, 95% v/v, Scharlau), sodium hydroxide (NaOH, 98% Scharlau), pH 2 citrate buffer (consisting of 0.03 M citric acid, 0.0082 M HCl, 0.061 M NaCl, Fluka) and ethanol (96% v/v, Scharlau) were used as received. The alkanethiol 2-mercaptoethanol (MCE, 99%) was obtained from Scharlau and 6-ferrocenylhexanethiol from Aldrich.

2.2. Methods

2.2.1. Electrode preparation

Polycrystalline gold (Poly-Au) electrodes from CH Instruments (US) and glassy carbon rods 3 mm in diameter (GCE) from Sigradur® (HTW, Germany) were mechanically polished with varying particle sizes (6 μm to 0.05 μm) of polishing suspensions (BUEHLER Metadi Supreme) on BAS polishing cloth. The electrodes were sonicated in water and further cleaned electrochemically. Poly-Au electrodes were subjected to wide potential scans between 0 V and 1.6 V at 50 mV s^{-1} in 1 M H$_2$SO$_4$ until a reproducible gold oxide stripping peak was obtained. GCE were conditioned by potential scanning from 0 V to 1.2 V in 1 M NaClO$_4$ for at least five complete scans at 50 mV s^{-1}. The prepared electrodes were used immediately after mechanical polishing and electrochemical cleaning.

2.2.2. Metal deposition

Palladium electrodes were prepared by potentiostatic deposition of PdCl$_2$ on cleaned GCEs. A constant potential of −0.3 V was applied for 1 min in a Pd deposition bath consisting of 7.5 mM PdCl$_2$

in citrate buffer. To prepare the deposition bath, 133 mg of PdCl$_2$ was added to 100 mL of pH 2 citrate buffer and sonicated for 15 min. The solution was further homogenised by shaking and left overnight in the dark after which period a clear solution was obtained. Finally, the pH of the solution was adjusted to 3 by addition of diluted NaOH. Mixed metal electrodes were prepared by shorter deposition time (1 or 5 s) of Pd on poly-Au electrodes 1.6 mm in diameter from the same Pd deposition bath [25].

2.2.3. Formation of self-assembled monolayers of alkanethiols

Mercaptoethanol (MCE) and 6-ferrocenylhexanethiol were dissolved in ethanol to a final concentration of 2 mM. The electrodes were exposed to 50 μL of the alkanethiol solutions and the formation of self-assembled monolayers allowed proceeding for at least 2 h in the case of mercaptoethanol, and 30 min in the case of 6-ferrocenylhexanethiol.

2.2.4. Electrochemical measurements

Cyclic voltammetry and potential step experiments were carried out using an Autolab model PGSTAT 12 potentiostat/galvanostat controlled with the General Purpose Electrochemical system (GPES) software (EcoChemie B.V., The Netherlands). A three-electrode set-up was adopted comprising of gold electrodes as working electrodes, and a platinum wire (BAS model MW-1032) and an Ag/AgCl (3 M NaCl) electrode as counter and reference electrodes respectively. All potentials were reported with respect to this reference electrode. The reductive desorption of SAM of MCE from poly-Au, Pd and poly-Au/Pd electrodes was realised in 0.5 M NaOH, under argon saturated atmosphere for 10 potential cycles within the studied window (either −0.2 to −1.1 V or −0.2 to −0.675 V) at a scan rate of 20 mV s^{-1}.

3. Results and discussion

3.1. Elucidation of metal specific potential windows for reductive desorption of MCE at Pd and poly-Au electrode

The potential window necessary to desorb MCE from each surface was initially elucidated by working on Au or Pd electrodes separately. Presented in Fig. 1(A), the reductive desorption of MCE from poly-gold surfaces was realised by repeatedly scanning the potential window −0.2 V to −1.1 V.

The first reductive scan exhibits two desorption peaks for the desorption of MCE, present at −0.834 V and −0.947 V (vs. Ag/AgCl), which progressively disappear in subsequent scans. This behaviour is consistent with the selective desorption from a poly-Au surface [15,26–29], where low index crystalline planes exhibit very narrow thiol reductive desorption potential windows.

The same experiment on Pd surface did not produce any clear desorption peaks. Due to the highly active hydrogen reduction taking place at potentials below −0.8 V no defined peaks could be measured. Thus, we determined the reductive desorption in an indirect manner, where the adsorption of the electroactive thiol 6-ferrocenylhexanethiol onto the palladium surface indicated that the alkanethiol previously adsorbed onto this surface had been desorbed. As shown in the voltammograms presented in Fig. 2 (2), the redox peaks attributed to the presence of ferrocene moieties due to the successful immobilisation of a monolayer of 6-ferrocenylhexanethiol on the palladium electrode from which a layer of MCE had been freshly electrochemically desorbed were observed.

The peak-to-peak separation of immobilised ferrocene on the freshly revealed Pd was 12.2 mV suggesting a non-diffusion limited redox process, the consequence of successfully surface immobilised ferrocene moieties [30,31]. Control experiments, where thiolated
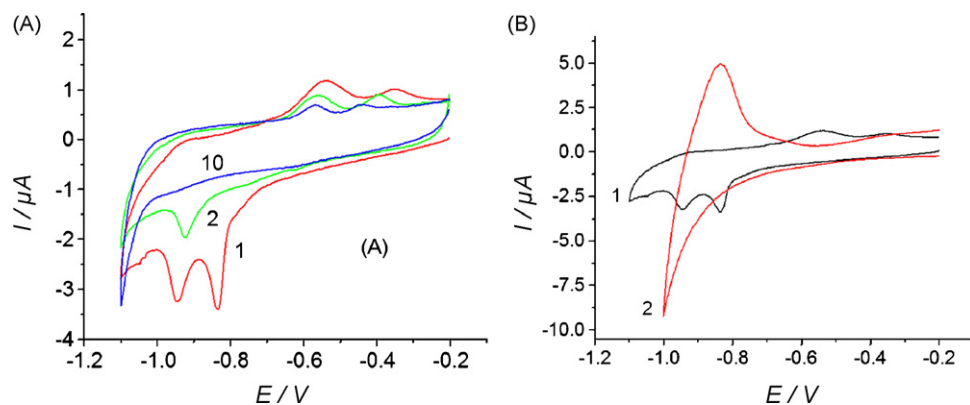
Fig. 1. Reductive desorption of MCE in 0.5 M NaOH from (A) gold surfaces following 1, 2 and 10 scans, and (B) from palladium surfaces (2) and gold (1).

ferrocene was immobilised on MCE coated electrodes and no desorption step was used, did not produce notable current values, although some ferrocene was immobilised following the surface displacement and rearrangement of the monolayer. Rapid exchange near defect points of SAMs and comparatively slow substitution of adsorbates within the crystalline domains are well known and have been widely reported [31–35].

Monitoring the current profile of Pd surface more closely, we found we could efficiently desorb MCE in the potential window −0.2 V to −0.675 V, which corresponds to an area of the polycrystalline Au potential window where no thiol reduction process can occur. These findings facilitated the realisation of metal-selective reductive desorption of short alkanethiols from Au/Pd electrodes and nanostructuring of the spatial distribution of the surface functionality based on the nature of the electrodes and not on a thermodynamically limited process such as chemisorption.

3.2. Electrochemical characterisation of mixed metal electrodes

We prepared Au/Pd electrodes by potentiostatically depositing Pd on plain gold electrodes. Deposition of Pd was realised at 0 V and the time of the deposition varied from 1 to 5 s (Fig. 3).

The resulting surfaces were characterised electrochemically in 1 M H_2SO_4 and the voltammograms are overlayed in Fig. 4. The deposition of Pd on Au is confirmed by the presence of the Pd

oxide formation at 0.900 V and subsequent reduction at 0.491 V for 1 s deposition and 0.422 V for 5 s deposition, while the formation and reduction of gold oxide is present at 1.200 V and 0.908 V for 1 s deposition and 0.918 V for 5 s deposition respectively.
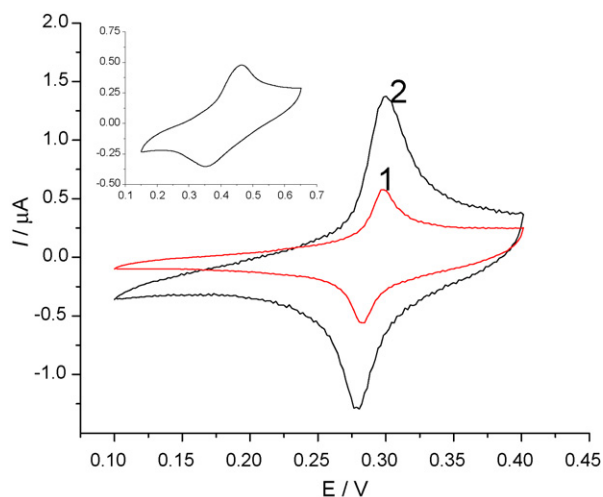

Fig. 3. Cyclic voltammetry in 1 M $NaClO_4$ of 6-ferrocenylhexanethiol immobilised on gold electrode (1) on which palladium deposited for 1 s (2) palladium deposited for 5 s. Inset: on bare gold electrode.
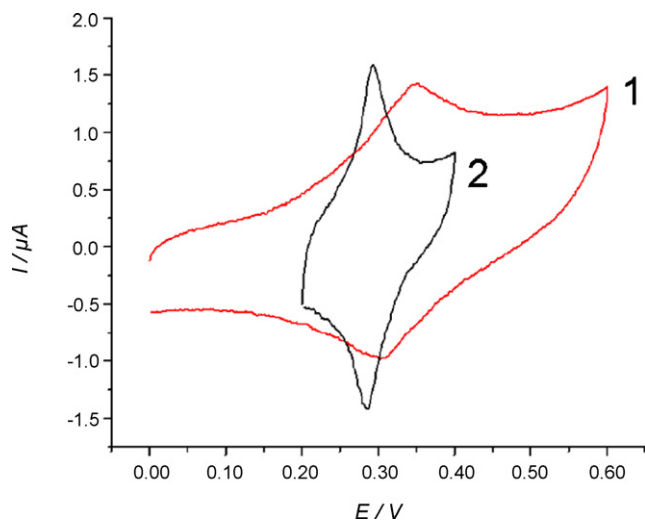

Fig. 2. Cyclic voltammetry in 0.1 M $NaClO_4$ of 6-ferrocenylhexanethiol immobilised on freshly desorbed MCE coated (1) gold and (2) palladium electrodes.
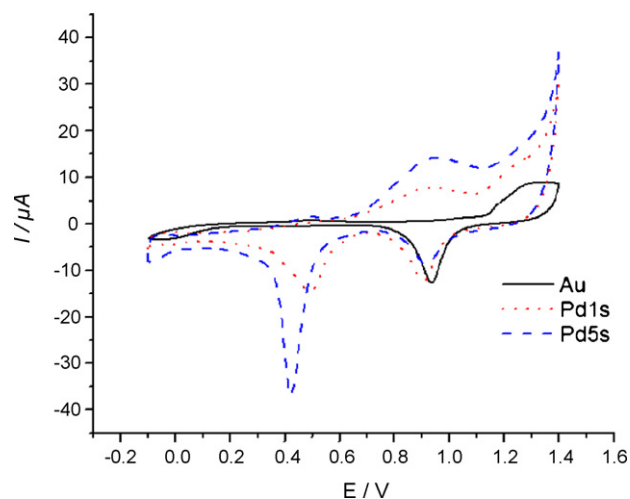

Fig. 4. Cyclic voltammetry of Au, and Au/Pd electrodes following variations in the deposition time of Pd in 1 M H_2SO_4.
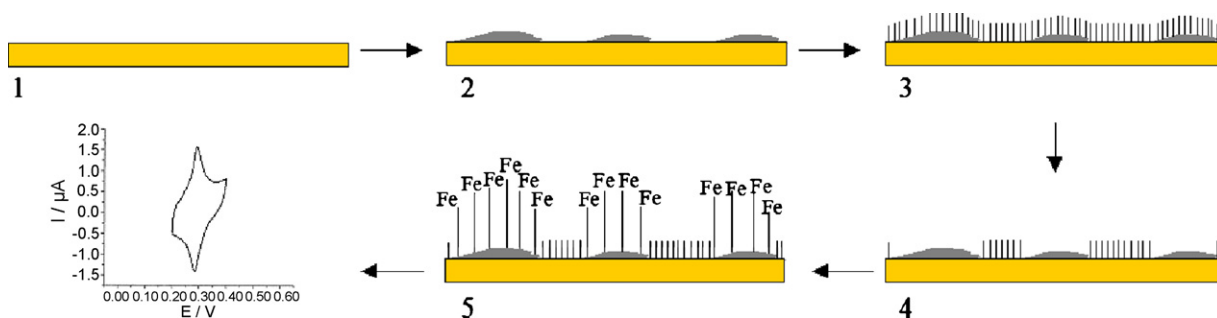
Fig. 5. Schematic of mixed metal electrode functionalisation (1, 2: partial electroplating of Pd on poly-Au electrode; 3: electrode surface blocking with MCE; 4: selective reductive desorption from Pd domains; 5: immobilisation of 6-ferrocenylhexanethiol on the bare Pd and resulting voltammetry).

The measured charges for the reduction of gold and palladium oxide and the corresponding area occupied by each metal are summarised for each electrodes in Table 1.

Interestingly, the amount of gold oxide formed at Au/Pd deposited for 1 s did not vary significantly from non palladium deposited poly-Au electrodes. Longer Pd deposition times did, however, affect the gold oxide formation more noticeably, attributable to the reduced gold active surface area. Finally, the total electrode surface area was considerably increased by factors of 2.18 and 2.83 following the deposition of Pd for 1 and 5 s respectively. As such, using short deposition times, we were able to control the surface ratio of gold to palladium, while avoiding a full coverage of the electrode with Pd. Longer deposition times and lower deposition potential have shown to very rapidly cover entirely gold substrates [24,36]. The deposition process was highly reproducible as was ascertained by monitoring the mass and thickness of palladium deposited on three separate electrodes, for each of 1 s and 5 s deposition times. The mass and thickness obtained was 2.15 μg/cm^2, (RSD = 2.83%, n = 3) and 1.79 nm (RSD = 2.79%, n = 3) for 1 s deposition, and 12.596 μg/cm^2 (RSD = 3.22%, n = 3) and 10.48 nm (RSD = 3.21%, n = 3) for 5 s deposition.

3.3. Metal selective electrochemical patterning of mixed metal electrodes

Finally, in order to assess the functionality of the mixed metal surfaces created, all three electrode types were subjected to the surface derivatisation steps depicted schematically in Fig. 5. The electrodes were coated with a monolayer of MCE (Fig. 5, step 1 to 3) and the selective reductive desorption from Pd domains only was attempted by cycling repeatedly in the potential window −0.2 V to −0.675 V previously elucidated (Fig. 5, step 4). Following this treatment, the mixed metal surface, with the MCE now desorbed selectively from the palladium domains only, was additionally exposed to a solution of 6-ferrocenylhexanethiol, expected to preferably anchor at free Pd regions, rather than MCE-occupied poly-Au (Fig. 5, step 5).

The successful immobilisation of 6-ferrocenylhexanethiol on Pd domains was assessed by cyclic voltammetry. The resulting voltamogramms are presented in Fig. 6. The presence of ferrocene
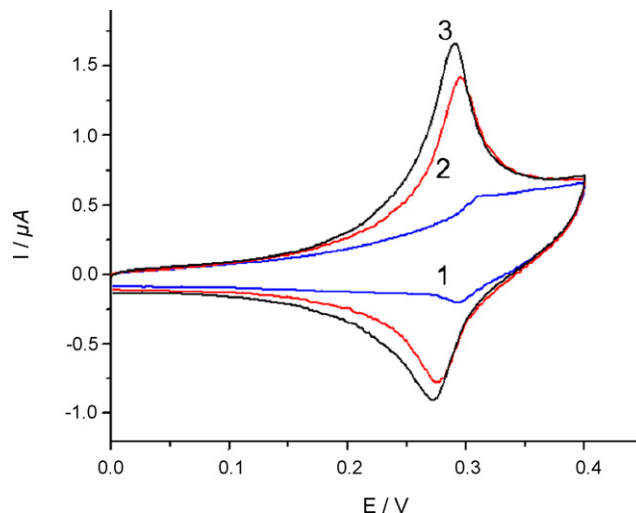

Fig. 6. Voltammetric responses for electrode initially coated with a monolayer of MCE, later subjected to selective reductive desorption, and finally exposed to ferrocene alkanethiols: (1) gold electrode, (2) Au/Pd deposited for 1 s and (3) Au/Pd deposited for 5 s.

moieties on Pd coated electrodes can be clearly seen from the pronounced ferrocene redox peaks, while very little signal can be recorded at the plain poly-Au electrode which followed the same treatment. Peak-to-peak separations were 26.3 mV, 19.1 mV and 19.7 mV for plain Au electrode, poly-Au/Pd 1 s and poly-Au/Pd 5 s electrode respectively. The plain poly-Au electrode served as a control to confirm that the peaks we observed could truly be attributed to the selective desorption of the MCE from palladium followed by immobilisation of 6-ferrocenylhexanethiol.

During the reductive desorption step performed in the potential window −0.2 V/−0.675 V, no peaks that could be attributed to the reductive desorption of MCE from the gold surface were observed, thus confirming that no MCE had been stripped from the gold surface. Following immersion in 6-ferrocenylhexanethiol, a small redox peak could be observed, most likely due to a small degree of displacement of the adsorbed mercaptoethanol at the boundary of defect points as previously explained in Section 3.1. The insignificance of the signals in comparison to those observed for both poly-Au/Pd 1 s and 5 s surfaces demonstrated the feasibility to employ such scheme to rationally design the chemical functionality of a solid–liquid interface.

4. Conclusions

In conclusion, we presented a rational approach to the formation of bi-functional surfaces via a metal-selective reductive process employing an initial sacrificial SAM layer of MCE. The spatial

Table 1
Current intensity recorded for the reduction of gold and palladium oxide and estimated surface area for a polycrystalline gold electrode (poly-Au) and for polycrystalline gold electrodes partially covered with Pd deposited for 1 s or for 5 s.

Electrodes	Oxide reduction peak (μC)		Surface area (cm^2)	
	Au	Pd	Au	Pd
Poly-Au	30.74	–	0.077	–
Poly-Au/Pd 1 s	27.22	42.54	0.068	0.10
Poly-Au/Pd 5 s	18.92	72.59	0.047	0.171

distribution of the surface functionality is therefore not controlled by a thermodynamically limited process such as chemisorption of alkanethiols, but rather takes advantage of the metal distribution at the surface. Such distribution is inherent to the material used and could be controlled during the fabrication process. The approach presented here may find particular application in the field of biosensors where surface-to-surface reproducibility is crucial to ensure a reliable performance and repeatability of the measurements, but also in heterogeneous catalysis.

Acknowledgements

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