Apparent enhanced underpotential voltammetry of lead(II) at a spontaneously adsorbed monolayer-coated gold electrode

The Analyst

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The ability of spontaneously adsorbed monolayers possessing terminal sulfonate groups to prevent electrode surface fouling by surfactant-containing solutions was examined. Films of 3-mercaptopropane sulfonate (MPS) on polycrystalline gold electrodes were prepared from acidic solution and characterised by reductive desorption. The voltammetric reduction of lead(II) ions at such electrodes revealed an enhanced current for underpotential deposition (upd) compared to the current observed at a clean polycrystalline gold electrode. The enhanced upd current was maintained in the presence of bovine serum albumin (BSA), indicating the ability of the MPS film to prevent adsorption of BSA on the gold electrode and the consequent fouling of the surface. Using the enhanced upd current, 1 μM Pb^{2+} could be detected in solution using square wave voltammetry. This work has implications for analytical applications of monolayer-coated electrodes.

Introduction

The formation of ordered structures by use of thiol chemisorption on gold or silver is now well established.[1,2] Use of alkane thiol compounds for chemisorption yields highly ordered monolayers referred to as self-assembled monolayers (SAMs). SAMs have proved beneficial in a range of potential applications, including surface wetting, studies of electron tunnelling and sensor development.[3–7] Formation of SAMs from alkane thiols is aided by the use of long alkyl chain compounds, since there is a greater lateral co-operative interaction between the methylene groups. Thus longer chains lead to more ordered structures. The less ordered shorter alkyl chain SAMs have been useful for analytical applications whereby the induced disorder in the film has allowed analyte partitioning and diffusion through the film.[5–7] The use of alkane thiols with additional functionality has been beneficial too; for example, SAMs with pyridinium end groups have shown extremely low detection capabilities for Cr(VI)[8] whereas SAMs with acidic end groups have been useful for detection of metal cations.[9]

In recent years a number of papers have appeared dealing with the behaviour of organo-monolayer films bearing sulfonate end-groups. Fawcett and co-workers[10] have studied the adsorption, electrochemical desorption and re-adsorption of 2-mercaptoethane sulfonate (MES) on single crystal gold electrodes. They suggested that MES does not form a compact monolayer, due to the short hydrocarbon chain minimising the lateral Van der Waal's interactions between chains, the bulky, negatively-charged end-group causing repulsion between adsorbed molecules and the high solubility of MES in water causing solvent incorporation into the surface film. Turyan and Mandler[11] studied monolayers of mercaptodecanesulfonic acid and showed that such films are disorganised, exhibiting a 'brush'-like organisation as well as being impermeable to inorganic anions and to organic species regardless of charge. An electrode modified with 10-mercapto-1-decanesulfonic acid allowed the selective detection of Fe^{2+} in the presence of a range of organic species which interfere with the Fe^{2+} oxidation at a bare gold electrode.[11] This group has also used these films for the deposition of two-dimensional conducting polyaniline films.[12] Finally, Anzai *et al.*[13] have shown that the electrochemistry of hexacyanoferrate(III/II) in protein solutions can be retained by use of a film of MES on a gold electrode. Identical electrochemical behaviour of hexacyanoferrate(III/II) was reported at bare and MES-coated gold electrodes.

The problems associated with the use of electroanalysis in many real samples, such as stripping voltammetric determination of trace metals in materials containing surfactants and proteins, are well known.[14] Various approaches to alleviation of these problems have been investigated,[15–19] including the use of thin polymer films on the working electrode surface in order to prevent foulant access to the electrode.[20–24] Applications of monolayer-coated electrodes in electroanalysis have not dealt with this problem, although stripping voltammetry-type measurements have been made. For example, Mandler's highly sensitive approaches to trace analysis with monolayer electrodes[8,9] and the anodic stripping voltammetric detection of Pb^{2+} and Cu^{2+} at SAM electrodes by Heineman and co-workers[25] illustrate the possibilities for stripping analytical approaches at such electrodes.

Given that monolayer films with charged, bulky end-groups induce a molecular brush organisation which is porous as well as highly charged,[10,11,13] we set out to study the effects of such films on the voltammetry of Pb^{2+} in the presence of protein as an initial step in the development of a new application area for monolayer-coated electrodes in electroanalysis. We envisaged that such a disorganised molecular film would allow small ions to permeate the film and gain access to the underlying electrode surface, whereas the large organic compounds associated with electrode fouling would be denied access by virtue of their size. Such an approach at gold electrodes would also provide a route to trace electroanalysis without mercury. During the course of our experiments we observed increased voltammetric responses for Pb^{2+} reduction at potentials positive of that for deposition of a bulk Pb phase. We report herein our investigations into both prevention of electrode surface fouling and enhancement of Pb^{2+} underpotential voltammetry at MPS-coated electrodes.

Experimental

3-Mercapto-1-propanesulfonic acid, sodium salt (MPS) was purchased from Aldrich (Poole, Dorset, UK) and used as

received. All other chemicals were of analytical grade and used as received. Water from a UHQ PS system (Elga Ltd., High Wycombe, UK) of 18 MΩ cm resistivity was used in the preparation of all solutions. Cyclic voltammetry was carried out with an Oxford Electrodes portable potentiostat/triangular wave generator (Oxford, UK), in conjunction with a Keithley 175A voltmeter and a Recorderlab 60000 XYt chart recorder (Sutton, Surrey, UK). Square wave voltammetry was performed with a Bioanalytical Systems CV50 Voltammetric Analyzer (BAS Technicol, Congleton, Cheshire, UK). Standard single-compartment, three-electrode cells were used for all experiments, consisting of gold disc (1.6 mm diameter discs, BAS Technicol), platinum wire and saturated calomel (SCE) as working, counter and reference electrodes, respectively. All potentials are reported with respect to the SCE. The polycrystalline gold electrodes were polished on aqueous 1 and 0.05 μm alumina slurries (Struers, Glasgow, UK) followed by cycling in 0.5 M H_2SO_4 until a stable gold oxidation/reduction cyclic voltammogram (CV) was obtained.

The MPS-coated gold electrodes were prepared as follows. The polished, acid-cycled gold disc electrode was immersed in a solution of MPS in 0.1 M $HClO_4$ for the desired time, removed and rinsed with water. For the reductive desorption[26] measurements, the electrode was then placed in a cell containing 0.5 M KOH (de-aerated by bubbling with N_2 gas for 10 min) and cycled between 0.0 and −1.3 V *vs.* SCE. The reductive desorption peaks were integrated by reference to a clean electrode scan in the same electrolyte in order to define the baseline. A sloping baseline was employed to prevent any overestimation of desorption charge by contributions from non-faradaic currents or currents due to other, non-reductive desorption faradaic processes. Peaks were cut-and-weighed for this integration procedure. The standard electrode modification time and MPS concentration were 5 min and 5 mM MPS in 0.1 M $HClO_4$.

Cyclic voltammetry of Pb^{2+} solutions were carried out in $Pb(NO_3)_2$–0.1 M KNO_3 mixtures with either clean gold or MPS-coated gold electrodes in solutions with or without added protein, bovine serum albumin, BSA (Sigma, Poole, Dorset, UK). The MPS-coated electrode was rinsed copiously with water before immersion in the Pb^{2+} solution. The potential range selected for the Pb^{2+} studies was dependent on whether bulk plus underpotential deposition or just underpotential deposition were to be studied. Solutions were de-aerated by bubbling with N_2 gas for 10 min.

Results and discussion

Film formation

Films of MPS on gold were formed by spontaneous adsorption from acidic aqueous solutions. Surface coverage was evaluated as a function of both the MPS concentration in solution and the adsorption time using the reductive desorption method.[26] In this method the chemisorbed thiolate (RS) is reductively cleaved from the gold surface

$$RS–Au_{(surface)} + e^- \rightarrow RS^- + Au_{(surface)} \quad (1)$$

and the charge required for this process was used as a measure of the surface coverage. Fig. 1(a) shows a typical voltammogram for this reductive desorption process. Two peaks were obtained, probably due to the use of a polycrystalline gold electrode. Fawcett and co-workers obtained a single peak for the reductive desorption of MES from a Au(111) electrode[10] and Porter and co-workers have shown that reductive desorption is sensitive to the surface crystal structure.[27] In our system, it is possible that the MPS molecules adsorb on predominantly two different types of gold crystal present in the polycrystalline structure, as revealed by this twin-peaked voltammogram in Fig. 1(a). Integration of the current in the two peaks gives the reductive desorption charge which is a measure of the surface coverage.

Figs. 1(b) and 1(c) show the evolution of the reductive desorption charge as a function of MPS concentration and adsorption time, respectively. In both cases the charge at saturation of the surface is approximately 1.6 μC, which corresponds to a saturation surface coverage of 6.9×10^{-10} mol cm^{-2}, taking into account Faraday's law, $n = 1$ (reaction 1), and a geometric surface area of 0.0233 cm^2 for the polycrystalline gold electrodes used (as determined by chronoamperometry).[28] This surface coverage is the same order of magnitude as that for MES on Au(111) reported by Fawcett's group (3.8×10^{-10} mol cm^{-2})[10] and for a close-packed *n*-alkanethiol SAM (7.6×10^{-10} mol cm^{-2})[29] which suggests that the MPS film forms a tightly packed structure. However, Fawcett estimated that this coverage of MES was approximately 0.65 in fractional coverage terms[10] which agrees with Mandler's report that mercaptodecane sulfonate yields fractional coverages of the order of 0.25–0.4.[11] We concluded that our MPS coating procedure yielded a gold surface coated with a submonolayer of MPS, presumably due to the highly charged nature of the molecules, their water solubility and their short alkyl chain. A disordered surface film may be assumed because of these factors.

Electrochemistry of redox probes in solution

The ability of MPS-coated gold electrodes to detect species in solution was tested using the hexacyanoferrate(III/II) redox couple. The cyclic voltammetric behaviour of this complex at the gold and MPS-coated gold electrodes was practically identical, indicating that the highly negatively charged film did not impede the transport of the anionic hexacyanoferrate to the

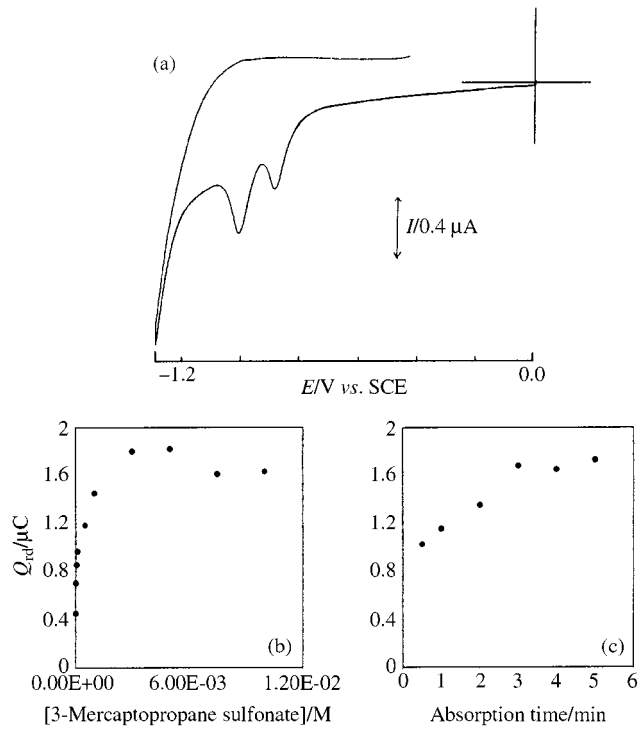

Fig. 1 (a) Reductive desorption of MPS film from polycrystalline gold electrode. MPS film formed by immersion in 1 mM MPS (in 0.1 M $HClO_4$) for 30 min. Reductive desorption carried out in 0.5 M KOH, 0.0 to −1.3 V, at 50 mV s^{-1}. (b) Reductive desorption charge as a function of solution concentration of MPS (in 0.1 M $HClO_4$), 30 min adsorption time in all cases. (c) Reductive desorption charge as function of adsorption time, all at 10 mM MPS (in 0.1 M $HClO_4$).

gold surface. This supports the idea that MPS films form disordered, porous, open structures amenable to solvent, electrolyte and probe anion permeation. This finding is in agreement with that of Anzai *et al.*, who found that hexacyanoferrate could be detected equally at bare and MES-coated gold electrodes.[13] Turyan and Mandler used much longer alkyl chains in their work and found that the electrochemistry of anionic probe ions was inhibited by such films.[11] Thus the short alkyl chain approach leads to a more disordered, porous structure which allows even ions of the same charge as the surface film to pass through and be detected at the underlying gold surface.

Detection of Pb^{2+} in solution: bulk processes

The cyclic voltammetric behaviour of a 1 mM Pb^{2+} solution in 0.1 M KNO_3 (pH 3.0) at an uncoated polycrystalline gold electrode is shown in Fig. 2(a). The peaks labelled C_1 and A_1 are the (cathodic) deposition and (anodic) stripping of bulk lead, respectively. These deposition and stripping peaks occurred at −0.53 V and −0.34 V, respectively. In the presence of 0.1% BSA in solution, the bulk deposition and stripping peaks were still evident, with peak potentials of −0.53 V and −0.27 V, respectively [Fig. 2(b)]. The increased peak–peak separation of these bulk lead processes indicated that the surface was somewhat fouled by the protein. The reduction peak current was decreased by *ca.* 40% and the peak became broader upon addition of the protein although there was no major effect on the stripping peak current (A_1).

Fig. 2(c) shows the cyclic voltammetric behaviour of Pb^{2+} at the MPS-coated gold electrode. The bulk lead deposition and stripping peaks, C_1 and A_1, were still present, with peak potentials of −0.52 V and −0.34 V, respectively. The peak currents and peak shapes were practically identical to that obtained at the bare gold electrode [Fig. 2(a)]. The presence of a film of MPS on the polycrystalline gold surface appears to have minimal effect on the electrochemistry of bulk lead deposition and stripping (a possible explanation for this is given below). Detection of Pb^{2+} in the presence of added protein, 0.1% m/v, at the MPS-coated gold electrode is illustrated in Fig. 2(d). In this case, the bulk deposition and stripping processes occurred at −0.55 V and −0.30 V, substantial changes from the case of both the MPS coated gold electrode in the absence of protein and the bare gold electrode in the presence of protein.

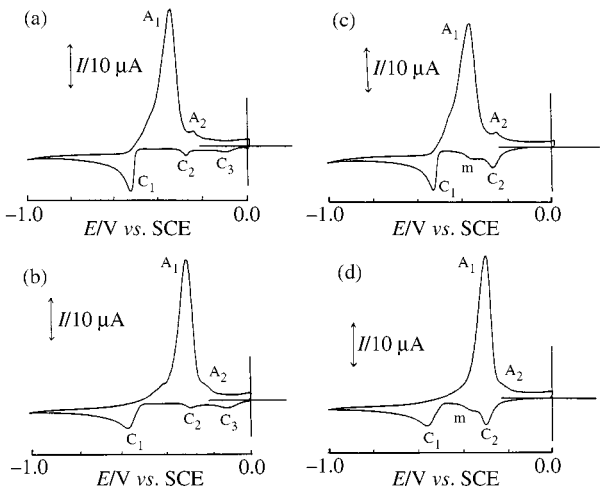

Fig. 2 Cyclic voltammetry of Pb^{2+} (1 mM) in 0.1 M KNO_3 pH 3.0 at: (a) bare gold electrode, (b) bare gold electrode plus 0.1% m/v BSA, (c) MPS-coated electrode and (d) MPS-coated electrode plus 0.1% m/v BSA. Sweep rate: 50 mV s^{-1}, MPS-coated electrode prepared by immersion of gold electrode in 5 mM MPS in 0.1 M $HClO_4$ for 5 min (see text for further details).

The peak current for reduction of Pb^{2+} was decreased by approximately 40% relative to that at the MPS coated gold electrode but was similar to that at the bare gold electrode in the presence of protein. There was no effect on the stripping current (A_1) although the slight pre-peak shoulder on A_1 in Figs. 2(a, b and c) was not evident. Overall, from these experiments we can summarise by saying that the effect of added protein on the deposition and stripping of bulk lead at bare and MPS-coated gold electrodes was negligible in practical terms: there was diminution of the reduction current and a change in the reduction peak shape, both of which were attributed to the effect of adsorbed protein on electron transfer kinetics, but there was no observable effect on the stripping process besides a slight change in the peak shape. BSA is known to adsorb on gold electrode surfaces from solution.[30] However the MPS film did not offer any benefit in prevention of the deleterious affects of BSA adsorption (see below for a possible explanation).

Detection of Pb^{2+} in solution: underpotential processes

At potentials positive of the bulk lead deposition/stripping processes small peaks were observed at all electrode and solution conditions studied (Fig. 2). At the bare gold electrode two such peaks were recorded, at −0.10 V and −0.27 V [peaks C_2 and C_3, Fig. 2(a)]. The formation of metal monolayers on foreign metal substrates at potentials positive of the reversible Nernst potential for bulk metal formation is referred to as underpotential deposition (upd).[31,32] The processes observed here are consistent with previous reports of Pb upd on polycrystalline gold.[33–35] Studies of Pb upd on single crystal gold show up as multiple peaks and these provide a sensitive indication of surface crystallinity.[36,37] The two peaks observed at the bare gold electrode [Fig. 2(a)] were maintained in the presence of added protein in solution [Fig. 2(b)] but on formation of the MPS film on the gold, there was a dramatic change in the current–potential curve in the upd region.

Figs. 2(c and d) illustrate this change, which resulted in an enhanced underpotential voltammetry of lead at the MPS-coated polycrystalline gold electrode in the absence and presence of 0.1% m/v BSA. The immediately obvious change relative to the experiments without MPS was that one major peak is now present (peak C_2, at −0.26 V without protein and at −0.29 V with protein), although a shoulder (labelled m) was present at −0.33 V and −0.35 V (absence and presence of protein, respectively). At 1 mM Pb^{2+} in solution, this upd peak current increased from a value in the region of 1–1.5 μA at the bare gold up to 4.5–5.8 μA at the MPS-coated gold electrode. The stripping of the underpotential deposit was observed at a peak potential of −0.24 V at the MPS-electrodes without added protein (A_2). At bare gold electrodes the stripping process was observed at −0.24 V but in the presence of protein at bare or MPS-coated gold the stripping of the underpotential deposit was observed as a shoulder at *ca.* −0.2 V (A_2). In all subsequent investigations we concentrated on the upd reduction process and its amplification by the MPS film. At the bare gold electrode, the upd response referred to in the following discussions is that at −0.27 V since this was the better shaped-response and was more repeatable.

The enhancement of the upd reduction current for Pb^{2+} was investigated as a function of Pb^{2+} concentration. Fig. 3(a) clearly illustrates this enhancement. Fig. 3(a) also shows that although 0.1 mM and 0.2 mM Pb^{2+} were not detected or gave only a small current signal at the bare gold in the presence and absence of added protein (BSA), at the MPS-coated electrode substantial currents were obtainable thus demonstrating clearly the advantage of using a self-assembled monolayer in the detection of Pb^{2+} ions in this way. It can be seen that the presence of the MPS film has a beneficial effect on the detection of Pb^{2+}, with or without protein being present. Fig. 3(b)

illustrates this with some representative voltammograms in the upd region. The apparent enhancement of the Pb upd peak at *ca.* −0.15 V [Fig. 3(b)B] by the presence of 0.1% m/v BSA requires further investigation.

The peak potentials for the upd of Pb^{2+} were shifted to less negative values at the MPS-coated electrode (absence of protein) compared to the bare gold (absence and presence of protein) and MPS-coated electrode (presence of protein). This shift of potential was of the order of 30–40 mV at Pb^{2+} concentrations in the range 0.1 to 0.5 mM. Less energy is required for the reduction; this may be due to the highly charged MPS film attracting lead closer to the gold surface, or a shift in potential of zero charge, something not observed in the presence of added BSA since some of the MPS charge is neutralised by the protein's net positive charge at the pH of this work (p*I* = 4.8).

In Fig. 2(c and d) a shoulder is evident at approximately −0.33 V (labelled m). This shoulder was not observed in the absence of the MPS film. On probing the stability of the Pb^{2+} upd signal at MPS and bare gold electrodes it became clear that the shoulder was due to desorption of the MPS film itself. This is illustrated in Fig. 4. Fig. 4(a) shows repetitive voltammograms in the Pb upd region at the MPS coated gold electrode. Although the enhanced reduction current signal and shoulder were in evidence on the first cycle, thereafter there was a decay in signal quality, and by the 10th cycle the voltammogram was identical to that obtained at a bare gold electrode. The corresponding experiment at the bare gold electrode is shown in Fig. 4(b). In this case the voltammogram was quite stable over the course of the 10-cycle experiment, in contrast to that observed for the MPS-coated electrode. Thus during the course of the detection of Pb^{2+} by this enhanced upd process the MPS film was desorbed and the electrode behaviour tended towards that of a clean gold electrode. This MPS desorption may explain why the bulk deposition process (C_1 in Fig. 2) was practically identical on both bare and MPS-coated gold electrodes in the absence and presence of added protein.

The sweep rate dependency of the current in the upd region was linear up to 100 mV s^{-1}, with a levelling-off thereafter; but plots of current *versus* square root of sweep rate had significant non-zero intercepts. It was concluded that the upd process, at bare and MPS-coated gold electrodes was a surface controlled process.

Low-level Pb^{2+} detection

Studies aimed at examining the ability of MPS-coated electrodes to detect Pb^{2+} in solution at lower concentrations than reported above were carried out, concentrating on the Pb upd region. Initially, CV studies of solutions containing 0.05 mM or 0.01 mM Pb^{2+} were carried out. In 0.05 mM Pb^{2+} two peaks were obtained, consistent with the peak and shoulder obtained at higher concentrations and were assigned to upd of Pb at −0.28 V and desorption of the MPS film at −0.33 V. At 0.01 mM Pb^{2+} one peak was observed, at −0.32 V, which corresponded to the reductive desorption of the MPS film. This result was confirmed by CVs with MPS-coated electrodes in solutions with no added Pb^{2+} whereby a peak was observed at −0.32 V (0.1 M KNO_3, pH 3.0) on the first cycle, but on repeated cycling the peak

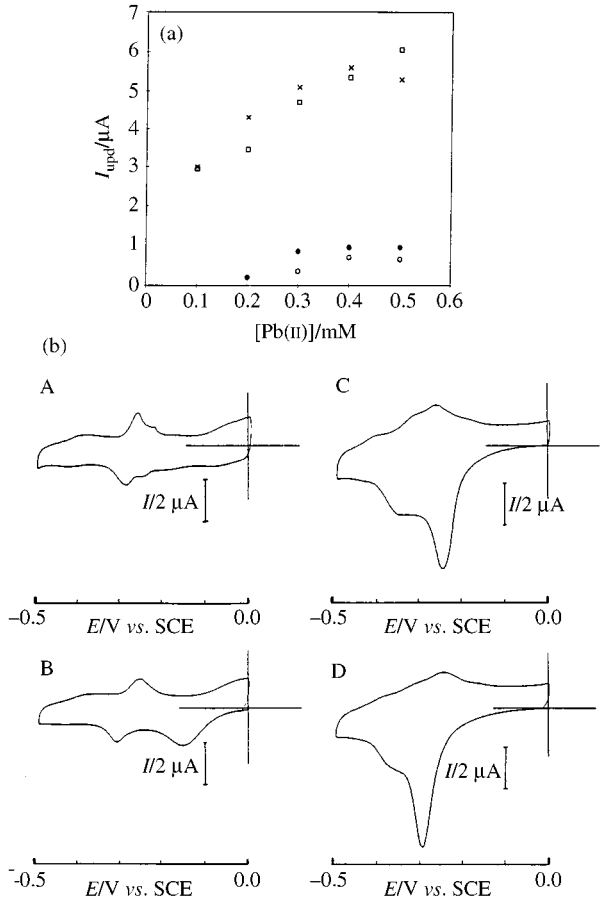

Fig. 3 (a) Reduction current for the upd of Pb^{2+} at: (●) bare gold, (○) bare gold plus 0.1% m/v BSA, (X) MPS-coated gold, and (□) MPS-coated gold in 0.1% m/v BSA. (b) Representative CVs for the upd region at: A, B, uncoated and C, D, MPS-coated gold electrodes in: A, C, 0.1 M KNO_3 pH 3.0 containing 0.5 mM Pb^{2+} and B, D, 0.1 M KNO_3 pH 3.0 containing 0.5 mM Pb^{2+} plus 0.1% (m/v) BSA. Other conditions as in Fig. 2.

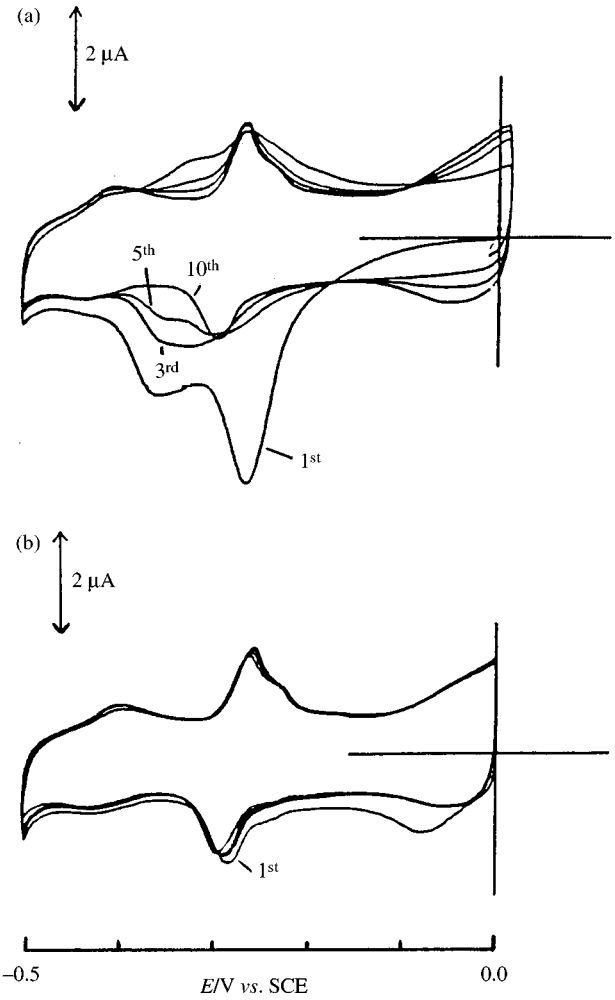

Fig. 4 Repetitive cyclic voltammograms in 1 mM Pb^{2+} at: (a) MPS-coated gold, and (b) bare gold. 1st, 3rd, 5th and 10th cycles shown. Other conditions as in Fig. 2.

disappeared indicating removal of the MPS film from the surface.

Application of square wave voltammetry[38] allowed detection of lower Pb^{2+} concentrations than by the linear sweep CV method above. Detection of Pb^{2+} at 1 μM was possible (see Fig. 5) and a linear dependence of the square wave differential current on the Pb^{2+} concentration was recorded in the range of 1–5 μM [$I(\mu A) = 0.081 \pm 0.008(\mu A\ \mu M^{-1})].[Pb^{2+}](\mu M) + 0.013 \pm 0.026(\mu A)$, $r = 0.981$, $n = 6$) using the differential current measurement. In Fig. 5, the peaks in the range from −0.15 to −0.20 V were assigned to the enhanced upd of Pb at the MPS-coated gold electrode and the peaks at −0.29 V were the reductive desorption of the MPS layer. Above 5 μM the current curved off as if towards a plateau at higher concentrations. Repeatability studies were carried out at 10 μM and 1 μM, and yielded RSD of 20.5% and 16.7%, respectively.

General discussion and conclusions

The charge for Pb upd followed the same trend as that in Fig. 3 for the upd peak current as a function of Pb^{2+} concentration in solution. At the higher concentrations there was a levelling-off of both the current and charge presumably due to a saturation of the surface by Pb atoms. The mean charge density for the highest two Pb^{2+} concentrations at MPS-Au electrodes both in the absence and presence of added protein was 3.44×10^{-4} C cm^{-2} ($s = 5.3 \times 10^{-5}$ C cm^{-2}). Assuming a two-electron reduction of Pb^{2+} in the upd region, this corresponds to a mean surface coverage of 1.78×10^{-9} mol cm^{-2} ($s = 2.8 \times 10^{-10}$ mol cm^{-2}). This surface coverage is close to that reported by Schmidt and Wuthrich[39] for a full surface coverage of a Pb upd layer on polycrystalline gold, 1.94×10^{-9} mol cm^{-2} and to that expected of any metal monolayer, approximately 2×10^{-9} mol cm^{-2}, as discussed by Kolb.[31] Our surface coverages were close to Pb monolayer coverage, despite the presence of a film of MPS on the gold surface, which itself is sub-monolayer in coverage. In the case of Pb upd at a bare gold electrode in the absence and presence of added protein, the corresponding surface coverages were 2.9×10^{-10} mol cm^{-2} (without protein) and 1.4×10^{-10} mol cm^{-2} (with added protein). These data indicate that the presence of protein had a serious affect on the upd of Pb on gold. However given the enhancement and similarity of data on MPS-coated gold with or without added protein it is unlikely that upd of Pb on bare gold would be required to be used for analytical applications. The smaller surface coverages on bare gold are due to the use of the best behaved and most repeatable peak for Pb upd, that occurring at *ca.* −0.27 V. Kolb *et al.*[33] reported that this peak was smaller than that at slightly more positive potentials. However in our investigation, the reduction peak at *ca.* −0.27 V was the better shaped and more reproducible.

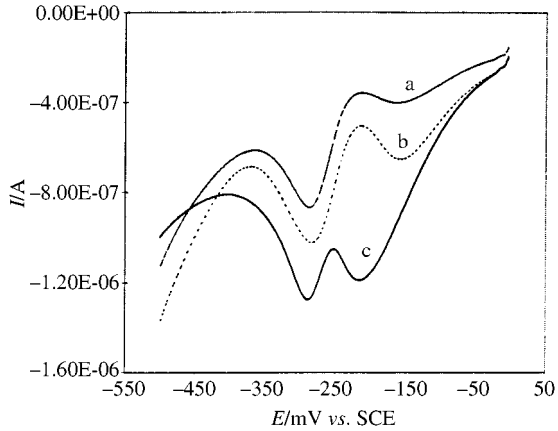

Fig. 5 Detection of low Pb^{2+} concentrations by underpotential square wave voltammetry at MPS-coated gold electrodes; (a), (b) and (c) are $[Pb^{2+}] = 1, 2.5$ and 5 μM, respectively. Square wave voltammetry parameters: step height, 5 mV; square wave amplitude, 25 mV; frequency, 15 Hz. Other conditions as in Fig. 2.

Underpotential deposition of metals at SAM films has been reported before but we are unaware of any upd work at highly charged monolayers such as we have investigated. Yoneyama and co-workers[40] investigated the upd of copper on gold(111)–propanethiol and concluded that Cu was deposited through the SAM film as a uniform Cu film between the SAM and gold; similar findings were obtained for Ag upd.[41] They found that the metal upd layer stabilised the SAM toward reductive desorption in alkaline solutions. Other workers have reported the intervention of Hg from the vapour phase between the SAM and gold inducing SAM re-orientation[42] and the stabilisation of SAMs towards thermal desorption by use of pre-deposited upd Ag layers on gold.[43] However all of these reports deal with the influence of the upd layer on the SAM. None have studied the role of the SAM on upd as reported in this paper. It is interesting to note that the upd layer is formed as an intermediary layer between the gold electrode and the SAM[40–42] and that a more stable SAM is produced in all cases.[40,41,43] Studies of bulk deposition at SAM electrodes, for stripping voltammetry applications, have been undertaken by Heineman and co-workers.[25,44] They found that upd peaks were actually removed from the voltammograms, leading to a better signal for analytical applications, using methyl and carboxylate-terminated SAMs. In contrast our approach appears to enhance the upd process.

It is possible that the MPS film is actually desorbed in the presence of Pb atoms on the gold surface at potentials more positive than MPS is desorbed in the absence of Pb atoms. MPS desorption in 0.1 M KNO_3 at pH 3.0 was observed at –0.32 V in the absence of Pb atoms. In the presence of Pb atoms, a peak and a shoulder at −0.28 V and −0.33 V were assigned to Pb upd and MPS desorption, respectively, since the process at less negative potentials was seen to vary with Pb^{2+} concentration [Figs. 3(a) and 5]. The possibility of MPS desorption is supported by the apparent lack of correlation of anodic peak processes to the cathodic peak processes in the upd region [Figs. 2 and 3(b)]. However this would be the direct opposite of previous reports of monolayer desorption from upd metal layers.[40,41,43] Whether the upd is enhanced by the MPS film or the desorption of the MPS film is enhanced by the deposited Pb atoms cannot be discerned from our data. However, an interesting phenomenon has been uncovered and merits further study. The enhancement of Pb upd could prove beneficial for analytical applications. Kirowa-Eisner and colleagues have demonstrated the very powerful analytical uses of upd. They first demonstrated this using Pb upd on silver,[45,46] whereby upd was employed as the deposition step and detection was by stripping of the underpotential deposit, and have recently extended this to Cu upd on gold.[47] Sub-parts per billion detection limits were achieved. However extensive sample pre-treatment was still required. It is possible that the use of a highly charged spontaneously adsorbed film at which upd can still occur will allow more simple sample pre-treatment strategies to be used.

In conclusion, we have shown that a film of MPS on polycrystalline gold can be prepared from acidic aqueous solution. This film exhibited a porous, disorganised structure, consistent with a submonolayer coverage and as expected for a highly charged, short alkyl chain species. Such a film has been shown to offer an apparent substantial improvement in the upd of Pb onto the gold surface and this enhancement is retained in the presence of added protein (as a model surface foulant). The improvement may also be attributable to a desorption of the organic film material in the presence of Pb atoms on the surface. In either case the effect observed is dependent on the concentration of Pb^{2+} ions in solution. These MPS-coated gold

electrodes may therefore offer a new route to the electroanalysis of trace metal ions in solutions containing potentially surface-fouling materials, so allowing the use of simpler sample pre-treatment methodologies. Our investigations into this phenomenon and its applications are continuing.

Acknowledgements

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