

## Ultramicroelectrode Arrays Modified With Ionomer-Entrapped Silica Films as Potential Voltammetric Sensors for Copper, Lead and Selenium

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Composite silica-polyelectrolyte thin films obtained by the sol-gel technique were used as surface modifiers for gold-based ultramicroelectrodes (UME) and gold and iridium based UME arrays (UMEA). Poly(dimethyldiallylammonium chloride) (PMDAAC) and polyvinylsulfonic acid (PVSA) were used as polyelectrolytes. The best response for the electrodes modified with a composite film was observed for film thickness of 0.7-0.9  $\mu\text{m}$  and a polyelectrolyte content of 1-2 %. Silica-polyelectrolyte modified gold-based UMEs were shown to be useful for determining trace levels of copper (II) via CV with a detection limit of  $5 \times 10^{-6}$  mol/L and for selenium(IV) by SWASV at  $10^{-9}$  mol/L levels. A mercury coated iridium-based UMEA covered with PVSA-silica composite film was used for lead (II) determination by SWASV. It was shown that silica-polyelectrolyte composite films increased selectivity for analyte determination and protected the surface of the electrodes from degradation and thus enhancing the life time of the electrode.

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Ultramicroelectrodes (UME) and ultramicroelectrode arrays (UMEA) with substrate materials such as platinum, iridium, and gold are of great importance in both voltammetric and amperometric analyses because of their high sensitivity and their ability to perform analysis in solutions with high resistance such as natural waters.<sup>1,2</sup> Such electrodes can be used as chip-based microelectronic devices for natural in-situ water monitoring. Iridium and gold-based UMEAs have been used to develop highly sensitive methods for determining  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Se}^{4+}$  in conjunction with SWASV.<sup>3,4</sup>

Improvement in the response, stability, lifetime, and detection limits of these electrodes can be accomplished by modifying the surface of the electrodes with stable porous films containing active functional groups. It has also been previously shown that silica modified by adsorption of high molecular weight quaternary ammonium salts (QAS) possess anion-exchange properties and can be used for preconcentration of different anions<sup>5</sup> High molecular weight polyelectrolytes can be entrapped within the porous silica film using a sol-gel process.<sup>6,7</sup> The sorbents are stable and possess ion exchange properties. They have been used as modifiers for carbon electrodes.<sup>8</sup>

Modification of gold and iridium based microelectrodes with polyelectrolyte containing sol-gel materials combines the advantages of ion-exchange preconcentration at ppb amounts of the analytes coupled with their subsequent voltammetric detection by UME arrays.

We present here the results of studies of surface modification effects and voltammetric characteristics for gold-based UMEs; microlithographically fabricated arrays of gold and iridium based UMEs with silica-poly(dimethyldiallylammonium chloride) (PMDAAC), and silica-polyvinylsulfonic acid (PVSA) composite films obtained by the sol-gel dipping technique.

### Experimental

#### Reagents and materials

Poly(dimethyldiallylammonium chloride) (PMDAAC, MW 240000), Tetraethyloxysilane (TEOS), Tetrabutyl orthosilica (TBOS), Poly(vinylsulfonic acid, sodium salt) (PVSA, MW 4000 – 6000), potassium hexacyanoferrate were purchased from Aldrich Chemicals. All reagents were analytical grade. Stock metal solutions were prepared from 99.999%  $\text{Cu}(\text{NO}_3)_2$  (Johnson Matthey) and 99.99%  $\text{SeO}_2$  (Aldrich) and diluted to required concentrations. Single  $10 \mu\text{m}$  gold ultramicroelectrodes were purchased from Cypress System, KS. The design of the microfabricated Ir and AuUMEs has been previously described.<sup>19</sup> Briefly, the UMEAs were fabricated on a standard 5in. silicon wafer substrate. The conductors were protected and insulated by a layer of silicon dioxide (5000 Å). Individual UMEAs chips ( $3.4 \text{mm} \times 3.1 \text{mm}$ ) were mounted on a  $80 \text{mm} \times 6 \text{mm}$  custom designed printed circuit board (CFC, Waltham, MA). Individual ultramicroelectrodes in the array were  $10 \mu\text{m}$  in diameter and spaced  $150 \mu\text{m}$  center-to-center from their nearest neighbor. Each UMEA contained 177 individual gold UMEs. Microscopic glass slides  $1 \times 1 \text{cm}$  dimension were used as support for the composite film in the spectrophotometric studies.

#### Apparatus

Cyclic voltammetry (CV) and Square Wave Anodic Stripping Voltammetry (SWASV) were performed using a EG&G PAR Model 273 potentiostat (Princeton, NJ) interfaced to a digital DECPc 420sx with EG&G M270 electrochemical software. A UV/VIS spectrophotometer Specord M-40

(Germany) with quartz cells was used for spectrophotometric measurements. AFM images were obtained using a Digital Instruments Nanoscope E controller (Digital Instruments, Santa Barbara, CA).

#### Procedures

Silica sol gel was obtained using hydrolysis and polycondensation reactions of TEOS and TBOS according to a previously described procedure.<sup>6,8</sup> Thin films were prepared from freshly formulated polyelectrolyte-containing sol-gel stock solution by spin coating on the polished surfaces of the gold UMEs and UMEAs. Electrochemical characteristics of the gold UMEs modified with the PDMDAAC and PVSA were studied using  $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{Cu}^{2+}/\text{Cu}$  systems. Electrode potentials were measured vs. a  $\text{Ag}/\text{AgCl}/\text{NaCl}$  reference electrode. The electrochemical cell consisted of the reference electrode, a platinum wire counter electrode and a sol-gel modified UMEA or UME working electrode. The ion-exchange properties of the silica film were also studied spectrophotometrically using glass slides coated with the sol-gel solution. The average thickness of the films was estimated based on AFM images of the modified electrodes and using an optical interference method for modified glass slides.<sup>10</sup>

#### Results and discussion

Preliminary studies showed that the PVSA and PDMDAAC can be easily entrapped into the sol-gel matrix. The obtained composite materials are mechanically and chemically robust. They possess high adhesion to the surface of glass slides, gold and iridium based UME and UMEAs. The silicon dioxide wafer surface of the UMEA appears to play an important role in fixing and stabilizing the film on the surface.

Atomic force microscopy (AFM) was used to visualize the microstructure of the composites on the surface of the glass slides and UMEs. It was shown that a crack-free flat surface is formed and provides a homogeneous bulk polyelectrolyte-silica film. The results obtained via the AFM indicate that the diameter of the pores of the film were less than 100 Å and the average thickness

PDMDAAC-silica and PVSA-silica films. It was shown that the polyelectrolyte molecules were not washed from the surface of the films by a 0.1M water solution of inorganic ions and 0.01 M  $\text{HClO}_4$ . The resulting PDMDAAC-silica film possess anion exchange properties and can be used for preconcentration of anions. Sorption of  $[\text{Fe}(\text{CN})_6]^{3-}$  onto the glass slide modified with a PDMDAAC-silica film was studied spectrophotometrically at  $\lambda_{\text{max}} = 315$  nm. It was shown that the adsorption equilibrium was reached within 30 minutes for  $[\text{Fe}(\text{CN})_6]^{3-}$  in the concentration range  $10^{-6} - 10^{-5}$  mol/L. The desorption of the analyte was observed after soaking the glass into a 0.1M NaCl solution for 10 min. The modified glass can be used repeatedly for more than 10 times. Composite films obtained in this manner can be used for preconcentration of anions and as possible modifiers of electrode surfaces.

The cyclic voltammetric characteristics of the gold UME and UMEA modified with PDMDAAC and PVSA silica composite films were studied using  $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{Cu}^{2+}/\text{Cu}$  systems, respectively. Cyclic voltammograms for the non-modified and modified UME are shown Fig 1 and 2.

A well defined sigmoidal response for the  $\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}$  couple was obtained for the non-modified and PDMDAAC-silica modified gold UME with a  $E_{1/2}$  of approx. 175 mV. No response was observed for UMEs modified with a bulk silica film without the ionomer.

The reproducible anodic peaks at +0.1 V for the  $\text{Cu}^{2+} / \text{Cu}^0$  couple were observed at both the non-modified electrodes and those modified with a PVSA-silica composite film. An increased response was obtained for the polyelectrolyte-modified UMEs. These results can be explained by the presence of charged groups of anion/ cation exchangers entrapped in the silica network after preconcentration of the ions and by their ability to thus enhance transport through the film. This result was also confirmed by spectrophotometric studies of the modified glass.

It has been previously shown that UMA arrays behave as a single UME but with a much higher and more stable response.<sup>1</sup> The gold based non-modified and sol-gel modified

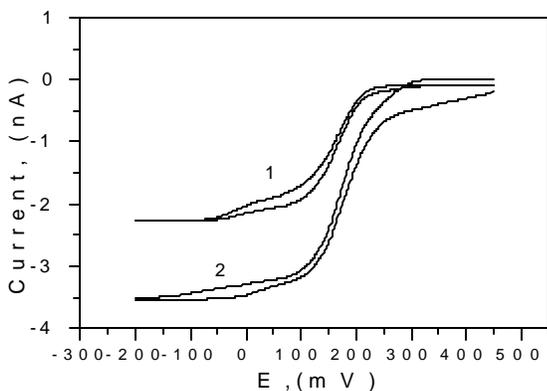


Fig. 1 Cyclic voltammograms for 5 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 0.1 M  $\text{KNO}_3$  at (1) non-modified; and (2) a silica-PDMDAAC modified gold UME. Preconcentration: 20 min, scan rate : 100 mV/s.

of the film was 700 nm. The thickness of the film on the glass slide obtained by optical interference was 1000 - 900 nm.

The properties of the films were determined using UV-VIS spectrophotometry on glass slides modified with composite

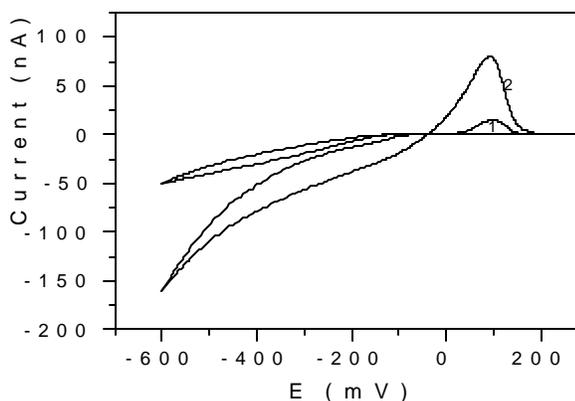


Fig. 2 Cyclic voltammograms for  $10^{-3}$  M  $\text{Cu}^{2+}$  in 0.01 M

$\text{HClO}_4$  at (1) non-modified; and (2) a silica-PVSA modified gold UME. Preconcentration: 30 min, scan rate 100 mV/s

UMEAs displayed the same properties as the single UME but with a response approximately 100 times greater than for the single UME. A broadening of the sigmoidal CV curve for the hexacyanoferrate/hexacyanoferrite system compared to the non-modified UMEA was observed.

### Optimization of the UMEs responses

The dependence of the peak anodic stripping current ( $i_p$ ) at a modified electrode for the  $\text{Cu}^{2+}/\text{Cu}$  couple as a function of the pre-concentration time ( $t_p$ ) and content of PVSA in the final sol is shown in Fig 3. It can be seen that at a PVSA content of 0.25% in the initial sol, a constant but relatively low response is achieved within 5 minutes; at a polyelectrolyte content of 0.5 and 1.0 %, a constant response is achieved within 10 and 20 minutes, respectively. For a PVSA content  $>1.0\%$ , a sol-gel with high viscosity is formed that directly influences the transport properties of the film as indicated by a decrease of  $i_p$  and an increase in  $t_p$ . Based on these results, the film with a PVSA content of 0.5 to 1.0% in the initial sol was then used for further work. A PDMDAAC content of 2.0 % in the sol was found to be optimal.

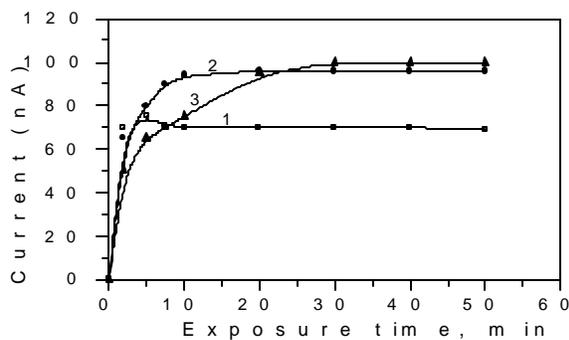


Fig 3. Dependence of the peak anodic stripping current on the pre-concentration time for 1 mM  $\text{Cu}^{2+}$  at a UME modified with a silica-PVSA film. PVSA content in the initial sol: (1) 0.25%; (2) 0.5%; (3) 1.0%

The dependence of the peak height on scan rate for the CV technique at non-modified and modified UMEA was studied. A linear dependence of peak height was observed for scan rates of 10 to 250 mV/s for the non-modified electrode and 10 to 100 mV/s for the silica-PDMDAAC modified electrode.

The reversibility of the modified electrode was also studied. After washing the electrode with water, the peak current in 0.1M  $\text{HClO}_4$  solution decreased but did not disappear. The regeneration of the electrode was attempted by soaking it in a 0.1 M NaCl solution. The anodic and cathodic peak current for copper and hexacyanoferrate disappeared completely after 10 min of immersion.

The decrease of the peak current for the  $\text{Cu}^{2+}/\text{Cu}$  couple at the non-modified electrode was observed using CV after 5 cycles and for SWASV after 2 measurements. On the other hand, the silica-PVSA modified electrode showed no change in the peak current during 10 cycles for both techniques. The response of the UMEA modified with PDMDAAC was stable for 5 days. Non-modified UMEAs were used for up to three days. The silica composite film protected the surface of the electrodes from degradation and enhanced the life time of the electrode.

### Analytical application of modified UMEs

The analytical characteristics, under optimal conditions, of the gold UMEAs modified with a silica-PVSA film were evaluated as a function of  $\text{Cu}^{2+}$  concentration. The best-fit linear calibration equation for  $\text{Cu}^{2+}$  detection at modified UMEA using CV is:

$i$  ( $\mu\text{A}$ ) =  $(0.069 \pm 0.033) + (0.082 \pm 0.006) \times C(\text{Cu}, 10^{-5} \text{ mol/l})$ , with  $R = 0.99$ . The linear portion of the graph was in the range:  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  mol/L. The detection limit was  $5 \times 10^{-6}$  mol/L. At the non-

modified electrode the linear portion was in the range of  $10^{-4}$  to  $10^{-2}$  mol/L, the detection limit was  $5 \times 10^{-5}$  mol/L.

The possibility of using PDMDAAC-silica as a protective membrane for the gold-based UME and UMEAs in conjunction with SWASV determination of selenium (IV) at ppb levels was demonstrated. The film containing the anion exchanger enhanced the selectivity for the selenium determination in the presence of interfering concentrations of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ . However, the presence of EDTA in solution for complexing lead was necessary due to the small size of the cation.

Iridium-based UMEAs with electrodeposited mercury have been shown to be useful for determining trace amounts of lead using the SWASV technique.<sup>1</sup> However, deposited mercury can be easily removed from the surface of electrode by merely shaking. To help prevent this, the mercury on the surface of the electrode can be covered by a PVSA-silica film. We have shown that an Ir-Hg/MEA modified with a composite silica-film was more stable over time and has a similar response to the non-modified Ir-Hg/MEA. The detection limit for determining  $\text{Pb}^{2+}$  using the modified UMEA by SWASV was 10 ppb for a deposition time of 120 s. The film does not appear to increase the sensitivity compared to the non-modified UMEA, however it does protect the mercury surface and thus increases the life time of the electrode.

Thus, modification of gold and iridium based UME and UMEAs with polyelectrolyte-silica composite films appears to be a promising technique for improving the electrochemical behaviour of such electrodes

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