Nanoengineered electrochemical sensor based on mesoporous silica thin-film functionalized with thiol-terminated monolayer

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A mesoporous silica thin film was synthesized *via* a surfactant-templating process, where a silica sol gel is spin-coated onto the surface of a microchip-based gold microelectrode. Within the film was a cubic lattice of pores having a primary size of 77 Å. Thiol (-SH) functional groups were subsequently immobilized onto the mesoporous silica thin film through a self-assembly process. The thiol-functionalized mesoporous silica (SH-FMS) thin film was used as the electrode sensing layer for detection of lead(II) in aqueous solutions by employing a square wave adsorptive stripping voltammetry technique. The electrode modified with the SH-FMS thin-film utilized the binding affinity of lead(II) to the thiol ligands to perform the preconcentration step under an open circuit, with no additional electrolytes. The voltammetric responses for lead(II) increased linearly with the preconcentration time from 1 to 30 min. The responses also increased linearly with lead(II) concentrations ranging from 250 to 5000 ppb after 5 min preconcentration and from 25–100 ppb after 30 min preconcentration.

Introduction

Mesoporous silica materials are becoming more attractive electrode modifiers than zeolites due to their much larger pore openings,[1] which improve diffusion and accessibility for larger analytes.[2] Most electrode modifications with mesoporous silica MCM-41 materials have been accomplished *via* composite coating of the silica materials on electrode surfaces[3,4] or mixing of the silica materials with conductive materials such as graphite powder.[5–7] These techniques often rely on graphite powder as a conductive additive or polystyrene as a binder between the mesoporous silica materials and the electrode surfaces. Better methods for preparation of mesoporous silica modified electrodes without binders and/or additives are desirable.

This study reports a method for preparation of a microchip-based gold microelectrode that is modified with a mesoporous silica film through an interfacial silica-surfactant self-assembly process, which does not require additives or binders. The self-assembly process allows surface layers to be constructed in a manner that is highly reproducible, which is very important for any two-dimensional surface reaction to be successful.[8] Organic thiol (–SH) functional groups were subsequently immobilized onto the surfaces of the mesopores of the silica film. The modified microelectrode was then used for detection of lead ions by employing adsorptive stripping voltammetry (AdSV) technique.

Mesoporous silica films with pore sizes of up to 100 Å have been synthesized from silica sol gels (normally consisting of silica precursor, acid solution, organic solvent, and water) by a surfactant-templating process in which the pores are formed upon removal of the surfactant by calcination.[9–13] The precise design and control of pore structure, pore size/volume, and pore orientation of the silica films can be achieved by using structure-directing agents, such as poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock co-polymers $(EO_nPO_mEO_n)$.[14] If a higher molecular weight surfactant (*e.g.* $EO_{106}PO_{70}EO_{106}$) is used, the resulting film will have a highly ordered, cubic lattice of pores with larger pore sizes and pore volumes. If a smaller molecular weight surfactant

(*e.g.* $EO_{20}PO_{70}EO_{20}$) is used instead, a well-ordered film with a planar hexagonal lattice of pores can be produced.[14] However, for a given triblock copolymer (*e.g.* $EO_{106}PO_{70}EO_{106}$) the pore structure of the film also depends upon the composition of the silica sol gel. At a high molar ratio of surfactant to organic solvent, a film with a planar hexagonal lattice of pores is formed; at lower molar ratios of surfactant to organic solvent, a film with a cubic lattice of pores is formed.[14] By controlling the film thickness (*e.g.* changing the compositions of the precursor solution), a continuous, defect-free, mesoporous silica thin film can be produced.[15]

Factors affecting the stability of silica thin films have been studied. Spin-coated silica thin films have been found to be unstable in basic aqueous solutions but stable in pure water and acidic electrolyte solutions.[15] The instability is caused by the dissolution of the mesoporous framework, which increases with increasing pH. Because electrodes modified with these silica films cannot be used in basic solutions, the silanol groups, inherent to the MCM-41 silica, are not useful in binding with metal ions in preconcentration step of AdSV. Silanol groups must be ionized in a basic solution (*e.g.* ammoniacal medium) in order to accumulate positively charged ion species.[2,16,17] Therefore, without functional ligands attached, the spin-coated films of mesoporous silicas are often used as molecular sieves in electrodes by either blocking or improving the voltammetric responses of the analyte species.[15]

In this work, organic thiol (–SH) functional groups were immobilized onto the surfaces of the mesopores of the silica film. Therefore, the preconcentration step can be performed in slightly acidic electrolyte solutions or neutral non-electrolyte solutions as long as the thiol ligands can adsorb the target analyte, based on previous pH study using batch adsorption experiments.[18] In non-basic solutions, the mesoporous silica films are more likely to remain stable for a long period of time.

To test the applicability of the thiol-functionalized mesoporous silica (SH-FMS) thin film as an electrode sensing layer, square wave voltammetry was conducted on a microchip-based gold microelectrode modified with a SH-FMS thin film for the detection of lead(II). Preconcentration of lead ions (*via*

coordination/chelation with thiols) occurred under open circuit potential in aqueous medium without adding other reagents as electrolytes. Effort was also focused on finding the best operating parameters, calibration curves, and detection limits for lead detection. To our knowledge, this is the first report on using a microchip-based electrode modified with functionalized mesoporous silica thin-film for metal ion detection based on AdSV.

Experimental

Chemicals and solutions

The non-ionic surfactant used in preparing the SiO_2 film was Pluronic F-127 ($EO_{106}PO_{70}EO_{106}$), obtained from BASF Corp. All solutions were of highest purity available, including ethyl alcohol (Gold Shield Chemical Co.), 2-propanol (Aldrich Co.), nitric acid (Aldrich Co.), tetraethyl orthosilicate (TEOS, Aldrich Co.), and 3-mercaptopropyl trimethoxysilane (MPTMS, United Chemical Technologies, Inc.).

Preparation of a SH-FMS thin film modified gold microelectrode array

The modification of a gold electrode array on microchip with a SH-FMS thin film consisted of two steps. First a mesoporous silica film was deposited onto the electrode surface by the spin-coating technique. Then the thiol functional groups were immobilized inside the mesopores of the film by self-assembly chemistry. To prepare the silica film solution, a 2.578 g quantity of Pluronic F-127 surfactant was dissolved in 3.430 g of de-ionized water and 8.846 g of ethyl alcohol. Then 0.108 g of concentrated HNO_3 was added into the mixture. Finally, a 5.0 g quantity of TEOS was added to the solution. The molar ratio of TEOS : water : ethanol : HNO_3 : Pluronic F-127 was 1 : 8 : 8 : 0.05 : 0.008. The solution was shaken for 24 h, then spin-coated at the speed of 3000 rpm onto the bare surface of a gold microelectrode array on microchip (part No. M1450110, Microsensor System, Inc.) for 30 s. Fig. 1a shows the schematic of the microelectrode array. The specific electrode array had 50 finger pairs (15 microns finger width and finger spacing) with gold as the electrode material and quartz as the substrate. The

electrical connection for the array was covered with plastic tape before spin coating with the film solution. After the spin coating, the tape was removed and the film-coated electrode was calcined on a hot plate at 350 °C for 8 min in air. Following the calcination, immobilization of the thiol groups onto the silica thin film was performed. The film-coated electrode was placed in a 100% humidity chamber at room temperature for 2 h, and then soaked in 400 mL of toluene at 75 °C under a nitrogen atmosphere. A 24 mL volume of MPTMS was added to the resultant electrode, placed within a 1000 mL reflux chamber, and refluxed at 110 °C for 5 h. Finally, the modified electrode was rinsed with copious 2-propanol and dried by blowing with N_2 gas. The final product was an electrode array modified with SH-FMS thin film. Fig. 1b depicts the electrode, which is composed of three layers: SiO_2/Au/SH-FMS.

Characterization of mesoporous silica thin film and SH-FMS thin film

Characterization of the untreated mesoporous silica film and the thiol-treated silica (SH-FMS) thin film was performed using N_2 gas adsorption/desorption (BET), scanning electron microscopy (SEM), XRD, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), an optical profilometer, and ellipsometry.

BET and TEM measurements were performed on untreated film that was detached from the substrate before the analyses. High-resolution TEM analysis was carried out on a JEOL JEM 2010F microscope operating at 200 kV with a specified point-to-point resolution of 0.194 nm. BET surface area, porosity, and pore size analyses were performed on a Quantachrome Autosorb 6-B gas sorption system. The thickness of the untreated film was measured using the Zygo optical profilometer (OMP-0347). Both untreated and functionalized films were analyzed using ellipsometry and FT-IR measurements. The FTIR characterization of the films was performed on a Nicolet MAGNA-IR 860 spectrometer equipped with an attenuated total reflectance (ATR) detector and a MCT-A detector.

Voltammetry measurement procedure

The voltammetric detection of lead(II) with the SH-FMS thin film modified gold electrode was investigated. The voltam-
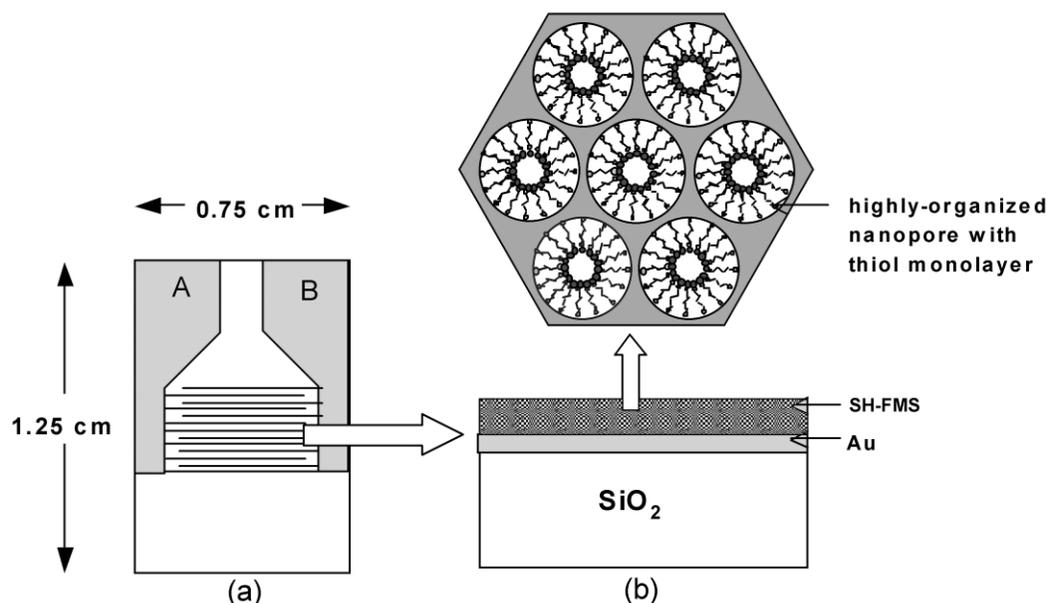

Fig. 1 A schematic of the gold electrode array with the SH-FMS thin film: (a) top-view of the array, and (b) side-view of the three-layer sensor (SiO_2/Au/SH-FMS).

metric procedure consisted of preconcentration, cathodic electrolysis, anodic stripping, and regeneration steps. Table 1 summarizes operating parameters during each step of the voltammetric detection experiments. Square wave voltammetry (SWV) experiments were performed on an electrochemical analyzer, model CHI660A (CH Instruments, Inc.), equipped with a three electrode system: a gold microelectrode array on microchip that was modified with a SH-FMS thin film as the working electrode, a platinum wire as the auxiliary electrode, and a KCl saturated Ag/AgCl electrode as the reference electrode. During the square wave voltammetry experiments, both sides of the electrode array were connected at points A and B (Fig. 1a) and used as the working electrode. All measurements were made in an ambient environment. Square wave voltammetry was operated with a frequency of 100 Hz, pulse amplitude of 50 mV, and potential step height of 5 mV. During preconcentration, the electrode was immersed (at 1 cm from the solution surface) in a 20 mL cell (id 2 cm) containing 15 mL of metal ion solution under an open circuit for a specified period of time. Lead (Pb^{2+}) solution was prepared daily by diluting atomic absorption (AA) standard solution (comprised of 1000 mg L^{-1} of Pb^{2+} in a 1% HNO_3 solution) from Aldrich Co. with high purity water (18 MΩ cm). The pH of the diluted metal ion solution was between 5 and 6. During preconcentration, the solution was stirred at over 300 rpm. The electrode was removed at the end of the preconcentration step, rinsed with DI water, and transferred to another 20 mL cell containing 15 mL of supporting electrolyte solution (*e.g.* 0.1 M HNO_3). During the cathodic electrolysis, a negative potential was applied to the electrode immediately after immersing it into electrolyte solution for a 60 s period (unless specified otherwise) to reduce the desorbed metal ion into elemental metal. Anodic stripping voltammetry was subsequently performed by sweeping a square wave potential toward positive values (*i.e.* from −0.8 V to 0.3 V). Quiescent conditions (no stirring) were used in both the cathodic electrolysis and stripping steps. No de-aeration of solutions was required in any step. The sweeping of a square wave potential toward positive values was performed one more time to insure that lead was completely removed from the electrode surface. Normally, when the electrolysis and stripping steps were performed in 0.1–0.2 M HNO_3, no regeneration of the electrode was required (no peak was detected after the re-sweep). Unless specified otherwise, each measurement was performed in duplicate and the average value was reported. The relative standard deviations (% RSD) were normally less than 5%.

Results and discussion

Characteristics of mesoporous silica thin film and SH-FMS thin film

The mesoporous silica film produced by the spin coating of silica sol gel appeared to be clear. From the SEM micrograph (not shown), the film surface was completely uniform with no cracking anywhere. The thickness of the film after calcination measured by the optical profilometer and the SEM micrograph was about 1.6 micron. Fig. 2 shows the TEM image of the

untreated mesoporous film. Short-range ordered mesopores with approximate pore size of 80 Å were observed.

Fig. 3a and b show the nitrogen adsorption/desorption isotherms and the pore size distribution of the untreated SiO_2 thin film. The N_2 adsorption and desorption isotherms are type IV with a clear H_2 type hysteresis loop.[19,20] The isotherm features are consistent with the film's large ratio of pore size to pore spacing[21,22] and cubic arrangement of pores.[14] The calcined film had a large primary pore diameter of 77 Å, a porosity of 60%, and a high BET surface area of 613 m^2 g^{-1}.

After the thiol immobilization, the refractive index of the mesoporous silica film increased from 1.16 to 1.36. If the refractive index of the sample was the sum of the refractive index caused by air (void fraction) and that caused by silica (solid fraction), it was estimated that the porosity of the film decreased from 66% to 23% as a result of thiol immobilization.
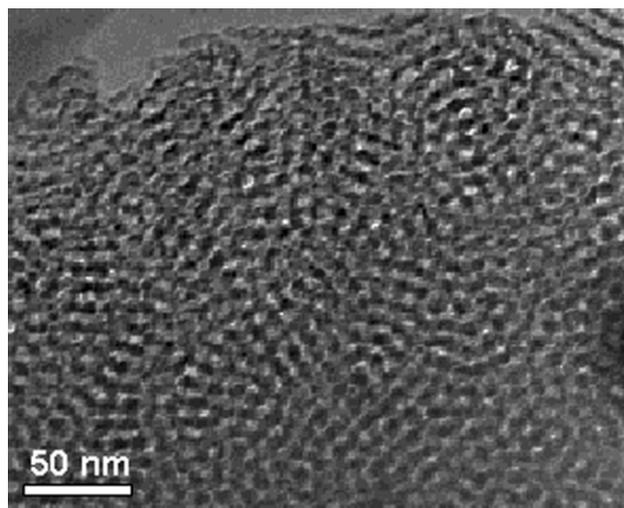

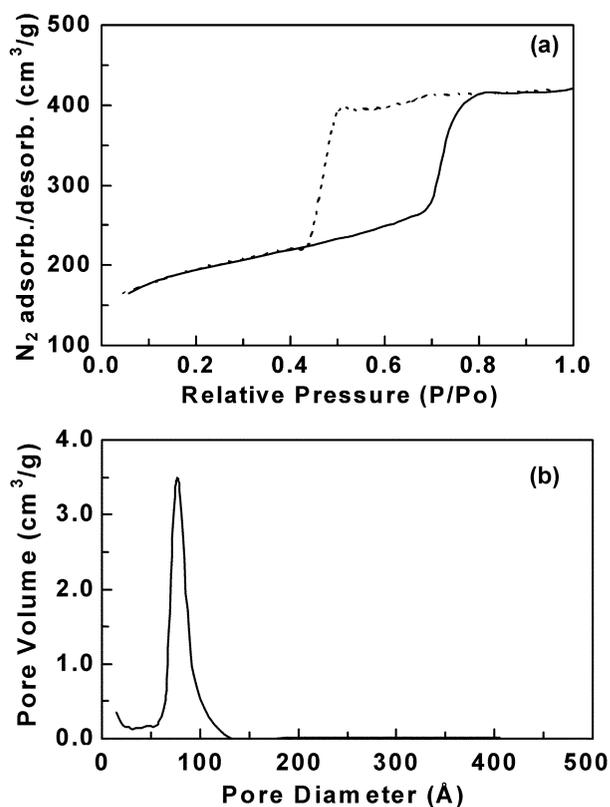**Fig. 2** TEM image of the mesoporous silica film.

Fig. 3 BET analysis: (a) — N_2 adsorption, --- N_2 desorption, (b) the pore size distribution of the untreated mesoporous silica thin film.

Table 1 Typical operating parameters during each step of the voltammetric detection experiments

Parameter	Preconcentration	Electrolysis	Stripping
Solution/electrolyte	25–5000 ppb Pb^{2+}	0.1 M HNO_3	0.1 M HNO_3
Solution volume	15 mL	15 mL	15 mL
Immersion time	2–30 min	1 min	—
Stirring speed	>300 rpm	0	0
Applied potential	Open circuit	−0.8 V	−0.8–0.3 V

Evidently, the immobilization of the functional groups on the pore surfaces reduced the film porosity. The structures of the mesoporous thin-film before and after the functionalization were measured with a Philips X'Pert MPD diffractometer using Cu K_a radiation. Both XRD patterns were alike, indicating that the structure of mesoporous film remained unchanged after the thiols attachment (figures not shown).

Fig. 4 shows the FTIR spectra of the untreated silica film and the thiol-treated film in the low and high wave number ranges. Absorbance bands at 1100–1000 cm^{-1} and 800 cm^{-1} were observed and attributed to Si–O–Si and O–Si–O vibration modes of the silica lattice.[23–25] The shoulder at around 960–940 cm^{-1} has been reported to be associated with stretching mode of Si–OH.[23–25] After the thiol-attachment, a weak-intensity band was observed at 2600–2550 cm^{-1}, and two strong-intensity bands were observed at 2960 cm^{-1} and 2870 cm^{-1}. The weak-intensity bands at 2600–2550 cm^{-1} was attributed to thiol S–H stretch[26] and the strong-intensity bands at 2960 cm^{-1} and 2870 cm^{-1} were attributed to the C–H stretch of the methylenes of the alkyl chain.[26] The FTIR spectra indicate that an organic thiol monolayer was successfully immobilized inside the nanopores of the mesoporous silica.

Voltammetric detection of lead(II)

The process of AdSV detection of Pb(II) using the SH-FMS thin-film electrode involves several steps. During the preconcentration step, Pb(II) ions are accumulated on the surface of nanopores by complexation with the thiol groups on the surface. In the detection step, accumulated Pb(II) ions desorb from the FMS surface in an acidic medium (*e.g.* 0.1 M HNO_3) and diffuse to the surface of gold electrode. These desorbed Pb(II) ions are cathodically electrolyzed at a negative potential (*i.e.* −0.80 V) for a certain period (*i.e.* 60 s), and subsequently detected by anodic stripping square wave voltammetry. The reactions occur between Pb(II) and SH-FMS (SiO_2–SH) thin-film electrode during each step in AdSV experiments can be summarized as follows:

Preconcentration of Pb(II) ions under an open circuit (eqn. (1)):

$$SiO_2 - SH + Pb(II) \rightarrow SiO_2 - S-Pb(II) + H^+ \qquad (1)$$

Desorption (eqn. (2)) and electrolysis deposition (eqn. (3)) of the Pb(II) ions onto gold microelectrode in acidic medium:

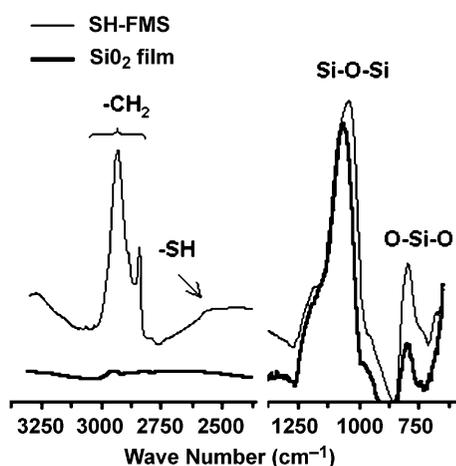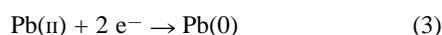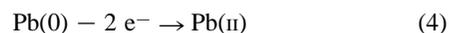$$SiO_2 - S-Pb(II) + H^+ \rightarrow SiO_2 - SH + Pb(II) \qquad (2)$$

$$Pb(II) + 2\ e^- \rightarrow Pb(0) \qquad (3)$$

Anodic stripping analysis (eqn. (4)):

$$Pb(0) - 2\ e^- \rightarrow Pb(II) \qquad (4)$$

Factors affecting the sensitivity of lead detection include: electrolysis and stripping medium composition, electrolysis time, and preconcentration time.

Electrolysis and stripping media. The effect of electrolysis and stripping media on the voltammetric response for Pb^{2+} at the SH-FMS-gold electrode was investigated using 0.05 M CH_3COONa (pH 2), 0.1 M HNO_3, and 0.2 M HNO_3. Because the SH-FMS thin film is an electrical insulator, desorption of the preconcentrated Pb^{2+} species from the SH-FMS to the electrode/solution interface must occur for the voltammetric detection to be possible. Then the desorbed Pb^{2+} may be detected directly by reduction from lead ion to elemental lead ($Pb^{2+} \rightarrow Pb(0)$). However, it is more sensitive and quantitative to perform a thorough electrolysis by applying a negative potential to deposit Pb(0) on the electrode surface, followed by anodic stripping voltammetry to oxidize the previously reduced Pb(0) to Pb^{2+}.[27]

The desorption of the preconcentrated species is normally accomplished by immersing the electrode in acidic solution. The 0.05 M CH_3COONa (pH 2) was ineffective as an electrolysis and stripping media: the sensitivity of the electrode to lead ions was negligible due to incomplete leaching of the adsorbed Pb^{2+} from the SH-FMS to the surface of the gold microelectrode. The 0.1 M HNO_3 solution was found to be best as an electrolysis and stripping medium because it could achieve complete desorption of Pb^{2+} while maintaining good stability of the voltammetric responses (less interference from hydrogen generation during electrolysis than when 0.2 M HNO_3 solution was used).

Electrolysis time. The effect of electrolysis time on the voltammetric response for Pb^{2+} at the gold microelectrode immobilized with SH-FMS thin film is shown in Fig. 5a. The experiments were performed in triplicate at conditions of: 1000 ppb Pb^{2+} preconcentration solution, 5 min preconcentration
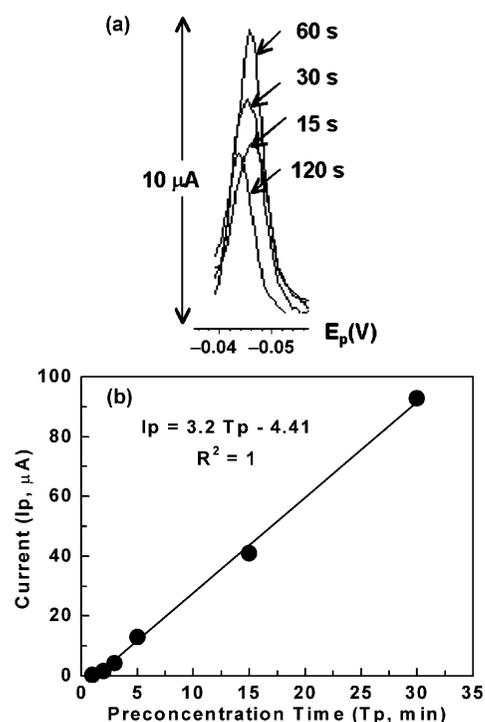
Fig. 4 FTIR spectra of the untreated mesoporous silica film and the SH-FMS thin film.

Fig. 5 The effects of (a) electrolysis time and (b) preconcentration time on the voltammetric response for 1000 ppb Pb^{2+} at the SH-FMS thin film modified gold electrode. Electrolysis/stripping media: 0.1 M HNO_3.

time, and 0.1 M HNO_3 as the electrolysis and stripping media. The voltammetric response increased as the electrolysis time was increased from 0 to 60 s, but decreased as the electrolysis time was increased to 120 s. Also, the reproducibility at a 120 s electrolysis period was poor, similar to our previous findings using a carbon paste electrode modified with powdered thiol-functionalized mesoporous silica.[28] The poor reproducibility is probably due to the generation of H_2 bubbles on the electrode surface, which affected the stability of the signals.

Preconcentration time. The effect of preconcentration time on the voltammetric response for Pb^{2+} at the gold micro-electrode immobilized with SH-FMS thin film is shown in Fig. 5b. The experiments were performed at conditions of: 1000 ppb Pb^{2+} preconcentration solution, 60 s electrolysis time, and 0.1 M HNO_3 as electrolysis and stripping media. The peak current increased linearly as preconcentration time increased from 0 to 30 min. For rapid detection of lead, a 5 min preconcentration period was found to be sufficient at this concentration range (*i.e.* 1000 ppb Pb^{2+}). For the detection of Pb^{2+} at a much lower concentration (*i.e.* 25 ppb Pb^{2+}), a 30 min preconcentration period may be required.

Calibration and detection limits. The calibration curve represents the voltammetric response (current) *versus* the metal ion concentration in the preconcentration solution. The experiments were performed under optimal conditions found in previous sections: 5 or 30 min preconcentration time, 60 s electrolysis time, and 0.1 M HNO_3 as the electrolysis and stripping media. Fig. 6 shows the calibration curves for Pb(II), measured after a 5 min preconcentration period. Inset (a) shows the representative voltammograms for Pb^{2+} concentrations (in the ascending order of peak height): 0 ppb, 500 ppb, 2000 ppb, 3500 ppb, and 5000 ppb Pb^{2+}. Inset (b) shows the calibration curves for Pb(II) in a low concentration range, measured after a 30 min preconcentration period. For a 5 min preconcentration period, the peak current was linear with respect to the metal ion concentration over the range of 250–5000 ppb. The limit of lead detection was 250 ppb after preconcentration for 5 min and improved to 25 ppb when the preconcentration time was increased to 30 min (Inset (b)).
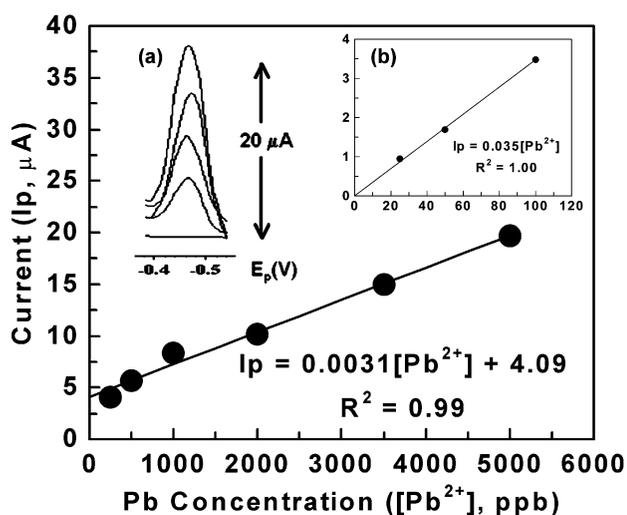
Conclusions

The microchip-based gold microelectrode modified with a SH-FMS thin-film was used successfully to detect lead in aqueous solution. The electrode has many appealing aspects: it has excellent stability (*i.e.* all voltammetic data reported in this paper were collected using the same electrode), it has low maintenance requirements (no activation and regeneration were required during this testing), and it can be easily mass-produced with highly reproducible surface properties and low costs. In addition, no de-aeration of the samples is needed, making the electrode suitable for use in the field. One potential drawback of AdSV based on conventional chemically modified thin-film electrodes is that the total number of binding sites in the thin films is limited, which may lead to narrow linear range of the calibration curves. The functionalized mesoporous thin-film can provide high binding site density due to high surface area of mesoporous structure, which leads to high sensitivity and large dynamic range for metal ion sensing. In addition, high binding site density in FMS thin-film is extremely important for miniaturized sensors. High-density binding sites will provide sufficient sensitivity at the electrodes of limited size. Manipulating the pore structure and pore orientation as well as the thickness of the SH-FMS film to improve the detection limits of metal ions and reduce the detection time will be further investigated. Incorporation of the microelectrodes modified with functionalized mesoporous silica thin films into micro-fluidic devices[29] for the detection of trace elements will be the next step in the development of this technology.

Fig. 6 The calibration curve for Pb^{2+}, measured after a 5 min preconcentration period with Inset (a) shows the representative voltammograms of Pb^{2+} concentrations (in ascending order) of 0, 500, 2000, 3500, and 5000 ppb Pb^{2+}, and Inset (b) shows the low-concentration-range calibration curve measured after a 30 min preconcentration period. All experiments were performed with a 60 s electrolysis period and 0.1 M HNO_3 as electrolysis/stripping media.

References

1 P. T. Tanev, J. R. Butrille and T. J. Pinnavaia, in *Nanoporous Materials: Chemistry of Advance Materials, An Overview*, ed. L. V. Interrante and M. J. Hampden-Smith, Wiley, New York, 1998, p. 239.
2 A. Walcarius and J. Bessière, *Anal. Chim. Acta*, 1999, **385**, 79.
3 Y. X. Jiang, W. B. Song, Y. Liu, B. Wei, X. C. Cao and H. D. Xu, *Mater. Chem. Phys.*, 2000, **62**, 109.
4 G. Villemure and T. J. Pinnavaia, *Chem. Mater.*, 1999, **11**, 789.
5 J. F. Diaz, K. J. Balkus, F. Bedioui, V. Kurshev and L. Kevan, *Chem. Mater.*, 1997, **9**, 61.
6 A. Walcarius, N. Lüthi, J. L. Blin, B. L. Su and L. Lamberts, *Electrochim. Acta*, 1999, **2**, 4601.
7 A. Walcarius, D. Despas, P. Trens, M. J. Hudson and J. Bessière, *J. Electroanal. Chem.*, 1998, **453**, 249.
8 J. J. Gooding, V. G. Praig and E. A. H. Hall, *Anal. Chem.*, 1998, **70**, 2396.
9 H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara and G. A. Ozin, *Nature*, 1996, **379**, 703.
10 H. Yang, N. Coombs, I. Sokolov and G. A. Ozin, *Nature*, 1996, **381**, 589.
11 I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger and S. M. Gruner, *Science*, 1996, **273**, 892.

12 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
13 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
14 D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka and G. D. Stucky, *Adv. Mater.*, 1998, **10**, 1380.
15 C. Song and G. Villemure, *Microporous Mesoporous Mater.*, 2001, **44–45**, 679.
16 A. Walcarius and J. Bessière, *Electroanalysus*, 1997, **9**, 707.
17 A. Walcarius, *Anal. Chim. Acta*, 1991, **384**, 1.
18 X. D. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu and K. Kemner, *Science*, 1997, **276**, 923.
19 R. Schmidt, E. W. Hansen, M. Stocker, D. Akporiaye and O. H. Ellestad, *J. Am. Chem. Soc.*, 1995, **117**, 4049.
20 P. J. Branton, P. G. Hall, K. S. W. Sing, H. Reichert, F. Schuth and K. K. Unger, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2965.
21 V. Luzzati, H. Delacroix and A. Gulik, *J. Phys. II*, 1996, **6**, 405.
22 Q. Huo, R. Leon, P. M. Petroff and G. D. Stucky, *Science*, 1995, **268**, 1324.
23 D. L. Wood and E. M. Rabinovich, *Appl. Spectros.*, 1997, **43**, 273.
24 R. M. Almeida, *J. Non-Cryst. Solids*, 1990, **121**, 194.
25 N. Primeau, C. Vautey and M. Langlet, *Thin Solid Films*, 1997, **310**, 47.
26 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 5th edn., 1991.
27 M. Etienne, J. Bessiere and A. Walcarius, *Sens. Actuators, B*, 2001, **76**, 531.
28 W. Yantasee, Y. Lin, T. S. Zemanian and G. E. Fryxell, *Analyst*, 2003, **128**, 467.
29 Y. Lin, C. A. Timchalk, H. Wu, D. W. Matson and K. D. Thrall, *Biomed. Microdevices*, 2001, **3**, 331.