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Highly sensitive detection of hexavalent chromium utilizing a sol-gel/carbon nanotube modified electrode

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Abstract

A pyridine-functionalized thin film has been fabricated to selectively preconcentrate Cr(VI) anions for electrochemical detection in the 5–300 $\mu\text{g L}^{-1}$ range. Glassy carbon electrodes were modified through physical deposition of single-walled carbon nanotubes (SWNTs) on the electrode surface, followed by electrochemical deposition of a sol-gel containing a 2-pyridine functional group. The use of SWNTs has increased sensitivity for Cr(VI) detection in aqueous solutions, providing a detection limit of 0.8 $\mu\text{g L}^{-1}$.

Graphical abstract

Keywords

chromium detection; single-walled carbon nanotubes; glassy carbon electrode; solgel; thin film; iridescence

1. Introduction

Chromium detection is of intense interest, as Cr(VI) is highly toxic even at trace (low mg L^{-1}) levels. Due to the strong oxidizing nature of Cr(VI), exposure leads to health problems that include lung cancer, stomach cancer, nasal cancer, allergic dermatitis, and mutagenesis [1–5]. Despite its known effects on human health Cr(VI) species are found in many places

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Dedicated to the 80th birthday of Prof. Hong-Yuan Chen

including common anti-corrosive materials, paints, dyes, tanned leather, coal ash, wood preservatives, welding materials, and chrome plating [6-8].

Trivalent chromium, on the other hand, is reported to be an essential trace element for mammals (ca. a few mg L⁻¹ in blood samples), and detection of Cr(III) has been actively studied [9]. Little is known about the specific roles of Cr(III) in the biological system, but it has shown to help treat glucose intolerance and certain types of diabetes [10]. Often biological samples are pretreated by using, e.g., H₂O₂ before Cr analysis and the pretreatments convert Cr(III) to Cr(VI). In such cases, subsequent Cr quantification in the biological samples becomes the analysis of Cr(VI), and electrochemical methods have often been used [11]. Recent studies have indicated that Cr(III) dietary supplements might be converted to Cr(VI) in the body by intracellular oxidation, leading to new concerns surrounding this type of Cr(III) intake [12].

Detection of trace Cr(VI) requires sensitive techniques. Currently, these include ion chromatography, atomic absorption (AA) spectrophotometry, spectrofluorimetry, spectrophotometry, chemiluminescence, inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and capillary zone electrophoresis [13-17]. Electrochemical methods are attractive because of their sensitivity, portability, and relatively low cost in comparison to other common techniques [18-35]. One of the largest steps forward in electrochemical analysis has been the combination of sol-gel thin films and electrodes [36-47].

Sol-gel films are formed through the hydrolysis and condensation of silicon alkoxides. These reactions can be catalyzed by either a base or an acid, each producing different porosities [48]. For trace analysis purposes, base catalysis tends to be favored over acid catalysis because it produces films with higher porosity and thus larger surface area [49]. This porosity and the electrochemical stability of the sol-gel films make them ideal for electroanalytical purposes. Additionally, functional groups are easily trapped in the gel by simply adding them to the sol before hydrolysis, producing films tailored for specific analyses [36, 38, 40, 41, 44-47, 50-53]. A very thin film is commonly desired because of a shorter diffusion pathlength of the analyte as well as a quicker response time.

Electrolytic sol-gel deposition is a fairly new development in the electroanalytical field and has been successfully employed to fabricate many new sensors [42-44, 46-47, 53]. By exposing an electrode to a sol consisting of alkoxysilane precursors and holding it at a sufficiently negative potential, hydroxide ions are generated at the electrode surface through the reduction of water and oxygen (Eqs. 1-3). The localized increase in pH catalyzes the hydrolysis of the sol, which immediately begins to condense onto the electrode. Because the gelation and the drying do not occur at the same time, as they do in physical depositions, the porosity is much larger [54]. Electrodeposition has proven to produce sol-gel films with more consistent film thicknesses than through past deposition techniques such as spin coating and dip coating [55]. The original pH of the sol, as well as the deposition potential and time, directly affect the thickness of the sol-gel film and can thus be used as parameters to control it.

Previously, our group has developed a sol-gel-based electrode containing pyridinium groups for Cr(VI) detection [46]. A new fabrication method has produced a more sensitive, Cr(VI) selective electrode. This new fabrication procedure reduces the limit of detection from $4.6 \mu\text{g L}^{-1}$ in the earlier work to $0.8 \mu\text{g L}^{-1}$ through the use of single-walled carbon nanotubes (SWNT), and through better control of the sol-gel film thickness. Films are deposited onto the glassy carbon electrode (GCE) using an electrodeposition technique and are believed to be between 75 and 100 nm thick due to their iridescence. Furthermore, the films are shown to remain completely intact and remain stable after many runs.

2. Experimental

2.1. Apparatus and materials

Scanning electronic microscopic (SEM) images were obtained with a LEO 1525 field emission scanning electron microscope. Electrochemical measurements were carried out on a modulated potentiostat (CHI 440a, CH Instruments). For the stripping step, a three-electrode configuration consisted of a modified glass encased GCE (3 mm in diameter, Cypress), a fritted Ag/AgCl (saturated KCl solution, CH Instruments) and a platinum wire (CH Instruments) as working, reference and counter electrodes, respectively. For the analytical step, a Ag/AgCl wire electrode was prepared by soaking a silver wire in bleach. This was used in place of the fritted Ag/AgCl reference electrode.

The following chemicals were used as received: chromium standard solution (1000 mg L^{-1} , Fluka), KCl (Certified ACS, Mallinckrodt), tetramethyl orthosilicate (TMOS) (Aldrich), NaCl (Certified ACS, Fisher Scientific), 2-[2-(trimethoxysilyl)ethyl]-pyridine (Gelest). Ultrapure water from a Millipore water purified system ($18 \text{ M}\Omega\cdot\text{cm}$, Barnstead) was used in all solutions. Other reagents were of analytical grade and used as received. All glassware was soaked in 1 M nitric acid bath and thoroughly rinsed with deionized (DI) water before use.

2.2. Carboxylation of SWNTs

SWNTs (40 mg) were added to a solution of 30% HNO_3 and then refluxed for 24 h at 140°C to obtain carboxylic group-functionalized SWNTs. The resulting suspension was centrifuged, and the sediment was washed with deionized water. Then, the oxidized SWNTs were dispersed in deionized water to a concentration of 0.5 mg mL^{-1} .

2.3. Preparation of electrode

Prior to fabrication, a GCE was polished carefully to a mirror-like surface on a standard electrode polishing kit (CH Instrument) including a 1200 grit Carbimet disk, 1.0 and 0.3 μm alumina slurry on a nylon cloth, and 0.05 μm alumina slurry on a microcloth polishing pad. After polishing, GCEs were successively sonicated with deionized (DI) water, ethanol and DI water for 5 min each. Carboxylated SWNTs were physically deposited by pipetting 4 μL (0.5 mg mL^{-1}) of the SWNT suspension directly onto the GCE surface. This was allowed to dry under nitrogen gas flow at room temperature for a minimum of 3 h. Any water trapped under the SWNTs could cause structural instability of the SWNT layer and thus the sol-gel film. The working electrode was then exposed to a sol consisting of 8 mL of 0.2 M KCl, 8 mL of EtOH, 1.3 mL of 2-[2-(trimethoxysilyl)ethyl]-pyridine, and 1.4 mL of TMOS that was acidified with HCl to pH 5.0. A potential of -1.1 V was then applied for 1800 s, followed by a rinsing of the working electrode with a 1:1 mixture of EtOH and DI water. Finally, the GCE was dried in the oven for 24 h at 70°C .

2.4. Analysis procedure

Prior to analysis, the modified GCE was soaked in a 0.1 M HCl solution to ensure that all of the pyridinium groups are protonated. The electrode was then exposed to solutions containing varying Cr(VI) concentrations in an electrolytic buffer of 0.1 M KCl and 0.1 M HCl. Accumulation took place at 0.6 V for 5 min while the solution was stirred. This positive potential helps to move anions, like our analyte, toward the working electrode and cationic interferers toward the counter electrode. The electrode was then moved to a Cr(VI) free buffer (3.5% NaCl) solution and determination of the accumulated analyte took place by reduction to Cr(III) through cathodic stripping. This was done by sweeping from 0.6 V to -0.3 V using SWV with a frequency of 15 Hz, step potential of 4 mV and an amplitude of 25 mV (Fig. 1). No stirring took place throughout the stripping step. The electrode was cleaned before every accumulation step by holding the potential at -0.2 V for 120 s in a buffer solution consisting of 0.1 M KCl and 0.1 M HCl while stirring.

3. Results and discussion

3.1. Surface analysis

The surface was analyzed using a LEO 1525 field emission scanning electron microscope (Fig. 2). An image taken at the border of the SWNT deposit area shows a contrast between the uniformity of the sol-gel coating on the bare GC surface versus the zone with SWNTs. This is strong evidence that the SWNT layer greatly increases the surface area of the electrodeposited sol-gel film.

The sol-gel film thickness and stability are controlled by the pH of the sol, the ratio of TMOS to 2-[2-(trimethoxysilyl)ethyl]-pyridine, the electrolytic content of the sol, the magnitude of the negative potential, and the deposition time. A sufficiently acidified sol helps to ensure that the deposited sol-gel film is thin. The low pH of the entire solution suppresses and localizes the high pH zone at the electrode surface where the OH^- ions are generated. Because the hydrolysis and condensation of the alkoysilanes are base catalyzed, less sol-gel is formed with lower amounts of hydroxide ions. This is directly related to the

deposition potential and deposition time. Therefore, many parameters were experimentally determined during optimization. Nanometer-thick films have many advantages. As stated previously, shorter path lengths as well as quicker reduction response times are obtained through thinner films. The stability of the film also depends upon its thickness. If the film is too thick (μm range) it tends to crack and flake off while drying, or comes off in solution most likely due to physical forces caused by the stirring. Using electrochemical quartz crystal microbalance (EQCM) experiments, our group determined that a ratio of TMOS to 2-[2-(trimethoxysilyl)ethyl]-pyridine greater than 1 resulted in unstable films due to poor gelation at the electrode surface [46].

One characteristic of a very thin film on a GCE is iridescent coloration. This is directly related to the thickness of the film and differences in refractive indices between the air, film and GC surface. As the light travels to the electrode, certain wavelengths are reflected off of the film while other wavelengths are refracted at the air/film boundary and reflect off of the GC surface causing a change in the color. The phase offset of the reflected light causes optical interferences which produce iridescence. This only occurs in very thin films; thus its appearance within this research is promising [44, 56, 57]. Although research has shown that the anodic treatment of a glassy carbon electrode in different silane-free electrolyte systems can lead to surface color changes, a KCl electrolytic system alone does not produce a color [58].

Because the iridescent hue depends on thickness [44, 56, 57], it is used to characterize the film. Not only is it a method for film thickness comparison, but also it reveals the uniformity of the film and thus aids in the formation of the experimental method. While this is unequal to imaging techniques such as SEM, it is a useful and cost-effective way to analyze the qualities of the film, as well as optimize the fabrication method.

Noting the changes in the color homogeneity of a film with respect to changes in the electrodeposition method led to the current parameters. A uniform, brown-hued iridescence is the most preferred in the films in this research. Brown films have shown to be the thinnest (between 75 and 100 nm), followed by light blue, as determined by Deepa and Collinson through the use of a surface profilometer [44, 54]. The thickest films that still show iridescence give yellow and red colorations [44, 54]. Fig. 3 displays the differences in film appearances throughout the optimization of the deposition process while Fig. 4 shows a final product after optimization.

3.2. Optimization of sol-gel thin film deposition

Because of the importance of the electrode surface uniformity and reproducibility, optimized parameters were based on the consistency of the modified glassy carbon electrode. As previously stated, the sol-gel film formation employs a base-catalyzed hydrolysis and condensation. Thus, making the solution slightly acidic allows for a more controlled film deposition as the hydroxide formed at the electrode surface maintains a short local residence time before being neutralized or catalyzing the sol-gel reactions. It was determined that performing the electrodeposition at pH 5 allows for a higher degree of control over the film, and much better uniformity, as the sol-gel hydrolysis and condensation can only take place very near to the electrode itself. After optimizing the solution pH, the ideal deposition

potential and time were determined based on the surface iridescence. Because the electrochemical reaction at the surface leads to the formation of one mole of H_2 gas to every two moles of OH^- (Eq. 1), it was discovered that too negative of a potential created enough bubbles on the electrode surface that it interfered with the film uniformity. A potential of -1.1 V was sufficient enough to catalyze the reactions without disrupting the surface. The final variable, deposition time, plays the largest role in the film thickness. Based on the iridescent color of the film, experimentation determined that a 30 min deposition lead to the ~ 75 nm brown film that was desired (Fig. 4). Ten more minutes produced a film with a blue iridescence.

3.3. Cr(VI) detection

The general process of Cr(VI) detection is outlined in Fig. 1. The modified GCE is successfully preconcentrated with Cr(VI) by interactions between the positively charged 2-[2-(trimethoxysilyl)ethyl]-pyridinium groups and the chromate anions. The reduction of Cr(VI) to Cr(III) consistently produces a potential peak at 0.26 V, and a calibration model with a correlation greater than 99% (Figs. 5 and 6). The $5 \mu\text{g L}^{-1}$ standard was repeated three times, producing a standard deviation of $8.3 \times 10^{-3} \mu\text{A}$. According to a signal to noise ratio of 3, the limit of detection (LOD) was determined to be $0.8 \mu\text{g L}^{-1}$. This LOD is 5.75 times lower than that of our sol-gel-based electrode containing pyridinium groups but *no* SWNTs, indicating that the SWNTs do increase the sensitivity as hypothesized [46]. Rudnitskaya and coworkers have recently reported potentiometric analysis of Cr(VI) using glassy carbon or Pt electrodes coated with films of carbon nanotube-doped, lignin-poly(propylene oxide) copolymers with the LOD of 5.3 mg L^{-1} [59]. Deep and coworkers have functionalized carbon nanotubes with phosphinic acid which, when spin-coated on boron-doped p-type (111) Si wafers as electrodes, demonstrate LOD of $0.01 \mu\text{g L}^{-1}$ [60]. A gold film modified carbon composite electrode, fabricated for the determination of Cr(VI) by Kachoosangi and coworkers, exhibits an LOD of $4.4 \mu\text{g L}^{-1}$ [61].

3.4. Real world sample

Swine blood was dry-ashed using the optimized method reported by Bragg and Xue [62]. A 16.3 g sample of the blood ash was dissolved in one mL of concentrated trace analytical grade HNO_3 , and was diluted to 50 mL with water and a buffer to form a final solution containing 0.1 M HCl, 0.1 M KCl, and 1.4% HNO_3 . The solution was then separated into two identical 20 mL aliquots. One aliquot was analyzed with the modified GCE, producing the potential peak seen in Fig. 7. The average peak current ($7.2 \times 10^{-7} \text{ A}$) after three potential sweeps correlates to a Cr concentration of $165.1 \pm 0.1 \mu\text{g L}^{-1}$ through the calibration curve in Fig. 6. The error is calculated using the standard deviation of the sample runs as the random error and the systematic error bars of the calibration curve. This value corresponds well with the ICP-OES analysis of the second aliquot which, after triplicate runs and in comparison to a Cr(VI) calibration model, determined that the same blood ash solution contains $199.5 \pm 44.0 \mu\text{g L}^{-1} \text{ Cr}$.

3.5. Interference studies

Interference studies were performed in solutions of $200 \mu\text{g L}^{-1} \text{ Cr(VI)}$ spiked with metallic species and ions that are judged most likely to interfere (3.0×10^{-6} , 1.0×10^{-4} , and $2.0 \times$

10^{-2} M [interfering ion]). The Cr(VI) reduction peak currents in the interference solutions are then compared to the Cr(VI) peak current in a non-spiked Cr(VI) solution. The ions chosen for the study (Na^+ , CH_3COO^- , Cr^{3+} , SO_4^{2-} , Cu^{2+} , Fe^{3+} , and VO_4^{3-}) can be found in both blood and ground water. The only interferences observed were Cu^{2+} and Fe^{3+} at concentrations of 2.0×10^{-2} M. Interestingly, the high concentrations of these metallic species increased the Cr(VI) peak current rather than decrease. Both copper(II) chromate CuCrO_4 and iron(III) chromate $\text{Fe}_2(\text{CrO}_4)_3$ are essentially insoluble in water [63]. At high concentrations, Cu^{2+} and Fe^{3+} ions are expected to form CuCrO_4 and $\text{Fe}_2(\text{CrO}_4)_3$ precipitation inside the sol-gel film on the electrode surface. The chromate ion in the precipitates may be reduced as well during the potential sweeping, contributing to the Cr(VI) peak currents, as illustrated in Fig. 8. No stable product between Cr(III) and Cr(VI) chromate has been reported, which may explain why Cr(III) cations do not show interference.

4. Conclusions

A glassy carbon electrode modified with SWNTs and an electrodeposited pyridiniumfunctionalized sol-gel thin film were used to successfully preconcentrate Cr(VI). The reduction of Cr(VI) to Cr(III), using square wave voltammetry, produces a current peak at 0.26 V and does not require a complexing ligand. The highly precise detection has been successfully performed in the low $\mu\text{g L}^{-1}$ range of Cr(VI) with a calculated LOD of $0.8 \mu\text{g L}^{-1}$. The analytical procedure here is unaffected by coexisting ions in expected biological and environmental concentrations. In comparison to earlier work from our group [47], the addition of a SWNT base layer, as well as thinner sol-gel films, has allowed for a three orders of magnitude increase in sensitivity.

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Highlights

- Cr(VI) detection: 5-300 $\mu\text{g L}^{-1}$ range; 0.8 $\mu\text{g L}^{-1}$ detection limit
- Sol-gel thin film electrodeposited over a carboxylated SWNT layer on GCE surface
- Sol-gel doped with 2-pyridinium to preconcentrate HCrO_4^-
- Lowering detection limit by three orders of magnitude through the use of SWNTs

Fig. 1.

Schematic of the accumulation of chromate followed by its reduction, resulting in its stripping from the electrode and subsequent detection.

Fig. 2. SEM images of the sol-gel coated GCE surface. Image B shows the strong difference in surface area that the sol-gel possesses between deposition on the bare GCE (bottom section) versus deposition on the SWNT-coated surface (top section).

Fig. 3.

Sol-gel film appearances throughout the optimization of the deposition process. Note the extreme variation in color and thus uniformity in A as opposed to B. Also worth noting is the transition from generally thicker blue and yellow films (A and B) to a very thin brown film (C) [54]. The areas of B and C that bare cortex patterns were located directly over the center of the stir bar during film deposition, causing less sol movement and thicker films in that area. Photographs were taken using a LEICA S8AP0 digital microscope.

Fig. 4.

Image of a bare GCE surface (A) compared to sol-gel film on the same electrode after the deposition procedure was fully optimized (B). Photographs were taken using a LEICA S8AP0 digital microscope.

Fig. 5. Square-wave voltammograms of various Cr(VI) concentrations collected at a pyridine-functionalized sol-gel electrode: 5, 50, 100, 150, 180, 200, and $250 \mu\text{g L}^{-1}$.

Fig. 6. The detection of Cr(VI) is modeled by an exponential function, possibly due to a Langmuir isotherm.

Fig. 7. Cr(VI) peak detected in an ashed swine blood solution. The peak shift from 0.26 V to 0.38 V was experimentally determined to be caused by a lower pH in the sample.

Fig. 8.

Graphical representation of interference studies. Note that the only interferences are Cu²⁺ and Fe³⁺ at levels higher than would be expected in environmental and biological samples.