Cupric Hexacyanoferrate Nanoparticle Modified Carbon Ceramic Composite Electrodes

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Graphite powder-supported cupric hexacyanoferrate (CuHCF) nanoparticles were dispersed into methyltrimethoxysilane-based gels to produce a conducting carbon ceramic composite, which was used as electrode material to fabricate surface-renewable CuHCF-modified electrodes. Electrochemical behavior of the CuHCF-modified carbon ceramic composite electrodes was characterized using cyclic and square-wave voltammetry. Cyclic voltammograms at various scan rates indicated that peak currents were surface-confined at low scan rates. In the presence of glutathione, a clear electrocatalytic response was observed at the CuHCF-modified composite electrodes. In addition, the electrodes exhibited a distinct advantage of reproducible surface-renewal by simple mechanical polishing on emery paper, as well as ease of preparation, and good chemical and mechanical stability in a flowing stream.

Keywords Sol-gel, carbon ceramic electrode, cupric hexacyanoferrate, nanoparticle, electrocatalytic oxidation, glutathione

Introduction

Preparation and characterization of metal hexacyanoferrate (MHCF) modified electrodes have attracted much attention in the past 20 years.[1-3] The promising and wide applications in electrocatalysis, ion-selective electrode, electrochromism, solid state battery, corrosion inhibition, and electroanalysis have undoubtedly given an intensive impetus to study further the system and fabrication procedures. Another motivation of the electrochemists is to make a better understanding of the processes occurring at these modified electrodes. Electrodeposition, adsorption, entrapping MHCF into polymer matrices, and mechanically immobilizing them onto electrode surfaces are often used to fabricate MHCF-modified electrodes. A serious drawback in the applications of these thin film electrodes is their poor long-term stability resulting from scratch, leakage, contamination, and passivation. Moreover, surfaces of these thin film electrodes can not be renewed under these conditions. Hence, it is necessary to explore and develop simple and reliable methods to fabricate surface-renewable MHCF-modified electrodes. In 1995, a surface-renewable Prussian Blue modified carbon paste electrode was developed by Scholz's group,[4] but this soft electrode lacked mechanical stability in flowing streams. After that, they also constructed a rigid reactive electrode containing a mechanical mixture of silver hexacyanoferrate (AgHCF), graphite powder, and solid paraffin for the determination of iron(III) ions in solution.[5] However, the AgHCF-modified composite electrode presented quasi-reversible voltammetric behavior with large peak-peak potential separation likely due to the inhomogeneous mechanical mixture of the components or the difference in AgHCF particle dimensions.

Sol-gel is a low-temperature process that involves the hydrolysis and polycondensation of suitable precursors to form three-dimensional inorganic network.[6-9] Sol-gel-based materials possess notable advantages for the encapsulation of various dopants and the development of practical sensors and catalytic supports, which feature ease of preparation, high porosity, photochemical and electrochemical stability, and enhanced mechanical and chemical durability. Recent advances in the various fields and

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applications of sol-gel in electrochemistry were described in several excellent review articles.[10-15] Since the pioneering work of Lev's group on carbon ceramic composite electrodes (CCE),[16] many efforts have been devoted to fabricating various chemically modified CCE and using them as sensors for metal ions, glucose, and other important chemical and biological substances.[16-21] An interesting feature of chemically modified CCE is that the active section of the electrodes is not clogged upon repeated polishing due to the brittleness of the sol-gel-derived silicate backbone, and thus the electrodes can be renewed by a mechanical polish if scratch, leakage, contamination, and passivation arise.

In the present article, we describe a novel strategy for the fabrication of surface-renewable MHCF-modified electrodes. As a representative, graphite powder-supported cupric hexacyanoferrate (CuHCF) nanoparticles were dispersed into methyltrimethoxysilane-derived gels to yield a conducting carbon ceramic composite. The composite was used as electrode material to construct CuHCF-modified electrodes. In this configuration, CuHCF acts as a catalyst, graphite powder ensures conductivity by the percolation mechanism, the silicate provides a rigid porous backbone, and the methyl groups endow hydrophobicity and thus limit the electrode wetting section. The CuHCF-modified CCE showed a high catalytic activity toward glutathione oxidation, a distinct advantage of surface-renewal by simple mechanical polishing on emery paper, and a good chemical and mechanical stability in a flowing stream.

Experimental

Materials

Methyltrimethoxysilane (MTMOS, >97%) was purchased from ACROS and used without purification. High purity graphite powder (average particle diameter, 1—2 μm) and glutathione were obtained from Aldrich. Cupric sulfate and potassium hexacyanoferrite were purchased from Beijing Reagent, Inc. The 600-grit emery paper was supplied by Shanghai Sand Wheel Plant. Other chemicals were of analytical grade and used as received. Deionized water used in all experiments was purified to a resistivity of 18 MΩ·cm with a Millipore Milli-Q water purification system.

Apparatus

Elemental analyses were performed on a TJA POEMS ICP atomic emission spectrometer. TEM was observed with a JEM-2010 transmission electron microscope. A computer controlled CHI 660 electrochemical workstation was used for voltammetric and amperometric measurements. A three-electrode cell, consisting of a glassy carbon electrode or a CuHCF-modified CCE as the working electrode, an Ag/AgCl (saturated KCl) reference electrode, and a platinum gauze counter electrode, was used. Prior to the experiment, the glassy carbon electrode was immersed in 0.10 mol/L nitric acid for 5 min and polished sequentially with 1, 0.3, and 0.05 μm alumina and cleaned ultrasonically for 1 min at the end. Amperometric detection in a flowing stream was performed using a home-made flow-through thin-layer electrochemical cell with a platinum disk counter electrode and a CuHCF-modified CCE working electrode. The potential was held at +0.71 V vs. an Ag/AgCl (saturated KCl) reference electrode. The background current was allowed to decay to a constant value before starting the sample injection. No action was taken to remove oxygen from solutions. All electrochemical experiments were conducted at (25±0.5) ℃.

Preparation of CuHCF *nanoparticles and graphite powder-supported* CuHCF

20 mL of (0.010 mol/L $CuSO_4$ + 0.010 mol/L HCl) aqueous solution was slowly dropped into 20 mL of (0.010 mol/L $K_3Fe(CN)_6$ + 0.010 mol/L HCl) aqueous solution to yield stable CuHCF collidal solution. The solution was properly diluted for TEM characterization.

2.5 g of graphite powder was dipped in the resulting CuHCF collidal solution (20 mL) at room temperature for about 24 h. A black solid was obtained after filteration through a sintered glass funnel. The solid was washed with cold water and dried at 50 ℃ *in vacuo*. The contents of K, Cu, and Fe were determined to be 0.31%, 0.56% and 0.48%, respectively, which confirmed the formula of CuHCF supported on graphite powder to be $K_{0.92}Cu_{1.03}[Fe(CN)_6]_{1.00}$. Thus, the weight ratio of CuHCF to graphite was calculated to be 1:36.

Fabrication of CuHCF-*modified* CCE

The CuHCF-modified CCE was constructed by the

following procedure. The solution of methanol (1.50 mL), MTMOS (0.75 mL), and hydrochloric acid (0.03 mL, 11 mol/L) was ultrasonically mixed for 2 min, then 1.50 g of graphite powder-supported CuHCF nanoparticles were added and shaken on a vortex agitator for an additional 3 min. The mixture was added to glass tubes with 3 mm inner diameter and 8 cm length, and the length of composite material in the tubes was controlled to be about 8 mm. In addition, a little extra mixture was needed to be retained on the top of the electrodes, and the mixture in the tubes was slightly pressed on smooth plastic paper with a copper stick through the back. After being dried at room temperature for about 48 h, the electrodes were polished with 600-grit emery paper to remove extra composite material and then wiped gently with weighing paper. Electric contact was made by silver paint through the back of the electrode.

Results and discussion

Fabrication of the CuHCF-*modified* CCE

In the present work, CuHCF nanoparticles were deposited onto graphite powder surface to yield graphite powder-supported CuHCF. Fig. 1 shows a typical TEM photograph of the resulting CuHCF nanoparticles.

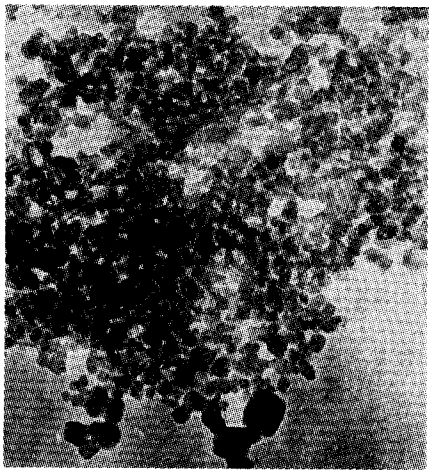

Fig. 1 The TEM photograph of CuHCF nanoparticles. Scale bar: 100 nm.

Additional water for the MTMOS hydrolysis step is provided by air humidity.[16] Base (NaOH or NH_4OH) or neutral (NH_4F) catalyst failed to produce rigid monoliths and yielded only silica-covered graphite powder. In addition, large doses of hydrogen chloride and MTMOS resulted in the rapid gelation before adding CuHCF supported on graphite powder and the bad conductivity of the composite,[22] respectively. The Si—C bonds remained unchanged during the hydrolysis and polymerization, and the methyl group remained exposed at the surface of porous silicate network. In the process of fabrication of the CuHCF-modified graphite organosilicate electrodes, a little extra mixture was needed to be retained on the top of the electrodes in order to conveniently obtain the whole and uniform surface when they were first polished on emery paper. Moreover, if the selected graphite particles were much bigger than those used in the present work or the gelation temperature was higher than 60℃, the composite material became fragile and thus it was difficult to obtain smooth electrode surfaces.

Voltammetric behavior of the composite electrode

After 5 min potential cycling scanning, the CuHCF-modified CCE presented a stable electrochemical behavior. Diagram A of Fig. 2 shows typical cyclic voltammograms for the CuHCF-modified electrode in 0.1 mol/L KCl aqueous solution at various scan rates. When the potential was scanned between 0.2 and 0.9 V, chemically reversible redox waves with the formal potential, $(E_{ox} + E_{red})/2$, at + 0.70 V, characteristic of CuHCF,[23-28] were observed. Because the cupric portion of CuHCF has no electroactivity in the investigated potential range, the electrode reaction should be attributed to the oxidation and reduction of hexacyanoferrate portion of CuHCF. The anodic and cathodic peak potentials shifted symmetrically, resulting in the constant of formal potential at various scan rates. As shown in Diagram B of Fig. 2, the anodic peak current I_{ap} is linearly proportional to scan rate v at scan rate lower than 40 mV/s, suggesting that peak current is surface-confined. At scan rate less than 40 mV/s, anodic and cathodic peak potential separation (ΔE_p) is less than 30 mV instead of the value zero expected for a reversible surface redox process.[29] The nonzero peak splitting might arise from two basic causes. First, the solvation of the redox centers or the structure of the electrode wetting section might change with oxidation state of the redox center. Second, CCE had larger resistance compared with the conventional gold, platinum and glassy carbon electrodes. The surface coverage was measured by integrating the area

under the anodic peak at 5 mV/s to be 1.93×10^{-9} mol/cm^2.

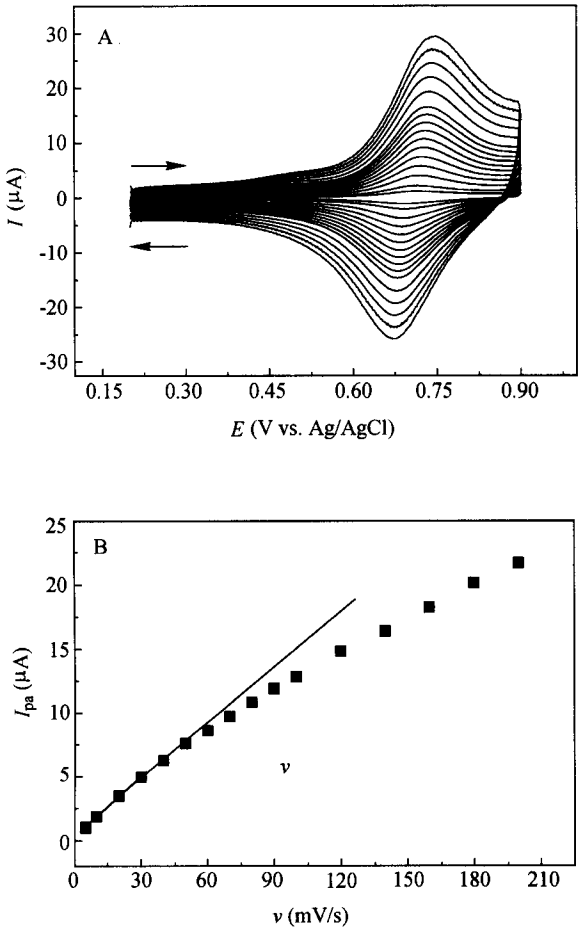

Fig. 2 (A) Cyclic voltammograms for the CuHCF-modified CCE in 0.10 mol/L KCl aqueous solution at various scan rates. From inner curve to outer curve: 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180, and 200 mV/s. (B) The dependence of anodic peak current on scan rate.

Additional observations are concerned with the strong dependence of voltammetric response on the choice of supporting electrolytes. Examples of four cyclic voltammograms for the CuHCF-modified electrode recorded in KCl, K_2SO_4, NH_4Cl, or NaCl electrolyte are shown in Fig. 3. In general, the redox waves are much better developed in the presence of K^+ (hydrated radius, 0.125 nm) than those in the presence of any other cations such as Na^+ or NH_4^+, whose hydrated radius is 0.183 or 0.125 nm, respectively. It is not surprising that the voltammetric responses are blocked in the electrolyte containing Na^+ with larger hydrated radius. However, the formal potential for the CuHCF-modified electrode in 0.10 mol/L NH_4Cl aqueous solution is relatively positive compared with that in 0.10 mol/L KCl solution although K^+ and NH_4^+ have the same hydrated radius, which indicates that the ion flux can not be explained by simple zeolitic selectivity as it was postulated for Prussian Blue and its analogues.[30] In addition, the slight difference in peak currents and formal potentials for the CuHCF-modified electrode in 0.1 mol/L KCl and 0.05 mol/L K_2SO_4 should be caused by the actual difference of actual K^+ activities in the two electrolytes. In general, electrochemical behaviors of the CuHCF-modified CCE are similar to those for CuHCF film modified glassy carbon electrode reported by Engel and Grabner.[28]

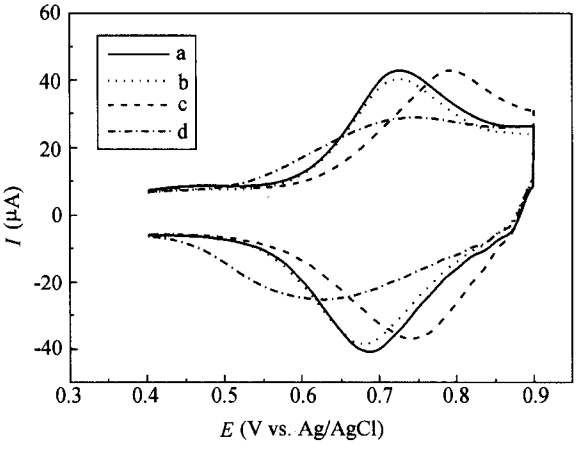

Fig. 3 Comparative cyclic voltammograms for the CuHCF-modified electrode in (a) 0.10 mol/L KCl solution, (b) 0.050 mol/L K_2SO_4 solution, (c) 0.10 mol/L NH_4Cl solution, and (d) 0.10 mol/L NaCl solution. Scan rate: 20 mV/s.

In order to study the dependence of electrochemical behavior on the K^+ activity a_K, Osteryoung square-wave voltammetry with an excellent sensitivity[31] was adopted to accurately measure formal potential E_f'. Diagram A of Fig. 4 shows square-wave voltammetric response of the CuHCF-modified electrode recorded in KCl electrolytes with K^+ concentration varied from 1.0×10^{-2} to 2.0 mol/L. The gradual decrease of peak currents can be explained by Fick's first law.[32] The voltammetric peak potentials were displaced in a negative potential direction with decreasing K^+ concentration. The result is in agreement with the involvement of potassium ions in the redox reaction. When the potentials were plotted versus the logarithm values of K^+ activities, a straight line shown in

Diagram B of Fig. 4 was obtained and the slope of 61.6 mV/pa_K is very close to the theoretical Nernst value (59 mV/pa_K) at the experimental temperature (298 K).[33]

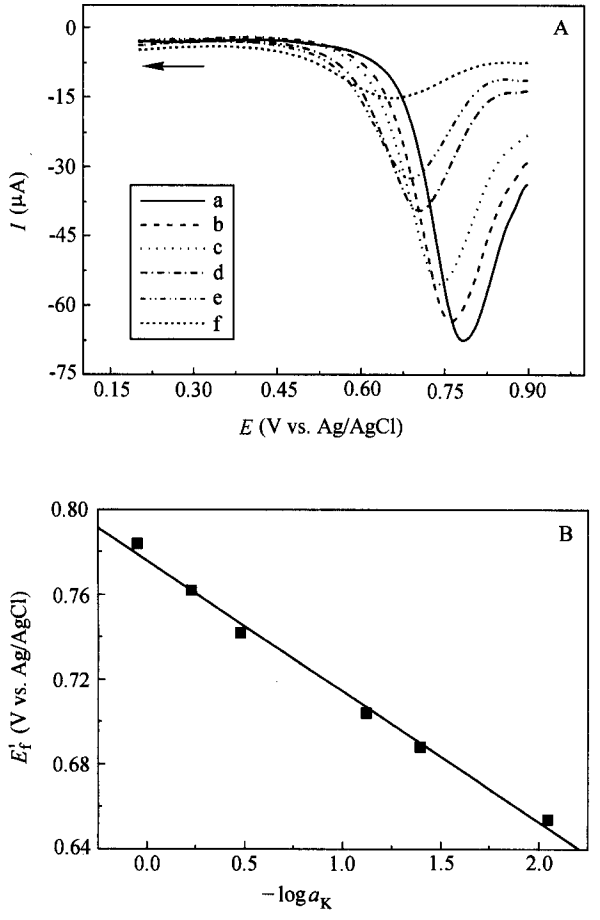

Fig. 4 (A) Square-wave voltammograms for the CuHCF-modified electrode in KCl solutions with different concentrations: (a) 2.00 mol/L; (b) 1.0 mol/L; (c) 0.50 mol/L; (d) 0.10 mol/L; (e) 0.050 mol/L; (f) 0.010 mol/L. Increment: 2 mV; frequency: 10 Hz; scan rate: 20 mV/s. (B) The relationship between formal potential E_f' and K^+ ion activity a_K.

Electrocatalytic oxidation of glutathione at the modified electrode

For better redox peak shapes and more convenient measurements, K^+-containing supporting electrolytes were selected. The oxidation of glutathione at a glassy carbon electrode or a CuHCF-modified CCE was carried out in 0.10 mol/L KCl solution. Typical cyclic voltammograms for glutathione oxidation are shown in Fig. 5.

There was no current response for glutathione oxidation at a glassy carbon electrode in the potential range from +0.30 to +0.80 V (curve b in Diagram A of Fig. 5. However, the glutathione oxidation wave negatively shifted to +0.71 V and the current obviously increased when the same amount of glutathione was oxidized at the CuHCF-modified electrode (curve b in Diagram B of Fig. 5). With the addition of glutathione, anodic peak current of the CuHCF-modified electrode increased while the cathodic peak current decreased, suggesting that glutathione be electrocatalytically oxidized by $KCu[Fe^{III}\text{-}(CN)_6]$.

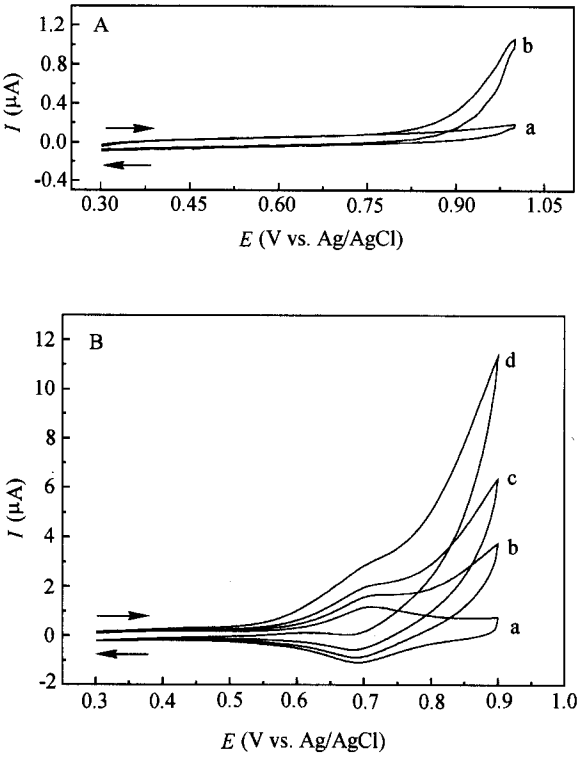

Fig. 5 (A) Cyclic voltammograms for a glassy carbon electrode in (a) 0.10 mol/L KCl solution and (b) 0.10 mol/L KCl + 0.20 mmol/L glutathione solution. (B) Cyclic voltammograms for the CuHCF-modified electrode in 0.10 mol/L KCl solutions containing (a) 0, (b) 0.20, (c) 0.50 and (d) 1.0 mmol/L glutathione. Scan rate: 5 mV/s.

On the basis of the voltammetric results described above, it appears that amperometric detection of glutathione using the CuHCF-modified electrode is possible. A typical *I-t* curve (Fig. 6) was obtained by successively adding glutathione to continuously stirred 0.1 mol/L KCl solution. The electrode response time was less than 5 s. The fast response is attributed to the thin wetting section

controlled by methyl groups and short penetration depth of glutathione. The inset of Fig. 6 shows the calibration graph for glutathione at the modified electrode. The electrode response is linear for glutathione within the concentration range from 5×10^{-6} to 8×10^{-3}mol/L, and the sensitivity is 7.78·μA/(mmol/L) (correlation coefficient of 0.9995). The detection limit was 1.2×10^{-6} mol/L when signal-to-noise was 3.

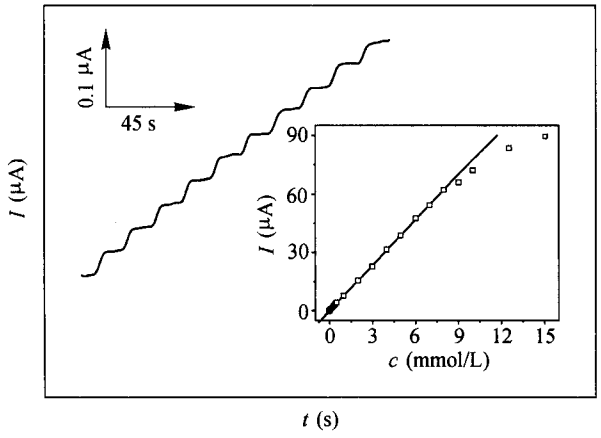

Fig. 6 Amperometric response of the CuHCF-modified electrode on successive increase of 5.0 μmol/L glutathione in 0.10 mol/L KCl solution. The inset is the steady-state calibration curve for current versus glutathione concentration. Applied potential: +0.71 V vs. Ag/AgCl; stirring speed: 600 rpm.

Long-term stability and repeatability of surface-renewal

Practical utility of chemically modified electrodes is often limited by a lack of long-term stability, which is attributable to dissolution or leaching of the electrocatalyst, especially in flowing streams. The stability of CuHCF-modified CCE was tested by cyclic voltammetry and amperometric detection in a flowing system. No current decrease for a CuHCF-modified electrode was observed after 10 h successive potential cycling in 0.10 mol/L KCl aqueous solution. Especially, the electrodes exhibited an excellent mechanical and chemical stability in a flowing stream. Fig. 7 shows the stable response of a CuHCF-modified CCE in flow injections of 0.10 mmol/L glutathione over about a 4 h period. It can be thought that the high stability of the modified electrode is related to the chemical and mechanical stability of the silicate matrix, the limited wetting section controlled by methyl groups, the strong adsorption of CuHCF nanoparticles on graphite powder, and the possible interactions between CuHCF and silanol groups. Another main attraction of the CuHCF-modified CCE is that the electrode surface can be renewed by simple mechanical polishing on emery paper and a fresh surface exposed whenever needed. This is especially useful for the electrocatalytic study since the catalytic activity is known to decrease when the electrode is fouled. Indeed, ten successive polishings resulted in a relative standard deviation (*RSD*) of 1.8% for a CuHCF-modified CCE.

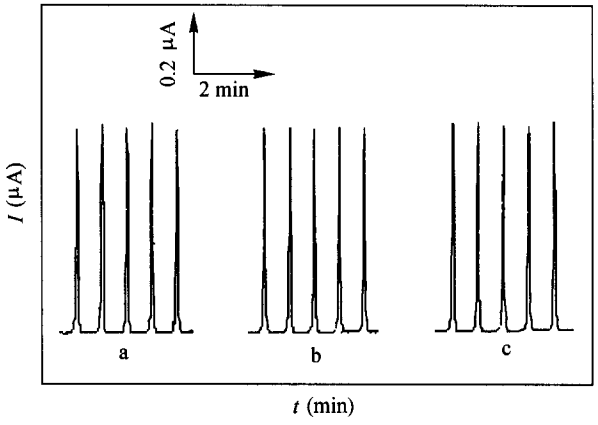

Fig. 7 Multiple flow injection response of 0.10 mmol/L glutathione using a CuHCF-modified electrode in a thin-layer electrochemical cell. (a) Initial flow injection response, (b) after 2 h, and (c) 4 h continuous operations. Electrolyte and carrier: 0.10 mol/L KCl; flow rate: 1.0 mL/min.

Conclusion

Surface-renewable CCE bulk-modified with CuHCF nanoparticles has been fabricated using sol-gel technique. The chemically modified electrode can electrocatalyze the oxidation of glutathione, and exhibit a distinct advantage of polishing, as well as ease of preparation, good chemical and mechanical stability. Like conventional chemically modified electrodes for electrocatalytic oxidation, the CuHCF-modified CCE will also lack specific selectivity for the determination of glutathione, yet the excellent stability of the composite electrodes indicates that it is possible to use them as a detector in HPLC analyses. Although the new method has been presented in the context of CuHCF-modified electrode, it can be readily extended toward the fabrication of other MHCF-modified CCE, which can be applied in electroanalysis, electrosynthesis, and other

fields.

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