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Renewable manganous hexacyanoferrate-modified graphite organosilicate composite electrode and its electrocatalytic oxidation of L-cysteine

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Abstract Manganous hexacyanoferrate (MnHCF) supported on graphite powder was dispersed into methyltrimethoxysilane-derived gels to yield a conductive composite, which was used as electrode material to construct a renewable three-dimensional MnHCF-modified electrode. MnHCF acts as a catalyst, graphite powder ensures conductivity by percolation, the silicate provides a rigid porous backbone, and the methyl groups endow hydrophobicity and thus limit the wetting section of the modified electrode. Cyclic voltammetry was exploited to investigate the dependence of electrochemical behavior on supporting electrolytes containing various cations. The chemically modified electrode can electrocatalytically oxidize L-cysteine, and exhibits a distinct advantage of polishing in the event of surface fouling, as well as simple preparation, good chemical and mechanical stability, and good repeatability of surface renewal.

Keywords Manganous hexacyanoferrate · Graphite organosilicate electrode · Electrocatalytic oxidation · L-Cysteine · Sol-gel synthesis

Introduction

Recently, there has been much interest in the preparation and characterization of Prussian Blue and related metal hexacyanoferrates (MHCFs) owing to their attractive physicochemical properties, which include electrochromism [1, 2, 3, 4, 5], ion-exchange and analytical sensing characteristics [6, 7, 8, 9, 10, 11, 12],

electrocatalysis [13, 14, 15, 16, 17], ionic and electronic (mixed-valence electron hopping) conductivities [18, 19, 20], charge storage [21, 22], and molecular magnetism [23, 24, 25, 26]. From a structural viewpoint, a MHCF of general stoichiometric formula $A_xM_y[Fe(CN)_6] \cdot qH_2O$ (where M is a metal, A stands for a counter-cation, and x, y, q are stoichiometric coefficients) forms a rigid three-dimensional framework of repeating -NC-Fe-CN-M-NC- units [27]. Attachment of MHCFs to electrode surfaces can be achieved by electrodeposition, adsorption, entrapping them into polymeric matrices, and mechanically transferring them onto the solid electrode surfaces [28]. A serious drawback in the applications of these two-dimensional thin film modified electrodes is their poor long-term stability due to scratch, leakage, contamination, and passivation. Moreover, electrode surfaces cannot be renewed under these conditions.

Sol-gel synthesis is a low-temperature process that involves the hydrolysis and polycondensation of suitable precursors to form a three-dimensional inorganic network [29]. This has led to intensive research in this area, particularly with regard to sensing and biosensing [30]. Studies on silica-modified electrodes have increased exponentially in past years. Recent advances in the various fields and applications of sol-gel synthesis in electrochemistry have been described in several excellent review articles [31, 32, 33, 34, 35]. Since the pioneering work of Lev's group [36] on graphite organosilicate electrodes, many efforts have been devoted to the fabrication of chemically modified graphite organosilicate electrodes and using them as sensors for metal ions, glucose, and other important chemical and biological substances. An interesting feature of the graphite organosilicate electrodes is that the active section of the electrodes is not clogged upon repeated polishing owing to the brittleness of the sol-gel silicate backbone, and thus the electrodes can be renewed by a mechanical polish after every use or contamination.

Although a renewable three-dimensional Prussian Blue-modified graphite paste electrode has been developed by Scholz and co-workers [37], its practical utility

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strongly depends on its durability under stress operations, such as hydrodynamic conditions. Subsequently, Scholz's group [38, 39] also developed renewable MHCF-modified graphite paraffin electrodes for electroanalytical applications. These studies represent important examples for renewable MHCF-modified electrodes. Recently, Cox and co-workers [40] have reported the solid voltammetric characterization of iron hexacyanoferrate encapsulated in silica. In the present work, we propose a novel procedure to fabricate a surface-renewable three-dimensional MnHCF-modified graphite organosilicate electrode. The chemically modified electrode can electrocatalytically oxidize L-cysteine and exhibits a distinct advantage of polishing in the event of surface fouling.

Experimental

Reagents

Methyltrimethoxysilane (MTMOS, >97%) was purchased from ACROS and used without further purification. High-purity graphite powder (average particle size 0.2–1 μm) was obtained from Shanghai Carbon Plant (China). Manganous chloride tetrahydrate and potassium ferricyanide were purchased from Beijing Reagent (China). Emery paper (600 grit) was supplied by Shanghai Sand Wheel Plant (China). L-Cysteine was purchased from Aldrich. MnHCF was prepared according to the literature method [41]. Other chemicals were of analytical grade and used as received. Ultrapure water obtained from a Millipore Milli-Q water purification system was used throughout the experiments.

Apparatus

Elemental analyses were performed on a TJA POEMS ICP atomic emission spectrometer. 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 MnHCF-modified graphite organosilicate electrode as the working electrode, an Ag/AgCl (saturated KCl) reference electrode, and a platinum gauze counter electrode, was used. All the experiments were conducted at 25 ± 0.5 °C.

Preparation of MnHCF supported on graphite powder

Under an argon atmosphere, 5 g graphite powder was suspended in 20 mL 0.02 M $\text{K}_3\text{Fe}(\text{CN})_6$ + 0.01 M HCl aqueous solution and stirred at room temperature, and then 20 mL 0.02 M MnCl_2 + 0.01 M HCl aqueous solution was slowly added dropwise and the stirring was continued for about 2 h. The resulting solution was filtered through a sintered glass funnel to yield a black solid. The solid was washed with cold water and dried at 50 °C in vacuo. A portion of the resulting solid was burnt at 800 °C and the residue was dissolved in 5 M HNO_3 solution for elemental analyses. The average contents (four times) of K, Mn, and Fe were determined to be 1.7%, 2.5%, and 2.6%, respectively, and the relative standard deviation (RSD) of the deposition experiments (four times) was 2.4%. Calculated from the results of the elemental analysis, the formula of MnHCF can be expressed as $\text{K}_{0.97}\text{Mn}_{1.01}[\text{Fe}(\text{CN})_6]_{1.03}$, and the ratio of graphite to MnHCF is 6.1.

Fabrication of the MnHCF-modified graphite organosilicate electrodes

Type-I MnHCF-modified graphite organosilicate electrodes were constructed by the following procedure. A solution of 1.2 mL

MeOH, 0.8 mL MTMOS, and 0.04 mL HCl (11 M) was ultrasonically mixed for 2 min, then 1.6 g graphite powder-supported MnHCF was 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 0.8 cm. In addition, a little extra mixture was retained on 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 drying at 30 °C for 24 h, the electrodes were polished with 600-grit emery paper to remove extra composite material and then wiped gently with weighing paper. Electrical contact was made by silver paint through the back of the electrodes. Type-II MnHCF-modified graphite organosilicate electrodes were fabricated using the procedure described above except that the mixture of graphite powder and MnHCF (weight ratio 4:1) ground in an agate mortar was substituted for the graphite powder-supported MnHCF. If there is no special statement, type-I electrodes were used in our experiments.

Results and discussion

Fabrication of the MnHCF-modified graphite organosilicate electrodes

In the present paper, the chemical deposition procedure was used to yield a homogeneous mixture of graphite powder and MnHCF for the first time. The deposition reaction was performed in an acidic solution to avoid hydrolysis of MnCl_2 . In the process of fabrication of the MnHCF-modified graphite organosilicate electrodes, it was necessary to retain a little extra mixture on the top of the electrodes in order to conveniently obtain whole and mirror-like surfaces when they were first polished. In addition, the composite material became fragile and thus it was difficult to obtain smooth electrode surfaces if the gelation temperature was higher than 60 °C.

Electrochemical behavior of the MnHCF-modified graphite organosilicate electrode

After 5 min potential cycling scanning, the MnHCF-modified electrode presented stable electrochemical behavior. Figure 1A shows typical cyclic voltammograms for the MnHCF-modified electrode in 0.1 M KCl aqueous solution at different scan rates. When the potential was scanned between -0.1 and $+0.9$ V, a well-defined redox wave with the formal potential of $(E_{\text{ox}} + E_{\text{red}})/2$ at $+0.545$ V, characteristic of MnHCF [28, 41], was observed. Because the manganous part of MnHCF has no electroactivity in the investigated potential range, the electrode reaction should be attributed to the reversible redox behavior of the hexacyanoferrate part of the MnHCF. The anodic and cathodic peak potentials shift symmetrically, resulting in a constant formal potential at various scan rates. As shown in Fig. 1B, the anodic peak currents (I_{pa}) are linearly proportional to the scan rate (ν) at scan rates lower than 40 mV/s, which should be an indication of the total conversion of the accessible microparticles; however, at scan rates higher than 40 mV/s, the anodic peak currents are proportional to the square

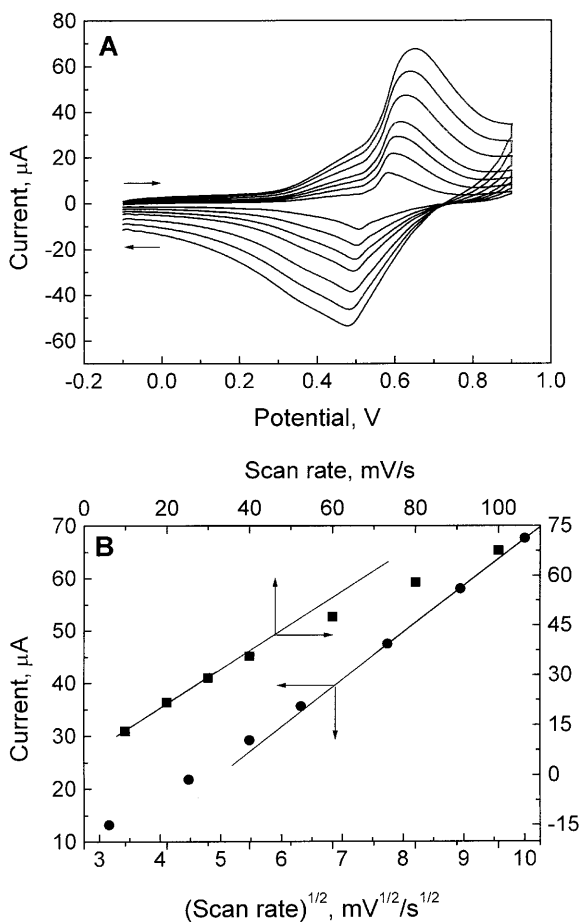


Fig. 1 A Typical cyclic voltammograms of the MnHCF-modified graphite organosilicate electrode in 0.1 M KCl solution at various scan rates (from inner curve to outer curve: 10, 20, 30, 40, 60, 80, and 100 mV/s, respectively). B The dependence of anodic peak current on the scan rate and on the square root of the scan rate

root of the scan rates, which indicates that the peak current is diffusion controlled. The shoulder at the reduction peak at higher scan rates may reflect that the distances between accessible MnHCF microparticles and the graphite surfaces are different. At lower scan rates, these accessible microparticles can all be reduced at one potential; however, at higher scan rates, the reduction of the more distant microparticles needs a larger overpotential and thus the shoulder appears. Wang and Collinson [42] have also observed multiple redox peaks for inorganic-organic hybrid films prepared from ferrocene-modified silanes. The surface coverage was measured by integrating the area under the anodic peaks at 10 mV/s and found to be 2.8×10^{-9} mol/cm². It should be pointed out that the coverage only reflects the coverage of accessible MnHCF microparticles rather than that of the overall microparticles because there may be some MnHCF microparticles without any contact with the graphite surface. Figure 2 shows the cyclic voltammograms for a typical type-II MnHCF-modified graphite organosilicate electrode in 0.1 M KCl solution. The anodic and cathodic potential difference of the type-II

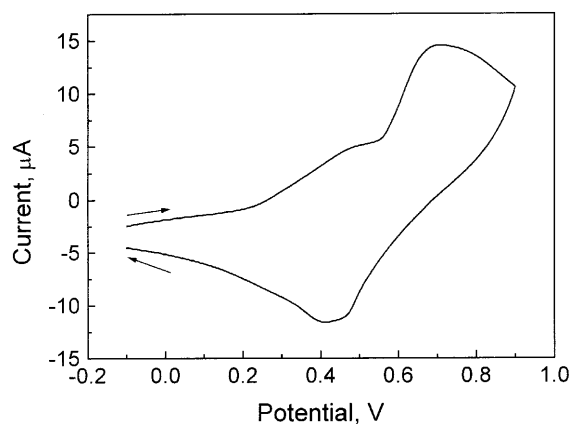


Fig. 2 Typical cyclic voltammogram of a type-II MnHCF-modified graphite organosilicate electrode in 0.1 M KCl solution at a scan rate of 20 mV/s

electrode is much larger than that of type-I. The results confirmed that the chemical deposition of MnHCF onto graphite powder should be a key step for the construction of three-dimensional MnHCF-modified graphite organosilicate electrodes.

Additional observations are concerned with the strong dependence of the voltammetric response on the choice of supporting electrolytes. Examples of four cyclic voltammograms for the MnHCF-modified electrode recorded in KCl, NH₄Cl, NaCl, and LiCl electrolytes are shown in Fig. 3. In general, the redox waves are much better developed in the presence of K⁺ (hydrated radius, 1.25 Å) than the Li⁺, Na⁺, and NH₄⁺ cations, whose hydrated radii are 2.37, 1.83, and 1.25 Å, respectively [43]. It is not surprising that the voltammetric responses are blocked in the electrolytes containing large Na⁺ and Li⁺ with larger hydrated radii. However, the anodic and cathodic peak currents for 0.1 M NH₄Cl are both smaller than those for 0.1 M KCl, which may be due to the poor mobility of NH₄⁺. This indicates that the ion flux cannot be explained by simple zeolitic selectivity as was postulated for Prussian Blue and its analogues [44].

In order to study the dependence of electrochemical behavior on the K⁺ activity (a_K), Osteryoung square-wave voltammetry with excellent sensitivity was adopted to accurately measure the formal potential (E°). Figure 4 shows the plot of E° versus $-\log a_K$ for the MnHCF-modified electrode in KCl solutions of different concentrations. The experimental value is 50 mV per decade, which is a little less than the theoretical value of the Nernst slope (59 mV per decade).

Electrocatalytic oxidation on the MnHCF-modified graphite organosilicate electrode

Recently, Narayanan and Scholz [41] immobilized microparticles of MnHCF onto the surface of a paraffin-impregnated graphite electrode and used the modified electrode to electrocatalytically oxidize hydrazine.

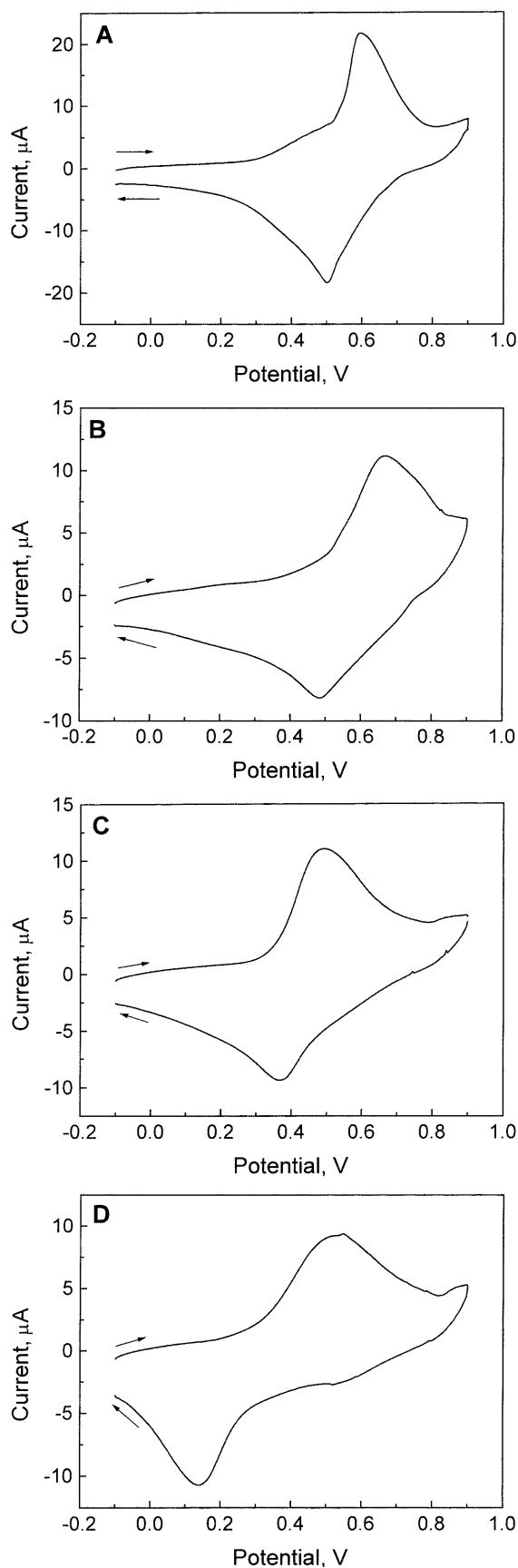


Fig. 3 Comparative cyclic voltammograms of the MnHCF-modified graphite organosilicate electrode in solutions with different supporting electrolytes at a scan rate of 20 mV/s: **A** 0.1 M KCl; **B** 0.1 M NH_4Cl ; **C** 0.1 M NaCl; **D** 0.1 M LiCl

Electrocatalytic oxidation of L-cysteine at Prussian Blue- and copper hexacyanoferrate-modified glassy carbon electrodes has been reported by Wang's group [45, 46]. In the experiments, we found that the MnHCF-modified graphite organosilicate electrode had a catalytic effect on the oxidation of L-cysteine. Figure 5 shows cyclic voltammograms for the electrocatalytic oxidation of L-cysteine at a glassy carbon electrode and a MnHCF-modified electrode. It can be clearly seen that electrochemical oxidation of L-cysteine on a glassy carbon electrode occurs at a potential more positive than +0.65 V (Fig. 5A), but L-cysteine can be electrocatalytically oxidized at +0.586 V on a MnHCF-modified electrode (Fig. 5B).

On the basis of the voltammetric results described above, it appears that amperometric detection of L-cysteine by the MnHCF-modified electrode is possible. Typical hydrodynamic amperometry (Fig. 6A) was obtained by successively adding 20 μL of 20 mM L-cysteine to 20 mL of continuously stirred 0.1 M KCl solution. The electrode response time was less than 5 s. The fast response is attributed to the thin wetting section controlled by the methyl group and the short penetration depth of L-cysteine. Figure 6B shows the calibration graph for L-cysteine at the modified electrode. The electrode response is linear for L-cysteine within the concentration range from 2×10^{-5} to 1×10^{-2} M, and the sensitivity is 1.555 $\mu\text{A}/\text{mM}$ (correlation coefficient of 0.999). The detection limit was 4.8×10^{-6} M when the signal-to-noise ratio was 3.

Stability and reproducibility of surface renewal

Much attention should be paid to the stability of chemically modified electrodes; thus the stability of the

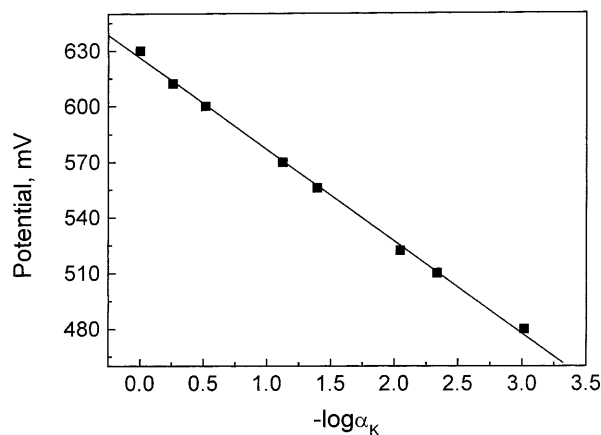


Fig. 4 The plot of $E^{\circ'}$ versus $-\log\alpha_K$

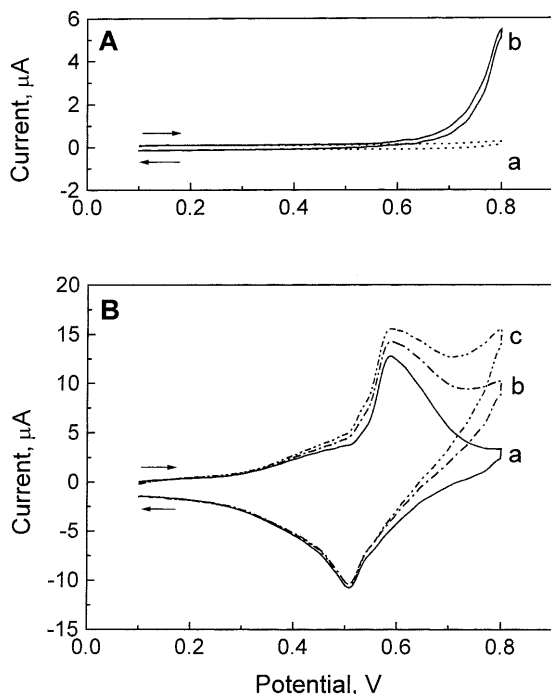


Fig. 5 A Cyclic voltammograms for a glassy carbon electrode in (a) 0.1 M KCl solution and (b) 0.1 M KCl+1 mM L-cysteine solution. B Cyclic voltammograms for a MnHCF-modified electrode in 0.1 M KCl solutions containing (a) 0 mM, (b) 1 mM, and (c) 2 mM L-cysteine. Scan rate: 10 mV/s

MnHCF-modified graphite organosilicate electrode was tested by cyclic voltammetry and amperometric detection in flow streams. As shown in Fig. 7, there was only 4.5% current decrease after 10 h successive potential cycling for the MnHCF-modified electrode in 0.1 M KCl aqueous solution. In fact, only 2.3% current decrease was observed when the electrode was measured in flow injections of 2 mM L-cysteine over about 2 h. We think 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 the methyl group, the strong adsorption of MnHCF on graphite powder, and the possible interactions between MnHCF and silanol groups. Another main attraction of the three-dimensional modified electrode is that the electrode surface can be renewed by simple mechanical polishing and a fresh surface exposed whenever needed. This is especially useful for electrocatalytic studies since catalytic activity is known to decrease when the electrode is fouled. Indeed, 10 successive polishings resulted in a RSD of 5.8% for a MnHCF-modified graphite organosilicate electrode by measuring the anodic peak area at the scan rate of 10 mV/s, which reflects the repeatability of surface renewal by polishing.

Conclusions

A new method based on chemical deposition and sol-gel techniques was developed to prepare a MnHCF-

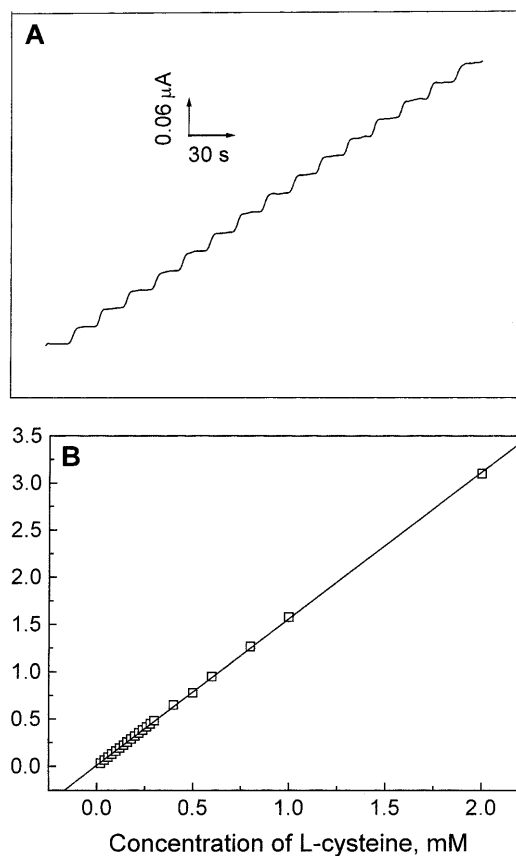


Fig. 6 A Amperometric response of the MnHCF-modified electrode on successive additions of 20 mM L-cysteine to 0.1 M KCl solution. B The steady-state calibration curve for current versus L-cysteine concentration. Applied potential: +0.586 V; stirring speed: 1000 rpm

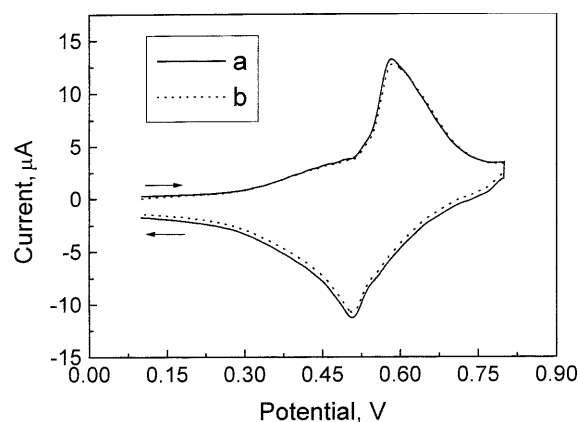


Fig. 7 Cyclic voltammograms of the MnHCF-modified electrode in 0.1 M KCl solution after (a) 5 min and (b) 10 h cycling potential scanning. Scan rate: 10 mV/s

modified graphite organosilicate composite electrode. Of particular interest may be the method that was devised to fabricate three-dimensional MHCF-modified electrodes which can be renewed by simple mechanical polishing in the event of scratches, leakage, contamination, and

passivation. In view of its good stability, the MnHCF-modified electrode holds promise for the quantitative detection of some important chemical and biological substances in flow systems when coupled to chromatographic and electrophoretic separation systems.

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