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Surface renewable graphite organosilicate composite electrode containing indium(III) hexacyanoferrate(II/III)

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Indium(III) hexacyanoferrate(II/III) (InHCF) supported on graphite powder was prepared using the *in situ* chemical deposition procedure and subsequently dispersed into methyltrimethoxysilane-derived gels to yield a conductive graphite organosilicate composite. The composite was used as the electrode material to fabricate a three-dimensional InHCF-modified electrode. InHCF 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. The chemically modified electrode can electrocatalyze the oxidation of thiosulfate, and exhibits a good repeatability of surface-renewal by simple mechanical polishing, as well as simple preparation, good chemical and mechanical stability.

Introduction

In the past twenty years, much effort has been made concerning the development and characterization of electrodes modified with metal-hexacyanometalate complexes.[1–5] Undoubtedly, the wide range of promising applications in the fields of electrocatalysis,[6–12] ion-selective electrodes,[13–15] electrochromism,[16–18] solid state batteries,[19,20] corrosion[21] and electroanalysis[22–25] has given an impetus to find out more about these systems and fabrication methods. Another motivation of the electrochemists is to gain a better understanding of the processes occurring at these modified electrodes.[26–30] Attachment of these electroactive species to electrode surfaces can be achieved by electrodeposition, adsorption and entrapping them into polymer matrices. A serious drawback in the applications of these two-dimensional thin film modified electrodes is their poor long-term stability due to scratching, leakage, contamination and passivation.[10,31] Moreover, electrode surfaces can not be renewed under these conditions. For example, Golabi and Noor-Mohammadi[32] found that the cobalt(II) hexacyanoferrate(II/III) film electrode exhibited a 10% decrease in the peak current after only 100 potential cycles. Yet, upon repetitive redox scans in acidic media the electrochemical activity of such a film eventually decays to zero.

Sol–gel is a low-temperature process that involves the hydrolysis and polycondensation of suitable precursors to form a three-dimensional inorganic network.[33] This has led to intensive research in this area particularly with regard to sensing and biosensing.[34] Many studies on silica-modified electrodes have been reported in the last few years. Recent advances in the various fields and applications of sol–gel in electrochemistry were described in several excellent review articles.[35–39] Since the pioneering work of Lev's group[40] on graphite organosilicate electrodes, many efforts have been devoted to the fabrication of chemically modified graphite organosilicate electrodes and their use 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 due 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 surface renewable Prussian Blue modified graphite paste electrode has been developed by Zakharchuk *et al.*,[41] its practical utility strongly depends on durability under stress operations, such as hydrodynamic conditions. Our recent interest has been focused on the fabrication and electroanalytical application of three-dimensional graphite organosilicate electrodes modified with metal-hexacyanometalate complexes.[42] There are several papers on the fabrication, physico-chemical characterization and application of indium(III) hexacyanoferrate(II/III) (InHCF) modified film electrodes.[43–50] In this paper, InHCF supported on graphite powder was prepared using the *in situ* chemical deposition procedure and subsequently dispersed into methyltrimethoxysilane-derived gels to yield a conductive graphite organosilicate composite for the first time. The composite was used as an electrode material to construct a surface renewable InHCF-modified electrode.

Experimental

Materials

Methyltrimethoxysilane (MTMOS, >97%) was purchased from ACROS and used without purification. High purity graphite powder (average particle size 0.2–1 μm) was obtained from Shanghai Carbon Plant. Indium sulfate and potassium hexacyanoferrite were purchased from Beijing Reagent Co. The 600-grit emery paper was supplied by Shanghai Sand Wheel Plant. 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

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of a glassy carbon electrode or an InHCF-modified graphite organosilicate electrode 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 0.1 M 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. No action was taken to remove oxygen from solutions. The surface morphology of the InHCF-modified electrode was observed with a JEOL JXA-840 scanning electron microscope (SEM). The back of the InHCF-modified electrode cut to be 0.5 cm was connected to the sample platform with electric paint. All the experiments were conducted at 15 ± 0.2 °C.

Preparation of graphite powder-supported InHCF

Under an argon atmosphere, 5 g of graphite powder was suspended in 20 ml 0.01 M $K_4Fe(CN)_6$ + 0.01 M HCl aqueous solution and stirred at room temperature, and then 20 ml 0.005 M $In_2(SO_4)_3$ + 0.01 M HCl aqueous solution was slowly added and the stirring was continued for about 2 h. The resulting solution was filtered through a sintered glass funnel to yield the black solid. The solid was washed with cold water and dried at 50 °C *in vacuo*. The K, In, and Fe contents were determined to be 1.36, 4.08 and 1.98%, respectively, which confirmed the formula of InHCF to be $KIn[Fe(CN)_6]$. Thus, the weight ratio of InHCF to graphite is calculated to be 6.7.

Fabrication of InHCF-modified graphite organosilicate electrodes

The InHCF-modified graphite organosilicate electrodes were constructed by the following procedure. The solution of 1.50 ml methanol, 0.75 ml MTMOS and 0.05 ml hydrochloric acid (11 M) was ultrasonically mixed for 2 min, then 1.70 g graphite powder-supported InHCF 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 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. 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 electrode.

Results and discussion

Fabrication and surface morphology of the InHCF-modified electrodes

In the present study, we exploited the *in situ* chemical deposition procedure to obtain a homogeneous mixture of InHCF and graphite powder. In the process of fabrication of the InHCF-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. 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.

Surfaces of the InHCF-modified graphite organosilicate electrodes are smooth although not mirror-like. A drop of water deposited on the surfaces does not spread indicating the apparent hydrophobic nature of the surfaces. A typical SEM photograph of the InHCF-modified electrode is given in Fig. 1 and shows that no cracks exist on the surface and the surface is uniform after a simple mechanical polishing. Since graphite powder is conductive, sputtering of the sample with gold was not necessary for the SEM study.

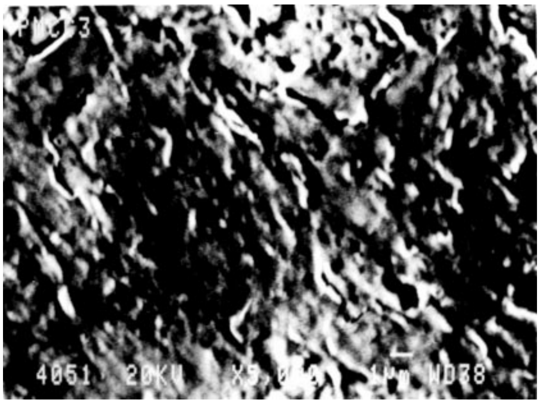

Fig. 1 The SEM photograph of the InHCF-modified electrode.

Electrochemical behavior of the InHCF-modified electrode

Fig. 2 shows the typical cyclic voltammograms for the InHCF-modified electrode in 0.1 M KCl solution at different scan rates. Since reduction of indium(III) requires highly negative potentials (about −1.0 V), the formal potential $E^{0\prime} = +0.75$ V (*vs.* Ag/AgCl) evaluated from the average of the oxidation and reduction peak potential values is due to the redox couple of iron centers in the potential range from +1.0 to −0.1 V.[43–50] The electrochemical process can be proposed as the following equation:

$$KIn^{III}[Fe^{II}(CN)_6] = In^{III}[Fe^{III}(CN)_6] + e^- + K^+ \qquad (1)$$

Additional experiments showed that another kind of InHCF-modified graphite organosilicate electrode fabricated by dispersing the physical mixture of graphite powder and InHCF in MTMOS-derived gels presented ill-defined cyclic voltammograms. The results confirmed that chemically homogeneous deposition of InHCF onto graphite powder should be a key step for the construction of three-dimensional InHCF-modified electrodes.

As shown in Fig. 3A, the anodic peak currents, I_{pa}, are proportional to the square root of the potential scan rate, $v^{1/2}$, not directly proportional to v as normally expected for surface reactants. That is to say, the properties of the waves in Fig. 2 are those expected for an electrochemical reaction controlled by diffusion. Fig. 3B shows the dependence of the anodic and cathodic peak potentials (E_{pa} and E_{pc}) for the InHCF-modified electrode on the logarithm of scan rate (log v). As predicted by the theory of Laviron *et al.*,[51] the anodic and cathodic peak

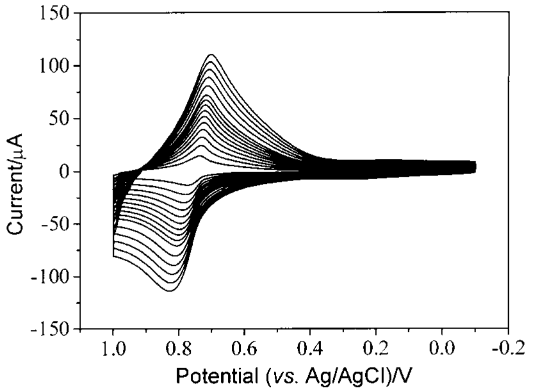

Fig. 2 The typical cyclic voltammograms for the InHCF-modified electrode in 0.1 M KCl solution at different scan rates (from inner to outer: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180 and 200 mV s^{-1}).

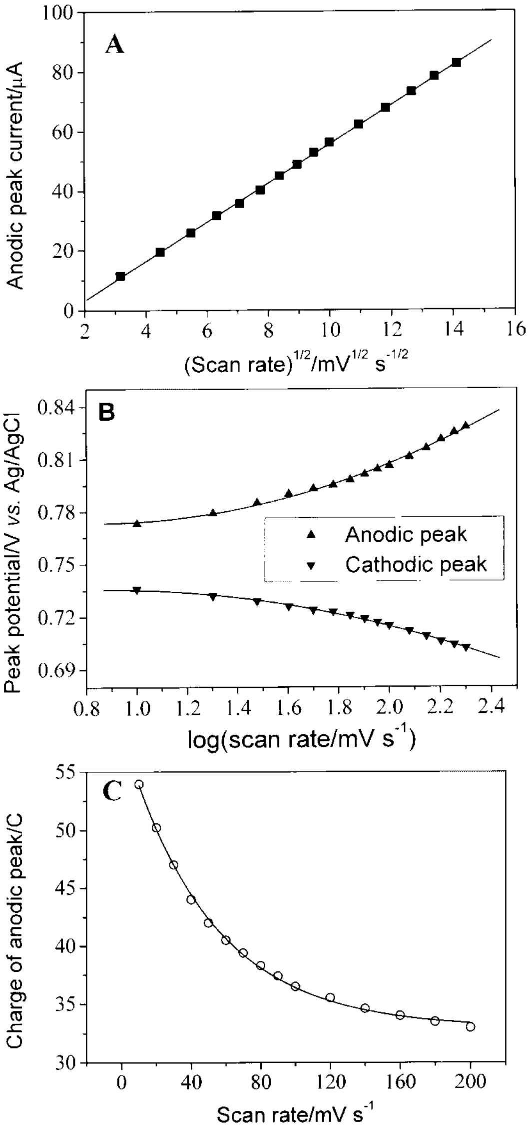

Fig. 3 (A) The dependence of anodic peak current on the square root of the scan rate; (B) the dependence of the anodic and cathodic peak potential on the logarithm of scan rate; (C) plot of the anodic peak charge *vs.* scan rate.

both present a tailing, which becomes more marked when the scan rate increases. The scan rate dependency of anodic charge presented in Fig. 3C is associated with the tailing wave shape. Obviously, a good deal of electroactive InHCF remains unoxidized as the potential is scanned through the anodic peak, more so at higher scan rates. Therefore, the rate of diffusion of electrochemical charge through the InHCF deposition layer must be very slow.

Ion effect on the electrochemistry of the InHCF-modified electrode

Additional observations are concerned with the strong dependence of voltammetric response on the choice of supporting electrolytes. Examples of four cyclic voltammograms for the InHCF-modified electrode recorded in KCl, K_2SO_4, NH_4Cl and NaCl electrolytes are shown in Fig. 4. In general, the redox waves are much better developed in the presence of K^+ (hydrated radius, 1.25 Å) than any other cations such as Na^+ and NH_4^+, whose hydrated radii are 1.83 and 1.25 Å, respectively.[1,27] It is not surprising that the voltammetric response is blocked in the electrolyte containing Na^+ ions with the larger hydrated radius. Our preliminary data with NH_4^+-containing electrolyte (Fig. 4, curve (c)) suggest that even smaller hydrated cations (NH_4^+) are not so easily transported in InHCF as K^+ ions. This indicates that the ion flux can not be explained by simple zeolitic selectivity as it was postulated for Prussian Blue and its analogues.[28] Poor mobility of NH_4^+, as well as the related irreversible cyclic voltammetric response, could be caused by electrostatic and ionic polarizability effects. In addition, the peak potentials in 0.1 M KCl and 0.05 M K_2SO_4 solutions are almost the same; however, the peak currents are different, which indicates anions may also participate in the redox process of InHCF.

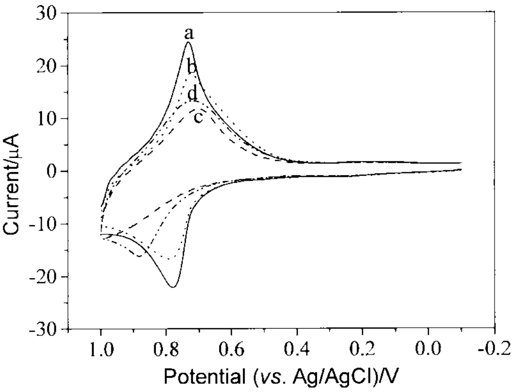

Fig. 4 Comparative cyclic voltammograms for the InHCF-modified electrode in: (a) 0.1 M KCl solution, (b) 0.05 M K_2SO_4 solution, (c) 0.1 M NH_4Cl solution and (d) 0.1 M NaCl solution.

In order to determine the dependence of formal potentials ($E^{0\prime}$) of the InHCF-modified electrode on K^+ concentration, we have performed Osteryoung square-wave experiments with an excellent sensitivity. Fig. 5 shows the square-wave voltammetric response of the InHCF-modified electrode recorded in KCl electrolytes where the K^+ concentration was varied from 2.0 to 1.0×10^{-3} M. The gradual decrease of peak currents can be explained by Fick's first law. The voltammetric peak (formal) 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^+ concentrations, a straight line (slope, 44 mV per decade change of K^+ activity; correlation coefficient, 0.9973) was obtained (Fig. 6). The shifts of 44 mV per decade change of K^+ activity were definitely lower than the theoretical value of 57 mV (Nernstian behavior) which would be expected for the sole involvement of K^+ in the reaction mechanism (eqn. (1)) at the temperature of the experiment. This less-than-Nernstian response can not be attributed to junction potentials. There is no doubt that K^+ ions do participate in the system's redox reaction. A possible explanation for the lower than 57 mV

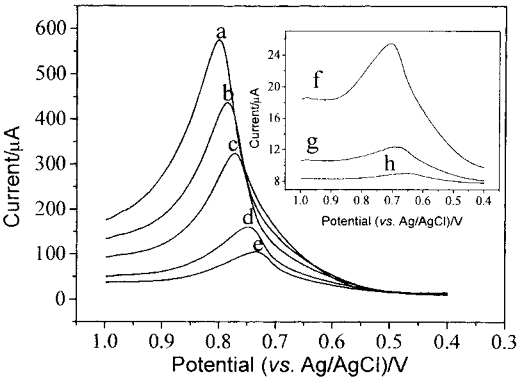

Fig. 5 Osteryoung square-wave voltammograms for the InHCF-modified electrode in KCl solutions with different concentrations: (a) 2.0, (b) 1, (c) 0.5, (d) 0.1, (e) 0.05, (f) 0.01, (g) 0.005, (h) 0.001 M. Increment: 2 mV, frequency: 10 Hz, scan rate: 20 mV s^{-1}.

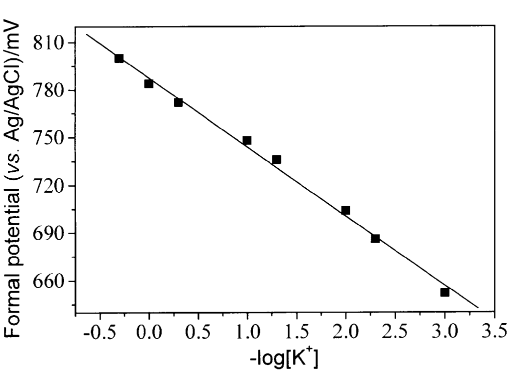

Fig. 6 The relationship between formal potentials and K^+ ion concentration.

slopes in Fig. 6 may be due to a more complex redox behavior of the InHCF-modified electrode (than expected from eqn. (1)) and/or to partial charge compensation anions from the electrolyte.

Electrocatalytic oxidation of thiosulfate at the InHCF-modified electrode

The oxidation of thiosulfate at a glassy carbon electrode and at an InHCF-modified electrode was carried out in a 0.1 M KCl solution. Typical cyclic voltammograms for thiosulfate oxidation are shown in Fig. 7. There was no electrochemical response for thiosulfate at a glassy carbon electrode in the potential range from 0.3 to 0.81 V. However, with the addition of thiosulfate, the anodic peak current of the InHCF-modified electrode increases while the cathodic peak current decreases, suggesting that thiosulfate was electrocatalytically oxidized by $In^{III}[Fe^{III}(CN)_6]$.

On the basis of the voltammetric results described above, it appears that amperometric detection of thiosulfate using the InHCF-modified electrode is possible. A typical hydrodynamic amperometric response (Fig. 8) was obtained by successively adding thiosulfate to continuously stirred 0.1 M KCl solution. The electrode response time was less than 3 s. The fast response is attributed to the thin wetting section controlled by the methyl group and the short penetration depth of thiosulfate. The inset of Fig. 8 shows the calibration graph for thiosulfate at the modified electrode. The electrode response is linear for thiosulfate within the concentration range from 1×10^{-5} to 1×10^{-2} M, and the sensitivity is 2.7 μA mM^{-1} (correlation coefficient of 0.9998). The detection limit was 4.2×10^{-6} M when the signal-to-noise ratio was 3.

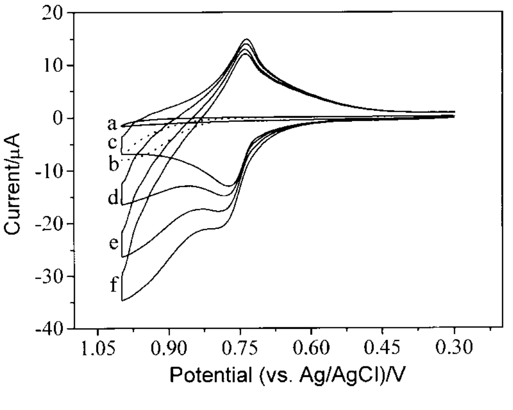

Fig. 7 Cyclic voltammograms for a glassy carbon electrode in (a) 0.1 M KCl solution and (b) 0.1 M KCl + 0.7 mM thiosulfate solution and for an InHCF-modified electrode in 0.1 M KCl solutions containing (c) 0, (d) 0.7, (e) 1.8 and (f) 3 mM thiosulfate. Scan rate: 10 mV s^{-1}.

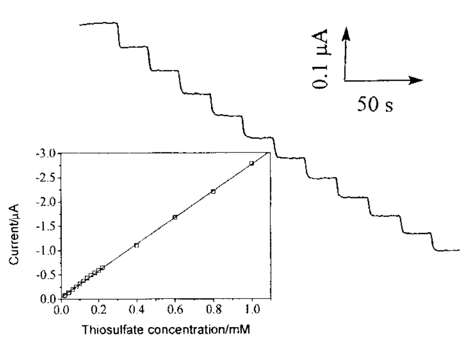

Fig. 8 Amperometric response of the InHCF-modified electrode on successive increase of 20 μM thiosulfate in 0.1 M KCl solution. The inset is the steady-state calibration curve for current *versus* thiosulfate concentration. Applied potential: +0.775 V; stirring speed: 800 rpm.

Stability and repeatability of surface-renewal

Much attention has been paid to the stability of chemically modified electrodes, so the stability of the InHCF-modified graphite organosilicate electrode was tested by cyclic voltammetry. As shown in Fig. 9, there was no obvious current decrease after 90 min successive potential cycling for the InHCF-modified electrode in 0.1 M KCl aqueous solution. 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 InHCF on graphite powder and the possible interactions between InHCF 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 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 3.6% for an InHCF-modified graphite organosilicate electrode.

Conclusions

A surface renewable three-dimensional InHCF-modified graphite organosilicate electrode has been fabricated using *in situ* chemical deposition and the sol–gel techniques. The chemically modified electrode can electrocatalyze the oxidation of thiosulfate, and exhibits a distinct advantage of polishing, as well as simple preparation, good chemical and mechanical stability. Although the new concept has been presented in the context of the InHCF-modified electrode, it could be readily extended towards the construction of other three-dimensional metal-hexacyanometalate modified graphite organosilicate

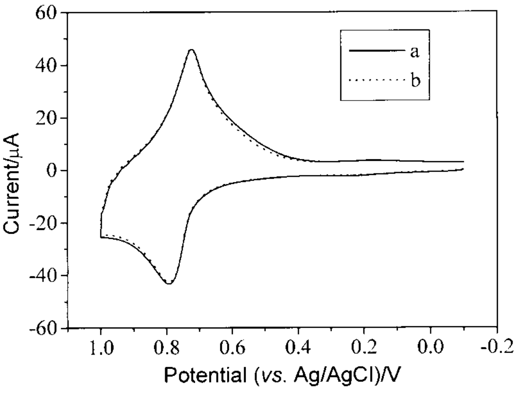

Fig. 9 Cyclic voltammograms for the InHCF-modified electrode in 0.1 M KCl solution (a) at the first cycle and (b) cycling continuously after 90 min. Scan rate: 50 mV s^{-1}.

electrodes and the measurement of other environmentally important compounds. The goal has been achieved and the results will be shown in our future papers.

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