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Renewable-surface amperometric nitrite sensor based on sol–gel-derived silicomolybdate–methylsilicate–graphite composite material

Peng Wang,[a] Xiangping Wang,[a] Lihua Bi[b] and Guoyi Zhu*[a]

[a] *Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: zhuguoyi@ns.ciac.jl.cn; Fax: +86 431 5685653*

[b] *Department of Chemistry, Northeast Normal University, Changchun 130024, China*

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A new type of silicomolybdate–methylsilicate–graphite composite material was prepared by the sol–gel technique and used for the fabrication of an amperometric nitrite sensor. The silicomolybdic anion acts as a catalyst, the 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, square-wave voltammetry and chronoamperometry were employed to characterize the sensor. The amperometric nitrite sensor exhibited a series of good properties: high sensitivity (1.771 μA mmol^{-1} dm^3), a short response time (7 s), remarkable long-term stability and especially reproducibility of surface renewal in the event of electrode surface fouling.

Introduction

Much concern has been shown about the level of nitrite in foods and beverages because nitrite can react in the stomach with dietary components to form toxic and carcinogenic nitrosamines.[1] Another danger that can occur after nitrite ingestion is that this ion in the bloodstream converts oxyhemoglobin to methemoglobin, thereby interfering with oxygen transport in the blood.[2] The elaboration of sensors sensitive to nitrite is an important challenge for medical and environmental applications. As is well known, direct electroreduction of nitrite ion requires a large overpotential on most electrode surfaces, but reduction can be catalyzed by the nitrite reductases,[3,4] which consist of an iron–sulfur unit and an iron isobacterio chlorin or siroheme in green plants. Thus various transition metal complexes have been employed as enzymatic models for nitrite reduction, including iron chelates,[5] iron porphyrins[6] and cobalt cyclam.[7] It has also been shown that a large variety of Keggin- and Dawson-type polyoxometalates (POMs) are efficient in the electrocatalytic reduction of nitrite and nitric oxide.[8–13] However, almost all these POMs were used directly in aqueous solutions or immobilized on the electrode surfaces as catalyst.[14] A serious drawback in the application of these surface modified electrodes is their poor long-term stability; moreover, the electrode surfaces can not be renewed in the event of leakage, contamination and passivation. It seemed desirable to exploit and develop a new simple and reliable procedure for POM-modified electrodes.

The sol–gel technique is a low-temperature process that involves the hydrolysis and polycondensation of suitable precursors to form ceramic materials.[15] This has led to intensive research in this area, particularly with regard to sensing and biosensing.[16–19] Studies on silica-modified electrodes have increased exponentially in recent years. Recent advances in the various fields and applications of the sol–gel technique in electrochemistry have been described in several excellent review articles.[20–24] Since the pioneering work of Lev's group[25] on ceramic graphite composite electrodes (CGCEs), much effort has been devoted to the fabrication of chemically modified CGCEs and using them as sensors for metal ions,[26] glucose[27] and other important chemical and biological substances.[28–30] An interesting feature of the CGCEs 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 the electrodes can therefore be renewed by mechanical polishing after each use or contamination incident.

Considering that POMs are a class of inorganic metal-oxide clusters in nature and may be uniformly dispersed in the silicate by the sol–gel process, our recent interest has been focused on the construction of CGCEs containing POMs. This paper describes the fabrication and electrochemical behavior of a CGCE containing 1 : 12-silicomolybdic acid ($SiMo_{12}$) and its use as an amperometric sensor for nitrite ion.

Experimental

Reagents and solutions

High purity graphite powder (average particle size 1–2 μm) was obtained from Aldrich (Milwaukee, WI, USA). Methyltrimethoxysilane (MTMOS, $>97\%$) was purchased from ACROS (Fair Lawn, NJ, USA) and used without further purification. Pure $SiMo_{12}$ was used as a gift from Professor Enbo Wang (Northeast Normal University, Changchun, China), and the water content in $H_4SiMo_{12}O_{40}\cdot 28H_2O$ was determined by thermogravimetric analysis. All other reagents were of analytical-reagent grade.

Ultra-pure water obtained from a Millipore (Molsheim, France) Milli-Q water purification system was used throughout the experiments. Solutions with different pH (0.00–3.51) were prepared by mixing 0.1 mol dm^{-3} Na_2SO_4 aqueous solution with 0.1 mol dm^{-3} Na_2SO_4–0.5 mol dm^{-3} H_2SO_4 aqueous solution. Natural spring water was supplied by Daqing Water

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Plant (Daqing, China) and concentrated 100-fold using a rotoevaporator. The resulting water was used to prepare sample solutions containing 0.5 mol dm^{-3} H_2SO_4. Solutions were deaerated by bubbling argon through them prior to the experiments and the electrochemical cell was kept under an argon atmosphere throughout the experiments.

Apparatus

A computer controlled EG&G PARC (Princeton, NJ, USA) Model 273 potentiostat with an M270 software system was used for voltammetric and amperometric measurements. A three-electrode cell, consisting of a modified CGCE as the working electrode, an Ag/AgCl (saturated KCl) reference electrode and a platinum gauze counter electrode, was used. A Cole-Parmer (Chicago, IL, USA) Model 3 pH meter was employed for pH measurements. All the experiments were conducted at 15 ± 0.2 °C.

Preparation of $SiMo_{12}$-modified CGCEs

A solution of 0.75 ml of methanol containing 3.75 mg of $SiMo_{12}$, 0.25 ml of MTMOS and 0.025 ml of hydrochloric acid (11 mol dm^{-3}) was mixed ultrasonically for 2 min, then 1.875 g of graphite powder was added and shaken on a vortex agitator for an additional 3 min. The mixture was placed in glass tubes of 3 mm id and 8 cm length, and the length of composite material in the tubes was controlled at about 0.8 cm. In addition, a small amount of 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 rod through the back. After drying at 30 °C for 24 h, the electrodes were polished with No. 3 emery paper to remove extra composite material and wiped gently with weighing paper. Electric contact was made by silver paint through the back of the electrode.

Results and discussion

Preparation and electrochemical behavior of the $SiMo_{12}$-modified CGCE

In the process of fabrication of $SiMo_{12}$-doped CGCEs, small amount of mixture was needed to be retained on the top of the electrodes in order to obtain conveniently a whole and uniform surface when they were first polished. In addition, the composite material became fragile and therefore it was difficult to obtain smooth electrode surfaces if the gelation temperature was higher than 60 °C.

The $SiMo_{12}$ anion, which has Keggin structure, is unstable in neutral and basic aqueous solution and undergoes a series of hydrolysis processes.[14] Therefore, electrochemical studies of $SiMo_{12}$-modified CGCE were carried out in acidic aqueous solutions.

Fig. 1 shows cyclic voltammograms of an $SiMo_{12}$-modified CGCE for different scan rates and the inset shows the corresponding dependence of the peak current on scan rate. Redox peaks I–I′, I–II′ and I–III′ correspond to reduction and oxidation through two-, four- and six-electron processes, respectively.[31–34] The linear relationship observed and the small peak separation between the corresponding cathodic and anodic waves indicate fast electron transfer to redox active species doped in the electrode wetting section. However, the peak potential separation ($E_{pa} - E_{pc}$) is < 35 mV instead of the value of zero expected for a reversible surface redox process, which might be due to non-ideal behavior.[35]

Effect of pH on the electrochemical behavior of the $SiMo_{12}$-modified CGCE

In order to study the pH-dependent electrochemical behavior of the $SiMo_{12}$-modifed CGCE, square-wave voltammetry with an excellent sensitivity was adopted to measure accurately the formal potentials ($E^{0\prime}$). Fig. 2 shows Osteryoung square-wave voltammograms for an $SiMo_{12}$-doped CGCE in 0.1 mol dm^{-3} Na_2SO_4 aqueous solutions of different pH. It can be clearly seen that with an increase in pH, the three redox potentials all gradually shift to the more negative potential direction and the peak currents also decrease. Reduction of $SiMo_{12}$ immobilized in the CGCE matrix is accompanied by the evolution of protons from solution to the wetted electroactive section of the electrode to maintain charge neutrality. With increase in pH, slower penetration of protons[36] to the wetting section of the $SiMo_{12}$-doped CGCE should be the reason for the current decrease, and the more negative reduction potentials can be elucidated using the Nernst equation.[37] Plots of $E^{0\prime}$ of the three successive redox waves *versus* pH for the $SiMo_{12}$-modified CGCE show good linearity in the pH range 0.00–3.51, as shown in Fig. 3. The slopes in this pH range are −65, −72 and −68 mV pH^{-1} for the I–I′, II–II′ and III–III′ couples, respectively, which are close to the theoretical value of −57 mV pH^{-1} for the 2e$^-$/2H$^+$ redox process at the experimental temperature. The electrochemical reaction of the $SiMo_{12}$-modified CGCE can be expressed as follows:

$$SiMo^{VI}{}_{12}O_{40}{}^{4-} + 2e^- + 2H^+ \rightleftharpoons H_2SiMo^{V}{}_2Mo^{VI}{}_{10}O^{4-}{}_{40}$$

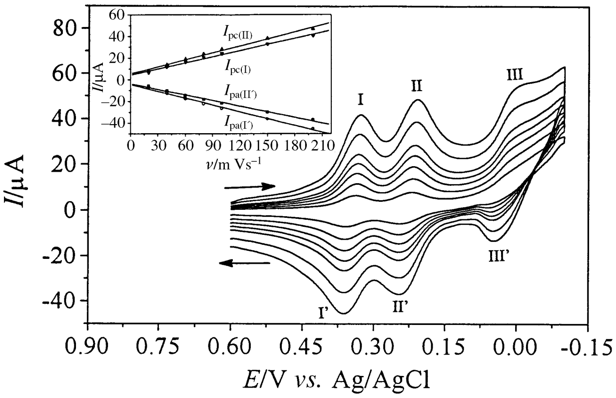

Fig. 1 Cyclic voltammograms for the $SiMo_{12}$-modified CGCE in 0.5 mol dm^{-3} H_2SO_4 aqueous solution at various scan rates (from inner to outer: 20, 40, 60, 80, 100, 150 and 200 mV s^{-1}). The inset shows the dependence of peak current on scan rate.

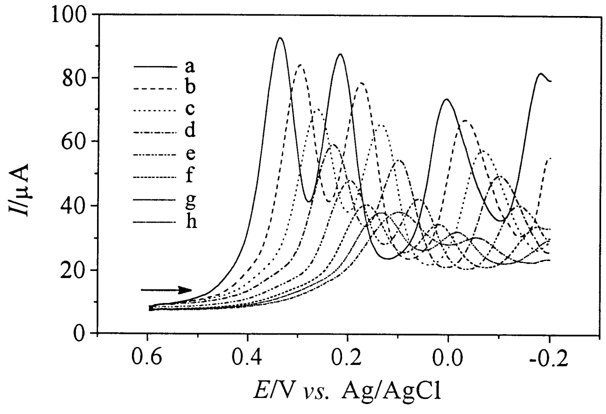

Fig. 2 Square-wave voltammograms for the $SiMo_{12}$-modified CGCE in 0.1 mol dm^{-3} Na_2SO_4 aqueous solutions with different pH: (a) 0.00; (b) 0.53; (c) 1.03; (d) 1.46; (e) 1.99; (f) 2.47; (g) 2.95; and (h) 3.51. Increment, 4 mV; amplitude, 25 mV; frequency, 15 Hz; scan rate, 60 mV s^{-1}.

$$H_2SiMo^V{}_2Mo^{VI}{}_{10}O^{4-}{}_{40} + 2e^- + 2H^+ \rightleftharpoons H_4SiMo^V{}_4Mo^{VI}{}_8O^{4-}{}_{40}$$

$$H_4SiMo^V{}_4Mo^{VI}{}_8O^{4-}{}_{40} + 2e^- + 2H^+ \rightleftharpoons H_6SiMo^V{}_6Mo^{VI}{}_6O^{4-}{}_{40}$$

Catalytic reduction of nitrite ions at the $SiMo_{12}$-modified CGCE

The direct electroreduction of nitrite requires a large overpotential at most bare electrode surfaces (including CGCE). A study of the electrocatalytic reduction of nitrite by $SiMo_{12}$ has been reported.[32] In the present work, we found that the $SiMo_{12}$-modified CGCE showed catalytic activity toward the reduction of NO_2^-. In view of the quasi-reversible voltammetric behavior of the III–III′ couple (shown in Fig. 1), we selected the potential range from +0.55 to +0.13 V to investigate the electrocatalytic reduction of nitrite. Fig. 4 shows the electrocatalytic reduction of nitrite on an $SiMo_{12}$-modified CGCE. With the addition of nitrite, both of the two reduction peak currents increase whereas the corresponding oxidation peak currents decrease, suggesting that nitrite is reduced by two- and four-electron-reduced species. It has been noted that the four-electron-reduced species has a larger catalytic activity toward nitrite than the two-electron-reduced species. Hence the catalytic activity of $SiMo_{12}$ toward nitrite increases with the extent that $SiMo_{12}$ is reduced. The catalytic process is regards as an EC catalytic mechanism and can be expressed as follows:

$H_2SiMo^V{}_2Mo^{VI}{}_{10}O^{4-}{}_{40} + NO^-{}_2 + nH^+ \rightarrow SiMo^{VI}{}_{12}O^{4-}{}_{40}$ + products containing N

$H_4SiMo^V{}_4Mo^{VI}{}_8O^{4-}{}_{40} + NO^-{}_2 + nH^+ \rightarrow H_2SiMo^V{}_2Mo^{VI}{}_{10}O^{4-}{}_{40}$ + products containing N

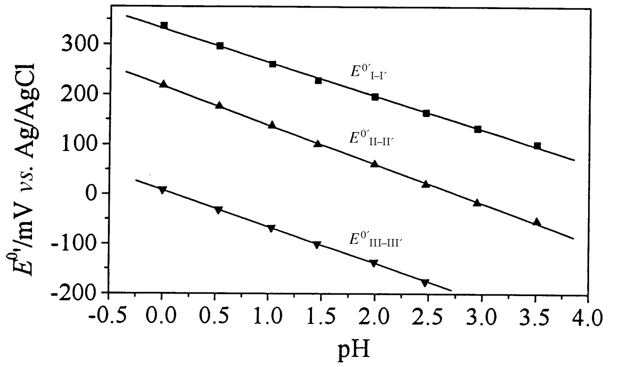

Fig. 3 Formal potential of three successive redox waves as a function of pH.

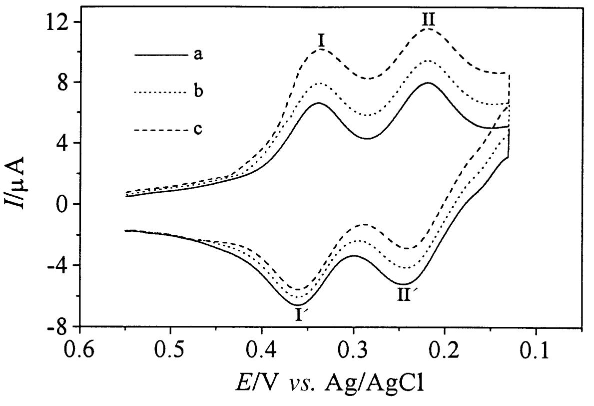

Fig. 4 Cyclic voltammograms for the $SiMo_{12}$-modified CGCE in 0.5 mol dm^{-3} H_2SO_4 aqueous solutions containing (a) 0.0, (b) 0.8 and (c) 2.0 mmol dm^{-3} nitrite. Scan rate, 20 mV s^{-1}.

Amperometric nitrite sensing and interferences

On the basis of the voltammetric results described above, it appears that amperometric detection of nitrite by the $SiMo_{12}$-modified CGCE is possible. According to the potential dependence of the nitrite electrocatalytic current under steady-state conditions, the optimum electrode potential was selected as +0.22 V *versus* the Ag/AgCl electrode in order to obtain constant and high sensitivity. A typical hydrodynamic amperometric response (Fig. 5) was obtained by successively adding nitrite to continuously stirred 0.5 mol dm^{-3} H_2SO_4 aqueous solution. The electrode response time was <7 s. The fast response is attributed to the thin wetting section controlled by the methyl group and a short penetration depth of nitrite. The inset in Fig. 5 shows the calibration graph for nitrite at the modified electrode. The electrode response was linear for nitrite within the concentration range 5×10^{-6}–1.5×10^{-2} mol dm^{-3}, and the sensitivity is 1.771 μA $mmol^{-1}$ dm^3 NO_2^- (correlation coefficient $r = 0.999$). The detection limit was 1×10^{-6} mol dm^{-3} when the signal-to-noise ratio was 3.

The interference effect was investigated by testing the response of the modified electrode to Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Ba^{2+}, Pb^{2+}, Zn^{2+}, F^-, Cl^-, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, CO_3^{2-}, HCO_3^- and Br^-, which are species that exist in natural mineral spring water. We found that a 1200-fold excess of Na^+, F^-, Cl^-, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, CO_3^{2-}, Br^-, HCO_3^-, Mg^{2+}, Ca^{2+}, Ba^{2+} and Fe^{3+} and a 1000-fold excess of Pb^{2+} and Zn^{2+} did not interfere in the detection of nitrite. Hence the sensor is selective for nitrite and was then applied to the determination of nitrite in natural mineral spring water by the standard addition method. The results of seven replicate analyses were a mean of 4.13×10^{-7} mol dm^{-3} with an RSD of 1.3% compared with 4.09×10^{-7} mol dm^{-3} obtained by a standard spectrometric method.[38] The agreement between the two methods is satisfactory.

Renewal reproducibility and long-term stability

Compared with polyoxometalates (POMs)-modified film electrodes fabricated by conventional methods, the $SiMo_{12}$-modified CGCEs based on the sol–gel technique have certain advantages. The hydrophobic MTMOS monomer results in a controlled wetting section of the composite electrode in aqueous solutions. Hence a bulk modified electrode can be polished using emery paper and a fresh surface exposed whenever needed. This is especially useful for electrocatalytic studies since the catalytic activity is known to decrease when the electrode is fouled. Indeed, 10 successive polishings of an $SiMo_{12}$-modified CGCE resulted in an RSD of 3.5%. In addition, little leakage was found when the electrode was immersed in 0.5 mol dm^{-3} H_2SO_4 aqueous solution for 50 d.

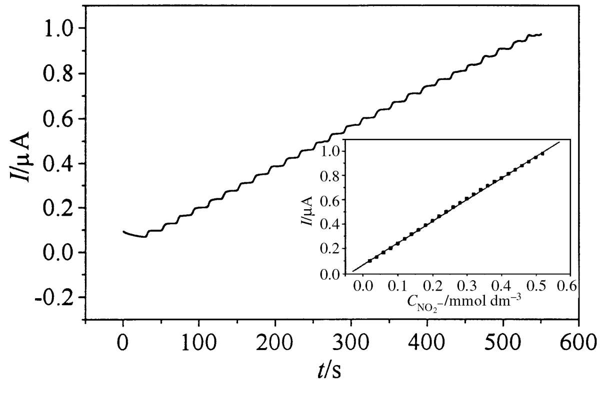

Fig. 5 Amperometric response of the $SiMo_{12}$-modified CGCE on successive additions of 20 μmol dm^{-3} nitrite to 0.5 mol dm^{-3} H_2SO_4 aqueous solution. The inset is the steady-state calibration curve for current *versus* nitrite concentration. Applied potential, +0.22 V; stirring speed, 500 rpm.

We think that the high stability of the $SiMo_{12}$-modified CGCE is related to the stability of the silicate matrix, the limited wetting section controlled by methyl groups, the strong adsorption of $SiMo_{12}$ on graphite due to the large neutral cage (Mo_nO_{3n}) with some aromatic properties[39] and the possible interactions between the doped $SiMo_{12}$ and silanol groups.

Conclusions

We have demonstrated a novel amperometric nitrite sensor based on sol–gel-derived silicomolybdate–methylsilicate–graphite composite material. The sensor exhibits good chemical and mechanical stability, excellent reproducibility and a distinct advantage of polishing in the event of surface fouling. Although the new concept has been presented in the context of $SiMo_{12}$-modified CGCEs, it could be readily extended to the construction of other three-dimensional POMs-modified CGCEs and the measurement of other environmentally important compounds.

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