Polishable Amperometric Hydrogen Peroxide Sensor Based on Sol-Gel-Derived Conductive Composite Containing Vanadium-17-molybdodiphosphate

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A new kind of conductive vanadium-17-molybdodiphosphate/graphite/methylsilicate composite was firstly prepared by the sol-gel technique and used as electrode material for the fabrication of amperometric hydrogen peroxide sensor. The remarkable advantage of the sensor is its excellent reproducibility of surface renewal by simple mechanical polishing.

It has been shown that a large variety of Keggin- and Dawson-type polyoxometalates (POMs) are efficient in the electrocatalytic reduction of NO_2^-, XO_3^- (X=Cl, Br, and I), H_2O_2, O_2, and other species.[1] However, almost all these POMs were directly used in solutions or immobilized on electrode surfaces as catalysts. A serious drawback in the application of two-dimensional POMs-modified electrodes is their poor long-term stability, moreover, electrode surfaces can not be renewed in the case of leakage, contamination, and passivation. Sol-gel is a low-temperature process that involves the hydrolysis and polycondensation of suitable precursors to form ceramic materials.[2] This has led to an intensive research in this area particularly with regard to sensing and biosensing.[3] Studies on silica-modified electrodes have increased exponentially in the last years.[4] Here we firstly prepared a kind of conductive vanadium-17-molybdodiphosphate/graphite/methylsilicate composite in silicate glass tube and used it as amperometric hydrogen peroxide sensor.

Vanadium-17-molybdodiphosphate[5] ($K_7P_2Mo_{17}VO_{62}{\cdot}24H_2O$) was synthesized according to the literature procedure and supplied by Prof. Enbo Wang (Department of Chemistry, Northeast Normal University). The content of crystal water was determined by thermogravimetric analyses to be 12.60%, and those of K, P, Mo, and V were determined by an inductively coupling plasma atomic emission spectrometer to be 7.90%, 1.82%, 47.34%, and 1.50%, respectively, which confirmed the formula of $K_7P_2Mo_{17}VO_{62}{\cdot}24H_2O$. All electrochemical measurements were carried out on a CHI 660 electrochemical workstation at room temperature (25 ± 1 °C) under argon atmosphere. A platinum plate and an Ag/AgCl (saturated KCl) electrodes were used as counter and reference electrodes, respectively. The vanadium-17-molybdodiphosphate modified electrode was prepared as follows: the solution of 0.75 mL methanol containing 5.63 mg $K_7P_2Mo_{17}VO_{62}{\cdot}xH_2O$, 0.25 mL methyltrimethoxysilane, and 0.025 mL hydrochloric acid (11 M) was ultrasonically mixed for 2 min, then 1.875 g graphite powder (average diameter, 1–2 μm) was added and shaken on a vortex agitator for an additional 3 min; the mixture was added to silicate glass tubes with 3 mm inner diameter and dried for 24 h at 30 °C; after drying, the electrodes were polished with 400-grit emery paper and the surface was swept with weighing paper; electric contact was made by silver paint through the back of the electrode.

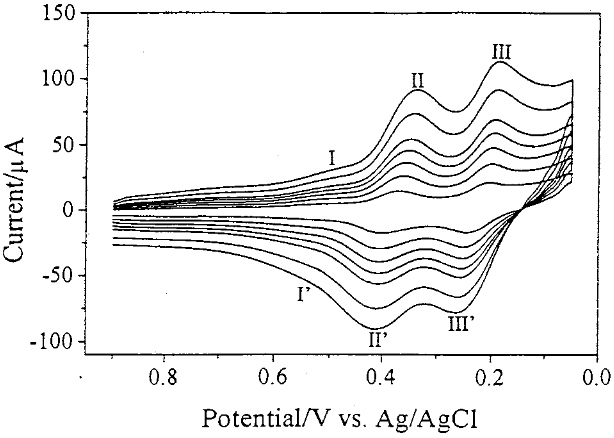

Figure 1. Cyclic voltammograms for the modified electrode in 0.5 M H_2SO_4 solution with different scan rates (from inner to outer: 20, 40, 60, 80, 100, 150, and 200 mV/s, respectively).

Figure 1 shows the typical cyclic voltammetric behavior for the sol-gel based sensor in 0.5 M H_2SO_4 solution at different scan rates. Redox peaks I-I', II-II', and III-III' correspond to reduction and oxidation through one-, two-, and two- electron processes, respectively.[5] The dependence of peak current on the scan rate (20–200 mV/s) was investigated in order to identify the type of current. The peak current was proportional to scan rate. This means that the redox current of the modified electrode is surface-controlled.

The pH effect of electrochemical behavior for the modified electrode was investigated by Osteryoung square-wave voltammetry[6] with high sensitivity. With increasing pH, the three redox formal potentials all gradually shift to the negative potential direction and peak currents also decrease. Reduction of vanadium-17-molybdodiphosphate immobilized in the methylsilicate graphite matrix is accompanied by the process of uptake of protons from solution to the wetting section of this electrode. The formal potential and current change can be explained by Nernst equation and Fick's first law,[6] respectively.

No obvious response was observed (Figure 2a) for hydrogen peroxide at glassy carbon electrode. As shown in Figure 2c–g, with the addition of hydrogen peroxide, all the three reduction peak currents increase while the corresponding oxidation peak currents decrease, suggesting that hydrogen peroxide is reduced by one-, three-, and five-electron-reduced species. It was also noted that the catalytic activity was enhanced with the extent the vanadium-17-molybdodiphosphate was reduced. Figure 3 shows the steady-state current response of the hydrogen peroxide sensor. The electrode response is linear within the concentration range from 1 to 75 mM with r = 0.9999. The

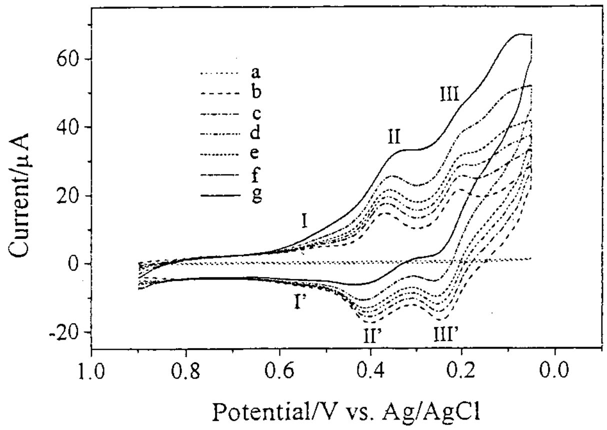

Figure 2. Cyclic voltammograms for a) the glassy carbon electrode in 0.5 M H_2SO_4+75 mM H_2O_2 and the modified electrode in 0.5 M H_2SO_4 containing b) 0, c) 10, d) 20, e) 30, f) 50, and g) 75 mM H_2O_2. Scan rate: 20 mV/s.

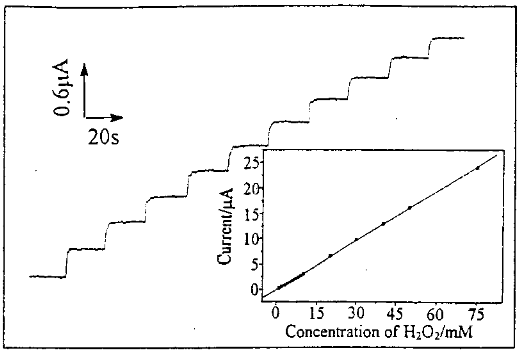

Figure 3. Amperometric response for the sol-gel-derived sensor on successive addition of H_2O_2. The inset is steady-state calibration curve for the hydrogen peroxide sensor. Conditions: 0.5 M H_2SO_4 solution; E_{appl}=+205 mV; stirring speed=500 rpm.

detection limit and slope of linear response were 0.4 mM and 324 nA/mM. The detection limit was calculated based on three times of the background current. The electrode response time was about 4 s. The rapid response is due to the limited thin wetting section controlled by methyl group and short penetration depth of hydrogen peroxide.

Compared with POMs-modified film electrodes fabricated by the conventional methods, the three-dimensional POMs-modified electrodes based on sol-gel technique have certain advantages. The hydrophobic methyltrimethoxysilane monomer results in a controlled wetting of the composite electrode in aqueous solutions. Hence, a bulk modified electrode can be polished using an 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 of a modified electrode resulted in a relative standard deviation (RSD) of 4.7%. The effective encapsulation of vanadium-17-molybdodiphosphate in the organosilicate-graphite material imparts the long term stability of the sensor. Little leakage was found when the electrode was immersed in 0.5 M H_2SO_4 aqueous solution for 20 days.

In conclusion, the methodology described here could be extended to the fabrication of other POMs-modified electrodes with smaller or larger scale, which could be used in electroanalysis and industrial electrolysis.

References and Notes

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