Hybrid Inorganic–Organic Material Containing 12-Molybdophosphate Bulk-Modified Carbon Paste Electrode

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The hybrid inorganic–organic electroactive material containing 12-molybdophosphate was synthesized and firstly used as a bulk-modifier to fabricate a chemically modified carbon paste electrode (CPE). The hybrid material bulk-modified CPE (HM-CPE) exhibits stable electrochemical behavior and good electrocatalytic activity. The remarkable advantage of the HM-CPE is its excellent reproducibility of surface renewal.

Polyoxometalates (POMs) have attracted much attention in electrode modification in the recent years owing to their excellent electrochemical and electrocatalytic properties.[1] The conventional modification methods are surface modification, including deposition, adsorption, immobilization in polymeric matrices and fabrication of monolayer and multilayer films. However, a serious drawback in the application of two-dimensional POMs-modified electrodes is their poor long-term stability, moreover, electrode surfaces cannot be renewed in the case of leakage, contamination and passivation. Sol–gel technique was used to prepare POMs bulk-modified composite electrodes in the last year.[2] In order to provide versatile modification method and meet various practical need, we explored another modification method to fabricate POMs bulk-modified electrode. The chemically modified carbon paste electrode is a mixture of a modifier, an electrically conductive graphite powder and a pasting liquid, and has been widely applied in electroanalytical chemistry owing to its many advantages: it is inexpensive, renewable, easy to handle, easy to prepare.[3] Here we designed and synthesized a hybrid inorganic–organic material containing 12-molybdophosphate: $(C_{21}H_{38}N)_3PMo_{12}O_{40}\cdot H_2O$, which is insoluble in water, ethanol and dioxane, but is soluble in acetone, above all, which is electroactive owing to the existence of the heteropolyanion $PMo_{12}O_{40}{}^{3-}$, and firstly fabricated an HM-CPE by direct mixing.

$H_3PMo_{12}O_{40}\cdot 14\ H_2O$ was synthesized according to the literature method.[4] To a solution of 30 mL ethanol containing 2.2 g (6 mmol) hexadecylpyridium chloride ($C_{21}H_{38}NCl\cdot H_2O$), 20 mL aqueous solution containing 4.2 g (2 mmol) $H_3PMo_{12}O_{40}\cdot 14\ H_2O$ was added and a yellow precipitate formed immediately. The precipitate was washed successively with water, ethanol and diethyl ether and was characterized by elemental analysis, IR and TG analysis. All electrochemical measurements were carried out on a CHI 660 electrochemical workstation at room temperature (25–30 °C) under argon atmosphere. A platinum gauze was used as counter electrode and an SCE was used as reference electrode. The HM-CPE was fabricated as follows: 1.0 g graphite powder was added to the solution of 2 mL acetone containing 30 mg $(C_{21}H_{38}N)_3PMo_{12}O_{40}\cdot H_2O$ and the mixture was ultrasonically mixed for 3 min, then allowed evaporation of acetone, which produced rather homogenously covered graphite particles; to the graphite particles 0.66 mL nujol was added and stirred with a glass rod; then the mixture was added to glass tubes with 3 mm inner diameter; electric contact was made by copper rod through the back of the electrode and the surface was swept with weighing paper.

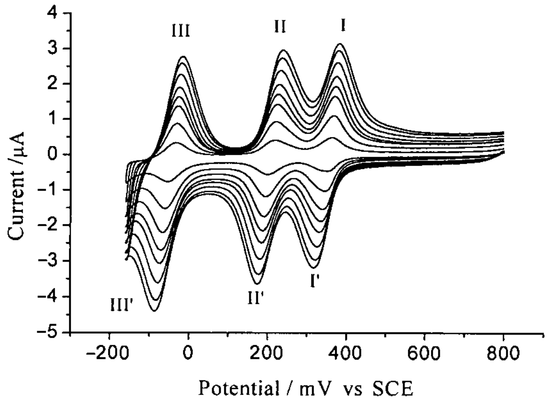

Figure 1. Cyclic voltammograms for the bulk-modified CPE in 1M H_2SO_4 solution with different scan rates (from inner to outer: 20, 50, 80, 100, 120, 150, 180, and 200 mV/s, respectively).

The typical cyclic voltammograms for three-dimensional HM-CPE (without activated treatment) in 1 M H_2SO_4 solution at different scan rates is shown in Figure 1. Redox peaks I–I', II–II' and III–III' correspond to reduction and oxidation of two-, two- and two-electron processes, respectively.[5] The peak current was proportional to scan rate, which indicates the redox process of the modified CPE is surface-controlled.

The HM-CPE possesses high stability. When the potential range is maintained at –200 to 800 mV, the peak currents almost keep unchanged over 500 cycles at a rate of 50 mV/s. After stored at room temperature for 15 days, the peak current only decreased 3% and could be renewed by squeezing a little amount of carbon paste out of the tube.

The pH of the supporting electrolyte has a marked effect on the electrochemical behavior of the modified electrode. With increasing pH, the three redox formal potentials all gradually shift to negative direction and the peak currents decrease. Plots of peak potentials of the three successive redox waves versus pH for the HM-CPE show good linearities in the pH range from 0.01 to 4.05. Slopes in this pH range are –63, –63, –65 mV/pH for the I–I', II–II' and III–III' couples, respectively, which are close to the theoretical value of –59 mV/pH for the $2e^-/2H^+$ redox process.[1] Just like the $H_3PMo_{12}O_{40}\cdot 14\ H_2O$, reduction of the hybrid material $(C_{21}H_{38}N)_3PMo_{12}O_{40}\cdot H_2O$ immobilized in the CPE is accompanied by the process of uptake of protons from solution. The formal potential and current changes can be explained by Nernst equation and Fick's first law,[6] respectively.

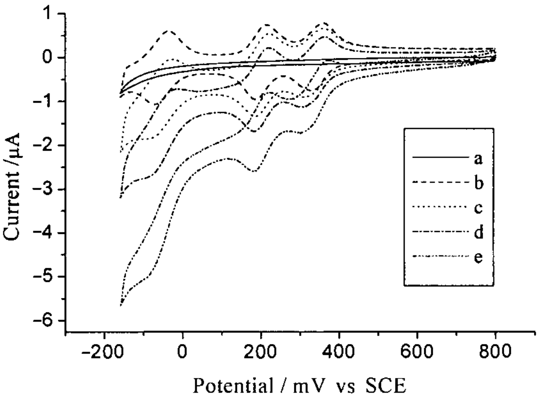

Figure 2. Cyclic voltammograms for a) the bare CPE in 1 M H_2SO_4 + 5 mM NO_2^- and the bulk-modified CPE in 1M H_2SO_4 containing b) 0, c) 1.25, d) 2.5, and e) 5 mM NO_2^-. Scan rate: 50 mV/s.

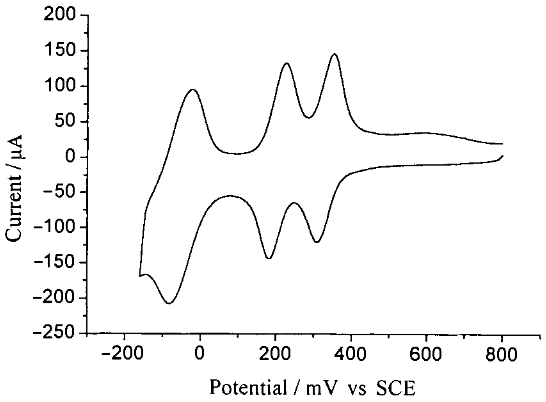

Figure 3. Cyclic voltammograms of the bulk-modified CPE in 1 M H_2SO_4 aqueous solution after activated in 50% (v/v) 1,4-dioxane + H_2SO_4 (1 M) solution for 15 min. Scan rate: 50 mV/s.

The electrocatalytic behavior of the HM-CPE toward the reduction of nitrite was shown in Figure 2. No obvious response was observed for nitrite at bare CPE. However, at the HM-CPE, with the addition of nitrite, all the three reduction peak currents increase while the corresponding oxidation peak currents decrease, suggesting that nitrite is reduced by two-, four- and six-electron-reduced species. It was also noted that the catalytic activity was enhanced with the extent the $(C_{21}H_{38}N)_3PMo_{12}O_{40}\cdot H_2O$ was reduced. The HM-CPE also shows good electrocatalytic activity toward the reduction of hydrogen peroxide and bromate.

It was noted that the cyclic voltammetric behavior of the HM-CPE in 50% (v/v) 1,4-dioxane + H_2SO_4 (1 M) solution is different from that in 1 M H_2SO_4. Initially, the peak currents continuously increase with potential scans and finally reach a steady state after 15 min. Compared with that in 1 M H_2SO_4, the peak currents increase about 150 times. The organic component hexadecylpyridium in the hybrid material probably is the reason for this phenomenon. In 1 M H_2SO_4 aqueous solution, only a little hybrid material molecules exposed on the surface of electrode, while in 50% (v/v) 1,4-dioxane + H_2SO_4 (1 M) solution, more hybrid material molecules exposed on the surface of electrode owing to the hydrophobic nature of the organic component. Figure 3 shows the cyclic voltammograms of the HM-CPE in 1 M H_2SO_4 aqueous solution after activated in 50% (v/v) 1,4-dioxane + H_2SO_4 (1 M) solution for 15 min. The peak currents of the activated HM-CPE almost keep constant over 500 cycles at a rate of 100 mV/s. The activated HM-CPE shows similar electrocatalytic activity to the unactivated HM-CPE.

Compared with POMs-modified film electrodes fabricated by the conventional methods, the three-dimensional HM-CPE has certain advantages. The organic component hexadecylpyridium in the hybrid material displayed a high affinity toward the nujol and avoided dissolution of hybrid material from the electrode surface during the measurement, which resulted in good reproducible currents and imparted the long-term stability of the modified CPE. The bulk-modified CPE can be renewed by squeezing a little amount of carbon paste out of the tube and a fresh surface exposes whenever needed. This is especially useful for the electrocatalytic study since the catalytic activity is known to decrease when the electrode is fouled.

In conclusion, the methodology described here can be extended to the fabrication of other POMs bulk-modified CPE, which can be used in electroanalysis and sensor.

References and Notes

1 M. Sadakane and E. Stechhan, *Chem. Rev.*, **98**, 219 (1998) and references therein.
2 P. Wang, X. Wang, and G. Zhu, *Chem. Lett.*, **2000,** 820.
3 a) K. Kalcber, *Electroanalysis*, **2**, 419 (1990) and references therein. b) D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **106**, 59 (1984). c) H. Tachikawa and L. R. Faulkner, *J. Am. Chem. Soc.*, **100**, 4379 (1978). d) K. Itaya and A. T. Bard, *Anal. Chem.*, **51**, 1487 (1978).
4 C. Rocchiccioli-deltcheff, M. Fournier, R. Franck, and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983).
5 a) S. Dong and Z. Jin, *J. Chem. Soc., Chem. Commun.*, **1987,** 1871. b) E. Wang, C. Hu, and L. Xu, "Polyoxometalate Chemistry," Science Press, Beijing (1997).
6 J. Wang, "Analytical Electrochemistry", VCH, New York (1994).