Inorganic-Organic Hybrid 18-Molybdodiphosphate Nanoparticles Bulk-modified Carbon Paste Electrode and Its Electrocatalysis

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A kind of inorganic-organic hybrid 18-molybdodiphosphate nanoparticles ($[(C_4H_9)_4N]_6P_2Mo_{18}O_{62}\cdot4H_2O$) was firstly used as a bulk-modifier to fabricate a three-dimensional chemically modified carbon paste electrode (CPE) by direct mixing. The electrochemical behavior of the solid nanoparticles dispersed in the CPE in acidic aqueous solution was characterized by cyclic and square-wave voltammetry. The hybrid 18-molybdodiphosphate nanoparticles bulk-modified CPE (MNP-CPE) displayed a high electrocatalytic activity towards the reduction of nitrite, bromate and hydrogen peroxide. The remarkable advantages of the MNP-CPE over the traditional polyoxometalates-modified electrodes are their excellent reproducibility of surface-renewal and high stability owing to the insolubility of the hybrid 18-molybdodiphosphate nanoparticles.

Keywords   18-molybdodiphosphate nanoparticles, inorganic-organic hybrid, chemically modified carbon paste electrode, electrochemical behavior, electrocatalytic reduction

Introduction

Polyoxometalates (POMs) are a large and rapidly growing class of compounds that generally undergo a series of consecutive one- or multi-electron reversible redox processes.[1-4] This property makes them very attractive in electrode modification. Sadakane and Steckhan[5] have presented detailed accounts of electrochemical properties and electrocatalytic applications of POMs and various procedures for the attachment of POMs onto electrode surfaces. The conventional electrode modification with POMs is surface modification, including electrodeposition, adsorption, entrapment into polymer matrices, self-assembly, layer-by-layer deposition, LB methods and sol-gel film modified electrode.[6-12] However, 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 a new kind of POMs-based material that maintains the electrochemical activity of POMs and improves the stability of conventional POMs-modified electrode, and develop a new simple and reliable procedure for surface-renewable POMs-modified electrodes. Recently, Zhu et al.[13,14] have fabricated POMs bulk-modified electrode by the sol-gel technique, which possesses a distinct advantage of reproducibility of surface-renewal. Our current interest has focused on the design and application of POMs-based inorganic-organic hybrid material in bulk-modified carbon paste electrode.[15,16]

The CPE is a mixture of an electrically conducting graphite powder and a pasting liquid, which has been widely applied in electrochemistry owing to its many advantages: it is inexpensive, easy to handle, easy to prepare, and above all, it can be used at both positive and negative potentials ranging from -1.4 to $+1.3$ V vs. the saturated calomel electrode (SCE).[17-19] Four preparative methods are used to modify carbon paste electrode: adsorption, covalent binding, dissolution in the pasting liquid and direct mixing, among which direct mixing is the most commonly used method.[17] In general, the modifiers used with direct mixing should be insoluble in the analytic solution, or they should at least strongly adsorb to

the paste components in order to avoid dissolution of the molecules from the electrode surface during the measurement. Various modifiers have been used in CPE for voltammetric analysis, including ion exchangers and absorbents; organic reagents for complexation, salt formation or covalent binding; inorganic and organic catalytic modifiers; biological modifiers and other modifiers.[17] Inorganic catalytic modifiers are mainly phthalocyanine, porphyrine and phenanthroline complexes.[20-24] To our knowledge, POMs and POMs-based material have not been used as catalytic modifiers in CPE.

Inorganic-organic hybrid POMs nanoparticles are insoluble in aqueous solution, whose electrochemical behavior and electrocatalytic activity have not been reported to our knowledge. In this paper, we employed an inorganic-organic hybrid 18-molybdodiphosphate nanoparticles as solid modifier to fabricate a bulk-modified CPE by direct mixing, and firstly described the electrochemical behavior of the MNP-CPE in H_2SO_4(1 mol/L) aqueous solution. The pH effect of the supporting electrolyte on the electrochemical behavior of the nanoparticles has been studied by square-wave voltammetry. The electrocatalytic behavior of the immobilized hybrid 18-molybdodiphosphate nanoparticles toward the reduction of nitrite, bromate and hydrogen peroxide was investigated, too. The MNP-CPE displays a distinct advantage of reproducibility of surface-renewal in the case of contamination and passivation, as well as long-term stability owing to the insolubility of hybrid nanoparticles.

Experimental

Materials and solutions

High purity graphite powder (average particle 1—2 μm) was obtained from Aldrich. $H_6P_2Mo_{18}O_{62} \cdot 14H_2O$ (P_2Mo_{18}) was synthesized according to the reported method[25] and was characterized by IR, elemental analysis and TG. $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles were prepared following our earlier work[26] and characterized by elemental analysis, TEM, IR and XRD. TEM image was shown in Fig. 1. Nujol and $(C_4H_9)_4NBr$ (reagent grade) were purchased from Beijing Chemical Plant and used as received. Other chemicals were of analytical grade and used without further purification.
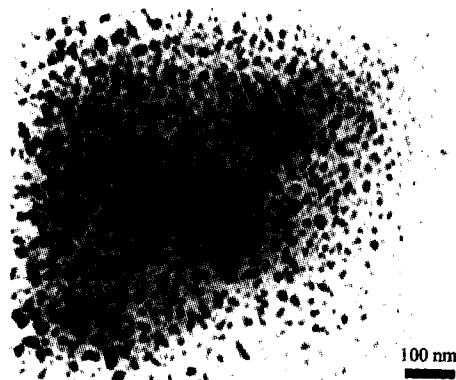

Fig. 1   TEM image of the $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles.

Thrice-distilled water was used throughout the experiments. Solutions with different pH were prepared by mixing the Na_2SO_4 (0.2 mol/L) aqueous solution with Na_2SO_4 (0.1 mol/L) + H_2SO_4 (0.5 mol/L) aqueous solution. Solutions were deaerated by pure argon bubbling prior to the experiments and the electrochemical cell was kept under an argon atmosphere throughout the experiment.

Apparatus

A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for the electrochemical measurements. A conventional three-electrode cell was used, consisting of a MNP-CPE or a bare CPE as the working electrode, a saturated calomel reference electrode and a Pt gauze counter electrode. All potentials were measured and reported vs. SCE. A pHS-25B type pH meter was used for pH measurement. All the experiments were conducted at room temperature (25—30 ℃).

Fabrication of the MNP-CPE and the bare CPE

The MNP-CPE was fabricated as follows: 1.0 g of graphite powder and 50 mg of $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles were mixed and ground together by agate mortar and pestle for approximately 20 min to achieve an even, dry mixture. To the mixture 0.66 mL of nujol was added and stirred with a glass rod, then the homogenized mixture was used to pack 3 mm inner diameter glass tubes to a length of 0.8 cm from one of their ends. In ad-

dition, a little extra mixture was retained on the top of the electrodes, and the mixture in the tubes was pressed lightly on smooth plastic paper with a copper stick through the back. The electrical contact was established with the copper stick. The bare CPE was fabricated using the same procedure as described above except that the modifier was not added. The surface of the CPE was wiped with weighing paper.

Results and discussion

Electrochemical behavior of the MNP-CPE

Considering that $P_2Mo_{18}O_{62}^{6-}$ anion is unstable in neutral and basic aqueous solution and undergoes a series of hydrolysis processes,[27,28] electrochemical studies of the MNP-CPE were carried out in acidic aqueous solutions.

Fig. 2 shows the cyclic voltammograms of the bare CPE and MNP-CPE in H_2SO_4 (1 mol/L) solution, respectively. It can be clearly seen that in the potential range of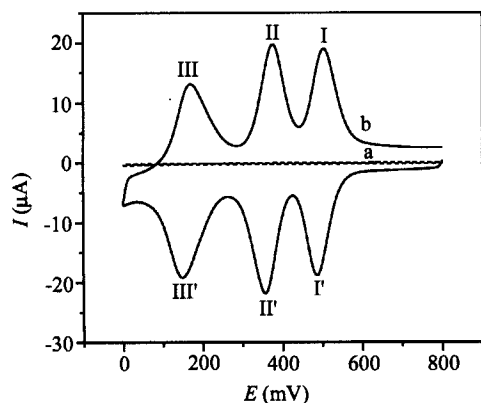 +800 to 0 mV, no redox peak at the bare CPE is observed (a), while at the MNP-CPE, three couples of reversible redox peaks appear (b). The mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are +495 mV (I), +367 mV (II) and +161 mV (III) vs. SCE, respectively. The shape of the redox peak and the peak potentials were similar to that of $P_2Mo_{18}O_{62}^{6-}$ anions modified electrodes. So the redox peaks I-I', II-II' and III-III' correspond to reduction and oxidation of $P_2Mo_{18}O_{62}^{6-}$ through two-, four- and six-electron processes, respectively.[5,27,28] The values of peak-to-peak separation between

the corresponding anodic and cathodic peaks (ΔE_p) at the MNP-CPE for the peak I-I', II-II' and III-III' are 16, 20 and 20 mV, respectively, instead of value of zero expected for a reversible surface redox process, which might be due to non-ideal reversible behavior.[29,30] Thus the surface coverage of electroactive species, Γ_c, can be approximately calculated by the following equation:[29,30]

$$Q = nFA\Gamma_c$$

Where Q is the background corrected charge, A is the electrode geometric surface area, and the other symbols have their usual meanings ($n = 6$). The total area under the three reduction peaks at the scan rate of 50 mV/s corresponds to ca. 1.8×10^{-9} mol/cm² of a reactant. The small peak separation indicates fast electron transfer to redox active species. In addition, if the amount of $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles is decreased, the resulting electrodes present cyclic voltammograms with smaller peak currents compared with that of the MNP-CPE described above.

Fig. 3A presents the cyclic voltammograms of the MNP-CPE at different scan rates in the potential rang of 0—800 mV in H_2SO_4(1 mol/L) solution, and the plots of peak current versus scan rates are shown in Fig. 3B. When the scan rate was varied from 20 mV/s to 400 mV/s, the cathodic peak currents were almost the same as the corresponding anodic peak currents. At scan rates lower than 150 mV/s, the peak currents were proportional to the scan rate, i.e., $i \propto v$, suggesting that the redox process is surface-confined; however, at scan rates higher than 150 mV/s, the relation between the peak current and scan rate gradually deviated from $i \propto v$ linear relation and was gradually close to $i \propto v^{1/2}$, which indicated the redox process was close to diffusion-controlled process. This is because at slow scan rate the inside molecules of nanoparticles can be fully utilized, which results in surface-controlled process, while at rapid scan rate the property of slower diffusion of nanoparticles is dominant, which makes the process become diffusion-controlled. In addition, with the increasing of scan rates, the value of peak-to-peak separation of anodic and cathodic (ΔE_p) gradually increases, which is different from $P_2Mo_{18}O_{62}^{6-}$ anions modified film electrodes. This is probably because the nanoparticles are solid and the electron exchanging rate between graphite and the nanoparticles is decreased to some extent.
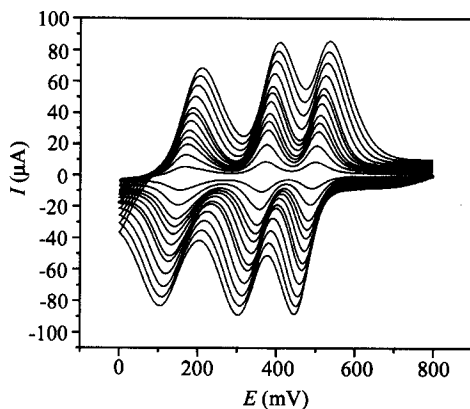

Fig. 2 Cyclic voltammograms of (a) the bare CPE and (b) the MNP-CPE in H_2SO_4 (1 mol/L) at a scan rate of 50 mV/s.

Fig. 3A Cyclic voltammograms of the MNP-CPE in H_2SO_4 (1 mol/L) at different scan rates (from inner to outer: 20, 50, 80, 100, 120, 150, 180, 200, 250, 300, 350 and 400 mV/s).
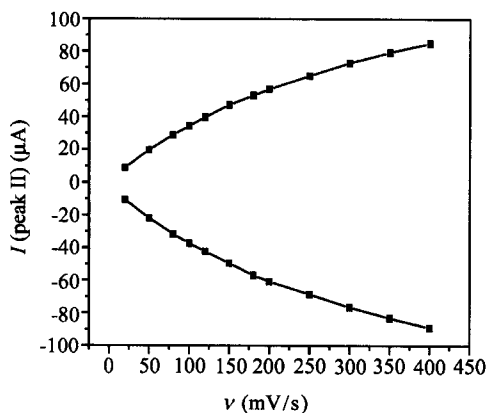

Fig. 3B Dependence of peak II current on scan rates.

Effect of pH *on the electrochemical behavior of the* MNP-CPE

In order to study the pH-dependent electrochemical behavior of the MNP-CPE, square-wave voltammetry with excellent sensitivity was adopted to measure accurately the formal potentials. Fig. 4A shows square-wave voltammograms for the MNP-CPE in Na_2SO_4 (0.2 mol/L) aqueous solution with different pH. It can be clearly seen that with an increase of pH, the three redox potentials all gradually shift to the more negative potential direction and the peak currents gradually decrease. Upon addition of H^+ to make the solution pH equivalent to that of H_2SO_4 (1 mol/L) again, the original I-E behavior is restored. Reduction of hybrid $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles is similar to that of $H_6P_2Mo_{18}O_{62}$ solution itself and is accompanied by the transport of protons from solution to the nanoparticles of the electrodes surface to maintain charge

neutrality. Along with increasing pH, decrease of H^+ concentration should be the reason for the current decrease according to the following Eqs. (1)—(3), and the more negative reduction potentials can be elucidated using the Nernst Eqs.[30,31] Plots of peak potentials of the three successive redox waves versus pH for the MNP-CPE were all linear in the pH range from 0.01 to 4.21, as shown in Fig. 4B. Slopes in this pH range are − 67,
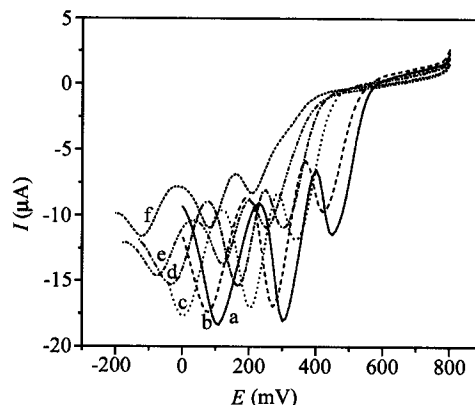

Fig. 4A Square-wave voltammograms for the MNP-CPE in Na_2SO_4 (0.2 mol/L) + H_2SO_4 (0.5 mol/L) solution with different pH: (a) 0.65; (b) 1.01; (c) 2.02; (d) 2.55; (e) 3.30; (f) 4.21. Increment: 10 mV; frequency: 10 Hz.
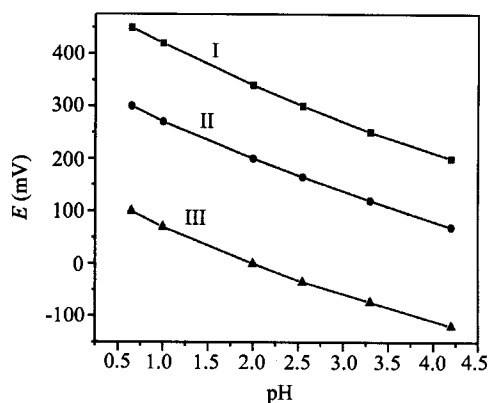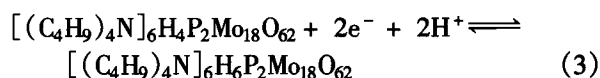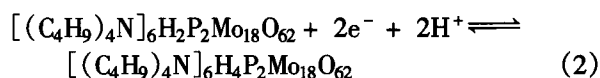

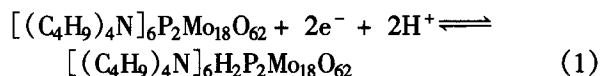**Fig. 4B** Relationship between peak potentials and pH. I, II and III are the first, second and third reduction peak of MNP-CPE, respectively.

− 65 and − 64 mV/pH for the I-I′, II-II′ and III-III′ couples, respectively, which are close to the theoretical value − 59 mV/pH for the $2e^-/2H^+$ redox process at the experimental temperature. The electrochemical reaction of the MNP-CPE can be expressed as follows [Eqs. (1)—(3)]:

$$[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} + 2e^- + 2H^+ \rightleftharpoons$$
$$[(C_4H_9)_4N]_6H_2P_2Mo_{18}O_{62} \qquad (1)$$

$$[(C_4H_9)_4N]_6H_2P_2Mo_{18}O_{62} + 2e^- + 2H^+ \rightleftharpoons$$
$$[(C_4H_9)_4N]_6H_4P_2Mo_{18}O_{62} \qquad (2)$$

$$[(C_4H_9)_4N]_6H_4P_2Mo_{18}O_{62} + 2e^- + 2H^+ \rightleftharpoons$$
$$[(C_4H_9)_4N]_6H_6P_2Mo_{18}O_{62} \qquad (3)$$

Electrocatalytic activity of the MNP-CPE

In H_2SO_4 (1 mol/L) solution, nitrite, bromate and hydrogen peroxide have no responses on bare CPE in the range of 0—800 mV (vs. SCE), because the direct electroreduction of these compounds requires a large overpotential. It has been shown that a variety of POMs and mixed-valence molybdenum, tungsten species are efficient in the electrocatalytic reduction of these compounds.[5,32-36] But in previous studies, all the catalysts used in the electroreduction are soluble POMs anions in solution or immobilized on the surface of electrode. So far the report of electrocatalytic reduction of these compounds with insoluble solid POMs nanoparticles was not found. In this article, we firstly investigated the electrocatalytic reduction of these compounds with solid inorganic-organic hybrid $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles bulk-modified in CPE.

Fig. 5 shows cyclic voltammograms for the electrocatalytic reduction of nitrite at a bare CPE and nitrite at the MNP-CPE. No obvious voltammetric response is observed in the potential range from + 800 to 0 mV for nitrite at the bare CPE. With the MNP-CPE, after the addition of nitrite, all 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 has been noted that the six-electron-reduced species has the largest catalytic activity toward the reduction of nitrite. That is to say, the catalytic activity of the $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles toward nitrite reduction increases with the extent that $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles is reduced. In the current experiment high scan rate (50 mV/s) has been used to register the electrocatalytic reduction of nitrite and obtained noticeable catalytic currents, which indicated the reduction of nitrite at the MNP-CPE was fast. Papaconstantinou *et al*.[37] have reported the electrocatalytic behavior of $P_2Mo_{18}O_{62}{}^-$ immobilized in polymeric

matrices on the surface of wax impregnated graphite electrodes (P_2Mo_{18}-WIGE) and the relation between the catalytic current and nitrite concentration is about 7.5 μA per mmol/L nitrite.[37] It is noticeable that at the MNP-CPE the relation between the catalytic current and nitrite concentration is about 35 μA per mmol/L nitrite, which indicates the MNP-CPE shows high electrocatalytic activity toward the reduction of nitrite. The MNP-CPE also shows good catalytic activity toward the reduction of bromate and hydrogen peroxide, as shown in Figs. 6 and 7. It can be clearly seen that two-, four- and six-electron-reduced species all have catalytic activity toward the reduction of bromate and hydrogen peroxide unlike other POM-modified electrodes where only the four- and six-
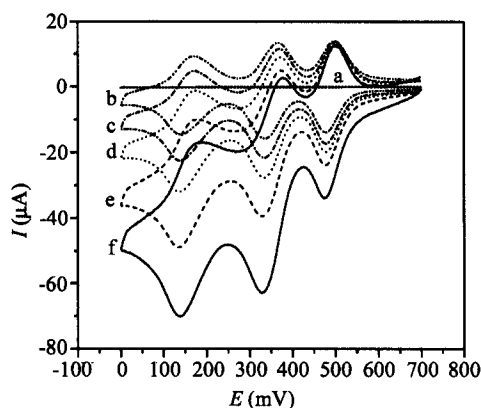

Fig. 5 Cyclic voltammograms of a bare CPE in the $NaNO_2$ (5 mmol/L) + H_2SO_4 (1 mol/L) solution (a) and a MNP-CPE in H_2SO_4 (1 mol/L) containing $NO_2{}^-$ concentrations of 0.0 (b); 0.25 (c); 0.5 (d); 1.0 (e); 1.75 (f) mmol/L. Scan rate: 50 mV/s.
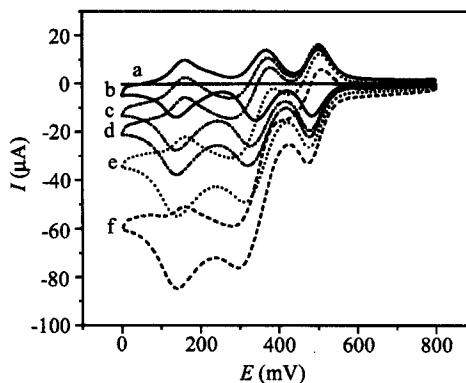

Fig. 6 Cyclic voltammograms of a bare CPE in the $NaBrO_3$ (5 mmol/L) + H_2SO_4 (1 mol/L) solution (a) and a MNP-CPE in H_2SO_4 (1 mol/L) containing $BrO_3{}^-$ concentrations of 0.0 (b); 0.375 (c); 0.75 (d); 1.5 (e); 3.0 (f) mmol/L. Scan rate: 50 mV/s.

electron-reduced species have electrocatalytic activity,[5,12] which is consistent with Zhu *et al.*'s report.[14] The scan rate is also 50 mV/s indicating the reduction of bromate and hydrogen peroxide at the MNP-CPE is fast, too. It is also noticeable that the relation between the catalytic current and bromate concentration is about 26 μA per mmol/ L bromate at the MNP-CPE, which is much higher than that at the P_2Mo_{18}-WIGE (about 5.5 μA per mmol/L bromate).[37] Compared with P_2Mo_{18}-WIGE, advantage of the MNP-CPE in the electrocatalysis is that the electrode surface can be renewed by means of squeezing a little carbon paste out of tube in the case of contamination.
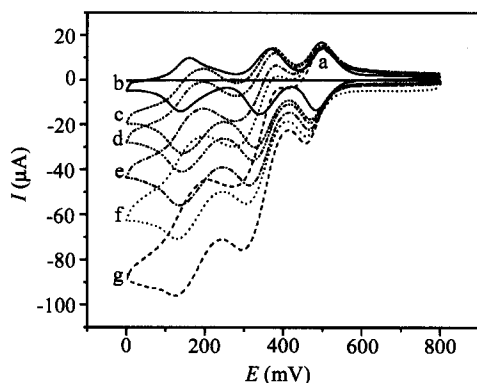

Fig. 7   Cyclic voltammograms of a bare CPE in the H_2O_2 (5 mmol/L) + H_2SO_4 (1 mol/L) solution (a) and the MNP-CPE in H_2SO_4 (1 mol/L) containing H_2O_2 concentrations of 0.0 (b); 4 (c); 6 (d); 10 (e); 15 (f); 22 (g) mmol/L. Scan rate: 50 mV/s.

Repeatability of surface-renewal and long-term stability

Compared with POMs-modified film electrodes fabricated by conventional methods, the three-dimensional $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles bulk-modified CPE has certain advantages. One of the main attractions of using the bulk-modified electrode is that the electrode surface can be renewed after every use. A fresh surface can be exposed by means of squeezing a little carbon paste out of tube whenever needed. This is especially useful for electrocatalytic study since the catalytic activity is known to decrease when the electrode is fouled. Indeed, ten successive surface-renewal resulted in a relative standard deviation (RSD) of 5.5% for the hybrid 18-molybdodiphosphate nanoparticles bulk-modified CPE.

Keita and Nadjo[38] have reported that entrapment of heteropolyanion (HPA) in poly(4-vinylpyridine) matrices

(PVP) on electrode surface resulted in new materials with remarkable stability, which is ascribed primarily to the insolubility of the HPA/PVP system. In this paper, we found the hybrid insoluble $[(C_4H_9)_4N]_6P_2Mo_{18}O_{62} \cdot 4H_2O$ nanoparticles bulk-modified in the CPE also presented remarkable stability. In our initial experiment, $H_6P_2Mo_{18}$-$O_{62} \cdot 14H_2O$ (P_2Mo_{18}) was used as a modifier to fabricate bulk-modified CPE. When the P_2Mo_{18}-CPE was continuously scanned in H_2SO_4 (1 mol/L) aqueous solution in the potential range from + 800 mV to 0 mV for 30 min, the peak current decreased by 8%. Dissolution of P_2Mo_{18} from the electrode surface resulted in the significant bleeding of the modifier. While the MNP-CPE was continuously scanned at the same conditions for 6 h, the peak currents only decreased by 6%. When the MNP-CPE was stored at room temperature for two months, the current only decreased by 3% and could be renewed by squeezing a little carbon paste out of tube. The high stability of the hybrid POMs nanoparticles bulk-modified CPE can be mainly attributed to insolubility of the hybrid nanoparticles, which is consistent with Keita's report.[38] In addition, the hybrid nanoparticles dispersed in the carbon paste cannot aggregate and also imparts the long-term stability of the MNP-CPE.

Conclusions

Inorganic-organic hybrid POMs nanoparticles were bulk-modified in the CPE by direct mixing, which were exemplified here by the 18-molybdodiphosphate nanoparticles bulk-modified CPE. Three couples of reversible redox waves were observed in acidic solution, which corresponded to two-, four- and six-electron redox process, respectively. The pH of electrolyte had a marked effect on the electrochemical behavior of the MNP-CPE. The MNP-CPE shows very good electrocatalytic activity toward the reduction of nitrite, bromate and hydrogen peroxide in acidic solution. Above all, the MNP-CPE exhibits distinct advantage of surface-renewal in the event of surface fouling and long-term high stability owing to the insolubility of the hybrid nanoparticles. In addition, the methodology described here can be extended the electrochemical study of other electroactive nanoparticles and fabrication of other nanoparticles bulk-modified CPE, which can be used in electroanalysis and sensor.

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