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ORIGINAL PAPER

Electrochemical behavior of an inorganic–organic hybrid based on isopolymolybdate anions and ethylenediamine

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Abstract The one-dimensional inorganic–organic compound, $(C_2H_{10}N_2)[Mo_3O_{10}]$, was synthesized hydrothermally, and characterized by single crystal X-ray diffraction. The compound was used as a bulk-modifier to fabricate a renewable three-dimensional chemically modified carbon paste electrode (Mo-CPE) by direct mixing. The electrochemical properties of $(C_2H_{10}N_2)[Mo_3O_{10}]$-modified Mo-CPE were investigated with respect to their pH-dependence, stability and electrocatalytic activity. The hybrid material bulk modified Mo-CPE not only displays good electrocatalytic activity toward the reduction of BrO_3^-, IO_3^-, NO_2^- and H_2O_2, but also exhibits good stability and multiple repeatability by simply polishing on the surface of a wet filter paper, a feature which is important for practical applications.

Keywords Carbon paste electrode · Electrochemistry · Electrocatalysis · Inorganic–organic hybrid

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1 Introduction

Transition metal polyoxometalates (POMs) represent a well-known class of structurally well-defined clusters with an enormous variation in size, metal-oxygen framework topology, composition and properties. Thus, they have attracted much attention for their applications in many fields of science such as medicine [1], biology [2], catalysis [3] and advanced materials [4]. Also, polyoxometalates possess superacid acidity, strong oxidizability, and exhibit fast reversible multiple electron redox transformations under rather mild conditions and high stability of most of their redox states [5–7] which make them very useful in the preparation of modified electrodes. The hybrid materials of POMs with organic or biochemical substances can combine both inorganic and organic qualities, possessing new synergistic properties and diverse applications in photo- and electro-chromism, magnetism, catalysis and medicine [8–17]. Therefore, the design of new kinds of hybrid materials containing both POMs and organic subunits and the development of their beneficial properties can be investigated for both fundamental and applied chemistry.

Carbon paste electrodes (CPEs) have attracted increasing attention since they were used by Adams in 1958 [18]. The most significant benefit of using CPEs is the simple and effective renewal of their surface, low cost, and ease of preparation [19–21]. They also give the possibility of controlling the electrochemical properties by varying the selection of the main constituents and of their ratios on the carbon paste electrode [22, 23]. Recent research interest has focussed on the preparation of insoluble inorganic–organic hybrid POMs and their application in electrode modification [24–29], especially in carbon paste electrodes [30–34], because inorganic–organic hybrid POMs modified CPE supply a wide range of solubility for POMs.

POMs containing molybdenum possess excellent electrocatalytic activity [35, 36]. Han and co-workers [37] studied the electrochemical behavior of $(pbpy)_4H[PMo_{12}O_{40}(VO)]$ and $(pbpy)_4H_4[SiMo_{12}O_{40}]$ via modified CPEs. $[Ru(bpy)_3]_3[PMo_{12}O_{40}]_2 \cdot 4H_2O$ [38], $(C_{21}H_{38}N)_3PMo_{12}O_{40} \cdot H_2O$ [39] also reveal the remarkable advantage of CPE for insoluble hybrid materials. In this work, we synthesized the inorganic–organic compound, $(C_2H_{10}N_2)[Mo_3O_{10}]$, which is electroactive owing to the existence of Mo_3O_{10}, and fabricated a three dimensional chemically modified CPE with the compound by direct mixing. Moreover, the electrochemical behavior and electrocatalytic properties of modified Mo-CPE were studied by cyclic voltammetry.

2 Experimental

2.1 General

The reagents used were commercially obtained, were of analytical grade purity and used without further purification. Electrochemical experiments were performed with a CHI 660 Electrochemical Workstation in a conventional three-electrode electrochemical cell using CPE as the working electrode, twisted platinum wire as the auxiliary electrode, and a Ag/AgCl reference electrode in aqueous media. The carbon paste was renewed mechanically after each measurement by smoothing and polishing the surface layer with a wet filter paper.

2.2 Hydrothermal synthesis of $(C_2H_{10}N_2)[Mo_3O_{10}]$ and fabrication of $(C_2H_{10}N_2)[Mo_3O_{10}]$-CPE

The compound was synthesized under mild hydrothermal conditions and autogenous pressure. A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.0438 g), ethylenediamine (0.0775 g), was dissolved in 18 mL of water with stirring, and H_3PO_4 was added in small portions to this mixture to adjust the pH value. Then the mixture was transferred and sealed into a 20 mL Teflon-lined stainless steel autoclave and heated to 443 K for 5 days. Colorless, transparent crystals were separated by filtration, washed with water and dried in air.

The Mo-CPE was fabricated as follows: 0.5 g graphite powder and 0.03 g $(C_2H_{10}N_2)[Mo_3O_{10}]$ were mixed and ground together by agate mortar and pestle to achieve an even, dry mixture, to which mixture 0.05 mL paraffin oil was added and mixed; then the mixture was used to pack a 3 mm inner diameter glass tube. The surface was pressed tightly onto weighing paper with a copper rod through the back.

3 Results and discussion

3.1 Crystal character

The crystals were characterized by X-ray single-crystal analysis. The results revealed that the compound is a one-dimensional polymer constructed of chains of MoO_6 octahedra and layers of ethylenediamine molecules, which is coincidentally the same as that reported previously [40]. The MoO_6 octahedra are linked by sharing one edge or face with parallel octahedra and one corner up or down octahedra into a 1D chain structure running along the direction of the axis. Between adjacent inorganic chains of MoO_6 octahedra, organic ethylenediamine molecules are located. The structure may be described as stacks of parallel chains of MoO_6 clusters with organic ligands sandwiched between the chains (Fig. 1). There are extensive hydrogen bonding interactions between inorganic anions and organic ligands based on the short distance of N–H···O (2.2445–3.2118 Å). The product is highly insoluble in water and common organic solvents.

3.2 Electrochemical behavior of the Mo-CPE

Figure 2 presents the cyclic voltammetric behavior of Mo-CPE at different scan rates in pH 2.37 H_2SO_4–$NaSO_4$ buffer solution. In the potential range −0.45 to 0.75 V, with the scan rate varying from 0.1 to 1.0 V s^{-1}, the current for the four reversible redox peaks increased gradually and the peak potentials were almost unchanged. Plots of peak current of the successive redox waves versus scan rate show good linearity (see inset), indicating the redox process of Mo-CPE is surface-controlled.

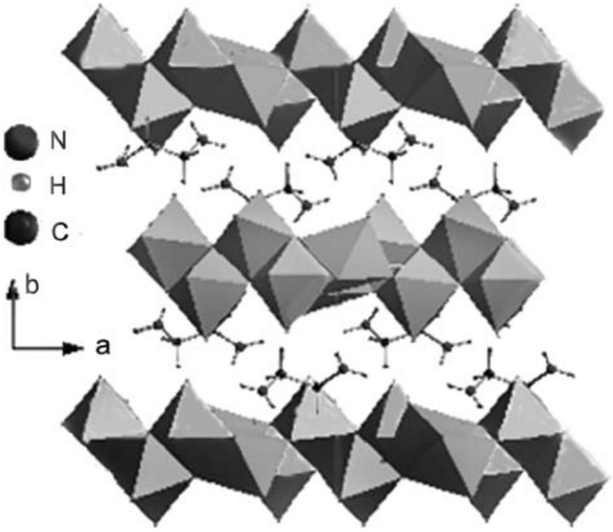

Fig. 1 A packing drawing of $(C_2H_{10}N_2)[Mo_3O_{10}]$ showing that the chains of inorganic anions and organic molecules array alternately

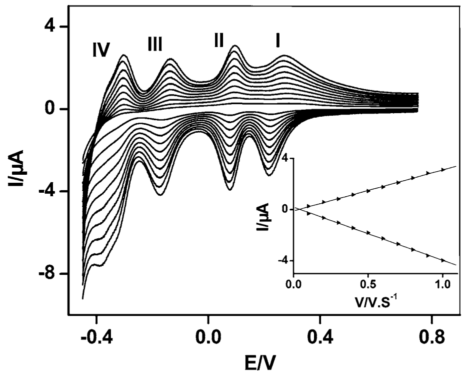

Fig. 2 Cyclic voltammograms for Mo-CPE in pH 2.37 buffer solution at different scan rates (from *inner* to *outer*): 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 V s^{-1}. The *inset* shows plots of the anodic and the cathodic peak currents for II against scan rates

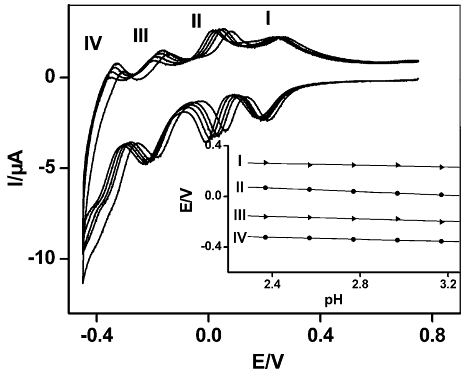

Fig. 3 Cyclic voltammograms for Mo-CPE in $Na_2SO_4 + H_2SO_4$ buffer solution with different pH values (from *left* to *right*): 2.37, 2.57, 2.77, 2.97 and 3.17. The *inset* the relationship between peak potentials of the four redox waves and pH

In general, the reduction of polyoxomentalate anions is accompanied by protonation. Figure 3 shows the cyclic voltammograms for the Mo-CPE in buffer solution at different pH values. With increasing pH, the peak potentials for four redox couples shifted negatively and the shapes of the redox peaks remained unchanged. The inset shows E_f versus pH lines. The lines have different slopes for the four redox couples: 34 mV for wave I, 70 mV for wave II, 60 mV for wave III, 52 mV for wave IV, suggesting that different levels of protonation accompany these redox reactions.

3.3 Electrocatalytic activities

The importance of POMs in the development of chemically modified electrodes has been recognized in recent years owing to their excellent electrochemical, electrocatalytic properties and thermal stability [5]. $(C_2H_{10}N_2)[Mo_3O_{10}]$ was predicted to provide heterogeneous electrocatalysis. We investigated the electrocatalytic reduction of four substrates of analytical interests, BrO_3^-, IO_3^-, NO_2^- and

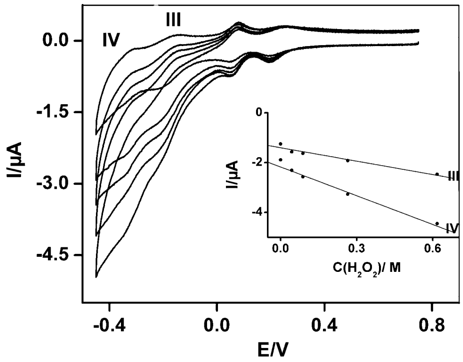

Fig. 4 Reduction of hydrogen peroxide at Mo-CPE in pH 2.37 buffer solution containing H_2O_2 in various concentrations (from *outer* to *inner*): 0, 0.044, 0.088 and 0.2646, 0.617 M. Scan rate: 0.5 V s^{-1}. The *inset* shows relationship between the fourth cathodic current and concentration of H_2O_2

H_2O_2 by Mo-CPE. In the present experiments, Mo-CPE showed high catalytic response towards the reduction of the four substrates.

3.3.1 *Electrocatalytic activity of Mo-CPE for the reduction of H_2O_2*

Figure 4 shows the cyclic voltammograms of the Mo-CPE in a pH 2.37 aqueous buffered solution in the absence and presence of H_2O_2, with the addition of hydrogen peroxide, for the redox couples at −0.31 V and −0.14 V. The cathodic peak currents increased while the corresponding anodic peak currents decreased; the other two cathodic peak currents of the Mo-CPE redox couple at 0.26, 0.08 V were almost unchanged. These results indicate that the waves III and IV posses good electrocatalytic activity for H_2O_2, suggesting that Mo-CPE is promising for use as a hydrogen peroxide sensor.

3.3.2 *Electrocatalytic activity of Mo-CPE for the reduction of NO_2^-*

Figure 5 shows the cyclic voltammograms of Mo-CPE at a scan rate 0.5 V s^{-1} in acid solution containing nitrite. As the amount of nitrite accumulated, the cathodic peak current of the latter three peaks increased, while the corresponding anodic peak current decreased, which is different from the reduction of hydrogen peroxide. The results suggest that nitrite was reduced in multiple steps by a reduced species of $(C_2H_{10}N_2)[Mo_3O_{10}]$.

3.3.3 *Electrocatalytic activity of Mo-CPE for the reduction of BrO_3^- and IO_3^-*

The cyclic voltammograms of Mo-CPE in the pH 2.37 buffer solution in the absence and presence of BrO_3^- and

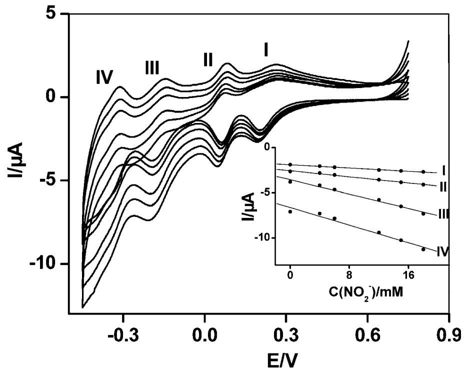

Fig. 5 Reduction of nitrite at Mo-CPE in pH 2.37 buffer solution containing NO_2^- in various concentrations (from *outer* to *inner*): 0, 4, 6, 12, 15, 18 mM. Scan rate: 0.5 V s^{-1}. The *inset* shows the relationship between the four cathodic current and concentration of NO_2^-

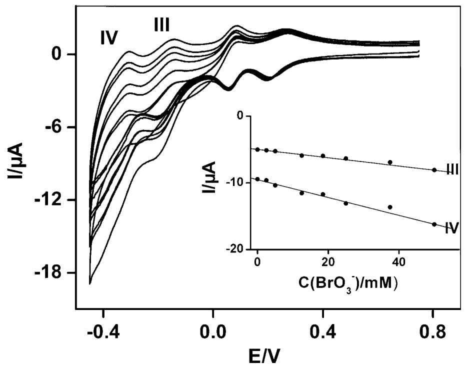

Fig. 6 Reduction of bromate at Mo-CPE in pH 2.37 buffer solution (from *outer* to *inner*): 0, 2.5, 5.0, 12.5, 18.5, 25.0, 37.5, 50 mM. Scan rate: 0.5 V s^{-1}

IO_3^- are shown in Figs. 6 and 7, respectively. The electroreduction of bromate and iodate requires a large overpotential. No obvious response was observed under the conditions used below for the Mo-CPE. It can be seen from Figs. 6 and 7 that the catalytic waves appear at the third and fourth redox waves of Mo-CPE, while peaks I and II are almost unaffected by the addition of bromate and iodate. These results indicate that Mo-CPE exhibits electrocatalytic activity towards the reduction of BrO_3^- and IO_3^-.

The carbon paste electrode surfaces were renewed by extruding approx. 0.5 mm of carbon paste from the holder and subsequently smoothing on wet filter paper. Typically, this mechanical renewal was made before starting a new set of experiments. When cyclic voltammetry was performed at different scan cycles, the peak currents were almost unchanged up to at least 500 cycles, indicating that this CPE is very stable.

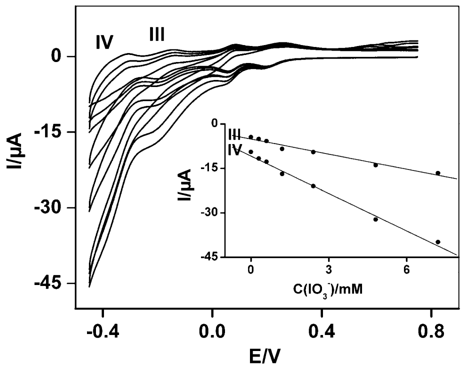

Fig. 7 Cyclic voltammograms for Mo-CPE in $Na_2SO_4 + H_2SO_4$ buffer solution (pH 2.37) containing IO_3^- in various concentrations (from *outer* to *inner*): 0, 2.5, 5.0, 12.5, 18.5, 25.0, 37.5, 50 mM. The *inset* shows a linear dependence of the third and fourth cathodic peaks

As a measure of the efficiency of this electrode for electrochemical reduction, the catalytic efficiency was calculated as defined by the equation [41]:

$$\mathrm{CAT} = 100\% \times \left[\mathrm{I_p(POM, substrate)} - \mathrm{I_p(POM)}\right]/\mathrm{I_p(POM)}$$

where I_p(POM, substrate) and I_p(POM) are the peak currents for the reduction of the POM with and without the presence of substrate (NO_2^-, BrO_3^-, etc.), respectively. To make a comparison between the Mo-CPE in this study and Mo-based POM hybrids from another study, the catalytic efficiencies are compared in Table 1. PANI $SiMo_{12}$ and P_2Mo_{18} are modified electrodes consisting of the polymolybdate supported on a polyaniline (PANI) matrix [41]. The I_p values were obtained from the insets of Figs. 2, 3, 4, 5, 6, 7 of wave IV at a scan rate of 0.5 V s^{-1}.

As seen in Table 1 the catalytic efficiency for the Mo-CPE is comparable to similar molybdenum-based modified electrodes, at least for the reduction of nitrite.

4 Conclusion

The inorganic–organic hybrid polyoxometalate based on Mo_3O_{10} and $C_2H_{10}N_2$ was used as a solid bulk modifier to fabricate a three-dimensional bulk-modified carbon paste electrode (Mo-CPE) by direct mixing. The inorganic–organic hybrid, $(C_2H_{10}N_2)[Mo_3O_{10}]$, being insoluble in water and common organic solvents, avoids bleeding of the modifier which makes the Mo-CPE modified electrode remarkably stable. The Mo-CPE modified electrode depends on pH as a result of protonation, and can catalyze the reduction of BrO_3^-, IO_3^-, NO_2^-, H_2O_2. It is expected to have potential applications in the fields of sensors, electron transfer and electrocatalysis.

Table 1 Catalytic efficiencies of the modified electrode used in this study and comparison to related modified electrodes

Substrate	CAT of Mo-CPE (conc. substrate)	CAT of PANI $SiMo_{12}$ (conc. substrate)	CAT of PANI P_2Mo_{18} [41] (conc. substrate)
NO_2^-	200% (18 mM)	120% (10 mM) [41]	64% (5 mM) [41]
BrO_3^-	325% (50 mM)	184% (10 mM) [42]	40% (5 Mm) [43]
IO_3^-	825% (50 mM)	433% (0.3 mM) [44]	455% (2 mM) [43]

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