Inorganic–organic hybrid polyoxometalate containing supramolecular helical chains: Preparation, characterization and application in chemically bulk-modified electrode

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Abstract

An inorganic–organic hybrid polyoxometalate (POM) (Hbpy)₄[SiMo₁₂O₄₀]₁⁺ (bpy = 2,4-bipyridine), has been prepared and characterized. X-ray diffraction study reveals that compound 1 contains interesting organic double helical chains. The hybrid nanoparticles was used as a solid bulkmodifier to fabricate a three-dimensional chemically modified carbon paste electrode (1-CPE) by direct mixing. The electrochemical behavior and electrocatalysis of 1-CPE has been studied in detail. The results indicate that 1-CPE has a good electrocatalytic activity toward the reduction of nitrite in 1 M H₂SO₄ aqueous solution. 1-CPE shows remarkable stability that can be ascribed to the interactions existed between POM anions and organic double helical bpy chains, which are very important for practical applications in electrode modification.

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1. Introduction

The synthesis and characterization of polyoxometalates (POMs) modified by organic molecules are currently of significant interest, owing to their intriguing architecture and tremendous potential applications in a wide number of fields [1]. Among those important properties of POMs, the ability to undergo reversible multi-electron redox processes [2] endows them with very attraction in chemically modified electrode (CME) and electrocatalytic research [3]. The traditional CME with POMs can be achieved by many methods [4]: (i) surface modification, including electrodeposition, adsorption, doping into polymer matrices, self-assembly, layer-by-layer deposition and LB methods; (ii) sol–gel technique; and (iii) other strategies [5]. However, a drawback in the application of the conventional POMs mentioned above is their poor long-term stability according to good solubility [6].

Recently, an interest has focused on the design and preparation of novel POM-based hybrid materials, as well as application of them in the three-dimensional bulk-modified carbon paste electrode (CPE) by direct mixing [7]. Chemically bulk-modified CPE is a mixture of a modifier, graphite powder and paste liquid, which has been widely applied in electrochemistry due to its many advantages: inexpensive, easy to handle, and easy to prepare [8]. Generally, 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 measurements. Therefore, the traditional POMs cannot be directly used as a bulkmodifier of CPE owing to their good solubility. However, inorganic–organic hybrids of POMs prepared by hydrothermal reaction are of usually poor solubility in water and in common organic solvent. This property is very advantageous to expand POM-based materials’ application in chemically bulk-modified electrode. A current development in this area is to explore novel lattice architectures resulting from the association of organic molecules and polyoxometalate anions.
We reported here the hydrothermal synthesis, single crystal structure and preliminary studies of electrochemical and electrocatalytic activities of (Hbpy)_4[SiMo_{12}O_{40}] (I) (bpy = 2,4-bipyridine). Interestingly, the hybrid forms in the solid state a supramolecular structure H-bonding drives the self-organization of the protonized brys as helical chains that in turn arrange around the polyoxometalate centers. The hybrid nanoparticles was used as a solid bulkmodifier to fabricate a three-dimensional chemically modified CPE (I-CPE) by direct mixing. Electrochemical behavior and electrocatalysis of I-CPE were investigated.

2. Experimental section

2.1. General methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses were carried on a MOD 1106 elemental analyzer. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a Mg Kα (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2 × 10^{-6} Pa during analysis. FTIR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FTIR spectrophotometer using a KBr pellet. Cyclic voltammograms (CV) were recorded on a 384B polarographic analyzer. A typical three-electrode cell having a CPE working electrode, a platinum counter electrode, and a silver/silver chloride reference electrode was used for the voltammetry experiments.

2.2. Hydrothermal synthesis

(Hbpy)_4[SiMo_{12}O_{40}] (I). A reaction mixture of Na_2MoO_4·2H_2O (2 mmol), Na_2SiO_3·9H_2O (0.3 mmol), bpy (0.3 mmol) and H_2O (10 mL) was sealed in an 18 mL Teflon-lined reactor under autogenous pressure at 170 °C for 4 days, followed by slowly cooling (10 °C h^{-1}) to room temperature. Yellow block crystals were obtained along with amorphous powder. The crystals were picked out, washed with distilled water, and air-dried at 50 °C (yield: 63%). Elemental Anal. Found: C, 19.8; H, 1.7; N, 4.4%. Calcd. for C_{40}H_{36}Mo_{12}N_{8}O_{40}Si: C, 19.6; H, 1.5; N, 4.6%.

2.3. Preparation of I-CPE

The I-CPE was fabricated as follows: 0.5 g graphite powder and 0.04 g compound I was mixed and ground together by agate mortar and pestle to achieve an even, dry mixture; to the mixture 0.50 mL paraffin oil was added and stirred with a glass rod; then the mixture was used to pack 3 mm inner diameter glass tube, and the surface was wiped with glass paper; electrical contact was established with copper rod through the back of the electrode.

2.4. X-ray Crystallographic study

Single crystal of I with dimension 0.297 mm × 0.193 mm × 0.133 mm was glued on a glass fiber. Data were collected on a CCD diffractometer with Mo Kα monochromated radiation (λ = 0.71703 Å) at 293 K. Psi-empirical from equivalents was applied. The structure was refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [9]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The H(1) and H(2) atoms were located from difference Fourier maps. Other hydrogen atoms were located in the idealized positions.

Crystal data: CuH_{4}Mo_{12}N_{8}O_{40}Si. Monoclinic, P2(1)/c, Mr = 2448.14, a = 15.4534(8) Å, b = 13.9512(10) Å, c = 20.0972(15) Å, β = 106.4050(10)°, V = 3080.64(4) Å³, Z = 2, Dc = 2.639 Mg m^{-3}, μ = 2.483 mm^{-1}, R_1 = 0.0723 and wR_2 = 0.1632 for I > 2σ(I). CCDC-243842 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax (internet): +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

3.1. Crystal structure

The crystal structure analysis reveals that compound I consists of one SiMo_{12}O_{40}^{4−} cluster and four brys molecules in a unit (see Fig. 1). The anion shows a structure typical of disordered 'o-Keggin' molecule [10]. The central atom
Fig. 2. Ball-stick and space-filling plots of the left-handed (L) and right-handed (R) chains.

Si is located at the inversion center (0, 1/2, 1/2) and is surrounded by a cube of eight oxygen atoms, with each oxygen site half-occupied. Si–O bonds range from 1.556(13) to 1.704(14) Å (mean 1.634 Å). The Mo=Od (Od = terminal oxygen) bonds are in the usual range of 1.648(8)–1.667(9) Å. A structural feature is that the anions extend the linkages into a two-dimensional (2D) inorganic framework due to a short distance of terminal oxygen O(5) and O(12) (the distance is 2.906 Å) in bc plane.

Among those interactions in fabricating large supramolecular structures, hydrogen bonding is more attractive because of its highly directional nature and relatively high bonding energy, and is also most commonly used as the supramolecular cement in constructing this kind of structure assemblies [11]. In compound 1, the organic part exhibits an interesting structural feature: supramolecular helical chains (see Fig. 2), which is rare in hybrids of polyoxometalate chemistry. Under the current reaction system, the terminal N atoms of bpy are protonized. These bpy molecules are connected each other via N=N—N hydrogen bonding to produce right- and left-handed helical bpy chains (N(1)···N(4) = 2.941 Å, N(3)···N(2) = 2.904 Å, $\theta_{N(3)···N(2)} = 135.39^\circ$ and $\theta_{N(1)···N(4)} = 157.48^\circ$) along b-axis. The right- and left-handed helical bpy chains alternately penetrate up and down the plane constructed by POM ions to form a cushion-shaped intertexture (see Fig. 3). In the structure point of view, the organic helical chains may just be the reason to promote the above-mentioned close contact of O(5) and O(12) of the anions.

Fig. 3. A view represents how the organic chains penetrate the plane of inorganic anions. Dark sphere: POM anion; dark band: organic helical chain.

3.2. IR and XPS spectra

The IR spectrum of 1 exhibits the characteristic peaks of the Keggin anion at 997, 950, 905 and 756 cm$^{-1}$ attributed to v(Si=O), v(Mo=Oc–Mo), v(Mo=Ob–Mo) and v(Mo=Od) (Od = terminal oxygen, Ob = bridged oxygen of two octahedral sharing a corner, Oc = bridged oxygen of two octahedral sharing an edge), respectively. The bands in the 3000–1080 cm$^{-1}$ region are attributed to characteristic vibrations of bpy. The XPS spectra give a peak at 235.35 eV, attributable to Mo$^{6+}$.

3.3. Voltammetric behavior

3.3.1. Voltammetric behavior of 1-CPE in aqueous electrolyte

Fig. 4 shows the cyclic voltammetric behavior for 1-CPE in 1 M H$_2$SO$_4$ aqueous solution at different scan rates. It can be clearly seen that in the potential range +800 to −100 mV, three reversible redox peaks appear and the peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are +333, +227 and +21 mV (50 mV s$^{-1}$), respectively. Redox peaks I–I$'$, II–II$'$ and III–III$'$ correspond to three consecutive two-electron processes, respectively. When the scan rate was varied from 20 to 500 mV s$^{-1}$, the cathodic peak currents were almost the same as the corresponding anodic peak currents, and the peak potentials changed gradually: the cathodic peak potentials shifted to the negative direction and the corresponding anodic peak potentials to the positive direction with increasing scan rates. At scan rates lower than 110 mV s$^{-1}$, the peak currents were proportional to the scan rate, which indicates the redox process of 1-CPE is surface-controlled; however, at scan rates higher than 110 mV s$^{-1}$, the peak currents were proportional to the square root of the scan rate, which indicates the redox process of 1-CPE is diffusion-controlled.
Fig. 4. The cyclic voltammograms of the 1-CPE in 1 M H₂SO₄ at different scan rates (from inner to outer: 20, 50, 80, 110, 140, 170 and 210 mV s⁻¹). The inset shows plots of the anodic and the cathodic peak II–II' currents against scan rates.

The peak-to-peak separations between the corresponding anodic and cathodic peaks increase with increasing scan rate, may be explained below: (i) the reduction of compound 1 immobilized in the CPE is accompanied by the evolution of protons from solution to maintain charge neutrality. The encapsulation of 1 nanoparticles into a CPE may slow down the penetration rate of protons from solution into the nanoparticles and thus decrease the electron exchange rate to some extent. With increasing scan rate, the diffusion rate of the protons into the nanoparticles begins to determine the electrochemical reduction rate. (ii) The electron exchange rate between the insoluble solid 1 nanoparticles and the electrode may be slower than that between the soluble POM anions and the electrode.

3.3.2. pH-dependent electrochemical behavior of 1-CPE

The pH of the supporting electrolyte has a slight effect on the electrochemical behavior of the 1-CPE in H₂SO₄ + Na₂SO₄ aqueous solutions. As seen in Fig. 5, with increasing pH, the three redox potentials all gradually shift to negative direction and the peak currents decrease. Reduction of hybrid 1 nanoparticles is similar to that of H₄SiMo₁₂O₄₀ itself and is accompanied by the evolution of protons from solution to the nanoparticles of the electrodes surface to maintain charge neutrality. The formal potentials and current changes can be explained by Nernst equation and Fick's first law [12], respectively.

3.3.3. Voltammetric behavior of the 1-CPE in a mixed solvent electrolyte

Many electrochemical studies of POMs have been carried out in order to make clear the redox properties of a series of Mo complexes known as a Keggin structure [13]. The previous voltammetric and polarographic investigations have shown that the redox processes of 12-heteropolyoxometalates in acidic solutions are influenced by the nature of organic solvent [14].

In the present experiments, a polar solvent (ethanol) and a non-polar aprotic solvent (1,4-dioxane) were used as media to investigate the solvent effect on the redox properties of the 1-CPE. Fig. 6 shows the comparative cyclic voltammograms of the 1-CPE in 1 M H₂SO₄ (a), in 50% (v/v) ethanol + 1 M H₂SO₄ (b) and in 50% (v/v) 1,4-dioxane + 1 M H₂SO₄ (c) media at 80 mV s⁻¹, respectively. It can be clearly seen that in 50% (v/v) ethanol + 1 M H₂SO₄, all the cathodic peak potentials (Eₓ) of the three redox waves slightly shift to the negative potential direction and the peak-to-peak separations between the corresponding cathodic and anodic peaks increase. Many results [15]
have proved the bridging oxygen atoms (Mo=O=Mo) are exclusively reactive and consumed in the early stages of the reduction of Keggin POMs. The result for the potential shift in the mixed electrolyte is similar to that reported by Wang and Dong [14]. In aqueous acidic solution, the protons diffused into POM nanoparticles are attached to the 0h atoms of the [Hbpy]4[SiMo12O40]2+ by bonding and this easily results in the redox reaction on 1-CPE in the presence of protons, while other protons may adsorb around I nanoparticles due to some other effect. However, in the presence of ethanol molecules, these organic solvent molecules may also be adsorbed around I nanoparticles and this adsorption effect is stronger than that of the protons, which hinders the diffusion of the protons and thus decreases the electron exchange rate between I nanoparticles and the electrode surface. It is noted that, when I-CPE was taken out and put into 1 M H2SO4 aqueous solution in the absence of ethanol, the voltammetric behavior of I-CPE was restored again and reached a steady state after immersion in 1 M H2SO4 aqueous solution for 2 min. These results show that the electrode surface was not destroyed in 1 M H2SO4 solution containing ethanol.

For 50% (v/v) 1,4-dioxane + 1 M H2SO4 (c), however, the medium effect on the electrochemical behavior of I-CPE is quite different from that in ethanol + 1 M H2SO4 solution. The peak potentials slightly shift to the positive direction rather than the negative direction. This is probably because non-polar aprotic solvent molecules cannot be adsorbed around I nanoparticles like ethanol, and on the contrary, the existence of 1,4-dioxane favors diffusion of protons into I-CPE and thus the peak potentials shift to the positive direction.

3.3.4. Stability and surface-renewal of I-CPE

In experiment, I-CPE showed higher stability. When the potential range is maintained at 800 to −100 mV, it is stable over 500 cycles at a rate of 100 mV s−1 and the current response remained almost unchanged. When the I-CPE was stored at room temperature (25–30 °C) for at least one month, the current response remained almost unchanged, which proved it to be very stable. The remarkable stability of the I-CPE should be ascribed to the insolvability of the inorganic–organic hybrid POM nanoparticles. Compared with POM-modified film electrodes fabricated by the conventional methods, the three-dimensional CPE has certain advantages. The most important advantage is, when needed, that squeezing a little carbon paste out of the tube can renew the bulk-modified CPE. Experiment results demonstrated that 15 successively renewals did not result in an observable change of currents whereas has a relative standard deviation of 5.8% for a gel film electrode [4]. This is especially useful for the electrocatalytic study since the catalytic activity is known to decrease when the electrode is dirtied.

3.3.5. Electrocatalytic activity of I-CPE

As is known, POMs has been exploited extensively in electrocatalytic reductions [16]. For example, Dong et al. [17] observed that SiW12O404+ could be used as an electrocatalyst for the reduction of nitrite; Keita et al. [18] observed that two-electron-reduced SiMo12O404+ can reduce nitrite in acidic solution; Toth and Anson [19] have applied the iron(III)-substituted Keggin type POMs as catalysts for the reduction of hydrogen peroxide and nitrite. Here, Compound I is employed to fabricate POM nanoparticle modified electrode to electrocatalyze the reduction of nitrite, chlorate and hydrogen peroxide.

The reduction of nitrite to ammonia involves a six-electron-eight-proton change. It is well known that direct electroreduction of nitrite ion requires a large overpotential at most electrode surfaces, and so no obvious response was observed for nitrite at bare CPE in the range of +800 to −100 mV in 1 M H2SO4 solution. Otherwise, the photoreduction of NO2− can be catalyzed by nitrite reductase enzymes which are present in green plants. Various transition metal complexes have been employed as enzymatic models for nitrite reduction, including iron chelate [20], iron [21] or cobalt porphyrin [22], or cobalt cyclam [23]. They behave as key intermediates of the catalysis and are reduced by multiple-electron processes. Fig. 7 shows the cyclic voltammograms of I-CPE under scan rate 80 mV s−1 in the acid solution containing nitrite. The results indicate that I-CPE has good electrocatalytic activity toward the reduction of nitrite. With the addition of nitrite, all the three reduction peak currents increase markedly while the corresponding oxidation peak currents decrease markedly, suggesting that the reduction of nitrite involves two-, four- and six-electron-reduced species. It was noted that the catalytic activity was enhanced with the extent that the (Hbpy)4[SiMo12O40]2+ was reduced. We have also noted that high scan rate (80 mV s−1) has been used to register the electrocatalytic reduction of nitrite and obtained noticeable catalytic currents, which indicates the reduction of nitrite at the I-CPE is fast.
Fig. 8. Cyclic voltammograms of the 1-CPE in 1 M H₂SO₄ containing different concentrations of ClO₃⁻. Scan rate: 80 mV s⁻¹.

Fig. 9. Cyclic voltammograms of the 1-CPE in 1 M H₂SO₄ containing different concentrations of H₂O₂. Scan rate: 80 mV s⁻¹.

Figs. 8 and 9 show cyclic voltammograms for the electrocatalytic reductions of chlorate and hydrogen peroxide by 1-CPE in 1 M H₂SO₄ aqueous solution, respectively. It can be seen clearly that with addition of chlorate and hydrogen peroxide, the third reduction peak current increases gradually while the corresponding oxidation peak current gradually decreases and the first two redox peak currents remain almost unvaried, suggesting that chlorate and hydrogen peroxide are reduced only by the six-electron-reduced species, which is different from the reduction of nitrite.

4. Conclusion

The inorganic–organic hybrid 1 is prepared by hydrothermal reaction. In compound 1, the organic moiety exhibits an interesting supramolecular helical chains structure. Compound 1 is employed to fabricate the POM nanoparticle modified electrode to electrocatalyze the reduction of nitrite, chlorate and hydrogen peroxide, which promises to compete well with traditional POM modified electrodes. The results indicate that the 1-CPE has a good electrocatalytic activity toward the reduction of nitrite. Compared with the conventional POM-modified electrodes, the 1-CPE presents remarkable stability due to the insolubility of the inorganic–organic hybrid POM nanoparticles, which is important for practical applications. The most important advantage of 1-CPE is, whenever needed, that squeezing a little carbon paste out of the tube can renew the bulk-modified CPE. This is especially useful for the electrocatalytic study since the catalytic activity is known to decrease when the electrode is dirtied.

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