



A general strategy for the preparation of polyoxometalate coordination polymer modified electrodes via an ionic liquid route and their electrocatalytic activities

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ABSTRACT

A general strategy for the preparation of polyoxometalate coordination polymer modified electrodes via an ionic liquid route was proposed. A polyoxometalate (POMs) coordination polymer **1**, $[\text{H}_2\text{bpy}]_2\{\text{Cu}(\text{bpy})_2\text{Mo}_5\text{P}_2\text{O}_{23}\} \cdot 4\text{H}_2\text{O}$ (bpy = 4,4'-bipyridine) was successfully reconstructed by electrolyzing in its ionic liquid solution on conducting glasses electrode coated with indium tin oxide (ITO). Polymer **1** is soluble in the an ionic liquids (ILs) 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄), not soluble in water and common organic solvents such as DMF, ether. The reconstructed polyoxometalate coordination polymer on the ITO electrode was characterized by XPS and XRD. XPS spectrums and the XRD patterns of the deposited POMs on ITO electrode show the deposited POMs had the same structure as the polyoxometalate coordination polymer **1**, which imply that the structure of the deposited POMs on ITO electrode keeps the same as the original the polyoxometalate coordination polymer **1**. Cyclic voltammetry technique was used to study the electrochemical properties of the as-prepared POM modified ITO electrode. The results implied that it had not only a good electrocatalytic activity toward the reduction of iodide, but also a high stability in aqueous solution. The proposed strategy for the construction of POMs coordination polymer modified electrode shows remarkable advantages, which should be important for practical applications.

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1. Introduction

In recent years, the construction of polyoxometalate (POMs) coordination polymer has attracted considerable attention in supramolecular and materials chemistry due to the formation of fascinating structures and potential applications as optoelectronic, magnetic, and porous materials [1–9]. One of the important properties of POMs is their ability to undergo reversible multi-electron redox processes [10,11], which makes them very attractive in catalytic and electrocatalytic fields [12–20]. As early as 1998, Klemperer and Wall reviewed and predicted that the future of polyoxometalate chemistry would finally move from solids and solutions to surfaces [21]. Numerous examples have emerged and fully supported this idea. Up to date, most of the work has so far focused on the assembly of the polyoxometalate coordination polymer. However, the applications of the coordination polymers based on polyoxometalates were less developed. This could be attributed to the tendency of low solubility for most of the polyoxometalate coordination polymers in both water and usual organic solvents.

The ionic liquids (ILs) are employed as novel solvents in this work. The ILs have attracted an increasing amount of interest, owing to their low volatility, non-flammability, high chemical and thermal stabilities, high ionic conductivity, and broad electrochemical windows [22]. Initial investigations concerning ILs focused on employing them as “green” solvents in chemical synthesis, catalysis, separation, and electrochemistry. Recently, ILs have emerged as templates or stabilizers for nanostructures [23]. Some task specific ILs have also been designed, because the structures and properties of ILs can be easily tuned by selecting the appropriate combination of organic cations and anions. It is also possible to utilize one ionic component to deliver a unique function and the other to deliver a different and independent function [24].

In this paper, we propose a general reconstructed synthetic strategy for the insoluble polyoxometalate coordination polymer **1**, $[\text{H}_2\text{bpy}]_2\{\text{Cu}(\text{bpy})_2\text{Mo}_5\text{P}_2\text{O}_{23}\} \cdot 4\text{H}_2\text{O}$ (bpy = 4,4'-bipyridine) by the electrolyzing it on conducting glasses coated with indium tin oxide (ITO) in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄). The results indicate that the individual structures and properties of the polyoxometalate coordination polymer are easily and successfully delivered to the surface of modified electrode. The proposed strategy for the reconstruction of polyoxometalate coordination polymer modified electrodes

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shows remarkable advantages, which should be important for practical applications.

2. Experimental

2.1. Materials

The polyoxometalate coordination polymer **1**, $[\text{H}_2\text{bpy}]_2\{\text{Cu}(\text{bpy})_2\}\text{Mo}_5\text{P}_2\text{O}_{23}\cdot 4\text{H}_2\text{O}$ (bpy = 4,4'-bipyridine) was prepared according to Ref. [25] and characterized by FTIR spectra, thermogravimetric analysis (TGA) and XRD. All results are in agreement with those reported previously [25] (see Figs. S1 and S2). Other chemicals were purchased commercially and used without further purification.

2.2. Reconstructing of polyoxometalate coordination polymer **1** on ITO electrode

An ITO electrode was washed by first placing it in a hot $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7:3) bath for 40 min and then in an $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$ (5:1:1) bath for 30 min. Prior to the experiment, the bare ITO electrode was scanned by successive cyclic voltammetry within the potential range of +2 to -2.5 V in freshly deoxygenated 1:1 BMIM⁺ and BF₄⁻ ionic liquids to obtain the clean surface of the ITO electrode and finally dried in air (S3). The insoluble polyoxometalate (POMs) coordination polymer **1**, $[\text{H}_2\text{bpy}]_2\{\text{Cu}(\text{bpy})_2\}\text{Mo}_5\text{P}_2\text{O}_{23}\cdot 4\text{H}_2\text{O}$ (bpy = 4,4'-bipyridine) was successfully reconstructed by electrolyzing in ionic liquids on indium tin oxide (ITO) electrode. The polyoxometalate coordination polymer is insoluble in aqueous solution and usual organic solutions, but soluble in the ionic liquid BMIMBF₄ at a constant potential of -1.2 V for 2 h. The modified ITO electrode was allowed to dry in air for hours and ready for characterization.

2.3. Characterization

A CHI 660C Electrochemical Workstation was used for the electrochemical measurements. A conventional three-electrode cell, consisting a reconstructed polyoxometalate coordination polymer **1** coated ITO electrode as the working electrode, a saturated calomel reference electrode (SCE) and a Pt counter electrode was used. All potentials were measured and reported versus the SCE. All the experiments were conducted at room temperature (25–30 °C). The XRD patterns were observed on a Rigaku DMAX/rC X-ray diffractometer with Cu K α radiation. The infrared spectrum was obtained on an Alpha Centaur FT/IR spectrometer with pressed KBr pellet in the 4000–400 cm^{-1} regions. A Perkin–Elmer TGA thermogravimetric analyzer was used to obtain TGA curve in N₂ with a temperature increasing rate of 10 °C min⁻¹. X-ray Photoelectron Spectrum (XPS) of the polyoxometalate coordination polymer reconstructed on ITO electrode is detected at a Kratos AXIS Hsi X-ray photoelectron spectrometer.

3. Results and discussion

3.1. Characterization of the polyoxometalate coordination polymer reconstructed on ITO electrode

3.1.1. The XRD pattern of the polyoxometalate coordination polymer **1** reconstructed on ITO electrode

The polyoxometalate coordination polymer **1** is soluble in the BMIMBF₄ ionic liquid, but insoluble in the water and usual organic solvents such as DMF and ether. Therefore, the compound **1** is a good material to realize our proposed reconstructed synthetic strategy. The ITO electrode was electrolyzed in the solution of

BMIMBF₄ ionic liquids containing the compound **1** for 2 h. It should be pointed out that the deposition process of POMs on the electrode surface is very complicated and still not clear in aqueous solution. For the present case, the detailed mechanism of this deposition process in the ionic liquid is also not clear for us. XRD technique is employed to investigate the structure of polymer **1** reconstructed on ITO electrode and polymer **1**, respectively. It suggests that they had the same structure, as shown in Fig. 1.

The result may imply that by reducing the POM ions to its lower valence, its solubility in the ionic liquid may decrease and thus deposit on the electrode surface, and the polyoxometalate coordination polymer **1** reconstructed on ITO electrode keeps the same structure as the original polyoxometalate coordination polymer **1**.

3.1.2. The XPS spectrum of the polyoxometalate coordination polymer **1** reconstructed on ITO electrode

The XPS spectra of polymer **1** reconstructed on ITO electrode and polymer **1** are showed in Fig. 2. The weak peaks at 932.8 eV and 952.8 eV correspond to the binding energy of Cu2p_{3/2} or Cu2p_{1/2}, and at 232.5 eV and 236.1 eV correspond to the binding energy of Mo3d_{5/2} or Mo3d_{3/2}, respectively. This indicates that Cu²⁺ and Mo⁶⁺ appear in the electrodeposition process. The XPS spectra indicate that polymer **1** is obtained on the ITO electrode by the potentiostatic electrodeposition.

3.2. Electrochemical behavior in aqueous solution

The typical cyclic voltammograms for the reconstructed polyoxometalate coordination polymer **1** on an ITO electrode in 0.5 M H₂SO₄ solution at potential range from +700 to +100 mV is shown in Fig. 3. Redox peaks I–I' and II–II' correspond to reduction and oxidation of two-electron processes of POMs [26]. By varying the potential scan rate, the redox peaks currents were both proportional to the scan rates, as shown in Fig. 4, where the potential scan rates were varied from 10 mV s⁻¹ to 70 mV s⁻¹.

In the reduction processes, the addition of electrons takes place at the delocalized band-like states, rather than at a specific Mo atom. Furthermore, the good linear relationship between the peak current and the potential scan rate indicates the redox reactions are surface confined. However, the peak potential differences (ΔE_p) are larger than the theoretical value (0 mV) expected for a reversible surface redox process [27] and increases along with increasing scan rate, suggesting a quasi-reversible electrochemical process (see Fig. 4). As a consequence, the electrochemical behaviors of the reconstructed polyoxometalate coordination polymer **1**

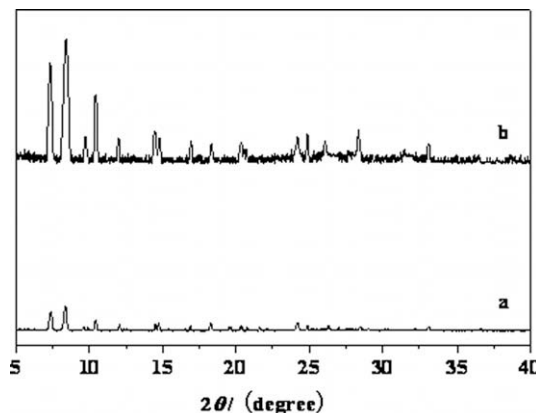


Fig. 1. X-ray powder diffraction patterns of the reconstructed polymer **1** on a ITO electrode (a) and polymer **1** (b).

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