

Electrochemical Behavior and Its Electrocatalytic Activity of A P-Mo Heteropolyanion Modified ITO Electrode

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Abstracts: A new method for the preparation of an organic-inorganic composite film of the heteropolyanion has been developed by modifying $P(Mo_2O_7)_6^{7-}$ to the indium tin oxide (ITO) electrode surface. The modified electrode displayed a strong catalytic activity towards the reduction of IO_3^- . In the range of $1.0 \times 10^{-6} \sim 5 \times 10^{-4}$ mol/L, the catalytic current was linear proportional to the IO_3^- concentration.

Keywords: Chemically modified electrode, heteropolyanion, indium tin oxide electrode, IO_3^- .

ITO is a versatile material in the electronic industry because of its special transparent and conductive properties. However, there are a few reports regarding the adsorption of organic or organometallic compounds on the ITO surface¹⁻⁴. The heteropolyanions are interested in the field of material science, catalytics, biology, and medicine owing to their chemical, structural, and electronic versatility⁵⁻⁷. One of the most important properties of polyoxometalate anions is their ability to accept a number of electrons giving rise to the mixed-valency species, which makes them suitable as the electrocatalysis and electrochromic materials⁸.

Several composite films containing heteropolyanion modified electrodes have been prepared by several groups recently⁹⁻¹³. The organized molecular assemblies with the precise control of layer composition and thickness become available by these techniques. But some undesirable characteristics of a monolayer, such as unstability in the typical hydrothermal conditions (high pH and high temperature), preclude the use. These promoted us to seek a well-organized heteropolyanions monolayer modified ITO electrode. We found that the covalent bonding of (3-aminopropyl) trimethoxysilane (KH-550) on ITO surface may provide a good substrate to attract $H_7[P(Mo_2O_6)_7]$ (HPA) molecules and to form the heteropolyanion film and it is found an extreme sensitive electrocatalytic action towards the reduction of IO_3^- . In addition, the electrocatalytic action towards BrO_3^- and ClO_3^- was examined as well.

Experimental

Electrochemical experiments were carried out with a BAS-100A (BAS. Inc. USA) and

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CHI-660 (CHI Company USA) with a three-electrode system: The saturated calomel electrode (SCE) was used as reference and platinum wire as counter electrode. All chemicals were in the analytical reagent grade. The solutions were prepared with double distilled water.

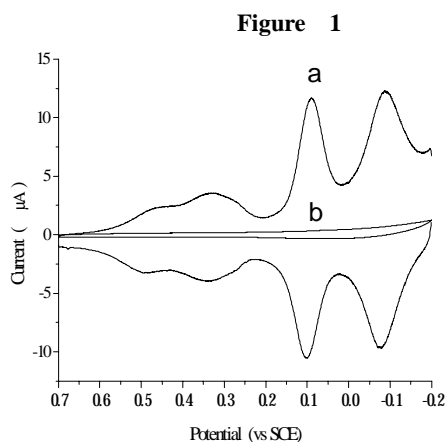
The ITO electrodes were cleaned by sonication. Then electrodes were immersed in 5 mol/L NaOH for 5 hour *prior to* rinsing with water and derivatization in an aqueous solution of 1% KH-550 for 10 min. The prepared $\text{-NH}_2/\text{ITO}$ was immersed into 5×10^{-4} mol/L P-Mo HPA solution for 30 min, then rinsed with 0.1 mol/L HCl. The modified electrode was ready. It is found that the redox properties of this electrode was influenced by the immersion time of the $\text{-NH}_2/\text{ITO}$ surface in the P-Mo-HPA solution and 30 min was chosen as a standard time according to the experimental result.

Results and Discussion

Electrochemical behavior of the modified surface

It is reported that HPA has a good redox behavior and is very stable in acidic medium. Its redox action is usually accompanied with the participation of protons.¹⁴ The solutions we used in this method was 0.1mol/L HCl. **Figure 1** shows the cycle voltammograms of HPA modified electrode and bare electrode respectively. The cycle voltammograms indicate that the HPA was modified on the $\text{-NH}_2/\text{ITO}$ surface. The four couples of reversible redox peaks presented in the range from 0.70 V~-0.20 V(*vs* SCE) in **Figure 1**. When the scan rate was 50 mV/s the cathodic peak potentials(E_{pc}) were -0.095 V(I), 0.073 V(II), 0.249 V(III) and 0.423 V(IV) respectively. The anodic peak potentials were -0.084 V(I), 0.084 V(II), 0.264 V(III) and 0.460 V(IV) respectively. The peak currents i_{pc} , i_{pa} were found linearly proportional to the scan rate in the range of 10-250 mV/s which was characteristic for the surface bounded species.

According to the related equation between the peak current (i_p) and the surface concentration, (): $i_p = n^2 F^2 A V / 4RT$, is obtained from the experimental data. $= 1.49 \times 10^{-10} / n^2$ mol/cm², where n is the number of electrons of the electrode reaction. The surface concentration was so high that the modified electrode can be considered as a monolayer modified electrode.

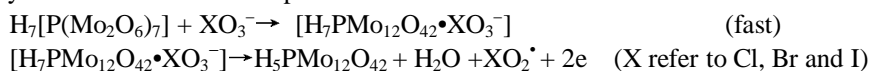


(a).P-Mo HPA modified NH_2/ITO surface (b). Bare ITO surface

Electrocatalytic effect of HPA/-NH₂/ITO on reduction of IO₃⁻

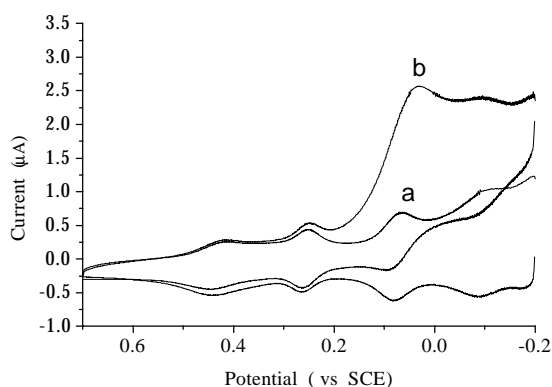
In 0.1 mol/L HCl, IO₃⁻ has no response to the -NH₂/ITO surface in the range from 0.70 V to -0.20 V (vs SCE). The electrocatalytic reduction of IO₃⁻ with a HPA modified -NH₂/ITO as investigated in this experiment.

The CV of a HPA modified -NH₂/ITO surface with the IO₃⁻ is shown in **Figure 2**. After additions of IO₃⁻, the second cathodic peak currents of the surface wave of the HPA modified -NH₂/ITO increased, but its anodic peak currents decreased and disappeared. At the same time, the other current did not change appreciably. According to the electrochemical properties of P-Mo anion and reference⁷ the catalytic activity on the modified surface decreases from IO₃⁻ to ClO₃⁻. The mechanism of the catalytic reduction could be expressed as follows:

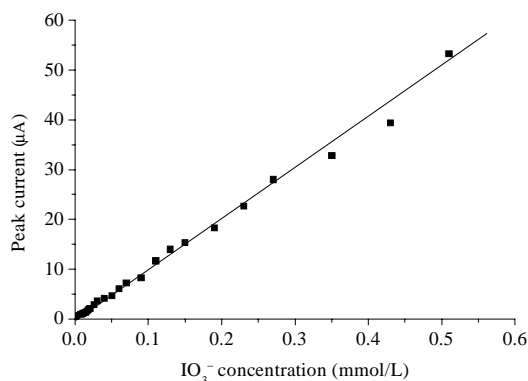


In this catalytic process, the catalytic currents of the second peak were related to the IO₃⁻ concentrations. The relation between IO₃⁻ concentration and the catalytic current of the second peak is shown in **Figure 3**. It showed that the IO₃⁻ concentration was linear proportional to the catalytic current of the second peak in the concentration of 2.0×10⁻⁶~5×10⁻⁴mol/L. This is a higher sensitivity than it reported in document. The relative standard deviation is 4.5% for six successive determinations at 1×10⁻⁵ mol/L solutions.

Figure 2



(a) CV of NH₂/ITO electrode (b) CV in 0.1 mol/L HCl + 2.0×10⁻⁵ mol/L IO₃⁻

Figure 3 The relation between IO_3^- concentration and the second peak current

Conclusion

A new HPA/ITO modified electrode has been prepared and developed to study the electrocatalytic activity of IO_3^- . This modified electrode can act as a sensitive sensor for the detection of IO_3^- . Satisfactory results are obtained.

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