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Photo-induced electron transfer and electrocatalytic properties of novel charge-transfer compound $(TMB)_3HPMo_{12}O_{40}$

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Abstract

A novel charge-transfer compound $(TMB)_3PMo_{12}O_{40}$ (TMB-PMo_{12}, TMB = 3,3′,5,5′-tetramethylbenzidine) was synthesized. There is a strong electronic interaction between organic donor TMB and $PMo_{12}O_{40}^{3-}$ heteropoly anion. Irradiation of ultraviolet light can cause the intramolecular electron-transfer between TMB and heteropoly anion in the complex. Electrochemical behavior of the TMB-PMo_{12} modified electrode in H_2SO_4 solution showed well-defined redox couples corresponding to the redox reactions of the incorporated TMB and heteropoly anion. The TMB-PMo_{12} modified electrode exhibits excellent catalytic activity for the reduction of IO_3^-, where the incorporated TMB may play an important role to activate the catalytic activity of the heteropoly anion.

Keywords: Charge-transfer; Heteropoly acid; 3,3′,5,5′-Tetramethylbenzidine; Electronic absorption; Electrochemistry

1. Introduction

Heteropoly acids possess good redox properties and structural versatility and have been widely applied in many fields, such as medicine [1,2], catalysis [3–5], and materials sciences [6]. They are also excellent inorganic building blocks for advanced materials. Recently, heteropoly acids incorporated with various organic moieties have received increasing attention, because such novel functional charge-transfer hybrid molecules exhibit some interesting properties, such as photochromism, magnetism, photocatalysis and third order optical nonlinearities as compared to their bases [7–13]. To develop rational methods for the modification and functionalization of heteropoly acid, systems can provide the means to chemical, structural and electronic versatility and exploit more fully desirable attributes [14].

In this paper, we reported the synthesis and charge transfer properties of a novel inorganic-organic hybrid complex, which consists of molybdophosphoric acid with keggin structure, $H_3PMo_{12}O_{40}$ (PMo_{12}) and 3,3′,5,5′-tetramethylbenzidine (TMB). The reduced TMB is colorless, which has π–π and *p*–π conjugation structure, leading to the molecule favorable to transfer its electrons to other electron-acceptor form charge-transfer compounds [15,16]. The present study shows that there is strong electronic interaction between TMB and heteropoly anion PMo_{12}. The results prove that photo-induced intramolecular electron transfer occurs in the hybrid complex, where PMo_{12} and TMB in the hybrid compound can actually serve as the electron acceptor and donor, respectively. The hybrid complex also exhibits good electrocatalytic activity for the reduction of iodate.

2. Experimental

2.1. Chemicals

TMB was purchased from Suzhou New District BEC Fine Chemicals Co. Ltd. and used without further purification. $H_3PM_{O12}O_{40} \cdot nH_2O$ was prepared by the literature method [17]. All other chemicals used were of reagent

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grade. Solutions used in all experiments were prepared with Millipore water.

2.1.1. Synthesis of TMB – PMo_{12} hybrid compound

An ethanol solution containing 1.5 mmol TMB (10 mL) was added dropwise to 10 mL of 0.5 mmol PMo_{12} ethanol solution. The mixture solution was heated to 60 °C on a water bath. Then, the solution was stirred at 60 °C for 3 h. The color of the solution was gradually turned from yellow-green to green, and to final black-green, and precipitate appeared in the mixture. The precipitate was separated by filtration, washed with ethanol, and dried in vacuum at room temperature. The final product was characterized by IR spectroscopy, ESR spectroscopy, and thermogravimetric analysis. The complex can be formulated as $(TMB)_3HPMo_{12}O_{40} \cdot 3H_2O$ by the elemental analysis, found: C, 21.7; H, 2.61; N, 3.18; P, 1.18; Mo, 42.30%; calcd.: (C, 22.2; H, 2.65; N, 3.23; P, 1.19; Mo, 44.31%),

2.2. Apparatus and methods

Electrochemical measurements were carried out on a CHI 660 electrochemical station. Traditional three-electrode system was employed with saturated calomel electrode (SCE) as reference electrode and a Pt electrode as counter electrode. The working electrode was prepared by the following procedure. A glassy carbon electrode was polished with 0.5 and 0.05 μm α-alumina powder, respectively. Then the electrode was sonicated in absolute alcohol, doubly distilled water successively, and dried at room temperature. Silica sol was prepared according to the literature protocol [18]. TMB-PMo_{12} hybrid (0.0015 g) was dissolved in 1–2 drops of DMF, and mixed with 0.25 mL of silica sol and 0.25 mL of H_2O. The dispersion was sonicated for 10 min. After that, 8 μL of the suspension was dropped on the surface of a glassy carbon electrode and dried in air for 24 h. The thickness of the resulting film on the electrode was estimated to be ca. 0.1 μm.

Electronic absorption spectra were obtained on a Shimadzu UV-240 spectrophotometer. The solid sample was prepared as KBr pellets. Photochemical behavior was determined using a 500 W high-pressure mercury lamp as the light source. The distance between the lamp and the sample is 15 cm.

3. Results and discussion

3.1. Intramolecular charge transfer of the hybrid complex

The appearance of black green color of the solution in the synthesis procedure and elemental analysis of the hybrid complex seem to be indicative of the formation of the "heteropoly blue", the reduced form of PMo_{12}. To clarify this, ESR spectrum of the hybrid complex was measured at room temperature; the result is shown in Fig. 1. A broad signal with $g = 1.967$, along with narrow signal centered at $g = 2.004$, was observed. The former can be ascribed to the existence of Mo(V). The peak-to-peak derivative width (ΔHpp) of narrow signal is about 15 G, which is a typical value for organic radical. Therefore, this signal is tentatively assigned to the $TMB^{\cdot+}$ radical cation. The ESR result clearly verifies the occurrence of the charge transfer of TMB to polyanion in the hybrid complex. To further demonstrate the intramolecular charge transfer of the hybrid complex, photo-induced electron transfer and electrochemical behavior of the complex were measured and described next.

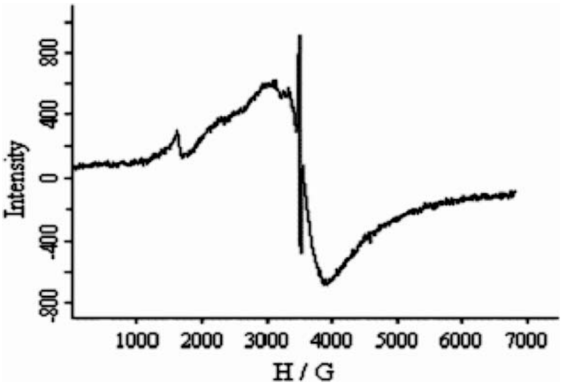

Fig. 1. ESR spectrum of the TMB-PMo_{12} hybrid complex at room temperature.

3.2. Electronic absorption spectra

The electronic spectra of the solid sample before and after irradiation are shown in Fig. 2. The TMB-PMo_{12} hybrid molecule in solid state exhibited a strong absorption band at 660 nm (Fig. 2 frame circle line). This band was not observed for the solid sample of PMo_{12} or TMB alone. The absorption of the reduced PMo_{12} should be located at 720 nm. Therefore, the band observed in Fig. 2 could come from the hybrid complex. A similar band was reported by Mecheria et al. [19] in their study of TMB as a redox mediator for molecular recognition of NADH. This band was attributed to the absorption of dimer TMB_2^{2+} (which is a charge-transfer complex of the oxidation product TMB^{2+}

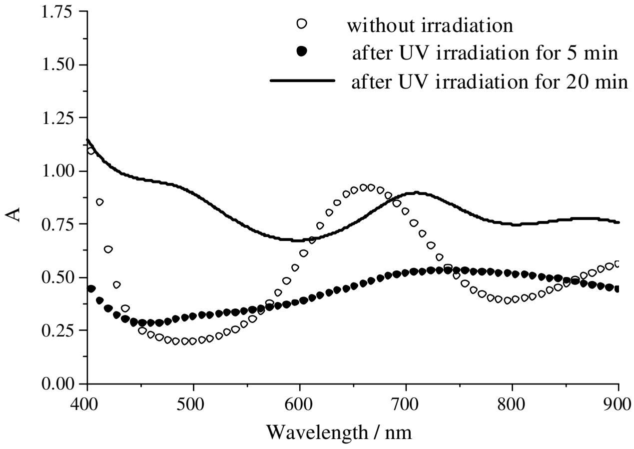

Fig. 2. Solid electronic-spectra of TMB-PMo_{12}.