



Electrochemical and Fluorescent Investigation of Inorganic-organic Hybrid from Butylrhodamine B and Keggin-Type Polyoxometalates

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A new inorganic-organic hybrid composed of butylrhodamine B (BRB) and Keggin-type polyoxometalates (PMO₁₂) was introduced. The UV-visible and FTIR results indicate the formation of hybrid is caused by the interaction of butylrhodamine B and polyoxometallate. The BRB-PMO₁₂ hybrid modified electrode shows the good electrochemical properties and catalysis to the reduction of bromate. Additionally, at the same condition, the fluorescence intensity of BRB-PMO₁₂ hybrid is almost 1.3 times than that of butylrhodamine B. The corresponding results have important implications for the design of multi-functional hybrid materials, which could be used widely in chemo/biosensing and catalysis.

Key Words: Butylrhodamine B, Polyoxometalates, Hybrid material, Electrochemistry, Fluorescence.

INTRODUCTION

The design and synthesis of inorganic-organic hybrid materials is of contemporary interest and becomes a major research theme in materials science¹⁻³. The hybrid materials are expected to exhibit improved properties and functions not seen in pure inorganic or organic phases and combine distinct properties of organic and inorganic components within a single molecular composite. Organic materials offer structural flexibility, convenient processing and tunable electronic properties; while inorganic compounds provide the potential for high carrier mobility, a range of magnetic and dielectric properties as well as thermal and mechanical stability. Recent researches in this area have resulted in one-, two- and three-dimensional hybrid systems⁴⁻⁶.

As a large and rapidly growing class of compounds, polyoxometalates are inorganic metal-oxygen cluster compounds that are outstanding in their topological and electronic versatility and attracted attention in materials, biochemistry, medicine and catalysis⁷⁻⁹. Keggin-type polyoxometalates of molybdenum are particularly attractive due to their ability to accept various numbers of electrons giving rise to mixed-valency species. Lately, Keggin-type polyoxometalates were reported to stabilize platinum nanoparticles and carbon nanoparticles^{10,11}.

Rhodamine B and their derivatives dyes are a group of xanthene dyes and have high fluorescence quantum yield, which

makes them very useful in applications like an active medium of dye lasers, fluorescence labeling and in bioanalytical chemistry^{12,13}. Recently, the uses of rhodamine B compounds in synthesis of composite materials have been reported¹⁴⁻¹⁶.

In this paper, we have explored the preparation of inorganic-organic hybrid material by combining electronic polyoxometalates and fluorescent butylrhodamine B at the first time. The electrochemical and fluorescent characteristics of hybrid materials were discussed.

EXPERIMENTAL

Butylrhodamine B (BRB) and Keggin-type POM (H₇PMO₁₂O₄₂, abbreviated PMO₁₂) were purchased from Chemical Reagent Company of Shanghai, China. All other reagents were of analytical grade and were used without further purification. Double-distilled water was used throughout.

Cyclic voltammetry measures were carried out in a conventional three-electrode cell controlled by CHI 660C Electrochemical Work Station (CH Instruments, Inc). Pyrolytic graphite (PG) electrode (surface area 0.06 cm²) was used as working electrode. A platinum foil was applied as the counter electrode and a saturated calomel electrode (SCE) served as reference electrode. All potential values given below refer to saturated calomel electrode. All experiments were performed at room temperature. The UV-VIS spectrum of BRB-PMO₁₂ was recorded with a DU 800 spectrophotometer (Beckman,

USA). The BRB-PMo₁₂ adduct was pressed into a KBr pellet for FTIR investigation (WQF-410 spectrometer, Beijing, China). The fluorescence spectrum was obtained in F-4500 fluorescence spectrophotometer (Hitachi, Japan) at room temperature.

BRB-PMo₁₂ hybrid was synthesized by addition of 0.05 g/mL aqueous solution of butylrhodamine B dropwise to a solution containing 0.1 g/mL PMo₁₂ under vigorous stirring. After complete addition, the mixture was stirred continuously for half an hour. The precipitates were centrifuged three times and washed each time with double distilled water to remove the excessive PMo₁₂. Finally, dried overnight in a vacuum at room temperature and red-wine products can be obtained.

BRB-PMo₁₂ hybrid was dispersed in *N,N*-dimethylformamide solution and sonicated for 5 min and result in 2 mg/mL homogeneous solution. Meanwhile, the pyrolytic graphite electrode (surface area 0.06 cm²) was polished with alumina, followed with being washed in double-distilled water and ethanol, respectively, then activated in 0.5 M H₂SO₄ solution. Then, 10 mL of BRB-PMo₁₂ solution was added on the surface of pyrolytic graphite and dry in ambient.

RESULTS AND DISCUSSION

UV-visible spectroscopy is a useful and facile technique to evaluate the optical property of hybrid. Fig. 1 shows the UV-visible absorption spectra of butylrhodamine B, PMo₁₂ and BRB-PMo₁₂ hybrid. The PMo₁₂ shows one strong characteristic peak at 211 nm (Fig. 1a), which can be ascribed to the O-Mo charge transfer transition. The butylrhodamine B exhibits one peak around 555 nm (Fig. 1b), which relates to the monomeric form of butylrhodamine B. As shown in Fig. 1c, the hybrid presents two characteristic absorption peaks at 216 nm and 554 nm, respectively, substantiating the optical characterization of butylrhodamine B and PMo₁₂ in the hybrid do not alter each other.

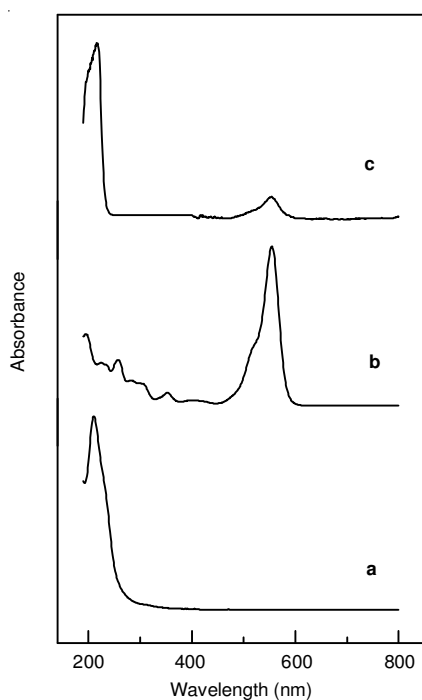


Fig. 1. UV-VIS spectra of (a) PMo₁₂, (b) BRB and (c) BRB-PMo₁₂ solution

FTIR measurements were also carried out for PMo₁₂, butylrhodamine B and BRB-PMo₁₂ hybrid. The corresponding results are shown in Fig. 2. The spectrum of PMo₁₂ exhibits four obvious peaks at 1065, 968, 869 and 790 cm⁻¹ (Fig. 2a). According to literatures^{10,17} peak at 1065 cm⁻¹ is assigned to inner P-O_a-Mo bond, peak at 790 cm⁻¹ to Mo-O_d-Mo bridges, peak at 869 cm⁻¹ to Mo-O_b-Mo, while peak at 968 cm⁻¹ is ascribed to external Mo=O_c bond. The formation of BRB-PMo₁₂ hybrid is evident from the FTIR spectrum because the unique bands of both PMo₁₂ and butylrhodamine B can be observed on composite (Fig. 2c). Additionally, the spectrum of PMo₁₂ is changed (from 1065 to 1052, from 968 to 958, from 869 to 880, from 790 to 805) due to its adsorption on the butylrhodamine B dye.

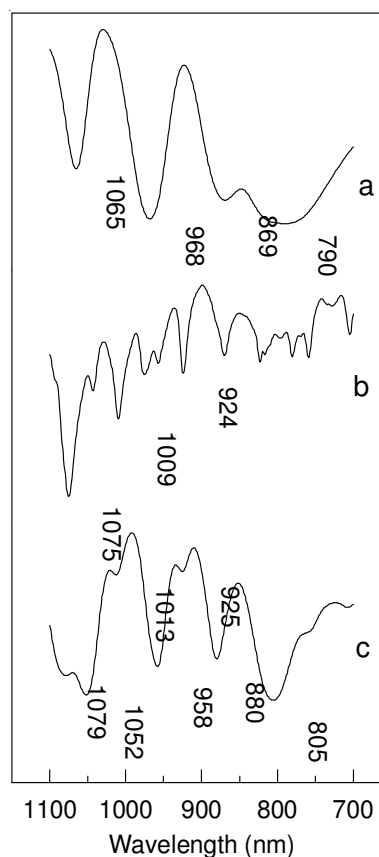


Fig. 2. FTIR spectra of (a) PMo₁₂, (b) BRB and (c) BRB-PMo₁₂

The cyclic voltammogram of bare electrodes with BRB-PMo₁₂ modification in 0.5 M H₂SO₄ aqueous solutions is presented in Fig. 3. At BRB-PMo₁₂ modified electrode, three reversible redox peaks can be observed clearly. The formal potential $E_{1/2}$ ($E_{1/2} = E_{Pa}/2 + E_{Pc}/2$) for three peaks are + 0.28, + 0.18, -0.09 V, respectively. The shape of the curves and the peak potentials are in accord with other work¹⁰. These results show that PMo₁₂ in the hybrid still keeps its electrochemical properties. The electrocatalytical reduction of BrO₃⁻ in 0.5 M H₂SO₄ solution at BRB-PMo₁₂ hybrid modified electrode was investigated preliminarily. It can be observed obviously that the reduction response currents decrease with the addition of the BrO₃⁻, which imply multi-reduction forms of PMo₁₂ anion have electrocatalytic ability to the reduction of BrO₃⁻.

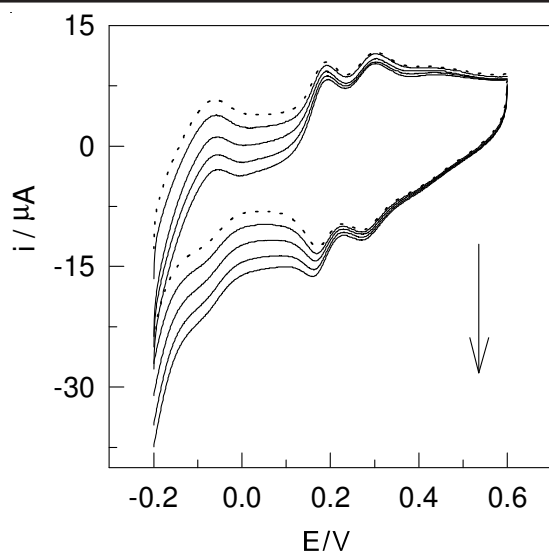


Fig. 3. Cyclic voltammograms of PG/BRB-PMo₁₂ electrode in a 0.5 M H₂SO₄ solution without (dotted line) and with 1, 2, 3, 4 mM (from inside to outside, solid line) BrO₃⁻.

The fluorescence excitation and emission spectra of butylrhodamine B and BRB-PMo₁₂ hybrid in DMF solution were shown in Fig. 4. It can be seen that butylrhodamine B solution shows apparent spectral characteristics with excitation maximum at 474 nm and emission maximum at 605 nm. However, the wider distance between excitation and emission maximum and the larger fluorescence intensity can be observed at BRB-PMo₁₂ hybrid in the same experiment condition. The excitation maximum and emission maximum are at 496 nm and 599 nm, respectively. The fluorescence intensity of BRB-PMo₁₂ hybrid is almost 1.3 times than that of butylrhodamine B. These imply that the existence of PMo₁₂ in hybrid does not change the original fluorescence property of butylrhodamine B but improve the fluorescence intensity because of the unique structure of PMo₁₂.

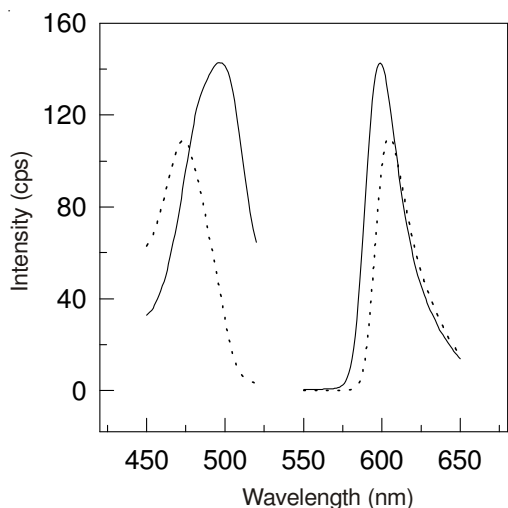


Fig. 4. Fluorescence spectrum of BRB solution (dotted line) and BRB-PMo₁₂ solution (solid line) in the same condition (PMT voltage 400 V, Ex slit 5.0 nm, Em slit 5.0 nm).

Conclusion

A new BRB-PMo₁₂ hybrid material was prepared here in a convenient and effective method. The resulting hybrid material can be used in chemically modified electrode for amperometric detection of bromate. More importantly, it has higher fluorescence intensity than pure organic phases. These results provide a useful avenue for preparing novel multi-functional hybrid materials, which can be used in catalysis, biosensing, magnetic and optical fields.

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