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Preparation of green luminescence composite film and study of electrofluorochromic performance

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ABSTRACT

A novel hybrid consisting of 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HOPTS) and graphene oxide (GO) was firstly synthesized as GO@HOPTS, which was confirmed to exhibit green luminescence emission. Then, GO@HOPTS and heteropolyanion $NaP_5W_{30}O_{110}^{14-}$ (P_5W_{30}) were utilized to fabricate the composite films $\{(PDDA/P_5W_{30})_5/[(PDDA/P_5W_{30})_5/PDDA/GO@HOPTS]_{15}/(PDDA/P_5W_{30})_5\}$ on quartz substrate and conductive ITO-coated glass electrode by the layer-by-layer (LBL) assembly deposition technique based on the electrostatic attraction of oppositely charged species. The composite films were characterized by cyclic voltammetry (CV), fluorescence spectroscopy, UV–vis spectroscopy and X-ray photoelectron spectroscopy (XPS). The electrofluorochromic performance of the composite film was investigated by in situ UV–vis spectroelectrochemical and fluorescence spectroelectrochemical measurements under electrochemical modulation. The results indicate that the composite film displays not only green luminescence emission but also reversible green luminescence switching behaviors manipulated by the redox process of P_5W_{30} via the energy transfer between the green luminescence component HOPTS and electroreduced species of P_5W_{30}.

1. Introduction

Since the discovery of the first example by Berzelius in 1826, the class of polyoxometalates (POMs) has been known for almost 200 years to date [1]. Nevertheless, the chemistry of POMs continues to receive considerable attention due to their enormous structural variety and interesting properties [2–5], which ensure their potential applications in many fields, such as catalysis [6–8], sensor [9], magnetochemistry [10], and materials science [11–15]. In particular, high chemical and long-term environmental stability, reversible redox activity and unique electronic property make POMs promising components for the functional materials [16–18].

In recent years, POM-based reversibly fluorescent switchable materials were investigated [19–21]. Usually, the realization of the fluorescent switch must encounter the following three conditions: (i) absorption spectrum of the energy acceptor should be overlapped with luminescence spectrum of the energy donor; (ii) the energy acceptor and energy donor should be arranged orderly; and (iii) the distance between energy acceptor and energy donor should be in the appropriate range. On account of the above conditions, the POMs were selected as the energy acceptor to regulate the fluorescent switch due to the following reasons: (i) POMs in reduced state exhibit a broad absorption band in the visible light region from 400 nm to 800 nm, which can overlap with the emission band of luminescence species; (ii) POMs and luminescence entities can realize order arrangement in the composite films via suitable design; (iii) the distance between POMs and luminescence species can be easily controlled by changing the fabrication sequence of POMs and luminescence species. So far, several examples of POM-based luminescence switching were reported [22,23]. The performance comes into three main categories, depending on the type of external triggers: POM-based fluorescent materials were switched by acid–base gases [24], UV–vis light irradiation [25], and electrochemical potential [26].

Our group used electrochemical technology to realize red luminescence switch based on Eu-POM composite film and the hybrid film comprising POM and red luminescence molecule for the first time [27,28]. At same time, our group investigated the effects of POM structures on electrochemically induced luminescence switchable behaviors [29], displaying that the fluorescence quenching efficiencies of the composite films depend on the POM structures under same experiment conditions, demonstrating that the desired electrochemically induced fluorescent switchable materials can be optimized by the choice of different POMs. However, it can be noticed that in almost all of the above

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examples POMs were used to switch red luminescence. There are only two reports on the other color luminescence switching manipulated by POMs [30,31]. Therefore, the rational design and investigation of other color luminescence switching materials based on POMs are a challenge.

Here, we fabricate a green luminescence composite film by the rational design. As expected, the composite film exhibits a reversible green luminescence switching behavior.

2. Experimental section

2.1. Materials

The heteropolyanion $NaP_5W_{30}O_{110}^{14-}$ (P_5W_{30}) was prepared according to the literature method [32] and identified by IR spectroscopy, UV spectroscopy and CV. 8-Hydroxypyrene-1,3, 6-trisulfonic acid trisodium salt (HOPTS) and poly(diallyldimethylammonium chloride) (PDDA, MW 100,000–200,000) were purchased from Sigma-Aldrich and used without further purification. Other related chemicals are of analytical grade. Water was purified using a Millipore Milli-Q water purification system. All measurements were done in 0.5 M H_2SO_4/Na_2SO_4 solution (pH = 2.5).

2.2. Instruments

UV–vis spectra were collected with a Varian Cary 50 UV–vis spectrophotometer. Fluorescence spectra were measured with a FLS980 spectrofluorometer. All the electrochemical experiments were carried out on a CHI 660C electrochemical workstation in a conventional three-electrode electrochemical cell using a reference electrode (Ag/AgCl), a counter electrode (a platinum foil) and a working electrode (ITO). Electrofluorochromic performance was performed by an in-situ spectroelectrochemical system through combining CHI 660C electrochemical workstation with a Varian Cary 50 UV–vis spectrophotometer and FLS980 spectrofluorometer. XPS was measured on modified ITO using an ESCALAB MK II Surface Analysis System (including X-ray photoelectron spectrometer) with aluminum Kα (1486.6 eV) as the X-ray source.

2.3. Preparation of GO@HOPTS solution

GO was prepared according to the literature procedure [33–35]. GO (100 mg) was dipped into 100 mL water for one day and dispersed in water with the help of ultrasonication. Under gentle stirring, HOPTS (20 mg) was added into the above dispersion solution. In order to make the HOPTS molecules completely adsorb on the surface of GO, above dispersion solution was stirred last for one day. Then the dispersion solution was centrifuged for 20 min under the rotating speed of 12,000 rpm and supernatant was removed. Remaining precipitate (GO@HOPTS) was re-dispersed in 100 mL water to form GO@HOPTS solution for the fabrication of the composite film. The hybrid GO@HOPTS was characterized by luminescence and FT-IR spectra.

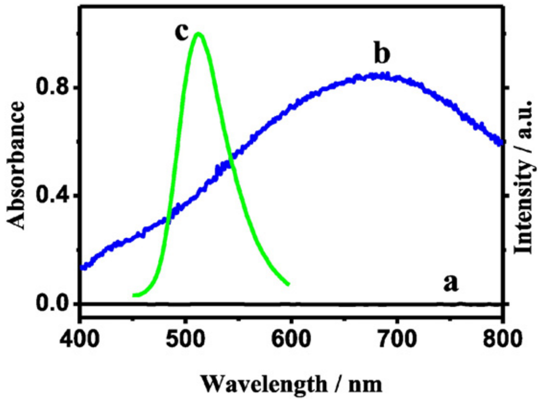

Fig. 1. UV–vis spectra of P_5W_{30} in its initial state (a) and electro-reduced state (b), and normalized luminescent spectrum of HOPTS (c) in 0.5 M H_2SO_4/Na_2SO_4 (pH = 2.5) aqueous solutions.

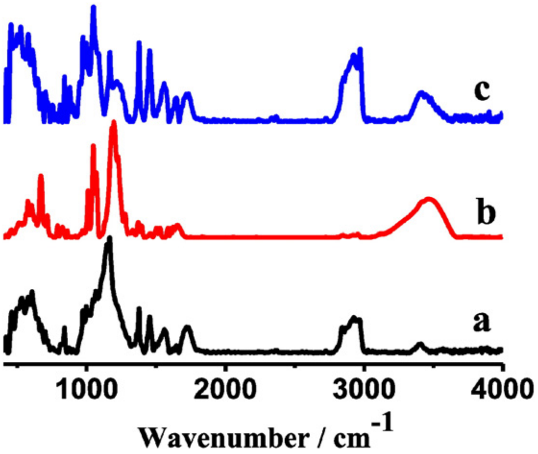

Fig. 2. FT-IR spectra of GO (a), HOPTS (b) and GO@HOPTS (c).

2.4. Fabrication of the composite films

Firstly, the quartz substrate and the conductive ITO-coated glass electrode were cleaned according to the literature methods [36]. Then, the composite films on the surface of the substrates were alternatively deposited from 10 mg/mL PDDA, 2 mM P_5W_{30} and GO@HOPTS aqueous solutions based on LBL assembly technology. In each deposited process, the immersion time was 20 min and the modified substrates were picked out and rinsed thoroughly by deionized water several times for removing partial physically adsorbed substances and followed by drying with nitrogen stream.

3. Results and discussion

3.1. The activity studies of P_5W_{30} and HOPTS in solutions

Oxidation state of P_5W_{30} is colorless and fully transparent (Fig. 1, black curve), but reduced state of P_5W_{30} is dark blue and exhibits a

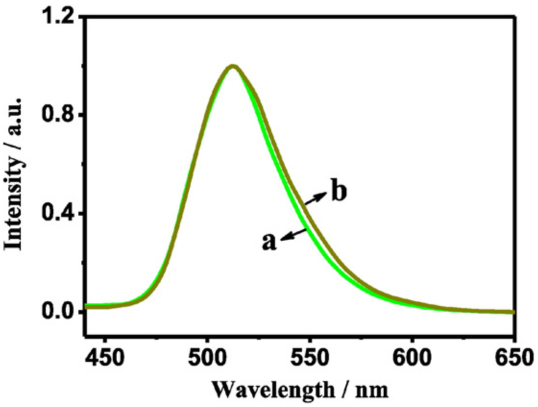

Fig. 3. Normalized luminescent spectra of HOPTS aqueous solution (a) and GO@HOPTS aqueous solution (b).