Investigation of the Electrochromic Properties of Dawson-type Polyoxometalate and Xylenol Orange

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ABSTRACT

This paper focuses on the electrochromic (EC) properties of the film material consisting of Dawson-type polyoxometalate (POM) and xylenol orange (XO). The composite film is prepared by the layer-by-layer self-assembly technique (LbL). A significant optical modulation (17% at 650 nm), fast switching time, high coloration efficiency (49 cm²/C at 650 nm) are achieved for the POM and XO film. In addition, the composite film shows adjustable colors, making it attractive for practical applications.

INTRODUCTION

Electrochromic (EC) materials can change their color in response to a small electric potential difference. Major EC materials can be divided into transition metal oxides, viologens, conductive polymers and Prussian blue [1-3]. Polyoxometalates (POMs) have been widely used as EC materials due to their low cost, fast response time and high optical contrast. Wang et al. fabricated three types of vanadium-substituted POMs-based thin film, whose optical contrast is up to 91.8% and switching time for coloration and bleaching is 3.5 s and 3.9 s, respectively [4]. The film based on POM is found to switch from transparent to blue due to the reduction of POM [5]. However, single color change of POM film limits its application.
Recently, layer-by-layer self-assembly method (LbL) relied on alternately electrostatic adsorption of oppositely charged species is an effective and convenient technique for the preparation of POM-based multilayer film. Ma et al. fabricated a composite film consisting of P2W17V and cadmium sulfide nanoparticles by LbL method, which displayed remarkably enhanced electrochromic properties in comparison with the CdS-free film [6].

In this paper, we present a convenient and fast way to prepare a POM and XO thin film at room temperature. The composite film displays well EC performances in terms of fast response time, high optical contrast and coloration efficiency. Furthermore, it can change color from pink to dark blue.

EXPERIMENTAL DETAILS

All chemicals were used as without any further purification. Dawson-type polyoxometalate (P2W18) was prepared according to the literature procedures. 3-aminopropyltrimethoxysilane (APS), poly(ethylene imine) (PEI) and xylenol orange (XO) were purchased from Aldrich. F-doped SnO2 transparent conducting glass substrates (FTO) were purchased from Nippon Sheet Glass.

FTO-coated glass and quartz were used as substrates. The deposition of the composite film was carried out as follows: the substrates were dipped in PEI and PSS solution. Then it was alternately immersed in the PEI (5×10^-3 mol/L), P2W18 (5×10^-3 mol/L), PEI and XO (5×10^-2mol/L) for 7 min, rinsed with deionized water, and dried in N2 after each immersion. The film can be expressed as P2W18-XO.

A three electrodes system was used with Pt wire as the counter electrode, Ag/AgCl as the reference electrode, FTO coated by the composite film as working electrode. UV-vis spectra were recorded using a TU-1901 PERSEE UV–vis spectrophotometer.

RESULTS AND DISCUSSION

![Figure 1. UV-vis spectra of [POM-AR]n film with n = 0-8 on a quartz substrate.](image-url)
Figure 1 displays the UV-vis transmittance spectra of $[\text{P}_2\text{W}_{18}\text{-XO}]_n$ ($n = 0$-$8$) film assembled on quartz substrate. The transmittance of the films increases systematically with the number of cycle, which is evidence for the deposition of $\text{P}_2\text{W}_{18}$ and XO. The multilayer films exhibit the characteristic transmittance peaks at 280 nm and 448 nm, which are corresponding to the strong band of $\text{P}_2\text{W}_{18}$ and XO, respectively.

The chronoamperometry results of P2W18-XO film are summarized in Figure 2. The optical transmittance spectra were measured at a wavelength of 650 nm with alternately applied potentials of -1.0 and +1.0 V for 22 s each. The color of the P2W18-XO film switched between pink and purple blue with variations in the electric potential.

![Figure 2. Potential (a) and chronoamperometry (b) of P2W18-XO film-coated FTO glass for the double potential stepping (-1.0 V and +1.0 V).](image)

![Figure 3. (a) Optical transmittance of P2W18-XO film at 650 nm. (b) Variation of the in situ optical density vs. charge density for P2W18-XO film.](image)
As shown in Figure 3a, the transmittance of $P_2W_{18}$-XO film was 87.2% in the bleached state and 70.4% in the colored state. The modulation range of the film at 650 nm is calculated to be 16.8%. The response times of 7.6 s and 5.3 s for colored and bleached state, respectively. Figure 3b displays plots of the in situ OD versus intercalation charge density of the $P_2W_{18}$-XO film at 650 nm. The coloration efficiency (CE) is calculated to be 49 cm²/C.

CONCLUSION

In summary, P2W18-XO film has been successfully constructed on the FTO glass substrates. The composite film displayed fast response time, high optical contrast and high coloration efficiency.

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