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High performance visible and near-infrared region electrochromic smart windows based on the different structures of polyoxometalates

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ABSTRACT

Polyoxometalates (POMs) are a kind of metal oxide nanoclusters with excellent electrical properties, which have proved to be an excellent candidate for electrochromism (EC) materials. In this paper, we present a better performance POMs-based EC material on the TiO_2 substrate through adjusting the structure of the Well-Dawson type POMs with the electrodeposition method, which can overcome the high cost of the traditional methods such as vacuum evaporation or sputtering. The performance of the EC smart windows was fully tested. The maximum optical contrast for the $K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$ (P_2W_{17})-based EC smart window is 93.1% at the wavelength of 620 nm and for the $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$ (P_2W_{18})-based EC smart window is 48.7% at 646 nm. The coloration time extracted for a 90% transmittance for the P_2W_{17}-based EC smart window is 0.9 s and for the P_2W_{18}-based smart window is 0.97 s; the coloration efficiency for the P_2W_{17}-based EC smart window is 205.3 $cm^2\,C^{-1}$ and the P_2W_{18}-based smart window is 176.8 $cm^2\,C^{-1}$. Both of the P_2W_{17}- and P_2W_{18}-based EC smart windows have the feature of remarkable durability over 1000 cycles. The P_2W_{17}-based smart window has larger optical contrast and higher coloration efficiency than the P_2W_{18}-based smart window. More significantly, the near-infrared behavior of the P_2W_{17} under different applied potentials was recorded for the first time by using the smart window. We believe the performance of the P_2W_{17}-based smart window is the state-of-the-art among the POMs-based EC smart windows.

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1. Introduction

The topics about energy are very popular among scientific research areas with the purpose of sustainable development [1–3]. The major publications are concerned about the utilization of the solar energy and exploration new energy, but energy-saving also plays an important role in sustainable development. Electrochromic (EC) smart windows are being developed for the application in building technologies that are at the forefront of emerging energy saving. These smart windows may be electronically darkened or lightened with small applied potential, allowing for tuning of daylight, solar heat gain, and internal heat loss through windows of the buildings [4–9]. Recently, the EC of near-infrared (NIR) to the microwave region of the spectrum has been focused on, owing to their potential applications in military camouflage, optical communication, data storage, and thermal control [10–13]. Thus the development of NIR and visible difunctional EC device is greatly desired [14–20].

The high performance WO_3-based EC device was prepared by the sputter or vacuum evaporation, which is shown to be a viable option for manufacturing. But for the purpose of cutting cost, the development of atmospheric pressure solution-based deposition methods has proved to be an effective strategy [7]. The electrodeposition method could be a promising route, the possible reasons are as follows: (1) it can be carried out under ambient temperature and atmospheric pressure; (2) it can be applied to complicated shape, large scale and porous substrate; (3) the process is easy to control [21,22]. There are some researches on preparing NiO and WO_3-based EC electrodes by electrodeposition method. However, the electrodeposited films need further annealing processes, which affects the crystal phase and morphology of the EC films [23,24]. The electrodeposition method has not been widely used because the performance of the EC films prepared by this method is worse [25,26].

The appropriate EC materials and the methods to prepare the films are two essential aspects in obtaining a high performance EC device. POMs represent a well-known class of metal oxide nanoclusters with intriguing structures and electrical properties, which

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have been applied in many areas such as catalysis, medicine, and material science [27–34]. POMs clusters can undergo reversible and stepwise multielectron-transfer reactions without changing their structures. And they would exhibit different colors after accepting different electrons. Comparing with the researches of the EC properties on the transition metal oxides, seldom have the research on POMs [35–37]. It is still unknown whether the POMs own the NIR EC properties or not. The successful preparation of the EC film is a crucial step in the fabrication of an EC device. The dominant method to prepare a POMs-based EC film is the LBL method [38–43]. The LBL method plays an important role in the investigation of the EC properties of POMs, but the disadvantages of the method gradually appeared, such as, when the film is thinner, the optical contrast and coloration efficiency will be low; when using thicker film to achieve relative high optical contrast, response time will be longer and the transparency of bleach state becomes worse; more importantly, it takes extremely long time to finish the LBL process, which may slow down the developing progress in studying the POMs-based EC films and the application of POMs in device [38–43]. Recently, our group developed an effective and experimentally convenient solution-based electrodeposition method for high performance EC film assembly, which is based on the intense interaction between POMs anion and TiO_2 substrate. Additionally, POMs show excellent solubility in water, which is different from the transition metal oxides. So it does not need to calcine the POMs-based electrodeposited film. This method has the following advantages: (1) the EC film with high optical contrast can be obtained in a very short time; (2) the deposit process is of low cost and easy to control; (3) the EC electrode made by electrodeposition method also performs long durability [44]. This is also beneficial for the fabrication of large-area EC devices.

The structures of the POMs play an important part in the properties of the POMs-based materials [45,46]. POMs have six basic structures. The derivates of the basic structures make the structures of the POMs versatile [47–49]. Derivates can be generated by adjusting the component of the basic structure. The structures of the derivates are alike, but have big differences of properties [50–52]. For transition metal oxides, the morphology of the materials makes great influence on the performance of the EC device [53–56]. In contrast, for POMs-based EC devices, the adjusting of the structure of POMs molecule would have huge influence on the performance of the device. A benefit of POMs is that the different structures could easily be prepared in pure phase directly. By using the electrodeposition method to prepare a POMs-based EC film, it would reduce the cost dramatically. The proper method is the precondition of fabricating a POMs-based EC smart window, thus, through adjusting the components of a POM molecule to hunt proper POMs EC materials is an extremely meaningful and crucial work.

In this paper, we choose the Well-Dawson type POMs $K_6[P_2W_{18}O_{62}]\cdot14H_2O$ and its derivative $K_{10}[P_2W_{17}O_{61}]\cdot20H_2O$ (abbreviate as P_2W_{18} and P_2W_{17}) as the EC materials by using the electrodeposition method to prepare the EC film on the porous TiO_2 substrate and fabricate high performance POMs-based smart windows successfully. Because the differences of the structures, the P_2W_{17}-based smart window exhibits NIR EC behavior when the applied potential up to −1.6 V. It is the first time to investigate the NIR EC properties of POMs. Meanwhile, the differences of the performance between the P_2W_{18}- and P_2W_{17}-based EC smart windows are compared in the paper.

2. Experimental

2.1. Materials

$K_6[P_2W_{18}O_{62}]\cdot14H_2O$ and $K_{10}[P_2W_{17}O_{61}]\cdot20H_2O$ were prepared according to literature procedures [57]. The TiO_2 paste with particle size of ca. 18 nm was bought from Dyesol. FTO glass (14 Ω/□, Nippon Sheet Glass) was purchased from Heptachroma (Dalian, China). The electrolyte is 0.1 M LiI PC solution. The other reagents were all purchased from purchased from Aladdin.

2.2. Instruments

Electrochemical experiments were performed on CS350 electrochemistry station (CH Instruments, Wuhan CorrTest® Instrument Corporation, China). Field emission scanning electron microscopy (FESEM) images and scanning electron microscopy with an energy dispersive X-ray analytical system (SEM-EDX) were taken using Hitachi S-4800 scanning electron microscope. Atomic force microscopy (AFM) measurements were performed in air with a SPI3800 N Probe Station. Visible light absorption spectra and transmittance spectra were obtained with a Varian Cary 500 UV-vis NIR spectrometer.

2.3. Preparation of the EC electrode

The TiO_2 film with the thickness of ca. 7 μm was prepared using the screen printing method. The electrodeposition process is as follows: the counter electrode is Pt wire; the reference electrode is Ag/AgCl and the TiO_2 film acts as the working electrode. The TiO_2 film was immersed in the P_2W_{17} or P_2W_{18} aqueous solution (pH ~ 2.0, 0.7 mM), then scanned using cyclic voltammogram method between −1.0 and 0.5 V at a scan rate of 100 mV s^{-1} for 30 cycles. After that, the film was rinsed with deionized water and dried with hot air, and then the film was placed in the oven with the temperature of 150 °C for 30 min.

2.4. Assemble of the EC smart window

A bare FTO with a hole acted as the counter electrode. The device was sealed with Surlyn film (45 μm), the electrolyte was injected from the hole of the FTO. The hole was sealed with another thin glass.

3. Results and discussion

An EC device is essentially a rechargeable battery, in which the EC electrode is separated by a suitable electrolyte from a charge balancing counter electrode. The structure of the POMs-based EC device is illustrated in Scheme 1. The transparent and porous TiO_2 film provides a substrate for the P_2W_{18} or P_2W_{17} molecules and transport electrons between the external circuit. Under a sufficient negative external potential, the electrons can pass through the TiO_2 film and inject to the vacant levels of the P_2W_{18} or P_2W_{17} molecules to form the heteropoly blue (colored process). In contrast, when a positive potential applied, the electrons was extracted from the heteropoly blue to the external circuit and the film return to transparency. This is the bleach process. The surface morphology and the homogeneity of the POMs-based EC film were detected by scanning electron microscope (SEM). As shown in Fig. 1. It exhibits the pores with the size of 20–50 nm in the EC films, which is similar to the photoanode used in dye-sensitized solar cells [58–62]. The size of the TiO_2 grain of the as-prepared TiO_2 substrate is 15–20 nm, and there is no aggregation of the TiO_2 particles in the substrate (Figure S1). After the P_2W_{18} or P_2W_{17} deposited to the TiO_2 substrate, the porous structure was still retained as shown in Fig. 1a and b. There is no sign of aggressive of POMs molecules in the pores of the TiO_2 substrate which is benefit for the diffusion of electrolyte in the TiO_2 matrix, resulting in the short response time of coloration and bleaching [63–65]. EDX taken by SEM is able to analysis the components of the POMs-based films. The element W appears in Figure S2a and S2b verify the existence of P_2W_{17} and P_2W_{18} polyanions

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