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Enhanced electrochromic performance of a vanadium-substituted tungstophosphate based on composite film by incorporation of cadmium sulfide nanoparticles

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ABSTRACT

A composite film consisting of vanadium-substituted tungstophosphate α_2-$K_7P_2VW_{17}O_{62}\cdot18H_2O$ ($P_2W_{17}V$) and cadmium sulfide nanoparticles (CdS) was fabricated on quartz, silicon and indium oxide substrates by layer-by-layer self-assembly method. The composite film $\{PEI/[P_2W_{17}V/PEI–CdS]_n/P_2W_{17}V\}$ was characterized by UV–visible spectra, cyclic voltammetry, chronoamperometry, atomic force microscopy, scanning electron microscope and X-ray photoelectron spectra. Visually optical contrast from light yellow to dark goldenrod can be seen for the composite film during the potential scanning between 0 and −1.1 V. The 30 bilayers composite film displayed the optical contrast of 59.8% and coloration efficiency of 38.29 $cm^2\,C^{-1}$ at 543 nm which were remarkably enhanced in comparison with the CdS-free film. Therefore, the CdS should be the attractive active component to improve performance of electrochromic materials.

1. Introduction

In recent years, polyoxometalates (POMs) as a well-known class of transition metal oxide nanoclusters with intriguing structures and diverse properties have attracted increasing attention worldwide [1–11]. They were widely used in several fields, such as catalytic activity, molecular conductivity, magnetism, luminescence, especially in photochromism and electrochromism [12,13]. One of the most important properties of these structurally well-defined POM clusters is their ability to undergo reversible multiple electron-transfer reactions without the substantial change of their structures [14,15], which endows POMs reversible electrochromic property. Kurth and his co-workers fabricated multilayer composite film containing POM cluster of $[Eu\text{-}(H_2O)P_5W_{30}O_{110}]^{12-}$ by LbL self-assembly technique and investigated their electrochromic properties [7]. Xu et al. carried out a lot of investigations about electrochromic properties of the composite films containing polyoxometalates. In 2004, they fabricated electrochromic composite films by combination of α-$K_{10}[P_2W_{17}O_{61}]\cdot17H_2O$ (P_2W_{17}) with copper(II) or iron complexes [13]. In 2005, they explored the electrochromic composite film of polyallylamine hydrochloride (PAH) and α-$K_8[P_2W_{17}]_{61}Ni^{II}$ $(H_2O)\cdot18H_2O$ ($P_2W_{17}Ni$) [15]. In the recent few years, they fabricated several composite films based on $K_6P_2W_{18}O_{62}\cdot14H_2O$ and nanoparticles or carbon nanotubes or PEDOT, which showed reversible electrochromic property with tunable color, high optical contrast and long-term stability [1,14,16,17]. We prepared the composite film consisting of Keggin-type polyoxometalate $[SiW_9V_3O_{40}]^{7-}$ (SiW_9V_3) and bismuth oxide nanoparticles (Bi_2O_3), which displayed reverse photochromic and electrochromic performance [8]. The multilayer composite films mentioned above displayed good electrochromism, suggesting that the composite films containing POMs with various structures decorated by other functional components are promising candidates for electrochromic materials and development of this kind of electrochromic films remains challenge.

Cadmium sulfide (CdS) as a kind of semiconductor material has been applied to many areas due to its suitable band gap (approximately 2.4 eV) and strong photoresponse in the visible region [18]. The CdS in nano-scale has special luminescence properties and semiconductor quantized performance. These outstanding properties make CdS nanoparticles attractive candidates for functional materials and widely used in many fields such as solar cells, photodetectors, photoelectrochemistry, photochromism and electrochromic materials [19–29].

In this paper, a composite film based on a polyoxometalate and CdS nanoparticles was fabricated by the layer-by-layer (LbL)

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self-assembly method and its electrochromic performance was explored. In our strategy, a V-substituted polyoxometalate α_2-$K_7P_2VW_{17}O_{62}\cdot 18H_2O$ ($P_2W_{17}V$) was chosen as the electrochromic active component of the proposed composite film. The reasons for selecting $P_2W_{17}V$ are as follows: (*i*) substitution of the metal ions in POMs can modify the electrochemical properties of polyoxometalates [15,30]. (*ii*) Compared to the P_2W_{18} ($K_6P_2W_{18}O_{62}$), $P_2W_{17}V$ contains an additional negative charge, which increases the electrostatic attraction between the $P_2W_{17}V$ layers and opposite layers. (*iii*) Overwhelming majority of the POMs are unstable in the range of high pH value. However, vanadium-substituted POMs could retrieve this shortcoming, which widens their application range. The selected $P_2W_{17}V$ in this work is stable even in pH = 7.0, making the proposed electrochromic film used in mild electrolyte solution which is friendly to the environment. (*iv*) The composite film $\{PEI/[P_2W_{17}V/PEI\text{–}CdS]_{30}/P_2W_{17}V\}$ can display tunable color from light yellow to dark goldenrod due to the mixed color of the reduced $P_2W_{17}V$ and CdS at negative potential.

The electrochromic property of the composite film is improved by incorporation of CdS nanoparticles into the $P_2W_{17}V$ film, resulting in the higher optical contrast, superior coloration efficiency and shorter switching time for bleaching and coloring than that of the CdS-free film. The information above indicated that incorporating CdS nanoparticles into POMs film may be effective to accelerate the occurrence of the redox reaction by increasing the rate of electron transfer [18,29].

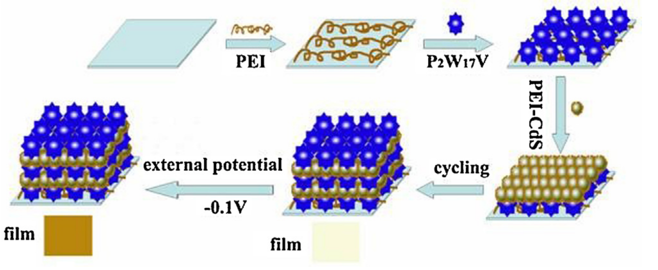
2. Experimental

2.1. Reagent

α_2-$K_7P_2VW_{17}O_{62}\cdot 18H_2O$ ($P_2W_{17}V$) was prepared according to the literature [31,32] and identified by UV–visible (UV–vis) absorption spectra and cyclic voltammetry. Poly(ethylenimine) (PEI MW 750,000) was commercially purchased from Aldrich and used without further purification. NaH_2PO_4, Na_2HPO_4, NaCl, Na_2S, $CdCl_2$ and hydrochloric acid were purchased from Yongchang Chemical Company. All chemicals were of analytical grade or better. The water used in all experiments was deionized to a resistivity of 18 MΩ.

2.2. Physical measurements

All the electrochemical experiments were performed on a CHI 760D Electrochemical Workstation. A conventional three electrodes system was used, with a composite film $\{PEI/[P_2W_{17}V/PEI\text{–}CdS]_n/P_2W_{17}V\}$ coated ITO electrode or a CdS-free film coated ITO electrode as a working electrode, Ag/AgCl (3 M KCl) as the reference electrode and platinum coil as the counter electrode. Atomic force microscopy (AFM) measurements were performed in air with a Dimension TM3100 series of AFM. Scanning electron microscopy (SEM) images were obtained with S-4300. Transmission electron microscope (TEM) images were obtained on an H-7650 TEM. The cyclic voltammetric (CV) and chronoamperometry measurements were carried out at ambient temperature (20 °C) in phosphate buffer solutions (PBS, pH = 7). Electrochromic experiments of composite film were performed by combining the U-3900 UV–vis spectrophotometer with the electrochemical workstation. The electrochemical measurements, electrochemical impedance spectroscopy and electrochromism investigation were measured in the 0.05 M phosphate buffer solution (NaH_2PO_4, Na_2HPO_4) for the electrocatalysis at room temperature.



Scheme 1. Scheme for the formation of the electrochromic composite film $\{PEI/[P_2W_{17}V/PEI\text{–}CdS]_n/P_2W_{17}V\}$.

2.3. Syntheses of the PEI–CdS nanoparticles

The colloidal cadmium sulfide nanoparticles were prepared according to the reported procedure [33]. In a classic process, 1 mL of 0.2 M $CdCl_2$ solution was added to 18 mL of 0.25 wt% PEI solution. The resulting viscous solution was added to 1 mL of 0.2 M Na_2S solution under vigorous stirring.

2.4. Preparation of the composite film

The surface of quartz was cleaned according to references [6]. Firstly, the substrate was thoroughly cleaned by treatment with Piranha solution (H_2SO_4:H_2O_2 = 7:3, v/v) at 80 °C for 20 min, and then rinsed with deionized water. Further purification was carried out by immersing the substrate in $NH_3\cdot H_2O$:H_2O_2:H_2O (1:1:5, v/v/v) solution at 70 °C for 20 min and extensively washing with water and drying with slow stream of nitrogen. The cleaned substrate was immersed in 10 mM PEI solution for one night to form a precursor layer. Then, a composite film $\{PEI/[P_2W_{17}V/PEI\text{–}CdS]_n/P_2W_{17}V\}$ was deposited onto the substrate-supported precursor by immersing the substrate alternately in POM solution (2 mM) and PEI–CdS solution (0.1 M CdS solution with 2.5 wt% PEI) for 30 min, respectively, followed by rinsing with deionized water and drying in a gentle nitrogen stream after each immersion. This process can be repeated until the desired number of bilayers of $\{PEI/[P_2W_{17}V/PEI\text{–}CdS]_n/P_2W_{17}V\}$ is obtained. Scheme 1 illustrates the fabrication process of the composite film. For comparison, a $\{PEI/[P_2W_{17}V/PEI]_n/P_2W_{17}V\}$ film also was prepared.

ITO glass substrates were ultrasonic cleaned by immersing into a KOH (30%)–ethanol solution for 20 min at 40 °C, and thoroughly rinsed with deionized water. Then, the substrates were immersed into ethanol for ultrasonic cleaning at 40 °C, followed by rinsing with deionized water and drying in a nitrogen gas. Finally, purification was carried out by immersing in deionized water for ultrasonic cleaning at 40 °C. With the fabrication procedure mentioned above, highly reproducible films with controlled thickness were obtained.

3. Results and discussion

3.1. UV–vis absorption spectra

UV–vis spectroscopy was used to monitor the growth process of the composite film. Fig. 1 shows the UV–vis absorption spectra of the multilayer composite film $\{PEI/[P_2W_{17}V/PEI\text{–}CdS]_n/P_2W_{17}V\}$ (with n = 1–12) assembled on a quartz substrate (on both sides). The composite film $\{PEI/[P_2W_{17}V/PEI\text{–}CdS]_n/P_2W_{17}V\}$ (n = 1–12) exhibits two characteristic absorption bands of $P_2W_{17}V$ at about 196 and 280 nm, which are owing to the terminal oxygen to tungsten ($O_d \rightarrow W$) and the bridge-oxygen to tungsten ($O_b/O_c \rightarrow W$) charge transfer transitions, respectively [14,34]. In comparison with the UV–vis spectrum of the $P_2W_{17}V$ solution, these two