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A reversible photochromic switch based on self-assembly of layered double hydroxide and decatungstate

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ABSTRACT

This paper reports the fabrication of photochromic anions/layered double hydroxide (LDH) films by alternate assembly of polyvinyl alcohol modified tungstate (PVA-$W_{10}O_{32}$) and CoAl-LDH nanosheets on quartz substrates using the layer-by-layer (LBL) deposition technique, and demonstrates their application as an optical switch through alternate irradiating using UV and visible light. UV–vis absorption spectroscopy indicates a stepwise and regular growth of the (PVA-$W_{10}O_{32}$/LDH)$_n$ film upon increasing deposition cycles. X-ray diffraction and scanning electron microscopy (SEM) demonstrate that the films possess a periodical layered structure perpendicular to the substrates with a thickness of ~2.53 nm per bilayer. Furthermore, the optical switch with film thickness of 65 nm (25 bilayers) exhibits a reversible photochromic property, rapid response for UV and visible light (5 min), high storage stability (~97.5% of its initial absorbance remained after one month) as well as mechanical stability. In addition, the study on mechanism of color change cycle of the optical switch shows that the reversible change of valence state for W element confirmed by XPS and ESR. Therefore, this work provides new opportunities for fabrication and application of photochromic anions/LDH films which can be used as optical devices and sensors.

1. Introduction

Photochromic materials, which show practical or potential applications in the fields of protection (spectacles, photobarriers, anti-fake, and camouflage), illumination, decoration, memory, display, photography, switches, photometry, data storage, photomechanics and so on, have attracted great interests [1]. In order to take advantage of the photochromic property, the active molecules must be dispersed in a medium (solvent or solid matrix) because the photochromic compound usually is inactive in its crystalline state [2]. Generally, organic solid polymers (PMMA) are used as the medium to disperse photochromic molecules [3]. However, some inherent demerits (relatively poor thermal or optical stability as well as toxicity) of the organic polymers greatly limit the practical application of this kind of photochromic material to date. Therefore, it is essential to search for materials to disperse the photochromic molecules, so as to achieve photochromic switches with high photochromic efficiency and stability, as well as environmental compatibility.

Inorganic material used as dispersive medium to disperse photochromic molecules due to its excellent stability is a type of preferable matrix, such as sol–gel derived silicates [4] and aluminosilicates [5]. However, these resulting photochromic materials have displayed slower response time than that of solution and organic solid matrices. Thus, it is vital to choose a suitable inorganic material to disperse photochromic molecules. Recently, the exfoliated inorganic nanosheets of layered double hydroxides (LDHs) have attracted strong attention thanks to its stability (light, temperature and mechanics) and environmental compatibility [6]. Especially, the optical films fabricated by electrostatic self-assembly of LDH building blocks and optical molecules show enhanced optical properties (intensity, efficiency and fluorescence resonance energy transfer) [7]. Inspired by this, we hypothesize similar assemblies of LDH nanosheets as dispersive medium and photochromic molecules may result in enhanced photochromic property. The LDH nanosheets provide a confined and stable microenvironment for dispersing and fixing photochromic molecules; the size of LDH nanosheets in nanoscale is beneficial for the decreasing of energy loss of triggering light, accelerating photochromic speed and enhancing photochromic efficiency of optical molecules; the inherent anisotropy of LDH nanosheets imparts a high orientation on photochromic molecules, which

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is expected to induce compact and order arrangement of photochromic molecules.

In this work, tungstate (WO_4^{2-}) was chosen as guest anion to assemble with LDH nanosheets by alternate layer-by-layer (LBL) method to obtain photochromic switches, since its wide application in electrochromic devices, photocatalysers, gas sensors, optical switching devices, etc. [8]. Exactly, tungstate has been studied for a long time. Generally, organic polymer was used as host material to disperse tungstate to obtain tungstate-based film material, so as to realize the application in photochromic sensor and devices. However, poor light and thermal stability of organic polymer greatly limit the wide application of tungstate-based film material. Moreover, non-uniformity of the polymer/tungstate composite also has effect on its property. In our work, LDH was used as host material to assemble with tungstate by layer-by layer method which can realize combination in nano-scale size and obtain a kind of uniform and new inorganic-inorganic composition film. Furthermore, stability of LDH material intensively enhanced the stability of composition film. In order to realize the assembly of tungstate and LDH nanosheets, polyvinyl alcohol (PVA) was utilized to modify tungstate to form decatungstate ($W_{10}O_{32}^{4-}$) [9]. The $(PVA\text{-}W_{10}O_{32}/LDH)_n$ films were obtained by alternate LBL assembly of LDH nanosheets and $PVA\text{-}W_{10}O_{32}$ on a quartz substrate, which shows potential application in the field of optical switch. UV–vis absorption spectra indicate a stepwise and regular film growth procedure, and the film surface is continuous and uniform confirmed by SEM images. The $(PVA\text{-}W_{10}O_{32}/LDH)_{25}$ film with a thickness of ~65 nm exhibits reversible photochromic switch triggered by UV and visible light, high storage (97.5% of its initial absorption intensity remains after one month) and mechanical stability. Therefore, we provide here a simple method to fabricate films with reversible photochromic property, which can be potentially used to develop advanced photochromic devices and sensors. These hybrid systems are potential candidates for applications involving UV-light-sensitive coatings, smart windows, information displays, high-density memory devices and UV dosimetry.

2. Experimental

2.1. Materials

Na_2WO_4 (biochemistry grade) was purchased from Sigma–Aldrich Company. Analytical grade chemicals including $Co(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, ethanol, ethylether, HNO_3, NaOH, PDDA (diallyldimethylammonium chloride), PSS (sodium polystyrenesulfonate) and PVA were used without further purification. The deionized and decarbonated water was used in all the experimental processes.

2.2. Fabrication of the $PVA\text{-}W_{10}O_{32}$

A Na_2WO_4 aqueous solution ($0.17\,g\,mL^{-1}$) was dropped into a 75 mL of HNO_3 ($1\,mol\,L^{-1}$), and a light yellow deposition was obtained. After 30 min, the deposition was stepwise washed by 170 mL of HNO_3 ($0.05\,mol\,L^{-1}$), 35 mL of ethanol and 20 mL of ethylether [10]. The $PVA\text{-}W_{10}O_{32}$ colloidal solution was prepared by adding a 0.25 g of deposition above in PVA aqueous solution at 60 °C for 1 h. The reaction formula was shown in Fig. S1.

2.3. Fabrication of the $(PVA\text{-}W_{10}O_{32}/LDH)_n$ films

The CoAl-NO_3 LDH precursor was synthesized by the hydrothermal method reported previously [11]. A 0.1 g of CoAl-LDH was shaken in 100 mL of formamide solution for 24 h to obtain a colloidal suspension of exfoliated CoAl-LDH nanosheets. The quartz glass substrate was cleaned in concentrated $NH_3{\cdot}H_2O$/30% H_2O_2 (7:3) and concentrated H_2SO_4 for 30 min each. After each procedure, the quartz substrate was rinsed and washed thoroughly with deionic water. The substrate was dipped in a solution of PDDA ($1.0\,g\,L^{-1}$) for 20 min followed by washing in water, and then the substrate was dipped in a solution of PSS ($1.0\,g\,L^{-1}$) for 20 min followed by washing in water. The modified substrate above was dipped in a colloidal suspension ($0.1\,g\,mL^{-1}$) of LDH nanosheets for 10 min followed by washing thoroughly, and then the substrate was treated with a 100 mL of $PVA\text{-}W_{10}O_{32}$ aqueous solution (0.025 wt%) for another 10 min followed by washing. Multilayer films of $(PVA\text{-}W_{10}O_{32}/LDH)_n$ were fabricated by alternate deposition of LDH nanosheets suspension and $PVA\text{-}W_{10}O_{32}$ solution for n cycles. The resulting films were dried with a nitrogen gas flow for 2 min at 25 °C. For comparison, $(PVA\text{-}W_{10}O_{32}/Mg\text{-}Al\text{-}LDH)_{15}$ and $(PVA\text{-}W_{10}O_{32}/Zn\text{-}Al\text{-}LDH)_{15}$ films were also synthesized by the same way.

2.4. The response to UV and visible light measurement

The film was irradiated by UV light with different times (0, 5, 10, and 15 min) in the room temperature, and then the irradiated film by UV light was put in the visible light environment. The film response to light was recorded by a UV–vis absorption spectra with a liquid holder.

2.5. Characterization techniques

The UV–vis absorption spectra were collected in the range from 190 to 900 nm on a Shimadzu T-9201 spectrophotometer, with the slit width of 1.0 nm. X-ray diffraction patterns (XRD) of the PTS/LDH UTFs were recorded using a Rigaku 2500 VB2+PC diffractometer under the conditions: 40 kV, 50 mA, Cu Kα radiation ($\lambda = 0.154056$ nm) step-scanned with a scanning rate of 0.5°/min, and a 2θ angle ranging from 2° to 10°. The morphology of thin films was investigated by using a scanning electron microscope (SEM ZEISS). X-ray photoelectron spectroscopy (XPS) measurement was performed with monochromatized A1-Kα exciting X-radiation (PHI Quantera SXM). The ESR spectra were recorded at room temperature with a Bruker ESP300 spectrometer. A standard 100 MHz field modulation and a 5–10 G modulation width were used.

3. Results and discussion

3.1. Characterization of the $(PVA\text{-}W_{10}O_{32}/LDH)_n$ films

3.1.1. Assembly of the $(PVA\text{-}W_{10}O_{32}/LDH)_n$ films

Fig. 1A shows the UV–vis absorption spectra of the $(PVA\text{-}W_{10}O_{32}/Co\text{-}Al\text{-}LDH)_n$ films with various bilayer numbers (n) deposited on quartz substrates. A stepwise and regular film growth procedure is observed by the linear correlation between the absorption band of $W_{10}O_{32}^{4-}$ at ~196 (valence band ~ conductive band transition) and at ~274 nm (other polyanion with W^{6+}) [12] with n (Fig. 1B). The UV absorption spectra of the $(PVA\text{-}W_{10}O_{32}/Mg\text{-}Al\text{-}LDH)_{15}$, $(PVA\text{-}W_{10}O_{32}/Zn\text{-}Al\text{-}LDH)_{15}$, and $(PVA\text{-}W_{10}O_{32}/Co\text{-}Al\text{-}LDH)_{15}$ film are shown in Fig. S2. It can be observed that the absorption intensity of the $(PVA\text{-}W_{10}O_{32}/Co\text{-}Al\text{-}LDH)_{15}$ is far larger than others. So, CoAl-LDH is chosen as the assembled unit to realize the photochromic performance. Compared with $PVA\text{-}W_{10}O_{32}$ colloidal solution (Fig. S3), the absorption spectra for the $(PVA\text{-}W_{10}O_{32}/LDH)_n$ films are similar to $PVA\text{-}W_{10}O_{32}$ colloidal solution, which excludes the aggregation of $PVA\text{-}W_{10}O_{32}$ during the assembly process. The LDH matrix offers a rigid and confined microenvironment for the guest molecule, which leads to a decrease of the rotation freedom of $PVA\text{-}W_{10}O_{32}$.