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# Visible-light photochromic nanocomposite thin films based on polyvinylpyrrolidone and polyoxometalates supported on clay minerals

Xiang-yu Wang[a], Qi Dong[a], Qing-ling Meng[b], Jun-Yan Yang[a], Wei Feng[a,*], Xiang-kui Han[b]

[a] Key Lab of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun 130021, PR China
[b] Key Laboratory of Songliao Aquatic Environment, Ministry of Education, Jilin Jianzhu University, Changchun 130118, PR China

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ABSTRACT

A novel reversible photochromic nanocomposite film was prepared by entrapping phosphomolybdic acid supported on the sodium bentonite (PMoA/Na-MMT) into polyvinylpyrrolidone (PVPd). The microstructure, thermal stability, photochromic behavior and mechanism of the hybrid film were investigated. Fourier transform infrared spectroscopy (FT-IR) results illustrated that the Keggin geometry of polyoxometalates (PMoA) and organic groups of PVPd were still preserved inside the composites and non-covalent bond interaction was built between PMoA/Na-MMT and PVPd polymer matrix. Transmission electron microscopy (TEM) image showed that PMoA nanoparticles were finely dispersed in Na-MMT which exhibited fine stratified structure. Atomic force microscopy (AFM) images indicated that the surface topography of polymeric matrix changed after adding PMoA/Na-MMT, and the surface appearance of nanocomposite film was different before and after visible-light irradiation. The stability of the hybrid film and the effect of the perturbation of Na-MMT on the stability were determined by means of the thermogravimetric analysis (TG) and differential thermal analysis (DTA). Irradiated with visible light, the ultraviolet-–visible spectra (UV–vis) showed that the hybrid films changed from colorless to blue and could recover the colorless state gradually in air, where oxygen played an important role during the bleaching process. The hybrid films exhibited excellent bleaching ability during the heating. According to the X-ray photoelectron spectroscopy (XPS) analysis, the appearance of $Mo^{5+}$ species indicated the photo-reduction reaction between PMoA/Na-MMT and PVPd matrix occurred according to the proton transfer mechanism, and the photochromic reactions were found to exhibit first-order kinetics.

## 1. Introduction

Photochromic materials are important for a number of applications in many fields such as chemical sensors, modified electrodes or holographic storage devices [1]. Polyoxometalates (POMs), a series of multi-core inorganic metal-oxide clusters, is one of the most attractive photochromic materials due to their fundamental structures and versatile electronic properties [2–4]. One of the most important properties of POM anions is the ability of accepting one or more electrons to yield mixed-valency colored species (heteropolyblues or heteropolybrowns), which makes them suitable as photochromic, thermochromic and electrochromic materials [5,6]. However, the fact that POMs is difficult to form films limits its applications. Therefore, to get transparent thin films and to improve their photochromic properties and stability, entrapping POMs nanoparticles into polymeric networks has been the focus [7–9]. The novel functional composite materials which POMs compound to polymeric system have already become the forward scientific research field in the inter-discipline of material science and chemistry, deeply rooted in its unique character bearing the inorganic performance as well as the property of organic polymers. Various polymers such as polyacrylamide (PAM) [10,11], polyvinylpyrrolidone (PVPd) [12], polyvinyl alcohol (PVA) [13,14] and polyether chains (PEs) [15] were used as matrix to construct POMs-based composite films. Normally, these hybrid films can change their color only in response to light in the ultraviolet region. However, UV light is only a small part of the whole solar energy and artificial UV light sources are both unstable and expensive,

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* Corresponding author. Tel.: +86 43188499792; fax: +86 43188499792.
*E-mail address:* weifeng@jlu.edu.cn (W. Feng).

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which limit the marketing process [16–20]. So extending the light response of these hybrid films to the visible-light region has a theoretical and practical significance, which provide a new method for the photochromism upon visible light.

Inorganic layered materials such as clay minerals, layered double hydroxides, and metal oxides have been interesting to use as a nano-sized building block [21]. The montmorillonite group of layered clay materials possesses a two-dimensional space, and various intercalated ionic or polar organic molecules can be accommodated within these interlayer spaces by ion-exchange reactions [22]. Clay minerals are especially attractive due to their large surface area and ion-exchange properties, and their interlayer properties have been modified for controlled functions requiring. In the study, the function of sodium bentonite (Na-MMT) is through the high specific surface area and water-swelling performance to load POMs, which makes POMs evenly dispersed on the Na-MMT and provides good mechanical property of composite films [23–25]. Additionally, polyvinylpyrrolidone (PVPd) was used as a polymeric matrix because of its good soluble ability and high reactivity of organic group.

In this paper, we have prepared a novel reversible photochromic nanocomposite film by entrapping phosphomolybdic acid supported on the sodium bentonite (PMoA/Na-MMT) into polyvinylpyrrolidone (PVPd). The microstructure of the hybrid film was studied with FT-infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The stability of the hybrid film was determined with the thermogravimetric analysis (TG) and differential thermal analysis (DTA) [26]. By means of ultraviolet–visible spectra (UV–vis) and X-ray photoelectron spectroscopy (XPS), the novel visible-light photochromic properties of the hybrid films were investigated. We found some new photochromic phenomena of such hybrid thin films and gave some reasonable explanation for the photochromic process.

## 2. Materials and methods

Keggin type PMoA was purchased from the Beijing Chemical Reagent and purified by recrystallized twice. Polyvinylpyrrolidone (PVPd) with 50,000 molecular weight was obtained from Aldrich and used as received. Bentonite (Na-MMT) obtained from Changchun, Ji Lin Province. The particle size was 75 μm. The chemical composition was found to be as follows: 72.05% $SiO_2$, 15.21% $Al_2O_3$, 1.66% $Fe_2O_3$, 1.85% MgO, 0.42% $K_2O$, 1.56% CaO, 0.28% $TiO_2$ and 2.06% $Na_2O$. All other chemical reagents were of analytical grade and used as received. Deionized water was used in all experiments.

## 3. Experimental

### 3.1. Preparation

0.02 g PMoA and 0.05 g Na-MMT were dissolved in deionized water with the volume of 10 ml, respectively. Then the 10 ml PMoA solution was slowly added to the 10 ml Na-MMT solution under vigorous stirring at 333 K. After stirring for 2 h, the composite solution was cooled to room temperature. Then the composite solution was added to the 10 mg/ml PVPd solution under vigorous stirring at room temperature. After stirring for 20 min, the final transparent solution was obtained and used to prepare composite films by dipping method on various substrates such as copper grids, silicon grids, KBr plates and quartz plates, which were used for TEM studies, AFM studies, FT-IR spectroscopy and UV–vis spectroscopy, respectively. All the hybrid films were dried at room temperature with protection from light. The thickness of hybrid films was approximately 2.5 μm, which was measured by a FCT-1030 Film Thickness Measurements System (LCD Lab, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science).

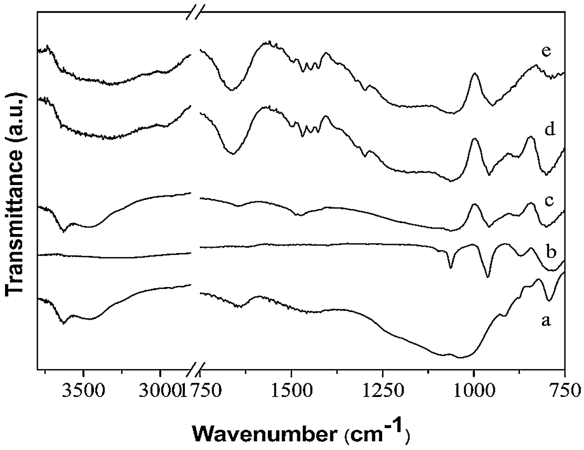

**Fig. 1.** FT-IR spectrum of pure Na-MMT (a), pure PMoA (b), and PMoA/Na-MMT hybrid film (c) PMoA/Na-MMT/PVPd before visible-light irradiation (d) and after visible-light irradiation (e).

### 3.2. Instrumental analysis

FT-IR spectra were determined at room temperature with a Nicolet Impact 410 FT-IR spectrometer in the range of 400–4000 $cm^{-1}$. The TEM images were obtained on a JEOL JEM-200CX transmission electron microscope by dropping onto that copper grid. The AFM measurements were obtained in air using an Auto Probe CP in contact mode. For in suit AFM measurements, the samples were not removed from the scanner so that the whole visible-light irradiation could focus on one position. Absorbance curves were determined on an UV–vis spectrometer (Shimadzu UV-1601PC) with 0.5 nm optical resolution in the range of 350–900 nm. During visible-light radiation, the xenon lamp was also placed over samples at a distance of 150 mm. After the irradiation for a certain time, the in suit images were obtained and all the experimental manipulations were conducted at room temperature. XPS was performed using ESCALAB 250 photoelectron spectrometer.

Photochromic experiments were carried out using a 300 W Xe lamp as the light source. The distance between the lamp and films was 150 mm. Films were exposed to air during the process of visible light irradiated. After irradiation for a certain time, in situ absorbance curve of film was obtained. The irradiation time was recorded until the curve was just the same as the before one. Film was sheltered from light under air conditions and absorption spectra were measured at regular intervals to monitor the bleaching process. All measurements were carried out at room temperature.

## 4. Results and discussion

### 4.1. FT-IR spectra

The FT-IR spectrum in range 3800–750 $cm^{-1}$ of the PMoA/Na-MMT/PVPd hybrid film before and after visible-light irradiation are given in Fig. 1. For comparison, the FT-IR spectra of the PMoA, Na-MMT and PMoA/Na-MMT were performed to confirm the structural features in the resulted composite film. For the pure PMoA, there were four characteristic bands which could represent the Keggin geometry structure at 1060, 962, 870 and 783 $cm^{-1}$ assigned to stretching vibration $\nu$(P-Oa), $\nu$(Mo-Od), $\nu$(Mo-Ob-Mo) and $\nu$(Mo-Oc-Mo) respectively, characterizing the Keggin unit. From Fig. 1c, it can be indicated that the bands in the PMoA/Na-MMT associated with the anions shifted by a few $cm^{-1}$, which shown that the