

Preparation and Photochromic Properties of Hybrid Thin Films Based on Heteropolyoxometallate and Polyacrylamide

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A series of photochromic hybrid films were prepared through entrapping Dawson type tungsten heteropolyoxometallates ($P_2W_{18}O_{62}^{6-}$) and molybdenum heteropolyoxometallate ($P_2Mo_{18}O_{62}^{6-}$) into polyacrylamide matrix. FTIR results showed that the Dawson geometry of heteropolyoxometallates is still preserved inside the composites and strong coulombic interaction is built between heteropolyoxometallates and polyacrylamide *via* hydrogen bonding. Irradiated with ultraviolet light, the transparent films change from colorless to blue and show reversible photochromism. The bleaching process occurs when the films are in contact with air or O_2 in the dark. The molybdenum heteropolyoxometallate hybrid film has higher photochromic efficiency and slower bleaching reaction than tungsten heteropolyoxometallate hybrid film. ESR results indicated that polyacrylamide is a hydrogen donor and the photoreduced process is in accordance with the radical mechanism.

KEY WORDS: Thin film, Heteropolyoxometallate, Polyacrylamide, Photochromism

1. Introduction

Photochromism and electrochromism of transition metal oxides have been a subject of much interest because of their potential technological applications in display, solar energy conversion, high density memory devices and other high technology fields^[1]. However, the low response speed, fatigability and higher cost for manufacture of these materials are not sufficient, which make them far from application. Heteropolyoxometallates (HPOM) have caused increasing attention because of their special structures and properties^[2]. One of the most important properties of these metal oxide clusters is that they can accept electrons or protons to become mixed-valency colored species (heteropolyblues or heteropolybrowns) which make them to be used as photochromic or electrochromic materials. But these kinds of materials are difficult to manipulate into practical devices, which limits their application^[3].

To realize practical applications, photochromic materials must be easily shaped as coatings, monoliths, or any other form. Thus, many studies are introducing HPOM particles into polymeric networks^[4]. Such HPOM-polymer composites are expected to have novel electrical, optical, magnetic and catalytic properties. Recently, our groups^[5,6] have reported the preparation and photochromic properties of HPOM nanoparticles embedded in organic or inorganic polymer. To the best of our knowledge, no one has made study about the photochromic hybrid inorganic polymeric thin film based on Dawson type HPOM entrapped into polyacrylamide *via* hydrogen bond. In this paper, a series of novel photochromic hybrid films were fabricated based on polyacrylamide (PAM) and Dawson HPOM molecules. Such hybrid film has a good photochromicity. The photochromic process is in accordance with the radical mechanism, which is entirely different from the previous works mentioned.

2. Experimental

2.1 Preparation of hybrid composites

Dawson type phosphomolybdic acid (P_2Mo_{18}) and phosphotungstic acid (P_2W_{18}) were synthesized according to a literature method^[7] and recrystallization was performed in aether-water. PAM (AR) (molecular weight is 780000) was purchased from Dow Chemical Co. Deionized water was used

in all experiments. P_2Mo_{18} , P_2W_{18} and PAM were dissolved in water with the concentration of 5 mg/ml, 5 mg/ml and 200 mg/ml, respectively. Then tungsten (or molybdenum) HPOM solution was slowly added into PAM solution with vigorous stirring at 333 K. After stirring for 2 h, the solution was cooled to room temperature. The final transparent solution was used to prepare photochromic inorganic-organic hybrid films on quartz or glass substrates *via* dipping process. Films (denoted PW and PMo, respectively) were dried in a chamber by controlling air humidity that could not exceed 60% in order to obtain optically perfect films. The thickness of the hybrid films, measured using a FCT-1030 film thickness measurement system (LCD Lab, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences), was approximately 2.1 μm .

2.2 Spectroscopy measurement

Fourier transform infrared (FT-IR) spectra were obtained at room temperature with a Nicolet Impact 410 FT-IR spectrometer. All absorption measurements were made on an ultraviolet-visible (UV-vis) spectrophotometer (Shimadzu UV-1601PC). The electron spin resonance (ESR) spectra were recorded on a Bruker ER200-D-SRC spectrometer at X-band. Photochromic experiments were carried out using a 500-W high pressure mercury lamp as the light source. The distance between the lamp and the sample was 15 cm. Samples were maintained in contact with air during irradiation.

3. Results and Discussion

3.1 FT-IR spectra

Since the two samples gave the similar IR vibration bands, we only list the IR spectra of PW film in Fig.1. To compare the characteristic IR bands of PAM with the composite materials, the IR spectrum of pure PAM is also shown. The vibration bands at 1313~1348 cm^{-1} , 1618~1656 cm^{-1} , 1402~1452 cm^{-1} and 2852~2924 cm^{-1} of organic groups are ascribed to vibration mode of C-C, C=O and C-H, respectively^[8]. Contrasted to pure PAM with 3190 and 3373 cm^{-1} for $\nu\text{N-H}$, the $\nu\text{N-H}$ of PW splitted into 3193, 3344 and 3434 cm^{-1} during the composite formation. It was suggested that hydrogen bonding was formed between P_2W_{18} and PAM^[9]. Very strong bands below 1100 cm^{-1} were observed in the infrared spectra of different composite films, due to the polyanions. For example, the infrared spectra in the 2000~700 cm^{-1} region for the PW film with and without

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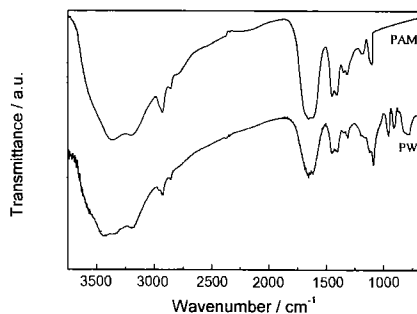


Fig.1 FT-IR spectrum of PW film and pure PAM

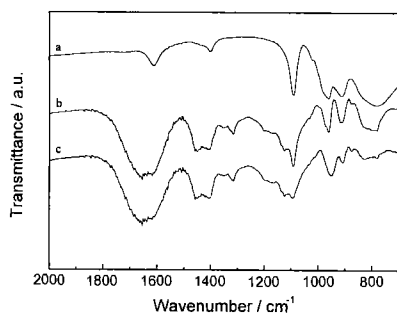


Fig.2 FT-IR spectrum of PW film: (a) P_2W_{18} in a KBr pellet, (b) PW film without UV irradiation, (c) PW film with UV irradiation for 90 min

UV irradiation are given in Fig.2; for comparison, the spectrum of P_2W_{18} in a KBr pellet is also shown. Clearly seen from Fig.2, the bands in composite films associated with the anions are all shifted by only a few cm^{-1} , which indicates that the Dawson geometry of HPOM is still preserved inside the hybrid films. A more detailed inspection of the vibrational band shifts revealed that the $W=O_d$ and $P-O_a$ bands of HPOM in the hybrid films had red shifts and the bands of $W-O_b-W$ had blue shifts. For $W-O_c-W$, in addition to the shoulder observed at 824 cm^{-1} approximately, the position of the $W-O_c-W$ vibrations underwent a blue shift from 779 to 789 cm^{-1} . Compared with the pure P_2W_{18} , a new vibration band appeared at 874 cm^{-1} . Based on the results above, we propose that strong coulombic interaction is formed between two components^[10]. After UV irradiation, the hybrid films changed from colorless to blue. Meanwhile, the frequencies of all characteristic vibrational bands of HPOM are all shifted by a few cm^{-1} compared with the unirradiated composite films, which is due to the formation of heteropolyblue^[11].

3.2 Electronic spectra

The dependence of UV-VIS-NIR absorption spectra of the composite films upon the irradiation of UV light is shown in Fig.3. The films showed no significant absorption from 350 to 1100 nm with the exception of an absorption edge in the UV region before UV irradiation. Figure 3(a) shows the coloration process of PW film with irradiation time. After irradiation, a broad absorption band located between $700\sim 672\text{ nm}$ were observed. Similarly, the PMo film showed one broad band at 722 nm , with the increase of irradiation time its blue shifts to 685 nm (Fig.3(b)). Those bands are characteristics of reduced HPOM molecular species with intervalence charge transfer (IVCT, $M^{5+} \rightarrow M^{6+}$) bands at about $800\sim 625\text{ nm}$ ^[12]. The appearance of IVCT bands shows that electron transfer occurs from the organic substrate to heteropolyanions. Those results indicate that HPOM entrapped in the hybrid matrices can be reduced under UV irradiation. The dependent change in absorbency with the irradiation time for PMo and PW films

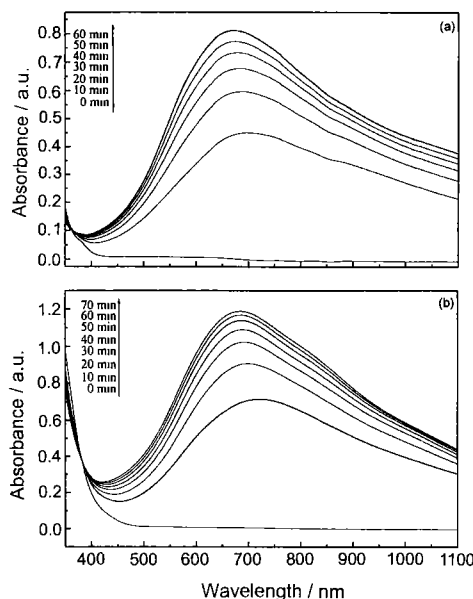


Fig.3 Coloration process. UV/VIS/NIR absorption spectra of the PW (a) and PMo (b) film with the irradiation time. In all cases the numbers on each figure indicates the time of irradiation in minutes

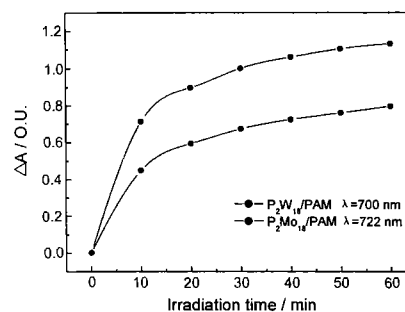


Fig.4 Change of absorbency for PMo film and PW film via UV irradiation time

is shown in Fig.4. It was found that the PMo film showed a strong photochromic effect. The change of absorbency at 700 nm was 1.1295 after the irradiation of the PMo sample for 60 min . The change of absorbency was only 0.7956 at 722 nm for PW sample under the same conditions as the PMo sample. Thus the color change in the PMo sample is 1.42 times stronger than that of the PW sample under same irradiation conditions.

Figure 5 shows the bleaching process of the composite films. After UV light has been turned off, the films begin to decolor gradually in air. The absorption spectra of the two films bleached are coherent with that without irradiation. Contrasting Fig.5(a) with Fig.5(b), we have noticed that the bleaching speed of PW film is faster than that of PMo film. Even 50 days later the intensity of absorption at 680 nm is three fourth of that of color saturation for PMo film, but for the PW film the intensity of absorption at 680 nm is one-fourth. If the colored films are stored in nitrogen, He, Ar or vacuum conditions, it could retain blue for a long time. But changing the ambient atmosphere back to air or oxygen, the bleaching process will start again. These results show that oxygen plays an important role during the bleaching process.

3.3 ESR spectra

The unirradiated samples exhibited no significant ESR signals at 84 K . After UV irradiation the hybrid films exhibited defined signals shown in Fig.6. The signal *b* with

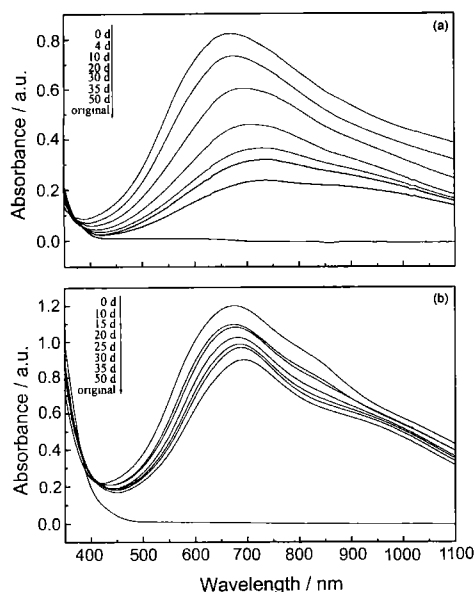


Fig.5 Bleaching process. UV/VIS/NIR absorption spectra of the PW (a) and PMo (b) films with the bleaching time. In all cases the numbers on each small figure indicates the time of irradiation in days

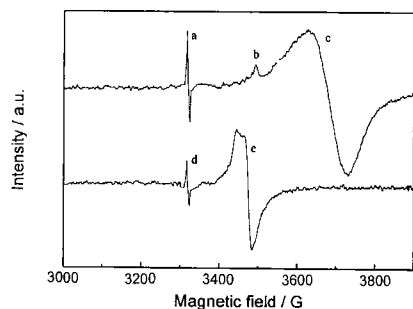
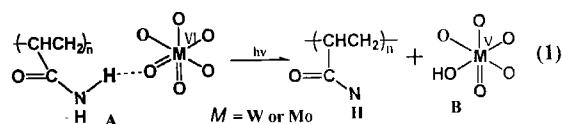


Fig.6 X-band ESR spectrum of the hybrid films at low temperature (84 K). A 500 W high pressure mercury lamp irradiated PW and PMo films for 90 and 70 min, respectively. Signals a and d are due to the formation of radical. Signal b is due to Mo impurities acting as selective electron traps. Signal c and e are due to the photoreduced $[P_2W_{18}O_{62}]^{7-}$ and $[P_2Mo_{18}O_{62}]^{7-}$, respectively

$g=1.957$ is ascribed to Mo^{5+} . The appearance of the Mo^{5+} is because small amounts of Mo (coming from the raw materials, about 0.005%) were always contained in the P_2W_{18} . They behave as selective electron traps under reducing condition^[13]. The broad isotropic signal c ($g=1.858$) is assigned to $[P_2W_{18}O_{62}]^{7-}$ and the signal e with $g=1.961$ is ascribed to $[P_2Mo_{18}O_{62}]^{7-}$. Above values are in agreement with that reported in the literature [14]. The appearance of W^{5+} and Mo^{5+} is an important proof for the oxidation reduction process happened between the heteropolyanions and the organic substrate. As to the radical signal at $g=1.997$ of the colored film, it is deduced that the photochromic mechanism is in accordance with the radical process. Equation (1) denotes the environment of the photoreducible MO_6 site and the subsequent formation of the charge transfer complex B in the hybrid films. The more detail of photoreduced process was indicated that the photoexcitation of the O=M ligand-to-metal charge transfer (LMCT) of WO_6 led to a transfer one hydrogen from PAM to the oxygen atom at the photoreduced site in the edge-shared MO_6 octahedral lattice. At the same time, the N-H and O=M bond decomposed. This was followed by the interaction of one electron of oxygen atom with the hy-

drogen and another electron of oxygen atom was transferred to the metal atom. Thus, the reduction of the polyoxometalates and oxidation of the polymeric matrix happened through radical process.



Complex B reflects the charge separation of the electron and hole, which keeps the colored state stable. The blue film can be bleached to colorless in the dark in contact with air or O_2 , but if it was stored deaeratedly, the blue can be retained for quite a long time. It shows the decoloration process is a chemical process, in which O_2 can oxidize M^{5+} to M^{6+} , but not an oxidation reduction process of the system itself. According to Pope and his coworkers' results^[15], the redox potential of P_2Mo_{18} is bigger than that of P_2W_{18} , which explains that the Mo HPOM-based hybrid film has the highest photochromic efficiency and much slow bleaching process.

4. Conclusion

A series of new photochromic hybrid films were prepared based on Dawson type HPOM in the polymeric network. HPOM clusters maintain Dawson structure and make up strong coulombic interaction with polymeric substrate via hydrogen bonding. The films have good photochromic properties. When exposed to UV light, the films turn blue due to reduction of HPOM and oxidation of polymeric substrate. The photochromic mechanism is in accordance with the radical process. The presence of W^{5+} and Mo^{5+} in the irradiated films was observed and IVCT ($M^{5+} \rightarrow M^{6+}$) transition is responsible for the color. These reactions are reversible in the presence of air or O_2 . The reason why the film containing Mo HPOM shows higher photochromic efficiency and much slower bleaching than that containing tungsten HPOM is attributed to the different redox potentials of the two polyanions.

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