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Article in *Journal of Materials Science Letters* · March 2002

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Controllable structure and photochromic properties of inorganic-polymeric nanocomposite films

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Heteropolyoxometallates (HPOM) have caused increasing attention because of their special structures and properties [1]. One of the most important properties of these polyanion clusters is that they can accept electrons or/and protons to yield mixed-valency colored species (heteropolyblues or heteropolybrowns), which are ideal for use as photochromic and electrochromic materials. But these kinds of materials are difficult to manipulate into practical devices, which limits their applications [2].

To realize practical application, photochromic materials must be easily shaped as coatings, monoliths or other forms. To a large extent, many studies are introducing nanometer-sized HPOM into inorganic and/or organic polymer networks [3–7]. An important advantage of inorganic-polymeric composites is that the polymeric matrix can make nanometer scale HPOM clusters disperse well in the composites and improve the stability of the material. Entrapment is related to chain orientation, chemical reaction and structural relaxation, as well as the interactions between HPOM and the polymeric matrix. The different final film structures would result in significantly different potential properties.

In our previous study, a new photochromic hybrid film was prepared based on Keggin structure phosphotungstic acid (PWA) dispersed into polyacrylamid (PAM) matrix. We found that PWA maintained Keggin geometry in the hybrid film and interacted with the polymeric matrix strongly via hydrogen bonding [8]. The present work is aimed to fabricate hybrid PWA/PAM thin films with controllable structure and photochromic properties via adjusting the PWA content.

PWA was purchased from Beijing Chemical Reagent Co. and used as received. PAM (Mw of 11000 ± 110) was from Dow Chemical Co. Deionized water was used in all experiments. PAM (0.1 g) was dissolved in $10 \times 10^{-6} \text{ m}^3$ water. Appropriate amounts of PWA were added to $10 \times 10^{-6} \text{ m}^3$ water, respectively. Then PAM solution was added to PWA solution under vigorous stirring at 333 K. After stirring for 2 h, the final transparent solution was cooled to room temperature. We prepared two kinds of PWA/PAM composites in which the weight percent of PWA was 9 wt% and 38 wt%, respectively.

Thin films were prepared by dipping method on CaF_2 and quartz substrates for FT-IR and UV-vis measurements. Films 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 was about $2.1 \mu\text{m}$.

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 $2.1 \mu\text{m}$. The TEM image was obtained on a Jeol JEM-200CX transmission electron microscope by dropping complex solution onto copper grids. FT-IR spectra were obtained in a Nicolet Impact 410 spectrometer. UV-vis spectra were performed on a diode array spectrophotometer (Shimadzu UV-1601PC UV-vis spectrophotometer). 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 150 mm. Samples were in contact with air during irradiation.

Fig. 1 shows the infrared spectra (IR) of PWA and the hybrid films with different concentrations of PWA. For pure PWA crystal there are four characteristic

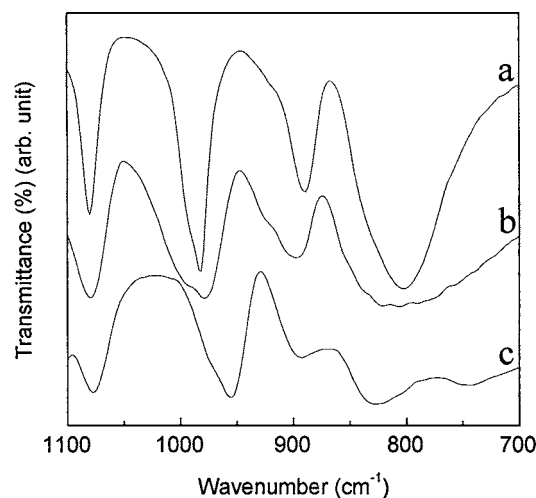


Figure 1 IR spectra of (a) PWA and the hybrid films doped with PWA (b) 38 wt% and (c) 9 wt%.

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bands: 1080 cm^{-1} for $\nu(\text{P-O}_a)$; 982 cm^{-1} for $\nu(\text{W-O}_d)$; 890 cm^{-1} for $\nu(\text{W-O}_b\text{-W})$ and 802 cm^{-1} for $\nu(\text{W-O}_c\text{-W})$. In the case of film doped with PWA, it is found that the bands associated with the polyanions all shifted by only a few cm^{-1} , which indicates that the Keggin geometry of HPOM is still present inside the hybrid film.

Generally, the W-O_d vibration can be considered as a pure stretching one, whose vibration wavenumber is an increasing function of anion-anion interaction. The W-O_d asymmetrical stretching frequency of the films with PWA wt% from 38% to 9% changes from 978 to 955 cm^{-1} . This is attributed to the weakening of anion-anion interactions of electrostatic type, due to the influence of PAM, which leads to the lengthening of the anion-anion distance. Because $\text{W-O}_b\text{-W}$ and $\text{W-O}_c\text{-W}$ vibrations are not pure stretching and cannot be free from bending character, there is a competition of opposing effects. The electrostatic anion-anion interactions lead to an increase in the bending vibrations [9]. Moreover, perturbations due to anion-cation interactions result in a decrease in the vibration frequencies. So, the change of the $\text{W-O}_b\text{-W}$ and $\text{W-O}_c\text{-W}$ asymmetrical stretching frequencies can reflect a difference of anion-cation interaction. A more detailed inspection of the vibrational band shifts reveals that the asymmetrical stretching vibrations of $\text{W-O}_b\text{-W}$ changes from 893 to 896 cm^{-1} and that of $\text{W-O}_c\text{-W}$ varies from 825 to 815 cm^{-1} with the increase of concentration of PWA from 9 to 38 wt%. Hasik *et al.* observed that a shift in $\text{Mo-O}_c\text{-Mo}$ vibration of $\text{PMo}_{12}\text{O}_{40}^{3-}$ incorporated into polyaniline was induced by the Coulombic interactions between the HPOM and the protonated polymeric matrix [10]. Because the PO_4 tetrahedron is assumed to vibrate almost independently, the stretching vibration shows no relation with the PWA dopant content.

The microstructure of hybrid films with different PWA concentration is observed in Fig. 2. The size of PWA particles in the hybrid films is uniform on the nanometer scale and the shape is regularly spherical. But we note that the particle size and conglomeration are effectively tailored by the PWA concentration. The PWA particles in hybrid films with PWA concentration of 9 wt% are smaller than with 38 wt%, having typical particle sizes of 45–55 nm and 55–65 nm, respectively. The nanoparticles in the film with low PWA concentration are well dispersed. In the case of high PWA concentration, the particles appear agglomerated. This tailoring effect of PWA concentration on hybrid films is mainly caused by the strong surface interaction between PWA and the polymeric matrix [11]. It is suggested that PWA particles can interact with the polymer via hydrogen bonding with different density as a function of the PWA concentration, which makes PWA particles exhibit different size and conglomeration.

In the films, a charge-transfer bridge is formed via hydrogen bonding between PWA and PAM and photochemical reaction can take place through this "bridge." Under UV irradiation, reduction occurs due to the transfer of active hydrogen protons in the amino groups from PAM to PWA and PAM acts as an electron donor and PWA as an electron acceptor. Typical absorption of the

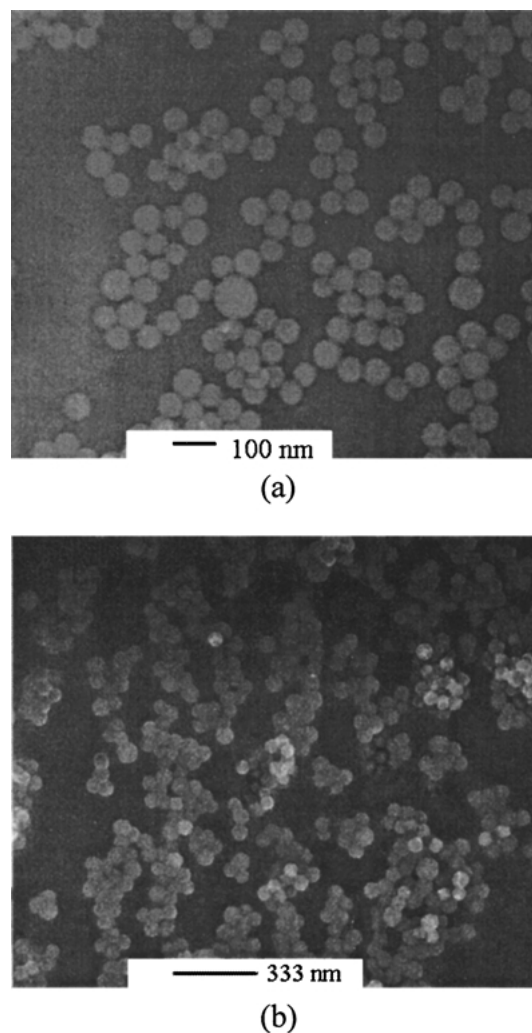


Figure 2 TEM micrographs of nanocomposite films with different PWA concentration: (a) 9 wt% and (b) 38 wt%.

hybrid films with different PWA concentration before and after UV irradiation is shown in Fig. 3. Before UV irradiation, there was no absorption band from 400 to 1000 nm, and the films are colorless. From Fig. 3, it can be found that the photochromic behaviors of the films were influenced by the PWA concentration after it was exposed to UV light. For the hybrid film with 9 wt% PWA concentration, two broad intense absorption bands appeared at 490 and 620 nm, respectively, and the film turned blue. Those bands are characteristic of reduced Keggin molecular species with d-d bands and intervalence charge transfer (IVCT, $\text{W}^{5+} \rightarrow \text{W}^{6+}$) bands, and could be easily assigned to two-electron reduction of HPOM by their characteristic spectra [12]. When PWA concentration is 38 wt%, however, only one absorption peak occurs, located at 540 nm and the film becomes brown. It is proposed that more electrons were transferred from PAM to polyanions and formed highly-reduced polyoxometallate products [13]. The above experimental results indicated that the photochromic behaviors of PWA/PAM composite films can be controlled by adjusting the PWA content. We argued that the phenomenon comes from the different interactions between polyanions and the polymeric matrix [14].

In summary, we fabricated a controllable structure and photochromic property hybrid film based on

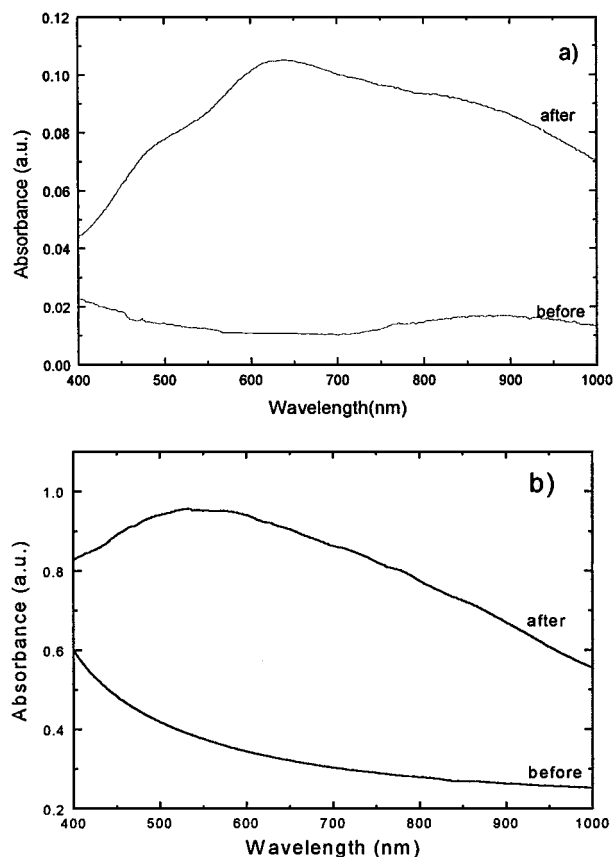


Figure 3 UV-vis spectra of the hybrid films with different PWA concentration: (a) 9 wt% and (b) 38 wt%.

PWA/PAM. IR spectra showed that Keggin structure of PWA existed in the hybrid films. The regularity of the varying of characteristic bands in the infrared spectra as a function of PWA concentration was described. The PWA particle size and conglomeration in the hybrid films can be obviously modified by controlling

the concentration of polyanions. Meanwhile, the hybrid film with low concentration of PWA can be reduced to polyheteroblue and that with high concentration to polyheterobrown.

Acknowledgment

The authors acknowledge the National Natural Science Foundation of China (NNSFC) for the provision of financial support.

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Received 26 October

and accepted 18 December 2001