

Preparation and Photochromic Behavior of Novel Hybrid Inorganic-Organic Thin Film

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Abstract: A novel photochromic complex comprising of Keggin type tungstophosphate acid (PW₁₂) and polyacrylamide (PAM) was prepared. FT-IR results showed that the Keggin geometry of PW₁₂ was still preserved inside the composite, and a charge-transfer bridge was built between PW₁₂ and PAM *via* hydrogen bond. AFM images indicated that surface topography of polymer matrix changed after adding PW₁₂. Under UV irradiation, the film was reduced photochemically to yield a blue species, which was reversible in the present of oxygen in polymeric network.

Keywords: 12-Tungstophosphate acid, polyacrylamide, photochromism.

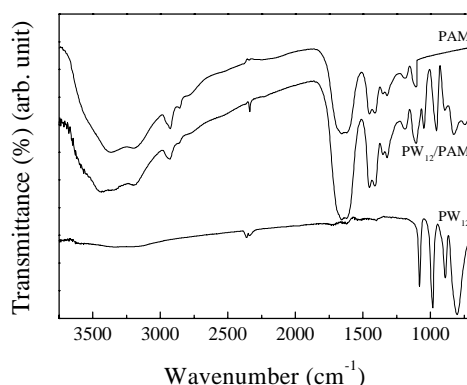
Heteropolyoxometallates (HPOM) have caused increasing attention because of their special structures and properties¹. One of the most important properties of these metal oxide clusters is that they can accept electrons or protons to form mixed-valency colored species (heteropolyblues or heteropolybrowns), which make them to be used as data storage and other informational function materials. Nowadays, many studies are introducing polyoxometallates nanoparticles into polymeric networks to get transparent thin films and to improve their photochromic property and stability². In this paper, we have prepared optically transparent thin film of PW₁₂/PAM complex and investigated their photochromic properties.

PW₁₂ was purchased from Beijing Chemical Reagent Co. and PAM from Dow Chemical Co.. PW₁₂ and PAM were dissolved in water with the concentration of 5 mg/mL and 10 mg/mL, respectively. Then PAM solution was slowly added to PW₁₂ solution under vigorous stirring at 333 K. After stirring for 2 h, the solution was cooled to room temperature. The complex of PW₁₂/PAM was formed. The supporting quartz plates were used for UV-vis studies, KBr pellet for FT-IR spectra, silicon for AFM. Thin film was made by dipping method. Films were dried in a chamber with controlled air humidity that did not exceed 60% in order to obtain optically perfect films. A 500-Watt high-pressure mercury lamp was used for the photochromic experiments.

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FT-IR spectra were measured in a Nicolet Impact 410 spectrometer. UV-vis spectra were performed on diode array spectrophotometer (Shimadzu UV-1601PC UV-vis spectrophotometer). All the AFM images were obtained in air using a AutoProbe CP (Park Scientific Instruments) in Non-contact mode.

Figure 1 FT-IR spectrum of hybrid film and corresponding pure PAM and PW_{12}



The FT-IR spectra of PW_{12} /PAM film and corresponding pure PAM and PW_{12} are shown in **Figure 1**. Signals $1315\sim 1352\text{ cm}^{-1}$ ($\nu\text{C-C}$), $1614\sim 1659\text{ cm}^{-1}$ ($\nu\text{C=O}$) and $1405\sim 1449\text{ cm}^{-1}$ and $2850\sim 2932\text{ cm}^{-1}$ (νCH_2) also confirm organic groups. There are two vibration bands at 3190 and 3373 cm^{-1} assigned to $\nu\text{N-H}$ for pure PAM and the $\nu\text{N-H}$ of PW_{12} /PAM splitted into 3193 , 3347 and 3449 cm^{-1} , which indicated that the hydrogen bond is formed between PW_{12} and PAM³. The infrared spectra of the composite films are characterized by very strong bands below 1100 cm^{-1} , due to the polyanions. Clearly seen from **Figure 1**, the bands in composite films associated with the anions are all shifted by only a few cm^{-1} contrasted to pure PW_{12} , which indicates that the Keggin geometry of HPOM is still preserved inside the hybrid film⁴. For example, the W=O_d and P-O_a bands of HPOM in the hybrid films have red shifts and the bands of $\text{W-O}_b\text{-W}$ and $\text{W-O}_c\text{-W}$ both have blue shifts. It is suggested that the infrared bands shift of HPOM in the hybrid films should be attributed to strong coulombic interaction between heteropolyanions and polymeric substrate. This result is also testified by AFM study.

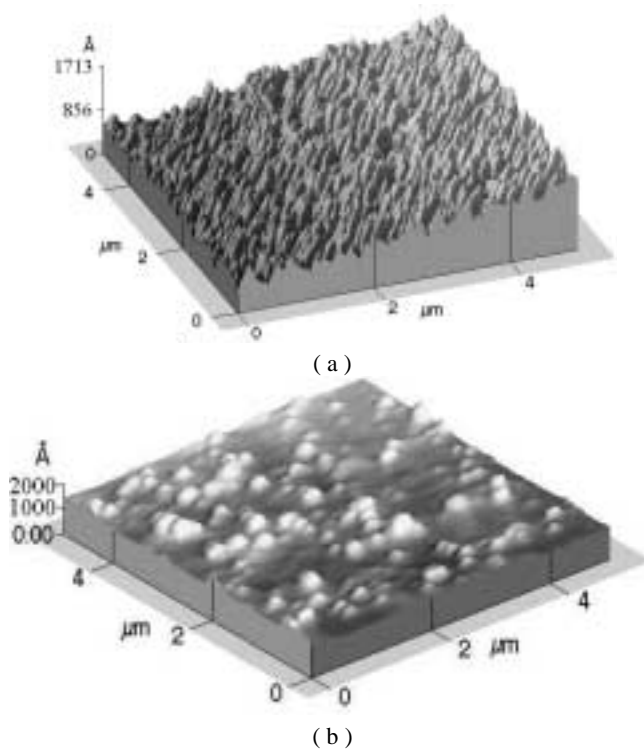
Figure 2a is an AFM image of PAM thin film. Regular resembled rolling mountain peaks over the surface were observed. As to PW_{12} /PAM film the topography changed from the peak to the hill structure (see **Figure 2b**). The hills are similar but their size is not uniform. It may be inferred that polymer matrix have surrounded PW_{12} clusters after the adding of PW_{12} .

The dependence of UV-VIS-NIR absorption spectra corresponding to the coloration process of the hybrid film with irradiation time upon UV light are shown in **Figure 3**. The film showed no significant absorption from 400 to 1100 nm before UV irradiation. After it was exposed to UV light, the film turned to blue with two broad intense absorption bands at $600\sim 700$ and 490 nm . These bands are attributed to metal-to-metal

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extra intervalence charge transfer (IVCT) ($W^{5+} \rightarrow W^{6+}$) and intensity-enhanced d-d transition, respectively⁵. On the other hand, the wavelength and density of IVCT band changed as the irradiation times increased. Because the d-d transition is not an intervalence transition, its wavelength is unaffected by the extent of anion reduction in UV-spectra⁵. When the film was exposed to UV light for 2 min the λ_{\max} of IVCT band was at around 720 nm, which could be easily assigned to one-electron reduction of polyoxometallates by their characteristic spectra⁶. As irradiation time increased, the wavelength of IVCT band shifted to short wavelength until a single minimum was obtained. When the irradiation time increased to 10 min the λ_{\max} of IVCT was at around 620 nm, which was assigned to the two-electron reduction of polyoxometallates⁶. Comparing with the one-electron reduction, the relative intensity of IVCT was almost as twice as that. It showed that with the increase of irradiation time the photoreduction proceeded from one-electron to two-electron blue stage during photochromism.

Figure 2 AFM image of pure PAM film (a) and hybrid film (b)



Such photochromism of blue hybrid films is reversible in air since oxygen is a good scavenger. **Figure 4** shows the bleaching process of the hybrid films. After UV light was turned off, the films begin to decolor gradually in air. Curve c in **Figure 4** gives the absorption spectra of the colored film which was kept in N_2 -saturated environment for two weeks. It is clear that the colored film is more stable upon non-oxygen environment. If the film was exposed in air for two weeks (see curve d), reduced

species were oxidized by oxygen partially. When the film was heated at 50°C for 2 hr, the colored species returned to their original color in the presence of oxygen. These results show that oxygen plays an important role during the bleaching process.

Figure 3 UV-vis-NIR absorption spectra of the hybrid film with different irradiation time

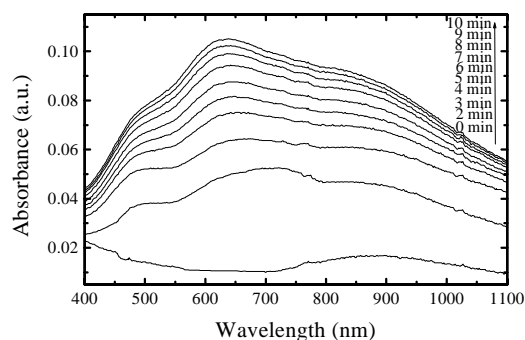
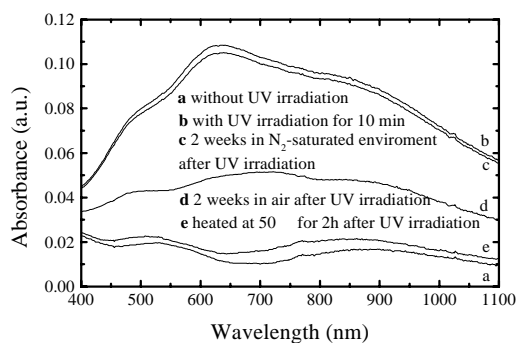


Figure 4 UV-vis-NIR absorption spectra of the hybrid film at different conditions



Acknowledgments

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