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Photochromic behavior of nanocomposite hybrid films of finely dispersed phosphotungstic acid particles into polyacrylamide

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A series of nanocomposite hybrid films consisting of phosphotungstic acid (PW12) and polyacrylamide (PAM) were prepared. TEM images showed that PW12 particles with average diameter of tens of nanometer were finely dispersed in the film. FT-IR results suggested that the Keggin geometry of PW12 was still preserved inside the matrix and a charge-transfer bridge was built between PW12 and PAM through hydrogen bonds. Under UV irradiation, PW12 was reduced photochemically to yield various mixed-valency colored species ("heteropoly blues" or "heteropoly browns"). The extent of photoreduction was concerned with the concentration of PW12 and irradiation time. The presence and diffusion of oxygen played an important role in reversibility of photochromism.

1. Introduction

Photochromic materials have been the focus of much attention because of their potential technological applications in information display, high-density memory devices and other high-technology fields [1–3]. Functionalized polyoxometallates are good candidates for the preparation of such materials because they can accept electrons or (and) protons to yield mixed-valency colored species (heteropolyblues or heteropolybrowns). However, the density, durability, and uniformity of these materials are not sufficient, which make them far from application. To a larger extent, the approach of using hybrid inorganic-organic materials to construct optically transparent thin films has also been fascinating [4–6]. The challenge for such materials is to optimize both inorganic and organic components on a molecular scale so as to obtain finely dispersed composites. Nowadays, many studies are introducing polyoxometallates nanoparticles into polymeric networks to get transparent thin films and to improve their photochromic property and stability [7–10].

Non-reduced polyoxometallates are characterized by O → M charge-transfer (CT) bands appearing in the ultraviolet region. Reduction of polyoxometallates to heteropoly blues or heteropoly browns results in decrease of the O → M CT bands and formation of an intervalence CT band (IVCT) located in the visible and near infrared region. The intensities and position of absorption bands are approximately proportional to the number of trapped electrons [11]. In this paper we have prepared novel uniform inorganic-polymeric photochromic nanocomposite films consisted of Keggin type phosphotungstic acid (PW12) particles well dispersed in polyacrylamide (PAM). Under UV irradiation, the films could be reduced to heterpoly blues or heterpoly browns. It was found that the concentration of PW12 in hybrid materials and the irradiation time had an effect on the photochromic process.

2. Experimental

2.1. Preparation of hybrid films

PW12 was purchased from Beijing Chemical Reagent Co. and PAM with density of 11000 ± 110 was purchased from Dow Chemical Co. PW12 and PAM were dissolved in water with the concentration of 5 kg/m^3 and 10 kg/m^3, respectively. Then PAM aqueous solution was added to PW$_{12}$ aqueous solution under vigorous stirring at 333 K. After stirring for 2 h, the solution was cooled to room temperature. We prepared five kinds of PW12/PAM composites in which the weight percent of PW12 was 9 wt%, 17 wt%, 28 wt%, 38 wt% and 44 wt%, respectively.

Thin films were prepared by the 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

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to obtain optically perfect films. The thickness of the hybrid films was about 2.1 μm.

2.2. Characterizations of hybrid films

Photochromic experiments were carried out using a 500-Watt high-pressure mercury lamp as the light source. FT-IR spectra were obtained in a Nicolet Impact 410 spectrometer. UV-vis spectra were performed on diode array spectrophotometer (Shimadzu UV-1601PC UV-vis spectrophotometer). The TEM image was obtained on a JEOL JEM-200CX transmission electron microscope using samples prepared by dropping complex solution onto copper grids.

3. Results and discussion

3.1. Composition of film

FT-IR spectra can give information on the structure of PW12 and the interaction between PW12 and PAM. Since the samples with different concentrations of PW12 showed similar IR vibration bands, we only listed the data and their assignments for the sample with 9 wt% PW12 in Table I. It was found that the frequencies of the PW12/PAM skeletal bands differ from the corresponding frequencies of pure PW12 by only a few wavenumbers as follows: the νW–Od band (986 cm^{-1}) and νP–O band (1081 cm^{-1}) exhibited red shifts with regard to pure PW12, while the inter νW–Ob-W and intra νW–Oc-W modes were shifted to higher wavenumbers, i.e., 2 cm^{-1} and 4 cm^{-1}, respectively. These results indicated that the Keggin geometry of PW12 was still preserved inside the hybrid film [12, 13]. Compared with pure PAM with 3190 and 3373 cm^{-1} for νN-H, the νN-H of PW12/PAM split into bands peaking at 3193, 3347 and 3449 cm^{-1}. It was suggested that hydrogen bonds were formed between PW12 and PAM [14].

3.2. Microstructure of film

From TEM image (Fig. 1) of the hybrid film containing 9 wt% PW12 we can find that PW12 particles with average diameter of ca. 50 nm were well dispersed. As the concentration of PW12 increased, the average diameter of PW12 particles changed from 50 nm to 65 nm and the PW12 particles were finely separated each other.

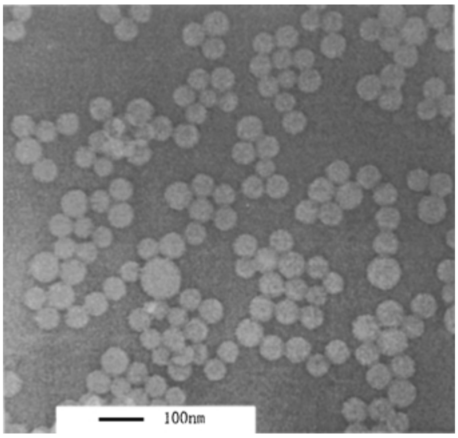

Figure 1 TEM image of the hybrid film with concentration of 9 wt% PW12.

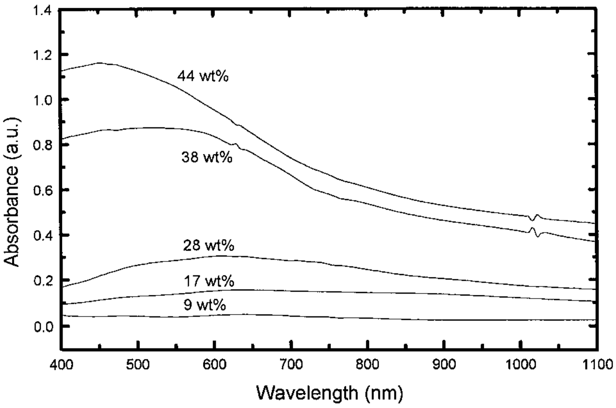

Figure 2 UV-vis-NIR absorption spectra of the hybrid films with different concentration of PW12. All samples were exposed upon UV light to saturated state.

3.3. Photochromic behavior of the film

Before UV irradiation there was no absorption band from 400 to 1100 nm in UV-vis spectra for PW12/PAM hybrid films with different concentrations. After UV irradiation new broad absorption bands appeared as shown in Fig. 2. We can find that the photochromic behaviors of the films were influenced by the concentration of PW12. Within the concentrations of PW_{12} from 9 wt% to 28 wt%, the absorption bands of films were located in the visible region, such as at 620 nm and 490 nm, and the films were blue. These bands are attributed to metal-to-metal extra intervalence charge transfer (IVCT) ($W^V \rightarrow W^{VI}$) and intensity-enhanced d-d transition, respectively [14]. According to Papaconstantinou's results we assumed that such photochromic process resulted from two-electron reduction of polyoxometallates [15]. On the other hand, when the concentration of PW12 was increased to 38 wt% and 44 wt% only one broad band appeared, at 540 and 460 nm, respectively. This result indicated that more electrons were transferred from PAM to polyanions, which led to brown species [16].

Fig. 3 shows the electron level variation of PW12/PAM films with different concentrations of PW12 during photochromic process. For the films with the concentration of PW12 from 9 wt% to 28 wt%, the IVCT

TABLE I IR data (ν/cm^{-1}) of pure PW12 and PAM and hybrid film

Sample	νP–O	νW–Od	νW–Ob-W	νW–Oc-W	νC-C(N)	νC-H	νN-H
PW12	1081	986	891	804	–	–	–
PAM	–	–	–	–	1414–1663	2854–2940	3190, 3373
PW12/PAM	1080	982	893	808	1412–1658	2843–2926	3193, 3347, 3449

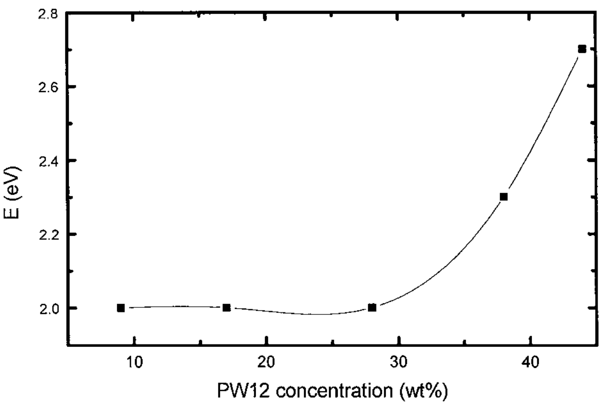

Figure 3 Electron level variation of hybrid films with different concentration of PW12 during photoreduction.

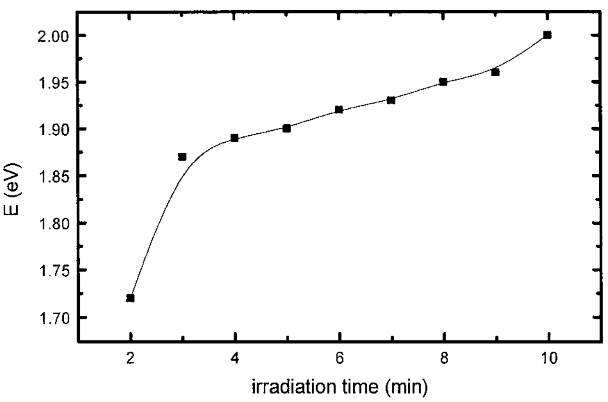

Figure 5 Electron level variation of the hybrid film with 9 wt% PW12 during photoreduction.

band gap of 2.0 eV was clearly observed. With increase of the concentration of PW12, such as to 38 wt% and 44 wt%, the corresponding IVCT band gap reached to 2.3 eV and 2.7 eV. It indicated that the heteropoly-blues could be obtained under lower energy and the heteropoly browns appeared under higher energy. The IVCT band gap of PW12/PAM hybrid films resulted from hydrogen transmission followed by trapping electrons [10]. Thus the reduction may be written as follows:

$$PW^{VI}{}_{12}{}^{3-} \rightarrow PW^{V}{}_{2}W^{VI}{}_{10}{}^{(3+n)-} \quad \text{(blue)}$$

$$PW^{VI}{}_{12}{}^{3-} \rightarrow PW^{IV}W^{VI}{}_{11}{}^{(3+n)-} \quad \text{(brown)}$$

where n refers to the number of accepted electrons of PW12 from PAM.

The irradiation time of UV light also plays an important role in the photochromic process under diluted concentration of PW12. UV-vis-near IR spectra of the film with 9 wt% PW12 with different irradiation time were given in Fig. 4. Before irradiation there were no absorption bands in the visible region due to W^{6+} with d^0 configuration of metals. After it was exposed under UV light, the film turned blue with two broad absorption bands at 600–700 and 490 nm. Meanwhile, the wavelength and intensity of IVCT band changed as irradiation time was prolonged, but the d-d transition band was still located at 490 nm since it was not an intervalence transition [15]. After the film was irradiated with UV light for 2 min, the IVCT band appeared at around 720 nm, which could be easily assigned to one-electron reduction of PW12 due to their characteristic spectra [15]. With increase of the irradiation time, the IVCT band blue-shifted. When the irradiation time increased to 10 min, it changed to around 620 nm, which was ascribed to the two-electron reduction of PW12 [15]. Comparing with the one-electron reduction, the relative intensity of IVCT band for two-electron reduction was almost twice as high. The change of IVCT band gap from one-electron to two-electron blue stage with increase of irradiation time was shown in Fig. 5. It was found that electron level of IVCT band increased as the irradiation time was prolonged, and the band gap changed from 1.7 eV to 2.0 eV. The process for the photoreduction was given as below.

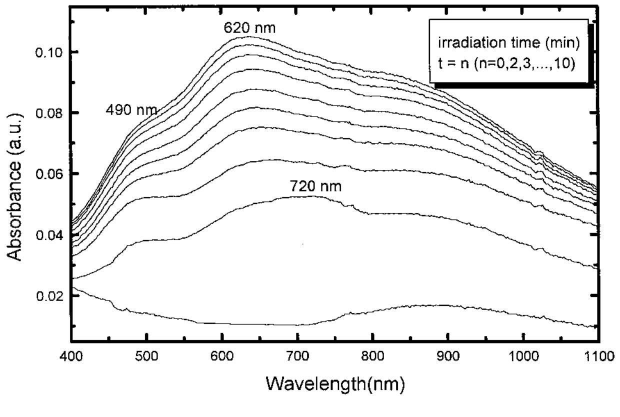

Figure 4 UV-vis-NIR absorption spectra of the hybrid film with 9 wt% PW12 irradiated with different time.

$$PW^{VI}{}_{12}{}^{3-} \rightarrow PW^{V}W^{VI}{}_{11}{}^{4-} \rightarrow PW^{V}{}_{2}W^{VI}{}_{10}{}^{5-}$$

Such photochromic behaviors of blue hybrid films are reversible in air since oxygen can oxidize W^{V} to W^{VI}.

$$PW^{V}{}_{2}W^{VI}{}_{10}{}^{5-} + 1/2\ O_2 \rightarrow PW^{VI}{}_{12}{}^{3-} + O^{2-}$$

We also studied the decoloration process of blue films under different conditions in detail. As shown in Fig. 6c, we found that the colored film with 9 wt% PW12 is more

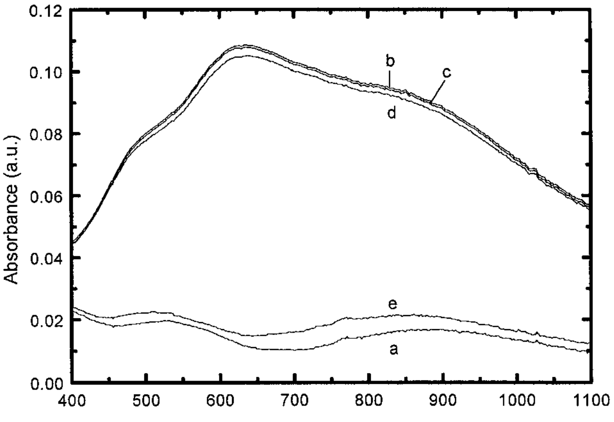

Figure 6 UV-vis-NIR absorption spectra of the hybrid film with 9 wt% PW12: (a) without UV irradiation, (b) UV irradiation for 10 min, (c) 2 weeks in N_2-saturated environment after UV irradiation for 10 min, (d) 2 weeks in air after UV irradiation for 10 min, (e) heated at 50°C for 2 h after UV irradiation for 10 min.

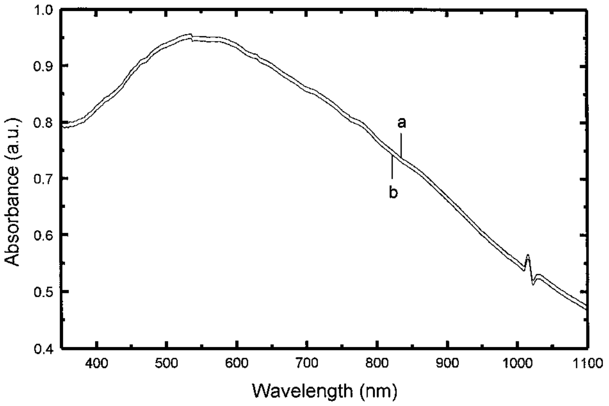

Figure 7 UV-vis-NIR absorption of the hybrid film with 38 wt% PW12: (a) UV irradiation for 25 min, (b) 2 months in air after UV irradiation for 25 min.

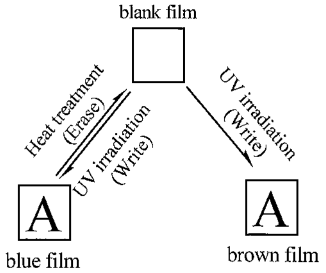

Figure 8 Promising application of various photochromic reactions.

stable in N_2-saturated environment for two weeks. If the sample was exposed in air for two weeks (Fig. 6d), reduced species were oxidized partially. When the blue film was heated at 50°C for 2 hr in air, it was decolored completely (Fig. 6e). It was illustrated that the decoloration of the reduced species was related to the presence of oxygen and it was a diffusion-controlled process [17, 18]. The brown hybrid film displayed irreversible photochromism in air whether heated or not, because W^{IV} is not easily oxidized (Fig. 7).

Due to their interesting photochromic properties, these PW12/PAM hybrid films may possibly be used as display and information storage materials. Fig. 8 shows the combination of the 'photon mode' to achieve those purposes. A desired pattern can be written onto colorless hybrid film by UV light. Brown films can be used as permanent optical storage materials and the information stored in blue films can be easily erased by heating in the presence of oxygen.

4. Conclusion

A series of novel nanocomposite PW12/PAM thin films were prepared. In the film PW12 with nanometer dimensions was well dispersed in the matrix. The Keggin geometry of PW12 was still preserved inside the complex and a charge-transfer bridge was built between PW12 and PAM via hydrogen bond. The hybrid films with different concentrations of PW12 exhibited interesting photochromic behavior, for example, reduction of the hybrid films with low concentrations of PW12 yielded blue mixed-valence species ("heteropoly blues") and those with higher concentrations of PW12 led to brown species ("heteropoly browns"). Under UV irradiation, the photoreduction species in the blue films changed from one-electron to two-electron reduction of polyoxometallates with increasing of irradiation time. The blue films exhibited reversible photochromic property and the brown films could not be decolored.

Acknowledgments

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