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Sonochemical preparation of photochromic nanocomposite thin film based on polyoxometalates well dispersed in polyacrylamide

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Abstract

Novel photochromic nanocomposite thin film containing phosphotungstic acid entrapped in polyacrylamide was prepared using ultrasound technique. TEM image revealed that the polyoxometalates nanoparticles with narrow size distribution were finely dispersed in polymer matrix. IR spectra showed that the Keggin geometry of polyoxometalates was still preserved inside the composite film and strong Coulombic interaction was built between heteropolyoxometalates and polyacrylamide via hydrogen bond. It was found that the thermal stability of the hybrid film was lower than that of pure polymer but the film was stable enough for photochromic application from the TG–DTA curves. The transparent film changed from colorless to blue under UV irradiation and showed reversible photochromism. The bleaching process occurred when the film was in contact with air or O_2 in the dark. The photoreduced process was in accordance with radical mechanism.

Keywords: Sonochemical; Preparation; Polyoxometalate; Polyacrylamide; Thin film; Photochromism

1. Introduction

Polyoxometalates have been widely studied as small compact oxide clusters [1]. Their redox properties and high electron density are ideal for their use as catalysts, stains for electron microscopy, and photochromic or electrochromic materials [2]. But these kinds of materials are difficult to manipulate into practical devices, which limits their application. As the promising application of polyoxometalates is coming true, films and fibers are of great interest as the final application form. For this reason, the good processability and large stability of polyoxometalates are necessary. Nanocomposite techniques provide a new method to improve the processability and stability of nanocrystals with intriguing novel electronic, optical, and magnetic capacities [3]. The general principles in the construction of nanocomposites involve the intimate mixing of crystals with processable matrixes. The matrix materials include polymers, glasses and ceramics, etc. Now, many studies are dealing with the stabilization of composite by entrapment of inorganic materials in polymeric networks [4–7]. One method of preparation of nanocomposite containing polyoxometalates is based on weak interactions between organic and inorganic components [8]. Other types of such hybrid materials require organically modified polyoxometalates, allowing the anchoring of organic moiety through chemical bonds in order to obtain macromolecules [9–11].

Dispersed nanocomposite materials are of great importance due to their special properties. Sonochemical processing has proven to be a useful technique for generating finely dispersed nanoparticles in composite materials [12]. Sonochemistry arises from acoustic cavitation phenomena, that is, the formation, growth, and implosive collapse of bubbles in a liquid medium. Using these extreme conditions, Gedanken and his coworkers [13,14] have successfully prepared magnetic metal polymer composite materials.

Till date, no one has studied on the photochromic hybrid inorganic–polymeric nanocomposites based on

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polyacrylamide thin film with entrapped polyoxometalates using ultrasonic method. In this work, we extend sonochemical method to prepare a composite film containing finely dispersed polyoxometalates nanoparticles with narrow size distribution in polyacrylamide. With transmission electron microscopy (TEM), X-ray diffraction (XRD) and infrared spectra (IR), the microstructure and composition of the film were studied. The thermogravimetric analysis (TG) and differential thermal analysis (DTA) revealed that the composite film was stable. The photochromic behaviors and mechanism were investigated using ultraviolet–visible adsorption spectra (UV–vis) and electron spin resonance (ESR). It suggested that the hybrid film had good reversible photochromism which was followed by radical mechanism.

2. Experimental

2.1. Preparation

Phosphotungstic acid (PWA) and polyacrylamide (PAM) were dissolved in water with concentration of 0.005% and 0.001% (by weight), respectively. Then, 10 mL PWA solution was slowly added to 10 mL PAM solution. The composite solution was irradiated by ultrasound (KQ-50B laboratory cleaner, 220 W, 40 kHz) at room temperature for 20 min. The final transparent solution was used to prepare hybrid films on various substrates via dipping process. 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, measured using an 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. Experimental technique

The TEM image was obtained on a JEOL JEM-200CX transmission electron microscope by dropping complex solution onto copper grids. IR spectra of the films deposited on KBr pellets were obtained at room temperature with a Nicolet Impact 410 FT-IR spectrometer in the range of 4000–400 cm^{-1}. X-ray diffraction (XRD) data were obtained using a Siemens D5005 diffractometer with a Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). TG and DTA were carried out in air on a NETZSCH STA 449C thermogravimetric analyzer with a heating rate of 20°C/min. All absorption measurements were made on a UV–vis spectrophotometer (Shimadzu UV-1601PC) with 1 nm optical resolution over the range 350–1100 nm. The electron spin resonance (ESR) spectra of samples were recorded on a Bruker ER200D-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. TEM measurements

In Fig. 1 we present the TEM image of the hybrid film. It shows that the PWA particles exhibit spheres structure with a narrow size distribution in which more than 90% populations are within the range 45–55 nm (average 50 nm). All the PWA nanoparticles are well separated from each other and are dispersed in the polymeric matrix homogeneously and randomly.

3.2. Infrared spectra

The IR spectra of the hybrid film and corresponding pure PAM and PWA are shown in Fig. 2. Vibration bands at 1316–1352 cm^{-1} (νC–C), 1615–1660 cm^{-1} (νC$=$O) and 1404–1450 and 2852–2932 cm^{-1} (νC$=$H$_2$) confirm organic groups. There are two vibration bands at 3190 and 3373 cm^{-1} assigned to νN–H for pure PAM and the νN–H of the hybrid film splits into 3193, 3347 and 3449 cm^{-1}, which indicates that the hydrogen bond is formed between PWA and PAM [15]. The formation of hydrogen bond is an important proof that the interaction happened between PWA and PAM. The infrared spectra of the composite films are characterized by very strong bands below 1100 cm^{-1}, due to the polyanions. The bands in composite film associated with the anions are all shifted by only a few cm^{-1} contrasted to pure PWA, which indicates that the Keggin geometry of HPOM is still

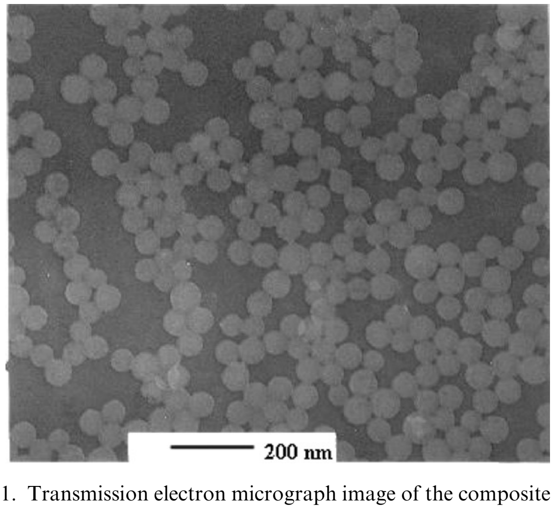


Fig. 1. Transmission electron micrograph image of the composite film.

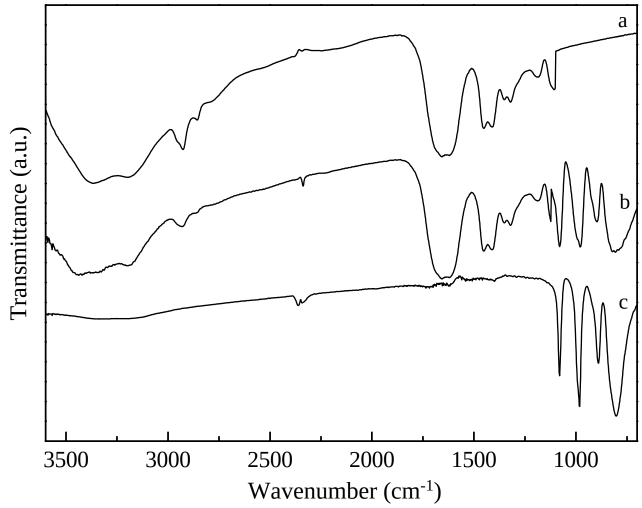


Fig. 2. IR spectra of pure PAM (a), composite film (b) and pure PWA (c).

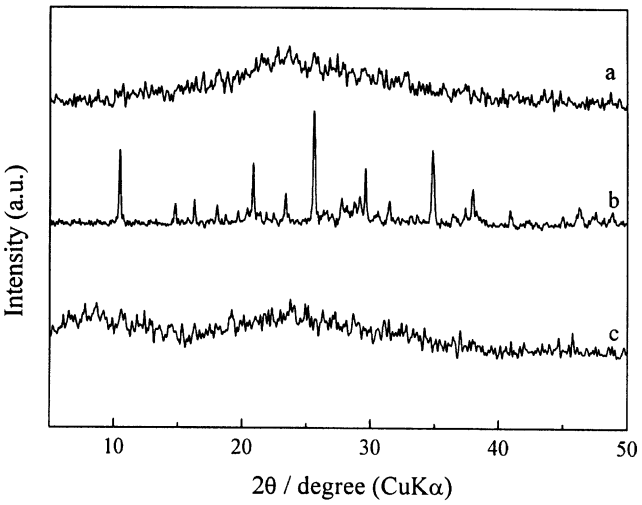


Fig. 3. XRD patterns of (a) pure PAM, (b) pure PWA and (c) composite film.

preserved inside the hybrid film [16]. For example, the $\mathrm{W{=}O_d}$ and $\mathrm{P{-}O_a}$ bands of HPOM in the hybrid film have red shifts and the bands of $\mathrm{W{-}O_b{-}W}$ and $\mathrm{W{-}O_c{-}W}$ have blue shifts. The shifts of infrared bands for HPOM in the hybrid film should be attributed to strong Coulombic interaction between polyoxometalates and polymeric matrix.

3.3. X-ray diffraction

XRD pattern of the hybrid film are shown in Fig. 3c. For comparison, the patterns of pure PAM and PWA are also given. It is clear that only pure PWA shows good crystalline structure and the hybrid film exhibits low crystallinity. In addition, due to the high content of PWA (33 wt%) in the film and the strong Coulombic interaction between PWA and PAM proved by IR spectra, we assume that the PWA nanoparticles are homogeneously dispersed inside the polymer matrix [17], which are in well agreement with the TEM result.

3.4. TG–DTA measurements

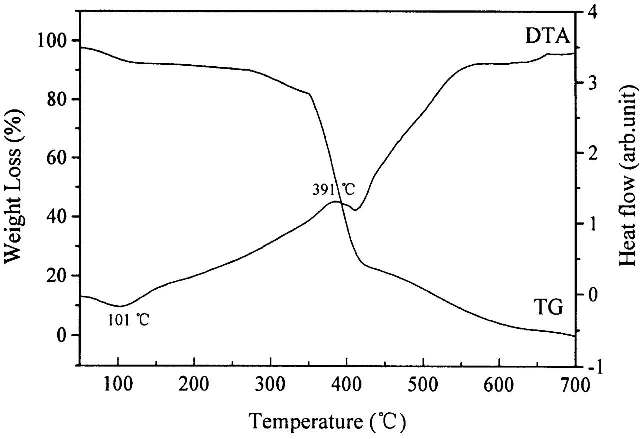


Fig. 4. The thermal analysis of the PAM film.

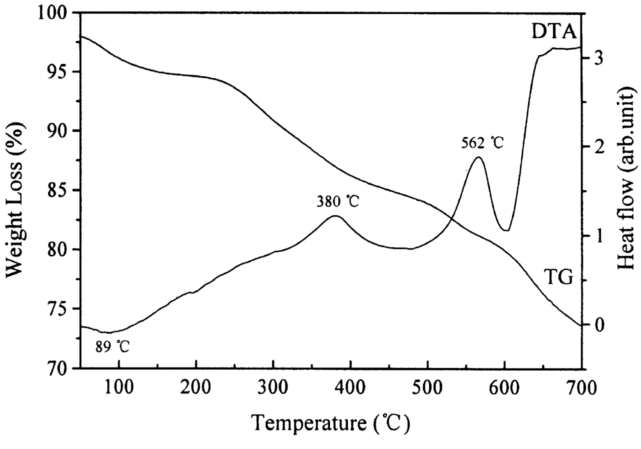


Fig. 5. The thermal analysis of the PAM film containing PWA.

To determine the stability of the film and the effect of the perturbation of PWA on the stability, we carried out TG–DTA measurements. In Figs. 4 and 5 we present the TG–DTA results of pure PAM film and the PWA/PAM hybrid film, respectively. For pure phase of PAM, the DTA curve shows an endothermic peak at 101°C, due to the removal of water trapped in the polymeric network. Thermal decomposition of the polymer begins at temperature higher than 250°C in air under atmospheric pressure accompanied by an exothermic peak appeared at 391°C. As to the DTA curve of the hybrid film, there are two exothermic peaks and one endothermic peak. The process of dehydration occurs at 89°C, which is an endothermic peak. One exothermic peak at 380°C is caused by the decomposition of the organic components in the hybrid film. The other exothermic peak at 562°C is due to the decomposition of the polyoxometalate [17]. From the above results, we found that the thermal stability of the hybrid film is lower than that of the pure polymer, but it is stable enough for photochromic application. The reason may be that the perturbation of PWA affects the three-dimensional structure of the polymer and weakens the interaction between the polymer chains [15,18].

3.5. Photochromic properties

The dependence of UV–vis absorption spectra of the composite film under UV irradiation is shown in Fig. 6. The film showed no significant absorption from 350 to 1100 nm before UV irradiation. Upon irradiation with UV light, the absorption spectral changes of the hybrid film were observed as shown in Fig. 6b. The absorption bands of 496 and 700 nm are characteristic of reduced Keggin molecular species with d–d transmission bands and intervalence charge transfer (IVCT, $M^{5+} \rightarrow M^{6+}$) bands, respectively [19]. Meanwhile, the film turns to blue from colorless. Such photochromism of blue hybrid film is reversible in air since oxygen is a good scavenger. After UV light is turned off, the film begins to decolor gradually in air. Curve c in Fig. 6 gives the absorption spectra of the colored film kept in air for 7 h. It is clear that the reduced species in hybrid film are unstable toward oxygen in air. When the film was exposed upon air for 15 h, the colored species returned to their original color. The photochemical reversibility has been examined by the irradiation with UV light for coloration and oxidation in air for decoloration. The absorption changes of the film at 700 nm are shown in Fig. 7. It indicated that the film has a good photochromic reversibility.

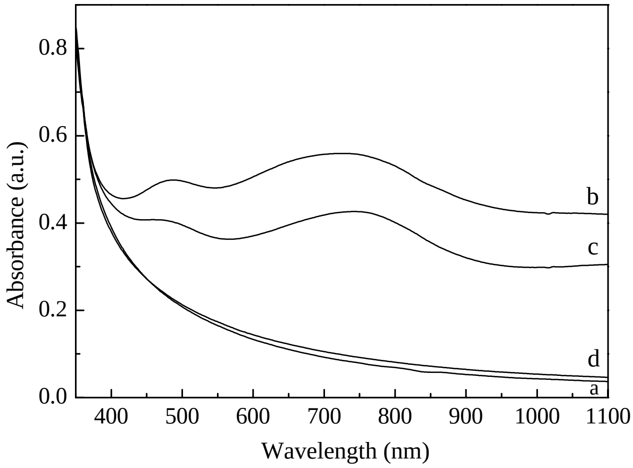


Fig. 6. UV–vis spectra of the composite film: (a) without UV irradiation, (b) after 40 min UV irradiation, (c) 7 h after 40 min UV irradiation, and (d) 15 h after 40 min UV irradiation.

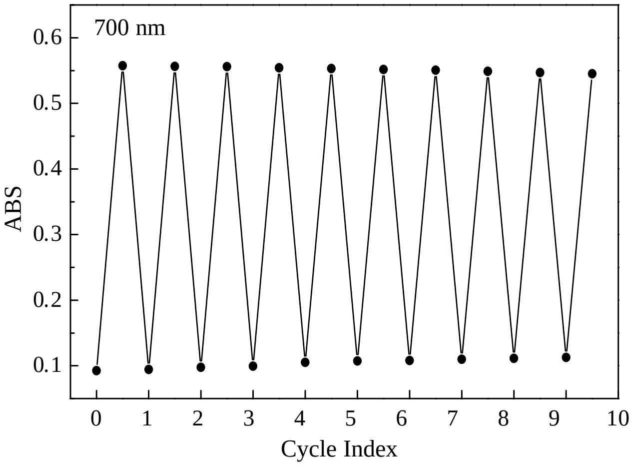


Fig. 7. The coloration–decoloration cycles of the film at 700 nm.

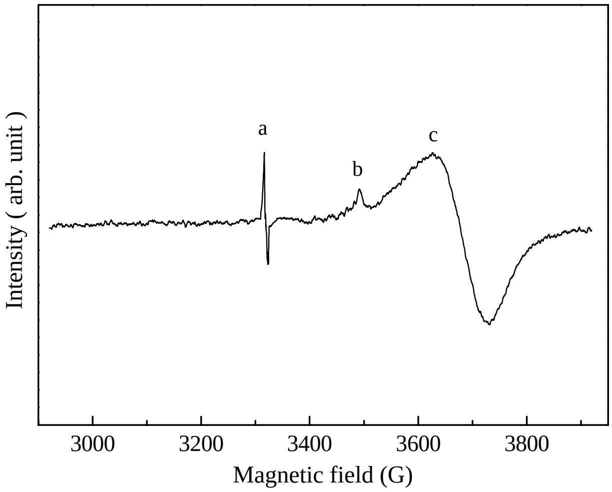
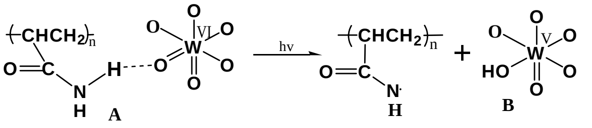


Fig. 8. X-band ESR spectrum of the composite film at low temperature (84 K). A 500-W high-pressure mercury lamp irradiated sample for 40 min. Signal a is due to the polymeric radical; signal *b* is due to molybdenum impurities acting and signal b is due to the photoreduced $(PW_{12}O_{40})^{4-}$.

3.6. Photochromic mechanism

To explain the photochromic behavior of the hybrid film, it was necessary to investigate the variation of electronic structure of the film during photochromism. Therefore, the ESR analyses of the hybrid film before and after photoreduction are given. The unirradiated samples exhibit no significant ESR signals at 84 K. After UV irradiation the hybrid film exhibits defined signals shown in Fig. 8. The signal b with $g = 1.950$ is ascribed to Mo^{5+}. The appearance of the Mo^{5+} is because small amounts of molybdenum (coming from the raw materials, about 0.005%) are always contained in the PWA. They behave as selective electron traps under reducing condition [20]. The broad isotropic signal c ($g = 1.833$) is assigned to $[PW_{12}O_{40}]^{4-}$. The above values are in agreement with that reported in the literature [20]. The appearance of W^{5+} proved that the oxidation–reduction process happened between the heteropolyanion and the organic substrate. The fact that these spectra are often isotropic down to quite low temperatures or show small hyperfine values results from the rapid intraionic hopping of the unpaired electron compared with the ESR time scale [20]. As for the radical signal coming from polymer ($g = 1.999$) of the colored film, it was deduced that photoexcitation of the O$=$W ligand-to-metal charge transfer (LMCT) of WO_6 led to a transfer of one hydrogen from PAM to the oxygen atom at the photoreduced site in the edge-shared WO_6 octahedral lattice. At the same time, the N–H and O$=$W bonds decomposed. This was followed by the interaction of one electron of oxygen atom with the hydrogen and another electron of oxygen atom was transferred to the metal atom. Therefore, the reduction of the polyoxometallates ($W^{6+} \rightarrow W^{5+}$) and oxidation of the organic matrix took place through radical process. Eq. (1) denotes the environment of the photoreducible WO_6 site and the subsequent formation of the charge-transfer complex B in the hybrid film, which agrees with our previous results [21].



(1)

Complex B reflects the charge separation of the electron and hole which is produced by the $O \rightarrow M$ LMCT transition in the heteropolyanions lattice. It is charge separation that keeps the colored state stable. On the other hand, the blue film can be bleached to colorless in the dark in contact with air or O_2, but if it was kept from air, the blue can be retained for quite a long time. It shows the decoloration process is a chemical process, in which O_2 oxidize M^{5+} to M^{6+}, but not an oxidation–reduction process of the system itself.

4. Conclusions

A new photochromic nanocomposite thin film based on polyoxometalates nanoparticles with narrow size distribution finely dispersed in polyacrylamide was prepared using ultrasonic method. In the hybrid film, PWA nanoparticles maintain Keggin structure and consist strong Coulombic interaction with polymeric matrix via hydrogen bonds. The film has good photochromic properties and coloration–decoloration reversibility. When exposed to UV light, the film turns blue followed by reduction of PWA and oxidation of polymer and the bleaching of film happens under the presence of air or O_2. The photochromic mechanism is in accordance with radical process.

Acknowledgments

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