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Photochromic polyoxotungstoeuropate $K_{12}[EuP_5W_{30}O_{110}]$/polyvinylpyrrolidone nanocomposite films

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Abstract

A novel photochromic nanocomposite film containing polyoxotungstoeuropate $K_{12}[EuP_5W_{30}O_{110}]$ entrapped in polyvinylpyrrolidone has been prepared through a spin-on coating technique. Thus-obtained amorphous nanocomposite film was characterized by IR spectra, UV–vis absorption spectra, XRD, SEM, TG-DTA, and ESR. Results show that polyoxotungstoeuropate interacts with polyvinylpyrrolidone strongly and disperses homogeneously in the matrix. The composite film exhibits good photochromic properties. When irradiated with UV light, the transparent film changes from colorless to blue. Then, bleaching occurs when the film is in contact with ambient air or O_2 in the dark. The photochromism of the composite film is due to charge transfer by reduction of polyoxotungstoeuropate and oxidation of polyvinylpyrrolidone.

Keywords: Nanocomposite; Photochromic; Polyoxotungstoeuropate; Charge-transfer

1. Introduction

Inorganic photochromic and electrochromic materials are important in high technological fields because of their potential applications in optical recording, information storage, optical switching, etc. [1–3]. Polyoxometalates (POMs) have won particular attention for their applications in many fields of science such as medicine, structural, catalysis, and materials owing to their chemical, structural, and electronic versatility [4–6]. One of the most important properties of these metal oxide clusters is the capability to accept various numbers of electrons giving rise to colored mixed-valence state species (heteropolyblue and heteropolybrown) while retaining their structural integrity, which makes them suitable as photochromic, electrochromic, and thermochromic materials [7,8]. Despite the potential of POMs, their implementation in advanced materials has remained elusive, mainly due to the fact that they are obtained as crystalline solids, which are difficult to process.

To move towards realistic technological implementations of POMs-based photochromic devices, we tentatively employed the europium (III) derivative of the Preyssler-type heteropolytungstate $K_{12}[EuP_5W_{30}O_{110}]$ (EPW) (Fig. 1) as an active component for its reversible electrochemical behavior accompanied by a large electrochromic response [9]. Polyvinylpyrrolidone (PVP) (Fig. 1) was chosen as a matrix for the composites because of its unique characteristics as follows [10–12]: (a) PVP has good film-forming and adhesive behaviors on many solid substrates and its formed films exhibit good optical quality (high transmission in visible range) and mechanical strength (easy processing) required for application; (b) the amorphous structure of PVP also provides a low scattering loss, which makes it an ideal polymer for composite materials for optical application; (c) PVP is highly soluble in water, so it is preferable to avoid phase separation in the reaction; (d) the pyrrolidone group of PVP prefers to complex with many inorganic salts resulting in fine dispersion of them; (e) the strong photosensitivity of PVP may be helpful to improve the photochromic performance of composite systems. The composite is constructed into thin film via spin-on coating technique which is a very convenient method for thin film preparations. Experimental results indicate the EPW/PVP film has good photochromism.

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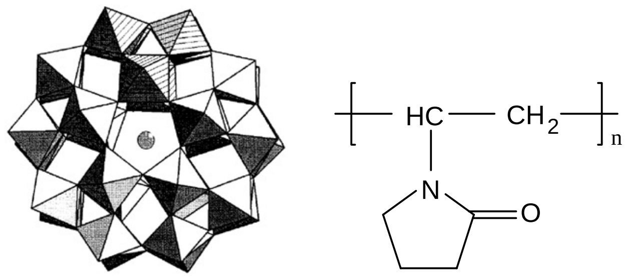

Fig. 1. Left: Polyhedral representation of the structure of $[EuP_5W_{30}O_{110}]^{12-}$ which consists of five PW_6O_{22} units (derived from the Keggin $[PW_{12}O_{40}]^{3-}$) arranged in a crown to form a cylindrical cavity where Eu^{3+} is encrypted. Right: PVP molecular structure.

2. Experimental section

2.1. Materials

Polyoxotungstoeuropate, $K_{12}[EuP_5W_{30}O_{110}] \cdot 54H_2O$ (EPW), was prepared according to Ref. [13], and the product was recrystallized twice. Polyvinylpyrrolidone (PVP) with M_w of 55,000 was obtained from Aldrich and was used without further purification. All other chemicals were of analytical grade and used as received. Deionized water was used in all experiments.

2.2. Preparation

1.11 g PVP was dissolved in 20 mL water and then 0.44 g EPW was added to the PVP aqueous solution under vigorous stirring. After 2 h, a homogenous, transparent solution was obtained. The transparent EPW/PVP film was obtained by spin-coating the mixture onto clean quartz, CaF_2, silicon wafer, and glass substrates at 1500 rpm for 30 s. The as-deposited films were dried for 2 days at 50°C for spectroscopic measurements. The thickness of the composite 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 0.9 μm. The whole process of preparation was carried out in the dark.

2.3. Methods

Fourier transform infrared (FT-IR) spectra were obtained with a Nicolet Impact 410 FT-IR spectrometer in the range of 772 to 4000 cm^{-1}. The samples were thin films deposited on CaF_2 substrates. All absorption measurements were made on a Shimadzu UV-2501PC ultraviolet-visible (UV–vis) spectrophotometer with 2 nm optical resolution over the range of 190–850 nm. X-ray diffraction (XRD) data were obtained using a Rigaku (Japan) D/max-rA X-ray diffractometer with a CuKα radiation ($\lambda = 1.5418$ Å). The angular scan range was from 5° to 50°. The thermal stability of the samples was checked with differential thermal analysis (DTA) and simultaneous thermogravimetry (TG) from room temperature to 750°C in air. Measurements were performed using a NETZSCH (Germany) STA 449C thermal analyzer, with a scanning rate of 10°C/min. Scanning electron microscopy (SEM) image was obtained on a Hitachi X-156 scanning electron microscope operating at 25 kV. The electron spin resonance (ESR) spectra of sample were recorded on a Bruker ER200-D-SRC spectrometer at x-band at 84 K. Photochromic experiments were carried out in air and a 500 W high-pressure mercury lamp was used as the light source with a 365 nm filter to filter out visible and infrared light. The distance between the lamp and the sample was 15 cm.

3. Results and discussion

3.1. FT-IR spectra

In the FT-IR spectrum of the EPW/PVP film, the band around 3300–3500 cm^{-1} is assigned to stretching mode of water. Several characteristic IR vibrational bands at 2952–2894 cm^{-1} (CH_2 or CH stretching), 1660 cm^{-1} (C = O stretching), 1462 cm^{-1} (CH_2 bending), 1424 cm^{-1} (CH_2 deformation), and 1290 cm^{-1} (C–N stretching) confirm organic groups of PVP [10]. Besides those bands, the FT-IR spectrum of the composite film shows very strong bands below 1200 cm^{-1}, due to the EPW [14]. Compared with the spectrum of EPW in a KBr pellet (Fig. 2a), all characteristic bands of EPW are present in the composite film with a little shift (Fig. 2b). It demonstrates that the EPW polyanions are “trapped” in the composite film and their chemical structure is preserved, but each characteristic bond becomes stronger or weaker to some extent. A more detailed inspection of the vibrational band shifts reveals that the bands of $W–O_b–W$ and $W–O_c–W$ bonds of EPW in the composite film both have blue shifts and the bands of $W–O_d$ and $P–O_a$ are red-shifted (Table 1). The infrared bands shift of EPW in the composite film can be attributed to electrostatic interactions between EPW and PVP (The N atom within PVP is a quasi-cation [10]). Generally, the $W–O_d$ stretching can be considered as pure vibration and is an increase function of anion–anion interaction. The red-shift of $W–O_d$ asymmetrical stretching frequency of the composite film compared with pure EPW crystal is due to the influence of PVP, which lengthens the anion-anion distances and weakens the anion–anion interactions. But the $W–O_b–W$ and $W–O_c–W$ asymmetrical stretching frequencies of the composite film are higher than those of pure EPW because they are different from $W–O_d$ stretching and present some bend characters. This can be assumed from geometrical considerations. As $W–O_b–W$ and $W–O_c–W$ vibrations are not pure and cannot be free from bending character, there is a competition of the opposite effects. The strong electrostatic anion–anion interactions lead to an increase in the stretching frequencies and a decrease in the bending vibrations [15]. Moreover, perturbations due to water molecules and anion–cation interactions result in a decrease in the frequencies of vibrations and can strengthen the decreasing effect of anion–anion interactions. In the competition of the opposite effects, the decreasing effect is stronger than the increasing one. Indeed, Lavrencic-Stanger et al., observed similar shifts of vibrations of $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ incorporated into the 3-isocyanatopropyltriethoxysilane-poly(propylene glycol)bis(2-aminopropyl ether) (ICS-PPG), which are induced by the coulombic interactions between the heteropolyanions and the protonated polymeric supports [16].

After UV irradiation, the film changed from colorless to blue. Comparing with the unirradiated composite film, we can find that the intensity of the bands relating to EPW in the spectrum of colored film (Fig. 2c) is decreasing strongly, meantime, a slight red-shift (Table 1) and a broadening of these bands are detectable, which results from the formation of heteropolyblue [17,18]. It indicates that EPW polyanions obtain electrons and are reduced. After decoloration in air, the color and the frequencies of all characteristic vibrational bands of EPW are all restored again (Fig. 2d).

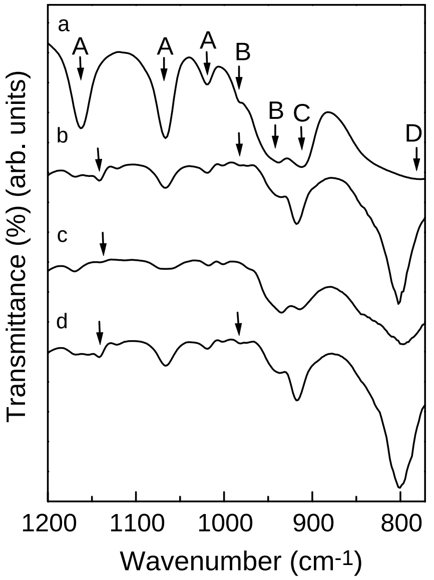

Fig. 2. FT-IR spectra of samples: (a) pure EPW in KBr pellet: A, ν(P–O$_a$); B, ν(W–O$_d$); C, ν(W–O$_b$–W); D, ν(W–O$_c$–W); (b) the EPW/PVP film without UV irradiation; (c) the EPW/PVP film with UV irradiation for 30 s; (d) the irradiated EPW/PVP film placed in air and sheltered from the light in the dark for 40 min.

3.2. X-ray diffraction

The XRD patterns of EPW solid powder, pure PVP film, and EPW/PVP composite film are given in Fig. 3. Well-defined sharp peaks are observed in EPW, indicating its crystalline nature. In the case of pure PVP, no such well-defined peaks are observed. Instead, two broad peaks are observed at $2\theta = 11.9°$ and 22.8°, suggesting its amorphous character [19]. No well-defined peaks corresponding to EPW are observed in the EPW/PVP film, indicating the absence of excess EPW in the composite material and EPW is well dispersed in PVP.

3.3. Scanning electron microscope

SEM can provide detailed information concerning the surface morphology and homogeneity of films. Fig. 4a

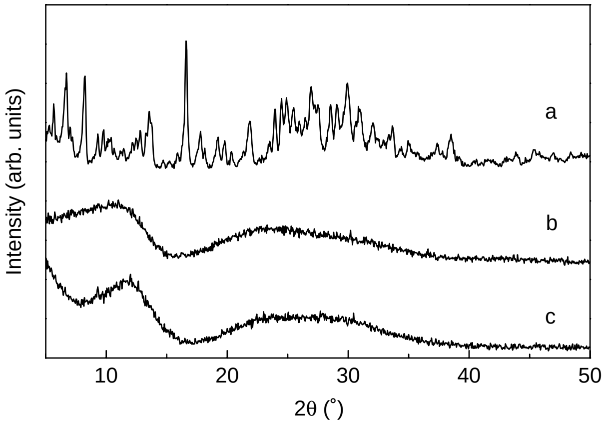

Fig. 3. XRD patterns of: (a) pure EPW; (b) the PVP film; (c) the EPW/PVP film.

Table 1
FT-IR Data (ν cm^{-1}) of EPW and EPW in the composite film

Sample	ν(P–O$_a$)	ν(W–O$_d$)	ν(W–O$_b$–W)	ν(W–O$_c$–W)
EPW	1162.2, 1066.5, 1019.2	982.2, 938.3	912.7	777.2
EPW/PVP (colorless)[a]	1141.6, 1066.5,1019.0	981.4, 935.1	917.7	801.8
EPW/PVP (blue)[b]	1141.4, 1066.4, 1017.6	934.8	914.3	798.5
EPW/PVP (colorless)[c]	1141.9, 1066.4, 1019.1	981.5, 935.5	917.3	801.5

[a] Without UV irradiation.

[b] Irradiation with UV light for 30 s in air.

[c] 40 min after UV irradiation.

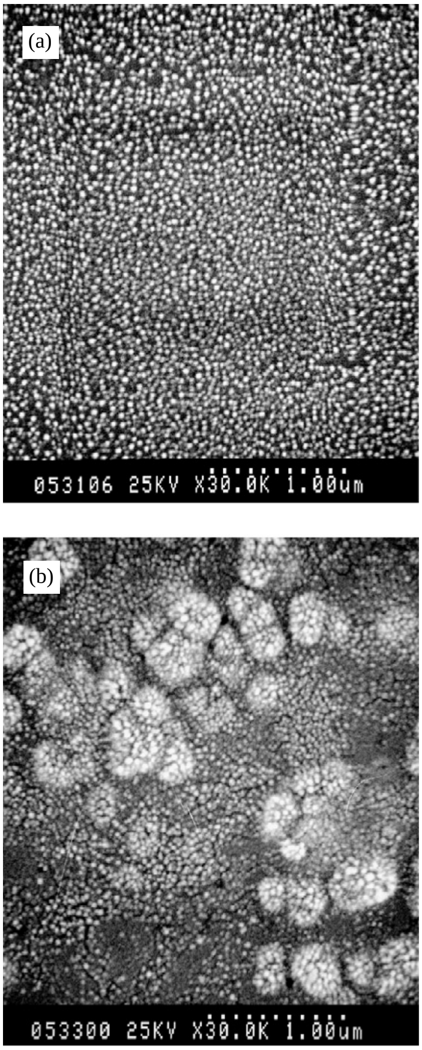

Fig. 4. SEM images of: (a) the pure PVP film; (b) the EPW/PVP film on silicon wafers (surface view).

and b show the SEM images of the PVP and EPW/PVP films on silicon wafers, respectively. One can easily see that the PVP film surface is very uniform and smooth and made up of a large number of microspheres with a narrow size distribution (ca. 45–50 nm). Besides those microspheres, some individual domains composed of lots of ca. 40–50 nm microspheres with diameters of ca. 300–520 nm along the horizontal axis can be seen in the surface of the EPW/PVP film. These domains are probably composed of complex ion pairs formed by the association of the EPW polyanions with PVP via coulombic interactions.

3.4. Thermogravimetry–differential thermal analysis

The thermal stability of the EPW/PVP film was studied by the thermal analysis depicted in Fig. 5. An early weight loss at temperatures below 160°C is seen from TG curve due to loosely bound water, followed by a steady weight loss due to loss of more strongly bound water (up to ca. 350°C) and then a further weight loss with a distinct inflection at ca. 350°C which is due to the oxidation of PVP [20]. The exothermic peak at ca. 350°C in the DTA curve determines the maximum temperature of utilization of the composite film in the presence of air.

3.5. Photochromism

Typical absorption spectra of the EPW/PVP film before and after UV irradiation are shown in Fig. 6. Before UV irradiation there are only two strong characteristic absorption bands of EPW polyanion at 198 and 276 nm which are ascribed to the O_d–W and $O_{b,c}$–W charge-transfer transition bands [21], respectively, substantiating the incorporation of EPW into the composite film without any structural alteration. After UV irradiation, the O → W charge transfer transition bands show no evident changes except a little decrease of its intensity. In addition, a new broad absorption band appears in visible region with a maximum at about

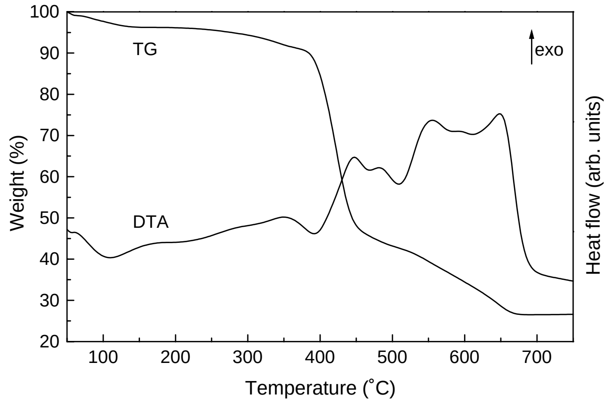

Fig. 5. The thermal analysis of the EPW/PVP composite (heating rate 10°C/min).

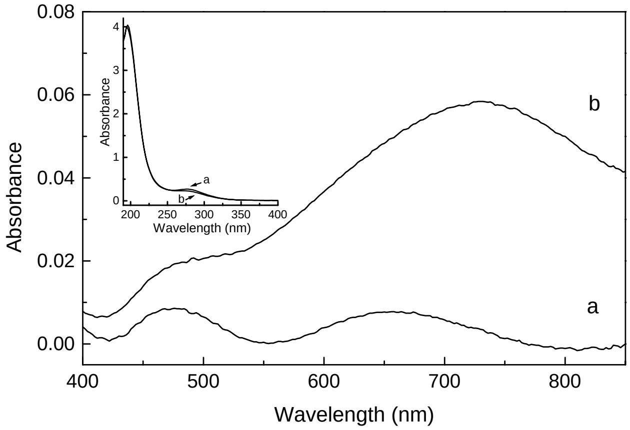

Fig. 6. Visible absorption spectra of the EPW/PVP film at 400–850 nm: (a) initial film; (b) after irradiation with UV light in air for 30 s. The inset shows the corresponding UV absorption spectra of the composite film at 190–400 nm.

730 nm, which is assigned to the intervalence charge transfer (IVCT, $W^{5+} \rightarrow W^{6+}$) band of the heteropolyanion and is characteristic band of heteropolyblue [6,22]; meantime, the film was colored with blue. The appearance of IVCT bands and the weaken of absorption peaks in UV region show that electron transfer occurs between the organic substrates and heteropolyanions under UV irradiation, converting heteropolyanions to heteropolyblues with simultaneous oxidation of the organic substrates.

After UV light was turned off, the film began to decolor gradually at room temperature in the dark. The dependency of absorbance at 730 nm on the bleaching time for the composite film at room temperature is shown in Fig. 7. The response speed is very fast at the beginning of bleaching process and becomes slow with prolonging the bleaching time. After 20 min, the bleaching process is nearly over. When exposed to UV light, the composite film can recover blue again. But if the colored films were stored in nitrogen, helium, argon 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 it is the oxygen in air that has reoxidized W^{5+} into W^{6+}, not the self-redox occurring in the system. In addition, the composite film shows a good reversibility in its coloration-decoloration process more than 50 times, suggesting good photochromic properties.

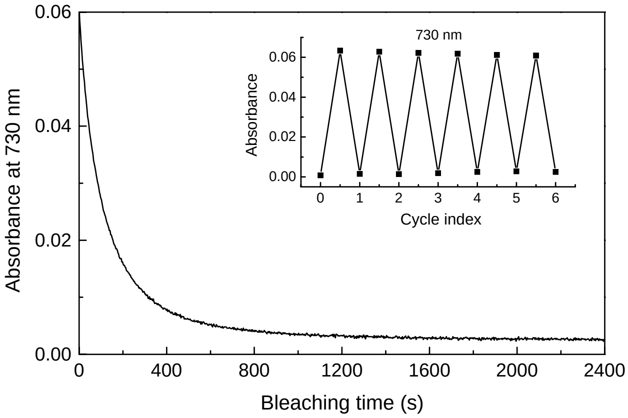

Fig. 7. The absorbance at 730 nm for the EPW/PVP film at room temperature as a function of the bleaching time. The inset shows the reversibility of the EPW/PVP film in the coloration–decoloration process.

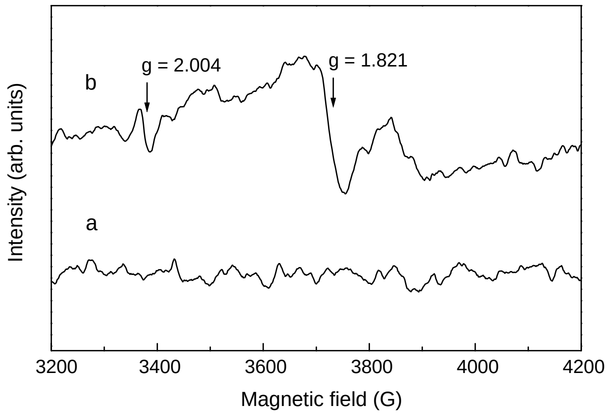

Fig. 8. X-band ESR spectra of the EPW/PVP film at low temperature (84 K): (a) unirradiated; (b) irradiated for 30 s.

3.6. ESR spectra

ESR is an efficient and sensitive spectroscopy to characterize polyoxometalates. The unirradiated EPW/PVP film exhibits no significant ESR signals (Fig. 8a). But after annealing the composite film exhibits two significant signals which are shown in Fig. 8b. One signal at about 3375 G is corresponding to the formation of W^{5+} with $g = 1.821$. This g value is in agreement with values reported in Ref. [23]. The other signal at about 3724 G is a typical radical signal with $g = 2.004$. Observation of UV-induced ESR signals is another proof for the charge-transfer process happened between the heteropolyanion and the organic substrate under UV irradiation, resulting in the reduction of EPW ($W^{6+} \rightarrow W^{5+}$) and oxidation of PVP through formation of radical.

4. Conclusion

A novel amorphous nanocomposite film with photochromic properties has been fabricated based on the stabilization of the functional materials EPW in the PVP matrix. EPW clusters are homogeneously distributed in the matrix and maintain the primary structure. The EPW/PVP film shows good photochromic properties and coloration–decoloration reversibility. Under UV irradiation, the film turns blue due to the charge-transfer process happened between EPW and PVP, and IVCT ($W^{5+} \rightarrow W^{6+}$) transition is responsible for the color. In fact, appropriate choice of POM and polymer matrix should be helpful for fabricating functional nanocomposite films having optical, magnetic, catalytic, photochromic and electrochromic properties.

Acknowledgments

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