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Preparation and Photochromic Properties of Keggin Type Tungstophosphate Acids/Dextran Hybrid Film

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Summary

A novel photochromic hybrid film containing 12-tungstophosphoric acid (PW_{12}) and dextran has been successfully prepared by solution casting method. The Fourier transform infrared (FTIR) and ultraviolet-visible (UV-Vis) spectra revealed that the Keggin geometry of the PW_{12} was still preserved in the hybrid film and a charge-transfer bridge was built between PW_{12} and dextran through hydrogen bonds. Wide-angle X-ray diffraction (WAXD) was used to investigate the morphology of the hybrid film. Under UV irradiation, the hybrid film was reduced photochemically to yield a blue species. The reversibility of the photochemical reaction of the hybrid film was observed. The characteristic signal of W (V) in the electron spin resonance (ESR) spectrum and the changes in the UV-Vis and FTIR spectra after irradiation was identified, indicating that PW_{12} was reduced to one-electron heteropoly blue and partial hydroxyl groups of dextran were oxidized to the carbonyl groups. A conceivable mechanism for the photochromic reaction was also proposed.

Introduction

Polyoxometalates based photochromic materials have attracted a widespread interest due to their special structures and properties [1]. They can be photochemically reduced to form colored species (heteropolyblues or heteropolybrowns) while retaining the structural integrity, which are ideal for use as photochromic and eletrochromic materials [2, 3]. However, for single inorganic photochromic species, they usually exhibit poor photochromic properties, low thermal stability of virgin or colored states, and sometimes a high-cost preparation with difficulty in tailor-make, and so forth [4]. It is desired to create photochromism in composite or hybrid materials in which a combination of properties is not available in any of the individual component of the composites or hybrids.

Polymers are introduced into the hybrid systems due to their versatile structural property and functionality. A main advantage of inorganic/polymeric hybrids is that the polymeric matrix can make nanometer scale polyoxometalate clusters disperse very well in the hybrids and improve the stability of the materials [5]. So far, the polymers used in the photochromic hybrids included polyacrylamide (PAM) [6], polyvinyl alcohol (PVA) [7], polyethylene glycol (PEG) [8], polyvinyl pyrrolidone (PVP) [9], and the like. In our previous study, a new photochromic hybrid was prepared based on 12-molybdenum phosphoric acid (PMo_{12}) with Keggin structure dispersed into dextran matrix. We found that PMo_{12} maintained Keggin geometry in the hybrid film and interacted with the dextran forming a supramolecular complex [10, 11]. The yellow complex irreversibly changes to blue-violet due to the formation of multivalent molybdenum (VI, V, IV) complex upon UV-light irradiation. The photochromic product was also a kind of supramolecular complex.

Dextran is a homopolysaccharide containing primarily (1→6) linked α-D-glucopyranose residues and is widely used in biomedicine, biochemistry and food industry [12], its main chain structure was represented in Fig. 1. As a continuous effort to explore this natural polymer, in this article, a novel hybrid was synthesized from dextran and another polyoxometalate, 12-tungstophosphoric acid (PW_{12}), with a Keggin structure as shown in Fig. 2. We have prepared a colorless and optically transparent thin film of PW_{12}/dextran hybrid and investigated its photochromic properties and mechanism.

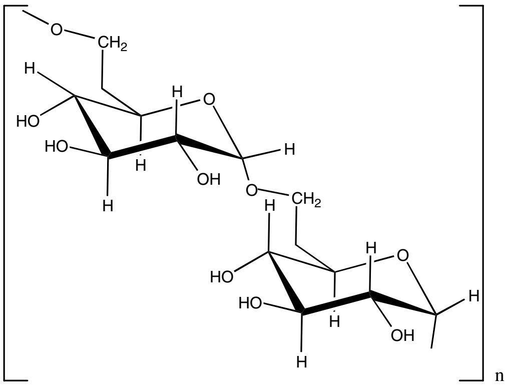

Figure 1. Main chain structure of dextran.

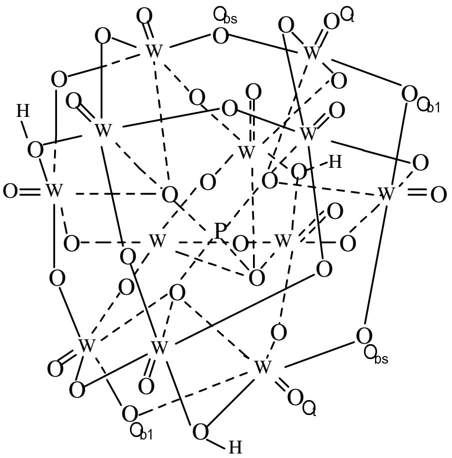

Figure 2. Scheme for Keggin structure of 12-tungsto phosphoric acid.

Experimental

Materials

12-Tungstophosphoric acid n-hydrate ($H_3PW_{12}O_{40} \cdot nH_2O$) was purchased from Wako Pure Chemical Industries, Ltd. (Japan). Dextran (M=90000) was obtained from Shanghai Changzheng Pharmaceutical Factory. They were dried, stored in a desiccator over $CaCl_2$ and used without further purification.

Preparation of PW_{12}/dextran hybrid film

The preparation of PW_{12}/dextran hybrid film was performed as follows: 1 g of dextran was dissolved in deionized water (10 ml) at room temperature. Then, 0.1 g of PW_{12} was added to the dextran aqueous solution under vigorous stirring for 4h at room temperature. The resultant solution was pour onto a glass plate and dried under vacuum in the presence of $CaCl_2$ in a dark chamber. A colorless and transparent film (d-W-1) of PW_{12}/dextran hybrid was obtained.

Photochromic reaction of PW_{12}/dextran hybrid film

The hybrid film (d-W-1) was evenly irradiated with a long wave UV lamp (360nm) for 30 min followed by drying in vacuo. The irradiation caused a photochemical reaction and color change of the hybrid film (d-W-1), leading to the formation of the blue photochromic product (d-W-2).

Characterization

Ultraviolet-visible (UV-Vis) absorption spectra of hybrids were recorded on a Lambda 850 UV-Vis spectrophotometer (Perkin Elmer). Fourier transform infrared (FTIR) spectra of all samples was taken with a Perkin Elmer FTIR-2000 spectrometer at frequencies from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The low temperature electron spin resonance (ESR) measurements were carried out on a Germany ER-420 spectrometer. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a Philips X'Pert-MPD X-ray diffractometer operating with a K-Alpha1 radiation source (wavelength = 1.54Å). The samples were mounted on a sample holder with Scotch tape and exposed at a scan rate of $2\theta = 2^{\circ}\ min^{-1}$ between $2\theta = 5$ and 55°.

Results and discussion

Structure and composition of PW_{12}/dextran hybrid film

The structural feature of PW_{12}/dextran hybrid and interaction between PW_{12} and dextran were investigated with FTIR. The FTIR data and assignment for PW_{12}, dextran and PW_{12}/dextran hybrids are listed in Table 1. It was found that the hybrid (d-W-1) exhibited the characteristic skeletal bands of PW_{12} [13, 14]. The frequencies of these bands were shifted away from the corresponding frequencies of pure PW_{12} by only a few wavenumbers as follows: νP-O (1082 cm^{-1}), $\nu W\text{-}O_b\text{-}W$ (896 cm^{-1}) and $\nu W\text{-}O_c\text{-}W$ (817cm^{-1}) were blue-shifted, while $\nu W\text{-}O_d$ (975cm^{-1}) had red shift, respectively. Further, the vibrational bands at 1015 cm^{-1} (νC–O), 1158 cm^{-1} (νC-O-C), 1431–1646 cm^{-1} (νC–C) and at 2874–2925 cm^{-1} (νC–H) of hybrid (d-W-1) were similar to those of neat dextran with a shift to shorter or higher wavenumbers only a few cm^{-1}. These results indicated that the Keggin geometry of PW_{12} was still preserved inside the hybrid film, and the PW_{12} was well dispersed in the dextran matrix. Compared with that for pure dextran, the *ν*O-H band of hybrid (d-W-1) becomes wide with the peak shifted from 3413 to 3445 cm^{-1}. Dextran containing hydroxyl groups can self-associate and form strong intra-molecular interactions through formation of hydrogen bonds [15]. The hydroxyl-hydroxyl bonds might be weakened by the formation of the inter-molecular interactions with PW_{12} partially. Therefore, it was suggested that the hydrogen bonds were formed between PW_{12} and dextran.

Table 1. FTIR data (ν, cm^{-1}) and assignment for dextran, PW_{12}, d-W-1 and d-W-2

Sample	PW_{12}	Dextran	d-W-1	d-W-2
νP-O	1080	-	1082	1081
ν W-O_d	978	-	975	983
νW-O_b-W	895	-	897	894
νW-O_c-W	810	-	817	804
νC-O-C	-	1159	1158	1155
νC-O	-	1010	1015	1019
νC-C	-	1423, 1644	1431, 1646	1428, 1640
νC-H	-	2871, 2920	2874, 2925	2871, 2924
νO-H	-	3413	3445	3432

The electronic spectrum of PW_{12}/dextran hybrid was compared with those of pure PW_{12} and dextran. As shown in Fig. 3, there was no apparent absorption band of dextran from 200 to 400 nm. In previous study, we have found that the electronic

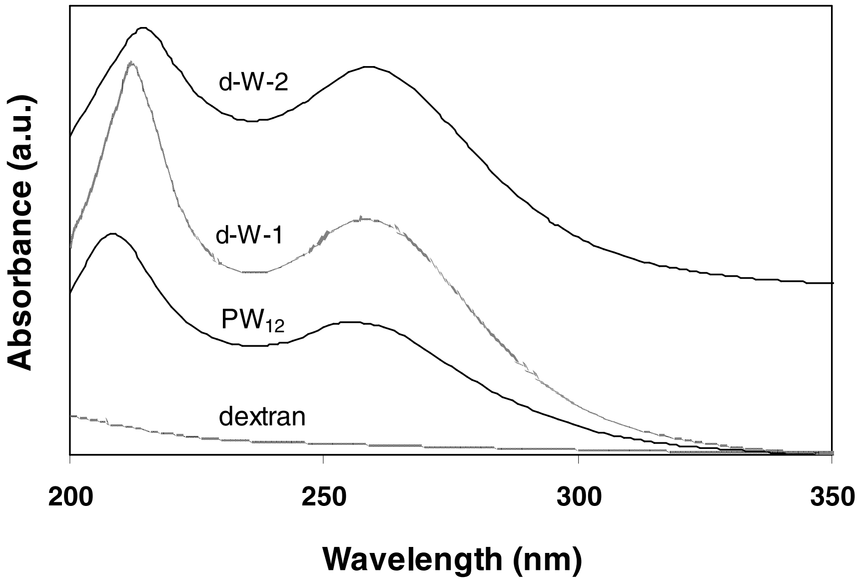

Figure 3. UV-Vis spectra (UV region) of pure and hybrid phases.

absorption of dextran was located in the far-ultraviolet region (<200 nm) due to the transition of n→σ* [10]. The absorption peaks for PW_{12} pure phase were found at 208 and 254 nm which are the characteristic absorption peaks of Keggin structure and assigned to the intramolecular (O_d →W and $O_{b,c}$ →W) charges transfer (CT) transitions [16, 17]. We observed two absorption bands around 212 and 258 nm in the UV spectrum of hybrid (d-W-1), probably resulting from the red-shift of the intramolecular (O→W) CT transition of PW_{12}.

In our previous study, we have proposed the formation of supramolecular complex or inclusion compound between PMo_{12} and dextran based on the observation of the characteristic absorptions and shifts in the FTIR and UV-Vis spectra [10, 11]. The appearance of the characteristic skeletal bands of PMo_{12} and dextran indicated the maintenance of chemical structures in PMo_{12} /dextran hybrid. On the other hand, the red- or blue-shifts of absorption bands may response to the change of electronic structures (electronic density and distribution) in PMo_{12} and dextran caused by the coulombic interaction between the organic donor (dextran) and heteropolyacid acceptor (PMo_{12}). Similarly, we observed the characteristic skeletal bands of PW_{12} and dextran and their shifts after formation of PW_{12}/dextran hybrids (d-W-1 and d-W-2) as mentioned above. Therefore, we believed that PW_{12} and dextran formed a supramolecular complex or inclusion compound rather than the simple blending.

Morphology of PW_{12}/dextran hybrid film

The morphology of hybrid was characterized by WXRD. Fig. 4 illustrates the WXRD patterns of the PW_{12}, neat dextran and PW_{12}/dextran hybrid with addition of 10wt% of PW_{12}. The WXRD pattern of the PW_{12} showed the characteristic diffraction peaks at 6.73 and 8.07° (2θ), respectively [14]. On the other hand, the dextran presented

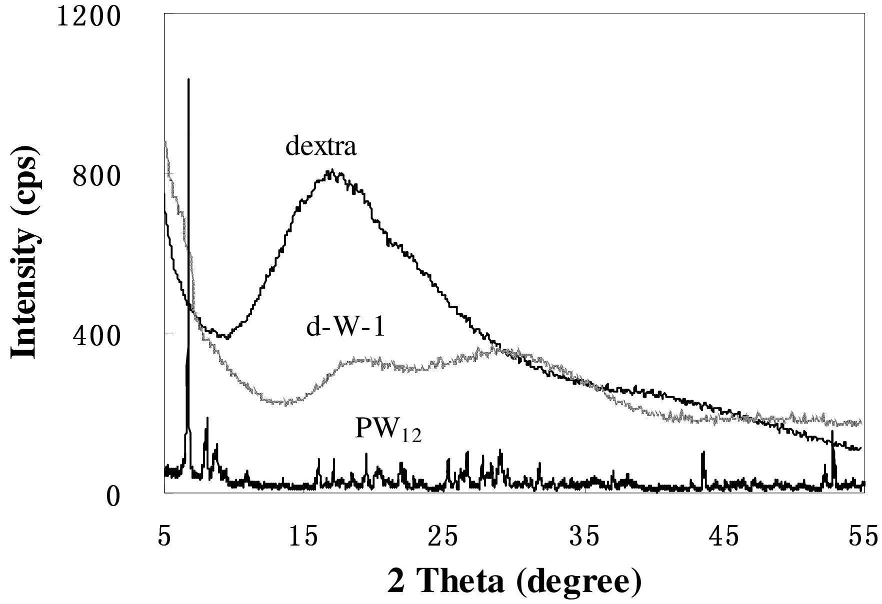

Figure 4. WAXD of dextran, PW_{12} and d-W-1.

a broad diffraction peak at 17.03 (2θ). After incorporating PW_{12} within dextran, the broad diffraction peak at 17.03 (2θ) of dextran and characteristic diffraction peaks of PW_{12} at 6.73 and 8.07° (2θ) disappeared, substituted by two quite weak and broad diffraction peaks at 19.19 and 29.61° (2θ), indicating an amorphous morphology. This result also provided another evidence for well dispersing of PW_{12} in the dextran matrix, probably in molecular scale.

Photochromic behavior of PW_{12}/dextran hybrid films

The UV-Vis absorption spectra of the PW_{12}/dextran hybrids before (d-W-1) and after irradiation (d-W-2) are shown in Fig. 5. Before UV irradiation, there was no apparent absorption band from 400 to 800 nm (Fig. 5a). After exposure to the UV light, two broad absorption bands appeared respectively at 757 and 496 nm in the UV–Vis spectrum of the colored film (Fig. 5b). They are assigned to the d-d transition band of W^{5+} and the intervalence charge transfer ($W^{5+} \rightarrow W^{6+}$) (IVCT) band of PW_{12} [3, 16], respectively. Both absorption bands are characteristic of the one-electron heteropoly blue [3, 16]. We also studied the decoloration process of the blue films under different conditions. It was found that the photochromic product d-W-2 with blue color could be bleached (Fig. 5c) by heating (70-80 ºC in air) within several minutes or faded under ambient conditions within several days. In fact, the colored specie was quite stable in ambient condition up to one week. After exposure to the UV-light irradiation, the decolored film can be photocolored again (Fig. 5d). This is quite different from our previous result for the PMo_{12}/dextran system in which the yellow inclusion compound irreversibly changes to blue-violet after irradiation [10, 11]. The reason accounting for such difference in reversibility may be that the multivalent molybdenum (VI, V, IV) complex, especially the Mo (IV), is not easily oxidized.

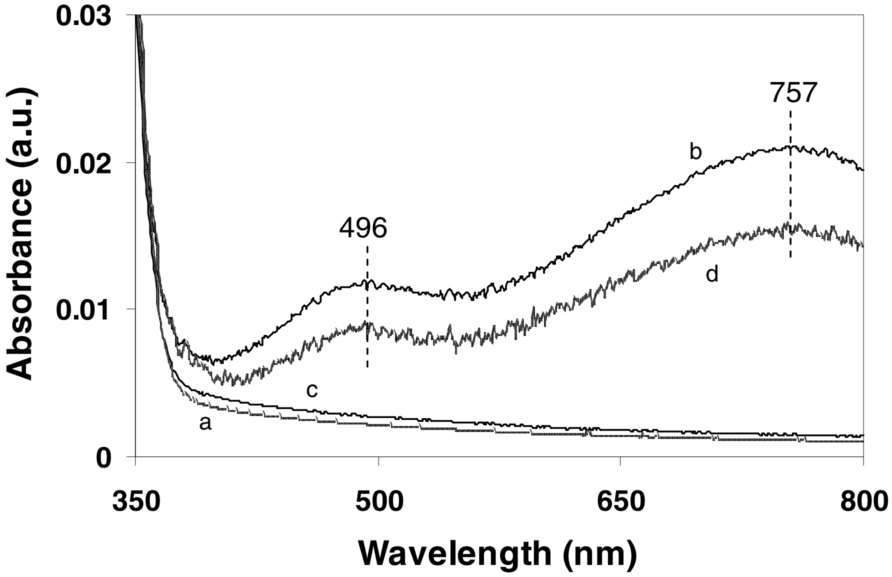

Figure 5. UV-Vis spectra (visible region) of the PW_{12}/dextran hybrids (a) d-W-1; (b) d-W-2; (c) heated at 70-80 ºC in air for 10 minutes for d-W-2; (d) recolored with UV irradiation for 10 minutes for bleached sample.

Photochromic mechanism of PW_{12}/dextran hybrid film

In order to determine the photochromic mechanism of PW_{12}/dextran hybrid film, the ESR spectra were conducted before and after the UV-light irradiation. No ESR signals were detected for the dextran, PW_{12} and d-W-1, indicating that dextran and PW_{12} did not contain the unpaired electron and the W atoms in the d-W-1 still maintain W^{+6}. After irradiation, an ESR signal with g =1.8605 was observed in the ESR spectrum of the d-W-2 (signal c in Fig. 6). According to literatures [16, 18], the ESR signal (g value) was similar to the characteristic of tungstic (W^{5+}) compounds and thus ascribed to W^{5+}. In addition, the signal (a) was ascribed to the alkoxy radical with g=1.9962, indicating the oxidation of dextran through the formation of the radical.

The structure of photochromic product (d-W-2) was further confirmed by its UV-Vis and FTIR spectra. After irradiation, two absorption bands in the ultraviolet spectral region were found at 215 and 261 nm, respectively. In comparison with the d-W-1 before irradiation, the intramolecular (O→W) CT transition band shifted away only a few nm. It is noteworthy that the FTIR spectrum of the d-W-2 showed a new absorption peak at about 1705 cm^{-1} that was absent in the neat dextran and d-W-1 spectra (Fig. 7). It may be normally assigned to the characteristic C=O stretching band, revealing the presence of carbonyl groups in the photoproduct of the d-W-1 [10, 11, 19, 20]. In other words, the partial hydroxyl groups of dextran in the d-W-1 were oxidized to the carbonyl groups through irradiation. In addition, the slight shifts in the PW_{12} Keggin structure bands at 804, 894, 983 cm^{-1} due to W-O_c-W, W-O_b-W and W-O_d stretching vibration were observed as a result of the reduction of W^{6+} as shown in Table 1.

Based on the aforementioned data, we may conclude that the photochemical reaction of dextran with PW_{12} in the d-W-1 and electron transfer between them occurred

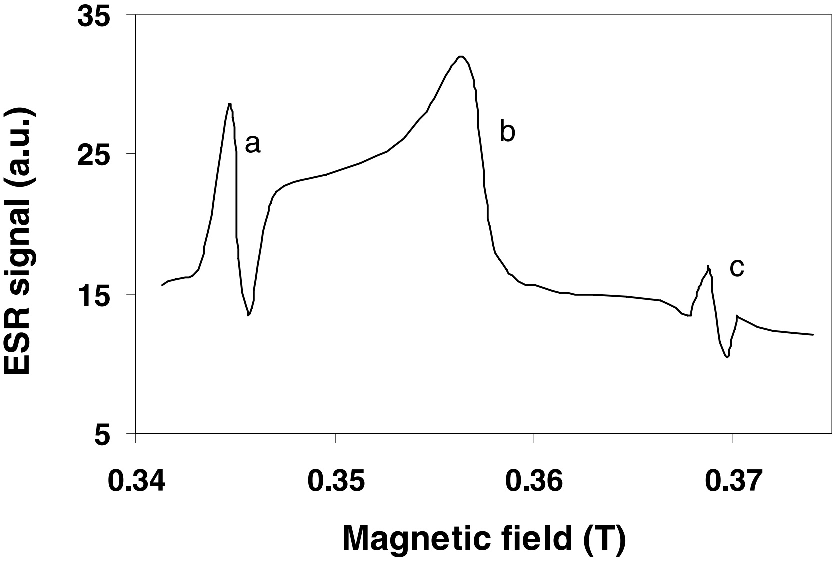

Figure 6. ESR spectrum of hybrid film exposed upon the UV irradiation for 10 min. (a) alkoxy radical with g =1.9962; (b) Mo impurities acting as selective electron traps; (c) photoreduced PW_{12}.

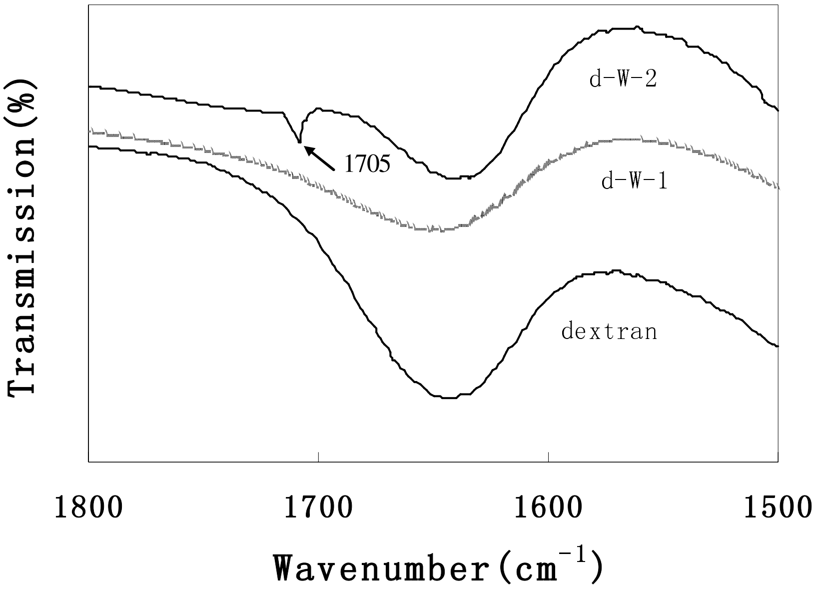

Figure 7. FTIR spectra of dextran, d-W-1 and d-W-2.

during UV irradiation. The photochromic mechanism of the d-W-1 could be represented by the following equations:

$$PW_{12}O_{40}^{3-} \underset{O_2}{\overset{h\nu}{\rightleftarrows}} PW_{11}^{VI}W^{V}O_{40}^{4-} \qquad (\mathbf{1})$$

$$\text{–CHOH–CHOH–} \xrightarrow{h\nu} \text{–CHOH–CHO}\cdot\text{–} \qquad (\mathbf{2})$$

$$\text{–CHOH–CHO}\cdot\text{–} \xrightarrow{h\nu} \text{–CHOH–CHO} + \cdot\text{CHOH–} \qquad (\mathbf{3})$$

For PW_{12}, it has been suggested that the bridging oxygen (Ob) has the exclusive reactivity and serves as the adsorption sites in the redox process. So the protons can be attracted to the Ob atoms to compensate the negative charges of the introduced reduction electrons [21-22]. In addition, it is said that the terminal oxygen (Od) is apparently the most active atom in the redox process since the Od is located at a protruding position of the Keggin unit and the Od–W bond is a double bond [21,22]. Therefore, it was deduced that the photoexcitation of the Od induced the transfer of the active hydrogen protons in the hydroxyl groups of dextran to PW_{12} under UV radiation. This is followed by one-electron transfer from dextran to PW_{12}. As a result, PW_{12} was reduced to the heteropoly blue (g =1.8605 in ESR) with simultaneous oxidation of the secondary hydroxy group in dextran to the carbonyl groups, respectively.

Conclusion

A novel hybrid film has been successfully prepared from PW_{12} and dextran by a facile method. The PW_{12} was well dispersed in the dextran matrix, probably existed in molecular scale with the Keggin's geometry. Dextran stabilized the PW_{12} phase via forming a supramolecular complex. The optically transparent hybrid film displayed an amorphous morphology supported by WAXD. The hybrid film exhibited excellent photochromism and good reversible coloration. The colored specie was quite stable in the ambient condition and returned to its original color under heating in air. According to the ESR and FTIR results, PW_{12} was reduced to one-electron heteropoly blue and the partial hydroxyl groups of dextran were oxidized to the unsaturated ketone or aldehyde during the photochromic reaction. A conceivable photochromic mechanism of the irradiated PW_{12}/detran was suggested.

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