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Thermochromic Organoaminomodified Silica Composite Films Containing Phosphomolybdic Acid

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A novel thermochromic sol–gel film has been prepared for the first time through entrapping phosphomolybdic acid into a kind of inorganic–organic matrix co-hydrolyzed from tetraethylorthosilicate and 3-aminopropyltriethoxysilane. The thus-obtained amorphous nanocomposite film was characterized by IR spectra, UV–vis absorption spectra, XRD, TG–DTA, and ESR. Results show that phosphomolybdate polyanions interact with R–NH_3^+ cations strongly and disperse homogeneously in the sol-gel matrix. The sol–gel film exhibits thermochromic properties. Annealed from 120 to 180°C, the transparent film changes from pale-yellow to blue. A possible charge-transfer process has been suggested to explain the thermochromism. © 2002 Elsevier Science (USA)

Key Words: **sol–gel; thermochromic; phosphomolybdic acid; charge transfer.**

INTRODUCTION

Inorganic thermochromic materials are important in highly technological fields because of their potential applications in optical switching devices (1), optical recording media (2), and advanced window coatings for buildings and vehicles to get an automatic control of the solar transmission (3, 4). So far, much effort in this field has been focused on transition metal oxides or sulfides such as MoO_3, VO_2, TiO_2, NbO_2, FeS, NiS, and so on (5–7), despite some weakness in visual transmittance and higher cost for manipulation. Polyoxometalate of transition metals (e.g., molybdenum, vanadium), due to reversible multivalence redoxidation and high electronic density, are ideal for use as photochromic, electrochromic, and thermochromic materials (8). Their structures can be depicted as molecular fragments of close-packed metal oxides of formula $X_aM_bO_c^{n-}$ (M = Mo, W, V, etc.; X = P, Si, Ge, As, etc.). The first and best known polyoxometalate structural type is the so-called Keggin structure. It consists of four M_3O_{13} groups of three edge-shared MO_6 octahedra, each group linked to the next M_3O_{13} by corner sharing and the whole arrangement enclosing a corner-sharing central XO_4 tetrahedron. In all polyanion structures the M-atoms are strongly displaced from the centers of their MO_6 octahedra towards the terminal unshared oxygen atoms (9).

In order to realize practical applications, thermochromic materials must be easily shaped as coatings, monoliths or any other form. The sol–gel method may be a good candidate for preparation of thermochromic materials via doping them into transparent matrices. Its advantage of low-temperature process allows synthesizing materials that cannot be prepared by conventional methods. Moreover, films of variable composition, microstructure, and thickness on different substrates as well as monoliths of various shapes can be easily prepared by simply adjusting reaction parameters, for instance the ratio of precursors to water, the nature of solvents, and reaction temperature, etc. (10). Moreover, the final products can exhibit good optical quality (high transmission in visible range) and mechanical strength (easy processing) required for application (11).

In the present work, a novel thermochromic sol–gel film was fabricated for the first time among which organoaminomodified silica clusters complex with phosphomolybdic acid molecules by electrostatic interaction, hydrogen bonding and van der Waals contacts. The thermochromic properties and mechanism of the composite material with regard to its structure are described.

EXPERIMENTAL SECTION

Materials

Phosphomolybdic acid ($H_3PMo_{12}O_{40}$, PMA for short) was prepared according to literature procedures (12).

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Tetraethylorthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTES) purchased from Aldrich Co were all used as received. Deionized water was used in all experiments.

Preparation

Hydrochloric acid (2.7 ml 8.9 mol lL^{-1}) was added to a mixed solution of 8.6 mL TEOS, 3.0 mL APTES, and 20.0 mL ethanol and the mixture was refluxed for 3 h under stirring. 1.9 g PMA was added to the solution and stirring for an additional 3 h; a transparent pale-yellow solution was obtained. The final solution was used to prepare thermochromic inorganic-organic composite film on quartz or glass substrates via spin coating process. The spin coating was performed using a four-step process (30 s with 1500 rpm each time). The as-deposited films were dried for 4 days at 50°C for spectroscopic measurements. The thickness of the composite film, measured using a FCT-1030 Film Thickness Measurement System (LCD Lab, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun), was approximately 1.0 μm. The preparation process of powder samples was depicted as follows. The solution was spread in a polystyrene-dish, and was under a flow of air at 40°C for 24 h, then the films were peeled off, cut up or powdered and stored in dry air at 50°C. Under these conditions, the residuals by products (water and solvent) were removed in a few days.

Methods

Fourier transform infrared (FT-IR) spectra were obtained with a Nicolet Impact 410 FT-IR spectrometer in the range 400–4000 cm^{-1}. The samples were thin films deposited on KBr pellets. X-ray diffraction (XRD) data were obtained using a Rigaku (Japan) D/max-rA X-ray diffractometer with a Cu*K*α radiation (λ = 1.5418 Å). The angular scan range was from 10 to 40°. 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 5°C min^{-1}. All absorption measurements were made on a Shimadzu UV–1601PC ultraviolet-visible (UV–vis) spectrophotometer with 1 nm optical resolution over the range of 350–1100 nm.The electron spin resonance (ESR) spectra of sample were recorded on a Bruker ER200-D-SRC spectrometer at X-band. In order to study the thermochromism of the sol–gel composite film, the material was annealed in the dark at different temperatures (from 120 to 180°C) for 1 h in a conventional furnace at atmospheric pressure. After annealing, the film was preserved out of light.

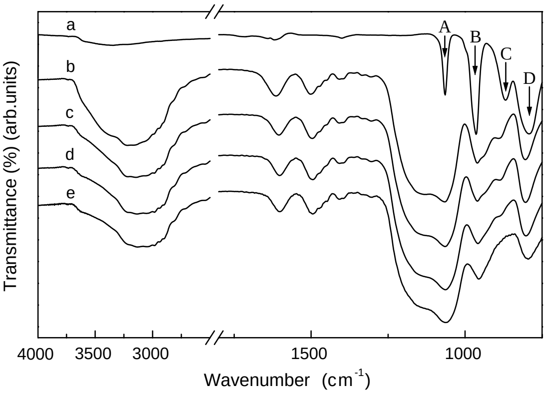


FIG. 1. FT-IR spectra of samples: (a) pure PMA: A, ν(P–O$_a$) O$_a$: oxygen atoms connected with MO$_4$ and XO$_4$ units; B, ν(Mo–O$_d$) O$_d$: external (corner) oxygen atoms; C, ν(Mo–O$_b$–Mo) O$_b$: bridge atoms linking MO$_4$ octahedral from the different M$_3$O$_{13}$; D, ν(Mo–O$_c$–Mo) O$_c$: bridge atoms linking MO$_4$ octahedral from the same M$_3$O$_{13}$; (b) the composite film unannealed (20°C); (c) the composite film annealed at 120°C; (d) annealed at 140°C; (e) annealed at 180°C.

RESULTS AND DISCUSSION

FT-IR Spectra

The IR spectra of pure PMA crystal and the composite film unannealed (as-prepared, 20°C) and annealed at different temperatures are given in Fig. 1. Several characteristic IR vibrational bands (see Table 1) at 1608 cm^{-1} (νNH$_3^+$), 1472 cm^{-1} (δCH$_2$ of propyl), 1448 cm^{-1} (δCH$_2$ of propyl), 1410 cm^{-1} (δSi-CH$_2$), 1130 cm^{-1} (ν_{as}Si–O–Si), 1067 cm^{-1} (ν_sSi–O–Si), and 942 cm^{-1} (νSi–OH) indicate the development of an inorganic-organic hybrid network during the gel formation (13). Except the P–O$_a$ band at 1064.9 cm^{-1} hidden by the more intense Si–O–Si vibrational bands, all characteristic bands of PMA are present in the hybrid film but with a little shift. This indicates the primary structure of the PMA anion has not been destroyed in the sol–gel composite film, but each characteristic bond becomes stronger or weaker to some extent.

TABLE 1

FT-IR Data (ν/cm^{-1}) of PMA and PMA in the Composite Film Unannealed (20°C) and Annealed at Different Temperatures (Fluctuation Range of Temperature Is ±0.5°C)

Sample	PMA	20°C	120°C	140°C	180°C
ν(Mo–O$_d$)	963.1	960.3	959.7	958.2	955.4
ν(Mo–O$_b$–Mo)	869.9	890.6	887.5	886.1	—
ν(Mo–O$_c$–Mo)	791.6	804.1	803.8	803.0	795.2

A more detailed inspection of the vibrational band shifts reveals that the bands of Mo–O_b–Mo and Mo–O_c–Mo bonds of PMA in the hybrid film both have blue shifts from 870 and 792 to 891 and 804 cm^{-1}, respectively, and the band of Mo–O_d is red-shifted from 963 to 960 cm^{-1}. We propose that the infrared bands shift of PMA in the sol–gel film should be attributed to strong coulombic interactions and H-bonding interactions between heteropolyanions and R–NH_3^+ cations (Fig. 2).

Indeed, Lavrencic-Stanger *et al.* (14) observed similar shift in vibration of $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ incorporated into the ICS-PPG induced by the coulombic and H-bonding interactions between the heteropolyanions and the protonated polymeric supports. Bi *et al.* (15) also found a similar phenomenon.

After annealing the film changed from pale-yellow to blue. Comparing with the unannealed composite film, we can find that the frequencies of all characteristic vibrational bands of PMA are all red-shifted by a few cm^{-1} after annealing, which is due to the formation of heteropolyblue (16) and indicates PMA have accepted electrons.

X-Ray Powder Diffraction

Powder XRD pattern of gel-containing PMA is shown in Fig. 3. For comparison, the pattern of the PMA crystal is also shown, which shows the characteristic peaks of heteropolyanion with the Keggin structure (17). No diffraction peaks characteristics of PMA crystal are observed in the XRD pattern of gel, there is only a broad dispersing band centered around 25° which displays a typical amorphous state. It suggests that PMA is well dispersed in the composite.

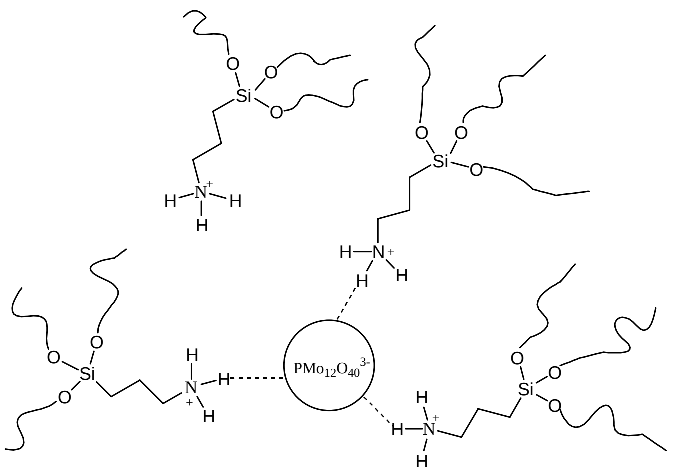


FIG. 2. Schematic illustration of coulombic interactions and H-bonding interactions between $PMo_{12}O_{40}^{3-}$ anions and *R*–NH_3^+ cations in the composite film.

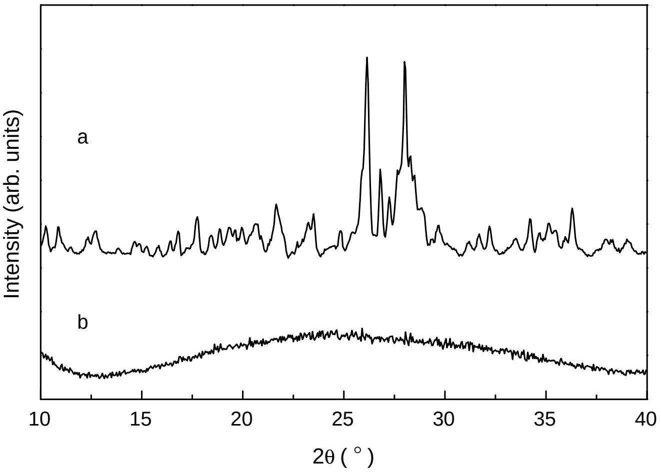


FIG. 3. Powder XRD patterns of: (a) pure PMA; (b) organoamino-modified silica gel containing PMA.

TG –DTA

The thermal stability of the xerogel was studied by the thermal analysis depicted in Fig. 4. An early weight loss at temperatures below 140°C is seen from TG curve due to loosely bound water and/or solvent, followed by a steady weight loss due to loss of more strongly bound water and silanol condensation (up to ca. 390°C) and then a further weight loss with a distinct inflection at ca. 390°C which might be due to organics (aminopropyl or ethoxy groups) desorbing (18).

Thermochromism

The unannealed composite film gives two strong absorption bands at 223 and 309 nm in UV region ascribed to the $O_d \rightarrow Mo$ and $O_{b,c} \rightarrow Mo$ charge-transfer transition, respectively, substantiating the incorporation of PMA into

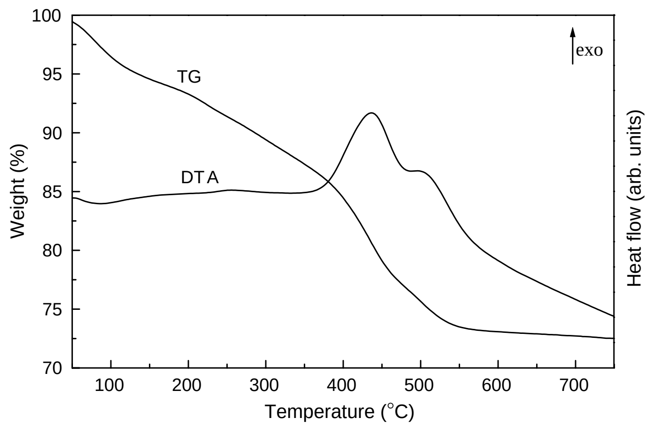


FIG. 4. The thermal analysis of the sol–gel composite (heating rate 5°C min^{-1}).

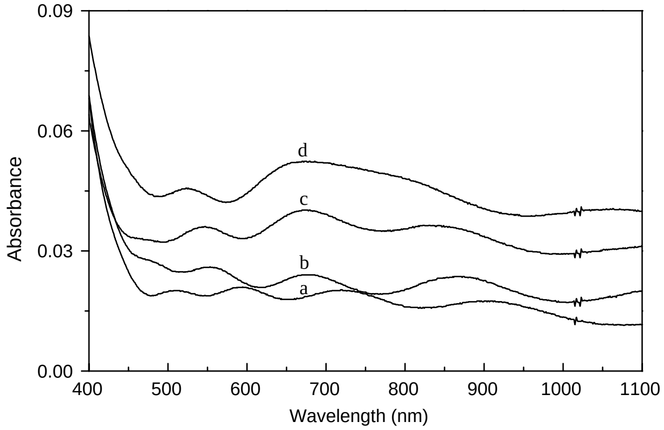


FIG. 5. UV–vis absorption spectra of the composite film: (a) unannealed (20°C); (b) annealed at 120°C; (c) annealed at 140°C; (d) annealed at 180°C.

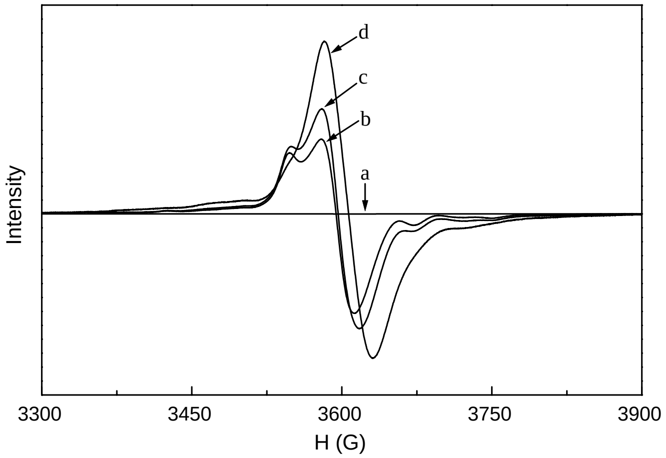


FIG. 6. X-band ESR spectra of the composite film: (a) unannealed (20°C); (b) annealed at 120°C; (c) annealed at 140°C; (d) annealed at 180°C.

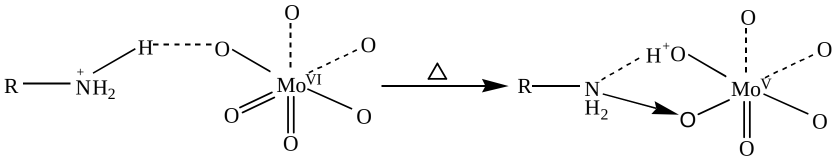
the composite film without any structural alteration. Figure 5 shows the UV–vis absorption spectra of the composite film unannealed and annealed at different temperatures. In addition to an absorption edge at 460 nm corresponding to the $O_{b,c} \rightarrow Mo$ charge-transfer absorption band of PMA, there is a broad absorption band centered around 700 nm.The intensity of absorption band around 700 nm increases as the annealing temperature increases from 120 to 180°C. This band is characteristic of reduced Keggin molecular species with intervalence charge transfer (IVCT, $Mo^{5+} \rightarrow Mo^{6+}$) band at about 625–769 nm (9). The appearance of IVCT band shows that electron transfer occurs between the organic substrate and heteropolyanion, converting heteropolyanion to heteropolyblue with simultaneous oxidation of the organic substrate. Those results indicate that PMA entrapped in the hybrid matrices can be reduced under annealing.

ESR Spectra

ESR is an efficient and sensitive spectroscopy to characterize polyoxometalates. The unannealed film exhibits no significant ESR signals. But after annealing the composite exhibits significant defined signals which are shown in Fig. 6. These signals are corresponding to the formation of Mo^{5+} with $g = 1.934$. These g values are in agreement with values reported in the literature (19). The signal intensity increases continuously as the temperature increases from 120 to 180°, which shows the content of Mo^{5+} increases with the temperature. This result correlates with the conclusion obtained from UV–vis absorption spectra. Observation of thermo-induced ESR signals is another proof for the charge-transfer process which occurs between the heteropolyanion and the organic substrate under annealing.

Thermochromic Mechanism

Thus, it is expected that the whole process of thermochromism in the sol–gel composite film may proceed in the following way:



A B

which is similar to the photochromic mechanism in alkylammonium polyoxomolybdate solids put forward by Yamase (20). The thermoexcitation of the MoO_6's $O \rightarrow Mo$ ligand-to-metal charge-transfer (LMCT) bands induces transfer of a proton from a hydrogen-bonded alkylammonium nitrogen to a bridging oxygen atom at the thermoreducible site in the edge-shared MoO_6 octahedral lattice. Simultaneously, the hole left at the oxygen atom as a result of the $O \rightarrow Mo$ LMCT transition interacts with nonbonding electrons on the amino nitrogen atom to form a charge-transfer complex B, where a paramagnetic electron localized at the distorted $MoO_5(OH)$ is responsible for the ESR signals in Fig. 6. The equation denotes the environment of the thermoreducible MoO_6 site and the subsequent formation of the charge-transfer complex B in the sol–gel composite film. Complex B reflects the charge separation of the electron and hole which are produced by the $O \rightarrow Mo$ LMCT transition in the heteropolyanions lattice. It is charge separation that keeps the colored state stable. It is obvious that this thermochromic mechanism only involves intermolecular charge-transfer process.

CONCLUSION

A novel amorphous sol–gel composite film with thermochromic properties has been fabricated based on the stabilization of the functional materials PMA in the inorganic–organic hybrid network. PMA clusters are homogeneously distributed in the network and maintain the Keggin structure. When annealed from 120 to 180°C, the film turns blue due to the charge-transfer process which occurs between PMA and organic substrate and IVCT ($Mo^{5+} \rightarrow Mo^{6+}$) transition is responsible for the color. According to the experimental results, we propose the thermochromic mechanism of the inorganic–organic hybrid system followed by charge-transfer process. In particular, the example demonstrates that many other kinds of molybdenum polyoxometalates also can be incorporated within this kind of sol–gel film, leading to new thermochromic materials.

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