



## Feature article

# Fabrication and visible-light photochromism of novel hybrid inorganic–organic film based on polyoxometalates and ethyl cellulose



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## ABSTRACT

Novel phosphomolybdic acid/ethyl cellulose hybrid film (denoted as PMoA/EC) was synthesized by entrapping PMoA particles into an EC matrix. The microstructure, visible-light photochromic behaviors and mechanism were fully investigated. The characterizations revealed that spherical PMoA particles dispersed uniformly in the hybrid film and their Keggin geometry were well preserved. The structure of EC was also maintained in the hybrid film after a composite process. Under visible light irradiation, the colorless transparent PMoA/EC hybrid film turned to blue and exhibited high photochromic responsiveness together with reversible photochromism in the presence of oxygen. The appearance of Mo<sup>5+</sup> species in XPS spectra indicated that photo-reduction reaction has occurred between PMoA particles and the EC matrix and suggested proton transfer mechanism during the photochromic process. To the best of our knowledge, EC was used to construct polyoxometalate-based hybrid film with visible light photochromism for the first time.

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## Introduction

Driven by potential technological applications such as high-density optical storage, information display devices and optical switching [1–4], investigations on photochromic materials have made great progress since photochromism was first discovered in 1876 [5–8].

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Polyoxometalates (POMs), a series of multi-core inorganic metal-oxide clusters, are one of the most attractive photochromic materials due to their fundamental structures and versatile electronic properties [9–11]. POMs can accept one or more electrons to yield colored species with mixed-valence while retaining their structural integrity which makes them outstanding inorganic candidates for the construction of functionally active solids [12–14]. By incorporating POMs into organic or hybrid inorganic–organic materials, various photosensitive systems with exceptional electro- and photochromic properties were built up [15–17]. One growing interest is to entrap POM nanoparticles into polymeric networks to fabricate transparent thin composite films with advanced photochromic and physical properties [18–20]. Various polymers such as polyacrylamide (PAM) [21,22], polyvinylpyrrolidone (PVP) [23], polyvinyl alcohol (PVA) [24,25] and polyether chains (PEs) [26] were used as matrix to construct POM-based composite films. However, the sensitivity of most photochromic effect is limited to the near-ultraviolet (UV) range. Since UV light is only a small portion of the whole solar energy and the wavelengths of most commercially available laser sources are usually in visible light range [27], the development of photochromic systems with superior visible light response is highly anticipated. By pretreatment with cathodic polarization, a  $\text{MoO}_3$  thin film became visible-light sensitive and presented reversible photochromism [28]. Leiderer et al. produced a  $\text{WO}_3$  film with visible light photochromism via introducing visible light sensitizer such as CdS into the film [29]. After that, Yao et al. reported the preparation of hybrid film fabricated from phosphomolybdic acid (PMoA) and PVP with photochromism under blue light (400–500 nm) and the absorbance can be enhanced significantly by subsequent thermal treatment [30]. In this work, ethyl cellulose (EC) which is a common film-former in coating, hot-melt adhesives and transfer inks, was chosen as an organic matrix to compose a PMoA-based hybrid inorganic–organic film. The high stability, great solubleness and strong flexibility EC possessed make it an outstanding substrate for plastic coating. Additionally, the abundant ethyl ether groups in EC allow facile charge-transfer between EC and PMoA particles. The prepared PMoA/EC hybrid film presented high visible-light photochromic responsiveness as well as reversible photochromism in the presence of oxygen.

## Materials and methods

### Materials

Phosphomolybdic acid (PMoA) was purchased from China National Pharmaceutical Group and recrystallized twice before use. Ethyl cellulose (EC) was purchased from Sigma (Ph Eur grade) and used as received. Ethanol and other organic solvents were purchased from Beijing Chemical Reagent.

### Preparation

PMoA and EC were dissolved in ethanol with concentrations of 75 mg/ml and 10 mg/ml, respectively. Then 5 ml PMoA ethanol solution was added to the same volume of EC solution drop by drop under vigorous stirring at room temperature. After stirring for 2 h, a yellow transparent solution was obtained. PMoA/EC hybrid films for structural characterization and photochromic properties were prepared by dipping the complex solution on different substrates with a 200  $\mu\text{L}$  syringe. Films were dried in a chamber with controlled air humidity below 60% in order to obtain optically perfect films. The thickness of the composite films was approximately 2.0  $\mu\text{m}$ , which was measured by a FCT-103 Film Thickness Measurement System (LCD Lab, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences).

### Physical measurements

TEM images were obtained with a JEOL JEM-200CX by dropping a complex solution onto copper grids. FT-IR spectra were collected using a Nicolet Impact 410 Fourier transform infrared spectrometer in the range of 4000–400  $\text{cm}^{-1}$ , and the samples were deposited on KBr pellets. AFM images were recorded by a Nanoscope III instrument under air atmosphere with hybrid film deposited on a silicon slice. Absorbance curves were collected on a Shimadzu UV-1601PC UV–vis spectrophotometer with 1 nm optical resolution over the range of 350–900 nm, and the samples for measurements were deposited on glass sheets on which surfaces were pre-modified by Piranha solution. XPS was performed using an ESCALAB 250 photoelectron spectrometer.

Photochromic experiments were carried out using a 300 W Xe lamp as the light source. The distance between the lamp and films was 15 cm. Films were exposed to air during the process of visible light irradiation. After samples were irradiated for a certain time, in situ absorbance curve was collected. The irradiation time was recorded until the curve was just the same as the previous one. Films were sheltered from light under air conditions and the absorption spectra were measured at regular intervals to monitor the bleaching process. All measurements were carried out at room temperature.

## Results and discussion

### TEM measurements

The microstructure of the PMoA/EC composite film was investigated by TEM. As presented in TEM image (Fig. 1), the PMoA particles exhibited regular spherical shape with an average diameter of 70 nm, and dispersed uniformly in the PMoA/EC hybrid film.

### FT-IR spectra

Comparisons of FT-IR spectra of the pure starting materials (PMoA and EC) and the PMoA/EC hybrid film were performed to confirm the structural features of the obtained hybrid film. As shown in Fig. 2, the characteristic stretching vibration for P–O, Mo–Od, Mo–Ob–Mo and Mo–Oc–Mo bands at 1064  $\text{cm}^{-1}$ , 971  $\text{cm}^{-1}$ , 875  $\text{cm}^{-1}$  and 788  $\text{cm}^{-1}$  in pure PMoA [31] were well retained after the composite process, but with a little variation due to the slight difference of chemical environments in the resulted PMoA/EC hybrid film. This result indicated that the Keggin geometry of PMoA was not destroyed in the composite process, and strong interfacial interaction was built between PMoA and EC [32]. After visible light irradiation, the vibration bands associated to PMoA in the hybrid film were preserved, however had a few  $\text{cm}^{-1}$  shift and the intensities were weakened which should be attributed to the formation of a heteropoly blue. Additionally, the presence of C–O–C vibration (at 1117 and 1067  $\text{cm}^{-1}$ ), C–C vibration (at 1370  $\text{cm}^{-1}$ ) and C–H vibration (at 2877–2978  $\text{cm}^{-1}$ ) which belong to EC was found in the hybrid film. This result revealed that the organic polymeric matrix was also well kept during the composite process.

### XPS spectra

To determine the formation of non-covalent interaction during the composite process, XPS spectra of C1s and O1s energy levels of pure EC and PMoA/EC hybrid film were both collected. As displayed in Fig. 3a, the C1s energy level of EC was divided into two levels at 285.91 eV and 284.59 eV via peak-resolution technique, which corresponded to the C–O bond and C–C bond, respectively. After the composite process, the main C1s energy value of EC was shifted to 286.14 eV and a new peak at 287.62 eV was resolved (Fig. 3b). Meanwhile, the O1s energy value of the pure EC and the resulted hybrid film was presented in Fig. 3c & d. The C–O–C bond (532.14 eV) and O–H bond (533.3 eV) could be found in the pure EC.

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