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Rapid Communication

# The first example of multilayer films with thermochromic properties

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**Abstract**

A novel thermochromic multilayer film containing polyoxometalate cluster $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]$ has been fabricated by layer-by-layer self-assembly method. In case of the multilayer film, the color changes gradually from yellowish to blue when it is subjected to temperatures between 120°C and 180°C for a period of time, and the multilayer film could be bleached in air at room temperature to recover its initial state. The novel thermochromic multilayer may be of practical benefit in the development of thermosensors, which would represent promising materials for future applications.


*Keywords:* Polyoxometalate; Layer-by-layer; Multilayer; Thermochromism

Considerable work has been focused on the development of chromogenic materials, such as photo-, electro- and thermochromic materials [1–3]. In particular, due to a large optical property change with change in temperature, thermochromic materials, known in the 1870s, can offer various potential applications in color and temperature sensors, large area displays with higher information density, and the so-called smart or intelligent windows [4]. Thermochromism has been seen in a great deal of organic and certain inorganic compounds. Also, some dyes have been embedded in polymer gel networks to obtain thermochromic hydrogel system [5]. It is necessary and challenging to explore a new strategy for constructing novel thermochromic materials.

A self-assembly method based on electrostatic interaction, layer-by-layer (LbL) technique [6], has been widely served as a powerful tool for design of novel ultrathin films. Especially, for polyoxometalates (POMs) [7], a versatile inorganic entity for the construction of functionally active solids, the formation and development of POM-based functional film mainly depended on the LbL method [8–10]. Therefore, in order to obtain new thermochromic materials, we incorporated given POMs into the polyelectrolyte matrix. Consistence with expectant thoughts, thermochromism was found, for the first time, in multilayers containing POMs. In this work, we employed the Preyssler-type heteropolytungstate $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]$ ($NaP_5W_{30}$) and poly(ethylenimine) (PEI) as building blocks to fabricate the POM-based ultrathin multilayer by LbL method. Here, $NaP_5W_{30}$ was prepared according to the method in Ref. [11] and the product was recrystallized twice. PEI (MW = 50,000) was obtained from Aldrich and used as received. Briefly, a substrate (quartz slide or silicon wafer) was cleaned prior to the film deposition by a method described in Ref. [12] and primed with PEI to introduce positive charge onto its surface. After rinsing with deionized water and drying with $N_2$, the PEI-coated substrate was alternately dipped into $10^{-2}$ M $NaP_5W_{30}$ solution and $10^{-2}$ M PEI (pH = 9.0) solution for 20 min each, followed by rinsing and drying. The architecture of multilayers can be expressed as PEI/$(NaP_5W_{30}/PEI)_n$, where the number of deposition cycles corresponds to the number of bilayers, $n$, on the quartz.

The growth process of the multilayer films was monitored by UV–vis absorption spectroscopy. Fig. 1 shows UV–vis spectra of $(NaP_5W_{30}/PEI)_n$ multilayers with $n = 1-20$ deposited on a precursor PEI film. The characteristic bands of $NaP_5W_{30}$ at 212 and 270 nm corresponding to the oxygen → tungsten charge transfer (CT) transition were observed in the multilayer films, which suggested $NaP_5W_{30}$ had been incorporated into the films. Plotting the absorbance at 212 and 270 nm as a function of the number of bilayers resulted in nearly

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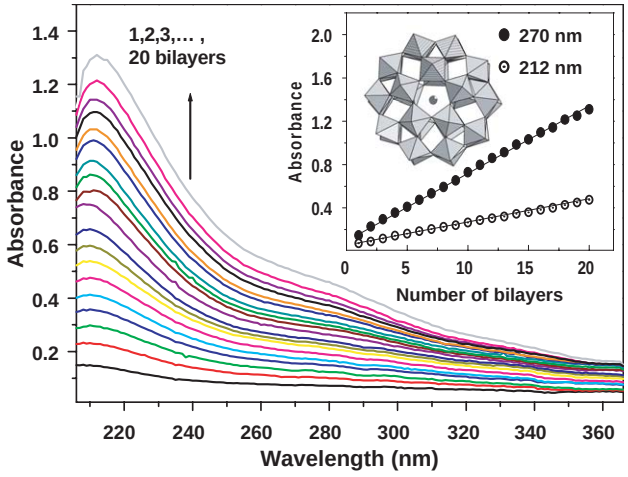



Fig. 1. UV–vis spectra of PEI/$(NaP_5W_{30}/PEI)_n$ multilayer films with $n = 1-20$ on quartz substrates (both sides). The inset shows plots of the absorbance values at 212 and 270 nm as a function of the number of $NaP_5W_{30}$/PEI bilayers ($n$) and the structure of $NaP_5W_{30}$.

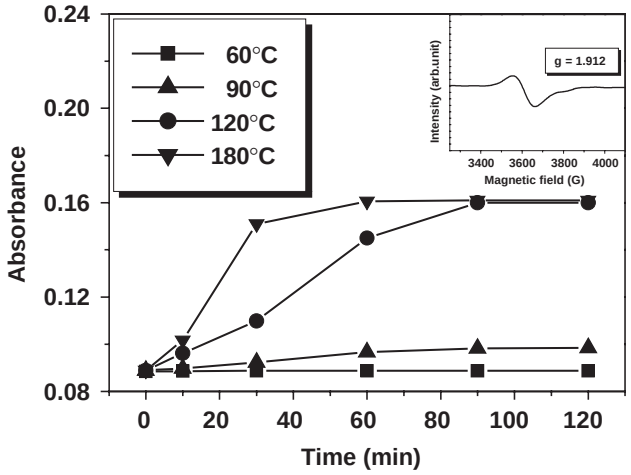



Fig. 2. The dependent change in absorbance at 700 nm on heating time under different temperatures for $(NaP_5W_{30}/PEI)_{80}$ multilayer films. The inset shows the ESR spectrum of $NaP_5W_{30}$/PEI sample heated at 180°C for 30 min.

straight lines (see inset in Fig. 1). It indicated that an approximately equal amount of $NaP_5W_{30}$ was deposited for each absorption procedure and the $(NaP_5W_{30}/PEI)_n$ films grew uniformly with each deposition cycle, although a partial loss of $NaP_5W_{30}$ clusters happened after each PEI deposition. Additionally, the FTIR spectrum recorded for $NaP_5W_{30}$/PEI multilayer film also presents characteristic vibration bands of $NaP_5W_{30}$ (vibration bands at 911 and 780 $cm^{-1}$, ascribed to the vibration modes of W = Od and W–Oc–W, and three well-resolved bands at 1165, 1082 and 1018 $cm^{-1}$ corresponding to P–Oa stretching bands), demonstrating $NaP_5W_{30}$ clusters have been incorporated into the multilayer films and the basic structure of $NaP_5W_{30}$ is still preserved inside the multilayers. Additionally, the wavenumber of N–H stretching band in PEI decreased from 3437 to 3432 $cm^{-1}$ after formation of the multilayers, which proved that the O–H hydrogen bond was formed between $NaP_5W_{30}$ and PEI. In a word, the electrostatic anion–cation interactions lead to an increase or a decrease in characteristic frequencies.

It is necessary to consider the effect of temperature on the optical absorbency properties of $NaP_5W_{30}$/PEI multilayer film. In order to avoid the effect of gas, all of heating experiments were carried out in vacuum. Fig. 2 shows the dependent change in absorbance on heating time under different temperature, for $(NaP_5W_{30}/PEI)_{80}$ multilayer film. At about 700 nm, a broad absorption band was observed. The band is characteristic of reduced Pressler molecular species with intervalence charge transfer (IVCT) band at about 600–800 nm [7]. The appearance of IVCT bands shows that an electron transfer occurs from the organic substance to heteropolyanions, indicating $NaP_5W_{30}$ entrapped in the PEI matrices can be reduced under heating. The multilayers present no changes in absorbance at 60°C, while a little changes could be observed at 90°C. However, with heating time prolonging, the multilayer film in the visible spectral range shows obvious increase of absorbance above 120°C. Moreover, the absorption gradually reached saturation and hardly changed upon further heating. Color changes below 120°C are scarcely perceivable. On the contrary, an obvious colorful sequence going from yellowish to blue was displayed when the $(NaP_5W_{30}/PEI)_{80}$ multilayer film was heated to 120°C for 90 min or 180°C for 30 min. Although chromatic changes are sensitive to higher temperature, the multilayer film will be unstable and easily destroyed at temperature above 200°C. Therefore, good thermochromic effects are yielded when the multilayer film is subjected to temperatures between 120°C and 180°C.

We also investigated the FTIR changes of wavenumbers for POM-based multilayers at 180°C. The bands of the colored films are narrower and slightly shifted when compared to the spectrum of uncolored films. The colored films reveal the characteristic bands of POMs as follows: W = Od, 913 $cm^{-1}$; W–Oc–W, 782 $cm^{-1}$; P–Oa, 1163, 1081 and 1021 $cm^{-1}$. Furthermore, the band assigned to the formation of O–H hydrogen bonding between PEI and POM have blue shifts from 3432 to 3428 $cm^{-1}$, due to transferring a hydrogen from the nitrogen of PEI to the bridge oxygen atom of POM [13].

When stopping heating, the multilayer film begins to discolor gradually in air as well as in dark. Fig. 3 shows the bleaching process of $(NaP_5W_{30}/PEI)_{80}$ multilayer film. The intensity of absorption bands decreased gradually and a few shifts in maximum absorption is observed with the increase of bleaching time from 0 to 180 min. The response speed is very fast at the beginning

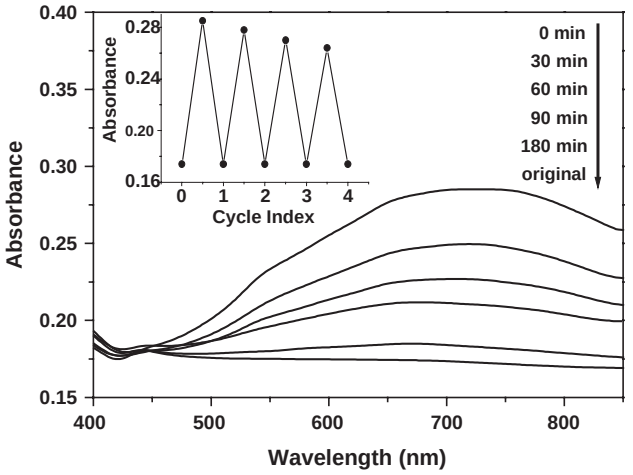
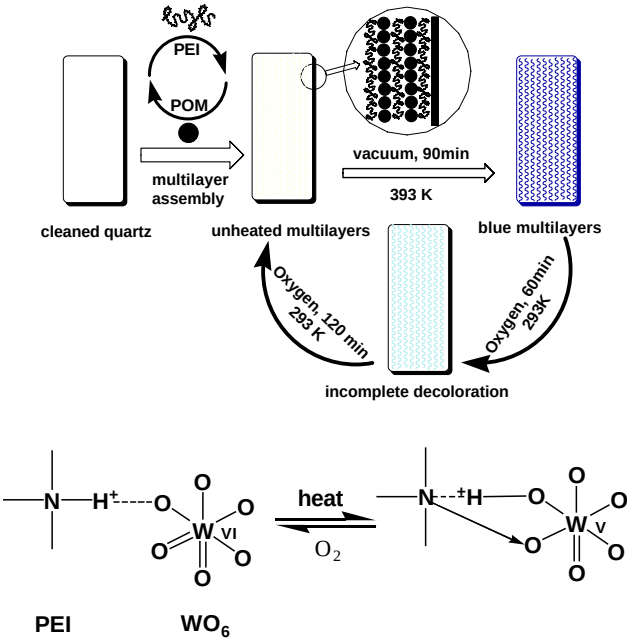



Fig. 3. Bleaching process, showing UV–vis absorption of the colored film as a function of the bleaching time. The inset shows its reversibility in the coloration–decoloration process at 700 nm.

of bleaching process and becomes slow with prolonged bleaching time. After 180 min, the bleaching process are nearly over. If the colored film is stored in nitrogen, argon or under vacuum condition, it could retain blue for a long period. However, changing the ambient atmosphere back to air or oxygen, the bleaching process will take place again. This results show that oxygen plays an important role during the bleaching process. The absorption spectra of $NaP_5W_{30}$/PEI film bleached completely are coherent with that without heating. However, more heating times, under the same condition, cannot make the film reach the original maximum absorbance. That is to say, the reversibility decreases with increasing heating number in multilayers (see the inset in Fig. 3).

To explain the thermochromic behavior of the system, electro spin resonance (ESR) was used to investigate the variation of electronic structure of the component in the system during the thermochromic process so as to elucidate the thermochromic mechanism. The $NaP_5W_{30}$/PEI sample exhibited no significant ESR signals at room temperature before heating. But after 30-min heating at 180°C, the sample exhibits a typical ESR signal of $W^{5+}$ at $g = 1.912$ (shown in the inset of Fig. 2). It was concluded that thermoexcitation of O = W in $WO_6$ ligand to metal charge transfer (LMCT) bands resulted in transferring a hydrogen from the nitrogen of PEI to the bridge oxygen atom at the thermoreduced site in the edge-shared $WO_6$ octahedral lattice. This is followed by the interaction of one electron with the proton, which was transferred to the oxygen atom. Simultaneously, the hole left at the oxygen atom as a result of the O→W LMCT transfer interacts with non-bonding electrons on the amino nitrogen atom to form a charge-transfer complex [14,15]. The bleaching, which occurs in the presence of oxygen molecules, is caused by the back




Scheme 1. Schematic illustration of self-assembly procedure (top) and thermochromic mechanism (below) of multilayer films.

reaction which is triggered by an electron transfer from the $W^V$ atom to the oxygen molecules. According to the above results, the thermochromic mechanism can be speculated as Scheme 1.

In order to further demonstrate thermochromic mechanism, X-ray photoelectron spectra (XPS) of the blue $NaP_5W_{30}$/PEI multilayer films was investigated. The binding energy values of W4*f* doublet for $W^{6+}$ and $W^{5+}$ are 35.6 and 37.7 eV, 34.5 and 36.5 eV, respectively. This implies that for the heated film part of $W^{6+}$ was reduced to $W^{5+}$ during the thermochromic coloration process, which is in agreeable to ESR result.

In conclusion, this communication describes the fabrication of thermochromic multilayer films containing heteropolytungstate ($NaP_5W_{30}$) and polyelectrolyte (PEI) constructed by the electrostatic LbL self-assembly method. A charge-transfer bridge was built between $NaP_5W_{30}$ and PEI by hydrogen bonding. The films exhibit certain reversibility of thermochromism. The results indicate the thermochromic properties displayed by the system may be of practical benefit in the development of thermosensors, which would represent promising materials for future applications.

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