

A novel photochromic multilayer based on preyssler's cluster†

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A novel photochromic multilayer film containing polyoxometalates has been fabricated using layer-by-layer self-assembly.

Photochromic materials, a kind of advanced materials, have received considerable attention in some highly technological fields in view of their potential applications in information displays, chemical sensors, modified electrodes, holographic storage devices and so on.^{1–5} Some research on photochromic materials based on organic molecules has been reported. In fact, insertion of functional inorganic components into polymeric matrices opens new avenues to functional materials with photochromic properties. The fabrication of such materials may rely on the principles of molecular self-assembly and self-organization. Most likely, thin film technologies will play a major role in future applications. Although there have been some reports⁶ on photochromic composite films based on both inorganic components and polymers obtained by spin-coating, the sol-gel method and Langmuir-Blodgett (LB)⁷ technology, it is too difficult to obtain large-area films with highly ordered structures. Due to the many advantages of the electrostatic layer-by-layer (LbL)⁸ self-assembly technique, such as ease of fabrication, independence of substrate size and topology, good mechanical and chemical stability of the prepared film, the LbL assembly technique has proved to be a powerful and versatile means for assembling multicomposite supramolecular structures with good control over the layer composition and thickness.⁹

Polyoxometalates (POMs) are typical inorganic metal oxide clusters with a wealth of topologies and chemical and physical properties, used in some fields such as catalysis, medicine and materials science.¹⁰ As versatile inorganic entities for the construction of functionally active solids, POMs can accept electrons or protons to become colored mixed-valence species, which make them suitable for photochromic and electrochromic materials.^{11,12} The LbL self-assembly method provides a powerful tool for the formation and development of POM-based functional materials and devices. To date, our group has reported the construction of photoluminescent POM-based LbL multilayer films¹³ and the preparation of ultrathin films containing POMs with nonlinear optical properties.¹⁴ Furthermore, we also *in situ* synthesized POM nanoparticles in polyelectrolyte multilayers by means of this method.¹⁵ Recently, Chen *et al.*¹⁶ reported the fabrication of photochromic multilayer films based on metal oxides and organic molecules. As we know, polymers are quite versatile for producing

self-assembly thin films due to their varied structural properties and functionalities. Numerous publications further indicate that polyelectrolytes can be widely used to self-assemble multilayer films. Here, we focus on the fabrication of photochromic multilayer films by alternate adsorption of the Pressler-type heteropolytungstate $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]$ (NaP_5W_{30}) cluster and poly(ethylenimine) (PEI). The results indicate the multilayer films have good photochromic reversibility and could be used for optical data storage, especially as holographic storage media.

In this work, NaP_5W_{30} was prepared according to the literature method¹⁷ 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 film deposition by a method described in the literature.¹⁸ (The substrate was firstly placed in an 80 °C $H_2SO_4-H_2O_2$ (7:3) bath for 1 h and then in a 70 °C $H_2O-H_2O_2-NH_3$ (5:1:1) bath for 20 min, and extensively rinsed with deionized water after each cleaning step.) The substrate was then primed with PEI to introduce a 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 procedure resulted in the buildup of a multilayer film containing NaP_5W_{30} , which can be expressed as $PEI/(NaP_5W_{30}/PEI)_n$, where n is the number of bilayers. Photochromic experiments were carried out using a 500 W high-pressure mercury lamp as the light source. The distance between the lamp and the sample was 10 cm.

The growth process of the multilayer films was monitored by UV-vis absorption spectroscopy. Fig. 1 shows the UV-vis spectra of $(NaP_5W_{30}/PEI)_n$ multilayers with $n = 1-12$ deposited on a precursor PEI film. The characteristic bands of NaP_5W_{30} at 212 and 270 nm corresponding to the oxygen-to-tungsten charge transfer (CT) transition were observed in the multilayer films, which suggests that 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 results in nearly straight lines (see inset in Fig. 1). This indicates that an approximately equal amount of NaP_5W_{30} is deposited in each layer and that the $(NaP_5W_{30}/PEI)_n$ films grow uniformly with each deposition cycle, although a partial loss of NaP_5W_{30} clusters happened after each PEI deposition step.

Fourier transform infrared (FTIR) spectroscopy is an effective experimental tool widely used for the characterization and determination of structure and composition of molecular films. The FTIR spectrum recorded for NaP_5W_{30}/PEI multilayer film showed the following features: vibration bands at 911 and 780 cm^{-1} , ascribed to the vibration modes of $W=O_d$ and $W-O_e-W$, and three well-resolved bands at 1165, 1082 and 1018 cm^{-1} corresponding to $P-O_a$ stretching bands.^{19,20}

† Electronic supplementary information (ESI) available: ESR spectrum of the NaP_5W_{30}/PEI sample after irradiation. See <http://www.rsc.org/suppdata/nj/b3/b305578g/>

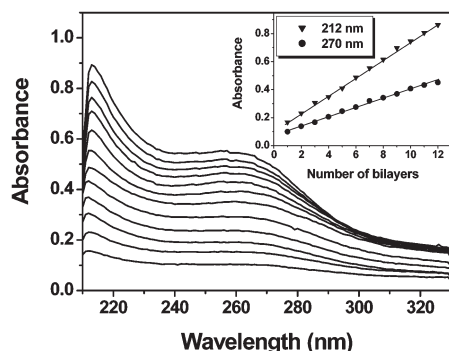


Fig. 1 UV-vis spectra of PEI/(NaP₅W₃₀/PEI)_n multilayer films with $n = 1$ –12 on quartz substrates (both sides). These curves, from bottom to top, correspond to $n = 1$ –12, respectively. The inset shows plots of the absorbance values at 212 and 270 nm as a function of the number of deposition cycles (n).

This result demonstrates that NaP₅W₃₀ clusters have been incorporated into the multilayer films and the basic structure of NaP₅W₃₀ is still preserved inside the multilayers, although the bands in the composite films associated with PEI are slightly shifted when compared to the spectrum of NaP₅W₃₀ in the KBr pellet. Furthermore, the multilayer films also exhibited absorption bands at 1450–1600 cm^{−1} (νC–C, νC–N) and at 2850–2950 cm^{−1} (νC–H) due to the PEI component. Additionally, the wave number of the N–H stretching band in PEI decreased from 3437 cm^{−1} to 3432 cm^{−1} after formation of the multilayers, which proves that a hydrogen bond is formed between NaP₅W₃₀ and PEI. In a word, the electrostatic anion-cation interactions lead to an increase or a decrease in the characteristic frequencies.

In order to obtain information involving the surface morphology and the homogeneity of the deposited films, an atomic force microscopy (AFM) image of a PEI/(NaP₅W₃₀/PEI)₃ multilayer film was obtained (shown in Fig. 2). Its surface exhibits a granular texture,²¹ which could be explained not only as a result of PEI deposition but as an indirect reflection of NaP₅W₃₀ aggregation. Particularly, it should be pointed out that the multilayers containing NaP₅W₃₀ can be considered as a very homogeneous composite material, which does not have obvious interfaces between the polyelectrolyte and inorganic components. Furthermore, the mean roughness of the surface was determined to be 0.530 nm, calculated over an area of $1.0 \times 1.0 \mu\text{m}^2$.

As shown in Fig. 3, the absorbance of the PEI/(NaP₅W₃₀/PEI)₃₀ multilayer film in the region above 600 nm increases with different UV irradiation time. It is characteristic of colored, reduced molecular species (heteropoly blues), with d-d band charge transfer intervalence transitions (W⁵⁺ → W⁶⁺) in the visible region. With irradiation time, the absorbance of the multilayer film gradually reached saturation. After

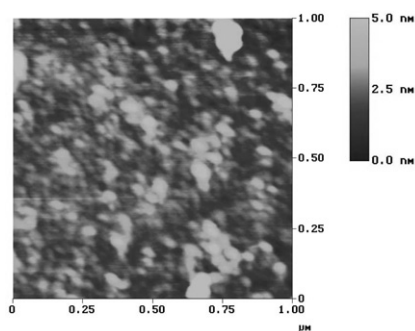


Fig. 2 AFM image of a PEI/(NaP₅W₃₀/PEI)₃ multilayer on a silicon wafer.

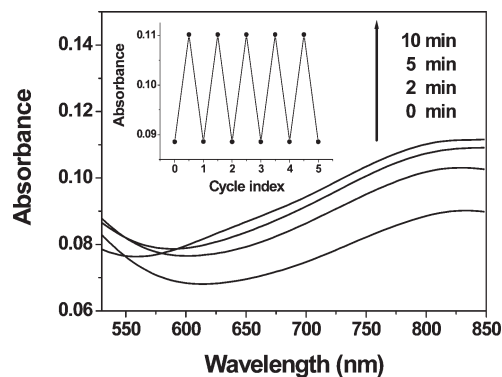


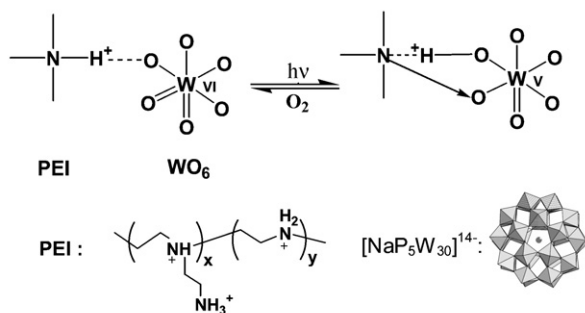
Fig. 3 UV-vis absorption spectra of PEI/(NaP₅W₃₀/PEI)₃₀ multilayer films as a function of the irradiation time. The inset shows its reversibility in the coloration-decoloration process at 800 nm.

the UV light was turned off, the blue film began to gradually discolor in air. The response speed is high and the bleaching process is nearly over after 5 min, which might be because the content of NaP₅W₃₀ and PEI are very low in the 30-bilayer film. If the bilayer number is increased to 100, the bleach speed is much lower than that of the 30-bilayer film and it needs about 30 min to reach complete decoloration. However, when storing the (NaP₅W₃₀/PEI)₃₀ films in nitrogen, it did not decolor for a long time. These results indicate that oxygen plays an important role during the bleaching process. The inset in Fig. 3 shows the good reversibility of the coloration-decoloration cycling of the multilayer films. The absorption spectra of the completely bleached films are consistent with that of the film without irradiation. That is to say, the irradiated NaP₅W₃₀/PEI multilayer films can be bleached and recover their initial state.

To explain the photochromic behavior of the system, electron spin resonance (ESR) was used to investigate the variation of the electronic structure of the component in the system during the photochromic process so as to elucidate the photochromic mechanism. The NaP₅W₃₀/PEI sample exhibited no significant ESR signals at room temperature before irradiation. But after UV irradiation, the sample exhibited a typical ESR signal for W⁵⁺ at $g = 1.868$ ($\Delta H = 46$ G) at 298 K (shown in the Electronic supplementary information). It is concluded that photoexcitation of O=W in the WO₆ ligand-to-metal charge transfer (LMCT) bands results in the transfer of a hydrogen from the nitrogen of PEI to the bridge oxygen atom at the photoreduced site in the edge-shared WO₆ octahedral lattice. This is followed by the interaction of one electron with the proton that 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.²² The bleaching that occurs in the presence of oxygen molecules is caused by the back reaction, which is triggered by an electron transfer from the W^V atom to the oxygen molecules. According to the above results and a similar conclusion put forward by Yamase,²³ the photochromic mechanism can be speculated as in Scheme 1.

In order to further demonstrate the photochromic mechanism, X-ray photoelectron spectra (XPS) of the blue NaP₅W₃₀/PEI multilayer film was investigated. The binding energy values of the W4f doublet for W⁶⁺ and W⁵⁺ are 35.2, 37.3 eV and 33.8, 36.4 eV, respectively. This implies that in the irradiated film part of the W⁶⁺ were reduced to W⁵⁺ during the photochromic coloration process, which is in agreement with the ESR result.

It is emphasized that the PEI employed in this study is especially attractive because its primary, secondary and tertiary amine groups provide various reaction sites to form



Scheme 1

charge-transfer complexes with polytungstate anions. Interestingly, a similar photochromic behavior was not found in the $\text{NaP}_5\text{W}_{30}$ /poly(allylamine hydrochloride) (PAH) multilayer films, leading to speculation that only the primary amine group in PAH cannot efficiently interact with polytungstate anions and form charge-transfer complex. The reason as to why this happens remains open. Further research on this aspect is underway.

In conclusion, this letter has described the fabrication of photochromic organic-inorganic multilayer films containing heteropolytungstate ($\text{NaP}_5\text{W}_{30}$) and polyelectrolyte (PEI) components, constructed by the electrostatic LbL self-assembly method. A charge-transfer bridge was built between $\text{NaP}_5\text{W}_{30}$ and PEI by hydrogen bonding. The films exhibit good reversibility of photochromism. The results indicate that such a thin film system might be used to fabricate a series of photochromic multilayer films by incorporating other POMs, which would represent promising materials for future applications.

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References

- 1 D. E. Katsoulis, *Chem. Rev.*, 1998, **98**, 359.
- 2 J. N. Yao, K. Hashimoto and A. Fujishima, *Nature (London)*, 1992, **355**, 624.
- 3 G. H. Brown, *Photochromism*, Wiley, New York, 1971.
- 4 J. N. Yao, P. Chen and A. Fujishima, *J. Electroanal. Chem.*, 1996, **406**, 223.
- 5 C. Bechinger, G. Definger and S. Herminghaus, *J. Appl. Phys.*, 1993, **74**, 4527.
- 6 T. R. Zhang, W. Feng, Y. Q. Fu and R. Lu, *J. Mater. Chem.*, 2002, **12**, 1453.
- 7 E. Coronado and C. Mingos, *Adv. Mater.*, 1999, **11**, 869.
- 8 G. Decher, *Science*, 1997, **277**, 1232.
- 9 X. Zhang and J. C. Shen, *Adv. Mater.*, 1999, **11**, 1139.
- 10 M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
- 11 I. Moriguchi and J. H. Fendler, *Chem. Mater.*, 1998, **10**, 2205.
- 12 S. Q. Liu, D. G. Kurth, H. Möhwald and D. Volkmer, *Adv. Mater.*, 2002, **14**, 225.
- 13 L. Xu, H. Y. Zhang, E. B. Wang and D. G. Kurth, *J. Mater. Chem.*, 2002, **12**, 654.
- 14 L. Xu, E. B. Wang, Z. Li, D. G. Kurth, X. G. Du, H. Y. Zhang and C. Qin, *New J. Chem.*, 2002, **26**, 782.
- 15 M. Jiang, E. B. Wang, Z. H. Kang and S. Y. Lian, *J. Mater. Chem.*, 2003, **13**, 647.
- 16 Z. H. Chen, Y. Ma, T. He, R. M. Xie and J. N. Yao, *New J. Chem.*, 2002, **26**, 621.
- 17 M. Filowitz, R. K. C. Ho, W. G. Klemperer and W. Shum, *Inorg. Chem.*, 1979, **18**, 93.
- 18 F. Caruso, D. G. Kurth, D. Volkmer, M. J. Koop and A. Müller, *Langmuir*, 1998, **14**, 3462.
- 19 S. Lis, *J. Alloys. Compd.*, 2000, **300–301**, 88.
- 20 M. H. Alizadeh, S. P. Harmalkar, Y. Jeannin, J. M. Frère and M. T. Pope, *J. Am. Chem. Soc.*, 1985, **107**, 2662.
- 21 S. Q. Liu, D. G. Kurth, B. Bredeneötter and D. Volkmer, *J. Am. Chem. Soc.*, 2002, **124**, 12279.
- 22 T. Yamase, *Chem. Rev.*, 1998, **98**, 307.
- 23 T. Yamase, *J. Chem. Soc., Dalton. Trans.*, 1991, 3055.