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Improving multilayer films endurance by photoinduced interaction between Dawson-type polyoxometalate and diazo resin

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Abstract

A composite multilayer film constructed of Dawson anion $[P_2Mo_{18}O_{62}]^{6-}$ and diazo resin (DR) was prepared by the electrostatic layer-by-layer (LbL) self-assembly method. The film could be stabilized by the photoinduced interaction between Dawson anion and diazo resin. IR spectra and X-ray photoelectron spectra revealed the possible occurrence of partial transformation from electrostatic interaction to covalent interaction between layers of the film after irradiation by UV light. Such transformation evidently increases the endurance of the film, which was demonstrated by AFM images and etching experiments with organic solvent. This study provides a new route to stabilze the polyoxometalate-based multilayer film by virtue of the photoinduced reaction with photosensitive polymer.

Keywords: Multilayers film; Polyoxometalate; Photoinduced interaction

1. Introduction

The fabrication of self-assembled ultrathin film has recently attracted considerable interest in view of their importance to nanomaterials with tailored structures and properties [1]. The layer-by-layer (LbL) self-assembly method, initially developed for pairs of oppositely charged polyelectrolytes [2], is a facile and versatile technique that has lately emerged as a viable approach to prepare large area ultrathin films. Because the composition, thickness, and orientation of each layer in the film can be controlled, the LbL technique provides a route to fabricate various regular structures at the molecule level, which offers potential advantages for device application. Polyoxometalates (POM), a class of molecularly defined inorganic metal-oxide cluster, hold intriguing structures and unexpected properties, and attract increasing attention worldwide [3,4]. Also, POMs have some properties related to developing functional materials, such as catalytic activity for chemical transformations [5], molecule-based conductivity [6], magnetism [7], photochromism, electrochromism, and luminescenece [8] and so on. Obviously, polyoxometalates are extremely versatile inorganic building blocks for the construction of functional materials. Several current researches have conducted to fabricate POMs-polyelectrolyte multilayer films by the layer-by-layer (LbL) self-assembly method so as to meet the requirement of device application [9,10]. Such multilayer films showing electrochromism, photoluminescence and nonlinear optical property have been reported recently [11–13], suggesting that the functional properties of POMs can be successfully incorporated into the multilayer film materials. However, the joining force between layers in the film was only electrostatic interaction, so that film's stability was insufficient and availability was limited.

It was well-known that polyoxometalate is generally an anionic cluster, in which its negative charges mostly distribute on the surface oxygen atoms of POM anion, thus photoinduced reactions can occur by activating these surface oxygen atoms [14]. In addition, a diazo resin (DR) can link POMs by electrostatic interaction between the cationic diazonium

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group ($-N_2^+$) and the anionic POMs (O^-) in order to form an LbL-ultrathin film. Since the photosensitive diazo resin could easily decompose under UV irradiation, the electrostatic interaction between $-N_2^+$ and O^- may partly transformed into covalent linkage under UV light [15]. For this consideration, we attempt to enhance the stability of multilayer films by photoinduced interaction between POMs and photosensitive polymer. Here, we report the preparation and characterization of a stable multilayer film constructed of Dawson anion $[P_2Mo_{18}O_{62}]^{6-}$ and diazo resin.

2. Experimental

2.1. Materials

$H_6P_2Mo_{18}O_{64}$ was prepared according to literature method [16]. Diazo resin (DR) was synthesized by polycondensation of diphenylamine-4-diazonium chloride with paraformaldehyde in concentrated sulfuric acid according to ref. [17] ($\eta_{sp}/C = 0.15\,dl\,g^{-1}$, $M_n = 2600\,g\,mol^{-1}$). Quartz and silicon wafers were cleaned in an 80 °C piranha solution (H_2SO_4–H_2O_2 (70:30, v/v)) for 20 min and rinsed in water. This procedure results in a hydrophilic substrate surface. Quartz wafers were used for UV–vis spectroscopy, silicon wafers for atomic force microscopy (AFM) imaging. The water used in all experiments had a resistivity higher than 17.5 MΩ cm.

2.2. Preparation of multiplayer films

The fabrication of the multiplayer film was carried out according to the following steps. The cleaned substrates (quartz, silicon, or mica) were immersed into a DR aqueous solution ($0.2\,mg\,ml^{-1}$) for 4 min, rinsed with water, and dried under a nitrogen stream. Then the DR-coated substrates were exposed to a P_2Mo_{18} aqueous solution ($2\,mg\,ml^{-1}$; pH 2–3) for 4 min, followed by rinsing and drying. One deposition cycle afford a bilayer of the film. This procedure was repeated several times to form an ultrathin multiplayer film on both sides of the substrates. The whole process was carried out in the dark.

2.3. Measurement

UV–vis spectra were measured on a 756CRT UV–vis spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector 22 FT-IR spectrometer. The CaF_2 wafers deposited with the composite films were used for IR spectra measurement. X-ray photoelectron spectra (XPS) were performed on an Escalab MKII photoeletronic spectrometer with ALK2 (1486.6 eV) as the excitation source. AFM images were taken using a Nanoscope IIIa instrument (Digital Instruments), operating in the tapping mode with silicon nitride tips. The photochemical experiment was performed using a 450 W high-pressure Hg lamp with a 365 nm filter.

3. Results and discussion

UV–vis spectroscopy was employed to monitor the layer-by-layer deposition process. Since compound of $H_6P_2Mo_{18}O_{64}$ can easily be dissolved in water (pH 1.5) to produce stable anionic cluster $[P_2Mo_{18}O_{64}]^{6-}$, it is possible to absorb $[P_2Mo_{18}O_{64}]^{6-}$ into the cationic DR layer by driving force of electrostatic attractions. The standard UV–vis spectra of $H_6P_2Mo_{18}O_{64}$ is shown in Fig. 1(a). Fig. 1(b) gives the UV–vis spectra of the multilayer film of $(P_2Mo_{18}/DR)_n$ ($n = 1$–6) deposited on quartz substrates. A broad peak at 380 nm is assigned to the absorption of the diazonium group of DR. The sharp peak at 213 nm and weak at 323 nm are a characteristic absorption of P_2Mo_{18}. But the weak peak at 323 nm is covered up by the broad peak at 380 nm. The gradual increase of the absorbance in UV–vis spectra (Fig. 1(b)) clearly indicate that full layer absorption has arisen after each deposition step. In addition, a good linear relationship between the absorbance and the number of P_2Mo_{18} /DR layers (inset plot in Fig. 1(b)) at both 380 and 213 nm shows that the layer-by-layer fabrication smoothly proceeds and the

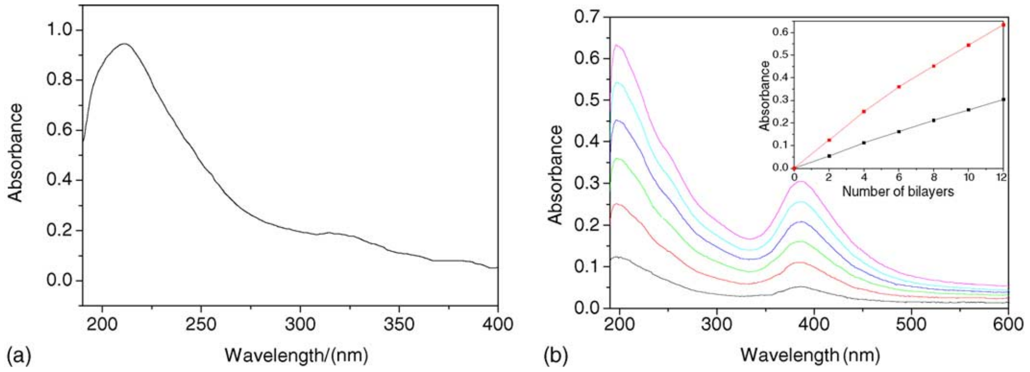


Fig. 1. (a) The UV–vis spectra of H6P2Mo18O64 in aqueous solution (1×10^{-5} M; pH 2). (b) UV–vis spectra of $(P_2Mo_{18}/DR)_n$ multilayers on quartz substrates. The number of bilayer is 2, 4, 6, 8, 10 and 12 (from bottom to top). The inset displays both the absorbance growth at 213 nm for P_2Mo_{18} and at 380 nm for DR as a function of the number of the bilayers for the $(P_2Mo_{18}/DR)_n$ multilayers.

P_2Mo_{18} anions are constantly incorporate in the multiplayer. Under UV irradiation, however, both the photodecomposition for DR and the photoreduction for P_2Mo_{18} could occur in the $(P_2Mo_{18}/DR)_n$ multiplayer films, so that the negative charge on the out oxygen atoms of P_2Mo_{18} anion increases evidently. After UV irradiation, a weak broad peak at ca. 690 nm could be observed, indicating the occurrence of the reduction for P_2Mo_{18}. According to the result of cyclic voltammetry measurement on $[P_2Mo_{18}O_{62}]^{6-}$ anion [18], it could behave in four reversible redox peaks, corresponding to two-, two-, two-, and four-electron process, respectively. Each redox step was accompanied with protonation of $[P_2Mo_{18}O_{62}]^{6-}$ anion. Taking account of the low absorption intensity at 690 nm and the insufficient proton supply in film, the extent of reduction of P_2Mo_{18} may only reach two electrons reduction, so that there were two Mo^{5+} ions in each $[P_2Mo_{18}O_{62}]^{6-}$ anion. At the same time, the cationic intermediate of DR was produced by losing a N_2 group. In view of the results of quantum chemical calculations for

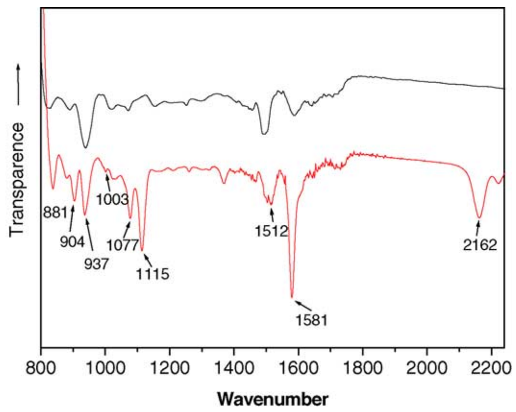
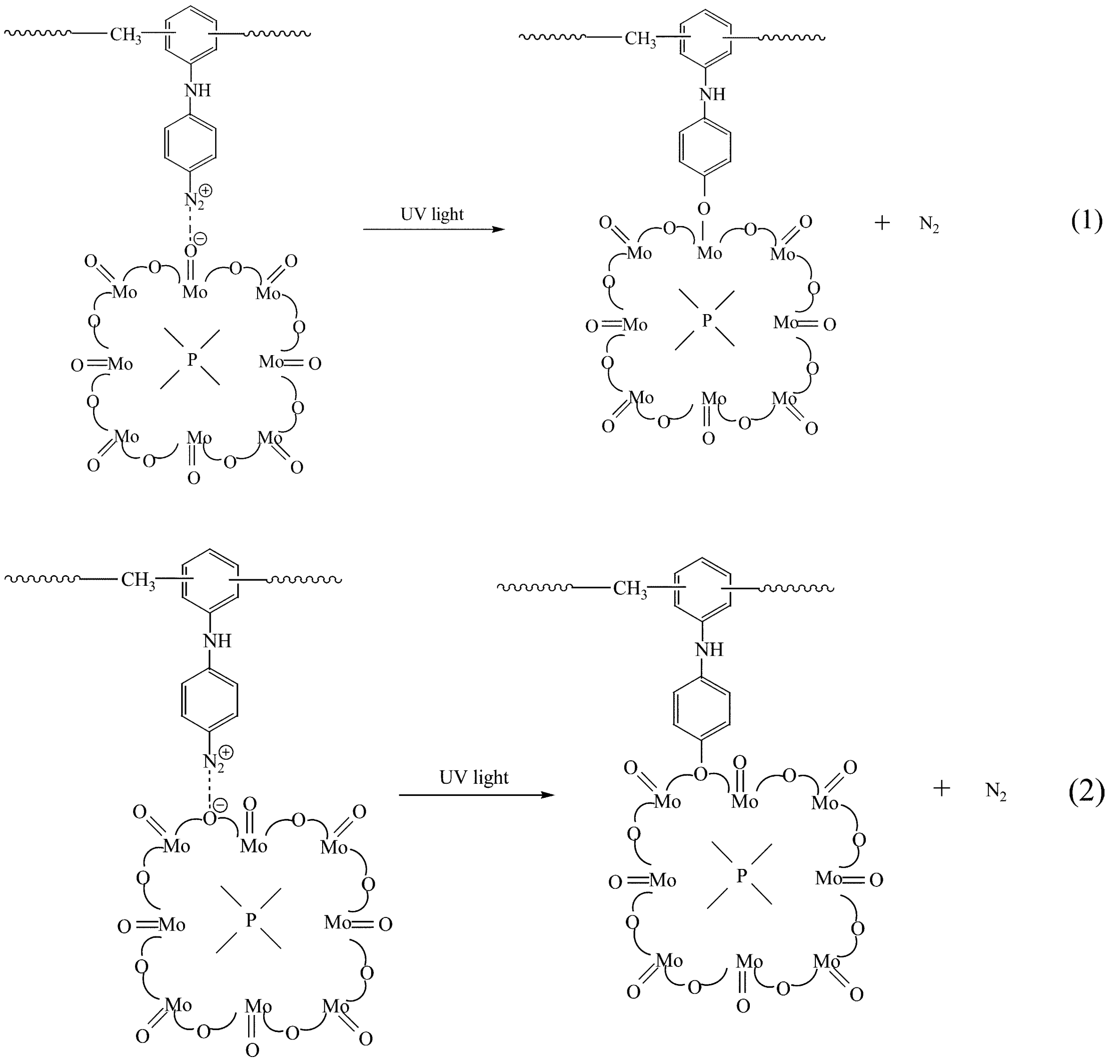


Fig. 2. IR spectra of a 40-bilayer P_2Mo_{18}/DR film fabricated on CaF_2 wafers before (bottom) and after (top) UV irradiation. Irradiation (at 365 nm), time: 20 min.



Scheme 1.

Keggin-type polyoxomolybdate anions, the bridge oxygen atoms of $[PMo_{12}O_{40}]^{3-}$ have higher negative charge density than terminal oxygen atoms of $[PMo_{12}O_{40}]^{3-}$ [19]. Noting that a strong interpolarization between cation and anion could result in a transformation from electrostatic interaction to covalent linkage [20], a possible mechanism is proposed as follows:

Before and after UV irradiation for a 40-bilayer film on CaF_2 wafers, their IR spectra could provide valuable information to reflect the photoinduced interaction between POMs and diazo resin. As shown in Fig. 2, the two peaks at 2160 and 1580 cm^{-1} are attributed to the stretching vibration of the dizanium group and the phenyl groups conjugated with the diazonium of DR, respectively. These two peaks disappear under UV irradiation, indicating that the diazonium groups in the P_2Mo_{18}/DR film decompose completely. In the 800–1200 cm^{-1}, there are five bands at 1077, 1003, 937, 904 and 881 cm^{-1}, which are respectively assigned to $\upsilon_{as}(P{-}O_a)$ 2 peaks, $\upsilon_{as}(Mo{-}O_d)$, $\upsilon_{as}(Mo{-}O_b{-}Mo)$ and $\upsilon_{as}(Mo{-}O_c{-}Mo)$ peaks. These five bands characteristically reflects the Dawson structure of the $[P_2Mo_{18}O_{64}]^{6-}$ anion [21]. Interestingly, after UV irradiation to the P_2Mo_{18}/DR film, some significant changes of IR spectra could be observed. Both a significant decrease in intensity for $\upsilon_{as}(Mo{-}O_b{-}Mo)$ and a slight red shift from 904 to 889 cm^{-1} simultaneously appear after UV irradition. Such changes suggest that the possible occurrence of partial transformation from electrostatic interaction to covalent linkage between the oxygen atom from Mo–Ob–Mo bond of P_2Mo_{18} and the carbon atom from cationic intermediate of DR, as illustrated in Scheme 1 (2). Further, $\upsilon_{as}(Mo{-}O_c{-}Mo)$ peak changed from 881 to 823 cm^{-1} after UV irradiation, suggesting that partial transformation from electrostatic interaction to covalent linkage between the oxygen atom from $(Mo{-}O_c{-}Mo)$ of P_2Mo_{18} and the carbon atom from cationic intermediate of DR has arisen, as illustrated in Scheme 1 (2).

The XPS measurements on the P_2Mo_{18}/DR ($n = 4$) films were carried out in order to identify the elemental composition of the multiplayer films. Although the XPS measurements give only a semi-quantitative elemental composition, the presence of C, N, O, P and Mo in the film could be confirmed, and the expected molar ratio of 2:18 for P to Mo could also approximately established. In the XPS measurements, O 1s peak at 532.1 cm^{-1} changed into 532.3 cm^{-1} after UV irradiation, which is attributed to the possible formation of Mo–O–C covalent bond in the P_2Mo_{18}/DR film by means of the photochemical reaction. Because the formation of Mo–O–C covalent bond could result in a little decrease of electron density on the related oxygen atom, the electron binding energy of O 1s increases to 532.3 eV. Moreover, a change for Mo 3d peak in the XPS measurement before and after UV irradiation was also observed. After UV irradiation, Mo $3d_{5/2}$ peak shifts from 235.6 to 234.8 eV, obviously resulting from the peaks overlap of both Mo^{6+} and Mo^{5+} components (Fig. 3).

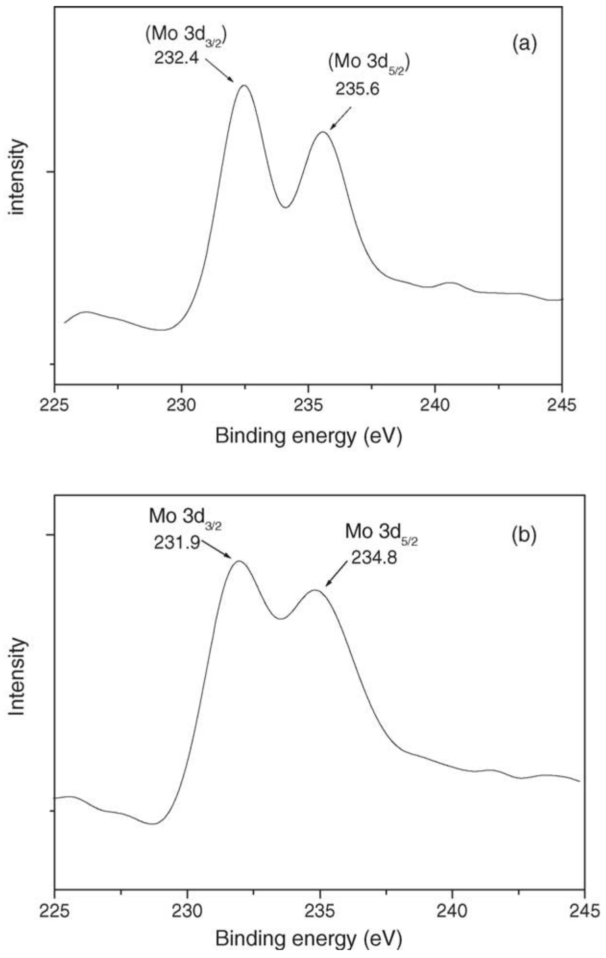


Fig. 3. Molybdenum atom peaks ($Mo3d_{3/2}$ and $Mo3d_{5/2}$) in the X-ray photoelectron spectrum for the P_2Mo_{18}/DR film: (a) before irradiation and (b) after irradiation.

AFM images of a $(P_2Mo_{18}/DR)_3$ film on a mica substrate before and after irradiation were taken to reflect the change of the surface morphology and the homogeneity of the film (Fig. 4). Before irradiation, the outer surface layer of the film is not enough uniform and smooth, with a mean roughness of 0.94 nm. After irradiation, the mean interface roughness decreased to 0.73 nm. In addition, it can be seen from Fig. 4(a) that the statistical film thickness should be ca. 10 nm, which is less than that ca. 15 nm (Fig. 4(b)) after irradiation. The increase of film thickness after irradiation suggests that the diazonium groups of DR have more outspread along the normal direction of layer plane, in order to meet the requirement of formation of partial covalent linkage between P_2Mo_{18} and DR. Thus, some small aggregates could be observed on the surface of film (Fig. 4(b)). The improved homogeneity of the film may be a result of the joint force transformation from electrostatic interaction to partial covalent linkage under the photoinduced interaction. Since the film structure changes from looseness to compactness, the uniformity and smoothness of the film surface could be improved considerably.

We made a preliminary investigation on the endurance of the irradiated film in organic solvent DMF. The UV–vis

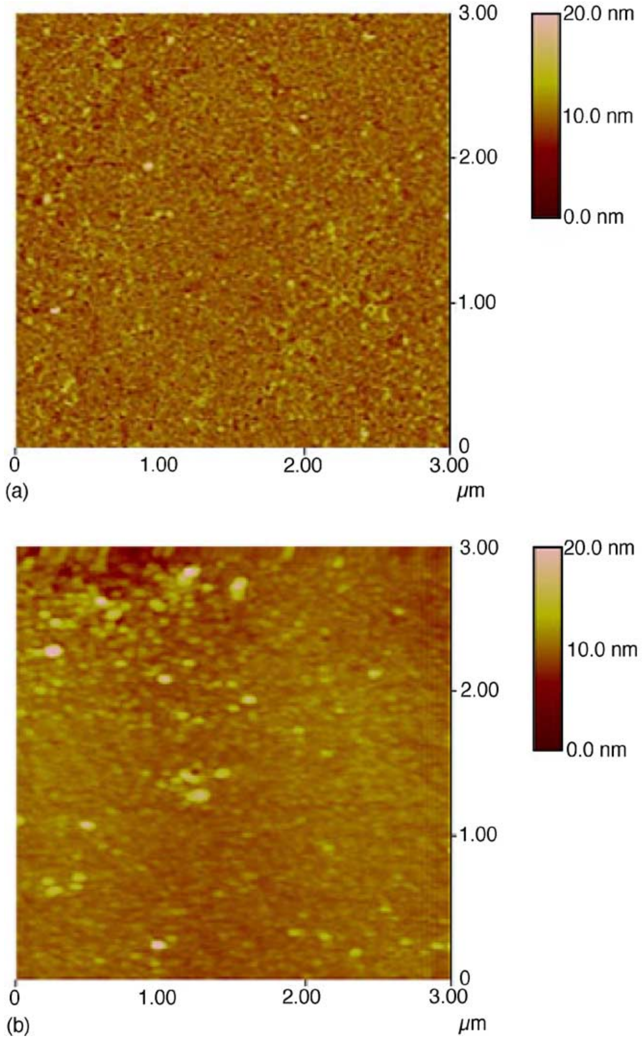


Fig. 4. Tapping mode AFM images for the $(P_2Mo_{18}/DR)_2$ film on mica substrates: (a) before irradiation and (b) after irradiation.

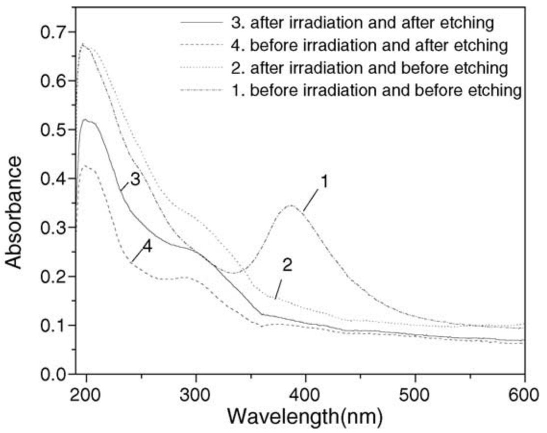


Fig. 5. UV–vis spectra of the 6-bilayer P_2Mo_{18}/DR film before and after etching in DMF for 48 h.

spectra of a 12-bilayer P_2Mo_{18}/DR film with different experimental conditions were recorded to reflect the change of the endurance of the film (Fig. 5). The absorbance drop (ΔA) for the irradiated film ($\Delta A = 0.16$) was clearly less than that for the non-irradiated film ($\Delta A = 0.24$) after the film sample was immersed in DMF for 48 h, showing the higher stability for the irradiated film. Taking account of the photoinduced interaction between P_2Mo_{18} and DR, the increased stability of the film should be ascribed to the formation of partial covalent linkage in the irradiated film.

4. Conclusion

An ultrathin multilayer film consisting of Dawson anion $[P_2Mo_{18}O_{64}]^{6-}$ and diazo resin has successfully been prepared by the electrostatic layer-by-layer self-assembly method. Some evidences to prove the partly transformed from electrostatic interaction to partial covalent linkage between layers have been obtained from IR spectra, XPS measurements, and AFM images. The increased endurance of the irradiated film, resulting from the photoinduced interaction between P_2Mo_{18} and DR, could be demonstrated by solvent etching experiments. This work provides a new route to stabilize the polyoxometalate-based multiplayer films by virtue of the photoinduced reaction with photosensitive polymer, which is of considerable signification toward the application of polyoxometalate-based film materials. In addition, further work to prepare a model compound giving the direct evidence for the formation of covalent bond has been in progress.

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