

Photo-Control of Adhesion Properties by Detachment of the Outermost Layer in Layer-by-Layer Assembled Multilayer Films of Preyssler-Type Polyoxometalate and Polyethyleneimine

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The ability to generate small-scale structures and assemble functional substances in the fields of micro electronics and optoelectronics continues to support advances in information technology. Here we present a novel type of “layer-by-layer” assembled films, whose surface properties can be controlled by UV irradiation in aqueous solution. We have designed a photochromic multilayer film of Preyssler-type polyoxometalate (NaP₅W₃₀) and polyethyleneimine (PEI) by using the layer-by-layer method. We found that the outermost PEI layer could be detached by UV irradiation in aqueous solution, and that this process could then cause inversion of the zeta potential. Furthermore, we achieved reversible-control of the surface properties first by UV irradiation, which induced the detachment of the outermost PEI layer, and by subsequent dipping into a PEI solution, which attached a new PEI layer. Finally, we successfully prepared photopatterned films with highly site-selective adsorption abilities by image-wise UV exposure.

Introduction

The ability to generate small-scale structures and to assemble functional substances in the fields of microelectronics and optoelectronics continues to support advances in information technology.¹ In order to design appropriate small-scale structures, increasing attention has been placed on the development of films whose adhesion properties can be controlled by external stimuli such as photoillumination,^{2,3} potential effects,^{4,5} surrounding media treatment,⁶ and so forth.⁷ One of the most popular and successful approaches is to apply photolithography⁸ on organic self-assembled monolayers (SAMs).⁹ By using this technique, the designed adsorption of functional particles onto profiled SAMs has

been demonstrated.^{3b,c,10} However, the conventional photolithographic technique has some disadvantages. For instance, it is expensive; it cannot be easily applied to nonplanar surfaces; it tolerates little variation in the materials that can be used; photoresist is not good for the environment; and it provides almost no control over the chemistry of the patterned surfaces.

On the other hand, the layer-by-layer (LbL) self-assembly method is a powerful and simple tool for constructing multilayered assemblies with tailored nanosize structures.^{11–14} When using the LbL method, there are fewer limitations in terms of substrates and components. In addition, many types of functional hybrid materials can be fabricated by the integration of various components such as polymers, nanoparticles, nanosheets, biorelated materials and carbon related materials.^{15–18} The LbL method also has the advantage that it offers the possibility of achieving low-cost and large-scale

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processing schemes. Today, microfabrication of LbL multilayer films is required^{19–24} and one of the most promising strategies is to control the adhesion properties by light irradiation.

To obtain LbL-assembled films whose surface properties can be controlled, we have focused on producing photochromic multilayer films consisting of a polyoxometalate²⁵ and a polyelectrolyte. Polyoxometalates consist of clusters of metal oxides and have been considered to be an attractive class of photo- and electrochromic materials.²⁶ It is known that some types of polyoxometalates show photochromic responses in polymer matrices containing protonated hydrogen.²⁷ The photochromic mechanism of these polyoxometalates can be explained by photoreduction. That is, valence electrons, which are mainly comprised of O 2p electrons in polyoxometalates, can be transferred to the conduction band of the polyoxometalates under UV irradiation. This induces reduction of the central metal atoms and results in a mixed-valency colored species known as “hetero-poly blue”. Coincident with the reduction, protonated hydrogen is transferred from the polymer to the bridge oxygen atoms at the photoreduced sites in the edge-shared WO₆ octahedral lattices of polyoxometalate.

In the present work, we have designed two types of multilayer films by using the LbL method. The first type of film, which we named Type 1, are photochromic multilayer films containing Preyssler-type polyoxometalate (NaP₅W₃₀)²⁸ and polyethyleneimine (PEI). On the other hand, the Type 2 structures are nonphotochromic multilayer films containing sandwich-type polyoxometalate (Co₄P₂W₁₈)²⁹ and PEI. As a result, we could demonstrate the detachment of the outermost PEI layers in the photochromic Type 1 films in response to UV irradiation in aqueous solution, which then resulted in the inversion of the zeta potential, whereas the Type 2 films did not show any such behavior. Moreover, we could succeed in reversibly controlling the surface properties of the Type 1 films by UV irradiation and by subsequent dipping into a PEI solution. Finally, we successfully prepared photopatterned films with highly site-selective adsorption properties.

Experimental Section

Material. NaP₅W₃₀, (NH₄)₁₄[NaP₅W₃₀O₁₁₀]·31H₂O was prepared according to the method described by Preyssler et al.²⁸ The NaP₅W₃₀ has the shape of a flattened ellipsoid with dimension 1.3 × 1.7 nm. Co₄P₂W₁₈, K₁₀P₂W₁₈Co₄(H₂O)₂O₆₈·20H₂O (volume is) was prepared according to the literature.²⁹ The Co₄P₂W₁₈ is a sandwich type polyoxometalate with ca. 1.6 nm length and 1.4 nm width. Poly(ethyleneimine) (PEI; MW 10 000, Wako) and poly-(sodium 4-styrenesulfonate) (PSS; MW 70 000, Aldrich) were used as-purchased without further purification. Fluorescent polystyrene particles were purchased from Duke Scientific Corp. (Aldehyde-modified fluorosphere (FR2040LA)).

Self-Assembly of the Multilayer Film. Glass and quartz were used as substrates for the self-assembly process. Well-cleaned glass or quartz substrates were ultrasonicated for 5 min in a mixture of 1 g of potassium hydroxide, 60 mL of ethanol, and 40 mL of water. After this procedure, the substrates were rendered completely hydrophilic, and negative charges were induced. For the precoating process, the substrates were alternately immersed in aqueous solutions of PEI (10 mM) and PSS (1 mM) for 20 and 10 min each. After each deposition, the substrates were rinsed 3 times in water for 1 min each.

After the precoating procedure, self-assembly films were fabricated using the following steps under these conditions: (1) immersion of substrate into a 10 mM branched PEI solution maintained at pH 5 (concomitant salt is 0.5 M NaCl) for 20 min; (2) rinse 3 times in water for 1 min each; (3) immersion in 0.5 mM NaP₅W₃₀ (for Type 1 films) or Co₄P₂W₁₈ (for Type 2 films) solutions for 20 min; (4) rinse 3 times in water for 1 min each. The portion of protonated nitrogen in PEI at pH 5 is about 50%.³⁰ Subsequently, steps (1–4) were repeated *n* times to produce ultrathin films containing *n* alternating layers of PEI and *n* layers of NaP₅W₃₀ or Co₄P₂W₁₈, which were defined as (PEI/NaP₅W₃₀)_{*n*}, or (PEI/Co₄P₂W₁₈)_{*n*}.

Photoirradiation. UV irradiation was carried out using an ultrahigh pressure mercury lamp (HYPERCURE 2000, Yamashita Denso, Japan). The films were irradiated at a distance of 15 cm without the use of focusing optics. The UV-exposed substrates were rinsed with deionized water and dried in Ar gas.

Image-wise UV irradiation was performed using a copper transmission electron microscopy (TEM) grid as a photomask. The grid was placed on the substrate in water, and was irradiated from a distance of 15 cm. Rinsing and drying steps were performed in the same manner as those used for the process without the photomask.

Instruments. FT-IR absorption spectra were recorded on an FT-IR 660 Plus spectrometer (JASCO, Japan). UV–vis spectra were recorded on a V-560 spectrometer (JASCO). The XPS spectra were obtained on an ESCA Model 1600 C-type spectrometer (ULVAC-PHI, Inc., Japan) using the Al K α line-source at 1486.6 eV. The binding energy scales were referenced to 284.0 eV, as determined by the location of the maximum peak in the C1s spectrum of PEI. The ζ potential measurements of the films were undertaken as the previous report said^{3a} using an Otsuka Electronics ELS-8000 electrophoretic light scattering technique. HPC-coated (hydroxyl-propyl-cellulose-coated) polystyrene particles of 520 nm in diameter were purchased from Otsuka Electronics and were used as standard probing particles to determine the ζ potentials of the substrates. The commercially available HPC-coated particles were dispersed in water and were diluted to about 500 times by adding a 10 mM aqueous solution of NaCl. QCM measurements were performed on an HC49/U type apparatus (Crystal Sunlife, Japan).

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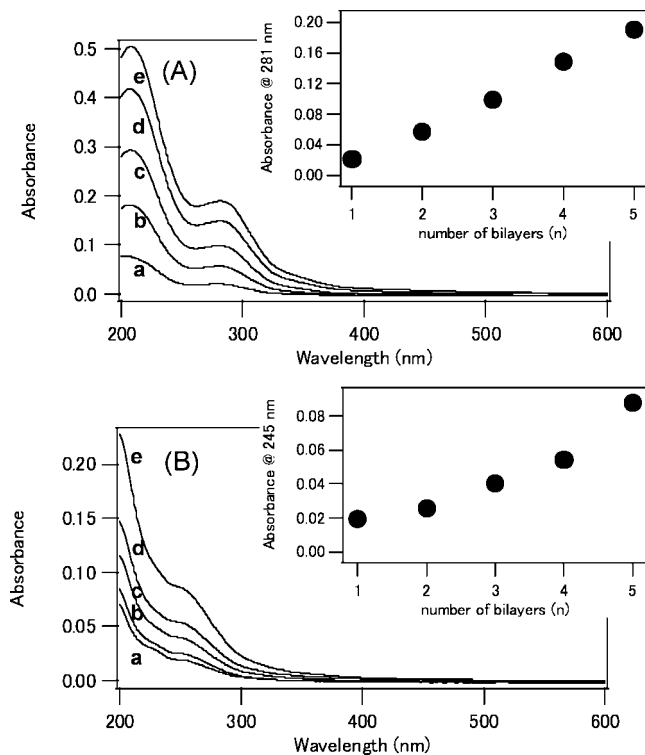


Figure 1. UV-vis absorption spectra of Type 1 films, (PEI/NaP₅W₃₀)_n (A) and Type 2 films, (PEI/Co₄P₂W₁₈)_n (B) [(a) $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 4$, (e) $n = 5$]. The insets show plots of the absorbance of the LMCT band containing the polyoxometalates against n .

Results and Discussion

Characterization of PEI/Polyoxometalate Multilayer Films. The fabrication processes for Type 1 films (NaP₅W₃₀/PEI)_n and Type 2 films (Co₄P₂W₁₈/PEI)_n were monitored by UV-vis spectroscopy and ζ potential measurements. Figure 1 shows the UV-vis spectra of (NaP₅W₃₀/PEI)_n (Type 1) and (Co₄P₂W₁₈/PEI)_n (Type 2) multilayer films with $n = 1-5$ on precursor PEI/PSS films deposited on quartz substrates. Absorption peaks were observed at 281 nm for the Type 1 films and at 245 nm for the Type 2 films, which were due to the characteristic absorptions of the ligand-to-metal charge transfer (LMCT) bands of each of the polyoxometalates. The insets in Figure 1 present plots of the absorbance values of the respective LMCT bands for these multilayer films as a function of the number of deposition cycles. The stepwise increase of the plots suggests gradual incorporation of the polyoxometalates into the multilayer films.

During the layer deposition process, the ζ potentials of the multilayers were also monitored (Figure 2). In both multilayer films, the ζ potentials were highly positive after dipping into PEI solution, whereas they were highly negative after dipping into the polyoxometalate solutions. This switching behavior in terms of the ζ potential suggests alternating changes in the surfaces of the multilayer films because of the differing molecular attachments. It is worth noting that only the outermost layer and not the underlying component determines the ζ potential. In addition, the occurrence of strong charge over-compensation is the principal reason for the existence of multilayers.¹⁴ Therefore, the above results are also consistent with the proper fabrication of multilayer films and suggested a certain stratification structure.^{35d}

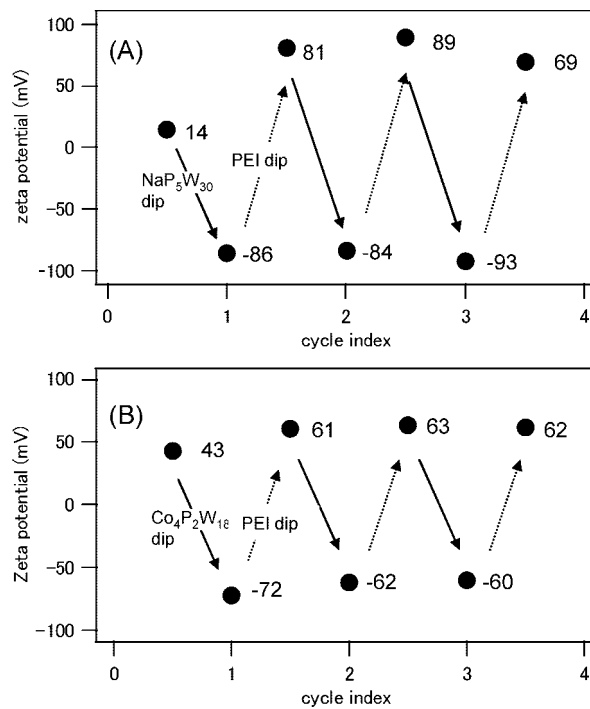


Figure 2. Changes in the ζ potential by alternate dipping in PEI and NaP₅W₃₀ solutions (A, Type 1) and Co₄P₂W₁₈ solutions (B, Type 2)

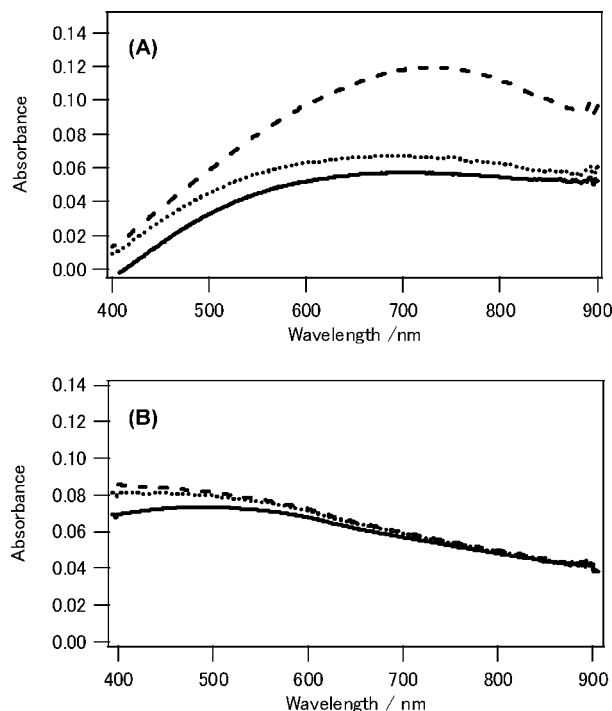


Figure 3. Changes in the UV-vis adsorption spectra of a 40 bilayer Type 1 film (PEI/NaP₅W₃₀)₄₀ (A) and a Type 2 film (PEI/Co₄P₂W₁₈)₄₀ (B) upon UV irradiation. In (A), the initial trans state (solid line) was first irradiated with UV for 10 min (dashed line). It was then bleached in air for 30 min (dotted line). In (B), the initial trans state (solid line) was irradiated with UV for 1 h (dashed line) and for 3 h (dotted line).

Photochromism of the Multilayer Films. First, we investigated the photochromic responses of 40 bilayer Type 1 films (Figure 3A). The absorbance at around 750 nm increased after UV irradiation (Figure 3A, dashed line). This is the characteristic intervalence charge transfer band of the polyoxometalate known as “Hetero poly blue”, and which

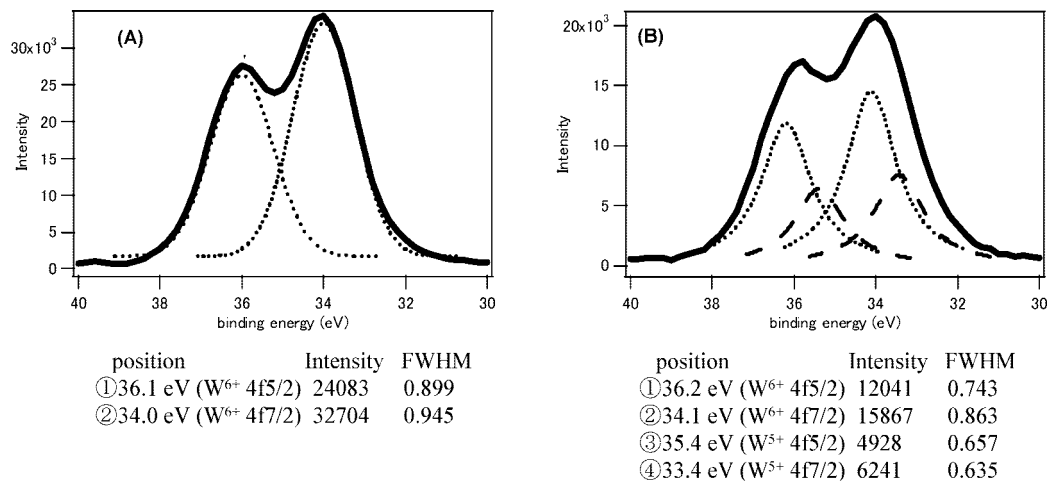
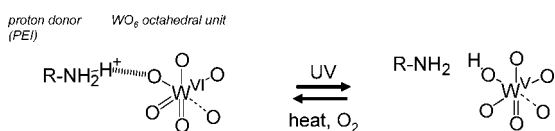


Figure 4. XPS spectra of the W 4f level of (PEI/NaP₅W₃₀)₃/PEI before (A) and upon UV irradiation (B). The tables show the deconvoluted results of the spectra.

Scheme 1



is attributed to the photoreduction of W⁶⁺ → W⁵⁺ in NaP₅W₃₀.^{26,27} XPS analyses of Type 1 films clearly support these changes in the electronic state of NaP₅W₃₀ upon UV irradiation (Figure 4). In the Type 1 films, only the W⁶⁺ species was observed before UV irradiation (Figure 4A). Upon UV irradiation, the W⁵⁺ species was then observed to rise in content up to 30% (Figure 4B, calculated by deconvolution of the spectra). This observation and the results of previous reports suggest that the photochromic reaction mechanism in this case is as follows (Scheme 1).²⁶ Photoexcitation of the LMCT band of O=W in WO₆ results in the transfer of a hydrogen atom from the nitrogen of the 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 that is left behind at the oxygen atom as a result of the LMCT transfer interacts with the nonbonding electrons on the amino nitrogen atom to form a charge-transfer complex.

After the UV light was turned off, the blue films began to discolor, gradually becoming transparent. The peak at around 750 nm also recovered to its initial state after 30 min (Figure 3A, dotted line). The reversibility of the coloration-discoloration could be repeated at least 3 times without almost any loss of color. This excellent photochromism is a characteristic of LbL film using the Preyessler type polyoxometalate.²⁷ It is noted that the coloration-discoloration was also observed in aqueous solution.

On the other hand, these photochromic responses were not observed for Type 2 films (Figure 3B). This behavior is predicated by the unsuitable reduction potential of Co₄P₂W₁₈ for the photochromic changes.³¹

Detachment of the Outermost PEI Layer by UV Irradiation in Aqueous Solution. The photoresponses of the ζ potentials for Type 1 films were monitored. For films in which the outermost layer was a NaP₅W₃₀ layer (i.e., (PEI/NaP₅W₃₀)₃), almost no changes in ζ potential were observed by UV irradiation (Figure 5A). On the other hand, for films in which the outermost layer was PEI (i.e., (PEI/NaP₅W₃₀)₃/PEI), the ζ potentials were gradually reduced as the UV exposure time was increased (Figure 5B). After 15 min of UV irradiation, the ζ potentials changed from +69 mV to -71 mV. Further UV irradiation did not decrease the zeta potential any further, which indicates that the changes had saturated. It is noted that this film was so stable in aqueous solution that these changes could not be observed after a few days of immersion into aqueous solution without UV irradiation.

XPS measurements were performed in order to study the changes that occur in Type 1 films before and after UV irradiation. For films in which the outermost layer consisted of NaP₅W₃₀ (i.e., (PEI/NaP₅W₃₀)₃), two intensity peaks corresponding to W 4f 5/2 and W 4f 7/2 were observed at 36.3 and 34.4 eV, respectively (Figure 6A). On the other hand, for films in which the outermost layer was PEI (i.e., (PEI/NaP₅W₃₀)₃/PEI), negative shifts in the peaks at 36.0 and 34.0 eV were observed (Figure 6B). This negative shift is caused by a core-level shift due to the adsorption of PEI.³² Next, for those (PEI/NaP₅W₃₀)₃/PEI films in which the ζ potentials were changed from +69 mV to -71 mV after 15 min UV irradiation in aqueous solution, intensity peaks were observed at 36.5 and 34.5 eV. The observed spectrum was almost the same as that of the film in which the outermost layer consisted of NaP₅W₃₀ (Figure 6C). This suggested that, after UV irradiation of the (PEI/NaP₅W₃₀)₃/PEI film, its surface was changed a condition similar to the NaP₅W₃₀ surface. This is consistent with the observed inversion of the ζ potential.

QCM measurements were then applied in order to investigate the effect of UV irradiation on Type 1 films. We can estimate the mass of a multilayer film on a substrate

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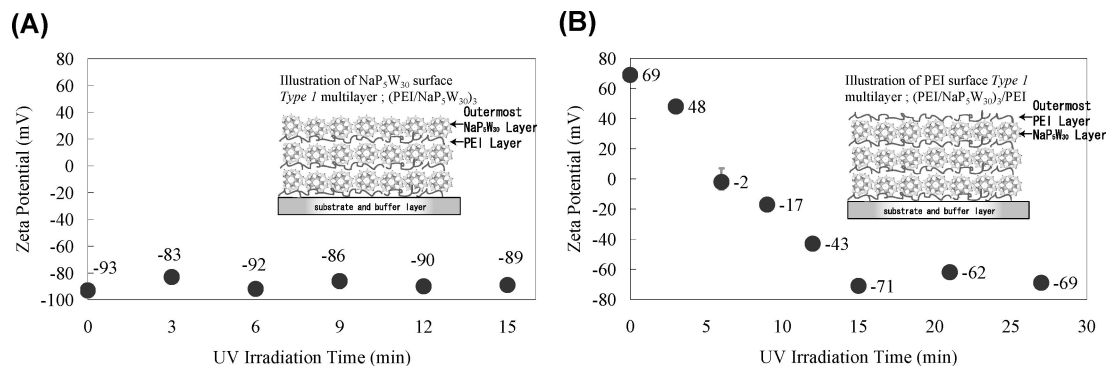


Figure 5. Changes in ζ potential upon UV irradiation of a (PEI/NaP₅W₃₀)₃ multilayer film (A), and of a (PEI/NaP₅W₃₀)₃/PEI multilayer film (B).

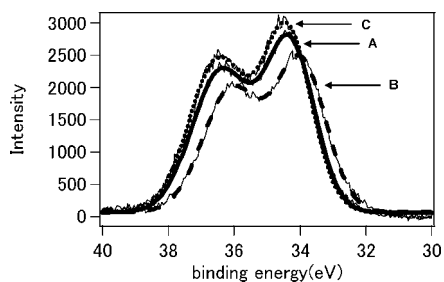


Figure 6. XPS analysis of W 4f edges in some Type 1 films for (A, solid line) (PEI/NaP₅W₃₀)₃, (B, dashed line) (PEI/NaP₅W₃₀)₃/PEI before irradiation, and (C, dotted line) (PEI/NaP₅W₃₀)₃/PEI after UV irradiation for 15 min in aqueous solution.

from the QCM frequency-shift by using the Sauerbrey equation.³³ The relationship between the frequency shift (ΔF) and the adsorbed mass (Δm) is given as follows

$$\Delta F = - \frac{2F_0^2}{A\sqrt{\mu\rho}} \Delta m \quad (1)$$

where F_0 is the frequency of the sensor (10 MHz in this case), A is the area of the electrode, μ is the shear stress of the quartz ($2.947 \times 10^{10} \text{ kg m}^{-1} \text{ s}^{-2}$), and ρ is the specific gravity of the quartz (2648 kg m^{-3}).

In the fabrication processes used to create Type 1 films, frequency decreases of $73 \pm 17 \text{ Hz}$ were observed because of the adsorption of one layer of PEI, which corresponded to a weight increase of $3.4 \pm 0.7 \text{ ng/mm}^2$ per one layer. On the other hand, the adsorption of NaP₅W₃₀ caused a frequency decrease of $146 \pm 10 \text{ Hz}$, which corresponded to a weight increase of $6.4 \pm 0.4 \text{ ng/mm}^2$ per one layer of NaP₅W₃₀. Here, the packing density of NaP₅W₃₀ in the films was estimated to be $0.47 \pm 0.2 \text{ cluster/nm}^2$ from the increase in weight. It should be noted that this packing density is almost the same as that of crystal packing.^{28b,34} High packing densities are often observed in LbL assembled multilayer films of small polyoxometalates because repulsive electrostatic and dipolar interactions are compensated as efficiently in a two-dimensional film as in the solid state.³⁵

Next, photoinduced changes in frequency were investigated. After 15 min of UV irradiation was applied to a Type 1 film in which the outermost layer was PEI (i.e., (PEI/

NaP₅W₃₀)₃/PEI)), the frequency increased by $58 \pm 14 \text{ Hz}$. This frequency change is nearly equivalent to the disappearance of one PEI layer.

To sum up the results from the XPS and QCM measurements, we concluded that the overall behavior was as follows. The outermost PEI layer was detached in response to UV irradiation and the first underlying NaP₅W₃₀ layer was exposed. As a result, the ζ potential was inverted. Figure 7 shows a schematic illustration of the mechanism proposed above.

On the other hand, for nonphotochromic Type 2 films, no changes in the ζ potential or in the frequencies under UV irradiation were observed during the QCM measurements, regardless of the outermost layer. These results suggest that the photochromic process plays an important role in the detachment of the outermost PEI layer that was observed for the Type 1 films.

In the case of Type 1 films, photochromic reactions occurred as shown in Scheme 1. As a result, protonated hydrogen transferred from the nitrogen of the PEI to the bridge oxygen atom at the photoreduced site in the edge-shared WO₆ octahedral lattice.²⁶ This transfer of protonated hydrogen then broke electrostatic bonds, generated new hydrogen bonds, and weakened the ionic strength of the PEI layer, because the ionic strength of PEI is determined by the degree of protonation.³⁰ Hence, the interface electrostatic interaction between the PEI layer and the NaP₅W₃₀ layer became weaker and therefore the outermost PEI layer detached. This behavior is consistent with statements in previous reports concerning the relationship between the ionic strength and the stability of multilayer films. For instance, Böhmer et al. reported changes that could be induced by adjusting the degree of protonation of the polymer.¹⁴ According to their report, when the polymer has a higher charge, then multilayer films become more stable, whereas when the polymer charge is lower, the electrostatic interaction is so weak that multilayer films become unstable or can not form poly ion complexes. In addition, it has also been reported that LbL assembled multilayers can be

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(34) In the crystal structure of (NH₄)₁₄[NaP₅W₃₀O₁₁₀]·31H₂O, the space per one cluster is 2.90 nm²/cluster in the [100] plane, 2.05 nm²/cluster in the [010] plane, and 2.09 nm²/cluster in the [001] plane.

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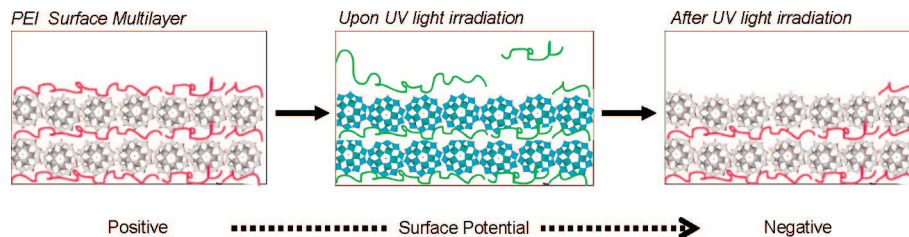


Figure 7. Schematic illustration of the photodetachment of a Type 1 film, $(\text{PEI}/\text{NaP}_5\text{W}_{30})_n/\text{PEI}$.

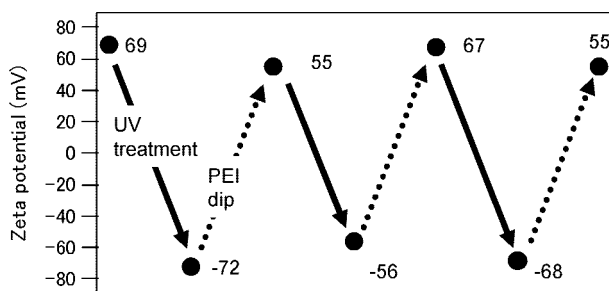


Figure 8. ζ potential switching in Type 1 films. A Type 1 film $(\text{PEI}/\text{NaP}_5\text{W}_{30})_3/\text{PEI}$ was alternately irradiated with UV for 15 min in aqueous solution and dipped in a PEI solution for 20 min.

decomposed by dipping the films into solutions of different pH and salt concentrations.^{36,37} Exposure to high-concentration salt solutions eliminates electrostatic interactions in the multilayer films and causes them to dissolve because the driving forces for dissociation are probably entropic in nature. Especially the outermost polyelectrolyte layer is actually always in equilibrium in aqueous solution,³⁸ it might be easier for the outermost PEI layer to detach in our study. Then, the reason why the outermost PEI is detached preferentially is discussed as follows. One possible explanation is that the $\text{NaP}_5\text{W}_{30}$ layer could be regarded as a bulk state because of the high packing density in the layer. In addition, although electrostatic bonds at the interface between

the PEI and $\text{NaP}_5\text{W}_{30}$ layers disappeared when the film exhibited photochromism, hydrogen bonding between nitrogen of PEI and transferred hydrogen generated instead of the electrostatic bonding,²⁶ hence the film could be still stable to some extent. Actually, we could not observe any changes in the film structure when it had exhibited photochromism in air. Therefore, it is reasonable to assume that the interaction between the PEI and $\text{NaP}_5\text{W}_{30}$ layers is weakened by the photochromic process, which makes the multilayer unstable and therefore the outermost layer of the PEI can be detached.

Switching in ζ Potential Plots in Type 1 Films. As stated above, we are able to fabricate LbL films whose outermost PEI layers can be controlled by UV irradiation. Taking this system into account, we then aimed at achieving reversible control of the ζ potentials of these films. Our strategy is to alternate between UV irradiation, which induces detachment of the outermost PEI layer, and dipping into a PEI solution, which induces adsorption in the outermost PEI layer. We then monitored the changes by carrying out measurements of the ζ potential (Figure 8). After the detachment of the outermost PEI layer on the Type 1 films by UV irradiation, the films were dipped into the PEI solution again. By this process, the decrease in the ζ potential (-72 mV) could be recovered to $+55$ mV, which is the same as the initial value before the detachment of the PEI layer. Subsequently, these

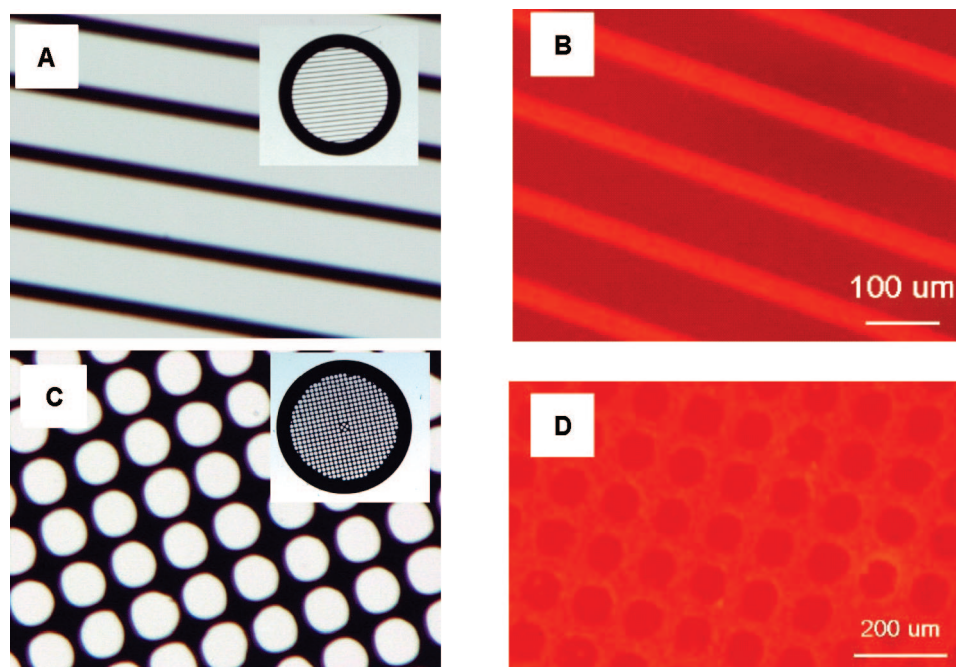


Figure 9. Optical microscope images of photomask (A, C) and fluorescence microscope images of fluorescent particles (B, D) assembled on a substrate on a photopatterned PEI surface Type 1 film, $(\text{PEI}/\text{NaP}_5\text{W}_{30})_3/\text{PEI}$. The inset images in A and C show overall images of the photomask (both of 3 mm diameter).

alternating steps were repeated at least three times. The surface changes were also confirmed by XPS spectra and QCM measurements (not shown). That is, reversible control of the surface properties by UV irradiation and dipping into PEI solution was shown to be possible for Type 1 films.

Adhesive Control of Latex Particles on Photopatterned Type 1 Films. One of the most important applications of the control of surface properties by photoirradiation is the site-selective adsorption of small particles of material.^{10b} Here we have demonstrated the photoinduced site-selective adsorption of fluorescent particles. We prepared films in which the outermost layer was photopatterned by image-wise UV irradiation. The films were of Type 1, in which the outermost layer of PEI was exposed to UV light through a photomask consisting of a copper TEM grid (Figure 9A and 9C). Then, commercially available fluorescent polystyrene particles, which were around 320 nm in diameter and exhibited negative ζ potentials (-38 mV in 10 mM NaCl solution), were used for easy detection of site-selective adsorption on the patterned substrates. The photopatterned multilayers were immersed in a suspension of the fluorescent particles for 20 min, rinsed thoroughly with deionized water, and then dried. Typical fluorescence microscope images of these multilayer films containing absorbed fluorescent particles are shown in images B and D

in Figure 9. It is reasonable that fluorescent particles exhibiting negative charges are adsorbed preferentially onto UV-unexposed areas in which the photodetachable cationic outermost PEI layer is present. Images B and D in Figure 9 show the site-selective adsorption of red fluorescent particles. This high site-selectivity is due to the dramatic ζ potential differences between the UV-exposed and non UV-exposed areas.^{3a,b}

Conclusions

We have designed photochromic multilayer films of $\text{NaP}_5\text{W}_{30}$ and PEI by the LbL method. Subsequently, we have succeeded in controlling the surface properties of the multilayer films by the detachment of the outermost PEI layer by UV irradiation in water. Our results demonstrated that the photochromic process plays an important role in this behavior because the transfer of protonated hydrogen from the PEI to the $\text{NaP}_5\text{W}_{30}$ in the photochromic process should weaken the interfacial interactions of $\text{NaP}_5\text{W}_{30}$ and PEI. Furthermore, we succeed in reversibly controlling the surfaces of the multilayers by UV irradiation and by dipping into a PEI solution. Finally, we successfully prepared a photopatterned multilayer by image-wise UV exposure with highly site-selective adsorption ability.

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