

Modification of photochromic inorganic/organic superlattice films by organic molecules

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A layered superlattice, WO_3 -polymer/1,10-decanediamine (1,10-DDA) self-assembled multilayer film, has been fabricated by means of alternating adsorption of tungstic acid and 1,10-DDA. The growth process, structure, and photochromic properties of the self-assembled multilayer film have been investigated and compared with those of the previously reported WO_3 /4,4'-bis(aminomethyl)biphenyl (4,4'-BAMBp) system. It was found that the exciting improved photochromic properties of WO_3 -polymer/1,10-DDA films result from the polymerization of WO_3 molecules in the inorganic layers. The results clearly show that the organic molecules can efficiently manipulate the microstructure of the inorganic layer as well as the photochromic properties of the self-assembled multilayer films.

Photochromic materials have received considerable attention because of their potential applications in a number of high technology fields.^{1–7} Transition metal oxides, the most extensively investigated inorganic photochromic materials, have been prepared by various physical and chemical deposition methods.⁸ However, these methods are generally expensive, complicated, and it is difficult to form large-area films with well-ordered structures. Most of all, these classic inorganic photochromic materials usually present some defects, such as low response speed and fatigue, which are very difficult to eliminate and this limits the application of these materials. It is necessary and challenging to explore a novel strategy for constructing dense, stable and highly ordered films composed of transition metal compounds with good photochromic properties. A self-assembly method based on the electrostatic interaction between oppositely charged species, as developed by Decher *et al.*,^{9–11} has been extended to many inorganic components^{12–18} and offers a powerful tool for the design of novel materials. In our previous work,¹⁹ the self-assembly technique has been confirmed to be an efficient method to construct novel photochromic materials. We have successfully fabricated self-assembly multilayer (SAM) films of WO_3 /4,4'-bis(aminomethyl)biphenyl (4,4'-BAMBp) with fine superlattice structure and photochromic properties using the alternating adsorption method. Here we report a simple and convenient method for the tailoring of photochromic properties of the WO_3 composite films by changing organic components. The photochromic response of layered nano-composite SAM film has been improved greatly when the organic molecules were changed from 4,4'-BAMBp to 1,10-decanediamine (1,10-DDA).

Results and discussion

Deposition process and the structure

The deposition process of the WO_3 /1,10-DDA SAM film was monitored by means of UV-visible absorption spectroscopy using a quartz slide as substrate. Fig. 1 shows UV-visible spectra of the SAM films with WO_3 as the outermost layers. The absorption peak at 196 nm can be assigned to an electronic transition from the valence band to the conduction band of WO_3 , while the absorption band around 263 nm corresponds to the characteristic absorption of polyoxometalate anion,^{20,21} suggesting that WO_3 has been polymerized in the inorganic

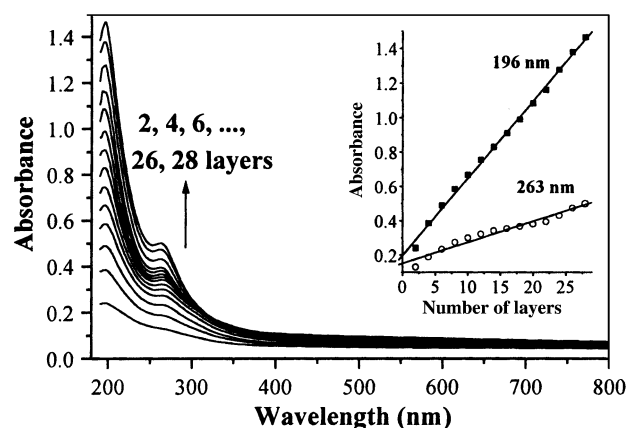


Fig. 1 UV-visible spectra of WO_3 -polymer/1,10-DDA SAM films fabricated on silanized quartz slides with increase in number of outermost WO_3 layers from 2 to 28 (from bottom to top). The insert shows the dependence of the optical absorbance of these films on the number of layers at different wavelengths.

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layer. The illustration inserted in Fig. 1 clearly shows a nearly linear relationship between the absorbance of the multilayers at different wavelengths (196 and 263 nm) *vs.* the number of layers, which indicates a nearly uniform growth and one vertical periodic structure of the organic-inorganic alternating films. The small deviation of the absorbance increase at 263 nm suggests the self-repairing ability of the self-assembly method.

The surface coverage, Γ , of WO_3 on the organic surface in the WO_3 -polymer/1,10-DDA SAM film (**A**) can be calculated using $\Gamma = [(A_\lambda/2) \varepsilon_\lambda^{-1} N_A] \times 10^{-3}$, where A_λ is the absorbance of WO_3 in the film at a given wavelength (λ), ε_λ is the extinction coefficient of WO_3 in solution ($\text{M}^{-1} \text{cm}^{-1}$) at λ , and N_A is Avogadro's number.^{22,23} Using the absorbance values around 195 nm (where absorbance is largest) and the corresponding extinction coefficients calculated from the solution absorption spectrum of a standard concentration of tungstic acid, the apparent surface coverage of WO_3 immobilized in each bilayer of film **A** is about $3.2 \times 10^{-9} \text{ mol/cm}^2$, while for $\text{WO}_3/4,4'$ -BAMBP SAM (**B**) film it is $1.1 \times 10^{-9} \text{ mol cm}^{-2}$. Thus, the apparent surface coverage of the SAM film **A** in each bilayer is about three times that of film **B**. The average area per WO_3 molecule in **B** is 0.15 nm^2 , corresponding to a diameter of about 0.44 nm, which agrees well with the size of a WO_6 octahedron.²⁴ This suggests that WO_3 molecules in every bilayer of the **B** film form a nearly uniform monolayer with edge and/or corner sharing, due to possible repulsion among the negatively charged WO_3 molecules. Meanwhile for the **A** system, WO_3 must have been polymerized in the inorganic layers so that its apparent surface coverage is three times that of the **B** system. This agrees well with the characteristic band of polyoxometalate around 263 nm in the absorption spectra of the **A** system (Fig. 1).

In addition, the UV-visible spectra of the **A** and **B** films do not show any distinctive absorption in the visible region due to an intervalence charge-transfer transition, implying that all tungsten atoms of WO_3 in the SAM films are in the oxidation state of +6, which is in agreement with the XPS results (35.8 and 38.2 eV for $\text{W}^{6+} 4f_{7/2}$ and $\text{W}^{6+} 4f_{5/2}$, respectively).⁸

The evidence for the periodic multilayer structure of film **A** can be confirmed by the small angle X-ray diffraction study of a 28-layer WO_3 -polymer/1,10-DDA SAM film prepared on a single crystal silicon substrate (see the insert of Fig. 2). The diffraction peaks are identified as the first (001, $2\theta = 3.05^\circ$) and the second (002, $2\theta = 6.12^\circ$) level diffraction peaks of the multilayered structure. The d space calculated from Bragg's equation is 2.897 nm. At the same time, the measured thickness of this SAM film from a surface profile measuring system was 80.0 nm and therefore the thickness of each bilayer was about 2.9 nm. This value agrees well with the 2.897 nm d space calculated from the XRD pattern. For the $\text{WO}_3/4,4'$ -BAMBP system, each bilayer was only 0.68 nm thick.

The lamellar order in multilayers of film **A** with different numbers of layers was also investigated by X-ray reflectivity (Fig. 2). The number of layers (WO_3 as the outmost layers) from bottom to top is 0, 2, 4, 6, 8, 16, and 28, respectively. In these X-ray reflectivity profiles, there are different numbers of oscillations originating from X-ray scattering from the top and bottom interfaces of the SAM films, implying uniform electron density throughout these films with low roughness. The number of oscillations is nearly proportional to the number of inorganic layers, suggesting a vertical periodical structure of these organic-inorganic alternating films. The analysis of these reflectivity profiles²⁵ leads to a thickness of 22.0, 30.3, 43.5 and 78.7 nm for 8, 12, 16 and 28 layers of SAM film **A**, respectively, which agree well with the above results from XRD and thickness measurement. In addition, Bragg scattering around 1.55° and 2.45° in some profiles ($n = 12, 16, 28$) also corresponds to a layer spacing (d) of 2.85 nm. These results demonstrate the finite superlattice structure of multilayer films and provide the direct evidence of a distinct and reproducible unit.

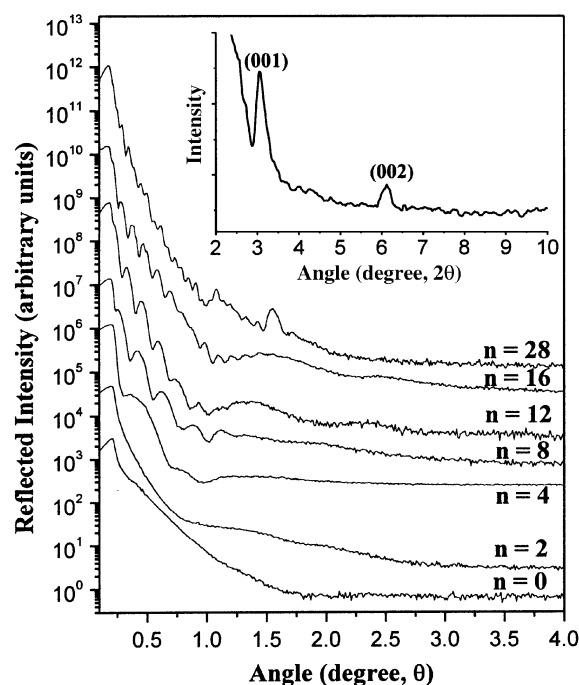
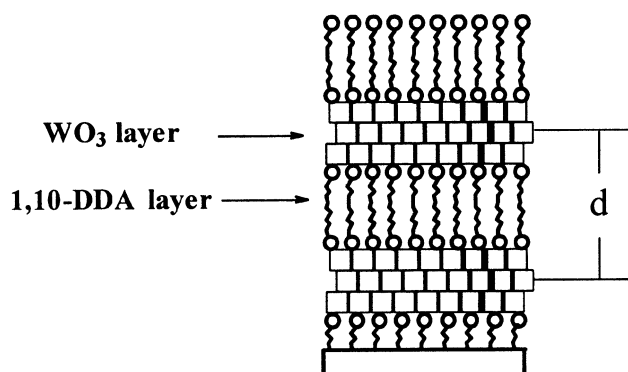


Fig. 2 Low angle X-ray reflectivity of a SAM film composed of alternating layers of WO_3 and 1,10-DDA. The insert gives the X-ray diffraction pattern of a 28-layer WO_3 -polymer/1,10-DDA SAM film.

XPS measurements were performed to identify the composition of the SAM films. From the XPS results of SAM films **A** fabricated on a single-crystal silicon substrate, the ratio of the elements O:C:N:W in the SAM film was determined to be 33.86:48.52:5.85:11.78.^{26,27} It is found that the ratio of C:N measured (8.3:1) does not agree well with the calculated value (5:1). This may be due to the low cross-section (0.24) of N and its low content in the film. It can be expected that the diamine molecule will not decompose during the deposition process. Thus, the stoichiometric formula of the film is suggested to be $[\text{H}_2\text{N}(\text{CH}_2)_{10}\text{NH}_2] \cdot 2\text{WO}_3 \cdot n\text{H}_2\text{O}$ based on the amounts of C, O and W. This ratio of the inorganic and organic components is the same as that of the $\text{WO}_3/4,4'$ -BAMBP (**B**) system.

One possible structure of the WO_3 -polymer/1,10-DDA SAM film (**A**) can be proposed from the above results (see Scheme 1): polymerized WO_3 molecules form two-dimensional networks by edge- and/or corner-sharing on organic molecule modified surfaces, and the 1,10-DDA organic molecules between networks complex with the inorganic component by the headgroups. The interaction may involve hydrogen bond, electrostatic and other non-covalent interactions. The thickness of the two-dimensional WO_3 -polymer network is about $0.4 \times 3 = 1.2 \text{ nm}$, since the amount of WO_3 in each bilayer of system **A** is 3 times that in the **B** system, in which each WO_3 layer is about 0.4 nm thick. The remaining 1.7 nm of the d spacing is the contribution of the organic component. Because the length of 1,10-DDA molecule is about 1.5 nm (the length is calculated based on the contribution of 0.125 and 0.15 nm per methylene and amino group, respectively, by supposing the organic molecule exists in the all-trans configuration), from this d value it is assumed that the densely packed organic molecules are arranged almost perpendicularly to the inorganic lamella. After the distance between the inorganic and organic molecules is taken into account, the structure will agree well with the above results.

During the self-assembly process, when the tungstic acid molecules are adsorbed onto the charged surface, driven by electrostatic coordination and hydrogen bonding interactions,



Scheme 1 Possible model of WO_3 -polymer/1,10-DDA SAM film.

the concentration of tungstic acid in the interfacial adsorption layer would be much higher than that in the bulk solution.²⁸ Therefore, the electrostatic and steric stabilizing effects of the stabilizer (oxalic acid)¹⁹ are weakened and the adsorbed tungstic ions readily form polytungstate species in the interfacial adsorption layer; at the same time the resulting loss of the negative charge should be able to induce further adsorption of tungstic ions.²⁹ As a result, even in the **B** system, WO_3 in the first layer on a 3-aminopropyltriethoxysilane (APS) modified surface (after protonation) has been polymerized as indicated by the absorption spectrum. But the coverage of WO_3 in the second or following layers of film **B** decreases by nearly a factor of 4 and thus no aggregation or polymerization is observed in these following layers (data not shown here). We think this is due to the much higher charge density of the first APS modified surface than that of the following surface modified with 4,4'-BAMBP. However, each inorganic layer, including the first one of film **A**, contained approximately the same amount of WO_3 , revealing that the charge density of the 1,10-DDA modified surface is close to the APS modified one and such a surface could condense the WO_3 molecules to polymerize. A series of divalent cations, $\text{NH}_3^+(\text{CH}_2)_n\text{NH}_3^+$ ($2 \leq n \leq 10$) have been tested but only 1,10-DDA could induce the polymerization of WO_3 , meaning that only 1,10-DDA can match and self-assemble the polymerized structure. On the surface of 1,10-DDA, therefore, the polytungstate species would rather form two-dimensional polynuclear networks by corner- and/or edge-sharing³⁰ and can act as multiple coordination sites for the adsorption of organic molecules in further self-assembly processes to form the superlattice WO_3 -polymer/1,10-DDA film.

Photochromism

The freshly prepared WO_3 -polymer/1,10-DDA (**A**) SAM film exhibits interesting photochromic properties as shown in Fig. 3. The film turns slightly blue when it is subjected to UV irradiation in air, similar to other amorphous WO_3 films. In the XPS spectra of the SAM film, the peaks corresponding to $\text{W}4f_{7/2}$ and $\text{W}4f_{5/2}$ are slightly broadened to asymmetric and shifted from 35.8 and 38.2 to 35.5 and 38.0 eV, respectively. This implies that photoinduced reduction take place between W^{6+} and W^{5+} in the SAM film during the photochromic coloration process.⁸ Clearly, the change in absorbance of film **A** (28 layers, 0.045 unit at 1050 nm) is much larger than that of system **B** (40 layers, 0.0055 unit at 1050 nm). Because the gross amount of WO_3 in the 28-layer WO_3 -polymer/1,10-DDA SAM film is nearly twofold that in the **B** film [$28 \times 3 \div (40 \times 1) = 2.1$], the absorption change of the former is obviously enhanced by as much as 3.9 times ($0.045 \div 0.0055 \div 2.1 = 3.9$). This means that the presence of WO_3 -polymer in the SAM film may play an important role in the improvement of the photochromic performance.

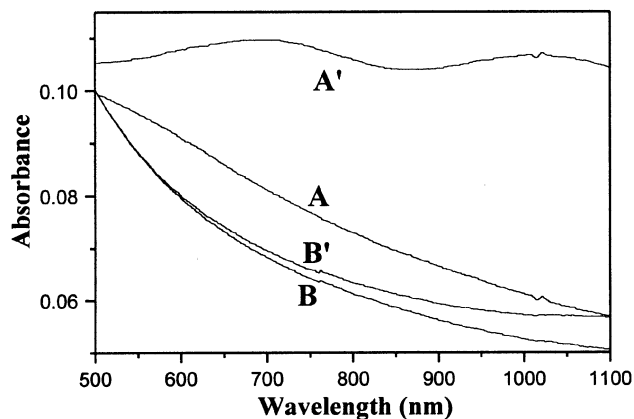


Fig. 3 Absorption spectra of a 28-layer WO_3 -polymer/1,10-DDA SAM film (**A**, **A'**) and a 40-layer WO_3 /4,4'-BAMBP SAM film (**B**, **B'**): **A** and **B**, spectra of freshly prepared and bleached films; **A'** and **B'**, spectra of the films irradiated with ultraviolet light in air for 3 min.

It is well known that when an alkylammonium/polyoxometalate composite material is irradiated with UV light, the photoexcitation of the $\text{O} \rightarrow \text{M}$ LMCT bands induces a transfer of a proton from a hydrogen-bonded alkylammonium nitrogen to a bridging oxygen atom at the photo-reducible site in the edge-sharing MO_6 octahedral lattice. This is followed by the interaction of the d^1 electron of the metal atom with the proton transferred to the oxygen atom. At the same time, the hole left at the oxygen atom interacts with non-bonding electrons on the nitrogen atom to form a charge-transfer complex (colored species), resulting in separation of the electron and the hole that are produced by the $\text{O} \rightarrow \text{M}$ LMCT in the inorganic lattice and stabilizing the colored state.⁷ The polymerization of WO_3 will increase the ratio of the edge-sharing WO_6 octahedral lattice.³¹ This not only facilitates the transfer of a proton from nitrogen of the hydrogen-bond associated alkylammonium to a bridging oxygen atom at the photoreducible site in the inorganic lattice,⁷ but also inhibits the fast bleaching process⁴ of the colored composite film or enhances the stability of the charge-transfer complex. Hence, the WO_3 -polymer/1,10-DDA composite film shows improved photochromic response in comparison with that of the WO_3 /4,4'-BAMBP system. This suggests that the UV photochromic response or photochromic behavior of the WO_3 composite film can be greatly improved by changing organic components.

When the irradiated WO_3 -polymer/1,10-DDA SAM film was heated for 10 min at 60 °C in ambient atmosphere, its absorbance reverses to the initial state. Moreover, the SAM film shows good reversibility in its coloration-decoloration process.

Conclusion

A novel inorganic/organic superlattice film with well-ordered structure and photochromic properties has been fabricated by the alternate adsorption method. The dependence of the photochromic effect on the polymerization of WO_3 molecules is discussed by comparison of the behavior of the WO_3 -polymer/1,10-DDA system with that of the previously reported WO_3 /4,4'-BAMBP system. The results clearly show that the organic molecules can efficiently manipulate the structure as well as photochromic properties of the self-assembly multi-layer films. That is to say, self-assembly techniques are suitable methods to fabricate new types of transition metal oxide materials with photochromic properties, offering a simple and convenient way to tailor photochromic properties of the composite films.

Experimental

The tungstic acid solution (stabilized with oxalic acid) used with a concentration of 5.0×10^{-3} M for the fabrication of these SAM films was prepared as previously reported.¹⁹ 1,10-Decanediamine (1,10-DDA) purchased from Aldrich Chemicals was dissolved in ultra-pure water to give a 0.1 mg mL^{-1} solution, with the pH value adjusted to 2. The alternate adsorption process was the same as previously reported. The 3-aminopropyltriethoxysilane (APS) modified substrate (either fused quartz or single crystal silicon (111)) was first dipped into 0.1 M HCl solution and protonated thoroughly, dried by nitrogen flow, then immersed in the tungstic acid solution for 60 min. Thus the substrate was covered with one layer of inorganic compound and its surface charge was reversed. After the substrate was rinsed with ultra-pure water and dried again, it was transferred into the solution of 1,10-DDA bipolar salt for 30 min. In this way a second layer was added and the original surface charge was restored. Repeating the above steps in a cyclic fashion for 30 min each, a well-ordered multilayer film of WO_3 alternating with 1,10-DDA was formed. $\text{WO}_3/4,4'$ -BAMBP films were prepared using the previous procedure.¹⁹ The thickness of the SAM film was measured with a surface profile measuring system (Detake 3 model JGP-560).

Photochromic experiments were carried out in air and a 500 W high-pressure mercury lamp was used as the light source with a 365 nm filter to filter out visible and infrared light. UV-visible spectra were obtained using a Shimadzu UV-1601PC double-beam spectrophotometer.

Small-angle X-ray diffraction (XRD) was carried out on a D/max-rB type X-ray diffraction instrument with the X-ray source being Cu-K α radiation ($\lambda = 0.15418 \text{ nm}$). The voltage of the tube was 40 kV, the electric current was 100 mA and the angular scan range was between 1.3 and 30° .

The low-angle X-ray reflectivity measurement was performed at the Beijing Synchronous Radiation Facility (BSRF). A focussed monochromatic X-ray beam ($\lambda = 0.15418 \text{ nm}$), provided by the 4W1C beamline, was incident on the sample of $0.3 \text{ mm} \times 0.5 \text{ mm}$ area. The sample and the detector were scanned in $\theta - 2\theta$ mode and the step of θ angle was 0.01° .

The X-ray photoelectron spectra (XPS) of the SAM films were recorded on a USW HA150 photoelectron spectrometer at BSRF using monochromated Al-K (1486.6 eV) radiation. The charging shift was corrected by the binding energy of carbon. The samples were maintained at room temperature and at a pressure of about 2×10^{-10} Torr throughout the investigation.

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