Self-assembled multilayer films of europium-substituted polyoxometalate and their luminescence properties

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Abstract

A new kind of hybrid self-assembled film was obtained by means of alternating deposition of the polyoxometalate (POM), K$_{13}$[Eu(SiW$_{11}$O$_{39}$)$_2$], and polyacrylamide (PAA) on the 3-aminopropylsilanized precursor film. The experimental results showed that the polyanions were successfully incorporated into the self-assembled multilayers of the polyacrylamide. The scanning electron microscopy (SEM) was taken to study the surface morphology of the film. The X-ray photoelectron spectra (XPS) verified that the polyoxometalates were incorporated into the multilayer films with a certain adsorption interaction. The effects of the polyacrylamide on the luminescence of the polyoxometalate were discussed in detail. The luminescence spectra showed that the energy was transferred from the ligands to the Eu$^{3+}$ ions in the self-assembled films.

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1. Introduction

Polyoxometalates (POMs) constitute a wide class of inorganic compounds with remarkable chemical, structural, and electronic versatility, having high potential for practical applications. They have been employed in the areas of catalyst, biology, and medicine [1–3]. In view of the ability of these molecular metal-oxide clusters to act as electron acceptors and accommodate functional rare earths, they were used in the construction of hybrid luminescent organic-inorganic materials. Luminescent rare earth complexes are of great interest due to their unique properties: high quantum yields of the emission, large Stokes shifts, long decay time, and very sharp emission bands. They have many important practical applications, such as the luminophores for lamps or screens, laser, electroluminescent optical devices and probes [4,5]. The luminescence characteristics of lanthanide-POMs and their intramolecular energy transfers have been reported [6–9]. The application of lanthanide-POMs in optical devices depends on their successful fabrication of thin films.

Several techniques could be employed to produce solid-state assemblies of rare earth-POMs. We have reported the construction of thin films containing lanthanide-POMs by Langmuir-Blodgett depositions and sol–gel method [10,11]. Recently, polyoxometalates/polymer multilayer films were successfully deposited by an alternate adsorption method [12–17]. The technique provides a way for the fabrication of ultrathin luminescent films containing lanthanide-POMs. Moreover, the self-assembled technique also gives a chance for studying novel optical properties of inorganic rare earth-polyoxometalates surrounded by organic layers.

It is well known that precursor is important for successful deposition of self-assembled films. The poly(ethyleneimine) (PEI) and poly(sodium-4-styrenesulfonate) (PSS) were used as the precursor films in the previous assembly of polymer/POMs [14–17]. In the present study, we successfully deposited the layer-by-layer self-assembled films of polyacrylamide (PAA)/europium-POMs using a substrate modified by 3-aminopropylsilane. UV spectroscopy was used for examining the growth of polymer films. The scanning electron microscopy (SEM) was used for the investigation of surface morphology. The luminescence spectra showed the energy could be transferred from the ligands to the rare
earth ions. The luminescence characteristics were discussed in detail.

2. Experimental

2.1. Materials

K$_{13}$[Eu(SiW$_{11}$O$_{39}$)$_2$] (EuSiW) was synthesized and purified according to [18]. 3-Aminopropyltriethoxysilane (APS) and polyacrylamide (MW: 10,000) were obtained from Aldrich. The products were used without further purification. The pure water for rinsing was first deionized and then distilled twice.

2.2. Film fabrication

The polymer/EuSiW multilayers were prepared as follows. A hydroxylated quartz substrate was first prepared to react with 3-aminopropyltriethoxysilane in benzene. 3-Aminopropylsilanized substrate was dipped into 0.1 mol/l HCl to obtain a positively charged surface, followed by immersion into an aqueous solution containing EuSiW with a concentration of $1 \times 10^{-4}$ mol/l for half an hour. After rinsing with pure water, the substrate was dried with a gentle stream of N$_2$. Thus, the precursor film APS/EuSiW was obtained. The substrate was transferred into an aqueous solution containing 0.1 mg/ml polyacrylamide (pH 3.0, adjusted by HCl), thus a polyacrylamide layer was formed on the APS/EuSiW film. Then the substrate was transferred into the solution of EuSiW. The polymer/EuSiW multilayers were obtained by repeating the last two steps. Rinse and drying procedures were performed after each adsorption step.

2.3. Characterization

UV-Vis absorption spectra were measured by using a Tu-1901 spectrophotometer. Luminescence spectra were obtained on a Spex FL-2T2 spectrophotometer equipped with xenon lamp as excitation source. The luminescence lifetime was recorded by a Spex 1934D-phosphorescence spectrophotometer. X-ray photoelectron spectra (XPS) were obtained by a VG ESCALAB MKII system. The excitation source was Mg K$_\alpha$ obtained by a VG ESCALAB MKII system. X-ray photoelectron spectra (XPS) were obtained by a VG ESCALAB MKII system.

3. Results and discussion

3.1. UV spectra

The formation of polymer/EuSiW multilayers was examined by means of UV spectroscopy. Fig. 1 shows the UV absorption spectra of polymer/EuSiW multilayers and the first APS/EuSiW layer on a quartz substrate, and the spectrum of EuSiW solution. As shown in Fig. 1, two strong absorption bands with maximum around 200 and 250 nm are observed in the spectrum of the EuSiW solution. The peak at 200 nm is assigned to O$_d$ → W charge transition and the other peak at 250 nm is assigned to O$_b$ → W charge transition, which are the two characteristic bands of Keggin heteropolytungstate complexes. In the spectra of the self-assembled films, two characteristic absorptions of the polyanions are observed. However, O$_b$ → W charge transition peak shows a red shift to 255 nm. The polymer PAA does not show any absorption at 255 nm, and its presence in the film does not contribute to the absorption spectra. The shifts of characteristic absorbance may be due to the interaction between the polyanions and the polymer. The inset in Fig. 1 shows the linear dependence of the absorbance on the number of layers of the film. For the films with n > 1, the absorbances of the films at 196 and 255 nm versus the number of layers are two straight lines. It is noticed that the absorbance values for APS/EuSiW monolayer are larger than those of PAA/EuSiW monolayer, indicating a greater amount of EuSiW deposited onto the APS precursor film.

3.2. XPS analysis

The elemental composition and the binding energy of the atoms in the films were analyzed by XPS. The signals from W, O, C, N, and H were observed in the XPS of the films. The XPS peaks corresponding to W core levels of the solid EuSiW and the multilayer films are shown in Fig. 2. The binding energy of W4f$_{7/2}$ is 34.9 eV in the solid EuSiW. The binding energy of W4f$_{7/2}$ is 35.2 eV in the self-assembled film. The binding energy of W4f$_{7/2}$ in the multilayer film is higher than that of the solid EuSiW. The data of XPS for W show that the polymer has an influence on the binding energy of W atoms in the polyanions, which shows that the static interaction lies between the polyacrylamide and the polyanions.
3.3. SEM investigation

The scanning electron micrographs were taken to provide further detailed information about the surface morphology and the homogeneity of the film to the nanometer scale. The SEM images of the APS/EuSiW precursor film and the multilayer films are shown in Fig. 3. The diameters of the polyoxometalate particles in the APS/EuSiW precursor film are larger than those of the multilayer films.

3.4. Luminescence properties

Fig. 4 shows the excitation spectra (normalized) of the solid EuSiW (a) and the self-assembled film (b), which were measured at the emission wavelength of 613 nm. Both the position and the shape of the spectra are quite different. The excitation spectrum of the multilayer films shows a wide band from 200 to 350 nm with a maximum at 255 nm, which is the ligands–metal charge transfer (LMCT) band. The excitation spectrum of the solid EuSiW only shows the characteristic excitation lines of Eu$^{3+}$. The excitation spectrum of the EuSiW solid shows that the excitation into the SiW$_{11}$ group is followed mainly by nonradiative transitions in this group and the Eu$^{3+}$ luminescence can only be excited into the Eu$^{3+}$ absorption lines in the visible region. As suggested by Blasse and Dirksen [9], the intramolecular energy
transfer from the excited level of the LMCT for the ligands to the emitting $^1D_0$ level of the Eu$^{3+}$ depends on the structure of the ligands of EuSiW. The hopping delocalization of a d$^1$ electron occurs predominantly in ligands SiW$_{11}$O$_{39}$$^{13-}$. The hopping delocalization of the d$^1$ electron over the lattice is a quenching channel against the energy transfer from the LMCT states to the emitting levels of the Eu$^{3+}$, due to the ease of recombination between the d$^1$ electron and the hole as a result of the decreased disparity between the nuclear configurations of the excited and the ground states of the ligands. Therefore, for the EuSiW solid at room temperature, the excitation spectrum only consists of sharp lines of Eu$^{3+}$ excitation and no band could be detected. However, a broad LMCT band appears in the excitation spectrum of the multilayer films. The charge transfer band is sensitive to the chemical surroundings of rare earth ions. The charge transfer band of the self-assembled film suggests that the electron energy levels of the oxygen atoms near the europium have been influenced by the formation of the hybrid films and the different energy transfer process existed in the two different states. For the multilayer film, the formation of the polymer/inorganic hybrid ligand may increase light absorption cross-section by “antenna effects.” The photoexcitation into the LMCT band of the ligands leads to an effective intramolecular energy transfer from the ligands to Eu$^{3+}$ via the triplet state of ligands, followed by emission due to the f-f transition within the Eu$^{3+}$ ions. Moreover, the formation of hybrid between the polymer and the polyanions may affect the LMCT energy levels of ligands and decrease the delocalization of d$^1$ electron, which may increase the communication between LMCT levels and excited Eu$^{3+}$ levels drastically [8]. The excitation spectra of the films indicate that the formation of the multilayer films results in the energy transfer from the ligands to rare earth ions [10].

The luminescence emission spectra for the multilayer film and the EuSiW solid, excited at 255 and 395 nm, respectively, are given in Fig. 5. Each of the luminescence spectra for the films and the solid shows five characteristic emission peaks. These peaks are assigned to five energy level transitions from $^5D_0$ metastable state to terminal levels, respectively: $^3F_j$ (j = 0–4) transitions. More clearly, the luminescence intensity of the induced electronic dipolar transition $^5D_0 \rightarrow ^7F_2$ and magnetic transition $^5D_0 \rightarrow ^7F_1$ are predominant transitions in the two states. For the EuSiW complexes, in the literature [9], the transition $^5D_0 \rightarrow ^7F_2$ peak splits into two peaks at 615 and 618 nm, and the secondarily intense transition $^5D_0 \rightarrow ^7F_1$ appears at 591 and 595 nm. The peak at 581 nm is ascribed to the $^5D_0 \rightarrow ^7F_3$, while the peaks at 651 and 701 nm correspond to $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. Compared with the spectrum of the solid, the spectrum of the multilayer films shows some differences in shapes, position, and splitting lines. The $^5D_0 \rightarrow ^7F_1$ emission transition occurs at 592 nm and the peak at 613 nm is $^5D_0 \rightarrow ^7F_2$, and no splitting is observed. The enhancement of the $^5D_0 \rightarrow ^7F_2$ is observed for the multilayer films, and the relative intensity between the two predominant transitions varies. It is well known that the hypersensitive emission $^5D_0 \rightarrow ^7F_2$ is expected to be more sensitive to the ionic environment in terms of shift in peak position as well as the relative intensity. The ratio between the electronic dipolar transition $^5D_0 \rightarrow ^7F_2$ intensity and magnetic dipolar transition $^5D_0 \rightarrow ^7F_1$ intensity is used as the measure of rare earth site symmetry [19]. The intensity ratio of $^5D_0 \rightarrow ^7F_2$/$^5D_0 \rightarrow ^7F_1$ for the solid EuSiW and the multilayer film is about 1.12 and 1.50, respectively. The fact suggests a more asymmetrical environment occupied by the Eu$^{3+}$ in the hybrid film than in the solid. The transitions between the resonance energy levels of Eu$^{3+}$ may be altered when the site symmetry of Eu$^{3+}$ is changed. The changes are possibly due to the formation of hybrids between the polyanions and the polymer.

The decay curves of the EuSiW solid and the self-assembled film were measured. The decay curves were singly exponential, from which the luminescence lifetimes were calculated. The lifetimes are 1.47 and 2.43 ms for the films and the solid, respectively. Our study, as well as others [10,20], has demonstrated that the lifetimes of the lanthanide complexes in assembled multilayer films were shorter than those of the corresponding solid. There are several possible reasons for the lifetime shortening of the ultrathin film, such as the lateral electron transfer, the different environments for the europium ions, thermal diffusion of the film, and the coordination water.

4. Conclusions

In this work, the multilayer PAA/EuSiW films were successfully fabricated on the APS precursor film. The X-ray photoelectron spectra indicated that the polyanions were incorporated into the multilayer films. The SEM was used to study the surface morphology and the homogeneity of the film. The emission and excitation spectra of self-assembled films were different in comparison with those of the EuSiW solid. It was found that the excitation spectrum of the self-assembled film showed a strong LMCT band, which
could not be observed in the excitation spectrum of the solid. The excitation spectra showed that the nonradiative transition probability within the POM could be reduced and the energy could be transferred from the hybrid ligands to the Eu$^{3+}$ ions in the self-assembled film. The emission spectrum showed that the ratios of the relative intensity between $5D_0 \rightarrow 7F_2$ and $5D_0 \rightarrow 7F_1$ transition became larger in the self-assembled films due to the change of the site symmetry of Eu$^{3+}$. The results showed that the interaction between the POM and organic matrix changed the site symmetry of the rare earth in POM and had an influence on the luminescence properties of Eu-POM.

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