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Orientations of Rare-earth-containing Heteropolyoxometalates with Different Sizes in the Interlayer of Synthetic Multibilayer Films

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Abstract: Three rare-earth-containing heteropolyoxometalates with different sizes, $Na_9[Eu(W_5O_{18})_2]$, $K_{13}[Eu(SiW_{11}O_{39})_2]$, and $K_{17}[Eu(P_2W_{17}O_{61})_2]$, have been incorporated by self-assembly into the interlayer of synthetic multibilayer films of dimethyldioctadecylammonium chloride and exhibited different orientations.

Keywords: Rare-earth-containing heteropolyoxometalate, synthetic multibilayer film, DODA, orientation.

Polyoxometalates (POMs) are received much interest currently because of their wide applications in catalysis and materials science[1]. We have prepared some inorganic composite materials by intercalating POMs into the interlayer space of layered double hydroxides (LDHs)[2,3]. These materials exhibit good catalytic activities and the C_2 axis of the intercalated Keggin-type POMs is found to be orthogonal to the layers of LDHs[2].

Synthetic multibilayer films are highly ordered molecular aggregates and their interlayer space is much similar to that of LDHs[4]. So far, only two isopolyoxometalates $[V_{10}O_{28}]^{6-}$ and $[W_{10}O_{32}]^{4-}$ have been incorporated into the interlayer of multibilayers by ion exchange or casting[5,6]. Here we report the incorporation and orientations of three rare-earth-containing heteropolyoxometalates with different sizes, $Na_9[Eu(W_5O_{18})_2]$ (EW), $K_{13}[Eu(SiW_{11}O_{39})_2]$ (ESW), and $K_{17}[Eu(P_2W_{17}O_{61})_2]$ (EPW), in the interlayer space of the synthetic multibilayer films of dimethyldioctadecylammonium chloride (DODA) by ion exchange. The photoluminescence properties of the organic-inorganic composite films were also obtained.

The three POMs were prepared according to the literature[7]. The DODA multibilayer film was formed by immersing a cleaned substrate in a solution of DODA in $CHCl_3$ (0.05 mol/L) at room temperature overnight. Composite films were prepared by self assembly, *i.e.* the substrate-supported DODA multibilayers were immersed in an aqueous POM solution (0.01 mol/L) at room temperature for a number of days. The substrate was taken out for recording the UV-vis spectra every day until the absorbance values of the characteristic bands were constant.

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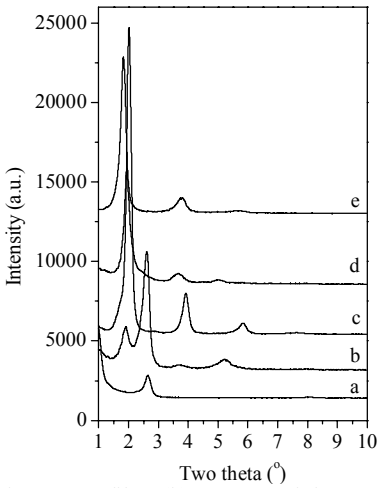
UV-vis spectroscopy was employed to monitor the ion-exchange process between the Cl^- ions of DODA and the polyanions. The results showed that the absorbances of the characteristic bands at 195 and 262 nm assigned to the O → W charge transfer transitions of the polyanions[8] increased with the exchange time. This indicated that the contents of the polyanions incorporated into the interlayer of DODA increased. More than ten days later, the absorbances did not increase any more, suggesting the complete substitution of Cl^- by the polyanions and finish of the ion exchange.

X-ray diffraction (XRD) has proved to be a potent and credible approach to investigate film structure[5-7,9] and orientations of the polyanions[6,7]. **Figure 1 a-e** showed the XRD patterns of the obtained films with different compositions. Several Bragg peaks can be clearly identified, confirming the existence of well-ordered multilayer structure in these films[9]. From the reflections the periodic thicknesses are *ca.* 33.2, 45.5, 46.0, and 48.5 Å respectively, which were calculated for the DODA single component film and the EW-, ESW-, and EPW-containing composite films. The last three values are much greater than the first one, confirming that the three polyanions have substituted small Cl^- ions and been incorporated into the interlayer of DODA. Based on these values and estimations of the DODA molecular length[10] and the cluster diameters of the polyanions[11-13], the orientations of the polyanions in the interlayer can be inferred. For the EW-containing film, the EW polyanions are oriented with their long axis normal to the surface of the substrate and form a monolayer with a thickness of *ca.* 13 Å. Thus, the remaining 32.5-Å thickness can be ascribed to one DODA bilayer and the DODA double-chains tilt with an angle of *ca.* 47.8° with respect to the substrate surface (**Figure 2a**). This thickness of a DODA bilayer is in good agreement with the periodicity of DODA multibilayers (33.2 Å), distinctly demonstrating the maintenance of ordered multibilayer structures after incorporation of EW. In contrast, the ESW and EPW polyanions are arranged with their long axis parallel to the substrate surface and form a monolayer with a thickness of *ca.* 10 Å and 12 Å. Accordingly, the thickness of the DODA bilayer is about 36.0 Å for the former (tilt of DODA: *ca.*54.9°) or 36.5 Å for the latter (tilt of DODA: *ca.* 56.0°) (**Figure 2b**). The dissimilar orientations may be associated with the different cluster diameters of the polyanions: the sizes of the polyanions increase as EW < ESW < EPW while the cluster diameters of ESW and EPW in the short axis are comparable with that of EW in the long axis[11-13]. The detailed mechanism needs further exploration.

In addition, for the EW-containing film with incomplete ion exchange (**Figure 1b**), the first two reflections ($2\theta = 1.92°$ and 2.6°) are quite close to the first-order reflections in **Figure 1c** and **1a**, respectively. This result confirms that the composite film at this time contains both EW and Cl^-, that is, the ion-exchange process has not finished yet.

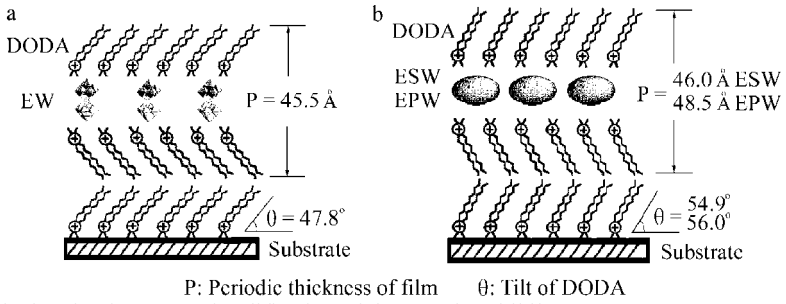
The photoluminescent properties of the POM-intercalated composite films were examined by fluorescence spectroscopy at room temperature and are briefly described here. These films all exhibit luminescence pertaining to the visible-region emission transitions $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 or 4) of Eu^{3+}, very similar to those found for the corresponding POM solids[8,14]. Again, this confirms the incorporation and stability of the polyanions in the composite films. However, some variations occur in the relative intensity, splitting, and width of individual bands compared with those of the POM

Figure 1 XRD patterns of the multibilayer films.



The five curves are (a) synthetic DODA film, (b) EW-containing composite film with incomplete ion exchange, (c) the completely ion-exchanged EW-containing film, (d) ESW- and (e) EPW-containing composite films. Individual curves are shifted in the y-axis direction for clarity.

Figure 2 Schematic representations of the orientations of (a) EW and (b) ESW and EPW in the interlayer of DODA multibilayers.



P: Periodic thickness of film θ: Tilt of DODA

Note that this drawing is an oversimplification of the actual multibilayer structure.

solids. Possible reasons may include the very low contents, different symmetries and distributions of the polyanions in the films and the interactions between the DODA cations and the polyanions are very weak.

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References

1. For a recent overview on polyoxometalate chemistry refer to *Chem. Rev.*, **1998**, *98* (1), 1 and references therein.
2. C. W. Hu, Q. L. He, Y. Zhang, Y. Y. Liu, Y. F. Zhang, T. D. Tang, J. Y. Zhang, E. B. Wang,

Chem. Commun., **1996**, 121.
3. Y. H. Guo, D. F. Li, C. W. Hu, Y. H. Wang, E. B. Wang, Y. C. Zhou, S. H. Feng, *Appl. Catal. (B Environmental)*, **2001**, *30* (3-4), 337.
4. S. Asakuma, H. Okada, T. Kunitake, *J. Am. Chem. Soc.*, **1991**, *113* (5), 1749.
5. I. Ichinose, T. Asai, S. Yoshimura, N. Kimizuka, T. Kunitake, *Chem. Lett.*, **1994**, 1837.
6. I. Moriguchi, K. Hanai, A. Hoshikuma, Y. Teraoka, S. Kagawa, *Chem. Lett.*, **1994**, 691.
7. R. D. Peacock, T. J. R. Weakley, *J. Chem. Soc. A*, **1971**, 1836
8. R. Ballardini, Q. G. Mulazzani, M. Venturi, F. Bolletta, V. Balzani, *Inorg. Chem.*, **1984**, *23* (3), 300.
9. M. Clemente-León, C. Mingotaud, B. Agricole, C. J. Gómez-garcía, E. Coronado, P. Delhaès, *Angew. Chem. Int. Ed. Engl.*, **1997**, *36* (10), 1114.
10. Y. Lvov, F. Essler, G. Decher, *J. Phys. Chem.*, **1993**, *97* (55), 13773.
11. M. Sugeta, T. Yamase, *Bull Chem. Soc. Jpn.*, **1993**, *66* (2), 444.
12. C. M. Tourné, G. F. Tourné, *Acta Cryst.*, **1980**, *B 36*, 2012.
13. V. N. Molchanov, L. P. Kazanskii, E. A. Torchenkova, V. I. Simonov, *Sov. Phys. Crystallogr.*, **1979**, *24*, 167.
14. G. Blasse, G. J. Dirksen, F. J. Zonnevijllle, *J. Inorg. Nucl. Chem.*, **1981**, *43* (11), 2847.

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