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Hybrid Self-Assembled Multilayer Films Formed by Alternating Layers of Keggin Polyoxometalates and 1, 10–DAD

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Abstract: Hybrid self-assembled multilayer films were prepared by alternate adsorption of 1,10-diaminodecane (1,10-DAD) and Keggin polyoxometalates of $SiW_{12}O_{40}^{4-}$, $SiW_{11}VO_{40}^{5-}$, and $PMo_{12}O_{40}^{3-}$, respectively. The films were reproducibly grown at each adsorption cycle as monitored by UV spectroscopy.

Keywords: Self-assembled films, polyoxometalates, hybrid materials.

Decher's technique has attracted much attention for the preparation of self assembled films[1]. However, polyoxometalates (POMs)-containing inorganic-organic hybrid films prepared by Decher's technique have not extensively studied[2-4]. Here, we extend Decher's technique to the preparation of three Keggin POMs-containing inorganic-organic hybrid films.

The general processes for multilayer films formed from POMs and 1, 10-DAD are illustrated in **Scheme 1**. The driving force for the assemblies is the electrostatic attraction between positively charged 1, 10-DAD protonated in strong acidic solutions and negatively charged Keggin polyanions. The Keggin POMs used are $H_4SiW_{12}O_{40}$, $K_5SiW_{11}VO_{40}$, and $H_3PMo_{12}O_{40}$, and multilayer films formed by them are abbreviated as SiW, SiWV and PMo films. We found that each alternate assembly is remarkably dependent on the following factors. The first one is the pH value of the 1,10-DAD solution, and the second one is the adsorption time of POM on 1,10-DAD layer and that of 1,10-DAD on POM and the last one is the use of freshly replaced 1,10-DAD and POM solution from time to time after several immersion cycles. Preliminary experiments revealed that alternate adsorption was not saturated with 1,10-DAD solution higher than pH 2 and the immersion time was less than 40 min.

Figure 1 shows the UV spectra for 7-layer SiW, SiWV and PMo films. The maxima were found to be 196 and 266 nm for SiW film, 198 and 267 nm for SiWV film, and 233 (sh) and 318 nm for PMo film. The spectra for the films are almost the same as those for corresponding aqueous $H_4SiW_{12}O_{40}$, $K_5SiW_{11}VO_{40}$, and $H_3PMo_{12}O_{40}$ solutions[5]. This implies that the POMs were successfully assembled in the multilayer films. The

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good linear relationships between the layer numbers and absorbances monitored at 266 nm for SiW film, 267 nm for SiWV film and 310 nm for PMo film, as shown in the **Figure 2**, demonstrate that assembling processes give vertically uniform multilayer films.

Scheme 1 Fabrication process of POM/1,10-DAD multilayer films (the balls represent $SiW_{12}O_{40}^{4-}$, $SiW_{11}VO_{40}^{5-}$, and $PMo_{12}O_{40}^{3-}$.)

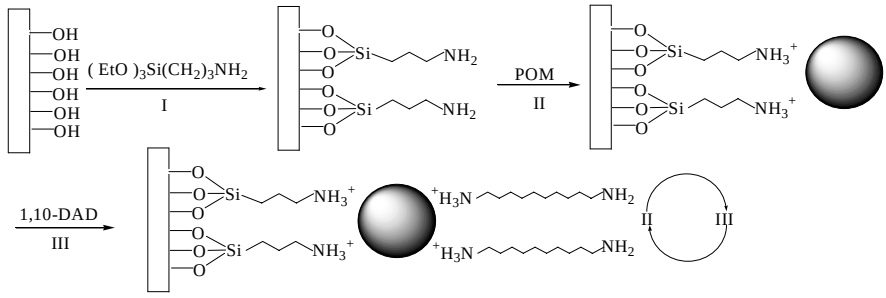


Figure 1 UV spectra of 7-layer POM/1,10-DAD self assembled films

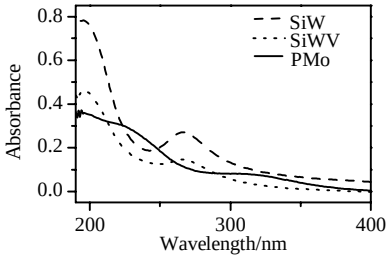
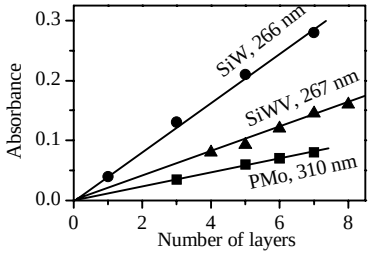


Figure 2 The relationships of absorbances of POM/1,10-DAD films *vs* the layer numbers



In conclusion, three Keggin POMs have been successfully assembled into multilayer films by Decher's technique. The efforts are being directed at studying on electrocatalytic and photochromic properties of these films.

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References

1. G. Decher, *Science*, **1997**, *277*, 1232**.**
2. M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl*., **1991**, *30*, 34.
3. Z. H. Chen, B. Liu, J. N. Yao, *Photographic Sci. Photochem.*, (in Chinese) **2000**, *18*, 198.
4. D. Ingersoll, P. J. Kulesza, L. R. Faulkner, *J. Electrochem. Soc.*, **1994**, *141*, 140.
5. T. J. R. Weakley, S. A. Malik, *J. Inorg. Nucl, Chem*., **1967**, *29*, 2935.

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