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Molecular Orientation of Copper Phthalocyanine in Thin Films and their Gas-Sensing Properties

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Copper phthalocyanine derivative Langmuir-Blodgett (LB) films were prepared by vertical dipping and horizontal lifting methods. Molecular orientation of copper phthalocyanine derivative in thin films was studied by polarized UV-Vis spectra. The relationship between the molecular orientation of copper phthalocyanine in LB films and their gas-sensing properties was investigated.

Keywords molecular orientation; metallophthalocyanine; thin film

INTRODUCTION

Metallophthalocyanines (MPcs) thin films have been aroused great interests in the past two decades[1] due to their high sensitivity of the tested gases. The sensing characteristics, including sensitivity, selectivity, and response-recovery time are found to be dependent on the central metal ions, substrates, film preparation methods,

heat-treatments and doping etc. [2,3]. It suggests that the properties of LB films might be tuned and improved by controlling the surface state of films, such as molecular orientation or stacking of molecules in the films. In this paper, the effect of orientation of copper phthalocyanine in the multilayers on the gas-sensing properties was studied.

EXPERIMENTAL

[4-(4′-benzyloxy phenyl sulfonyl) phenoxy]-tris-4-(2,4-di-t-amylphenoxy) copper phthalocyanine ($CuPcA_3$) was synthesized by the method [4] and purified by column chromatography. The chemical structure was shown in Figure 1. The concentration of copper phthalocyanine solution in chloroform was 1.4×10^{-4}mol dm^{-3}. $CuPcA_3$ LB films were deposited onto hydrophilic substrate by vertical dipping method as Y-type film at the dipping speed of 5mm min^{-1} and onto hydrophobic substrate by horizontal lifting method as X-type film under the surface pressure of 30mN m^{-1}.

Polarized UV-Vis spectra were recorded on Shimadzu UV-3000 UV-Vis spectrophotometer. The incident light was 0° and 30°. Gas sensitivity of thin films was measured as before [3].

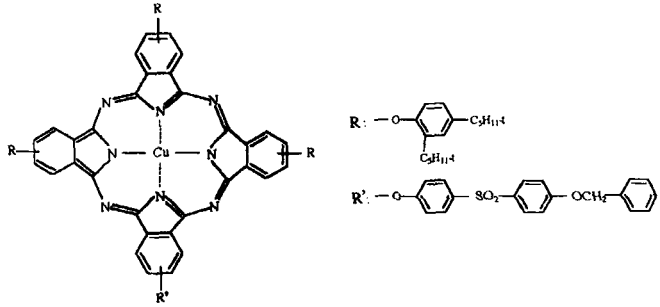

FIGURE 1. The chemical structure of $CuPcA_3$ derivative molecule

RESULTS AND DISCUSSION

There are two absorption bands (~330nm, 620nm) in the UV-Vis spectra of $CuPcA_3$ films that were transferred by vertical dipping and horizontal lifting methods under the surface pressure of 30mN m^{-1}. They are assigned to π-π^* electron transition from Soret-band and Q-band, respectively. The orientation of copper phthalocyanine molecules in LB films can be obtained from the tilting angle (θ) of the phthalocyanine ring axis with the surface normal, which is calculated according to Yoneyama's method [5]. The experimental data and calculation results of copper phthalocyanine derivative films are listed in Table 1. It can be found that the orientation angle of the phthalocyanine ring in the films is related to the deposition method. The inclined degree of phthalocyanine ring in the horizontal lifting film is bigger than that in the vertical one.

Table 1 Polarized UV-Vis experimental data, calculated results and sensitivity of $CuPcA_3$ thin films

Thin Film		Vertical dipping	Horizontal lifting
$\beta'= 0°$	$A_{//}$	0.236	0.309
	$A_{\perp}$	0.247	0.332
$\beta'= 30°$	$A_{//}$	0.256	0.335
	$A_{\perp}$	0.251	0.345
D_0		0.952	0.931
D_β		1.021	0.971
$\langle\theta\rangle$ (°)		38.8	46.2
Sensitivity	MeOH(35ppm)	30	7.5
	EtOH(35ppm)	10	5
	i-PrOH(35ppm)	3	2

Notes: $A_{//}$ and $A_{\perp}$ is the absorbance of the film for polarized light with electric vectors parallel (//) and perpendicular ($\perp$) to the dipping direction, respectively. D_0 and D_β is the dichroic ratio with incident angles of 0 and 30° respectively. β and β' is incident angle of light and reflection angle. Definition of sensitivity is given in detailed [3].

Gas sensitivity of these two films, summarized in Table 1, indicates that the orientation of phthalocyanine ring in the films also influence the sensitivity of the films to alcohol. The smaller the tilting angle of phthalocyanine ring in the film is, the larger the sensitivity of the films to alcohol is. This means that gas-sensing properties of the films are related to the surface state of the films. The orientation of the copper phthalocyanine derivative is important for the gas-sensing properties.

CONCLUSION

The research on the polarized UV-Vis spectra and gas-sensing properties of thin films shows that the sensitivity of the films to alcohol can be affected by the inclined degree of phthalocyanine ring in the films.

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