

The influence of heat-pretreatment on the gas-sensing properties of novel zinc phthalocyanine LB films

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ABSTRACT: A novel asymmetrically substituted amphiphilic phthalocyanine, 1,4-di(2-hydroxyethoxyl)-8,9,16,17,23,24-hexapentyloxyphthalocyanin zinc (asy-PcZn), was synthesized. It can be deposited as well-ordered LB films. Significant structural changes of the films were observed by UV-vis absorption spectra and low-angle X-ray diffraction after the films were annealed at 150 °C. What is more interesting is that the initial conductance of the films in air decreases and the response signal to NH₃ is weaker with longer response time after annealing compared with that of the untreated films. Copyright © 2002 Society of Porphyrins & Phthalocyanines.

KEYWORDS: phthalocyanine, gas sensor, ammoniac, LB films.

INTRODUCTION

Phthalocyanines (Pcs) are p-type organic semiconductors. Their conductance changes after being exposed to both electron-acceptor gases such as NO₂ and electron-donor gases such as NH₃. It is believed that the gas adsorption is followed by a charge-transfer interaction that results in conductance changes. Gas sensors using phthalocyanines have been aroused increasing interest in recent years because of rising levels of atmospheric pollution. The performance of phthalocyanines gas sensors is based on large changes in the dark conductance which are directly related to the adsorption of ppm or even ppb levels of toxic gases, such as NO₂, NH₃, Cl₂ etc., on the surface of Pcs films. It is also well known that the structure and morphology of phthalocyanine thin films have pronounced effect on their gas-sensing characteristics [1, 2]. Sadaoka

and his co-workers [3, 4] studied the effect of heat pretreatment on the morphology and electrical conductance of sublimed lead phthalocyanine films for NO₂ gas detection. They found that gradual increase in conductance was attenuated and response time was slightly prolonged by heat pretreatment at temperatures above the operating temperatures. Luo and coworkers [5, 6] reported the observation of an optical hysteresis behavior in the CuPc LB films during heating and cooling. However the absorption spectra of ZnPc LB films show obvious changes with increasing temperature and the spectra were then retained after cooling to room temperature. We found that a novel asymmetrically substituted amphiphilic phthalocyanine LB films gave a strong and fast response on exposure to NO₂ [7] ($\delta = 21.05 \times 10^{-9} \Omega^{-1}$ exposed to 20 ppm NO₂) while its zinc complex showed very weak response to NO₂ [8] ($\delta = 2.57 \times 10^{-9} \Omega^{-1}$ exposed to 20 ppm NO₂) but strong response to NH₃ ($\delta = 70 \times 10^{-9} \Omega^{-1}$ exposed to 20 ppm NH₃). In this paper the effect of heat pretreatment on the gas-sensing behavior was investigated and the correlation between gas adsorption characteristics and the film structure is discussed.

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EXPERIMENTAL

Synthesis of materials

Figure 1 gives the structure of the titled compounds. The synthesis of its metal free precursor was reported previously [9]. 1,4-di(2-hydroxyethoxyl)-8,9,16,17,23,24-hexapentyloxyphthalocyanine 46 mg (0.04 mmol), anhydrous acetate zinc 11 mg (0.06 mmol) and a little amount of anhydrous potassium carbonate suspended in 10 ml dry DMF were refluxed for 5 hours. After cooling to room temperature, the reaction mixture was poured into 200 ml H₂O. The precipitate was filtered and washed with water until the washings became neutral. It was chromatographed over silica gel (GF₂₅₄ column) using a mixture of CHCl₃:acetone (50:1) as eluent. 48 mg green solid asy-PcZn was obtained, yield 87%. UV-vis/CHCl₃(λ , log ϵ): 698, 5.12. MS(ToF) (M⁺+1): 1213.

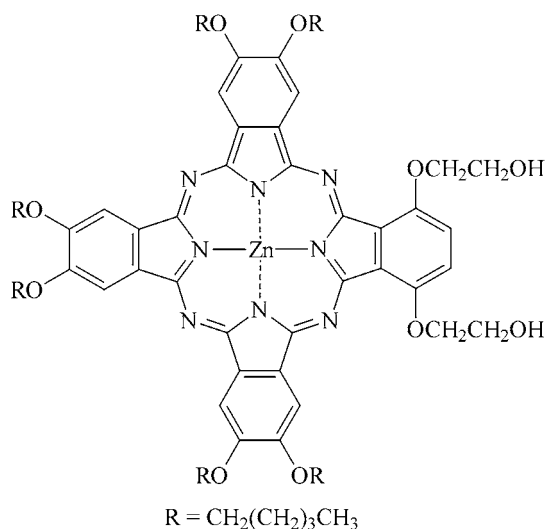


Fig. 1. The chemical structure of asy-PcZn

Monolayer and LB film deposition

A KSV-5000 twin-compartment LB trough was used for the preparation of LB films. The monolayers were spread from chloroform solution (5.2×10^{-4} mol/L) on double distilled water (pH = 5.6). The LB films were built up on glass and aluminum interdigital electrodes for spectroscopic and conductance measurements after the film was annealed at 150 °C, respectively. A constant surface pressure of 27 mN/m was maintained, resulting in fairly good deposition of typical Z-type films with the transfer ratio being about 0.8–1.0.

Instrument

UV-visible absorption spectra were measured on Hitachi 557 UV-visible spectrometer. Mass spectra

were determined on a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF-MS) using a Bruker Biflex III. The low-angle X-ray diffraction analysis was measured by Hitachi Natural D/max-RB diffractometer.

The lateral conductance of the LB films and dynamic gas-sensing response characteristic were monitored using a current-voltage (*I-V*) measuring apparatus composed of a DH1718DC power supply, a microvolt amplifier and a L23-100 x-y function recorder linked with a Teflon and glass gas-testing system consisted of inlets and flowmeters for introduction of gases, a mixture chamber and a testing chamber [10]. The compounds were deposited as thin films by LB technique onto a glass substrate precovered with interdigital aluminium electrodes (12 × 38 mm). The interdigital aluminum electrodes consist of 50 pairs of fingers, each 50 μ m wide and 10 mm long with a gap of 50 μ m between fingers. The bias voltage is 5 V and 15 V for the measurement of gas-sensing properties for 9-layer LB films before and after heat pretreatment, respectively.

RESULTS AND DISCUSSION

The structural characterization of LB films

Figure 2 shows the absorption spectra of 21-layer asy-PcZn LB films on glass at room temperature compared with that annealed at 150 °C. The peak at 710 nm assigned to monomer absorption is blue-shifted to 690 nm and a broad peak at around 645 nm assigned to dimer absorption increased after being annealed at 150 °C. According to molecular exciton theory [11], the blue-shift absorption is a consequence of molecular aggregation with a cofacial phthalocyanine ring orientation within the films.

Figure 3 shows the X-ray diffraction patterns of 21-layer asy-PcZn LB films that have been cooled down

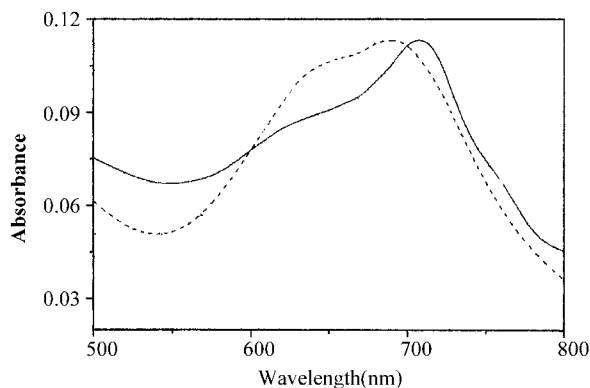


Fig. 2. Absorption spectra of 21-layer asy-PcZn LB films before (solid line) and after (dashed line) annealing at 150 °C for 1 hour in air

in air after annealing at 150 °C for 1 hour compared with that without heat pretreatment. There is a clear Bragg peak for the film before heat pretreatment with $d = 1.90$ nm while the peak intensity increased markedly after annealing at 150 °C with $d' = 2.14$ nm. From CPK model we estimated the distance, w , from the OH group to the end of fully extended alkyl chains on the opposite side of the molecule to be 2.24 nm. Here for the film without heat pretreatment, $d < w$, implies that the macroring of the molecules are tilted to some extent and/or there is interdigitation of chains of molecules in adjacent layers. After the films were annealed at 150 °C for 1 hour, $d \approx w$, indicates that the macroring of the molecules in the films are somewhat perpendicular to the substrate and the alkyl chains is almost fully extended. In other words, the molecules in the films were packed more tightly after heat pretreatment. The orientation of phthalocyanine molecules in LB films is schematically shown in the inserts of Fig. 3.

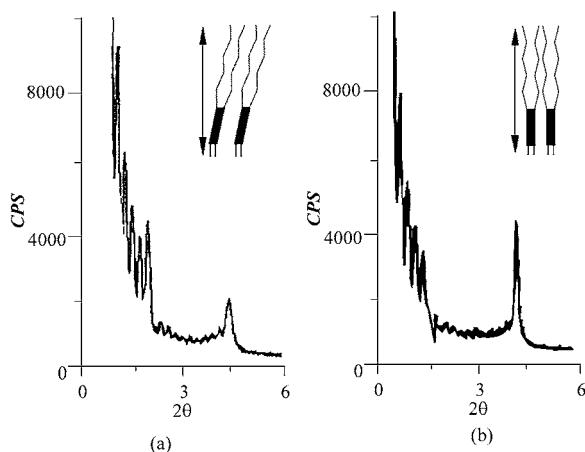


Fig. 3. The x-ray diffraction of 21-layer asy-PcZn LB films before (a) and after (b) annealing at 150 °C for 1 hour in air. Inserts are the tentative orientation of phthalocyanine molecules in LB films

The electrical properties of the films

I-V characteristics. The *I-V* characteristics of the films were determined by measuring the current flow through the film at different applied voltages as shown in Fig. 4. There is a good linear relationship between *I* and *V* at the voltage range of 3–10 V and 15–40 V for the film with and without heat pretreatment, respectively. All of the following experiments for the determination of gas-sensing properties were carried out at this voltage range. The curves do not pass through the origin may be ascribed to the contact resistance in the circuit [12]. It is shown that the slope of the straight line corresponding to the film conductance δ decreased from $6.83 \times 10^{-9} \Omega^{-1}$ to $3.08 \times 10^{-9} \Omega^{-1}$ after heat pretreatment. Most of the

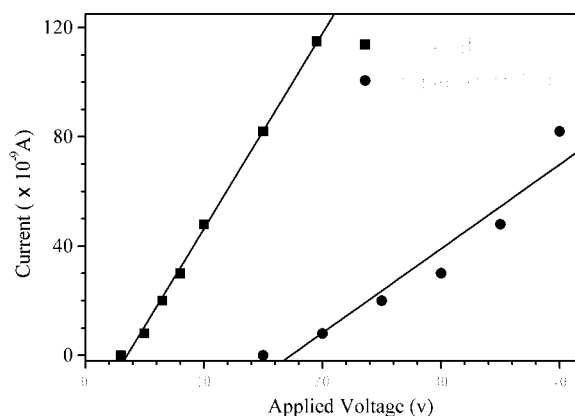
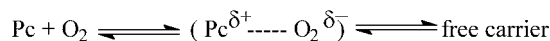


Fig. 4. The *I-V* characteristics of 9-layer LB films of asy-PcZn LB films before and after annealing at 150 °C for 1 hour in air

metal phthalocyanines are p-type semiconductors and their conductance increases following the adsorption of oxidizing gas molecules. It is generally accepted that O_2 is an almost unavoidable dopant of Pc thin films resulting in a weak charge transfer interaction that causes conductance change. The concentration of adsorbed oxygen decreases after heat annealing so that the conductance decreased compared with that of unheated films.

The gas-sensing properties of the films. Figure 5 shows the gas-sensing behavior of a 9-layer LB film to NH_3 of different concentrations before and after annealing at 150 °C for 1 hour. It is generally accepted that O_2 is an almost unavoidable dopant of phthalocyanine thin films resulting in weak charge transfer equilibriums:



We suggest that on ligation by NH_3 the energy gap of asy-PcZn and hence the activation energy

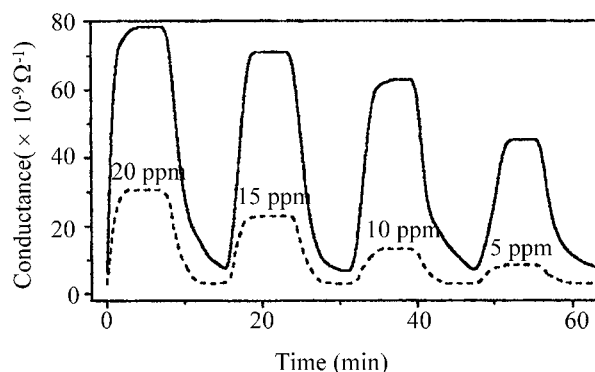


Fig. 5. The gas-sensing behavior of 9-layer LB films of asy-PcZn to NH_3 of different concentrations before and after annealing at 150 °C for 1 hour in air

is lowered, so that the equilibrium will be shifted to the right. The charge carriers thus created lead to the increase of conductance of the asy-PcZn LB films [8]. The gradual increase in conductance is attenuated by heat treatment that may be ascribed to the closer packing of molecules after heat treatment so that diffusion of NH_3 molecules into the bulk of the films became more difficult. It was suggested that the response and recovery processes could be expressed using the following equations [7]:

$$\text{adsorption: } I_a = I_0 \{1 - \exp(-t/\tau)\} \quad (1)$$

$$\text{desorption: } I_d = I_0 \exp(-t/\tau') \quad (2)$$

Here, I_a and I_d are the film conductance during adsorption and desorption, respectively, I_0 is the saturation conductance, τ and τ' are the response time and the recovery time, respectively.

Equations (1) and (2) can be rewritten to give equation (3) and (4):

$$-\ln(1 - I_a/I_0) = t/\tau \quad (3)$$

$$-\ln(I_d/I_0) = t/\tau' \quad (4)$$

For a response and recovery cycle in Fig. 6, plotting $-\ln(1 - I_a/I_0)$ vs. t gives a straight line as shown in Fig. 7. The reciprocal of the slope gives the response time τ . The recovery time was obtained by plotting $-\ln(I_d/I_0)$ vs. t . Here we take the response behavior of the LB film to 5 ppm NH_3 as an example. The response time is 59 s and 76 s and the recovery time is 283 s and 163 s for the LB films before and after heat pretreatment at 150 °C, respectively. The difference in response and recovery time of these two films may be ascribed to the difference in the physical structure and molecular packing of the two films. The LB films annealed at 150 °C are more tightly packed so that the penetration of the gas molecules into the bulk of

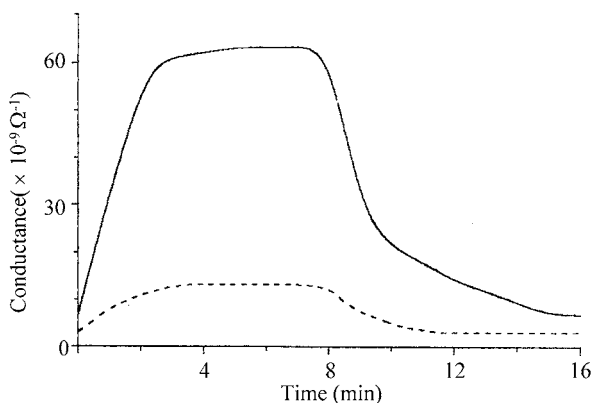


Fig. 6. The first cycle of response and recovery of 9-layer LB films before(solid line) and after(dotted line) annealing at 150 °C for 1 hour in air

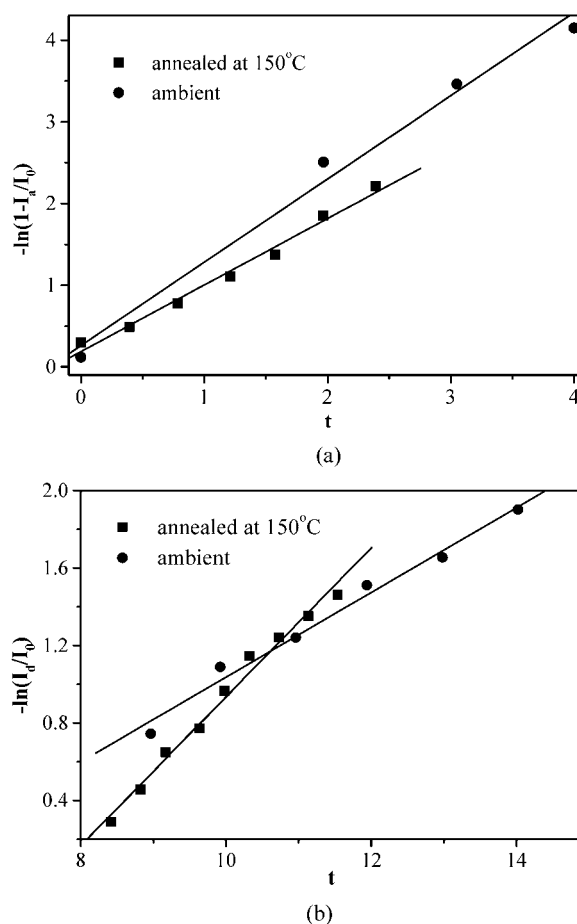


Fig. 7. Linear plots of (a) $-\ln(1 - I_a/I_0)$ and (b) $-\ln(I_d/I_0)$ against time t for the exposure to 10 ppm NH_3

the films became more difficult and a longer time is required to establish equilibrium compared with that of the unheated films. In the desorption process, the concentration of the adsorbed gases on the surface decreased more slowly because this process is controlled by the rate of gas diffusion from bulk to the surface so that the recovery time is much longer than the response time. However, as mentioned above, the concentration of the adsorbed gases decreased after annealing, the recovery time which corresponds to the time to return to the initial conductance value is shorter compared with the unheated films.

CONCLUSION

The effect of structure and molecular packing of the phthalocyanine LB films on the gas adsorption characteristic can be used to explain the observed response and recovery times of conductance changes. The films became more ordered and tightly packed after annealing at 150 °C so that the penetration of gas molecules into the bulk of the film became more difficult. The initial film conductance decreased and the response time was prolonged after heat treatment compared with the unheated films.

Acknowledgements

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