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The gas response behavior of spin-coated phthalocyanine films to NO_2

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Abstract

The spin-coated films of 2,9,16,23-tetra(heptyloxy)phthalocyanine showed very good gas sensing properties to NO_2 at room temperature. The response and recovery are rapid and complete with good reproducibility and high sensitivity. The magnitude of response of the film to NO_2 are enhanced by irradiation with light. This may be ascribed to the decrease in the activation energy for the charge transfer interaction between the phthalocyanine donor and the gas acceptor by light excitation.

Keywords: Phthalocyanine; Gas sensing; Spin-coated film

1. Introduction

The semiconducting properties of phthalocyanine films are modulated by the absorption and desorption of gases. This, together with the good chemical and thermal stability toward many environments of phthalocyanine, has led to significant efforts toward their incorporation in chemical sensors [1–3]. Recent research progress shows that phthalocyanine films have become outstanding candidates for use as highly sensitive gas sensors [4–9].

The principal obstacle for exploiting phthalocyanine thin films in practical gas-sensing devices has been the slow response and recovery times [6,8,9]. These properties are influenced by both chemical and physical structure of the films, which, in turn, is determined by the deposition technique of the film onto electronic substrates. There are two phthalocyanine film deposition technique that are commonly used. These are vacuum sublimation and Langmuir–Blodgett film transfer technique. It is apparent that there are significant differences in gas response behavior between these two kinds of films [10]. Alternatively, ordered thin films can also be constructed using spin-coating technique. There are relatively few reports of spin-coating phthalocyanine films for application in gas sensors in the open literatures, but the convenience of the technique has attracted the attention of industrial and applied groups. We report here the preliminary results on the formation of spin-coated phthalocyanine thin films and studies of gas response behavior of the films, showing that these films have unique properties of very fast reversible response to NO_2 at room temperature. The results are in contrast to the results reported in the literature showing that this kind of gas-sensor materials usually perform slow adsorption and desorption kinetics.

2. Experimental

2,9,16,23-Tetra(heptyloxy)phthalocyanine was synthesized in our laboratory following the procedures of Ref. [11]. The structure and the purity of the compound were determined by FDMS (field diffusion mass spectrum) M^+ 970 (calculation for $C_{60}H_{74}N_8O_4$ is 970); ^{1}HNMR (proton nuclear magnetic resonance) ($CDCl_3$) δ 7.3–8.0 (br, 12H aromatic), 2.25 (t, 8H, OCH_2), 1.5 (br, 40H, CH_2), 1.15 (t, 12H, CH_3); Elemental analysis (%): Found (calculated): C 74.09 (73.92); N 11.63 (11.54); H 7.61 (7.68). The films were spun onto a glass substrate bearing an interdigital aluminium electrode (which was lithographically patterned on a glass substrate; the substrates were cleaned and then deposited by evaporating a 200 nm aluminium film; they were patterned lithographically and etched to form 50 finger pairs of electrodes having a width of 50 μm and gap-width of 50 μm) rotating at 3000 rpm for 5 min, using 1×10^{-2} mol l^{-1} phthalocyanine solution in $CHCl_3$.

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The lateral conductance of the spin-coated film and dynamic gas sensing response characteristics were monitored using a current–voltage (I–V) measuring apparatus (which is composed of a DH1719 DC power supply, a microvolt amplifier and a LZ3-100 X-Y function recorder) linked with a Teflon and glass gas-testing system consisting of inlets and flowmeters for the introduction of gases, a mixing chamber and a testing chamber as shown in Ref. [9]. All the experiments were carried out at room temperature (25–30°C). The light source used to illuminate the film was a QHJ-4 He–Ne laser apparatus.

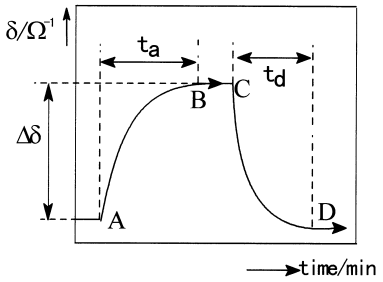

Fig. 2. The response process of phthalocyanine films to NO_2 followed by recovery in air.

3. Results and discussion

3.1. I–V characteristics of the spin-coated film

The I–V characteristics of the film were determined by measuring the current flow through the film at different voltage as shown in Fig. 1. At the voltage range 5–11 V, there is a good liner relationship between I and V in coincidence with the relationship $I = V/R$. All the following experiments for the determination of gas sensing properties are carried out at this adscititious voltage range.

3.2. Gas response properties of the film

The response and recovery process of a film to NO_2 gas is described in Fig. 2. A response cycle can be divided into two processes: adsorption process (A to B) and desorption process (C to D). The gas response characteristics of the film were described by four parameters: t_a, the time needed for adsorbing NO_2 to saturated; t_d, the time needed for desorption processing; t_h, the response time, which is taken to be the time after a 50% change in the stationary signal; and $\Delta\delta$, the difference in the conductance before and after exposure. The response characteristics of the spin-coated film to different concentrations of NO_2 gas are listed in Table 1. From the data, we can see that this spin-coated film possesses very short t_h and t_d. The response time, t_h, keeps almost constant with increasing concentration of NO_2. $\Delta\delta$ increases with the augment of the concentration of NO_2.

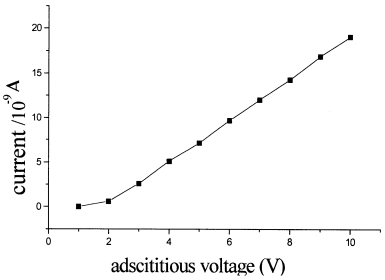

Fig. 1. The current flow through the film at different adscititious voltages in daylight.

For the purpose of inspecting the reproducibility of the response, we exposed the film to 5 ppm NO_2 repeatedly. Every cycle of exposure lasted for 2 min followed by recovery in air for 2 min. From the results in Fig. 3, we can see that the response of the film to NO_2 is rapid and nearly completely reversible under these conditions. The response of the film to same concentration of NO_2 are reproducible. Several measurements were also made for other concentrations of NO_2, and similar results were obtained. Repeat experiments on separately prepared films of the same material gave similar results.

3.3. The effects of light on the response behavior

The response behavior of the film to NO_2 was affected by light. The response of the film to NO_2 in the dark and under illumination with 632.8 nm light were measured. From Fig. 4, we can see that the conductivity of the film is enhanced upon irradiation by light.

The gas sensing properties of the phthalocyanine under illumination by light or in the dark were also determined. The results in Table 2 indicate that the response of the film is rapid and nearly completely reversible both in the dark and under illumination by light. It is also shown that both the response and recovery are enhanced by irradiation. In the dark, the response ($\Delta\delta$) of the film is 1.4×10^{-10} Ω^{-1}, while under illumination, the response of the film to the same concentration of NO_2 increased to 3×10^{-10} Ω^{-1}.

In order to explain the result, a charge transfer interaction is suggested, where a mobile hole carrier creation process takes place on the film surface. Since phthalo-

Table 1
The response characteristics of the film to NO_2 with different concentrations[a]

Concentration of NO_2 (ppm)	t_a (s)	t_d (s)	t_h (s)	$\Delta\delta$ (Ω^{-1})
1.25	120	155	10	1.59×10^{-9}
2.5	140	150	9	1.92×10^{-9}
5	130	145	9	3.54×10^{-9}
10	145	135	10	4.63×10^{-9}

[a]All the experiments were carried out in daylight.

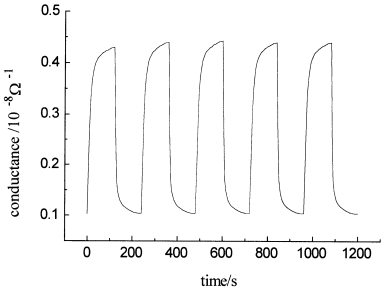

Fig. 3. Response cycles of the film to 5 ppm NO_2 in daylight at adscititious voltage of 7 V.

cyanine is a p-type semiconductor, the adsorbed NO_2 gas acts as an acceptor in the phthalocyanine lattice through the following reversible doping process (Eq. (1)) [4]:

$$P_c + NO_2 \overset{1}{\leftrightarrow} P_c^+ + NO_2^- \overset{2}{\leftrightarrow} h^+ + P_c + NO_2^- . \quad (1)$$

When the phthalocyanine molecules were excited by light, the reaction can be illustrated as process (Eq. (2)):

$$P_c \overset{\text{light}}{\leftrightarrow} P_c^* + NO_2 \overset{1}{\leftrightarrow} P_c^+ + NO_2^- \overset{2}{\leftrightarrow} h^+ + P_c + NO_2^- , \quad (2)$$

where h^+ refers to mobile hole. The energy required to transfer an electron from phthalocyanine film to the adsorbed NO_2 gas molecule is determined by the ionization potential of phthalocyanine, the electron affinity of the acceptor gas. The free energy changes of the electron transfer reaction in processes 1 and 2 can be expressed by the following equations:

$\Delta G_s = E^0_{(Pc^+/Pc^-)} - E^0_{(NO_2^-/NO_2)}$ in the dark,

$\Delta G_s = E^0_{(Pc^+/Pc^-)} - E^0_{(NO_2^-/NO_2)} - E_s$ under illumination,

where E_s refers to the first excited state energy that is the difference in energy of the phthalocyanine before and after illumination. Since the electron transfer process is more thermodynamically favorable in the latter case, the charge-carrier generation process is facilitated by light excitation and the magnitude of conductivity is enhanced.

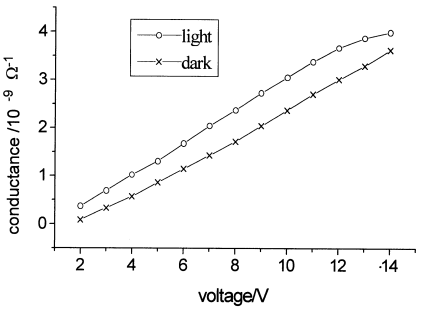

Fig. 4. The conductivity of the film at different adscititious voltage.

Table 2
The comparison of gas response properties of the film to 1 ppm NO_2 in the dark and under illumination

	t_h (s)	t_d (s)	$\Delta\delta$ (Ω^{-1})
Dark	10	110	1.4×10^{-10}
Light	8	120	3×10^{-10}

4. Conclusion

Spin-coated thin films of a symmetrically substituted 2,9,16,23-Tetra(heptyloxy)phthalocyanine exhibited very good gas sensing properties to NO_2 at room temperature. They show very quick response and recovery behavior in contrast to the results reported in the literature showing that this kind of material usually performs slow adsorption and desorption kinetics to NO_2. The response of the film can be enhanced by irradiation with light. It is suggested that a charge transfer interaction, which is facilitated by light, is responsible for the enhancement.

Acknowledgements

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