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Chlorine gas sensors using hybrid organic semiconductors of PANI/$ZnPcCl_{16}$*

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Abstract: PANI/$ZnPcCl_{16}$ (polyaniline doped with sulfosalicylic acid/hexadecachloro zinc phthalocyanine) powders were vacuum co-deposited onto Si substrates, where Pt interdigitated electrodes were made by micromachining. The PANI/$ZnPcCl_{16}$ films were characterized and analyzed by SEM, and the influencing factors on its intrinsic performance were analyzed and sensitivities of the sensors were investigated by exposure to chlorine (Cl_2) gas. The results showed that powders prepared with a stoichiometric ratio of $(ZnPcCl_{16})_{0.6}(PANI)_{0.4}$ had a preferential sensitivity to Cl_2 gas, superior to those prepared otherwise; the optimal vacuum co-deposition conditions for the films are a substrate temperature of 160 ℃, an evaporation temperature of 425 ℃ and a film thickness of 75 nm; elevating the operation temperature (above 100 ℃) or increasing the gas concentration (over 100 ppm) would improve the response characteristics, but there should be upper levels for each. Finally, the gas sensing mechanism of PANI/$ZnPcCl_{16}$ films was also discussed.

Key words: PANI/$ZnPcCl_{16}$; hybrid organic semiconductors; chlorine gas sensors; vacuum co-deposition
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1. Introduction

During the past few decades, organic semiconductor materials have been attracting considerable attention in polyaniline (PANI), metallophthalocyanines (MPcs), polypyrrole and polythiophene. Among them, PANI and MPcs have been identified as promising candidates for gas sensors because they can operate at low temperatures (below 200 ℃) or even at room temperature, while for metal oxides, the gas sensing can only operate at rather high temperatures (above 300 ℃) which is suitable for sensing in high-temperature surroundings[1−3]. Furthermore, PANI shows good environmental and chemical stability, ease of processing, an inexpensive monomer as well as high sensitivity, reversible response and short response time[4]; and MPcs exhibit high sensitivity to both electron acceptor gases such as Cl_2 and hole donor gases such as NH_3 in low concentration[5].

Unfortunately, there are few studies of Cl_2 gas sensing despite its toxicity and widespread occurrence in industrial synthesis and processing[6]. The high electronegativity of Cl_2 gas suggests that it should significantly affect the electrical behavior of MPc films and that the variation of conductivity of MPc films may be appropriate for Cl_2 gas detection. Recently, we have demonstrated newly developed high sensitivity Cl_2 gas sensors using hexadecachloro zinc phthalocyanine ($ZnPcCl_{16}$) films; however, these sensors still have several unsolved problems such as high resistance, long-term recovery and poor reproducibility[7]. Therefore, it is hopeful to obtain novel materials with synergetic and complementary behaviors between PANI and $ZnPcCl_{16}$. It is generally believed that films of PANI or MPc (e.g. thickness, uniformity, viscosity, and adhesive strength) impressively account for the sensor performance. Nowadays, various techniques are employed to prepare the films, such as vacuum deposition, spin-coating and the Langmuir–Blodgett technique, depending on the structure and solubility of the adopted materials[8−10]. Due to the thermal/chemical stability of these compounds and their rather small solubility in organic solvents, vacuum deposition is widely used to fabricate the films.

In order to improve the performance of gas sensors based on $ZnPcCl_{16}$ films, we have investigated PANI/$ZnPcCl_{16}$ films in this work. The hybrid films were fabricated by vacuum co-deposition and characterized by SEM, and their sensitivities to Cl_2 gas were measured. Finally, the gas sensing mechanism of PANI/$ZnPcCl_{16}$ films was also discussed.

2. Experimental

2.1. Synthesis of gas sensing materials

The PANI-SSA composite was prepared by *in-situ* polymerization of aniline using ammonium persulfate ($(NH_4)_2S_2O_8$) as an oxidant in the presence of sulfosalicylic

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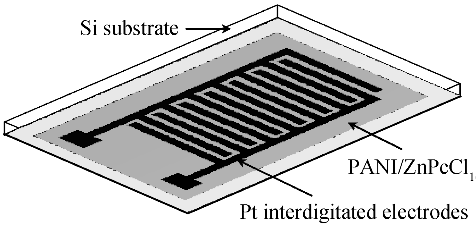


Fig. 1. Schematic diagram of interdigitated electrodes for PANI/$ZnPcCl_{16}$ sensors.

acid (SSA) at room temperature in air. Before dissolving in SSA solution (500 mL, 1 mol/L), aniline monomer was distilled and supplied with rations, and then $(NH_4)_2S_2O_8$ solution in a known concentration was slowly added to the mixtures drop by drop under magnetic stirring. In this process, the temperature for the reaction (normally at 4–6 ℃) should be controlled using an ice-water bath. The reaction was held for 8 h, the compound was filtered and then washed with HCl (1.5 mol/L), deionized water and absolute ethanol, respectively. Following that, the compound was dried (at 65 ℃) in a vacuum drying oven for 24 h, and an emeraldine PANI-SSA composite (half-oxidization and half-deoxidization state) was obtained. In the title, abstract and the following paragraphs, we will use PANI which indicates PANI-SSA synthesized here.

With regard to $ZnPcCl_{16}$ the blue powder which we have synthesized before, details were presented previously[7]. Considering the purity influencing the quality of the film, $ZnPcCl_{16}$ was dissolved in concentrated H_2SO_4 and then diluted with deionized water to remove the undesired products, repeatedly until the mixed solution completely turned blue, and then filtered with deionized water and dried (at 80 ℃) in a vacuum drying oven for 12 h.

2.2. Fabrication of PANI/$ZnPcCl_{16}$ films

As mentioned above, $ZnPcCl_{16}$ is so difficult to dissolve in ordinary organic solvents that we obtained hybrid films by vacuum co-deposition of $(ZnPcCl_{16})_x(PANI)_{1-x}$ powders with different stoichiometric ratios. These powders were sublimated in a vacuum at 8×10^{-4} Pa and 250 ℃ before vacuum co-deposition, mixed uniformly and then coevaporated onto silicon substrates in a diffusion-pumped vacuum system operating at a base pressure of 8×10^{-4} Pa. The substrates, whose size is 3.5×5 mm^2, provide 7 pairs of Pt interdigitated electrodes whose width is 200 μm and the spacing of which is 75 μm. A sandwich structure can be illustrated with Si substrate as the bottom layer, Pt interdigitated electrodes as the middle layer and PANI/$ZnPcCl_{16}$ films as the top layer, as shown in Fig. 1. For this purpose, quite a few micromachining techniques are introduced in electrode fabrication, mainly including the following procedures: template design, substrate cleaning, vacuum drying, photoresist coating, pre-baking, exposure, developing, post-baking, magnetron sputtering, resist stripping, heat treating, and laser cutting, respectively. The substrate temperature was varied from 80 to 160 ℃. The evaporation temperature of PANI/$ZnPcCl_{16}$ was varied from 325 to 450 ℃. The PANI/$ZnPcCl_{16}$ film thickness produced in this manner ranged from 50 to 350 nm.

Table 1. Sensitivity data of PANI/$ZnPcCl_{16}$ sensors to a variety of gaseous species (150 ppm).

x	Cl_2	NO_2	NH_3	CO	CH_3OH
0.9	0.58	0.97	1.10	1.37	1.02
0.8	0.45	0.92	1.12	1.55	1.03
0.7	0.33	0.85	1.16	1.75	1.03
0.6	0.25	0.78	1.21	1.86	1.05
0.5	0.35	0.73	1.29	2.18	1.06
0.4	0.52	0.65	1.26	2.32	1.09
0.3	0.78	0.58	1.25	2.37	1.12
0.2	0.86	0.62	1.28	2.45	1.15
0.1	0.95	0.53	1.35	2.58	1.18

2.3. Measurement system

The sensing performance of the sensors was investigated using a “static gas sensing system”. PANI/$ZnPcCl_{16}$ sensors were set on a heater in a glass bell jar. The current flowing through the electrodes of the heater in the atmosphere was under the limit of detection at an applied voltage ranging from 0 to 3 V. The sensitivity of the PANI/$ZnPcCl_{16}$ sensors at various operating temperatures was estimated by measuring the resistance during the repeated introduction and removal of the required gas whose concentration was calculated first. The sample gas was introduced by a gas injecting syringe into the glass bell jar. Here, gas sensitivity “S” is defined as the ratio R_g/R_0, where R_g and R_0 are the resistance of sensors after and before gas introduction, respectively.

3. Results and discussion

3.1. Analysis of PANI/$ZnPcCl_{16}$ films

It is already known that both PANI-SSA and $ZnPcCl_{16}$ are p-type organic semiconductors[11, 12]. When exposed to oxidizing gas or reducing gas, the resistance of PANI/$ZnPcCl_{16}$ films will decrease or increase correspondingly, depending on the injecting gas. We have prepared films with the same thickness of 200 nm, but different stoichiometric ratios. Sensitivities of 5 gaseous species were examined at room temperature in a given stoichiometry value x ranging from 0.1 to 0.9, as shown in Table 1. It should be emphasized that a value of sensitivity deviating farther from 1 suggests better sensitivity, responsible for both the oxidizing gas and the reducing gas. Comparing the data in Table 1, we can learn that the films show inert behavior to CH_3OH and NH_3, a favorable response to NO_2 and CO, and preferable sensitivity to Cl_2. Interestingly, the same sensitive properties to the oxidizing gas Cl_2 and NO_2 are often taken for granted, but the result indicates that by increasing the value x, the sensitivity to NO_2 increases and the sensitivity to Cl_2 almost decreases. In particular, when the films are prepared with $(ZnPcCl_{16})_{0.6}(PANI)_{0.4}$, the sensors are highly sensitive to Cl_2 with a sensitivity of 0.25. The sensitivity data from Table 1 further demonstrate the selectivity of the films to different gaseous species, which helps us to discriminate the miscellaneous gases.

Besides the stoichiometric ratio, the sensitivity of the PANI/$ZnPcCl_{16}$ sensors was tightly related to the preparation conditions of the PANI/$ZnPcCl_{16}$ films. Learning from Table 1, we chose $(ZnPcCl_{16})_{0.6}(PANI)_{0.4}$ for vacuum coevaporating the films and PANI/$ZnPcCl_{16}$ sensors were operated at 50 ℃

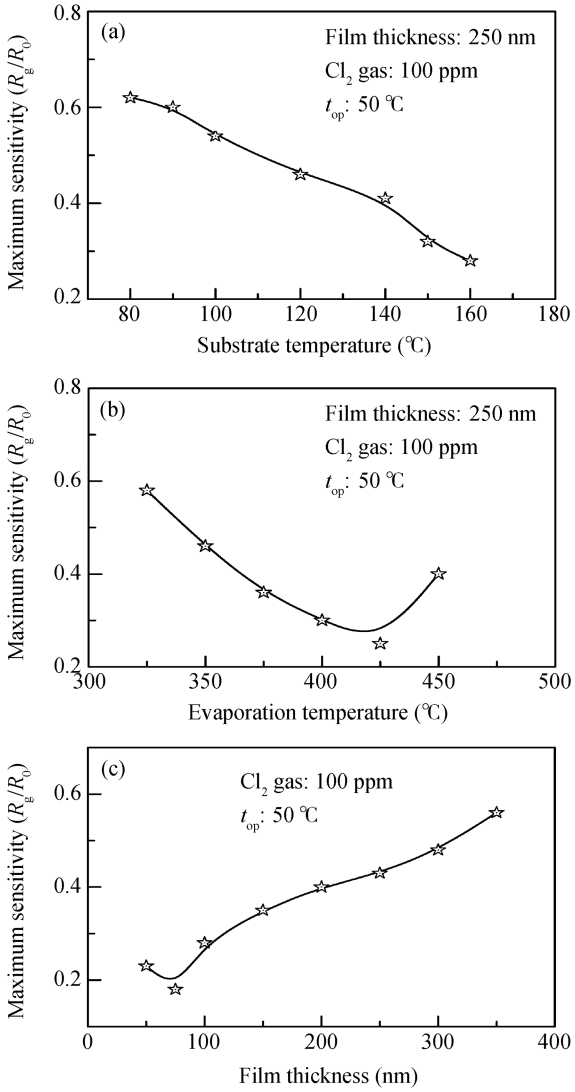


Fig. 2. Maximum sensitivity of PANI/ZnPcCl$_{16}$ sensors influenced by the coevaporation condition. (a) Substrate temperature. (b) Evaporation temperature. (c) Film thickness.

by exposure to Cl$_2$ gas with a concentration of 100 ppm, as shown in Fig. 2. The maximum sensitivity of PANI/ZnPcCl$_{16}$ films decreased as the substrate temperature was increased from 80 to 160 ℃, and we found that the films were unable to deposit on the substrate well if the substrate temperature was increased further. As can be seen from Fig. 2(a), the optimal sensitivity was obtained at a substrate temperature of 160 ℃.

At the same time, the evaporation temperature of PANI/ZnPcCl$_{16}$ films was investigated, and the maximum sensitivity of PANI/ZnPcCl$_{16}$ sensors was found to be strongly dependent on the evaporation temperature. It is understandable from Fig. 2(b) that with the increase of the evaporation temperature from 325 to 425 ℃, the maximum sensitivity decreased dramatically, but it failed to stay the course after 425 ℃. This phenomenon can be attributed to the thermolysis of PANI, which degrades PANI/ZnPcCl$_{16}$ molecular interaction. It also can be explained by the carbonization of the composites because the temperature reaches the ceiling temperature of both. Therefore, the evaporation temperature of 425 ℃ should be thought the best in this experiment.

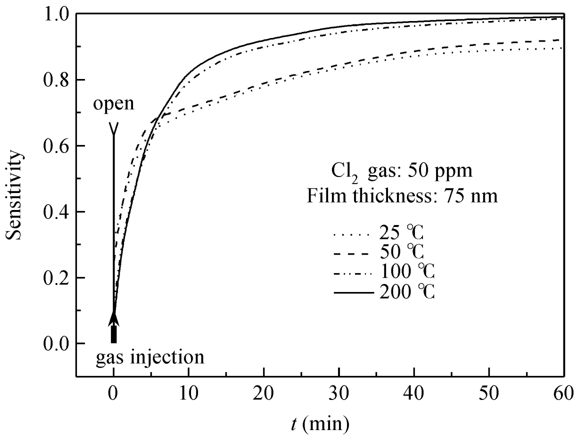


Fig. 3. Transient response of PANI/ZnPcCl$_{16}$ sensors operated at different temperatures.

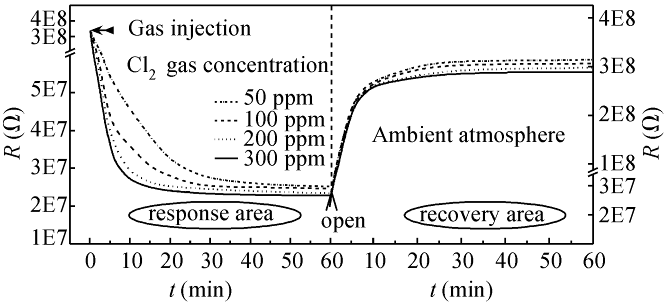
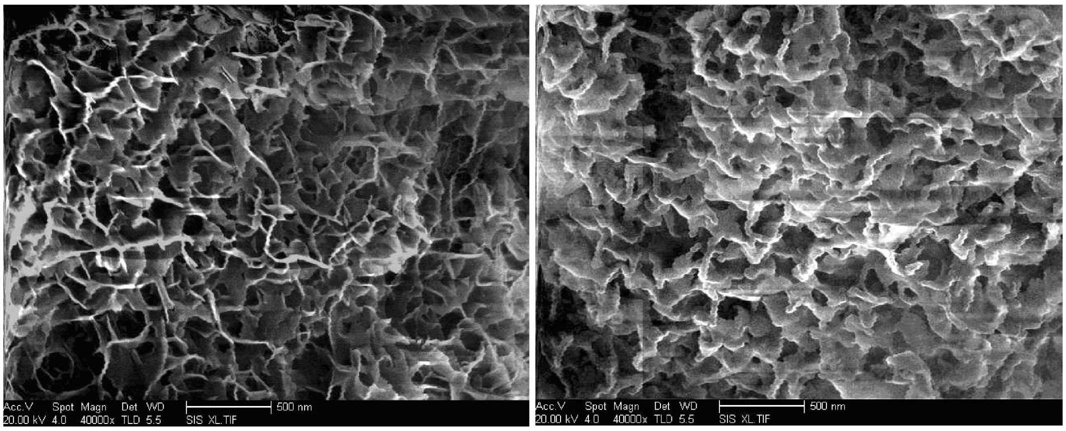


Fig. 4. Response and recovery of PANI/ZnPcCl$_{16}$ sensors operated at 100 ℃ (film thickness: 75 nm).

Theoretically, reducing the thickness of PANI/ZnPcCl$_{16}$ films can realize a short-term response and recovery purpose, but most reports reveal that if the thickness is below the bottom level, the films would be markedly unstable under long term operation. Figure 2(c) shows that the maximum sensitivity of the PANI/ZnPcCl$_{16}$ sensors was increased when the film thickness increased from 75 to 350 nm. Films that are too thick restrain the gas diffusion, which can be attributed to the compact accumulation of the molecules. As shown in Fig. 2(c), the optimal sensitivity could be satisfied with a thickness of 75 nm.

3.2. Sensing properties of PANI/ZnPcCl$_{16}$ sensors

It has been confirmed that the conductivity of semiconductors is closely associated with the operating temperature. For this, we have prepared PANI/ZnPcCl$_{16}$ sensors based on the analysis of PANI/ZnPcCl$_{16}$ films mentioned above. The sensors were operated at different temperatures, initially exposed to Cl$_2$ gas with a concentration of 50 ppm and simultaneously the gas was let out immediately, and their transient response is illustrated in Fig. 3. Comparison of the four curves suggests that the response time shortened as the operating temperature was increased. However, when the atmosphere was returned to ambient air, the recovery time remained relatively long (about 10 min to reach 90% of the initial level). Nevertheless, it should be noted that the recovery characteristic was much improved as the operating temperature was raised to approximately 100 ℃, which ensures that the sensors can be utilized in most cases.



(a) (b)

Fig. 5. SEM images of PANI/$ZnPcCl_{16}$ and $ZnPcCl_{16}$ films. (a) PANI/$ZnPcCl_{16}$. (b) $ZnPcCl_{16}$.

In the meantime, we also examined the response and recovery characteristics of PANI/$ZnPcCl_{16}$ sensors to Cl_2 gas of different concentrations. The sensors were operated at 100 ℃, and Cl_2 gas was fully injected each time. We can clearly see from Fig. 4 that quick response and recovery characteristics are revealed in the first 10 min (as shown in the response area and recovery area, respectively), and then gradually slow down until going steady in the following 50 min. However, the initial resistance (in the response area) is bigger than the ultimate one (in the recovery area), which can be blamed for the remaining gas adsorption on the films. Moreover, significant differences are observed at different gas concentrations as Figure 4 shows that the higher concentration of the gas is, the harder it is for the sensors to recover. The reason for this reluctant recovery (as shown in Figs. 3 and 4) can be interpreted by the sensing mechanisms of PANI/$ZnPcCl_{16}$ sensors, which will be discussed in the subsequent section. Concerning the resistance before and after gas injection, we are aware of the resistance being decreased by one order of magnitude, which may be good for sensitivity. Last but not least, judging from the response area, we can predict that the sensors should be very stable in a high concentration Cl_2 gas atmosphere. The experiment was repeated many times, and we found that there was a small drift of the resistance for each repeating operation.

3.3. Morphology of PANI/$ZnPcCl_{16}$ and $ZnPcCl_{16}$ films

In order to investigate the above results in more detail, the morphology of the films was characterized by SEM. The PANI/$ZnPcCl_{16}$ and pure $ZnPcCl_{16}$ films were vacuum co-evaporated onto interdigitated electrodes, and deposited with gold on the surface for SEM observation. The surface morphologies of PANI/$ZnPcCl_{16}$ and pure $ZnPcCl_{16}$ films are shown in Fig. 5, and they obviously show a honeycomb-like structure, where the particle dimensions fall in the nanometer range.

It can be clearly seen from Fig. 5 that the size of pores on the PANI/$ZnPcCl_{16}$ film is well-regulated and much larger than that of the pure $ZnPcCl_{16}$ film, which significantly enhanced the diffusion due to its larger exposure area and penetration depth for gas molecules. Therefore, the response characteristic of PANI/$ZnPcCl_{16}$ sensors was well improved for its high surface-to-volume ratio. Then, it willingly occurs to us that the microstructure of the nanocomposite films is in good agreement with the sensor performance as suggested by the SEM analysis of the PANI/$ZnPcCl_{16}$ and $ZnPcCl_{16}$ film surfaces. Based on this analysis, it may be widely acceptable that the sensor response is determined not only by the character of the organic semiconductor films, but also by the morphology of the sensitive films.

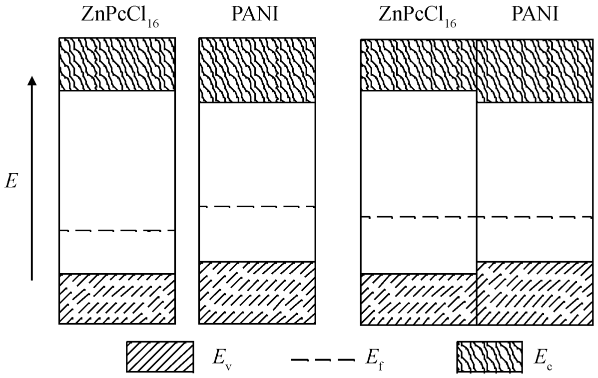


Fig. 6. Presumable energy bands of PANI, $ZnPcCl_{16}$ and the hybrid composites.

3.4. Sensing mechanism of PANI/$ZnPcCl_{16}$ films

As a matter of fact, the interactions of gases with solid MPc film surfaces are complex. Previous mechanistic studies of solid-state gas sensors can be described by one of two mechanisms: the conduction mechanism or molecular interactions. In most cases, atmospheric oxygen has always been considered as being the doping agent mainly responsible for the increase in electrical conductance of the MPcs, but De Haan and Van Faassen *et al.* demonstrated that the main effect of conductance change must rather be attributed to traces (ppm) of strongly oxidizing gases present in air[13, 14].

According to the classical theories, we propose a mechanism of physisorption and electron transfer based on energy band theory. A presumable model of energy bands of PANI, $ZnPcCl_{16}$ and the hybrid composites is depicted in Fig. 6. Although both PANI and $ZnPcCl_{16}$ are p-type semiconductors, their band-gaps are unlikely to be identical to each other and also differ in Fermi level (E_f); when co-working, the Fermi level of both will recombine (using a band-bending model) and ultimately reach the same level. The recombination must strengthen the mobilization of charges between PANI and ZnPcCl$_{16}$ molecules, leading to the redistribution of the charges. Finally, the redistribution of charges and recombination are more likely to change the band-gap and ability of absorbing charges. In the beginning, we assume that the Cl$_2$ molecules absorb only at the air/film interface, and then the formation of charge transfer complexes by coordination of Cl$_2$ to the films at the air/ZnPcCl$_{16}$ interface and at the air/PANI interface gives rise to appearance of the electron and hole charge carriers. Some of these charge carriers will be mobilized across the forbidden gap providing that the energy of these carriers is enough to compensate for band-gap, which brings a shift to the resistance (conductivity) of the sensors. This often happens in the response period, and the recovery is quite the opposite. If this assumption is correct, then it will provide at least a qualitative understanding of the fundamental phenomena in hybrid organic semiconductors.

4. Conclusions

A chlorine gas sensor was made on PANI/ZnPcCl$_{16}$ hybrid films and its sensitivity was investigated under different operation conditions. According to the results, it can be concluded that the stoichiometric ratio of PANI/ZnPcCl$_{16}$, the conditions of film deposition, the operating temperatures and the concentrations of Cl$_2$ gas have intimate relationships with the sensing characteristics of PANI/ZnPcCl$_{16}$ films. When operated at room temperature, PANI/ZnPcCl$_{16}$ films of different stoichiometric ratios showing prejudice to different gases reveal a good selectivity, and in particular a preferable sensitivity to Cl$_2$ gas. By analyzing the sensitivity of PANI/ZnPcCl$_{16}$ films to Cl$_2$ gas, the optimal coevaporation conditions were shown to be a substrate temperature of 160 ℃, an evaporation temperature of 425 ℃ and a film thickness of 75 nm. Either elevating the operation temperature or increasing the gas concentration would improve the response characteristics, but there should be upper levels for each.

To some extent, PANI/ZnPcCl$_{16}$ sensors are superior to the ZnPcCl$_{16}$ sensors we have made before, mostly in reducing the resistance by not less than one order of magnitude and partly in shortening the response and recovery. It clearly appears that the PANI components influence the morphology of the nanocomposite film, which led to the variation of the sensor response-recovery behavior. However, the response and recovery characteristics are still far behind those of the inorganic sensing materials. Therefore, quite a lot of scientific research should be done on these organic semiconductor materials. Further work will be devoted to improving the film preparation of these materials and fabrication of the devices.

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References

[1] Agbor N, Petty M, Monkman A. Polyaniline thin films for gas sensing. Sensors & Actuators B: Chemical, 1995, 28(3): 173

[2] Chengjun Q, Yanwei D, Quanliang Z, et al. Nitrogen dioxide sensing properties and mechanism of copper phthalocyanine film. Chin Phys Lett, 2008, 25: 3590

[3] Fan H, Zhang T, Qi Q, et al. Preparation and C_2H_2 sensing characteristics of Sm_2O_3-doped SnO_2 gas sensors. Journal of Semiconductors, 2008, 29(2): 319 (in Chinese)

[4] Deshpande N, Gudage Y, Devan R, et al. Room-temperature gas sensing studies of polyaniline thin films deposited on different substrates. Smart Materials and Structures, 2009, 18: 095010

[5] Azim-Araghi M, Krier A. The influence of ammonia, chlorine and nitrogen dioxide on chloro-aluminium phthalocyanine thin films. Appl Surf Sci, 1997, 119(3/4): 260

[6] Lim M, Chiang K, Amal R. Photochemical synthesis of chlorine gas from iron (III) and chloride solution. Journal of Photochemistry & Photobiology A: Chemistry, 2006, 183(1/2): 126

[7] Yunbo S, Tingping L, Zan L, et al. Synthesis of organic semiconductor hexadecachloro zinc phthalocyanine and its gas sensitivity. Journal of Semiconductors, 2009, 30(3): 034009

[8] Spadavecchia J, Ciccarella G, Siciliano P, et al. Spin-coated thin films of metal porphyrin-phthalocyanine blend for an optochemical sensor of alcohol vapours. Sensors & Actuators B: Chemical, 2004, 100(1/2): 88

[9] Ceyhan T, Altndal A, Erbil M, et al. Synthesis, characterization, conduction and gas sensing properties of novel multinuclear metallo phthalocyanines (Zn, Co) with alkylthio substituents. Polyhedron, 2006, 25(3): 737

[10] Manigandan S, Majumder S, Ganguly S, et al. Formation of nanorod and nano-particles of polyaniline using Langmuir–Blodgett technique. Mater Lett, 2008, 62(17/18): 2758

[11] Misra S, Chandra S. Electronic applications of semiconducting polymers. Indian Journal of Chemistry Section A, 1994, 33: 583

[12] Taira S, Miki T, Yanagi H. Dye-sensitization of n-TiO_2 single-crystal electrodes with vapor-deposited oxometal phthalocyanines. Appl Surf Sci, 1999, 143(1/4): 23

[13] De Haan A, Debliquy M, Decroly A. Influence of atmospheric pollutants on the conductance of phthalocyanine films. Sensors and Actuators B, 1999, 57: 69

[14] Van Faassen E, Kerp H. Explanation of the low oxygen sensitivity of thin film phthalocyanine gas sensors. Sensors and Actuators B: Chemical, 2003, 88(3): 329