

Comparison of Interaction Mechanisms of Substituted and Unsubstituted Copper Phthalocyanine thin Films towards Organic Vapours

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Abstract—The variations in electrical conductivity of Copper Phthalocyanine (CuPc) with adsorption of chemical vapours allow its utilization as chemical sensors. In the present study we have compared the sensitivities of unsubstituted CuPc and CuPc functionalized with tetrasodium tetraulfonic acid (CuPcS) towards benzene vapours. CuPc is a p-type semiconductor and on its functionalization with this peripheral group, it changes to n-type semiconductor. Therefore, it shows different values of sensitivities towards the same organic vapour. The variations are observed in the response-recovery times of CuPc and CuPcS thin films and also in the sensitivity values. The interaction mechanisms are also studied optically using UV-Visible spectroscopy by taking analysis of as prepared CuPc and CuPcS thin films and after exposure of benzene vapours.

1. INTRODUCTION

Metal Phthalocyanines (MPcs) are organic materials that can be used as chemiresistor sensors, in their metallated, metal free and substituted forms [1]. The electrical conductivity of phthalocyanine thin films can be altered by the presence of small gaseous molecules [2]. MPcs sensitivities to vapour phase molecules may be tuned by modifying or replacing the metal center and by substitution of functional groups on the organic ring [2]. In the present study, we have studied the sensing mechanism of Copper Phthalocyanine (CuPc) and tetrasulfonated tetrasodium salt copper phthalocyanine (CuPcS) towards benzene vapours and found the effect of the functionalized substituent group namely; tetrasulfonic acid tetrasodium salt on sensing of unsubstituted CuPc thin film towards benzene vapours. Benzene and other hydrocarbons are amongst the toxic chemical vapours affecting human health. Therefore, it has become necessary to develop sensors that can detect them and hence prevent their exposure to general public. Benzene is a stable aromatic compound which enables charge transfer with MPcs on account of its electron clouds on its apposite cyclic rings. In our previous work, we have studied the effect of the functional group, tetrasulfonic acid tetrasodium salt on interaction behaviour of unsubstituted CuPc thin film towards methanol vapour [3, 4]. We have

found that CuPcS thin film show increase in current after methanol vapours exposure [4] whereas CuPc thin film show decrease in after methanol vapours exposure [3]. The sensitivity of CuPcS is more as compared to CuPc thin film. The different trends of CuPc and CuPcS thin films towards same vapour is attributed to their different magnetic state as well as different contribution of charge carriers from the substituent group. Therefore, the present study is motivated to compare the interaction mechanisms and sensitivity values of unsubstituted and substituted CuPc thin films towards stable aromatic vapour benzene that is neither reducing nor oxidizing. Benzene participates in charge transfer phenomena by overlapping its electron clouds with CuPc and CuPcS thin films

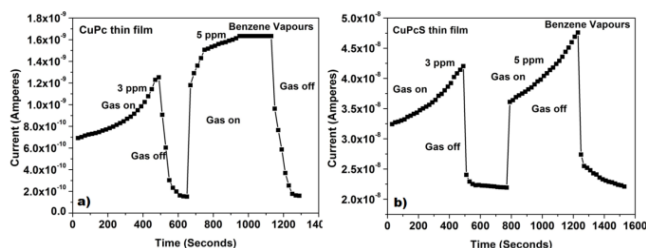
2. EXPERIMENTAL

Copper phthalocyanine (CuPc) powder and Copper phthalocyanine 3, 4', 4'', 4''' tetra-sulfonic acid tetrasodium salt (CuPcS) and benzene have been used without further purification and purchased from sigma aldrich. Thin films of CuPc and CuPcS of same thickness have been prepared using thermal evaporation and drop casting methods respectively [3, 4]. Silver electrodes with 1 mm electrodes gaps are used as contact electrodes for both the films of same thickness. The electrical currents of CuPc and CuPcS thin films under room temperature in dry air atmosphere and vacuum conditions is found to be 6.50×10^{-10} and 3.16×10^{-8} amperes, respectively under the applied voltage of 1 V. These currents were taken as the initial baseline currents. The initial current of CuPcS is more as compared to unsubstituted CuPc. This may be due to the presence of peripheral substituent which has tendency to increase the density of current carriers leading to an increase in current [3-5]. The sensitivity (in ppm⁻¹) and sensing responses (in %) of CuPc and CuPcS thin films have been calculated using same equations as used in our previous works [3-4, 6]

3. RESULTS AND DISCUSSION

3.1 Response-Recovery Curves of CuPc and CuPcS thin films towards benzene vapours

In order to study the effect of benzene vapours on CuPc and CuPcS thin films, we have exposed benzene vapours of 3 ppm and 5 ppm concentrations and ran two cycles of sensing with vapour on and off stages as shown in Figures. 1(a) and 1(b). From Figs. 1(a, b), we observe that there is an increase of currents of CuPc and CuPcS thin films with exposure of benzene vapours and decrease of current during vapour suction stage. This indicates that when benzene vapours bind with central copper ion, they lead to increase in its majority charge carriers. This increase in majority charge carriers is due to charge overlap of electron clouds of benzene with central metal site of CuPc [8]. The response time of CuPc thin film is around 473 seconds at 3 ppm and 277 seconds at 5 ppm concentrations, respectively. This indicates that response time decreases with increase in benzene vapours concentrations.



FIGURES 1 (a, b). Response-Recovery curves of CuPc and CuPcS thin films towards benzene vapours.

The response time of CuPcS thin film at 3 ppm concentration is around 487 seconds and around 438 seconds at 5 ppm concentration. We observe that for both CuPc and CuPcS thin film, response time decreases with increase in benzene vapours concentration. However, response times of CuPcS thin films are more as compared to CuPc thin films. The steady state current values are also reached in shorter time for CuPc thin film, whereas for CuPcS thin film, these values are not achieved even at higher time periods. This indicates that there is delay in interaction mechanism of CuPcS with benzene vapours as compared to CuPc thin film. This delay in the interaction mechanism may be attributed to the steric hindrance effect of the functionalized group attached to CuPcS that does not allow efficient overlap of the electron clouds from the π delocalized orbitals of benzene ring with central metal site of CuPcS [6, 9]. This implies that, the functionalized substituent group may act as an obstacle for effective interaction of benzene vapours with central metal site of CuPcS. In order to confirm our assumption, we calculated the sensitivity and sensing responses of CuPc and CuPcS thin films using equations (1) and (2). The calculated values are listed in table 1. We find that current increases sharply from 3 ppm to 5 ppm concentration. However, the sensitivities calculated using equation (1) is more at 3 ppm concentration

as compared to 5 ppm concentration for both the films. This increase might be due to dominance of vapour-vapour interaction over interactions between benzene vapours and surface atoms of thin films at 5 ppm concentration that leads to diminishing of their sensitivity [4].

Table 1 Sensitivity and Sensing response values of CuPc and CuPcS thin films towards benzene vapours.

Material	S (in ppm ⁻¹)		S %	
	3 ppm	5 ppm	3 ppm	5 ppm
CuPc	0.31	0.30	48	60.3
CuPcS	0.11	0.10	22.6	32.6

3.2 Optical interaction studies of CuPc and CuPcS thin films with benzene vapours

In order to study the effect of benzene vapours on electronic transition levels of CuPc and CuPcS thin films, UV-Vis spectra of CuPc and CuPcS thin films before and after benzene vapours exposure is taken. The spectra of CuPc [6] and CuPcS (Figure 2) thin films show two bands namely B band (Soret band) in the spectral range of 300 nm to 400 nm and the Q-band lying in range of 600 nm to 750 nm. The appearance of Q band is attributed to the π - π^* transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine [5, 9]. The B-band absorptions in the UV region are observed due to the transitions from deeper π levels to the LUMO [9, 10]. From Figure 2, we observe that for CuPc thin film a sharp shoulder band corresponding to Q band is present, whereas no such sharp shoulder band is observed for CuPcS thin film. This band is related to the symmetry of CuPc thin film, which is not present in CuPcS thin film [4,6]. This lack of symmetry in CuPcS thin film is due to the presence of peripheral substituent groups on phthalocyanine rings [3-4, 9-10]. From Figure 2 we observe that there occur more shifts in B and Q bands of as prepared CuPcS thin film after benzene exposure as compared to CuPc thin film [6]. This might be due to lack of symmetry present in CuPcS thin film that leads to more deviations in the electronic transition levels as compared to symmetric CuPc thin film [3-4, 6].

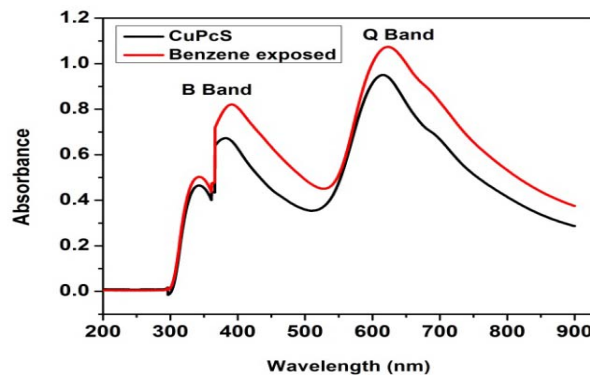


Figure 2. Uv-Visible Analysis of CuPc thin film with and without benzene exposure

Table 2 Variations on B and Q bands of CuPc and CuPcS thin films after benzene exposure.

Material	Absorption band positions (nm)			
	Soret (B band)		Q Band	
	As prepared [3-4, 6]	Benzene exposed	As prepared [3-4, 6]	Benzene exposed
CuPc thin film	341, 368	339, 368	613, 692	615, 694
CuPcS thin film	344, 380	342, 391	614	625

4. CONCLUSIONS AND DISCUSSIONS

Thin films of substituted and un-substituted CuPc of similar geometry and dimensions were exposed to a stable aromatic benzene vapour, whose interaction mechanism is primarily dependent on the central metal site of MPc. The present study highlighted the effect of functionalized group attached to CuPcS in affecting its interaction with benzene vapours. CuPcS in spite of its high mobility of charge carriers leads to comparatively lesser sensitivity as compared to unsubstituted CuPc. This implies that the interaction mechanism in chemresistors is not only dependent on its charge mobilities, but also on its molecular structure constituting the central metal site. Although for methanol vapours, CuPcS showed enhanced sensitivity and preferred over CuPc, but for benzene vapours, it acted as an obstruction for its efficient interaction mechanism. As benzene interaction is strongly dependent on the metal site, therefore metal atoms having high electro-affinity than copper can be preferred for benzene sensing. The functionalized group attached to the MPc ring should be supportive for benzene sensing unlike the functionalized group used in the present case. Therefore, our future aspect will be to tune MPcs in a way to enhance the sensitivity of CuPc towards benzene vapours.

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