

RESEARCH PAPER

Optical Characterizations and Gas Detection Study of Metallo-Phthalocyanine Thin Film Species

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ARTICLE INFO

Article History:

Received 27 March 2022

Accepted 10 June 2022

Published 01 July 2022

Keywords:

Band gap

Copper phthalocyanine

Gas sensing

UV-Visible

Zinc phthalocyanine

ABSTRACT

Copper and zinc phthalocyanines (CuPc and ZnPc) were deposited onto glass slides and platinum-interdigitated electrodes using spin coating technique to investigate the optical properties and sensing capability towards some odorants. The optical properties have been studied using UV-Visible absorption spectroscopy. The red shift in the absorption band in case of thin films indicated that phthalocyanines tend to make aggregation of dimer and trimer in comparison to solution where only monomers exist. Energy gap calculations, utilizing Tauc plot, show that the CuPc and ZnPc having band gaps of 3.87 eV and 3.93 eV respectively and the transition of charge carriers is direct transition. Detection of some gases has been carried out using resistive based sensor measurements. ZnPc has shown no obvious behavior towards chloroform, dimethylformamide and nitrogen dioxide gases, while CuPc was selective to nitrogen dioxide gas and shown very high sensitivity and reversibility. The response and recovery times of copper phthalocyanine thin film due 100 ppm nitrogen dioxide were 20 and 142.6 sec respectively.

How to cite this article

Shaty A A., Banimuslem H A. Optical Characterizations and Gas Detection Study of Metallo-Phthalocyanine Thin Film Species. J Nanostruct, 2022; 12(3):491-502. DOI: 10.22052/JNS.2022.03.002

INTRODUCTION

Phthalocyanines are aromatic organic compounds having semiconducting properties. Besides, they are chemically stable having dense colors suitable to be used as dyes and pigments in textile. In addition, phthalocyanine compounds may have the potential to be used in a variety of studies ranging from electronic devices to sensing applications [1-4]. Copper and zinc Phthalocyanines are currently regarded as optical materials because, it has a good light absorption in the (UV-Vis) region and also can absorb light on side of a blue green region in the spectrum [1,2]. Metal free Pc's contains two hydrogen atoms in the center of the molecule, but the various metal Pc's occur when the hydrogen

atoms are replaced by a single metal atom [5]. A phthalocyanine molecule consists of a central cavity that can accommodate different metal ions, and a phthalocyanine containing one or two metal ions is called a metal phthalocyanine (MPC). Introduction of metal cations (e.g. Zn, Fe, Cu, etc) into the central cavity of Pc molecule influences its physical properties greatly. For example, when a metal cation is introduced to the Pc molecule, the macrocycle exists as dianion and can be oxidized or reduced to different oxidation states. Many metal atoms can fit exactly into the central cavity without destruction of the planar structure of the phthalocyanine, however, some metal ions are too large to be accommodated in the central cavity of the phthalocyanine, causing distortion

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of the planar structure of the macrocycle. The nature of the chemical bonding between the central metal ion and the four nitrogen atoms of the two groups is of interest [6]. Phthalocyanine has become distinguished in material science and nanotechnology because it is thermochemically stable when exposed to high electromagnetic radiation. Importantly, phthalocyanine is remarkably versatile because the two hydrogen atoms in the central cavity allow the incorporation of different alternatives and can be replaced with more than 70 metals. This means that the structure allows adjusting the physical properties. This modification is possible in the periphery of the structure and in the axial locations. Possible structural adjustments can allow the creation of analogues phthalocyanine. Generally, the extension of the π -system, different number of isoindole units, an exchange of isoindole units with other heteroaromatic ring moieties lead to the construction of these phthalocyanine analogues [7]. The emerging functions of MPCs are mainly based on electron transfer reactions resulting from the π -conjugated ring system, interaction of the π -electrons with center metal atoms and the substituents in their structure [8,9]. In this work, CuPc and ZnPc thin films have been optically investigated and employed to utilize as gas sensing devices.

MATERIALS AND METHODS

Zinc 2,3,9,10,16,17,23,24-octakis(octyl)oxy)-29H,31H-phthalocyanine (ZnPc) with purity ~96% and copper(II) 2,9,16,23-tetra-tert butyl-29H,31H-phthalocyanine (CuPc) with purity ~95% have been purchased from Sigma Aldrich. Chloroform was used to dissolve the initials. The concentration has been kept to 5mg/ml.

Thin films of ZnPc and CuPc were deposited by spin coating technique onto the glass substrates ($1^{\circ}25^{\circ}75\text{ mm}^3$) at room temperature and platinum-interdigitated electrodes (IDE). Glass substrates were used to carry out the UV-Visible absorption spectra which were recorded on Shimadzu 1800 UV-visible spectrophotometer. On the other hand, Sensing measurements were performed on films deposited onto interdigitated electrodes and carried out using home made sensing equipment. All substrates have been ultrasonically cleaned with chloroform and deionized water.

Interdigitated electrodes (IDE) were prepared on 1cm by 1cm glass slide using sputtering technique

of type GSL-1100X-SPC16-3. platinum was deposited using stainless steel mask in the argon ambient.

RESULTS AND DISCUSSION

UV-Visible Absorption Spectra. The UV-vis spectrum observed for phthalocyanines originates from molecular orbitals within the aromatic 18 π electron system and from overlapping orbitals on the central metal atom [10]. A close examination of this band shows the characteristic splitting (Davydov splitting) present in all phthalocyanine derivatives [11]. The high-energy peak of the Q-band has been assigned to the first π - π^* transition on the phthalocyanine macrocycle [10]. The low-energy peak of the Q-band has been previously explained as a second π - π^* transition [10,12]. In the high-energy region of the B (Soret) band near 300 nm, the main suggestion of the large differences occurring in the absorption spectra of the phthalocyanines in this region indicate the presence of a d - band associated with the central metal atom. It is thought that π -d transitions are involved since strong absorption occurs near 320 nm, the V peak, in CuPc and the other metal phthalocyanine derivatives [13]. This is because CuPc has partially occupied d-bands. The absorption bands in the region of 275–210 nm, the S-band, may be due to d- π^* transition [10,12]. Which implies a broader d-band. UV-Vis absorption spectra of the copper, zinc phthalocyanines solution in chloroform are shown in Fig. 1. Absorption peaks at UV and visible light regions are due to B and Q bands, respectively. The absorptions of Q-band have two peaks at approximately 615nm and 695nm and the relative intensity of absorption at 615nm was smaller than that at 695nm, these two peaks are due to the monomer and aggregate of CuPc, ZnPc, respectively [13]. In the Q band, an intense absorption peak at 695nm is due to the transition between the bonding and antibonding (π - π^*) at the dimer part of the phthalocyanine molecule. Copper atom of the phthalocyanine molecule is associated with the d-band. Therefore, within the UV region of the spectrum, a strong absorption peak at 335nm is attributed to partially occupied d - π^* transitions. The variations in absorbance with B band are greater than the variations in Q band. In case of Zn phthalocyanine, in the Q-band the electronic transition occurs from higher occupied molecular orbital (HOMO), which

has an electronic density mainly located on the phthalocyanine molecule, to the lower unoccupied molecular orbital (LUMO), which has a small electronic density on Zn–N bond. The B-band electronic transition occurs between HOMO-4/LUMO orbitals. The electrostatic potential surface and contours of ZnPc, where the $+\delta$ and $-\delta$ charges are residing on Zn and on N-atoms, respectively. The electrostatic potential surfaces can give us an idea about how the ZnPc molecules are stacking in the nanostructure system. The most probable aggregation in the system is the H-aggregation due to high energy shift in the absorption spectrum.

The absorbance spectra for ZnPc CuPc, in case of thin film (100 nm thickness) was recorded and compared as shown in Fig. 2. The Figure shows that both of two spectra have two band in the visible region which is Q-band at the range about 523-775nm, and by comparison to the results of the ZnPc,CuPc solution, It produces a little red shift. In addition, the peak that assigned to aggregations of dimer and trimmer molecules in the thin films

became more intense in comparison to monomer peak which was higher in the solution. That could be explained by the fact that, in the solid case, phthalocyanine tend to form more aggregation of dimer and trimmer chain of molecules instead being monomers.

The best transmittance is at room temperature and that is conformable to the results of absorption spectra, also there is two bands; Q and B. The Q is in the region of 628-695nm and B band at the wavelength of 340nm as shown in Fig. 3. The transmittance spectra for CuPc thin films, having UV- exposure intensity are shown in Fig. 4, which shows that the maximum transmittance value of CuPc is at the range of 390- 540nm, while at ZnPc, the maximum transmittance value is at the range of 350- 555nm. The transmittance decrease clearly with UV- exposure intensity increasing for both B and Q band, where the increase of UV- irradiation led to increased absorbance and therefore cause a decrease in the value of transmittance [14]. From the transmittance values, the refractive index (n)

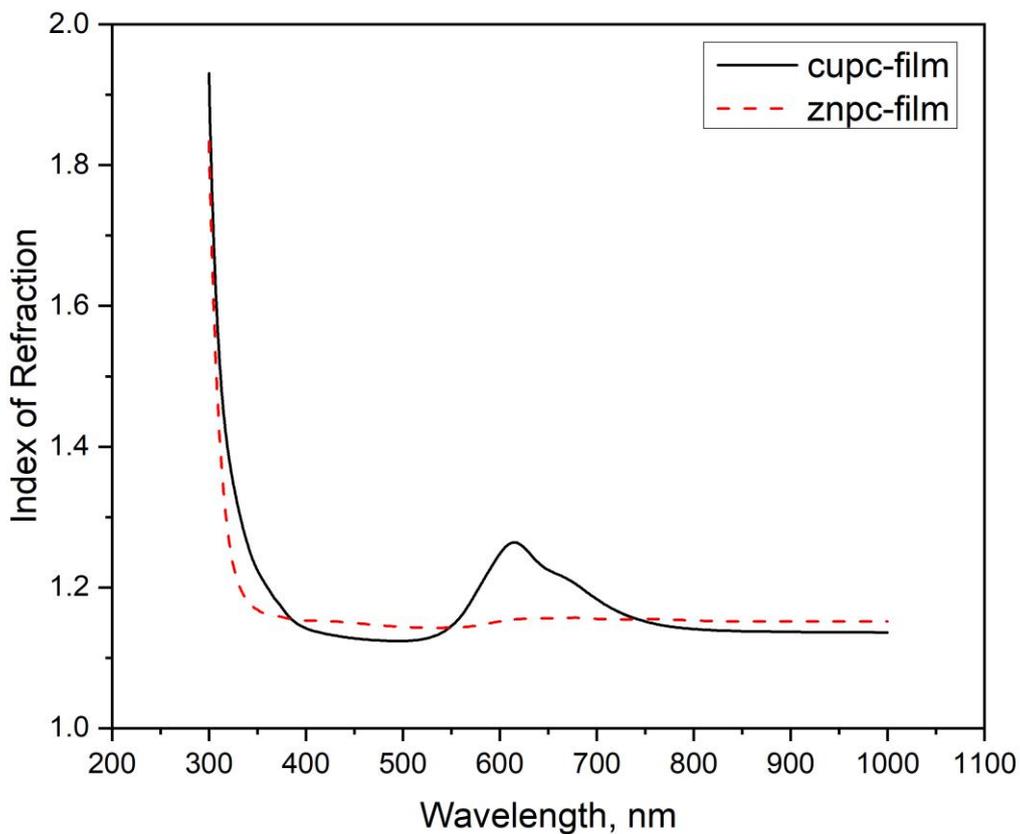


Fig. 1. Absorption spectra of CuPc and ZnPc solution in chloroform.

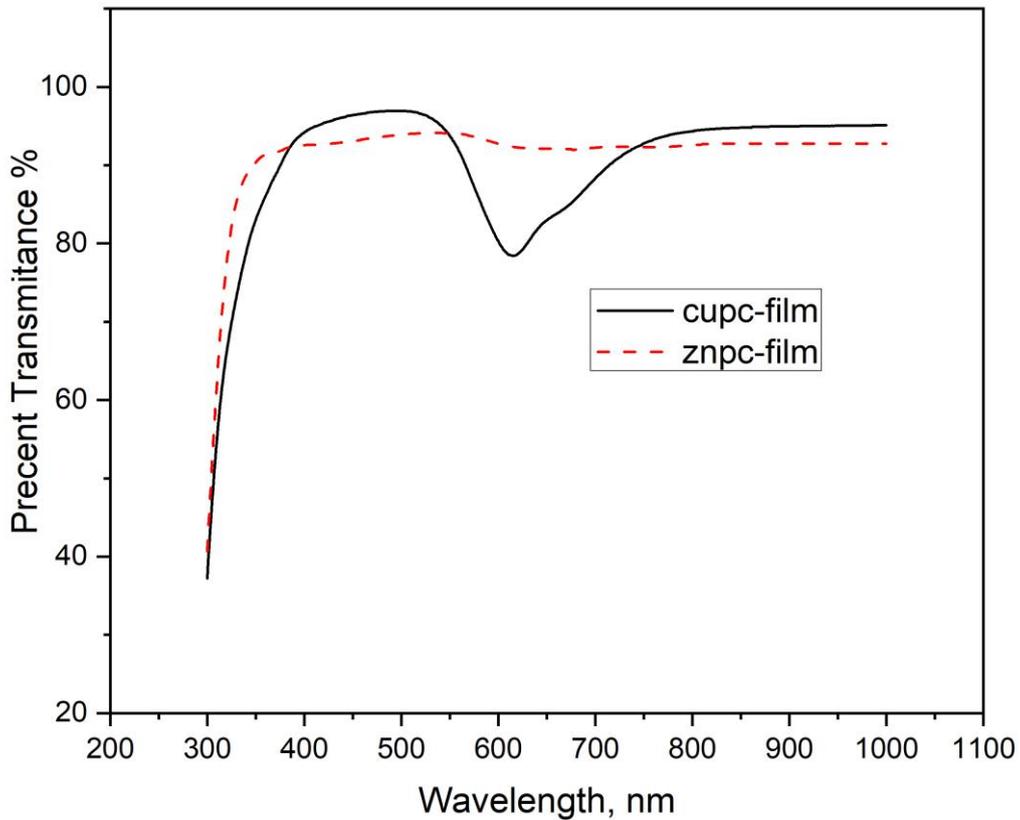


Fig.2. Absorption spectra of CuPc and ZnPc thin films deposited on glass substrate using spin coating technique.

were calculated using the following equations:

$$n = \frac{1}{T_s} + \sqrt{\frac{1}{T_s} - 1} \quad (1)$$

$$T_s = 10^{-A} \times 100 \quad (2)$$

Where T_s ; transmittance, n ; refractive index, A ; absorbance.

In Fig. 5, solid line shows the variation of refractive index at wavelength range 550-750nm, the behavior of refractive index change of preparation conditions and method used in preparation. From this Figure, slightly increase in refractive index in CuPc upon λ of 745nm to 618nm, and then started to decrease until λ equals to 538nm. These findings are reported previously [14]. The absorption coefficient (α) were determined from the region of high absorption using the equation [15]:

$$\alpha = 2.303(A/t) \quad (3)$$

Where t is the thickness of thin films (nm). α is the absorption coefficient ($1/\text{cm}$).

The absorption coefficient helps to conclusion the types of electronic transitions. When the values of absorption coefficient are higher than ($\alpha > 10^3 \text{ cm}^{-1}$) at high photonic energies, direct electronic transitions are expected and the electron momentum energy is conservation, but when the values of the absorption coefficient are lower than ($\alpha < 10^3 \text{ cm}^{-1}$) at low photonic energies, indirect electronic transitions are expected, in which the momentum of electron and photon are conservation with the help of a phonon [16]. The maximum wavelength (λ_m) of the incident photon which creates the electron-hole pair is defined as [17].

$$h\nu = \frac{1240}{\lambda m} \quad (4)$$

The optical energy gap values (E_g) for CuPc ZnPc, thin films have been determined by using

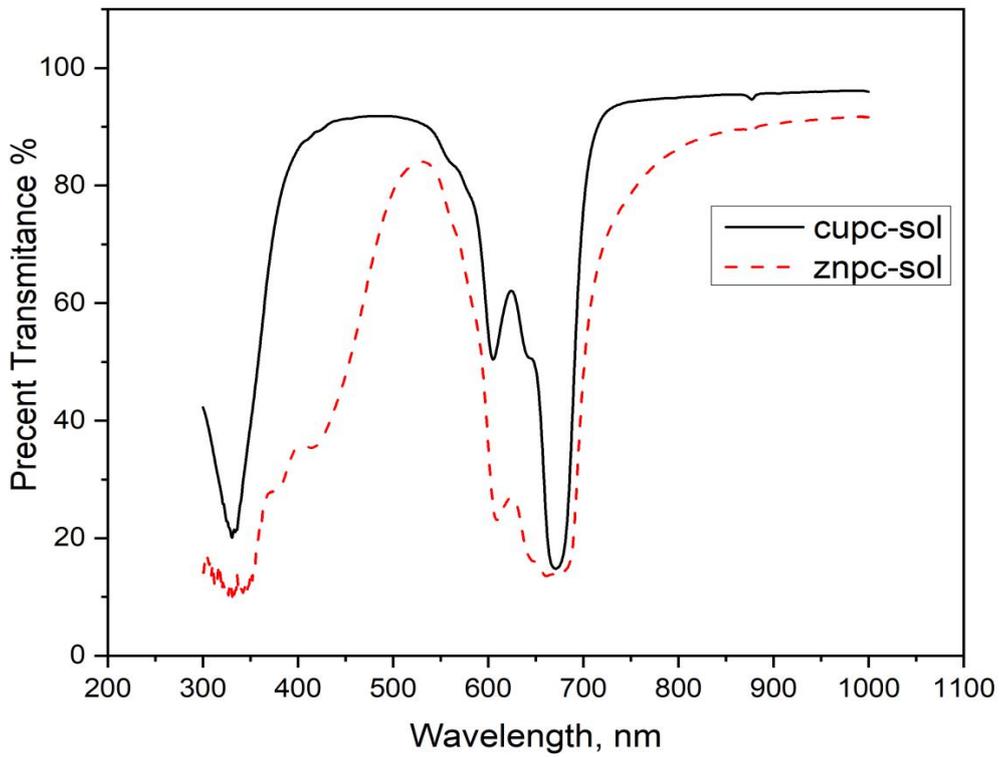


Fig. 3. Percent transmittance spectra of CuPc and ZnPc solution in chloroform.

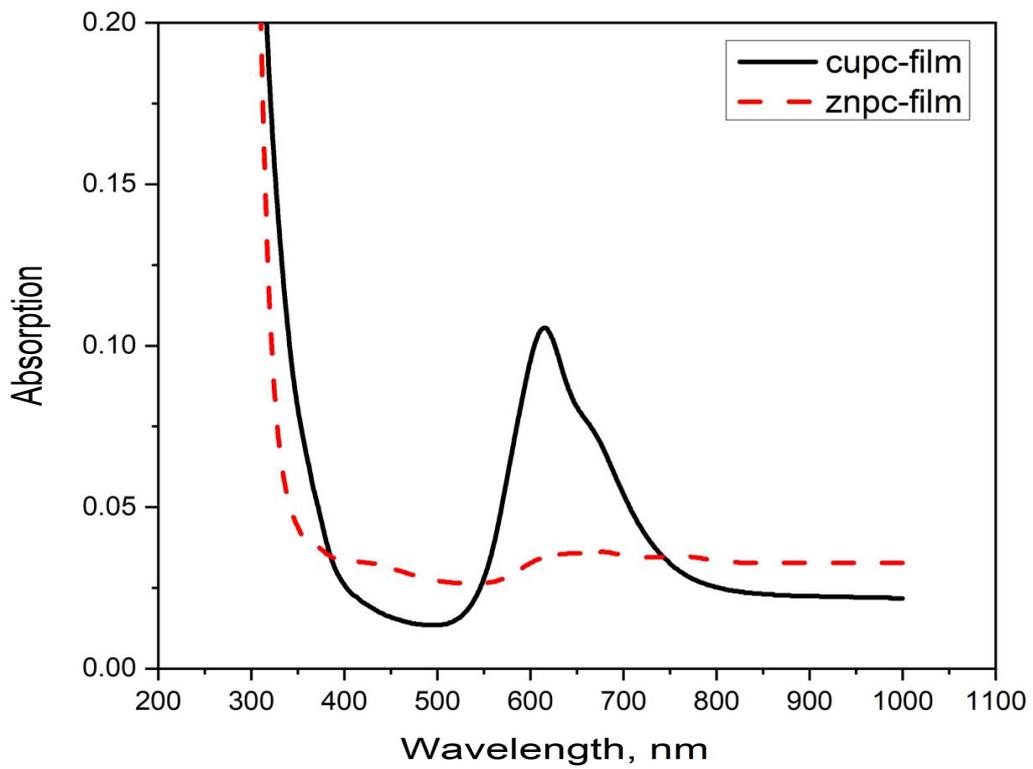


Fig. 4. Percent transmittance of CuPc and ZnPc thin films deposited on glass substrate using spin coating technique.

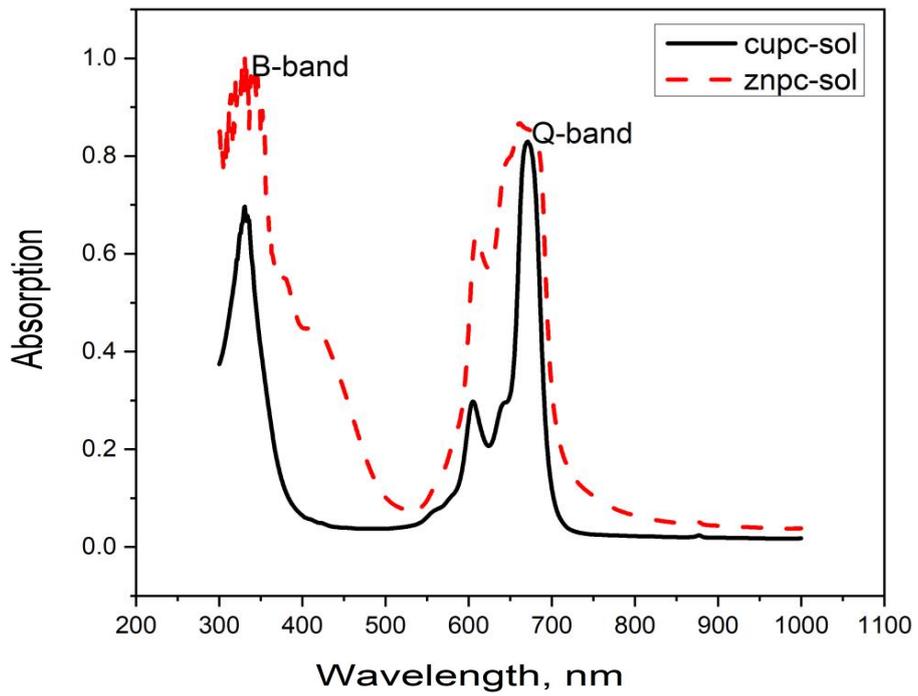


Fig. 5. Index of refraction of CuPc and ZnPc thin films deposited on glass substrate using spin coating technique.

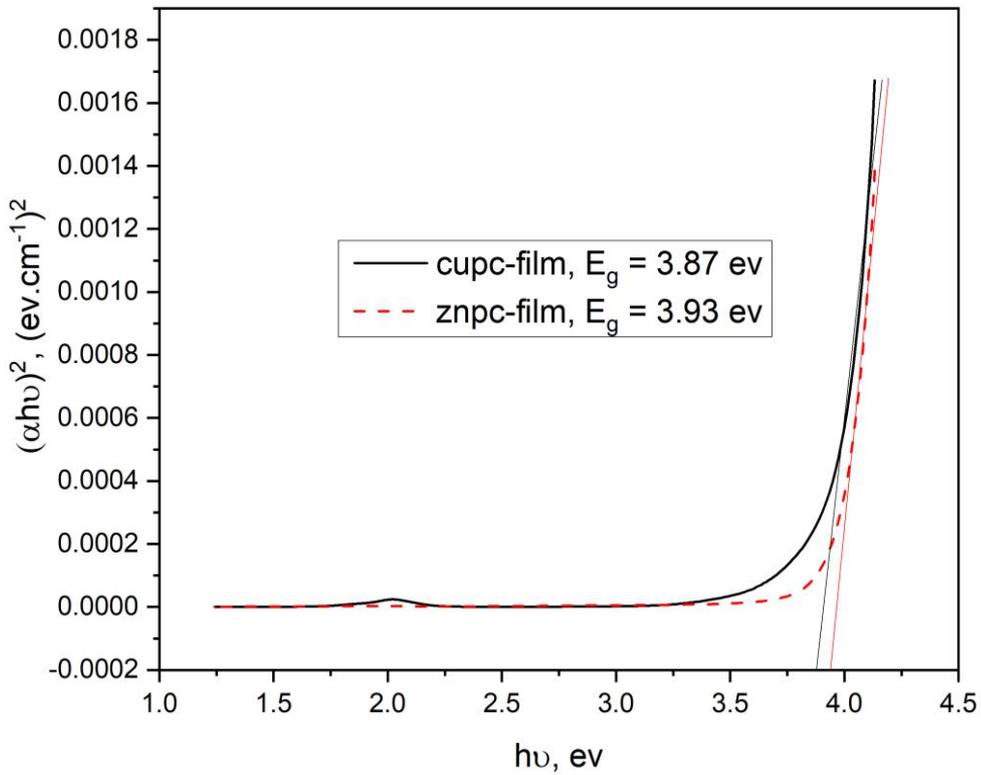


Fig. 6. Tauc plot and optical energy gap calculations of CuPc and ZnPc thin films deposited on glass slides using spin coating technique.

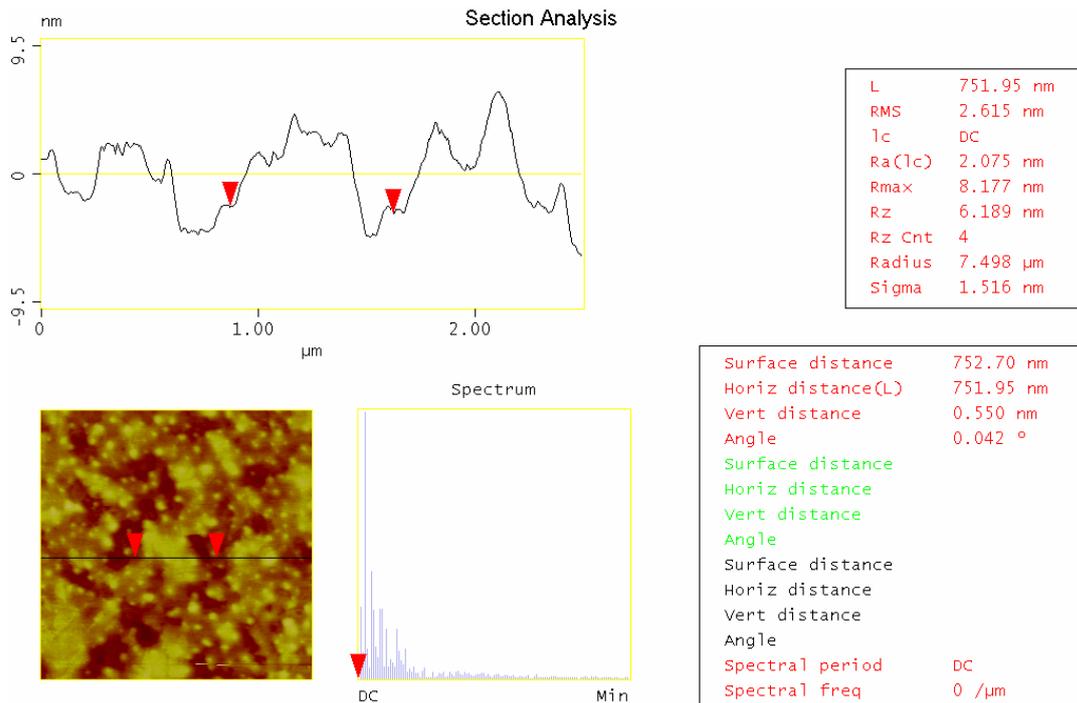


Fig. 7. AFM image and analysis of CuPc thin films deposited on silicon substrate using spin coating technique.

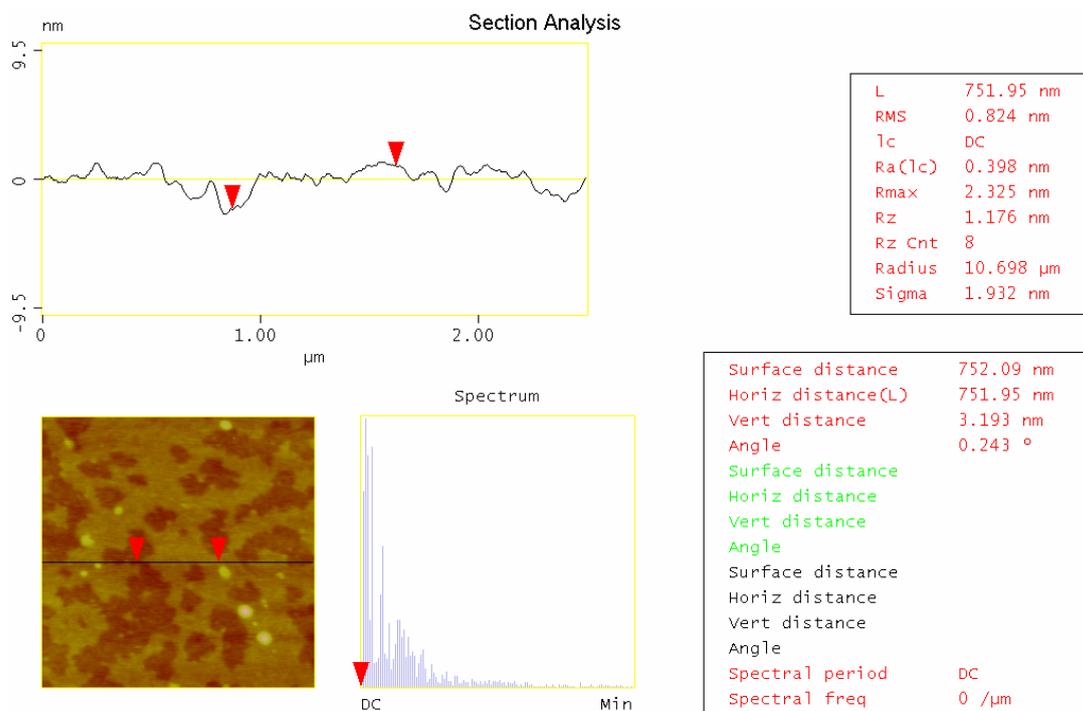


Fig. 8. AFM image and analysis of ZnPc thin films deposited on silicon substrate using spin coating technique.

Tauc equation [18]:

$$\alpha h\nu = B(h\nu - E_g)^2 \quad (5)$$

For an allowed direct transition, the transition

occurs from the top of the valence band to the bottom of the conduction band. When graphing the relation between each of the $(\alpha h\nu)^2$ with photon energy of incident radiation, through which it is possible to calculate the value of

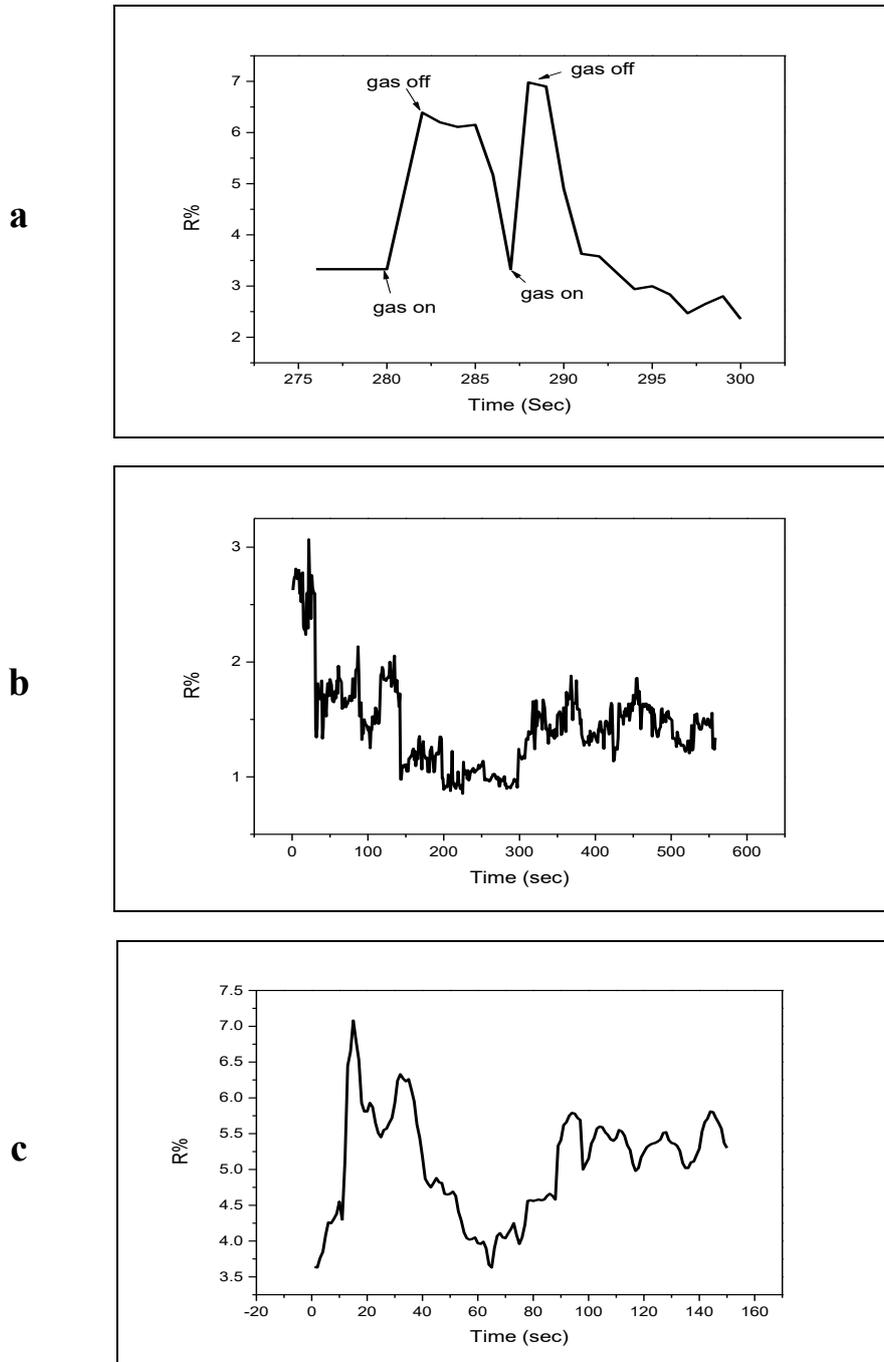


Fig. 9. Response vs. time of ZnPc deposited on interdigitated electrodes at room temperature for NO_2 (a), Chloroform(b), and DMF(c) vapors at 100 ppm.

allowed direct energy gap, and best graph obtained that can be the extension of the straight line that intersects the $h\nu$ - axis to determine the value of energy gap for allowed direct transition of the ZnPC, CuPC thin films, as shown in the Fig. 6,

and the values of energy gaps was 3.87 eV, 3.93eV respectively. Similar findings have also been reported elsewhere [18]. Fig. 6 shows a linear change at high energy range did not appear with the other curves, which indicates the occurrence

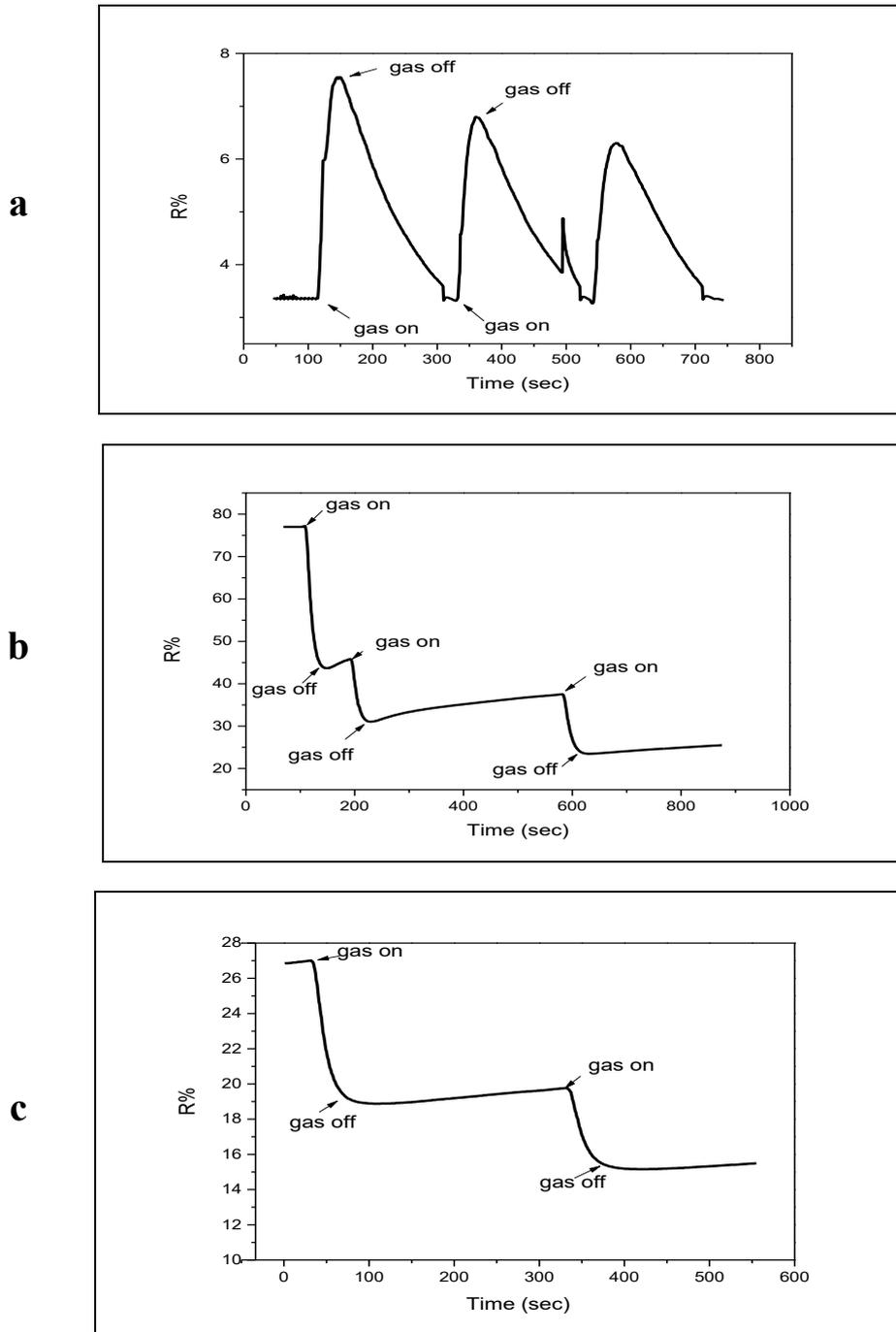


Fig. 10. Response vs. time of CuPC deposited on interdigitated electrodes at room temperature for NO_2 (a), Chloroform(b), and DMF(c) vapors at 100ppm.

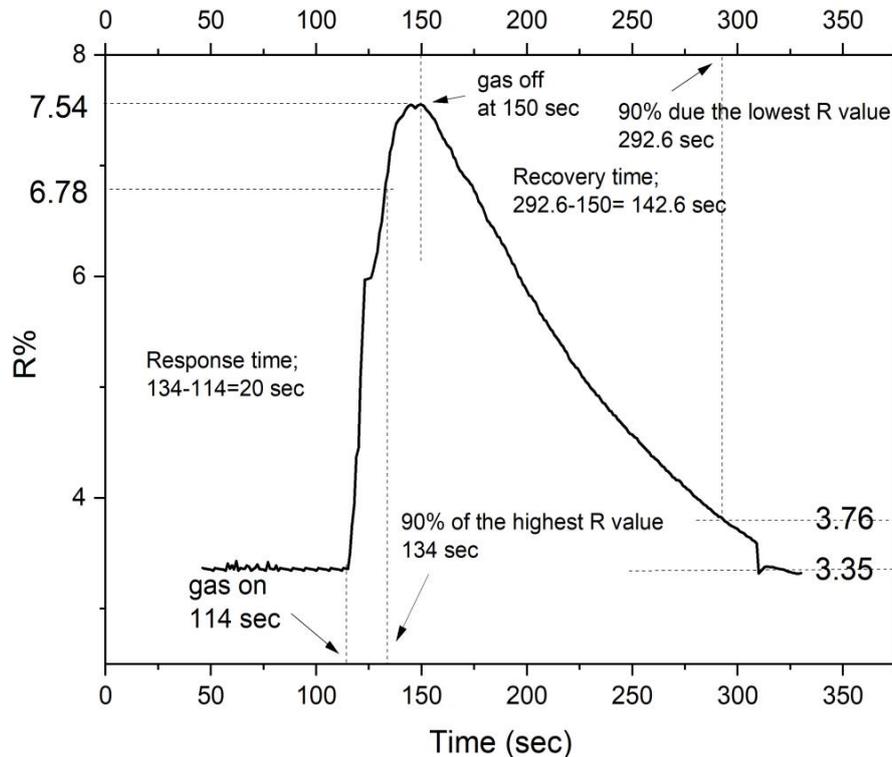


Fig. 11. Response and recovery times of copper phthalocyanine film upon exposure to NO_2 .

of the allowed direct electronic transition in the prepared films. There are variation between energy gap values and it is impact by mechanism a formation thin films and conditions accompanying the preparation process. Energy gap value and type depends on crystal structure of material and how atoms distribution in crystalline lattice and the levels energy structure, this mean that any change in structure properties can being caused by the change occurring of energy gap and transitions type which occurring in thin films [19].

Figs. 7 and 8 show AFM images of CuPc and ZnPc films spun onto silicon substrates with the roughness analysis presented AFM measurements in tapping mode have been performed on all samples in this study. Typical fibre features of phthalocyanine has been obviously seen in the films, which is similar to the topology of phthalocyanine and almost all organic dyes which tend to make very dense aggregations in the solid state. These aggregates are represented as a coplanar association of rings developing from monomer to dimer and higher order complexes and are driven by π - π interaction and van der Waals forces [4].

In present work, the sensitivity of CuPc and ZnPc devices were studied during exposure to 100 ppm concentration of chloroform, dimethyleformamide and nitrogen dioxide odorents at room temoerature. The samples were fixed in a special per- evaluated chamber. After that gaswas separately introduced to the chamber. The change in resistance ratio R_g/R_a (where R_g is the resistance in the present of gas and R_a is the resistance in zero grade air) on exposure to contaminated air at room temperature for 10 s. ZnPc have shown no obvious behavior towards contaminations as exhibited in the time dependence Fig. 9. Zn atom is a little bigger than the cavity of phthalocyanine, results in a deviation in the position from the plane of the molecule. Consequently, hindering of orientation took place and the adsorption of odorant would be random and not reversible. On the other hand, CuPc thin film has shown quite reasonable performance towards gases and presented in Fig. 10. From this Figure, the response of CuPc film to NO_2 gas was oposite to other gases which makes it selective to this particular gas. The reason for the decrease in resistance of the devices can be understood in

terms of a change in the surface conductivity of thin films. Such effects can be interpreted within the framework of the band theory. If we consider the adsorbed gases to produce appropriate donor or acceptor levels within the band gap of the organic materials at the film surface. CuPc and ZnPc are a p-type organic semiconductor, upon exposure to the oxidizing gases such as O_2 , the hole concentration near the surface will be enhanced through a doping mechanism, resulting in the increase of electrical conductivity[20]. In the case of chloroform and DMF odorants,

film resistance decreased rapidly and no reversibility occurred. The recovery rate of the film resistance was slower and did not recover to the original value before exposure. The present recovery characteristic is less than that in a previous work operated at the same temperature [21]. These results confirm that the sensitivity of phthalocyanine as gas sensor depend on different factors such as ambient condition, method of device fabrication, sensing temperature and the type of central metallic element. The response and recovery times have been calculated as 90% of the highest R value and 90% due the lowest R value and found to be 20 sec and 142.6 sec respectively. Fig. 11 represent clearly the calculations of both response and recovery times.

CONCLUSION

Thin films of zinc and copper phthalocyanine have been prepared in the mean of spin coating mechanism. UV-Visible spectra have revealed that thin film has shown a little red shift in the position of Q band in comparison to solution spectra and formation of dimer and trimer molecules instead of being monomers. The optical energy gaps were found to be 3.87 eV and 3.93 eV for copper and zinc phthalocyanine respectively. Films of copper phthalocyanine have been quite sensitive and selective to nitrogen dioxide gas while zinc phthalocyanine performed randomly upon exposure to contaminated ambient.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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