EFFECT OF THE CHLOROFORM AS A CHEMICAL TREATMENT ON GAS SENSING FOR CuPcTs/Alq$_3$ THIN FILMS

GHADA A. KADHIM, MAHDI A. MOHAMMED[*]
Department of Physics, College of Science, Wasit University, Al Kut, Iraq

The effect of chemical treatment by chloroform at different immersion time values of 30, 50, and 70 min has been studied on the structural, morphological, electrical properties, and gas sensitivity against NO$_2$ gas for CuPcTs/Alq$_3$ thin films. The X-ray diffraction (XRD) was shown that the crystal size decreased from 4.8 to 2.7 nm with increasing immersion time to 50 min and then transferred to amorphous at 70 min. The atomic force microscopy (AFM) measurements for the untreated and chemically treated films with chloroform was shown that the average particle diameter decreased at 50 minutes of immersing time and then increased at 70 minutes. At 50 minutes of treatment time, the electrical properties of the thin films improved and the gas sensor measurements for NO$_2$ were shown the best sensitivity at 373 K.

1. Introduction

Copper Phthalocyanine (CuPc) is one of the metal phthalocyanines (MPc) [1]. It is a p-type semiconductor and has the feature of being suitably stable towards heat and chemical treatment. In general, Phthalocyanines are difficult to dissolve in solvents, such as deionized water, methanol, ethanol, etc. However, to dissolve the MPc in solvents, various functional groups have joined. Phthalocyanine, (CuPcTs) is one of the organic semiconductors and a typical example of water-soluble phthalocyanines. CuPcTs have a structure similar to that of CuPc except the polar (SO$_3$Na) connects in the corners of the benzene rings, which makes the compound dissolves in water [2, 3]. Aluminum tris(8-hydroxyquinoline) (III) (Alq$_3$) is widely used in photovoltaic devices due to its excellent thermal and electronic properties. It has been used successfully as an electron-emitting layer and/or transporting layer. Lately, the use of Alq3 and its derivatives in organic solar cells as buffering and/or dopant layers has been reported to increase the lifetime and the efficiency of the cell. Alq3 can be in two diverse geometric isomers: facial and meridional. As the optical properties of materials can be calculated using computer software [4, 5], LUMO and HOMO levels are predicted for the two isomers that are expectant to influence the injection barrier and could labor as traps for charge carriers [6-9].

The organic and donor materials are the most promising materials for use in many bi-layers or bulk heterojunction applications. The properties of organic semiconductor materials can be improved either by heating treatment [10, 11] or by chemical treatment [12, 13]. The process of immersing low solubility solvents may improve the topographical, optical, or electrical properties of the samples. This occurs by increasing the absorption of light or transferring the charge or altering the roughness of the surface which may improve the machine performance that depends on the ingenuity of these qualities [14]. Verification of the use of organic matter is a broad area of research for the development of different sensor types due to the diversity of its properties and the large chemical stability of many of them [15, 16].

The most important factors that the chemoresistance gas sensor works on are the sensitivity and rapid response at low gas concentrations. Sensitivity is the ability of a device to detect the difference in a chemical or/and physical property of the sensing substance under gas exposure with a certain gas concentration. The percentage of sensitivity (S) can be determined in

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[*] Corresponding author: mahmed@uowasit.edu.iq

many ways, (a) (S = Resistance of air/Resistance of gas), (b) S = 100 $\times$ (R_{air} - R_{gas})/R_{air} or (c) S = (conductance of gas – conductance of air)/ conductance of air $\times$100 [17]. Response time is the time required for a gas sensor to reach 90% of the total response of the signal. Recovery time is the time required for a gas sensor to return 90% of the original baseline signal upon removal of the target gas [18]. Polymers are characterized by chemical or physical adsorption properties that are different from inorganic materials and are sensitive to the deposition process and chemical treatment [19].

The selection of organic compounds spin-coated thin films as sensing layers offer assistance in the device's sensitivity perfection via change molecular structure through structural modification. Several components have been investigated for the sensing of nitrogen oxides NO_x, such as PbPc [20], WO_3 [21], and Zn_2SnO_4 [22]. Experimentally, the thin metal layers of CuPc, NiPc, and PbPc phthalocyanine were made using a plasmon resonance spectrometer, which is an optical technique and can monitor physical and chemical processes. This method was sensitive to detect small changes in dielectric properties within the metal-phthalocyanine boundary as a result of exposure to the target gas. The sensitivity was found to be dependent on the thickness of layers [23].

Gas sensors are mainly based on the adsorption of gases on the sample surface [24]. The fundamental of the gas response of chemoresistance sensors mechanism depends on the bound of electrons by the oxygen molecules that are absorbed and cause the bending of energy bands upward. This is because the electrons captured on the surface in the form of negative ions and the formation of a depleted electron zone cause a change in the electrical conductivity of the semiconductor compared to the flat band [25]. The interaction of gas with oxygen or competitive adsorption reduces and can reflect the bands' curvature, leading to increase conductivity due to the release of electrons within the material [26].

NO_2 is considered to be risky to the environment and human health. Therefore, the development of sensors to detect NO_2 gas is very important. In our research, the NO_2 gas was selected and found to be good sense to the materials that make up the compound separately (CuPcTs, Alq_3) better than the rest of other gases.

2. Experimental

2.1. Materials
CuPcTs, Alq_3, and chloroform were bought from Sigma-Aldrich.

2.2. Synthesis
5 ml of both CuPcTs and Alq_3 were mixed in 10 mg/ml of chloroform using a magnetic stirrer about 30 min at 40 ^{o}C to obtain CuPcTs/Alq_3 solution that was then filtered by 0.4 µm filter. The final solution was used to prepare thin films on glass substrates by the spin-coating technique at 700 RPM, and then the films were dried at room temperature. Thin films were immersed in chloroform at different time values (30, 50, and 70) min to study the effect of chemical treatment on optical, morphological, and gas sensing for the blend thin film.

After the chemically treated, films were left to dry at room temperature. Sufficient time was needed to absorb the solvent deeper into the material, but the longer time may cause dislocation of some deposited substance and negatively affected film properties.

2.3. Characterization
The structural parameters for the blend thin film were analyzed using XRD system model Shimadzu XRD 6000 with Cu (Kα) X-ray tube. Shimadzu FTIR was used to study the effect of chemical treatment on chemical bonds. Sample surface morphological was examined using the CSPM AFM spectrometer to calculate the average particle size.

2.4. Examination of gas sensor
Samples were examined as gas sensors against oxidized gas (NO_2). Throughout the experiment, the humidity, volume of the test chamber, and the flow rate of the gas were constant,

which were 50%, 5301.44 cm^3, and 60 pmm, respectively. The concentration of gas ratio was adjusted by two flow-meters to be 5% of incident air inside a chamber vacuumed by a rotary pump. The electrical resistance of the sample was measured by the multimeter, which is the probe to sense the target gas flow and is connected with a computer as shown in Fig. 1. The sample temperature was controlled by a hot plate heater. The thermometer and automatic thermostat controller were used at different temperatures to find the optimum working temperature for a gas sensor to satisfy the suggested sensing mechanism.
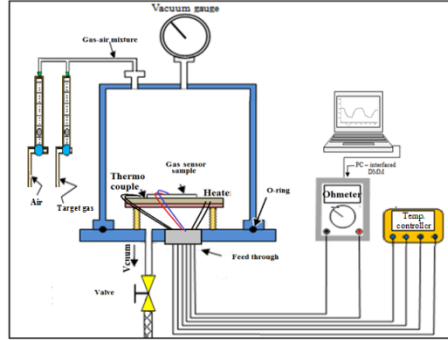

Fig. 1. Gas sensor examination system.

3. Results and discussion

Fig. 2 shows the XRD patterns for as-deposited CuPcTs/Alq3 blend thin films on a substrate of glass and chemically treated with Chloroform at various immersing time values (30, 50 and 70 min). This figure illustrates that the 001 peak increases at 50 min immersing time then decreases with increasing the immersing up to 70 min due to absorbing the liquid and penetrates deeper into thin films. This causes to break the bonds and leads to increase amorphously. The broad peak of each immersing time, which begins from 15° to 35°, refers to the glass substrate. Most chemical treatment solutions affect the surface properties and depend on the granular size of the solution. In this research, the chloroform solution entered the material because it contained small particles and led to break material chemical bonds. Therefore, when we increased the immersion time, it led to a decrease in the crystallite size. This behavior agrees with the reference [27]. The average crystallite size was calculated using the Scherrer formula [28-30]

$$G.S = \frac{k\,\lambda}{FWHM\,.\,cos(\theta)} \tag{1}$$

where k is a shape factor for average crystallite that equals 0.9, θ is the angle between the incident and reflected rays and λ is the wavelength of the X-ray, which is 1.54 Å for Cu target.

The calculated FWHM and average crystalline size (G.S) are given in Table 1. The table shows that the crystallite size decreases with increasing immersing time to 50 min. After this time, the material converts to amorphous.
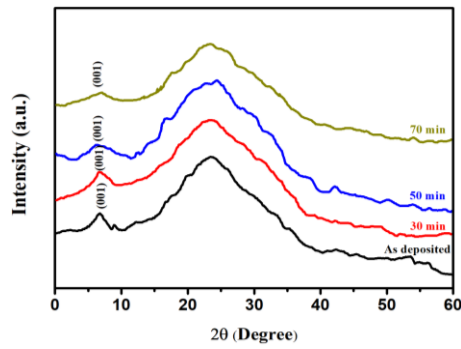
*Fig. 2. XRD analysis of the CuPcTs/ Alq₃ thin films chemically treated
at different immersing times by chloroform.*

*Table 1. The (FWHM) and (G.S) of the CuPcTs/Alq₃ thin films chemically treated
with chloroform at different time.*

Time (min.)	2θ (Deg.)	FWHM (Deg.)	G.S (nm)	phase	hkl
As deposited	6.65	1.650	4.8	CuPcTs	(001)
30	6.93	2.321	3.4	CuPcTs	(001)
50	7.014	2.981	2.7	CuPcTs	(001)
70	Amorphous				

Fig. 3 shows AFM images and the particle size distribution of the CuPcTs/Alq₃ blend thin films deposited on glass substrates via a spin coating method and chemically treated with chloroform at different time values.
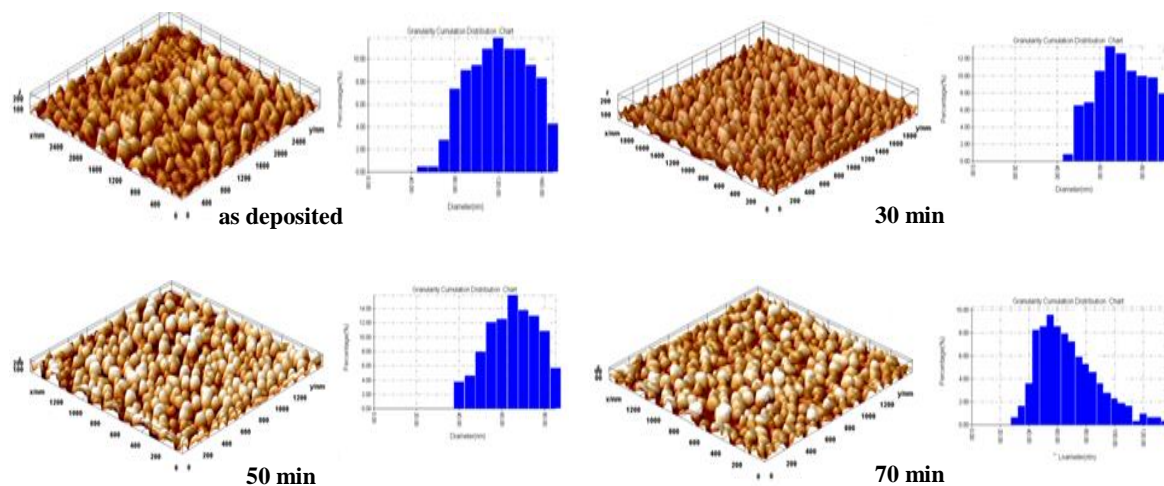

*Fig. 3. AFM measurement of the CuPcTs/Alq₃ blend thin films immersed in chloroform at different
time values.*

Table 2 illustrates the variation of average particle diameter and surface roughness for the AFM examination test of the CuPcTs/Alq₃ with different chemical treatment times. From the table, the average particle diameter drops from 111.22 to 65.12 nm at 50 minutes' immersion time in chloroform then increasing to 98 nm at 70 minutes. Increased immersion time reduces granular

size and increases roughness as well, thus leads to increase sensitivity and reduces response time and recovery time. However, surface roughness has reverse behavior. As a result of decreasing the particle size and increasing the surface roughness (i.e. increase surface area exposure to gas target), traps are created to capture O after exposure to the target gas. Because the thin film material is of n-type, the electrons in the material combine with the positive charges, so the resistance increases, which leads to an increase the sensitivity [31].

Table 2. AFM parameters of the CuPcTs/ Alq$_3$ thin films immersed in chloroform at different time values.

Time with chloroform (min)	Average diameter (nm)	RMS roughness (nm)	Peak-peak (nm)
As deposited	111.22	0.56	3.76
30	80.43	0.86	5.22
50	65.12	1.05	2.42
70	98.73	0.99	3.90

Fig. 4 demonstrates the FTIR patterns of the CuPcTs/Alq$_3$ thin films at different treatment time values in the chloroform. The observed bands were matched with the characteristics values for Phthalocyanine [32]. The peaks appear at 3940.03, 3901.88, 3843.47, 3749.25, 3706.42, and 3660.48 cm^{-1} for the N-H bond. The peaks of 3365.43, 3419.07, and 3433.09 cm^{-1} belong to the O-H bond, and the peaks of 2912.13, 3923.18, and 3038.28 cm^{-1} refer to the C-H stretch. The 1619.40, 1677.09, 1716.02, and 1778.38 cm^{-1} peaks are for the C=C aromatic bond, and the 1346.6, 1402.2, 1441.14 and 14467.6 cm^{-1} are for the C-N bond. The peaks of 1163.14 and 1244.90 cm^{-1} correspond to the C-C bond. The peaks of 1105.51 and 1067.53 cm^{-1} are for C-O and S=O bonds, respectively. The 649.18, 699.80, 752.75, 796.36, 900.71, and 1037.76 cm^{-1} are shown for C-H out of plane bend vibration, and the 418.86, 428.03, 461.51, and 498.11 cm^{-1} are for Cu-N bond. Other peaks appeared in the range at 2024.39, 2087.47, 2108.50, 2147.43 and 2205.84 cm^{-1} correspond to triple C≡C bond, which is stronger than the C–C single bond or the C=C double bond [33], and in the range at 2340.55, 2417.65, 2465.93, 2526.67, 2623.23 and 2747.8 cm^{-1} correspond to triple C≡N bond [34] as a result of making the blends. The peaks that correspond to both the triple C≡C and C≡N bonds are weak with chemical treatment. Also, the peak intensities that belong to the O-H bond increase with immersing time values, but other bonds decrease.
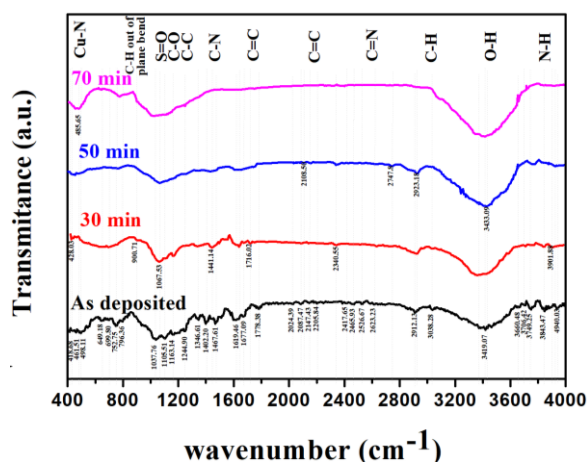

Fig. 4. FTIR of the CuPcTs/Alq$_3$ composite thin films chemically treated with chloroform at different time values.

Hall effect measurements for CuPcTs/Alq$_3$ thin films show that all films behave as n-type. Table 3 shows the many important parameters: carrier concentration (n), mobility (μ_H), and conductivity (σ). The electric carrier concentration increased with immersing time to 50 min in chloroform and then decreased at 70 min while electron mobility decreased with immersing time.

Table 3. Hall effect measurements for the CuPcTs/Alq$_3$ blend on glass slides immersed in chloroform with different time values.

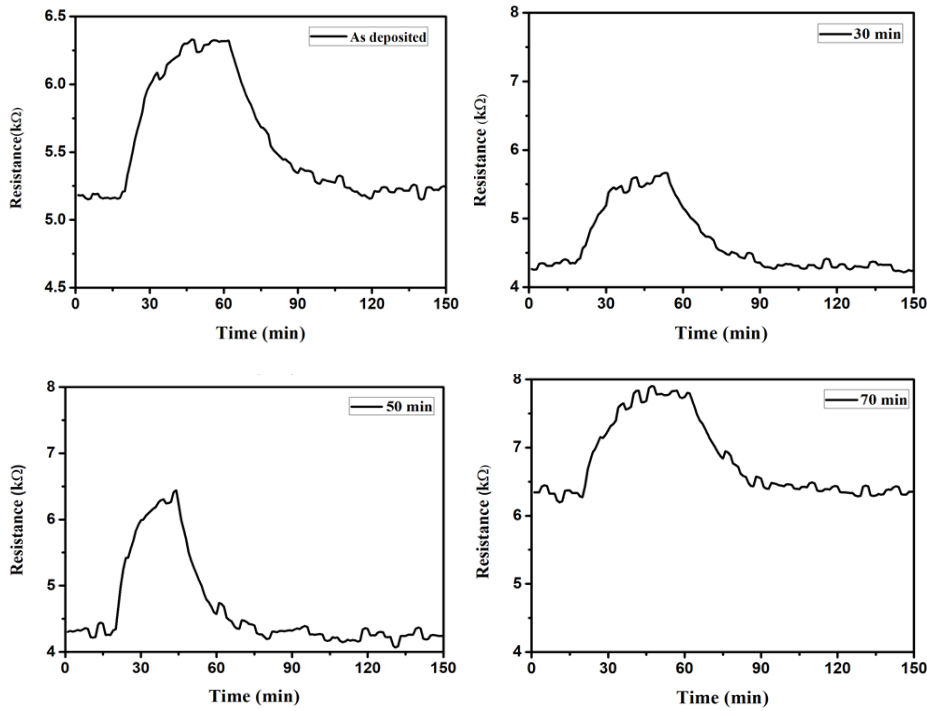| Immersing time in Chloroform (min.)	n×10^{15} (cm^{-3})	μ_H (cm^2/v.sec)	σ_{RT} ×10^{-2} (Ω^{-1}.cm^{-1})
As deposited	6.50	16.35	1.70
30	7.90	14.87	1.88
50	8.70	14.15	1.97
70	7.10	11.53	1.31

Fig. 5. Resistance variation of as deposited CuPcTs/Alq$_3$thin films chemically treated with chloroform at different treatment time values using 5% NO$_2$ gas.

One of the gas sensors working principle depends on the chemoresistance principle, in which the interaction of target gas with the adsorbed oxygen from the ambient on the sample surface. This is a result of the release of the captured electrons from oxygen ions into the sample and causes variation in both free charge carriers and sample resistivity. All samples exhibit small sensitivity, which is 25% at the best immersion time to NO$_2$ gas at room temperature. Fig. 5 illustrates the variation of the CuPcTs/Alq$_3$ thin film resistance at 373 K operating temperature at exposure to NO$_2$ gas target for samples chemically treated with chloroform at different treatment time values (30, 50, and 70) min. We chose the 373 K directly after room temperature (RT), and it was shown to obtain good results, but in this study, we wanted to know the characteristics of the gas sensor for the samples due to the different time values of chemical treatment at a constant temperature.

All of the samples behave as n-type semiconductor sensors, where they are more resistant to electricity when it is exposed to an oxidizing gas, especially at 373 K temperatures where $O2^-$ converts to $2O^-$ that attracts more electrons at the surface. The transition causes an increase in surface charge density with corresponding to variations of band bending and surface conductivity [34].
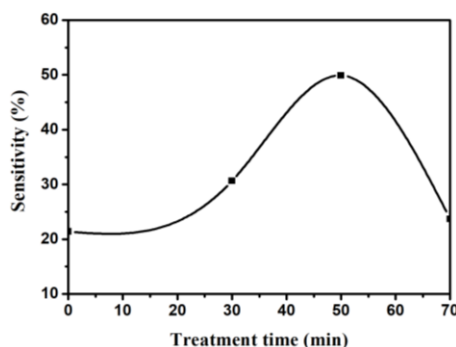

Fig. 6. NO$_2$ sensitivity versus time of chloroform treatment.

Fig. 6 shows a clear difference in the sensitivity of the samples to NO$_2$ gas, reaction time, and recovery time according to the time of chemical treatment of chloroform for CuPcTs/Alq$_3$ gas sensor. The sensitivity of these samples increased from 21.4 to 29.9 %, when the immersion time was increased to 50 min due to the decrease in granular size and increase the surface roughness. However, with an increase of immersing time up to 50 min, the sensitivity decreased and the minimum response time and recovery time increased due to the increase in particle size that came from the negative effect of increasing immersion time on the surface of the sample, see fig.7. This behavior agrees with the XRD and AFM measurements.

Table 4 shows the gas sensor parameters of sensitivity, response time, and recovery time with different values of treatment time with chloroform and operating temperature at 373 K.
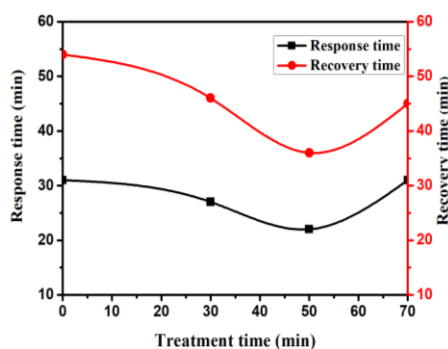

Fig. 7. NO$_2$ response time and recovery time with time of chloroform treatment.

*Table 4. CuPcTs/Alq$_3$ gas sensor parameters chemically treated
at different time values with chloroform.*

Treatment time	Sensitivity%	response time(min)	recover time (min)
As deposited	21.385	31	54
30	30.626	27	46
50	49.882	22	36
70	23.659	31	45

4. Conclusions

Fabrication bulk heterojunction blends based on organic semiconductors (CuPcTs/Alq$_3$) were achieved by a low-cost spin coating technique. According to the XRD measurement, the crystallite size decreased from 4.8 nm to 2.7 nm at 50 min immersing time and then became amorphous at 70 min immersing time. AFM measurements were shown that the average particle diameter decreased from 111.22 nm to 65.12 nm at 50 min immersing time and then increased to 98.73 nm at 70 min. This means the AFM measurement agrees with XRD results. The maximum roughness was found at 70 min immersing time. The FTIR measurement was shown that the O-H bond had a different behavior than other bonds, which increased with increasing immersing time. The sensitivity of both response time and recovery time for CuPcTs/Alq$_3$ samples was good at 50 min in chloroform, while more immersing time causes to retard these properties of the gas sensor

References

[1] Varghese, S., et al., Determination of the energy band gap of thin films of cadmium sulphide, copper phthalocyanine and hybrid cadmium sulphide/copper phthalocyanine from its optical studies. Materials Letters, 2002. 56(6): p. 1078-1083.

[2] Tedesco, A.C., J. Rotta, and C.N. Lunardi, Synthesis, photophysical and photochemical aspects of phthalocyanines for photodynamic therapy. Current Organic Chemistry, 2003. 7(2): p. 187-196.

[3] Abbas, N.K., et al., The Effect of Heat Treatment on Optical Properties of Copper (II) Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt (CuPcTs) Organic Thin Films. Silicon, 2019. 11(2): p. 843-855.

[4] Al Ogaili, H. and M. Mohammed, IMPACT OF THE HYDROGENATED ON CHARACTERIZATIONS OF ZnSe WURTZOIDS BASE ON DFT. Chalcogenide Letters, 2019. 16(11): p. 507-511.

[5] Al Ogaili, H., S. Abbas, and M. Mohammed, RAMAN SPECTRA AND ELECTRONIC FEATURES FOR NANOTUBES OF ZnSSe WURTZIOD: AB-INITIO. CHALCOGENIDE LETTERS, 2020. 17(5): p. 251-255.

[6] Tolkki, A., et al., Organometallic tris (8-hydroxyquinoline) aluminum complexes as buffer layers and dopants in inverted organic solar cells. Thin Solid Films, 2012. 520(13): p. 4475-4481.

[7] Wang, N., et al., Effect of buffer layers on the performance of organic photovoltaic cells based on copper phthalocyanine and C60. Solar Energy Materials and Solar Cells, 2010. 94(2): p. 263-266

[8] Du, H., et al., The effect of small-molecule electron transporting materials on the performance of polymer solar cells. Thin Solid Films, 2011. 519(13): p. 4357-4360.

[9] Omar, W.A., Synthesis and photophysical properties of aluminium tris-(4-morpholine-8-hydroxyquinoline). Journal of advanced research, 2013. 4(6): p. 525-529.

[10] Evangelos, V., et al., Conductivity degradation study of PEDOT: PSS films under heat treatment in helium and atmospheric air. Open Journal of Organic Polymer Materials, 2012. 2(1): p. 7-11.

[11] Harikumar, P. and V. Sivasankara Pillai, Electrochemical studies on metal Phthalocyanines. 1990, Cochin University of Science and Technology.

[12] Lu, X., et al., In situ surface chemical modification of thin-film composite forward osmosis membranes for enhanced organic fouling resistance. Environmental science & technology, 2013. 47(21): p. 12219-12228.

[13] Basu, B., S. Satapathy, and A. Bhatnagar, Merox and related metal phthalocyanine catalyzed oxidation processes. Catalysis Reviews—Science and Engineering, 1993. 35(4): p. 571-609.

[14] Helander, M.G., Electrode/Organic Interfaces in Organic Optoelectronics. 2012, University of Toronto.

[15] Muzikante, I., et al., A novel gas sensor transducer based on phthalocyanine heterojunction devices. Sensors, 2007. 7(11): p. 2984-2996.

[16] Muckley, E.S., et al., Multi-mode humidity sensing with water-soluble copper phthalocyanine for increased sensitivity and dynamic range. Scientific reports, 2017. 7(1): p. 1-11.

[17] Arafat, M., A. Haseeb, and S.A. Akbar, A selective ultrahigh responding high temperature ethanol sensor using TiO2 nanoparticles. Sensors, 2014. 14(8): p. 13613-13627.

[18] Arafat, M., et al., Gas sensors based on one dimensional nanostructured metal-oxides: a review. Sensors, 2012. 12(6): p. 7207-7258.

[19] Harbeck, M., New applications of organic polymers in chemical gas sensors. 2005, der Eberhard-Karls-Universität Tübingen.

[20] Ho, K.-C. and Y.-H. Tsou, Chemiresistor-type NO gas sensor based on nickel phthalocyanine thin films. Sensors and Actuators B: Chemical, 2001. 77(1-2): p. 253-259.

[21] Prajapati, C.S. and N. Bhat, ppb level detection of NO 2 using a WO 3 thin film-based sensor: material optimization, device fabrication and packaging. RSC advances, 2018. 8(12): p. 6590-6599.

[22] Patil, M., et al., Fast response and highly selective nitrogen dioxide gas sensor based on Zinc Stannate thin films. Materials Science for Energy Technologies, 2020. 3: p. 36-42.

[23] Pustelny, T., J. Ignac-Nowicka, and Z. Opilski, Experimental Investigations of Thin Metalphthalocyanine Layers CuPc. PbPc, NiPc by Plasmon Resonance Method to be Applied in NO2-Sensors, Optica Aplicata, 2004. 34(2): p. 246-255.

[24] Ferro, R., et al., Gas-sensing properties of sprayed films of (CdO)/sub x/(ZnO)/sub 1-x/mixed oxide. IEEE sensors Journal, 2005. 5(1): p. 48-52.

[25] Barsan, N., M. Schweizer-Berberich, and W. Göpel, Fundamental and practical aspects in the design of nanoscaled SnO2 gas sensors: a status report. Fresenius' journal of analytical chemistry, 1999. 365(4): p. 287-304.

[26] Williams, D.E., Semiconducting oxides as gas-sensitive resistors. Sensors and Actuators B: Chemical, 1999. 57(1-3): p. 1-16.

[27] Nada, K., A. Abdulameer, and R. Ali, Nanostructure Investigation of Organic Semiconductor Copper (II) PhthalocyanineTetrasolfonic Acid Tetrasodium Salt (CuPcTs) Thin Films by Structural and Surface Morphological Measurements,". Journal of Applied Physics, 2016. 8(1): p. 61-67.

[28] Mohammed, M.A., et al., The removal of zinc ions from their aqueous solutions by Cr2O3 nanoparticles synthesized via the UV-irradiation method. Egyptian Journal of Chemistry, 2020. 63(2): p. 425-431.

[29] Rheima, A.M., et al., Inhibition effect of silver-calcium nanocomposite on alanine transaminase enzyme activity in human serum of Iraqi patients with chronic liver disease. Drug Invention Today, 2019. 12(11): p. 2818-2821.

[30] Rheima, A.M., et al., Adsorption of selenium (Se4+) ions pollution by pure rutile titanium dioxide nanosheets electrochemically synthesized. Desalination and Water Treatment, 2020. 194: p. 187-193.

[31] Hsieh, J., C. Liu, and Y. Ju, Response characteristics of lead phthalocyanine gas sensor: effects of film thickness and crystal morphology. Thin Solid Films, 1998. 322(1-2): p. 98-103.

[32] Gómez, A.R., et al., Optical absorption and visible photoluminescence from thin films of silicon phthalocyanine derivatives. Materials, 2014. 7(9): p. 6585-6603.

[33] Patrick, G.L., Organic Chemistry. 2nd ed. 2004: London: Bios Scintific Publishers Taylor & Francis Group Distributed.

[34] Sun, Y.-F., et al., Metal oxide nanostructures and their gas sensing properties: a review. Sensors, 2012. 12(3): p. 2610-2631.