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Study of the Effect of Methanol Vapours on Copper Phthalocyanine Salt sol-gel Glass

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Abstract— *Copper Phthalocyanine (CuPc) is a p-type material and has the tendency to be functionalized easily with addition of specific ligands to its central atom to enhance its properties which makes it a promising material for sensing applications due to its increased selectivity. The present study deals with the study and analysis of chemical interaction of methanol vapours with the CuPc sample by studying the effect of the concentration of methanol vapours on the electrical current of CuPc with respect to time. CuPc sample has been doped in the sol-gel glass by chemical sol-gel method using CuPc tetrasuphonic tetra sodium salt and silicate precursors. The UV-Visible analysis confirms the synthesis of CuPc in glass form. Characteristic B (Soret) and Q bands of CuPc have also been observed which indicates the successful dispersion of CuPc salt in porours glass form. The chemical interaction of methanol vapours and the effect of its concentration have been studied by measuring the conductivity before and after the exposure of methanol vapours of respective concentration with respect to time. An increase in sensitivity with increase of concentration has been observed.*

1. INTRODUCTION

The management of toxic gases is of vital importance in regard to the concern of environmental issues. This has lead to the need of economical, gas selective and gas sensitive sensors [1]. Phthalocyanines (Pcs) and Metal Phthalocyanines (MPcs) are promising materials for gas sensing applications because of their increased selectivity, sensitivity, chemical and thermal stability which makes them ideal sensors. They can be operated even at elevated temperatures.

Phthalocyanine is a macrocyclic compound consisting of 4 isoindole units linked through nitrogen atoms. Most of the elements are able to coordinate to the Pc macrocycle. Furthermore, the central metal of a MPc can take additional ligands. The great advantage of Pcs and MPCs over other metal oxide sensors lies in the fact that they have increased selectivity. This is due to the fact that Pcs can be modified easily by replacing their central metal atom or by functionalizing them with certain substituent groups and by adding specific ligands to the cental metal atom. Therefore, by changing these parameters Pcs and MPcs can be made selective to different types of gaseous species which makes them highly selective and sensitive materials. Pcs are hydrophobic in nature, therefore commonly used method for their synthesis is to prepare the thin films of Pcs using thermal evaporation method [2]. But they can be made hydrophilic by functionalizing them with certain functional groups. Therefore, the salts of MPcs can be prepared by using chemical sol-gel method. CuPc tetrasufonic tetrasodium salt can be dispersed in glass using sol-gel method. CuPc has an added advantage to be used as sensor because it is comparatively stable metal which acts as a promising material for practical applications [3]. Prepartion of CuPc salt in sol-gel glass enables the uniform adsorption of the gaseous vapour onto the CuPc sol-gel glass on account of its porous structure, which allows effective chemical interaction of the organic vapour with CuPc sol-gel glass.

2. EXPERIMETAL

In the present work we have synthesized CuPc sol-gel glass by sol-gel method by using copper pthalocyanine-3, 4′, 4″, 4‴ tetrasulfonic acid tetrasodium salt as the dopant into the silicate solution. The sol-gel process involves the formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid. A typical sol-gel method involves the hydrogenation of the reacting precursor (generally alka-oxide solutions) solutions to form the sol part of the sample which after heating and polycondensation leads to the formation of gel that is dried to form monoliths, thin films, powder or glass [4].

The preparation of CuPc salt in sol-gel glass form is done by chemical route sol-gel method. We initially prepared a silicate solution using ethanol and tetraethoxysilane in 50:50 mole ratio. HCl was added to enhance solubility of the various solvents in the solution and maintaining the required pH value. 4mL of Distilled water was also added to the solution. The whole solution was then stirred for around 3 hours until a clear transparent solution was obtained. Thereafter 5 mg of CuPc salt dissolved in 5mL distilled water was added into the prepared silicate solution with heating and stirring for about 2-3 hours. The obtained gel was vacuum dried for about 12 hours at room temperature to get the final CuPc salt sol-gel glass.

3. RESULTS AND DISCUSSION

The prepared sample is characterized spectroscopically using UV-Visible absorption, the chemical interaction and hence the sensing behavior is analyzed using electrical measurements by taking variation in current after the exposure of methanol vapours of different concentrations.

4. OPTICAL ANALYSIS

The optical analysis of the sample has been conducted by taking UV-Visible analysis using Perkin Elmer LS-35 Spectrometer in the wavelength range of 200 to 900 nm. The obtained UV-Visible results are shown in Fig. 1. The trace 1 represents the UV-Visible spectra of prepared CuPc salt sol-gel glass. The appearance of B band at around 295 nm and 332 nm indicates direct electronic excitations from π* to π orbital of the isoindole units of the macrocycle of CuPc salt and the Q bands which are indicative of onset of energy are observed at around 630 nm and 668 nm which are due to the functional substituent groups, that is the tetrasulfonic tetrasodium salts [5]. Similarly trace 2 is the UV-Visible spectra of CuPc salt in distilled water and its respective B and Q bands are also shown in the Figure. The third trace corresponds to the peak of the silicate glass and no such bands are appeared because of its transparency and absence of any dopant. By comparing the three graphs we can conclude that the CuPc salt has been dispersed successfully into the silicate solution to form CuPc salt sol-gel glass and the characteristic absorption peaks of CuPc salts have been observed.

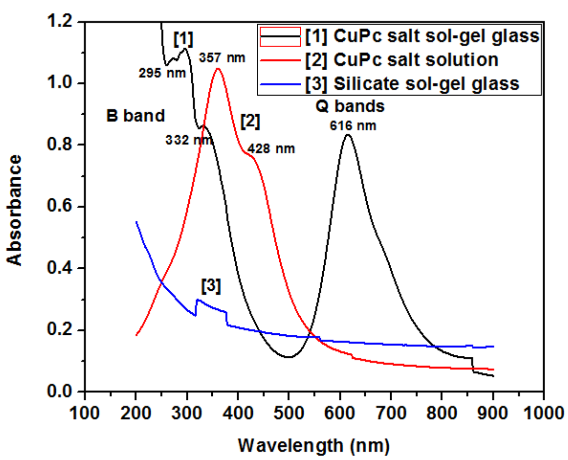

Fig. 1: Uv-Visible Analysis of CuPc salt.

5. STUDY OF CHEMICAL INTERACTION

To study the chemical interaction of methanol vapours on the CuPc salt sol-gel glass, we have measured the variations in electrical conductivity with and without the exposure of vapours using digital Picoammeter (DPM-111 Model) by two probe method. Voltage was applied with the help of Keithley (224 programmable current source) and was kept constant as 1 Volt. Thereafter the methanol vapours were passed initially with 1 mL concentration volume and accordingly the variation in current was observed and it was found (Fig. 2) that the current increased after the exposure of vapours. The increase in current may be attributed to the charge transfer mechanism between CuPc salt and the methanol. The charge transfer involves the functionalized substituent group (tetrasulfonic acid tetrasodium salt) which tends to accept the electrons leading to increase in current of the sample. Also from the graph (Fig. 2) we observed that with increase in concentration of methanol vapours the increase in current was more which indicated increase in the charge transfer. We further observed that at all the concentrations the conductivity attained its initial value after the vapours were removed, which indicated that this phenomena was reversible. Therefore it can be inferred that CuPc salt may behave as an efficient sensor.

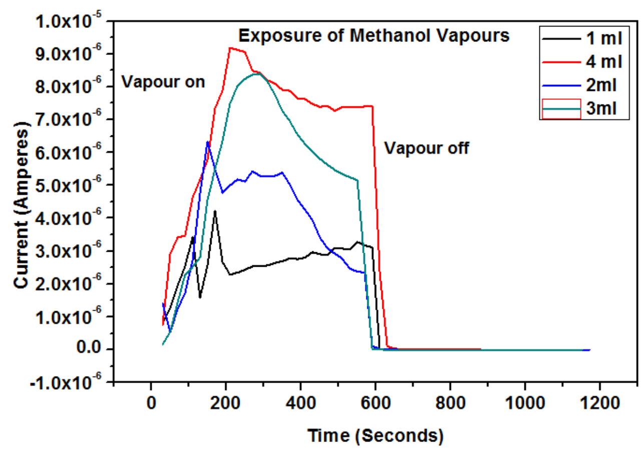

Fig. 2: Variation in current on exposure to methanol vapours.

6. CONCLUSIONS AND DISCUSSIONS.

CuPc salt sol-gel glass has been prepared using chemical route sol-gel method by exploiting the property of enhanced solubility of CuPc salt in organic solvents because of the presence of sulfonic acid and sodium salts groups into it. The advantage of using copper as the central atom in the Pc group lies in its greater stability as compared to other metals. The UV-Visible absorption spectra confirms the successful dispersion of CuPc salt into the silicate solution to form the porous glass structure. The effect of concentration of methanol vapours on CuPc salt sol-gel glass is shown by variation in the electrical current onto the exposure of vapours and has been found to increase with increase in concentration.

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