Copper Phthalocyanine Based Ammonia Gas Sensor Working at Room Temperature

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Abstract

A sensor for ammonia gas sensing has been fabricated using copper phthalocyanine (CuPc) as a sensing material. The sensor sample was prepared in the form of pellet. The CuPc sensor sample for ammonia was operated at different concentrations at room temperature and change in resistance was monitored. Sensitivity of CuPc pellet sensor for ammonia concentration 5 volume % (ratio of volume of ammonia to volume of air) is 91 %. The response and recovery time is 2 minute and 6 minute respectively. The study revealed that the conductivity of the CuPc sensor sample increases with increase in ammonia gas concentration.

Key Words: Ammonia sensor; Metallophthalocyanine, Copper phthalocyanine, response time, recovery time, sensitivity

1. Introduction

The importance of environmental gas monitoring is well understood and much research has been focused on the development of suitable gas sensitive materials. Because air pollution is getting serious gradually, research on the gas sensors based on metal macrocyclic may be important and find practical applications. Ammonia is one of the pollutant gases which is a foal smelling and toxic. High volume control of combustibles in the chemical industry[1], Leak-detection in air conditioning systems, breath analysis for medical diagnosis, animal housing etc. needs ammonia sensors[2, 3].

Recently there has been a considerable interest in exploiting organic substances such as metallophthalocyanines (MPcs), porphyrins, and doped conducting polymers. For getting higher surface area and maximum sensing these materials are suited in the form of thin or thick films. MPc is a well known material because of its extensive applications in different areas[4]. They possess electronic and morphologic characteristics which are very favorable for semiconductive properties. The resistance of a device varies by exposure to chemical substance. Moreover MPcs have high thermal and chemical stabilities[5, 6].

Presently we are working on the study of CuPc as ammonia sensor due to its good sensor properties. These types of sensors are attractive because of its low cost, sensitivity and reliability. This paper deals with the ammonia gas sensor in the pressed pellet form based on CuPc as the sensor material working at room temperature.

2. Experimental

CuPc was synthesised by chemical method from phthalic anhydride, urea and copper salt as precursors. Various methods for synthesis of MPcs were reported in the literature, from which the one with phthalic anhydride and urea route was selected as it is low cost and simple to work out[7]. Figure 1 shows the reaction scheme for synthesis of CuPc using this route.

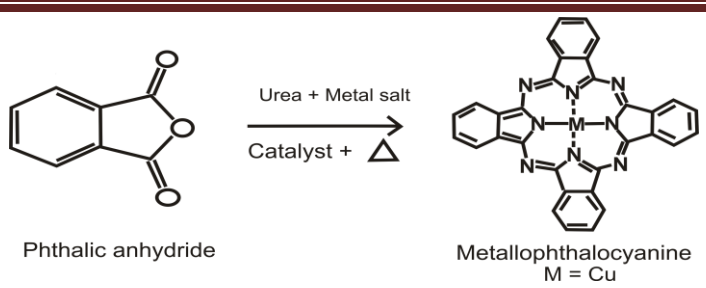

Fig. 1. Reaction scheme used in synthesis of CuPc.

Typically, it involves mixing of phthalic anhydride, urea, metal salt, proper catalyst and heating the mixture. Reaction was observed to be very vigorous at about 250 ^{o}C. After completion of the reaction, residue was washed number of times with distilled water and methyl alcohol for purification. The powder was then air-dried and crushed uniformly to fine grains. The synthesised powder was used for different characterizations and for preparation of sensor samples. In order to prepare sensor samples, synthesized CuPc powder was compacted in the form of pellets of diameter 13 mm and thickness 0.7 mm using press technique with optimized pressure and time of application of pressure. For electrical measurements, silver paste contacts were made on either surface of the sample.

2.1. *Material Characterization*

The structural properties of CuPc powder were investigated by X- ray diffraction patterns using Philips X- ray diffractometer PW 1729 with Cu K_{α} radiation (λ= 1.5406 Å). The UV-Vis absorption spectra of CuPc pellet is recorded using JASCO SPECTRO PHOTOMETER Model V-630. Infrared spectroscopy of CuPc is performed at room temperature using JASCO *FT/IR-6100 type A* infrared spectrophotometer in the spectral range 2000 cm^{-1} - 400 cm^{-1}.

Ammonia sensing properties of CuPc were carried out using a specially designed airtight chamber. Schematic diagram of test chamber is shown in figure 2. The sensor element was exposed to ammonia of variable concentrations. The electrical resistance of a sensor in air and in ammonia was monitored using two probe technique with Keithley-2000 multimeter.

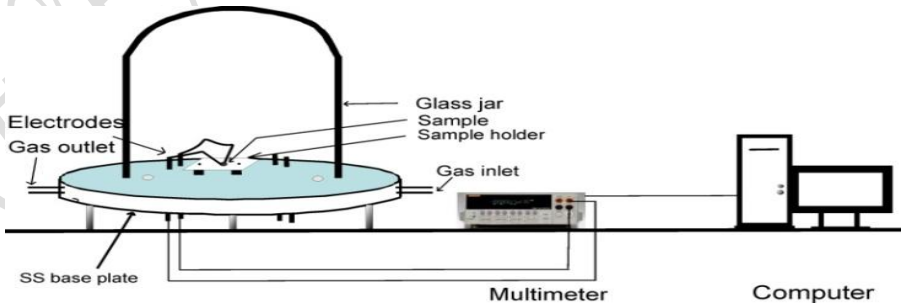

Fig. 2. Schematic diagram of test chamber

3. Results and discussion

CuPc is synthesised using phthalic anhydride urea route. The cyclotetramerization reaction took place at about temperature 250 ^{o}C. Sensor samples were prepared using press techniques with optimized parameters. Resistivity of sample of CuPc was determined and it was equal to 1.066 x 10^{9} Ωcm.

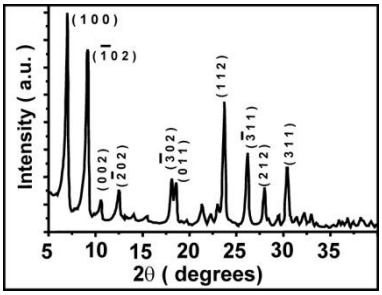

Fig. 3. X-ray diffraction pattern of powder copper phthalocyanine

3.1. *Material Characterization*

X-ray diffraction characterization of synthesised copper phthalocyanine powder was carried out. XRD spectra and positions of XRD peaks of copper phthalocyanine are shown in figure 3. It is found to be in good agreement as in literature[8] and PCPDF file number 11-0893. CuPc is found to be in stable β form. UV-Vis absorption spectra of CuPc are shown in figure 4. λ_{max} = 669 nm[9]. Q-band is clearly seen in the UV visible spectra.

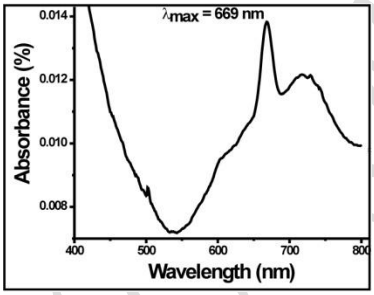

Fig.4. UV- Visible spectra of copper phthalocyanine

Infrared spectroscopy of CuPc powder was performed at room temperature in the spectral range 2000 cm^{-1} - 400 cm^{-1}. The IR spectra of a substance are markedly dependent on the chemical composition. IR spectrum of synthesised CuPc powder shown in figure 5 indicates that the region between 400 cm^{-1} - 1350 cm^{-1} is same as any MPc because this region is the skeleton region of MPc macromolecule. The peak at 728 cm^{-1} corresponds to C - H out of plane bending vibrations. The peak at 900 cm^{-1} corresponds to C - H in plane bending vibrations.

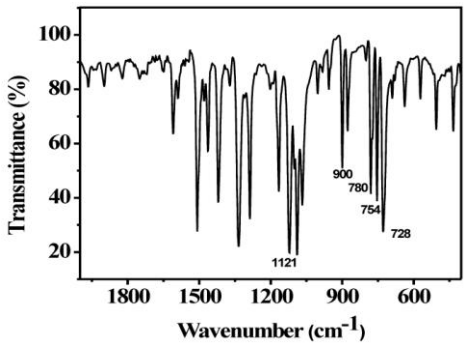

Fig. 5. FTIR spectra of CuPc in powder form

3.2. *Ammonia Sensing Properties*

The response resistance of CuPc pellets upon an exposure to NH_3 concentrations of 0.05, 0.1, 0.5, 3, 5 and 9 volume % were recorded. NH_3 being the donor gas and CuPc the P-type semiconductor, it is expected that on exposure to ammonia, CuPc sample show increase in its resistance. However, we observed decrease in its resistance on exposure to ammonia gas. Such type of behavior may be due to exposure of sample to ammonia in the air atmosphere. The sensitivity of samples to each ammonia concentration was calculated using formula (1).

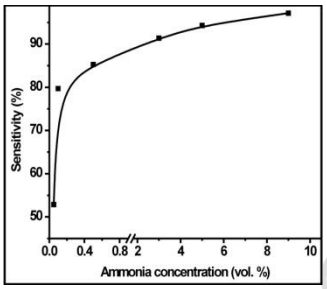

Fig. 6. Sensitivity versus ammonia concentration.

$$S\ (\%) = \frac{R_a - R_g}{R_a} \times 100\ \% \qquad (1)$$

Where R_a is the resistance of sensor sample measured in air and R_g is the resistance in air containing tested gas respectively. The sensitivity plot in figure 6 shows the maximum and constant sensitivity of CuPc samples obtained at ammonia concentration approximately greater that 7 volume %. The CuPc sensor was repetitively exposed to optimized NH_3 concentration 9 volume % for stabilization and figure 7 shows that after 4 to 5 cycles it was stabilized.

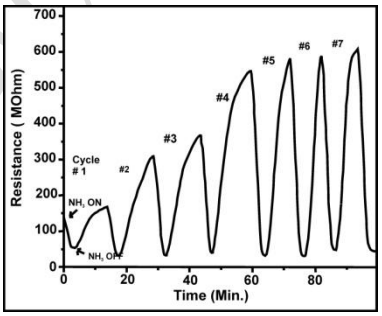

Fig. 7. Repetitive exposure of CuPc sample with NH_3 concentration 9 volume % at room temperature

The same sample was allowed to recover sufficiently and then exposed to different NH_3 concentrations following the decreasing order of 9 volume %, 7 volume %, 5 volume %, 3 volume % and 1 volume % at room temperature and 76 % relative humidity. The response is shown in figure 8. The response time and recovery time determined from this graph upon the exposure to NH_3 concentration 5 volume % at room temperature was 2 minute and 6 minute respectively. It is observed that the change in resistance (ΔR) decreases from high NH_3 concentration to low NH_3 concentration in surrounding air of the sample. At NH_3 concentration 9 volume %

change in resistance is 355 MΩ while for 1 volume % concentration it is 258 MΩ. Decrease in ΔR with decreasing ammonia concentration corresponds to decrease in conductivity.

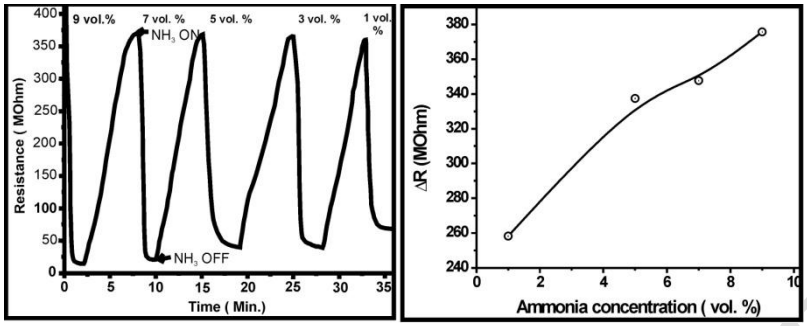

Fig. 8. Response of sensor with decreasing ammonia concentration.

4. Conclusion

The CuPc is successfully synthesised using phthalic anhydride and urea route, confirmed using different characterization techniques and prepared sensor samples. The CuPc sensor sample was studied with different concentrations of ammonia at room temperature and change in resistances was monitored. Sensitivity of CuPc pellet sensor for ammonia concentration 5 volume % is 91 %, response time is 2 minute and recovery time is 6 minute. The study revealed that the conductivity of the CuPc sensor sample increases with increase in ammonia gas concentration.

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