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Room temperature ppb level Cl_2 sensing using sulphonated copper phthalocyanine films

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ABSTRACT

We present room temperature chemiresistive gas sensing characteristics of drop casted sulphonated copper phthalocyanine (CuTsPc) films. It has been demonstrated that these films are highly selective to Cl_2 and the sensitivity in the 5–2000 ppb range varies linearly between 65 and 625%. However, for concentrations ≥2000 ppb, the response becomes irreversible, which is found to be due to the chemical bond formation between Cl_2 and SO_3Na group of CuTsPc films. The X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) data confirms the oxidation of SO_3Na group by Cl_2 gas.

1. Introduction

Concerns for clean environment require strict regulations on toxic gas emission from industries and automobiles. In order to enforce these regulations, there is a need for more sensitive gas-sensing devices that are able to detect toxic gases in the parts-per-billion range [1]. For instance, Cl_2 gas is widely used in various useful processes, such as, water purification, bleaching of pulp in paper mills, treatment of sewage effluents and as insecticides. Cl_2 is notoriously toxic gas, which can be lethal at low doses. The toxic limit of Cl_2 for 8 h time weighted average is 0.5 ppm [2]. This requires development of sensors that can detect Cl_2 in ppb level. In recent years, many results were reported on Cl_2 sensing, and Table 1 summarizes several materials used for chemiresistive (i.e. a change in conductance on gas exposure) Cl_2 detection. From Table 1, it can be seen that there are only few materials such as bisporphyrin, cobalt phthalocyanine (CoPc), and $Zn_2In_2O_5$–$MgIn_2O_4$, which can sense the ppb level of Cl_2 gas. The working temperature of these devices is very high i.e. in the range of 180–300 °C. It can also be seen from Table 1, the materials such as polypyrrole–ZnO nanocomposite, SnO_2 with Sb doping and fluorinated ethylene propylene (FEP)/polyanniline, which can detects the Cl_2 gas at room temperature but at ppm level. Therefore there is a need of material which can detect the ppb level of Cl_2 gas at room temperature. Apart from this, for a practical commercial gas sensing application one requires: (i) large area and cost effective methods of films making, (ii) low temperature of operation hence low cost of instrumentation and as at low temperature of operation no structural reorganization of the films takes place, therefore the sensing characteristics will be reproducible for prolonged operations. In this context we tried to explore the gas sensing characteristics of sulphonated copper phthalocyanine (CuTsPc) thin films. It has been reported that sulphonated metal phthalocyanine has got enhanced solubility and higher mobility (~1.08 $cm^2 V^{-1} s^{-1}$) compared to their non-sulphonated counterpart [21]. The chemical structure of CuTsPc is shown in Fig. 1. The structure of CuTsPc is very similar to the copper phthalocyanine (CuPc) except that polar SO_3Na group attached to the corners benzene ring and makes this compound water soluble [22]. In this paper, we for the first time report a room temperature chemiresistive sensors based on a drop casted CuTsPc films. The results of chemiresistive response to various oxidizing (Cl_2, NO, CH_4) and reducing (H_2S, NH_3, CO) gases indicate that these films are sensitive to only Cl_2 gas with a fast response and recovery at room temperature.

2. Experimental

The commercially available Aldrich make CuTsPc powder (dye content: 85%) was used for preparation of films. The cleaning of quartz substrates (used for deposition of films) of size 10 mm × 10 mm × 0.3 mm were carried out by sonicating them in the Aldrich makes, electronic grade try-chloro-ethylene, acetone

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Table 1
Different materials used for chemiresistive detection of chlorine.

Materials used	Working temperature (°C)	Detection limit (in ppm)	Ref.
Polypyrrole–ZnO	25	1	[3]
SnO_2 with Sb doping	25	3	[4]
FEP/polyanniline	25	100	[5]
Cu-phthalocyanine	170	0.18	[6]
Co-phthalocyanine	180	0.005	[7]
Bisporphyrin	180	0.01	[8]
Mg-phthalocyanine	200	0.18	[9]
$WO_3/FeNbO_4$	230	2	[10]
$CdIn_2O_4$	250	0.2	[11]
$CdSnO_3$	250	0.1	[12]
$CuO–CdIn_2S_4$	250	400	[13]
In_2O_3	250	0.5	[14]
$In_2O_3–Fe_2O_3$	250	0.2	[15]
$NiFe_2O_4$	250	1000	[16]
SnInO	300	3	[17]
$Zn_2In_2O_5–MgIn_2O_4$	300	0.01	[18]
WO_3	300	1	[19]
ZnO	400	300	[20]

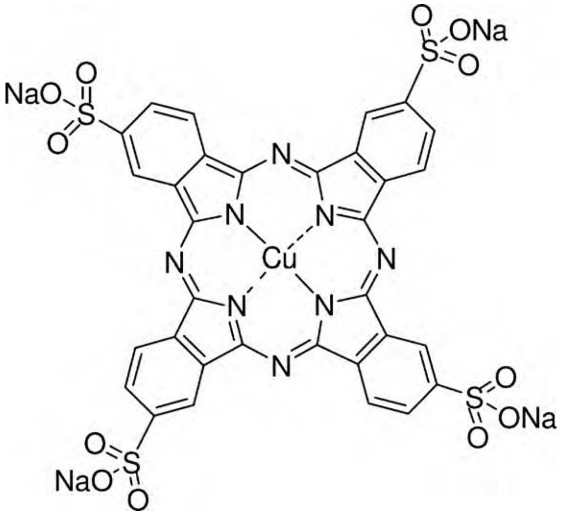

Fig. 1. Chemical structure of the sulphonated copper phthalocyanine (CuTsPc) molecule.

and methanol solutions for 10 min in each solution, respectively. After this substrates were dried using high velocity argon gas jet stream. Thin films of nominal thickness ~1 µm were prepared using drop casting method. The solution is prepared by dissolving 5 mg of CuTsPc in 0.1 ml of de-ionised water and 0.4 ml of methanol (Aldrich make, electronic grade). After sonicating it for 10 min the droplets were spreaded on pre-cleaned quartz substrate. Deposited films were dried for few hours under ambient conditions and finally vacuum annealed at 250 °C for 15 min. All the deposited films were very uniform in thickness.

The surface morphology of the films was imaged by scanning electron microscope (VEGA, TESCAN make). The structure of the grown films was determined by grazing incidence X-ray diffraction (GIXRD) using Cu K_α radiation (Seifert-XRD 3003TT) in out-of-the-plane geometry with an incidence angle of 0.1°. The Fourier transform infrared spectroscopy (FTIR) spectrum of the films was recorded using Bruker spectrometer (Vertex 80v) in reflectance mode from 4000 to 400 cm^{-1} with a resolution of 1 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) of the deposited films was carried out using Mg K_α (1253.6 eV) source and a MAC-2 electron analyzer. The XPS-analysis chamber has a base vacuum of 10^{-9} mbar. The XPS binding energy scale was calibrated to C-1s line at 284.5 eV.

In order to measure the gas sensing characteristics of the films, the electrical contacts were prepared by first thermally evaporating two gold pads (120 nm thick, size 2 mm × 2 mm at a spacing of 1 mm) and then attaching silver wires to them by silver paint. A change in resistance of the film as a function of time (response curve) was recorded at room temperature for 500 ppb concentration of different gases (i.e. Cl_2, H_2S, NH_3, CH_4, CO and NO), which were commercially procured from M/s Chemtron Science Pvt. Ltd. in the gas filled canister (gas pressure 20 kg/cm^2) of volume 0.5 l and having concentration of 1080 ppm (rest content is N_2). The response curves were recorded using a static gas testing setup. Briefly, the sensor was mounted upside down in a leak tight stainless steel chamber (net volume: 983 cm^3). A desired concentration of the test gas in the chamber is achieved by injecting a known quantity of gas using a micro-syringe. The response data was acquired by using a personal computer equipped with Labview software. Once a steady state was achieved, recovery of sensors was recorded by exposing the sensors to air, which is achieved by opening the lid of the chamber. From the response curves, the sensitivity (S) was calculated using the relation: $S = \{(C_e - C_0)/C_0\} \times 100\%$, where C_0 and C_e are the conductance values in air and at the saturation level after exposing the gas. Response and recovery times were defined as the time needed for 90% of total resistance change on exposure to gas and air, respectively. The conductance was measured by Keithley 6487 voltage source/picoammeter system using lab-view software.

3. Results and discussion

Typical GIXRD pattern and SEM image of the drop casted CuTsPc films are shown in Fig. 2. The film consists of a dense morphology.

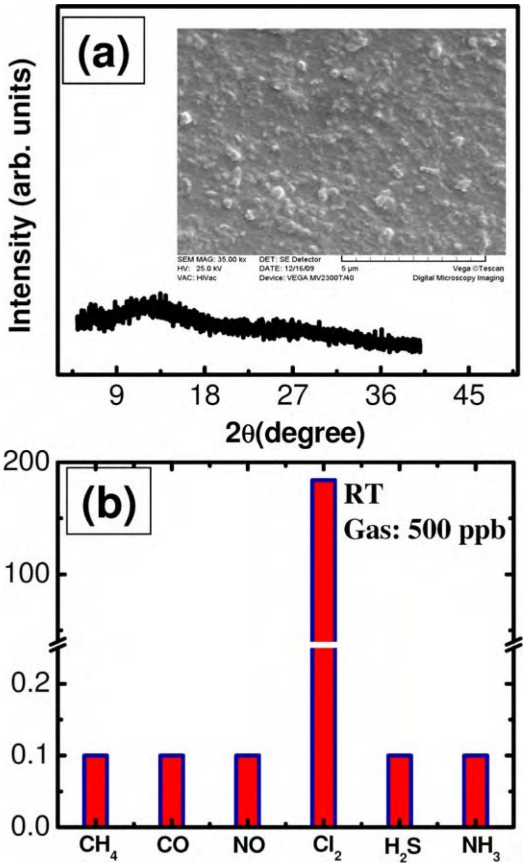

Fig. 2. (a) GIXRD pattern and scanning electron microscope (SEM) image of the drop casted CuTsPc film on quartz substrate. (b) Selectivity histogram of CuTsPc films towards 500 ppb of different gases at room temperature.

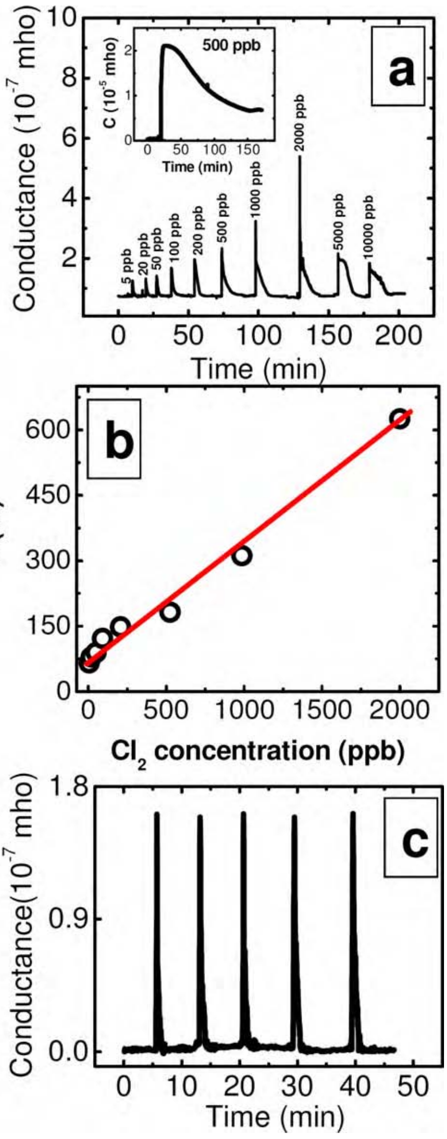

Fig. 3. (a) Response curves of CuTsPc films recorded after exposing to different doses of Cl_2 gas. Response curves are highly reversible up to 2000 ppb dose. Inset shows the response curve of CuPc films for 500 ppb of Cl_2 gas. (b) Variation of sensitivity (S) as function of Cl_2 concentration, which shows a linear dependence. (c) The response curve of the CuTsPc films for a repeated exposure of 100 ppb of Cl_2 gas.

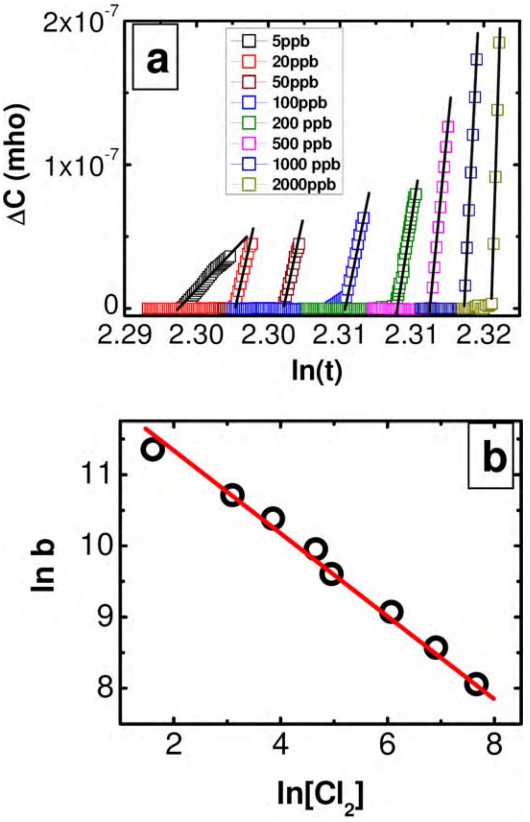

Fig. 4. (a) Change in conductance (ΔC) as a function of ln(t), which was derived from the response curves in Fig. 3(a). Straight-line fit of data is in accordance with Elovich equation and the slope of linear fits yields parameter b. (b) Linear correlation between ln b and ln[Cl_2].

The absence of any peak in the diffraction data shows that films are amorphous in nature.

Now we discuss the sensing characteristics of the CuTsPc films at room temperature. For this purpose, response curves (change in conductance of the film as a function of time) were recorded at 500 ppb concentration of different gases i.e. Cl_2, H_2S, NH_3, CH_4, CO and NO. The histogram showing the sensitivity for different gases (Fig. 2(b)). It may be noted from the histogram that films are highly selective to the Cl_2, and the sensitivity value is ~184%. For all other gases, the sensitivity was <0.1%. Typical response curves recorded at room temperature for different Cl_2 concentrations are shown in Fig. 3(a). It may be noted that Cl_2 exposure up to 2000 ppb, resulted in a highly reproducible response curves, with a very fast response time (~4 s) and a full recovery in ~10 min at 2000 ppb. It suggest that CuTsPc films can be used as chemical sensor in the gas exposure range of 5–2000 ppb, however for gas concentration >2000 ppb, the degradation of films limits their sensing application. The possible explanation for the reversible behavior in the range of 5–2000 ppb and irreversible for >2000 ppb will be presented later. For comparison purpose in the inset of Fig. 3(a), we have plotted the response curve for amorphous copper phthalocyanine (CuPc) films for a Cl_2 exposure of 500 ppb at room temperature. The base conductance of the CuPc films is 5.4×10^{-7} Ω, on exposure to 500 ppb of Cl_2 gas; the conductance value increases to 2.1×10^{-5} Ω in 3 min. It can be seen from the conductance versus time plot, the full recovery to base resistance does not takes place even after 150 min, hence the irreversible response of CuPc films disqualify it for room temperature Cl_2 gas sensing. Under the similar conditions the base conductance of CuTsPc film is 7×10^{-8} Ω and on exposure of 500 ppb of Cl_2 it increases to 2.5×10^{-7} Ω in 4 s and full recovery to base resistance takes place in 2 min. The faster response time and full recovery to the base resistance indicates the superiority of CuTsPc films over the CuPc films.

The sensitivity of the CuTsPc films based gas sensors has been defined as $S = \{(C_e - C_0)/C_0\} \times 100$, where C_0 and C_e are the conductance values in air and at the saturation level after exposing the gas. The variation of S as a function of Cl_2 concentration is shown in Fig. 3(b). At 5, 20 and 50 ppb of Cl_2 concentrations, the sensitivity values are 65, 79 and 89%, respectively. It is seen that for Cl_2 concentration in the 5–2000 ppb range, S increases linearly between 65 and 625%. However, for Cl_2 doses >2000 ppb, not only the S value decreases, the full recovery also never completes. To test the reproducibility of the response curve, we have recorded the response curve of the CuTsPc films for a repeated Cl_2 exposure of 100 ppb for many times, the data shown in Fig. 3(c) is only for five times exposure. The same value of conductance on every time exposure of the films shows that the response curves are highly reproducible.

Now we try to explain why the response is reversible at ≤2000 ppb Cl_2 concentrations and irreversible at higher concentrations. CuTsPc films are intrinsically insulators and turn

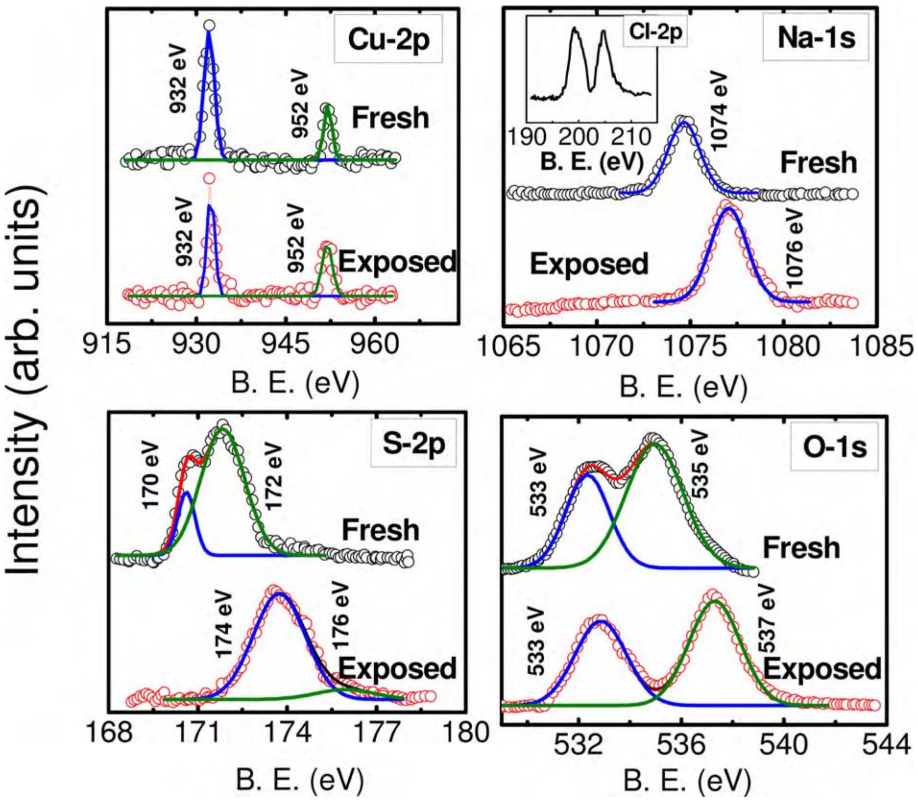

Fig. 5. Cu-2p, Na-1s, S-2p and O-1s XPS spectrum recorded for fresh and 10 ppm Cl_2 exposed CuTsPc films. Inset of Na-1s spectra shows the presence of Cl-2p peak in the exposed films.

semiconductors only when they are exposed to atmosphere. This is because oxygen from ambient chemisorbs at the film surface. The presence of adsorbed oxygen ($O_2{}^-$), corresponding to the binding energy at 533 eV was confirmed by the XPS analysis (as shown later in Fig. 5). Once the films is exposed to the low concentration of Cl_2 gas, it replaces the adsorbed oxygen (as being more electronegative than oxygen) as well as get adsorbed at other free sites on the films surface, and pick up the electron from there. As a result the conductance rises, but later this adsorbed Cl_2 is replaced by the atmospheric oxygen due to its abundance in the surrounding and results in the lowering of conductance. This reversible response is a prerequisite for chemiresistive sensors. It may also be noted that CuTsPc films will have more adsorbed oxygen at the surface compared to pure CuPc films due to the strong affinity of sulphonated group to the oxygen. Therefore the CuTsPc films show better response then the pure CuPc films at room temperature.

Whatever may be the adsorptions sites on CuTsPc films, the reactions involving the chemical absorption of Cl_2 gas on the solid CuTsPc surface, the adsorption rate will decrease with time due to an increase in surface coverage [23]. One of the most useful models to describe such activated chemical absorption is the Elovich eq., which is expressed by [23,24]:

$$\frac{d\theta}{dt} = a\exp(-b\theta) \tag{1}$$

where θ is the amount of gas adsorbed at time t and a, b are constants. In the Elovich equation, constant a is regarded as the initial adsorption rate because $d\theta/dt$ approaches a when θ approaches 0 and it depends on the activation energy. Constant b is related to a measure of the extent to which the surface has been screened by the potential barrier for successive adsorption. Given that $\theta = \theta_t$ at time equals t and $\theta_t = 0$ at $t = 0$, the integrated form of Eq. (1) is

$$\theta_t = \left(\frac{1}{b}\right)\ln(ab) + \left(\frac{1}{b}\right)\ln\left[t + \left(\frac{1}{ab}\right)\right] \tag{2}$$

In the present case, we assume that the change in the conductance (ΔC) is proportional to the amount of adsorbed Cl_2 molecules θ. As shown in Fig. 4(a), the plots of ΔC versus $\ln t$, which are derived from Fig. 3(a), are linear, indicating that the interaction obeys the Elovich equation. From the slopes, values of b are calculated for different Cl_2 concentration. As shown in Fig. 4(b), $\log b - \log[Cl_2]$ plot is linear in nature. Therefore, Cl_2 concentration apart from the sensitivity plot, as shown in Fig. 3(b), can also be determined from b that is derived from the response rate $\Delta C/dt$.

The irreversible response of the CuTsPc films at higher Cl_2 concentrations (>2000 ppb) indicates oxidation of the CuTsPc molecules. Since oxidation implies formation of a chemical bond, therefore energy and the presence of other species are required to reverse this process. Otherwise the process will be irreversible, as observed in the present case. In order to confirm the oxidation of CuTsPc, XPS and FTIR spectra were recorded for the freshly prepared films and after their exposure to a high dose (10 ppm) of Cl_2. The obtained XPS results are presented in Fig. 5. As shown in Fig. 4, first we look at Cu-2p XPS spectrum, as in metal phthalocyanine it is the preferable site for gas adsorption [25]. The peak at 932 and 952 eV corresponds to the Cu-$2p_{3/2}$ and Cu-$2p_{1/2}$, respectively. As seen there is no change in the spectrum after gas exposure, so it rules out the possibility of gas reaction at copper sites, which are the most prominent reaction sites for CuPc materials.

The major changes in the XPS spectrum occurs at sulphonated group site. The core level O-1s XPS spectrum of fresh CuTsPc films indicates presence of oxygen in two different chemical states. The peaks at 533 and 535 eV correspond to correspond to chemisorbed oxygen at films surface and oxygen present in the sulphonated group, respectively [26]. However, for Cl_2 exposed film, there is

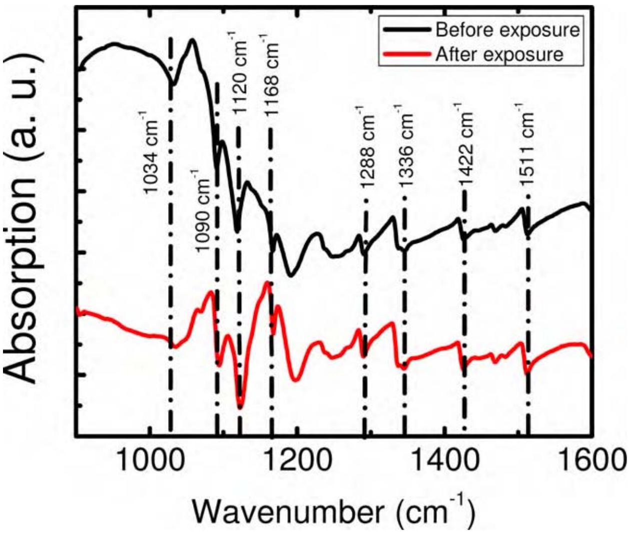

Fig. 6. Fourier transform infrared spectra (FTIR) data recorded for fresh and 10 ppm Cl_2 exposed CuTsPc films.

a large shift in the O peak at 535 eV i.e. related to S/Na atoms, indicating possibility of Cl_2 at oxygen sites of sulphonated group. This can possibly happen if the Cl_2 molecules get attached to O and form an oxychloride compound. The reaction will also lead to increase in the binding energies of S-2p and Na-1s peaks, as seen in Fig. 5. The presence of Cl-2p peak (shown in the inset of Na-1s XPS data) at 199 and 205 eV in exposed films verifies the existence of physisorbed and chemisorbed chlorine, respectively. This inference is further supported by the FTIR data presented in Fig. 6.

For fresh film the noticeable FTIR peaks are: 1034 cm^{-1} (SO_3 symmetric stretching bond), 1090 cm^{-1} (C–N stretching bond), 1120 and 1168 cm^{-1} (C–H in plane banding vibration), 1288 cm^{-1} (SO_3 asymmetric stretching bond) and 1336, 1422, 1511 cm^{-1} (characteristic of C–N stretching) [27]. However, after Cl_2 exposure, the intensity of the peak at 1034 cm^{-1} (SO_3 stretching bond) becomes significantly lower. All other peak do not show any shift or intensity change after Cl_2 exposure. The intensity of any FTIR peak is related to the dipole-moment. The lowering of intensity indicates the lowering of the dipole-moment of SO_3 group. This result can be explained by Cl_2 attacks on the oxygen sites of SO_3 group, which pick up some charge from it and results in lowering of dipole-moment.

4. Conclusions

We have investigated the gas sensing properties of CuTsPc films at room temperature, these films are highly sensitive and selective to the Cl_2 gas in concentration range of 5–2000 ppb. The CuTsPc films have distinct advantage over other materials such as metal oxides, metal phthalocyanines, and porphyins, etc., employed for chemiresistive Cl_2 detection, such as: (i) the films can be prepared by simple drop cast method, (ii) films can reproducibly detect ppb level of Cl_2 at room temperature with low response time (∼4 s) and recovery time ∼10 min. However, for concentrations >2000 ppb, the response becomes irreversible, which is found to be due to the chemical bond formation between Cl_2 and SO_3Na group of CuTsPc films.

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