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# High Performance CuO Nanorectangles based Room Temperature Flexible NH<sub>3</sub> Sensor

Bhuvaneshwari Sakthivel, Libu Manjakkal, Gopalakrishnan Nammalvar

**Abstract**— Here, we report the fabrication of a flexible room temperature ammonia gas sensor using surfactant-free hydrothermally synthesized copper oxide (CuO) nanorectangles. The structural analysis revealed that the CuO nanorectangles possessed monoclinic structure with an average length and breadth of 950 nm and 450 nm respectively. The specific surface area of CuO nanorectangles was determined to be 29 m<sup>2</sup>/g. The sensor was fabricated on a flexible polyethylene terephthalate substrate by screen printing technique. The room temperature ammonia sensing measurement exhibited significant response down to 5 ppm of ammonia with a quick response time of 90 s and recovered to baseline within 120 s. Maximum response of 0.99 was recorded for 100 ppm of ammonia. The rate constants for adsorption and desorption were estimated for 6.5 to 100 ppm of ammonia from the exponential conductance changes during response and recovery process. The sensor showed appreciable stability and reproducibility of the sensing performance over a period of 3 months. The fabricated flexible sensor demonstrated its ability to detect a wide range of ammonia concentrations at room temperature irrespective of the mechanical deformations applied. Thus, the fabricated sensor is promising and can be suitably employed for practical applications in environments where efficient gas sensing is vitally important.

**Index Terms**—CuO, Nanorectangles, Flexible gas sensor, Screen printing, Rate constants.

## I. INTRODUCTION

Toxic gases such as ammonia (NH<sub>3</sub>), carbon monoxide (CO), hydrogen sulphide (H<sub>2</sub>S), etc. from industrial exhausts or wastes cause long term health issues [1, 2] and could have grave impact on the quality of life of the workers. The continuous observation of these gases will allow monitoring the health of workers. The development of NH<sub>3</sub> various gas sensors has reported by several researchers, and ammonia is one of the gases taken seriously due to its natural and industrial origin [3-5].

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However, low level detection of NH<sub>3</sub> is still requires robust and inexpensive systems for real-time monitoring at ppb-ppm levels in environmental monitoring, food processing and medical applications.

In this regard, wearable electronics, which has gained significant attention recently, opens a new window possibly enabling self-health management. For better integration with wearable systems, sensors should be flexible, small in size, and portable. Flexible sensors based on metal oxide (MO<sub>x</sub>) nanostructures have attracted significant attention considering their high sensitivity, low production cost, ease of fabrication, wear-ability and eco-friendliness [9, 10]. There have been several reports on MO<sub>x</sub> based sensors such as SnO<sub>2</sub>, ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, InO<sub>3</sub>, CuO, Co<sub>3</sub>O<sub>4</sub> and NiO due to their extremely high sensitivity to hazardous gases (for instance H<sub>2</sub>S) as well as better selectivity to certain volatile organic compounds (VOCs) [11-19]. The adsorption induced variation in electrical resistance of MO<sub>x</sub> based gas sensors have been used for the detection of gases such as NH<sub>3</sub> in ppb (parts-per-billion) range [6]. The features such as long-term stability and low-power consumption have been recently demonstrated in nanostructures (nanorods, nanosheets, and urchin-like) based metal oxide gas sensors for the detection of NH<sub>3</sub>, CO, H<sub>2</sub>S, etc. [6-8]. However, these reported sensors require undesirably high operating temperatures to yield stable response whereas for wearable applications, ambient temperature operation of gas sensors is desirable.

Copper oxide (CuO) is a well-known *p*-type, thermo-stable MO<sub>x</sub> semiconductor with a narrow band gap of 1.4 eV and has been widely used as catalytic and adsorption material [19]. CuO with different morphologies such as nanowires, nanorods, nanoribbons, etc. structures have been utilized for sensing different gases [20-23]. The unique properties and sensing mechanism of CuO nanostructures have exhibited promising gas sensing properties towards various gases such as ethanol, methanol, other volatile organic compounds (VOCs) and other toxic gases [23]. Few reports have shown the long-term stability and low power consumption by fabricating gas sensors using CuO nanorods, nanowhiskers, nanoflowers, urchin-like towards for target gases like NH<sub>3</sub>, CO, H<sub>2</sub>S etc. However, most of the sensors needed higher operating temperature as mentioned above to show stable response. Moreover, only few sensor parameters were explored.

This work presents the development of CuO based flexible gas sensors for NH<sub>3</sub> detection at room temperature. Single phase CuO nanorectangles (NRs) were synthesized by a simple hydrothermal route and characterized for various

physio-chemical properties. The sensor was fabricated using screen printing, which is a well-established cost-effective technique for the fabrication of sensor systems on flexible and other different types of substrates [24, 25]. The fabricated sensors are operable at room temperature and exhibited superior response as compared to similar type of sensors reported in literatures. The flexible CuO sensor capable of sensing NH<sub>3</sub> of concentrations as low as 5 ppm. In this work, the detailed kinetics of sensing response is analyzed using non-linear regression models and the relationship between time constants and sensor response is also established. Apart from this, stability experiments were performed on the sensor which revealed the high reproducibility of sensing performance towards various concentrations of NH<sub>3</sub>.

## II. MATERIALS AND METHODS

### A. Synthesis of CuO nanostructures

CuO nanostructures were synthesized by mixing 0.1 M of Copper nitrate hemi pentahydrate (Alfa aesar, 98 % purity) and 0.7 M of NaOH (Alfa aesar, 98 % purity) in 75 ml de-ionized water under vigorous stirring for 60 min at room temperature. The dark blue solution obtained following these steps was transferred to a Teflon lined autoclave and kept in the furnace for 12 h at 160°C. The obtained precipitate was washed by centrifugation with water and ethanol several times and dried in air for 24 h.

### B. Flexible CuO sensor device fabrication

Initially, the CuO sensitive layer was prepared by mixing the synthesized CuO nanopowder with 50 wt.% of copolymer which comprised of PMMA-PMBA [Poly (methyl methacrylate)-poly (butyl methacrylate)] as binder and BCA [butyl carbitol acetate (ZCHO, Poland)] as solvent in an agate mortar for 1 hour. The screen for interdigitated electrode (IDE) was prepared with the following dimensions: finger lengths of 10 mm, electrode width of 0.5 mm and spacing between fingers of 0.5 mm. Fig.1a shows the screen-printed IDE using silver (Ag) paste (DuPont 5000) on PET substrate (Fig.1b). After printing, the electrode layer was dried at 120 °C for 20 min. Further, the CuO sensing element with an area of 1×1

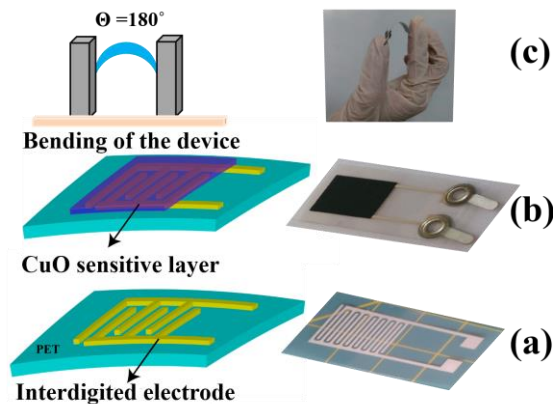


Fig.1. (a) Schematic and digital images of the fabricated sensors and (b) & (c) shows the bending condition enforced and the flexibility of the fabricated device.

cm<sup>2</sup> was printed on the top of the IDE layer as shown in Fig.1b. The fabricated CuO layer then dried at 120 °C for 2 hours. The bending condition and the flexibility of the device is shown Fig.1c.

### C. Gas sensing measurements

The NH<sub>3</sub> sensing efficiency of the device at room temperature was examined in an indigenous gas sensing setup [7]. In brief, static state distribution method was followed for the sensing measurement as follows. Initially, the stable data collection was ensured by preheating the sensor device inside the test chamber to overcome the storage related reversible resistance drift. Further, a predetermined volume of NH<sub>3</sub> was introduced in the sensing chamber. The required concentration of NH<sub>3</sub> vapor was calculated using the following equation [26];

$$C_{ppm} = \frac{V_{\mu L} D_{g/mL}}{M_{g/mol} V_{mL}} \times 2.24 \times 10^7 \quad (1)$$

where,  $C_{ppm}$  is the required vapor concentration,  $V_{\mu L}$  is the volume of liquid analyte,  $D_{g/mL}$  is the density of the liquid,  $V_{mL}$  is the volume of test chamber and  $M_{g/mol}$  is the molecular weight of the liquid analyte (all the subscripts are the respective units). Sensing studies were carried out using the commercially available NH<sub>3</sub> (99 % purity) at room temperature and under ambient conditions (temperature – 27 °C and laboratory relative humidity (RH) 55 - 70 %). A constant voltage of 3V was applied to the sensor and the relative change in sensor resistance was monitored and recorded as sensing signal. Prior to introduction of NH<sub>3</sub> every time, the baseline resistance was measured. The sensing response is calculated from the relative change in sensor's electrical resistance under NH<sub>3</sub> environment by the following equation [26],

$$S = \frac{R_G - R_a}{R_a} \quad (2)$$

where,  $R_a$  is sensor resistance in air ambience, and  $R_G$  is the resistance in NH<sub>3</sub> atmosphere.

### D. Characterization techniques

The crystal structure and phase analysis of the sample (powder and film) were carried out using X-ray diffractometer [Rigaku Ultima III, with Cu K<sub>α</sub> ( $\lambda=1.514$  Å) radiation]. Spectrum RX-FT-IR spectrometer (Perkin Elmer, USA) was utilized for vibration spectroscopy and functional group analysis. The 514.5 nm line from a Renishaw Micro Raman spectrometer with 5 mW argon ion laser as excitation source was used to confirm the structural properties of the CuO nanopowder and the sensor device. Morphological and elemental analyses were performed in a Zeiss ULTRA 55 field emission scanning electron microscopy (FESEM). Transmission Electron Microscopy (TEM) analysis was carried using a Philips CM 200 microscope. The surface morphology and roughness of the film were investigated in non-contact mode by Atomic Force Microscopy (AFM) (Park System's NX-10, South Korea) with a silicon nitride cantilever. For AFM analysis, a scan size of 10 μm and scan rate of 0.5 Hz was used. Surface area and porosity measurements were carried out at liquid nitrogen temperature using a Quantachrome Nova-1000 surface analyzer. N<sub>2</sub> adsorption-desorption isotherm cycle measurements were

performed up to the saturation vapor pressure of nitrogen ( $-196\text{ }^{\circ}\text{C}$ ) and the pore size distribution was determined from the adsorption data using BJH and de Boer's t-method.

### III. RESULTS AND DISCUSSIONS

#### A. Structural analyses of CuO powder and film

The XRD patterns (Fig.2a) of the samples is indexed according to the monoclinic structure (JCPDS data 45-0937) of CuO and there is no evidence of any impurity phases in XRD spectra of both as-prepared powder and fabricated sensor. The lattice parameters ( $a \neq b \neq c$  and  $\alpha = \gamma = 90^{\circ} \neq \beta$  for monoclinic structure) were evaluated from the following equations (3) and (4);

$$n\lambda = 2d \sin \theta \quad (3)$$

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{\sin^2 \beta}{b^2} + \frac{l^2}{c^2} - 2hl \cos \frac{\beta}{ac} \right) \quad (4)$$

The obtained values are  $a = 4.688\text{ \AA}$ ,  $b = 3.427\text{ \AA}$ ,  $c = 5.132\text{ \AA}$ , for CuO powder and  $a = 4.688\text{ \AA}$ ,  $b = 3.427\text{ \AA}$ ,  $c = 5.132\text{ \AA}$  for CuO based sensor device. The average crystallite size of 35 nm was estimated using the standard Scherrer's relation  $D = k\lambda / \beta \cos \theta$ , where D is the crystallite size, k the shape factor,  $\beta$  is the fullwidth half maximum. It is clear that there is no change in crystal structure observed for the film. The calculated lattice parameters found to closely match with those reported in literatures [3, 27].

The FTIR spectra recorded in the range 400 to 4000  $\text{cm}^{-1}$  for the CuO powder and CuO thick film is shown in Fig. 2b. The three signature peaks observed at 418, 496 and 603  $\text{cm}^{-1}$  belongs to the Au, Bu and the other Bu modes of CuO. The high frequency peak at 603  $\text{cm}^{-1}$  can be attributed to the Cu-O stretching along the (-101) direction. Absence of any peaks in the 605-660  $\text{cm}^{-1}$  range rules out the existence of  $\text{Cu}_2\text{O}$  phase. The broad absorption at 3394  $\text{cm}^{-1}$  can be attributed to the stretching vibration of absorbed  $\text{H}_2\text{O}$  or surface hydroxyls of the sample, and the bands at 1553 and 1378  $\text{cm}^{-1}$  are assigned to the asymmetrical stretching vibration and symmetrical stretching vibration of  $\text{RCOO}^-$  absorbed on the surface of CuO, respectively. It is evident that there is no presence of vibrational modes related to the binder molecules on the surface of CuO film observed indicates the purity of the device. Fig.2c shows the micro-Raman spectra recorded for the CuO nanopowder and film. The monoclinic phase of CuO belongs to the  $\text{C}_{6h}^{2h}$  space group, for which the primitive cell contains two molecular units. Thus, from the

selection rule, it is clear that there are twelve vibrational modes at the zone center, including three acoustic modes ( $A_u + 2B_u$ ), six IR active modes ( $3A_u + 3B_u$ ) and three Raman active modes ( $A_g + 2B_g$ ) [27]. Based on group theory, these lattice vibrations at the  $\Gamma$  point of the Brillouin zone are given as,

$$\Gamma = 4A_u + 5B_u + A_g + 2B_g \quad (5)$$

From Fig.2c, it is seen that the peaks are broadened and downshifted as compared to the CuO single crystal vibrations [8]. The spectrum shows three peaks at 271, 320 and 596  $\text{cm}^{-1}$ . The  $A_g$  mode observed at 271  $\text{cm}^{-1}$  is associated with the in-phase/out-phase rotations of the CuO asymmetric stretching mode whereas while  $B_{1g}$  bending mode existing at 320  $\text{cm}^{-1}$ . The  $B_{2g}$  mode observed at 596  $\text{cm}^{-1}$  is associated with the symmetric oxygen stretching. The three active Raman modes identified here are in accordance with the literature reports [27]. These significant peaks also indicate the single phase and good crystallinity of the as-synthesized CuO nanostructures. The broadening of the peaks can be attributed mainly to the quantum confinement effect of CuO nanostructures [28]. In the case of fabricated film only the three vibrational modes corresponding to CuO nanoparticles are present which rules out the possibility of impurities or binder left over.

#### B. Morphological and surface analyses of CuO powder and film

Fig.3a shows the FE-SEM image of synthesized CuO nanostructures which illustrates the rectangle-like morphology with smooth surfaces. The thin nature of the NRs with an average thickness of 45 nm can be seen from the TEM image represented in Fig 3b. The NRs are well shaped, blunt edged and are quite transparent. From TEM analysis, the average length is found as 950 nm and while breadth as 450 nm. Fig.3c shows the 2D AFM image of the CuO film. The  $5 \times 5\text{ }\mu\text{m}$  scan of the AFM image reveals that the CuO sensing layer composed of near uniform distributed nanostructures and void areas. The root mean square surface roughness of the film was found as 130 nm. The statistical analysis revealed the height profile of the film as shown in Fig.3d.

BET surface area analysis was performed on the samples to find examine the adsorption and desorption properties. The  $\text{N}_2$  adsorption and desorption curves shown in Fig. 3e indicates the type III isotherm behavior due to multilayer adsorption with a narrow H3 type hysteresis loop

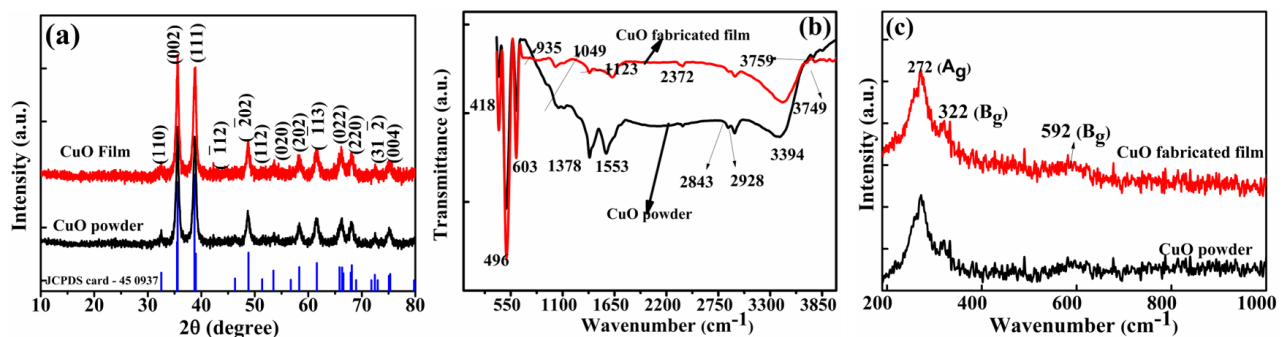


Fig. 2. (a) XRD spectra, (b) FTIR spectra and (c) micro Raman spectra of CuO powder and screen printed CuO film.

between 0.8 to 1  $P/P_0$ . The specific surface area of 29  $m^2/g$  was estimated from the adsorption/desorption isotherm. In addition, pore size distribution was calculated from the adsorption data using BJH and de Boer's method (inset in Fig.3e). The characteristic  $N_2$  adsorption and desorption isotherms and pore size distribution analyses reveal that the sample is mesoporous ( $> 2$  nm) with average pore diameter of

8 nm. It is important to mention that there is no visible pore structure observed from the morphological analysis. This indicates that the estimated pore size may be from the slit-like pores raised during the assembly of rectangle-like structures. The porosity of the nanomaterial is known to have strong influence on the sensing performance [29].

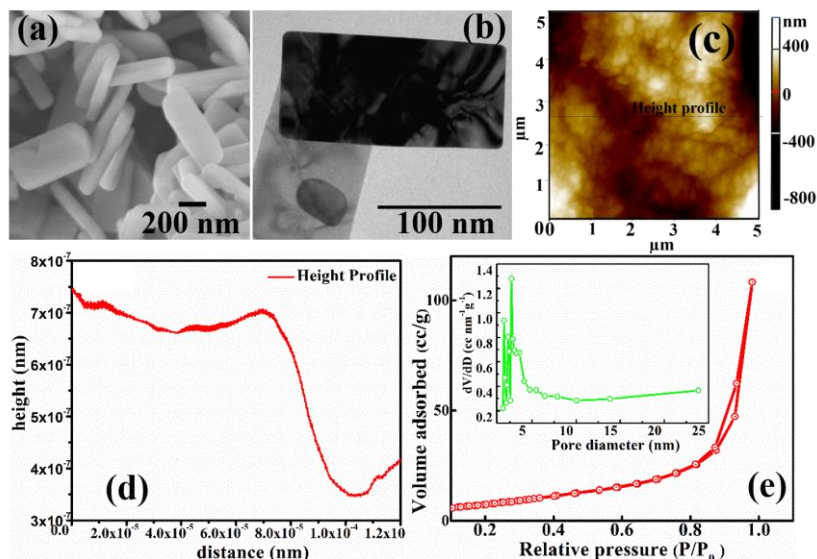


Fig.3: (a) FE-SEM (b) TEM images of CuO NRs (c) AFM image (d) height profile of the CuO film and (e)  $N_2$  adsorption - desorption curves of CuO NRs (the inset shows pore size distribution calculated from de-Boer's method).

### C. $NH_3$ sensing performance of the flexible CuO sensor

Before being exposed to  $NH_3$ , the ohmic nature of the fabricated CuO NRs electrode was checked. Fig.4 shows the I-V plot of the sensor device. The output current measurements were made with voltage sweeping between -10 V and +10 V. The linear I-V characteristics of the device shows the good ohmic contacts with no interfacial barrier or traps between the CuO sensing layer and Ag (IDE) electrodes. To check the effect of bending on the electrical properties, the sensor was bent at an angle  $90^\circ$  and kept in this condition for 24 h. The sensor was then brought back to flat condition (this mode of measurement will be mentioned as "after bending") and I-V measurement was carried out. It is seen that the sensor showed I-V characteristics similar to the one before bending it. The average resistance could be calculated from the slope of these lines. The initialization of the sensing response measurement

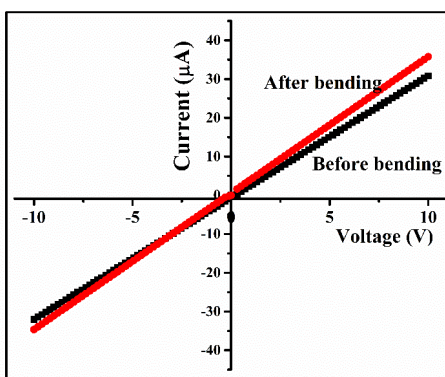


Fig. 4. I-V Characteristics of nanostructured flexible CuO film.

When the predetermined concentration of  $NH_3$  is allowed into the chamber,  $NH_3$  molecules interact with the adsorbed oxygen on the surface of CuO sensor, and releases electrons thereby increasing the sensor's resistance. Afterwards, the original base resistance can be retrieved back to the baseline by removing the  $NH_3$  supply, and the time taken to bring back the resistance within 10 % of the baseline is known as the recovery time. The sensing performance of the sensor was

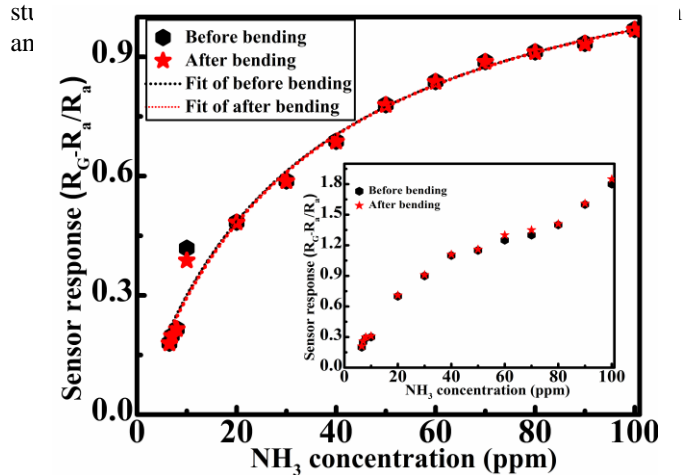
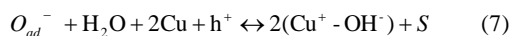


Fig.5. Sensing performance of flexible CuO sensor before and after bending for different concentrations of  $NH_3$  at RT and dotted lines are the corresponding fit (Inset- response of sensors @ RH=50 %).

The sensor response is found to increase with increasing NH<sub>3</sub> concentration which is a typical behavior of MO<sub>x</sub> sensors [26]. In order to observe the effect of bending on the sensor response, the sensor response was measured after recovering the sensor from bending as mentioned earlier. It is seen that the sensor response is not affected even after a day-long bending and the estimated response is shown in Fig.5. It should be noted that the sensor shows good response down to 5 ppm of NH<sub>3</sub>. It is worth mentioning that for automotive industries, the meaningful concentration is from 25 mg/s to 8 ppm [30] and long term allowed concentration is 20 ppm in passenger cabinets [31] for which our sensor showed impressive response of 0.18, 0.20, 0.22 and 0.52 for 5, 7, 8 ppm and 20 ppm, respectively. A maximum response of 0.98 observed for 100 ppm NH<sub>3</sub>.

The gas sensing mechanism is a process between the adsorbed species and the MO<sub>x</sub>s surface [19,26,27]. Upon exposure to air, the atmospheric oxygen is physisorbed on the sensor's surface which is typically temperature dependent. In the case of SnO<sub>2</sub>, it was found that the adsorption of O<sub>2</sub> takes place at the sensor's surface at low temperatures [32]. Here, the sensing experiments were carried out in RH ≥ 50 % which is comparable to the sensor's environmental conditions for real time applications. Hence, in addition to the physisorbed oxygen, the capillary condensation of water vapor in the adsorption sites of the sensor's surface as per the Grotthus mechanism [33] will be also taken into the account. By considering these two factors, the sensing response of the present sensor was carried out in RH of 50 % and the results are given in inset of Fig.5. It is seen that the sensor response to NH<sub>3</sub> at low concentrations from 5 to 10 ppm is greater by 0.8 % and from 10 – 100 ppm it is greater by 2 %. In addition, the response at RH=50 % found to move towards attaining a linear relationship with the NH<sub>3</sub> concentration. The lower humidity level favors more adsorption of NH<sub>3</sub> while higher humidity level leads a competition of NH<sub>3</sub> and physisorbed oxygen along with water vapor present in the atmosphere. The most probable interaction between the physisorbed oxygen and water vapor is explained for SnO<sub>2</sub>. In the view of this, the present sensing mechanism is explained by the following reactions,



The reaction eqn. 6 shows the adsorption of oxygen molecule on the surface while eqn.7 shows the subsequent reaction with the water vapor in the case of humid atmosphere. This interaction implies that under these adsorption/desorption conditions at high humid conditions, there will be a competition between water vapor and NH<sub>3</sub> for oxygen. Hence, the lesser sensor response observed at laboratory RH compared to 50 % RH. At high humid atmosphere, the formation of dipoles in eqn. 7 hinders the escape of electrons by increasing the work function of the MO<sub>x</sub> [34]. This mechanism however, further requires prove from direct spectral evidences similar to the reports available for SnO<sub>2</sub> [32, 35]. The observed ultra-high response for such low concentrations of NH<sub>3</sub> can also be attributed to the more

adsorption sites facilitated by the high surface area (29 m<sup>2</sup>/g) of CuO NRs.

Chemi-resistive sensors rely on the change in resistance mechanism due to the adsorption and desorption of the detected matter. Hence, the change in resistance should be proportional to the amount of the adsorbed and desorbed species onto the surface. The sensing mechanism can be explained in terms of the depletion layer model, using the adsorption-desorption (A-D) kinetics that take place at the crystalline interface and causing the change in carrier concentration. In such a case, the operating temperature, morphology, porosity play a major role along with the concentration and nature of the target gas. The observed response behaviors of Fig. 5 were analyzed with non-linear regression model corresponds to Langmuir adsorption isotherm as follows (dotted lines in Fig. 5) [36, 37],

$$\frac{\Delta R}{R_0} = \frac{Q_{sat} \times k \times c^n}{1 + k \times c^n} \quad (10)$$

where,  $\Delta R/R_0$  is the amount of NH<sub>3</sub> adsorbed by the sensor's surface (ppm),  $Q_{sat}$  is the maximum adsorption,  $k$  is a constant (kJ<sup>2</sup>/mol<sup>2</sup>) related to energy. In both cases, the sensor response behaviors showed good agreement with the Langmuir model. From this model, the saturation response of 1.35 and 1.33 was observed before and after bending mode measurements and the parameters are listed in Table I.

The sensor response time is the time required to cause a change in electrical resistance/conductance (R/C) on introducing NH<sub>3</sub> in a specific range by 90%. The calculated response time of the flexible CuO sensor lies between 5-9 min for different NH<sub>3</sub> concentrations. Fig. 6a shows the response and recovery kinetics of the fabricated sensor for different concentrations of NH<sub>3</sub> (5, 10, 20, 60 and 100 ppm).

It is worthy to mention that the sensor responded to 5 ppm of NH<sub>3</sub> in 90 s and recovered in 185 s. Fig.6b shows the variation of response and recovery items with respect to NH<sub>3</sub> concentration. It is seen that the response time decreases with increase in concentration while recovery time increases. In order to further analyze the A-D process of NH<sub>3</sub> on flexible CuO surface, the adsorption and desorption rate constants ( $\tau$ ) were estimated.

TABLE I  
LANGMUIR ISOTHERM FITTING PARAMETERS OF FLEXIBLE CUO SENSING RESPONSE TOWARDS DIFFERENT CONCENTRATION OF NH<sub>3</sub>

Mode	R <sup>2</sup>	k	c	Q <sub>sat</sub>
Flat mode	0.98	0.03	0.06	1.35
After bending	0.98	0.03	0.04	1.33

By considering the monolayer adsorption of reducing gas at T (Room Temperature), Langmuir adsorption kinetics for a single adsorption site with the conductance transient can be given as [34, 35],

$$C(t)_{resp} = C_0 + C_1[1 - \exp(-t/\tau_{resp})] \quad (9)$$

$$C(t)_{rec}^* = C_0^* + C_1^*[-\exp(-t/\tau_{reco})] \quad (10)$$

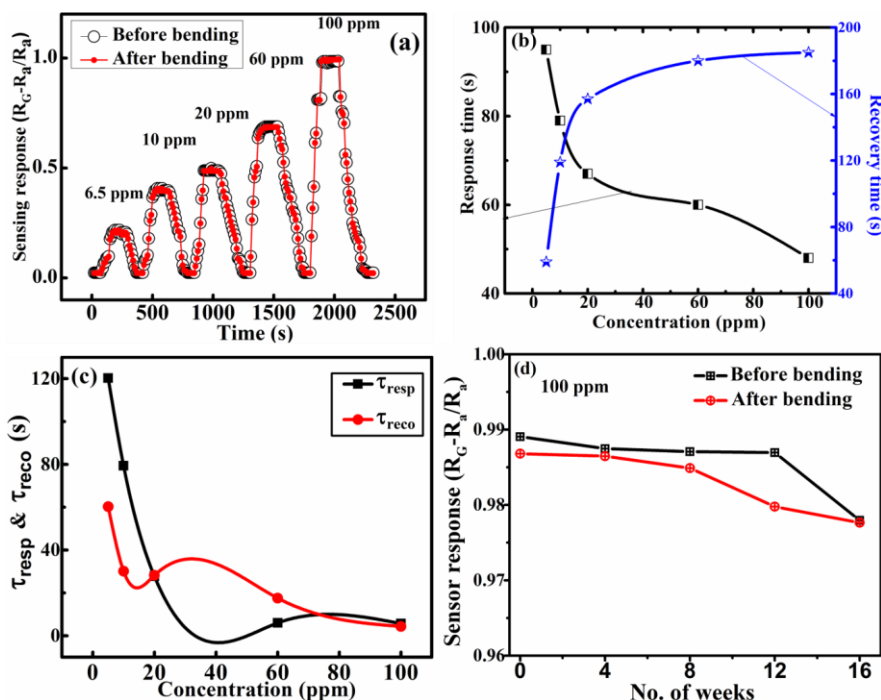


Fig.6. (a) Response - recovery plot of flexible CuO sensor for different concentrations of ammonia at Room Temperature, (b) variation of response and recovery times with ammonia concentration, (c) the time constant calculated from the regression analysis and (d) stability analysis of the sensor for 100 ppm of  $\text{NH}_3$ .

where,  $[C(t)_{\text{resp}}]$  and  $[C(t)_{\text{rec}}^*]$  are the conductance transients of response and recovery, respectively,  $C_0$  and  $C_0^*$  baseline conductance of the sensor and  $\tau_{\text{resp}}$  &  $\tau_{\text{reco}}$  are the relaxation times. The conductance corresponds to response of the flexible CuO sensor to different concentrations of  $\text{NH}_3$  measured at room temperature is fitted according to the equation 9 and the results are presented in table. II (ESI† See supporting information Fig. S1). The  $R^2$  values show that the fits are in good agreement. The non-significant change in the  $C_0$  value suggests the negligible baseline drift with increase in gas concentration. Similarly, the conductance corresponding to recovery curve was also analyzed using desorption model in equation 10. The recovery plots of the flexible CuO sensor for different  $\text{NH}_3$  concentrations are fitted well and the parameters obtained are also listed in Table II. Similar results were observed as response, the value of  $C_0^*$  varied slightly which indicate the marginal baseline drift in the sensor. It can be observed that the metric of how rapid the  $\text{NH}_3$  A-D process decreases as the gas concentration increases.

TABLE II  
ADSORPTION AND DESORPTION RATE PARAMETERS OBTAINED FROM THE FITTING OF TIME DEPENDENT CONDUCTANCE CHANGE IN THE PRESENCE AND ABSENCE OF AMMONIA.

C	Response transients			Recovery transients		
	$\tau_{\text{resp}}(\text{s})$	$C_0$ ( $10^{-7}$ )	$R^2$	$\tau_{\text{reco}}(\text{s})$	$C_0^*$ ( $10^{-7}$ )	$R^2$
6.5	120.25	40.14	0.98	60.28	2.15	0.98
10	79.36	39.55	0.99	30.12	0.80	0.98
20	8.75	40.35	0.99	28.23	0.92	0.97
60	6.02	40.12	0.98	22.56	1.92	0.99
100	5.7	40.21	0.98	4.36	2.81	0.98

Fig.6c shows the plot of concentration vs. relaxation times. As seen in figure the linear relationship is maintained up to 20 ppm and it deviates from the linearity at around 60 ppm, from this aspect, it can be concluded that the response time with  $\text{NH}_3$  concentration are likely governed by a physical process that involves the physio-adsorption of  $\text{NH}_3$  on the CuO surface.

Stability of the flexible CuO sensor towards  $\text{NH}_3$  gas was analyzed for 3 months with an interval of 21 days for 100 ppm of  $\text{NH}_3$ . From the Fig. 6d, it can be seen that there is no significant drift in the sensor response over a period of 2.5 months and a very slight drift afterwards can be observed. However, a decrease in response of about 0.07 % was observed which may be due to the humidity induced effect [38]. This long-term measurement reveals the good stability of the flexible CuO sensor. The observed sensing response of the flexible CuO sensor towards  $\text{NH}_3$  at room temperature is comparable with the response observed for CuO thick films prepared on other substrates like glass slides [39].

TABLE III  
COMPARISON OF SENSING PERFORMANCES

No	Material	Max. response/ $\text{NH}_3$ concentration	Ref
1	CuO Rods	0.98/1000	[40]
3	ZnO Rods	0.3/100	[41]
4	CuO Spheres, needles	0.8/100	[42]
5	rGO	0.8/100	[43]
7	CuO NRs	1/100	This work

Table III shows the comparison of sensing properties observed for different materials. It is interesting to reveal that the

fabricated flexible CuO sensor shows much better response at room temperature. Thus, the present investigation suggests that the fabricated flexible CuO sensor can selectively be used to detect low concentration of NH<sub>3</sub> at room temperature.

#### IV. CONCLUSION

CuO nanorectangles were successfully synthesized by a simple surfactant-free hydrothermal method. The X-ray diffraction analysis revealed the monoclinic phase of CuO with high crystallinity and purity. Flexible NH<sub>3</sub> sensor was fabricated by screen printing of CuO nanorectangle sample on flexible PET substrate. The sensor was able to respond to as low as 5 ppm to 100 ppm of NH<sub>3</sub> at room temperature. The highest response of 0.98 was achieved towards 100 ppm of NH<sub>3</sub>. The response of the sensor at room temperature can be attributed to the large surface area available for gas adsorption to take place. The main advantage of the sensor is that it is operable at room temperature and does not require any external stimulus for response and recovery. Additionally, even after being subjected to bending deformation for 24 h, the sensor was able to reproduce the response with negligibly small drift. The stability measurements showed that the sensor response is not significantly affected by any humidity etc. over a period of 3 months. The overall superior performance of the sensor implies that it can be used in wearable and other hand-held sensor devices employed in diverse applications. As a future application, the sensor can be attached to cloths with low power electronics and the data will be transferred to mobile phones via radio frequency identification (RFID) methods.

#### References

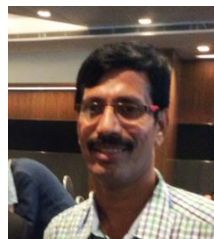
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