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CeO_2 thin film as a low-temperature formaldehyde sensor in mixed vapour environment

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Abstract. Nanostructured cerium oxide thin film was deposited onto the glass substrate under optimized condition using spray-pyrolysis technique. X-ray diffraction result indicates polycrystalline nature of the film with fluorite-type face-centered-cubic structure. The atomic force micrograph indicates the presence of nanocrystallites over the film surface. The vapour sensing characteristics of the annealed film were studied by chemiresistive method for various concentrations of formaldehyde vapour at room temperature (~ 30 °C). For 0·5 ppm of formaldehyde vapour, the film shows a response and recovery time of 36 and 1 s, respectively. The vapour sensing properties of the cerium oxide film in mixed environment were studied and reported.

Keywords. Nanostructure; spray pyrolysis; cerium oxide; chemiresistive; formaldehyde; breath analysis.

1. Introduction

Formaldehyde is one of the important volatile organic compounds used in many household products such as in detergents, paints and also in drugs (Korpan *et al* 2000). The occupational safety and health administration (OSHA) has adopted the permissible exposure level (PEL) of 0·75 ppm. However, formaldehyde is also a clinically important vapour observed in the human exhaled breath due to imbalance in pulmonary organ system (Poli *et al* 2010). The formaldehyde analysis in the exhaled breath is a good biomarker for diagnosing lung cancer at an earlier stage (Fuchs *et al* 2010). Hence, there is a need for formaldehyde detection in diseases diagnosing as well as for environmental monitoring.

Different traditional techniques were available to detect formaldehyde such as gas chromatography (Poli *et al* 2010), electrochemical (Marzuki *et al* 2012), conductometry (Sosovska *et al* 2008), calorimetric (Feng *et al* 2010; Wang *et al* 2012), potentiometric (Korpan *et al* 2000) and bio sniffers (Kudo *et al* 2012). But these techniques were expensive and require experienced operators and skillful interpretation of results. Hence, there exists a demand for simple, portable, high selective and cost-effective formaldehyde sensors.

Various undoped and doped binary metal oxide semiconductors such as SnO_2 (Wen and Tianmo 2009) ZnO (Zhang *et al* 2011), In_2O_3 (Wang *et al* 2009), NiO (Dirksen *et al* 2001), Ga-doped ZnO (Han *et al* 2009), Fe, Ti, Sn doped ZnO (Han *et al* 2010) CdO-mixed In_2O_3 (Chen *et al* 2008a,b) and Cd-doped TiO_2–SnO_2 (Zeng *et al* 2009) were reported as formaldehyde sensitive materials. The electrical resistance of these materials changes upon exposure to formaldehyde vapour at elevated temperature. However, much work has not been reported at low temperature and selectivity of the materials in mixed environment.

Cerium oxide (CeO_2) is one of the wide bandgap metal oxide semiconductors used as solid oxide fuel cells (Kharton *et al* 2011), electrochromic material (Porqueras *et al* 2003), catalyst (Trovarelli 2012), corrosion protection (Zhong *et al* 2008) as well as gas sensors (Barreca *et al* 2007). Due to chemical stability and high diffusion coefficient for oxygen, CeO_2 is used as an oxygen sensor (Jasinski *et al* 2003). Depending upon the size of microstructure, CeO_2 has both ionic and electronic conductivities (Chiang *et al* 1997). Therefore, the properties strongly depend on microstructure and in turn depend on processing condition. Different techniques were available to obtain CeO_2 thin films such as sputtering (Hollmannt *et al* 1992), epitaxy (Chen and Meng 2012), chemical vapour deposition (CVD) (Barreca *et al* 2007), e-beam evaporation (Porqueras *et al* 2003), sol–gel-dip (Murali 2008), etc and each technique has its own merits and demerits to achieve controlled and reproducible properties. Of many techniques, the spray pyrolysis is a simple and cost-effective and requires less purity precursor materials. The properties of the spray-deposited film can be controlled through substrate temperature, solute–solvent type, solute concentration and carrier gas pressure. In the present work, cerium oxide thin films consisting of

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nanocrystallites were prepared by spray-pyrolysis technique and its structural, morphological and formaldehyde sensing characteristics were investigated at room temperature in mixed environment.

2. Materials and methods

2.1 *Preparation of sensing element*

The thin film of cerium oxide was deposited onto the glass substrate by spray-pyrolysis technique. The fabrication and optimization of home-made spray pyrolysis unit have been reported earlier (Jeyaprakash *et al* 2011). The precursor solution was prepared by dissolving 0·025 M of cerium nitrate (III) hexahydrate ($Ce(NO_3)_2{\cdot}6H_2O$, 99·99% purity, Sigma Aldrich) salt in 50 mL of deionized water. The precursor solution was then sprayed as a fine mist over the pre-heated glass substrate of 25 × 15 × 1·5 mm dimension. The deposition temperature was fixed at 250 °C, which was monitored using a microcontroller-based thermostat with an accuracy of ± 1 °C. The pyrolytic reaction given in (1) will occur on the substrates and forms well-adherent CeO_2 film. The deposited films were then annealed at 300 °C for 3 h to improve the crystallinity

$$Ce(NO_3)_3{\cdot}6H_2O \rightarrow CeO_2 + 3NO_2 \uparrow + 6H_2O \uparrow + \frac{1}{2}O_2 \uparrow . \quad (1)$$

The structural studies of the film were carried out through X-ray diffractometer (D8 focus, Bruker) with CuKα radiation at a generator setting of 30 mA and 40 kV. The microstructure of the film surface was observed using atomic force microscope (AFM, Park System, XE-170).

2.2 *Vapour sensing set-up and measurement*

The vapour sensing characteristics of the CeO_2 film were carried out using home-made glass test chamber (1·5 L capacity). It consists of a sample holder with heater, septum provision to inject liquid volatile organic compounds, outlet port and electrical terminals for heater and film resistance measurements. Electrical contacts on the film surface were made by using thin copper wire and silver paste. The terminals were attached in series with 10 MΩ standard resistor to a 9 V d.c. power supply. The voltage drop across the standard resistor was connected to an operational amplifier with a gain of 100. The output signal from the op-amp is connected to a computer-controlled National Instruments–data acquisition board (NI-DAQ 6212) interfaced with LabVIEW software to record voltage and, then, to convert into electrical resistance of the film. The schematic representation of vapour sensing set-up and measurement system is shown in figure 1. Before sensing studies, the film was conditioned at 250 °C for 5 h to remove undesirable pre-adsorbed organic and water molecules. The resistance of the film measured in dry air atmosphere was found to be 560 GΩ and is taken as baseline resistance (R_o). The high resistance of the film is due to scattering of charge carriers at the boundaries of small crystallites. A calibrated volume of liquid formaldehyde is injected into the test chamber

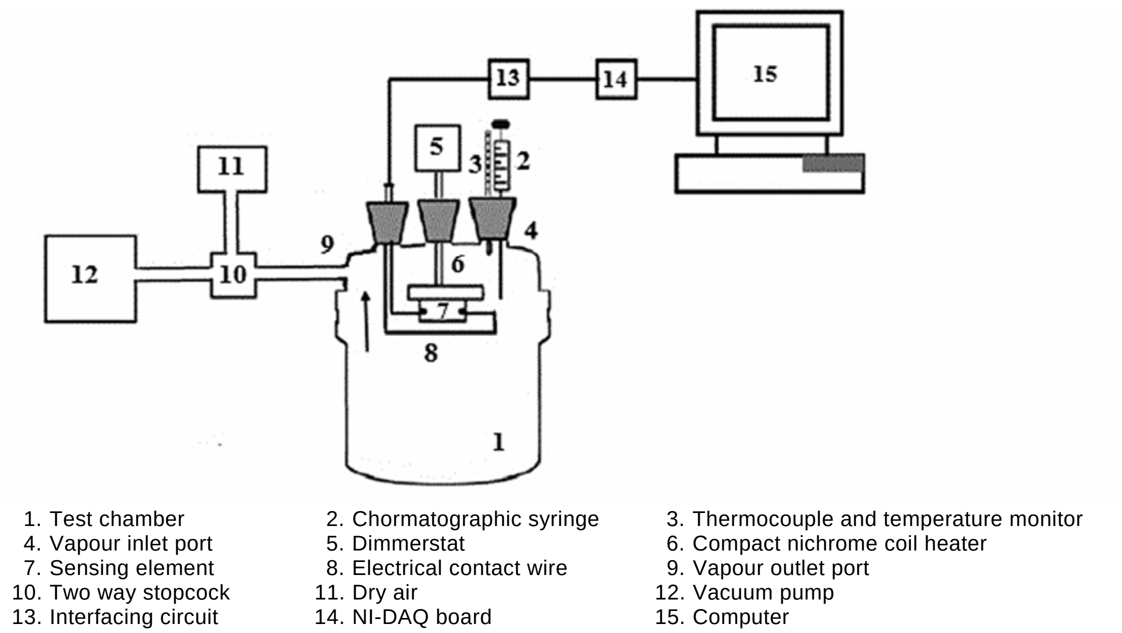

Figure 1. Schematic representations of thin film vapour sensing set-up and measurement system.

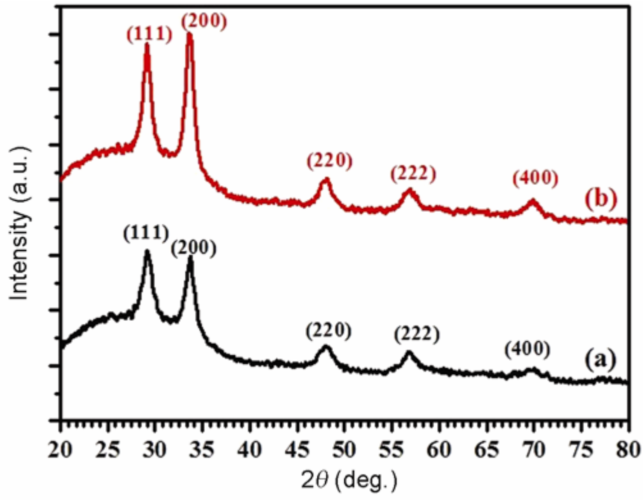

Figure 2. XRD pattern of (**a**) as-deposited and (**b**) annealed CeO_2 thin films.

using chromatographic syringe and simultaneous resistance measurement was made for every 500 ms. In the presence of vapours, the saturated electrical resistance (R_g) was obtained and the sensing response was calculated using (2)

$$S\% = \frac{(R_o - R_g)}{R_g} \times 100, \quad (2)$$

where R_o and R_g are the film electrical resistance in dry air and in formaldehyde environment, respectively.

3. Results and discussion

3.1 *Structural studies*

The X-ray diffraction (XRD) patterns of as-deposited and annealed CeO_2 thin films were shown in figure 2. When compared to as-deposited film pattern, the annealed film has little bit sharp and high intense preferential peaks due to increase in the crystallinity. Also, both the patterns indicate polycrystalline nature with fluorite-type face-centered-cubic structure as indexed with standard JCPDS card no. 34-0394. The crystallites size obtained from the preferential peak using Scherrer formula was found to be 20 and 25 nm for as-deposited and annealed CeO_2 thin films, respectively. The calculated lattice parameter value was 5·401 Å, which is in good agreement with the previously reported value (Avellaneda *et al* 2008).

3.2 *Surface topography*

The atomic force micrograph shown in figure 3 indicates that the crystallite size of the annealed film is slightly higher than as-deposited film, which is well in accordance

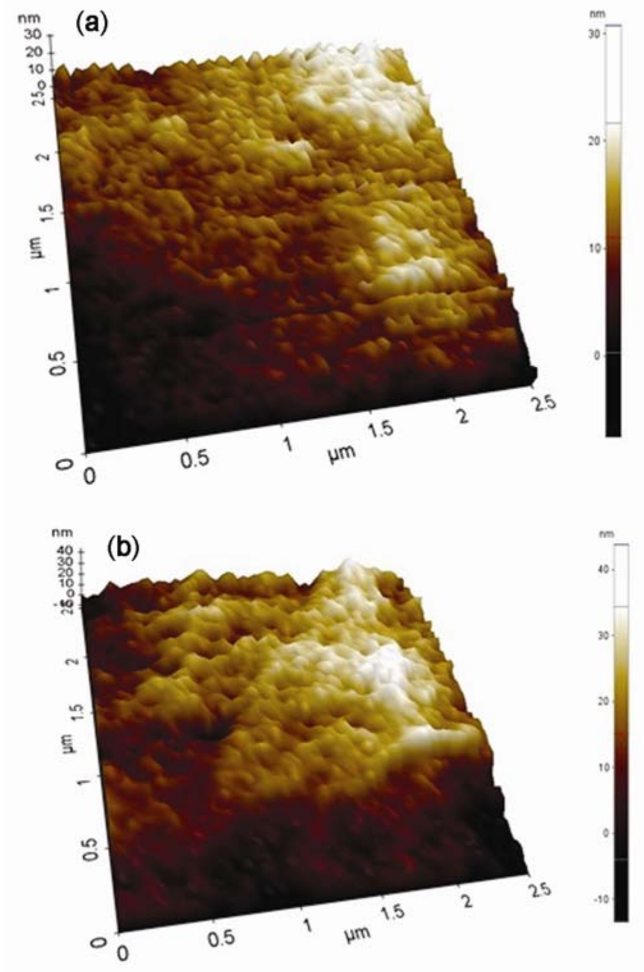

Figure 3. Surface topography of (**a**) as-deposited (**b**) annealed CeO_2 thin films.

Table 1. Surface profile parameters of spray-deposited CeO_2 thin films.

Parameters	As-deposited CeO_2	Annealed CeO_2
Mean roughness (R_a)	4·492 nm	8·135 nm
Peak valley line (R_{pv})	33·920 nm	57·198 nm
Root mean square roughness (R_{rms})	5·619 nm	9·811 nm
Skewness (R_{sk})	0·351	0·065
Kurtosis (R_{ku})	2·798	2·477

with the XRD results. The surface profile parameters, namely, average roughness (R_a), peak valley distance (R_{pv}), skewness (R_{sk}), Kurtosis (R_{ku}) for as-deposited and annealed CeO_2 thin films are given in table 1.

Annealed films show high R_a, R_{pv} and R_{rms} and lesser R_{sk} and R_{ku} values when compared to the as-deposited CeO_2 films. A similar result for annealed $La_2Ce_2O_7$ film was reported earlier by Lim *et al* (2011). The annealed film promotes a better crystallinity with small crystallites and high surface roughness. This favours more adsorption of atmospheric oxygen on the film surface, resulting in an increase of sensing sites (Min and Choi 2004; Mirabbaszadeh and Mehrabian 2012; Prajapati *et al* 2013), which will enhance the gas/vapour sensing performance of the film.

3.3 *Vapour sensing studies*

In ambient condition, the atmospheric oxygen molecules trap the conduction band electron from the surface of CeO_2 crystallite and chemisorbed as O_2^- ion at low temperature (Barsan and Weimar 2001). This will increase the surface resistance of CeO_2 film. As such, when the film surface is exposed to formaldehyde vapour, reduction reaction will occur with removal of adsorbed oxygen ion. This will decrease the CeO_2 film resistance and lead to detection of formaldehyde vapour. Equations (3) and (4) give the reaction scheme in the detection of formaldehyde vapour through change in CeO_2 film resistance

$$O_2 + e^- \xrightarrow[\text{CeO}_2\text{ surface}]{} O^-_{2(\text{ads})}, \quad (3)$$

$$\text{HCHO} + O^-_{2(\text{ads})} \xrightarrow[\text{CeO}_2\text{ surface}]{} CO_2\uparrow + H_2O\uparrow + e^-. \quad (4)$$

The decrease in CeO_2 film resistance towards different concentrations of formaldehyde vapours is shown in figure 4. It indicates an appreciable decrease in film resistance from 560 to 100 GΩ as formaldehyde concentration increases from 0 to 10 ppm. Above 10 ppm, no appreciable change in resistance was observed. Also the sensitivity (resistance change per unit concentration of vapour, i.e. slope of the figure 5) was observed to be good for low range of formaldehyde vapour concentration (1–5 ppm) and is shown as a table in the inset of figure 4. This may result in lesser oxygen ions on the CeO_2 film surface, and, hence, the excess of formaldehyde vapours could not react at higher concentration.

3.3a *Response and recovery studies*: Figure 5 displays the transient response of the CeO_2 film for different formaldehyde concentrations from 0·5 to 100 ppm. An instantaneous change in film resistance was observed when exposed to formaldehyde vapour. This indicates the rapid response of CeO_2 film towards formaldehyde vapour and is due to nanocrystallite present over the surface of the film, which enhances the reaction rate. The response time was calculated over the time taken for the film to attain 90% of baseline resistance after the exposure of formaldehyde vapour, while the time elapsed for the film to reach 10% of baseline resistance after venting the formaldehyde vapour was taken as recovery time. Figure 6

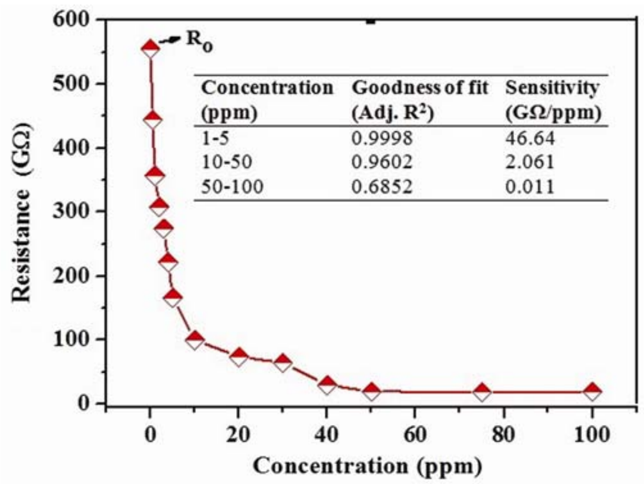

Figure 4. Surface electrical resistance variations in CeO_2 thin film as a function of formaldehyde concentration. (Insert table displays the adjusted R^2 values and sensitivity in three different concentration ranges.)

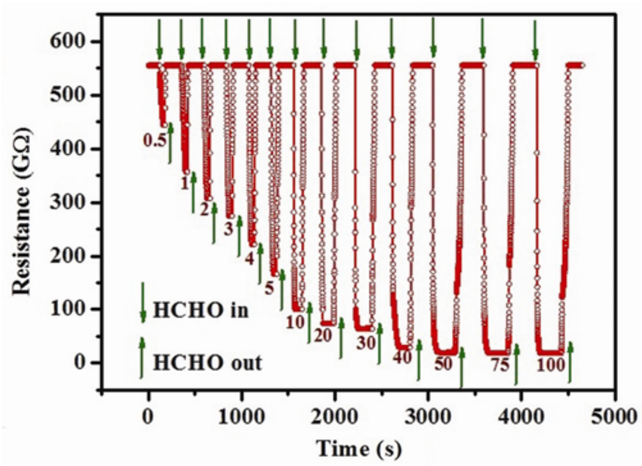

Figure 5. Transient response of CeO_2 film for different formaldehyde concentrations.

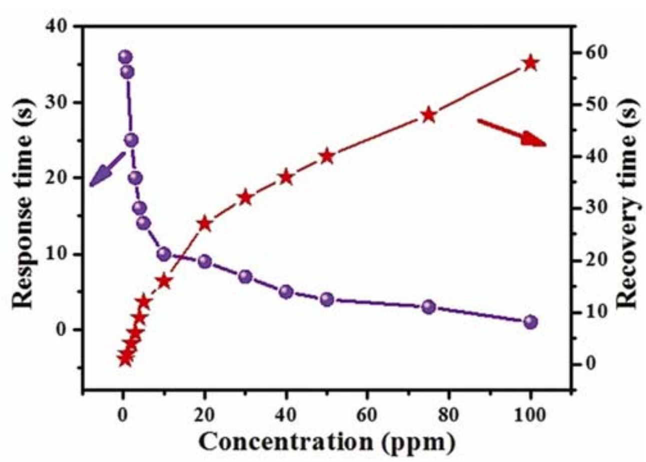

Figure 6. Variation in response and recovery times for different formaldehyde concentrations.

indicates the response and recovery times for different concentrations of formaldehyde vapours. At higher formaldehyde concentration, the interacting rate of the molecules over the surface of the film is high, thereby fast response was observed. On the contrary, at higher concentration, more number of adsorbed molecules could not be desorbed at room temperature, causing an increase in recovery time. The response and recovery times for 0·5 and 50 ppm vary from 36 to 1 s and 1 to 58 s, respectively. Also, no appreciable change in response was observed for the concentration less than 0·5 ppm and indicates the minimum detection limit at room temperature.

3.3b *Sensing response to different reducing vapour and stability*: The sensing response of the spray-deposited CeO_2 thin film towards other reducing vapours such as humid air (relative humidity = 75%), ammonia, acetone, ethanol, toluene, xylene and trimethylamine in dry air atmosphere was studied without changing other experimental conditions. Figure 7(a) picturizes the sensing response of CeO_2 film for individual vapours of nearly 1 ppm concentration. The result revealed that CeO_2 film had a good sensing response towards formaldehyde than towards other reducing vapours at room temperature. The selectivity of the film towards a particular vapour can be expressed as (5)

$$\text{Selectivity} = \frac{S_{\text{TV}}}{S_{\text{IV}}}, \quad (5)$$

where S_{TV} and S_{IV} are the sensing responses of the film towards target vapour and interfering vapour, respectively. The obtained result shown in figure 7(b) indicates that CeO_2 thin film is highly selective towards formaldehyde vapour. The catalytic effect (Godinho *et al* 2007) of nanostructured CeO_2 thin film increases the number of chemisorbed oxygen ions over the film surface and promotes the reaction with formaldehyde vapour. Moreover, the crystalline film being highly oriented could be a potential reason for increased selectivity (Tricoli *et al* 2010) towards formaldehyde vapour at room temperature. Yet, the understanding of selective gas detection of metal oxide semiconductor is a challenging one and makes it a striking area of research. The stability of the film was tested with 1 ppm of formaldehyde concentration for a period of 6 months and figure 8 substantiates the observed good stable response of CeO_2 film towards formaldehyde vapour at room temperature. A relative comparison of CeO_2 with the reported chemiresistive-type formaldehyde sensing materials is shown in table 2. It shows that the spray-deposited nanocrystalline CeO_2 thin film has better sensing response towards formaldehyde vapour at room temperature with shorter response and recovery times.

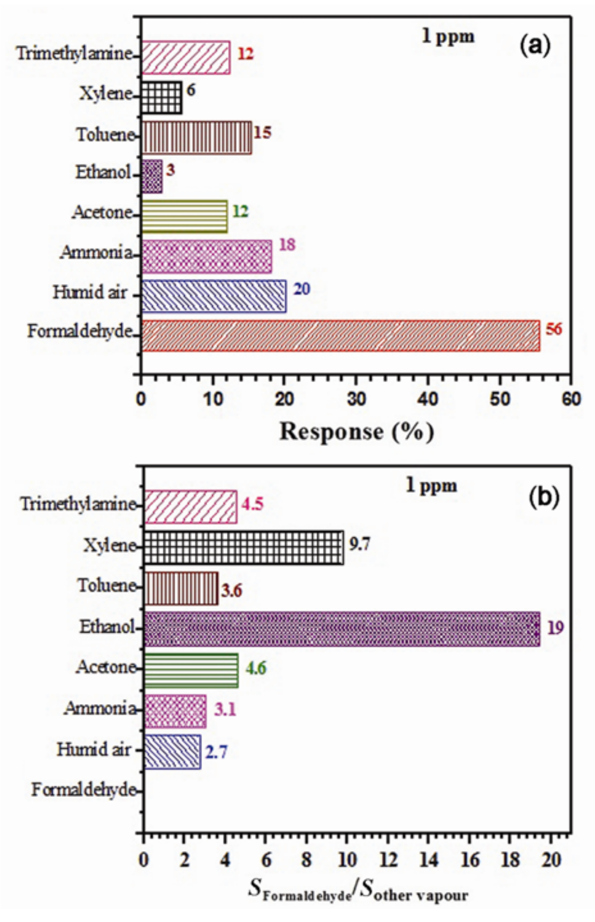

Figure 7. (**a**) Sensing response and (**b**) vapour selectivity plot of CeO_2 film.

3.3c *Response of CeO_2 film in mixed environment*: To study the vapour selectivity of CeO_2 film in mixed environment, initially, the film was exposed to formaldehyde vapour and simultaneous resistance measurement were made for every 500 ms. After observing the stable film

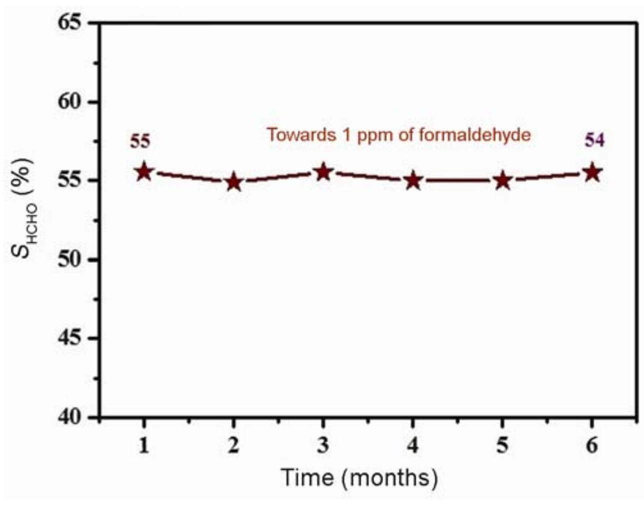

Figure 8. Stability of CeO_2 film as a function of time for 1 ppm of formaldehyde concentration.

Table 2. Comparison of formaldehyde responses of various metal oxide materials.

No.	Metal oxide	Preparation method	Detection range (ppm)	Sensor response (a.u.)	Response time (s)	Recovery time (s)	Operating temperature (°C)	Reference
1.	SnO_2	Sol–gel	50–400	20–90	28	17	200–400	Wen and Tianmo (2009)
2.	ZnO	Precipitation	1–1000	20–650	46	13	250–450	Zhang *et al* (2011)
3.	In_2O_3	Solvothermal	100–1000	150–750	8	13	200	Wang *et al* (2009)
4.	NiO	Sputtering	0·8–30	15–35	13·2	40	150–300	Dirksen *et al* (2001)
5.	CdO–In_2O_3	Chemical synthesis	10–100	100–420	400	150	80–150	Chen *et al* (2008b)
6.	CdO–Sn–ZnO	Precipitation	1–205	5–2500	150	50	150–400	Han *et al* (2011)
7.	CdO–In_2O_3–SnO_2	Chemical synthesis	10–100	50–550	120	100	100–170	Chen *et al* (2008a,b)
8.	Cd/TiO_2–SnO_2	Sol–gel	50–500	10–60	30	20	450–700	Zeng *et al* (2009)
9.	Au/ZnO–$ZnSnO_3$	Hydrothermal	2–50	2·5–35	15	12	300	Xu *et al* (2007)
10.	CeO_2	Spray pyrolysis	0·5–50	25–2833	36	1	30	Present work

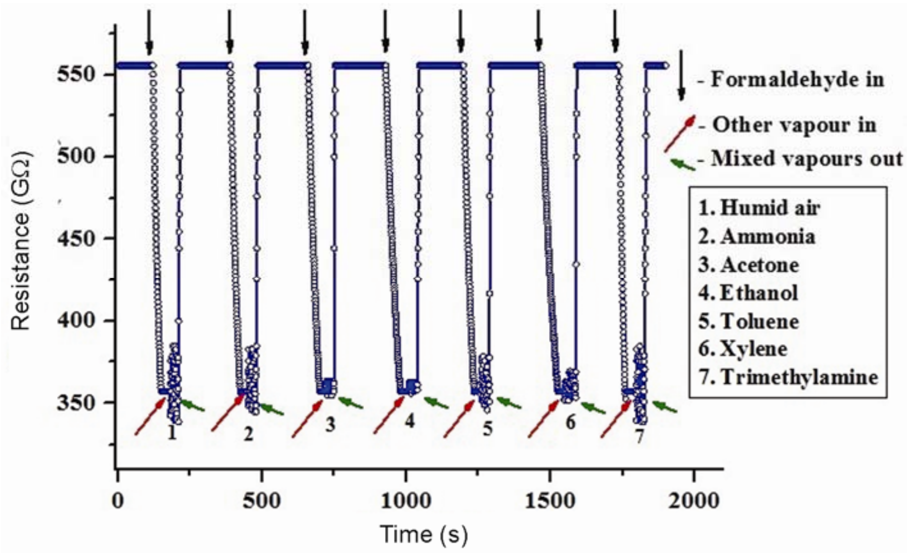

Figure 9. Transient response of CeO_2 film in mixed environment.

resistance, mixed vapour (formaldehyde–ammonia) was created in the test chamber by injecting calibrated amount of liquid ammonia and simultaneous resistance measurements were made. Similarly, studies were made for different mixed vapours such as formaldehyde–humid air, formaldehyde–acetone, formaldehyde–ethanol, formaldehyde–toluene, formaldehyde–xylene, formaldehyde–trimethylamine and the transient response of the CeO_2 film is shown in figure 9. No appreciable change in surface resistance of CeO_2 film was observed in any mixed vapour atmosphere. This indicates that CeO_2 film is highly selective towards formaldehyde vapour in mixed environment.

4. Conclusion

In summary, the CeO_2 thin film obtained by home-built spray-pyrolysis technique has nanocrystallites over the surface with face-centered-cubic structure of polycrystalline nature. The film shows a good sensing response, fast response–recovery time and selective detection of formaldehyde vapours at room temperature in mixed environment. The preliminary results carried out in the present work suggest that CeO_2 thin film having nanocrystallites on the surface can be studied further for analysing exhaled breath towards diagnosing lung cancer at an earlier stage by simple chemiresistive method.

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