



Nano ceria as xylene sensor – Role of cerium precursor

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ABSTRACT

Cerium oxide (CeO₂) thin films were deposited on glass substrates by spray pyrolysis technique using three different precursors namely cerium chloride heptahydrate, cerium nitrate hexahydrate and cerium acetate hydrate. Structural, morphological, optical, electrical and sensing properties of the CeO₂ thin films were examined. X-ray diffraction patterns of spray deposited CeO₂ thin films confirmed the formation of polycrystalline cubic fluorite crystal structure. The surface morphologies of CeO₂ films were observed using field emission scanning electron microscope. The optical band gap observed from luminescence spectra varied from 3.23 to 3.57 eV. Room temperature sensing characteristics of CeO₂ thin films towards acetone, ethanol, xylene and toluene were observed. CeO₂ thin film deposited using cerium acetate hydrate at 0.1 M concentration exhibited a better response towards xylene with fast response and recovery times of 224 and 13 s respectively at ambient temperature.

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1. Introduction

Environmental pollution is a growing threat to the entire living organisms in the earth. Though the fast-growing economies of the world have devised a mechanism to reduce the carbon footprints, the immediate threat of air pollution, especially from automobile, petrochemical and other chemical industries, have to be controlled with stringent threshold levels to save earth against surging impacts. Air pollutants are fatal, spanning at least two million lives every year [1]. One of the dominant air pollutants is xylene (C₈H₁₀), an aromatic hydrocarbon, which enters the atmosphere due to its wide usage across various industries. Xylene is the primary associate evolved in due course of crude oil fractionation. It is used as a solvent in printing, rubber, coal, concrete sealer, histopathological laboratories [2] and industries (cleaning agents for steel <http://www.newworldencyclopedia.org/entry/Steel>, silicon wafers, and Integrated circuits). It is also used as a major constituent in the

unleaded petrol. According to United States Environmental Protection Agency (EPA) [2], xylene is released into the environment at an alarming rate from various industries. As per EPA, people exposed for a short-term duration of 10 min (200 ppm) can cause neurological effects, chronic effects and irritation to eyes, nose, throat resulting in tremors, headache, fatigue, respiratory disorder, dizziness, and cardiovascular disorders [3,4]. In this context, it is imperative to develop a cost-effective, compact and low power xylene sensor.

Metal oxide thin films deposited on various substrates by various physical and chemical deposition techniques have been used as potential sensing elements for a wide range of applications [5]. Metal oxide thin films have already been deployed as catalytic [6], electrochemical [7], infrared [8], thermal conductivity [9], surface-acoustic wave [10], chemiresistive [11] and optical sensors [9]. Among these types, chemiresistive sensors have received maximum attention due to their natural compatibility with semi-conducting electronic devices, compactness and tunable structure to enhance specific detection [12]. Until now, many types of metal oxide compounds such as ZnO [13], CeO₂ [14], In₂O₃ [15], V₂O₅ [16], SnO₂ [17], Fe₂O₃ [18], WO₃ [19], TiO₂ [20] have been extensively employed as sensing materials for detecting Volatile Organic Compounds (VOCs).

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In recent times, various scientific groups have explored nanostructured metal oxides for the detection of xylene vapour. Keng Xu et al. [21] prepared hierarchical Co_3O_4 microspheres and utilized it for the detection of xylene (5 ppm) at 150°C , which resulted in a selective response of 37.9. Gao et al. [22] developed hierarchical Sn-doped NiO for detecting 100 ppm of xylene at 225°C with a sensing response of 20.2. Cao et al. [23] synthesized nanostructured ZnO by solid-state chemical reaction technique for simultaneous detection of methanol and xylene at 300 and 150°C and the response and recovery times were of less than 20 s. Li et al. [24] prepared mesoporous $\alpha\text{-Fe}_2\text{O}_3$ nanostructures by the solid-state chemical reaction and observed a sensing response of 6.45 towards 100 ppm of xylene at 340°C . Li et al. [25] synthesized Au loaded $\text{WO}_3 \cdot \text{H}_2\text{O}$ by hydrothermal technique and exhibited a sensing response of 26.4 towards 5 ppm of xylene at 255°C . Kim et al. [26] prepared NiO and Cr-doped NiO by solvothermal self-assembly reaction, which exhibited ultrasensitive detection of 5 ppm xylene with a maximum sensing response of 24.5 at 425°C . Unfortunately, a significant number of developed sensors have not fulfilled all the ideal gas sensing characteristics like stability, limit of detection, high selective response and faster response and recovery times. Moreover, most of the existing gas sensing materials was operated at elevated operating temperatures to detect xylene gas, which could lead to deterioration of stability of sensing elements. In this context, nanostructured cerium oxide (CeO_2), a rare-earth metal oxide has been used to fabricate room temperature xylene sensor. CeO_2 has unique physical/chemical properties, which make it an ideal candidate for optical [27], microelectronic [28], electronic [29], optoelectronics [30], photocatalytic [30] and gas/bio-sensing applications [31,32]. CeO_2 can be deposited on various substrates using spray pyrolysis [37], sol-gel [35], co-precipitation [36], pulsed laser deposition [37] and chemical bath deposition techniques [38]. Among these techniques, spray pyrolysis is found to be simple, cost-effective and can achieve high uniformity of deposition over large area [39]. Owing to these advantages, spray pyrolysis deposition technique was preferred over other deposition techniques [40]. In the present work, effects of different functional group of cerium precursors on the structural, morphological, optical and electrical properties of CeO_2 thin films were investigated. Furthermore, deposition parameters such as substrate temperature, nozzle – substrate distance, deposition time and diameter of the nozzle, carrier gas, carrier gas pressure and solution flow rate were optimized to develop thin film sensing element to detect xylene at room temperature.

2. Materials and methods

2.1. Film deposition

Cerium oxide thin films were deposited on preheated (250°C) glass substrates by spray pyrolysis system (Holmarc, HO-TH-04, India). The substrates were thoroughly cleaned following the procedure: First, glass substrates were cleaned in diluted detergent solution in order to remove viscous residues on the surface. Then, substrates were cleaned by ultra-sonication in acetone and ethanol for 20 min. Later, they were washed gently with deionized water and dried in a hot air oven. The cleaned glass substrates were placed on the substrate-holder. 0.1 M of three different cerium precursor solutions (purchased from Sigma Aldrich, USA) such as cerium (III) acetate hydrate ($\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot \text{xH}_2\text{O}$), cerium (III) chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$), cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were prepared using deionized water as a solvent. The deposition parameters were (i) spray gun nozzle – substrate distance of 13 cm, (ii) spray rate of 1 mL min^{-1} , (iii) spray duration of 10 s and (iv) carrier gas (compressed dry air) flow rate of

12 kg/cm^2 . With these optimized deposition parameters, CeO_2 thin films were deposited on glass substrates at a constant substrate temperature (250°C). A digital temperature controller was used to control the substrate temperature with an accuracy of $\pm 1^\circ\text{C}$. The deposited CeO_2 thin films were labeled as CeAc, CeCl and CeNi for $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot \text{xH}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursors respectively.

2.2. Characterization techniques

X-ray diffractometer (XRD) (Model X'Pert Pan analytical, The Netherlands) with Cu $K\alpha$ source ($\lambda = 1.5406 \text{ \AA}$) was used to study the structural characteristics of CeO_2 thin films. The morphologies of CeO_2 thin films were observed using a field emission scanning electron microscope (FE-SEM) (JSM-6701F, JEOL, Japan). The chemical compositions of CeO_2 thin films prepared using three different precursors were examined using a Fourier transform infra-red (FTIR) (Spectrum RX I, PerkinElmer Inc., USA) spectrometer in the range of $400\text{--}4000 \text{ cm}^{-1}$. The absorbance spectra of CeO_2 thin films were measured using UV–Vis spectrophotometer (Perkin Elmer, Lambda 25, USA; scan rate 50 nm min^{-1}) in the range of $350\text{--}600 \text{ nm}$. The electrical conductivity studies of were carried out using an electrometer (Keithley 6517B, USA). The sensing characteristics of the CeO_2 thin films towards xylene were investigated under humidity/dry air conditions at room temperature with a custom made gas testing chamber reported in our previous works [41].

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD patterns of spray deposited CeO_2 thin films using three different precursors CeAc, CeCl, CeNi at the moderate substrate temperature of 250°C . The diffraction peaks at $2\theta = 29.2^\circ$, 33.7° , 48.1° and 56.9° correspond to (111), (200), (220) and (311) crystallographic planes of CeO_2 and no other peaks corresponding to impurities were detected. XRD patterns also confirmed the formation of polycrystalline cubic fluorite crystal structure of CeO_2 thin films. All the diffraction peaks are matched with the JCPDS card number 81-0792 [42]. XRD patterns also showed a predominant (111) plane for all the films. An increase in the (311) plane was also observed for all the films, which might be due to the presence of n-functional group present in the different cerium precursor solutions. The parameters including average crystallite size, lattice constants, strain, inter-planar spacing values were calculated for all the diffraction peaks of CeO_2 thin films and are presented in Table 1.

The average crystallite size of CeO_2 (D) was calculated using the Debye's Scherrer formula (Eq. (1)) [43],

$$D_{hkl} = \frac{\kappa \lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad (1)$$

where, D_{hkl} is the average crystallite size of the (hkl), κ is the shape factor (0.89), λ is the wavelength of the incident X-ray (1.5406 \AA), β_{hkl} is the full width at half maximum (FWHM) of the (hkl) diffraction peak, θ is the Bragg diffraction angle.

The strain due to lattice mismatch and alteration in the crystal arrangement in CeO_2 films was calculated using eq. (2) [44],

$$\epsilon = \frac{\beta_{hkl}}{4 \tan \theta} \quad (2)$$

The lattice plane spacing and lattice constants were also calculated using Eq. (3) [45],

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