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1D Cerium Oxide Nanorods: Synthesis, Characterization and their Humidity Sensing Application

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***Abstract:** The formaldehyde-assisted hydrothermal system is used to synthesize CeO_2 nanorods by using precursor like cerium nitrate. Concentration of precursors and hydrothermal temperature affects the morphologies of these one-dimensional (1D) CeO_2 Nanomaterial's. This is achieved to control the reaction degree of Cannizzaro disproportionation tuned by Na/Ce molar ratio. The XRD, FESEM, FTIR and TEM these characterization techniques have been used to characterize the crystal structure and morphology of the as-synthesized CeO_2. Humidity sensing characteristics such as hysteresis, repeatability, impedance-relative humidity (RH) characteristics, response and recovery behavior, and stability of CeO_2 nanostructure have been investigated in detail for given precursor. The sensor showed rapid response and recovery, prominent stability, high humidity sensitivity, good repeatability and narrow hysteresis loop i.e. suitable candidate for the fabrication of the humidity sensors.*
***Keywords:** Nanorods, cerium nitrate, humidity sensor, XRD, FESEM*

I. INTRODUCTION

One-dimensional (1D) Nanostructured materials such as nanowires, nanotubes, nanorods and nanobelts offer opportunities for fundamental research concerning the influence of size and
dimensionality of a material on its physical and chemical properties.[1–3]. Cerium oxide (CeO_2) is a technologically important rare earth material because of its wide range applications as oxygen sensors [1,10], polishing agents [7], fuel cells [9], catalysts [8], and UV blockers [11]. Indirect synthetic pathway of 1D CeO_2 Nanorods results in increasing complexities and difficulties in the design and synthesis of their desired morphologies [12]. Formaldehyde, may used as an organic chemical, because of its rich abilities in synthetic reactions. [12-15] the Cannizzaro disproportionation reaction occurs immediately, when formaldehyde solution is mixed with strong alkali under the heated conditions in presence of the aldehyde group according to eq^n (1) and the formate is produced simultaneously.[12,19]

$2HCHO + OH^- = HCOO^- + CH_3OH$ (1)

$HCHO + HCOO2 + OH = CO_3^{2-} + CH_3OH$ (2)

According to the cross disproportionation reaction, the aldehyde groups presented at formate can further react with formaldehyde to produce carbonate under superfluous alkali conditions
(eq^n (2)). We can convert, formaldehyde into formate or/and carbonate by controlling the reaction conditions. The formate and carbonate are the great precursors for the synthesis of 1D CeO_2 Nanorods.[16-20] we can synthesize 1D precursors by controlling the reaction degree of the Cannizzaro disproportionation reaction. We can also state that formaldehyde solution is the most efficient solvent to synthesize 1D CeO_2 precursors among all attempted solvents such as acetaldehyde, isopropyl alcohol, ethanol, glyoxal, ethylene glycol, acetone,[18] etc

II. EXPERIMENTAL

A. Preparation of 1D CeO2 nanorods

Typically 1.0 gm of cerium (iii) nitrate $Ce(NO_3)_3$ hex hydrated was fully dissolved in 30 ml formalin solution at room temperature [1-4]. Then the desired quantity of NaOH or KOH was slowly added to the mixed solution by stirring, followed by the transfer of suspended solution in to 40 ml Teflon-lined stainless autoclave and heated up to 140^0 C to 20 hrs under autogenously pressure and static condition in electric oven[20]. The solution then cooled to room temperature, the precipitates were filtered, washed with double distilled water in several time and dried at 60^0C for 24 hrs [7,19]. The dried powders were calcinated to 400^0C for 3 hrs. The light yellow powder was obtained.

B. Preparation of Sensors Electrode

In present work the sensor consisting of CeO_2 nanorods layer coated on the top of an interdigitated electrode (IDE) was fabricated [10-13]. The IDE consists of five pairs of Cu tracks screen printed onto epoxy glass substrate (20 mm x 25 mm) [4]. The IDE-epoxy glass substrates were cleaned by an ultrasonic treatment in acetone and then rinsed with double-distilled water and dried in vacuum [17]. The powder of CeO_2 nanorods was mixed with double-distilled water in a weight ratio of 100: 25 to form a paste. The electrodes were used to evaluate the humidity sensing characteristics [14].

III. RESULTS AND DISCUSSION

A. Characterization of CeO_2 nanorods.

The XRD pattern of the CeO_2 nanorods as-synthesized by cerium nitrate after calcinated at 400^0C is depicted in Fig.1 (a). All the diffraction peaks in the XRD pattern of CeO_2 are exactly matched with JCPDS file (JCPDS No.: 01-078-6853), indicating the formation of cubic CeO_2 nanorods [1]. No impurities were present and pure CeO_2 nanorods are obtained [16-18]. The average crystallite size of the CeO_2 nanorods from XRD graph was found to be in the range of 21-27 nm.

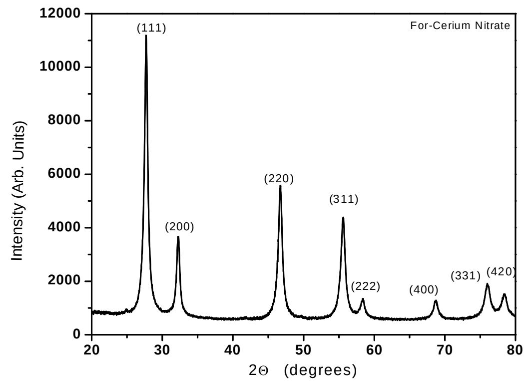

Fig 1 – XRD Pattern of the CeO_2 nanorods

The FTIR spectrum of the CeO_2 nanorods synthesized by cerium nitrate figure shows the bands around 451 and 853 cm^{-1} corresponding to a stretching vibrations characteristic of Ce-O [1]. The bands around 1064 and 1327 cm^{-1} shows to the characteristic vibrations of CeO_2. The stretching vibrational mode of the O-H group bonded to the Ce atom i.e. Ce-OH is given by band at ~ 3410 cm^{-1}. There is no distinction between FTIR of commercial and our obtained CeO_2 powders [18].

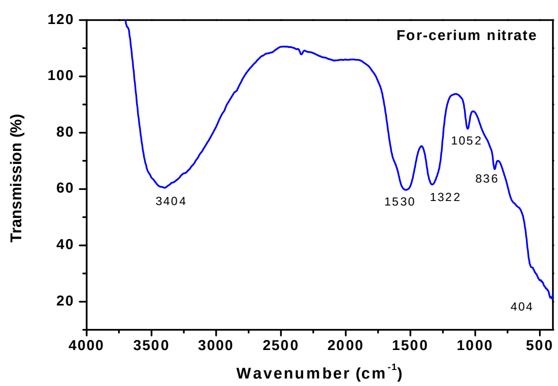

Fig.2 : FTIR of cerium nitrate after calcinated at 400^0C

The FESEM images of as-synthesized precursor using cerium Nitrate before and after calcinated CeO_2 nanorods (after calcinations of precursor at 300^oC) shows uniform CeO2 nano rods having breath 0.2 micron length 5-8 micron [1,2]

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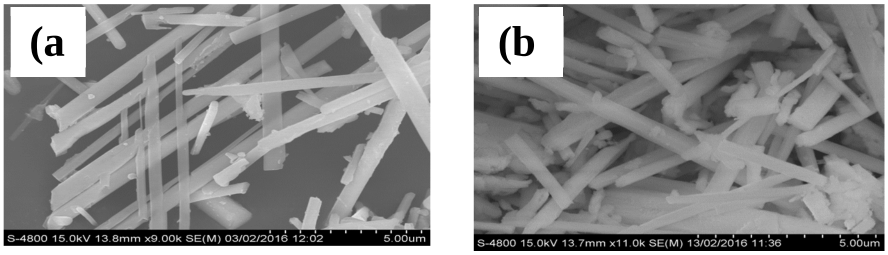

Fig.3 : (a) FESEM images of as-synthesized CeO_2 nanorods precursor using cerium nitrate and (b) CeO_2 nanorods (after calcination of precursor at 400^0C)

The TEM image of as-prepared product exhibits a uniform CeO_2 nanorods having breath approximately 300 nm and length approximately 2000 nm [4,5]. The corresponding selected area electron diffraction (SAED) pattern shows and confirms that the random orientations of the CeO2 nanorods and there is no secondary phase [14].

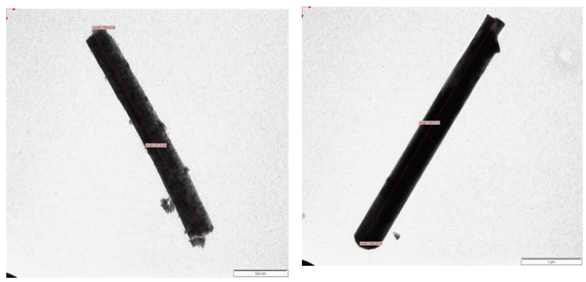

Fig.4 : (a) TEM images of as-synthesized CeO_2 nanorods precursor using cerium nitrate and (b) CeO_2 nanorods (after calcinations of precursor at 400^0C)

B. Humidity Sensing Measurements.

Different RH levels were generated by the different saturated salt solutions in air tight closed glass bottles at room temperature [3]. The six different standard saturated aqueous salt solutions of LiCl (11±0.30 %RH), $MgCl_2$ (33±0.14 %RH), K_2CO_3 (43±0.20 %RH), NaCl (75±0.15 %RH), KCl (85±0.24 %RH) and K_2SO_4 (97±0.16 %RH) were used to act as humidity source [18-20]. The sensing element was placed successively into the bottles with different RH levels at room temperature and the impedance of the sensor was measured as a function of RH at 27 oC (± 1 oC). The frequency range was varied between 60 Hz to 1 kHz for 1V applied voltage [14]. A humidity probe was also placed into the bottles along with the sensing element to monitor the RH during the measurement [4]. The response and recovery times were measured by switching the sensors back and forth between two closed bottles with RH values of 11% and 97% RH respectively [11-12]. The hysteresis was measured by switching the sensor between the closed bottles with 11%, 33%, 43%, 75%, 85% and 97% RH and then transferred back[5].

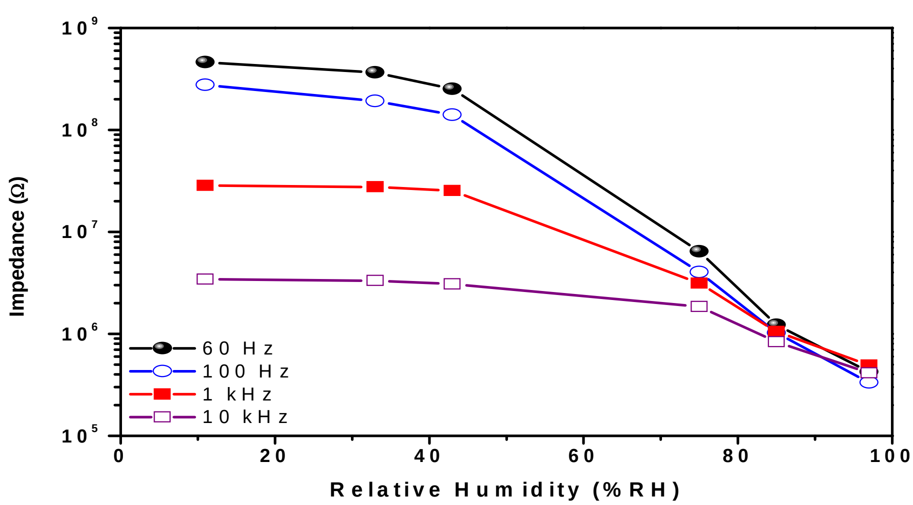

Fig.5 : Variations in impedance of CeO_2 nanorods based humidity sensor with change in RH (%) measured at various frequencies

The humidity-sensing performance, the impedance of the sensors based on CeO2 nanorods was measured as a function of RH at different frequencies at room temperature and the results are depicted in Fig.5. The impedance of the sensor depends on frequency and decreases with increase of frequency [12] .The linear response in the entire RH range is observed at relatively low frequency i.e. at 60 Hz[7]. The impedance of the sensor changes by three orders of magnitude from 0.3 x 10^6 to 0.4 x 10^9 Ω as RH increases from 11% to 97%.

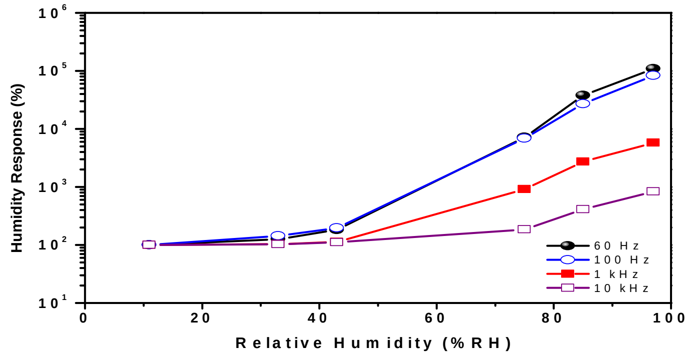

Fig.6 : Dependence of response on RH and frequency for CeO_2 nanorods based sensor, (c) and (d) Humidity hysteresis.

The response at different frequencies as a function of RH is shown in Fig.6, which reveals that the overall response is higher at the lower frequency (i.e. 60 Hz).Due to the best linearity

Response is observed at 60 Hz [1-5]. were employed in further studies to investigate the other characteristics of the sensor such as response and recovery behavior, hysteresis, reproducibility and stability

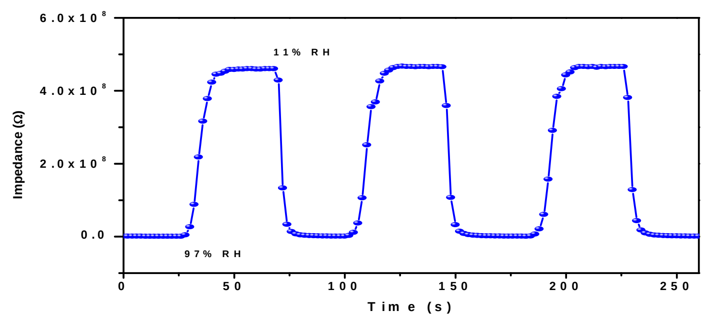

Fig.7 : (a) and (b) Dynamic response of the sensor when exposed to six high (90% RH) –low (10% RH) – high (90% RH) cycles.

The dynamic response of the CeO2 nanorods based sensor to rapid variations in the RH values of 11% and 97% is shown Fig.7(a & b),Dynamic response time (humidification from 11% RH to 97% RH) and the recovery time (desiccation from (97% RH to 11% RH) were approximately 5. s and 12-15. s, respectively demonstrating that the present sensor rapidly responds to the ambient RH.

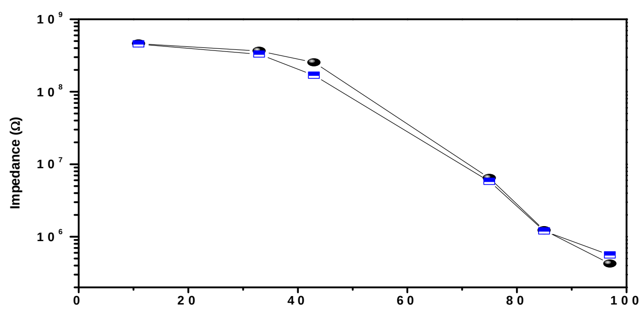

Fig.8 Humidity hysteresis

Hysteresis is one of the most important characteristics of a humidity sensor, which is defined as the maximum difference between the adsorption and desorption curves [9]. The humidity hysteresis of CeO2 nanoparticals based humidity sensor is shown in Fig.8. The sensor exhibits highly reversible sensing properties and the sensing curves for the humidification and desiccation processes almost overlap with each other, showing very small hysteresis. The maximum absolute value of humidity hysteresis error γH is found to be ~2% in the range of 11-97% RH indicating a good reliability of the sensor.

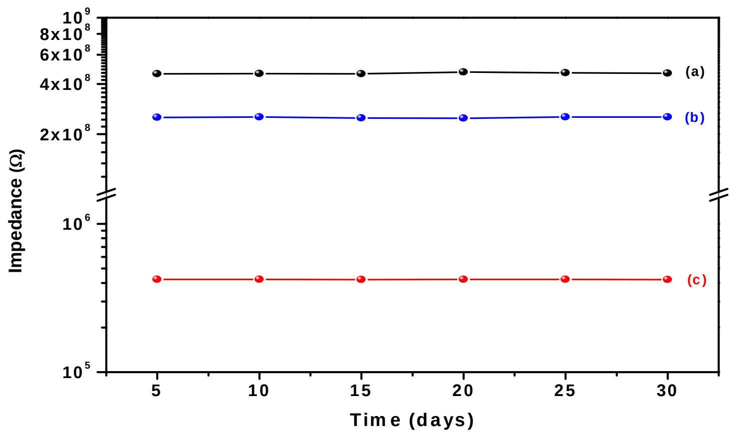

Fig.9 : Stability of the sensor measured at 11, 43 and 97 % RH.

The stability is an important parameter of humidity-sensing properties [7,11]]. In the period of 30 days the sensor was tested repeatedly once in five days under fixed humidity levels (11%, 43% and 97% RH). The impedance variation (Fig.9) is less than 3% at each humidity region for one month at 60 Hz, which shows that the impedance of the sensor fluctuates slightly with time and the data show good consistency [18-20].

IV. CONCLUSIONS

CeO_2 nanorods were successfully synthesized at low cost by using a simple hydrothermal method. The XRD results reveal the formation of cubic phase of CeO_2 nanorods with good crystallinity and the crystalline size ranging from 21 -27 nm.The TEM images shows CeO_2 nanorods structure with 300 nm in breadth and 2000 nm in length.The FTIR bands around 1064 and 1327 cm^{-1} show to the characteristic vibrations of CeO_2. FESEM shows CeO_2 Nanorods of 0.2 micron in breadth, 5 – 8 micron in length.The CeO_2 Nanorods exhibit excellent humidity sensing characteristics such as higher response, fast response time (~ 5 s), rapid recovery (~ 12-15 s), hysteresis within 2.0%, excellent reproducibility and broad range of operation (11-97% RH). It was demonstrated that the CeO_2 Nanorods can be used as reusable sensing material for the fabrication of humidity sensors.

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