Cerium Oxide-based Nanoparticles Thin Film: Sensitive and Selective for detection of NO_2 gas

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Abstract:

CeO_2 nanoparticles (NPs) gas sensor was fabricated on glass substrate by using spin coating technique. The developed CeO_2 NPs thin films influence the gas sensing performance towards NO_2 gas in the range of 5-200 ppm. For 100 ppm of NO_2, the response of NPs thin film is 44%. The morphology of CeO_2 NPs thin film exhibited high sensitivity, good selectivity and excellent repeatability for 100 ppm level of NO_2 gas at 200°C operating temperature. The gas-sensing measurements demonstrate that the CeO_2 NPs sensing material is an excellent candidate for NO_2. The CeO_2 NPs thin films were characterized for their structural and chemical properties using XRD, SEM and FTIR spectroscopy.

Key words: Sol-gel method; CeO_2 Nanoparticles, nanocrystalline, Structural analysis; Morphological analysis, NO_2 sensing properties.

Introduction

Nitrogen dioxide (NO_2) is one of the majority toxic air pollutants and is the key source of acid rain and photochemical smog which is very damaging for humans, animals and plants also [1]. For public health and environmental safety, it is desirable to develop NO_2 gas sensor with good selectivity, fast response-recovery time and excellent chemical stability. In n-type metal semiconductors CeO_2 (cerium dioxide) is one exhibits good oxidation-reduction properties at broad range of temperature with excellent properties for gas sensing application [2].

Experimental

The CeO_2 nanoparticles were synthesized by a sol-gel method by using Cerium (III) nitrate hexahydrate as a source of Cerium oxide. Cerium nitrate hexahydrate was dissolved into methanol and the solution stirred vigorously for 1 h at 60°C, leading to the formation of yellow color powder. The dried powder was thermally treated at temperature 700°C for a fixed processing time 1 h in an ambient air to form CeO_2 nanoparticles with different crystallite sizes. For the deposition, the CeO_2 powder was dissolved in m-cresol and the resulting solution was spin coated on to a glass substrate.

Structural analysis

Fig. 1(a) shows the XRD patterns of CeO_2 NPs thin films processed at 700°C temperatures. The diffraction peaks are indexed to the cubic phase structure of CeO_2 with lattice parameters, a=b=c=5.4137Å. The average crystallite size of CeO_2 NPs was 20nm at the processing temperature 700°C.

Composition analysis

Fig. 1(b) shows the FTIR spectra of CeO_2 synthesized nanoparticles processed at 700°C. The large broad band at 3323cm^{-1} is assigned to the O-H stretching vibration in OH−groups. The intense band at 500cm^{-1} corresponds to the Ce-O stretching vibration [3]. The bands located at around 713, 857 and 1063cm^{-1} have been attributed to the CO_2 asymmetric stretching vibration, CO_3^{-2} bending vibration, and C-O stretching vibration, respectively. The observed peaks were confirming the formation of cerium dioxide.

Morphological analysis

Fig. 1(c) shows the scanning electron micrograph (SEM) of CeO_2 films annealed at 700°C. From the micrograph, it is seen that CeO_2 film consists of nanocrystalline grains with uniform randomly oriented morphology and the CeO_2 film's surface is highly porous and consists of interconnected nanocrystalline grains, such type of morphology is preferred for gas sensing application.

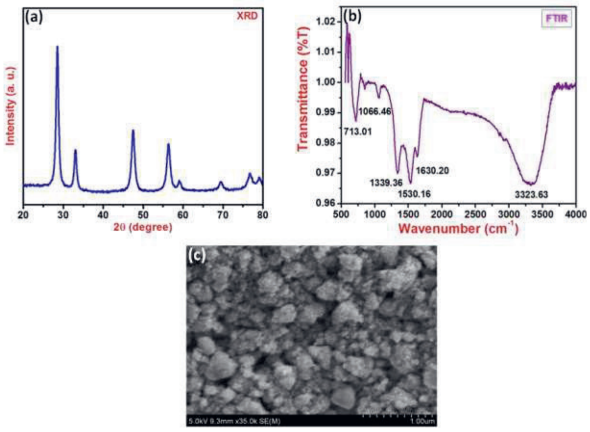

Fig.1. (a) XRD pattern (b) FTIR spectrum of CeO_2 nanoparticles, (c) SEM images of CeO_2 thin films processed at 700°C.

Gas sensing properties

Selectivity is the characteristic of a sensor that determines whether a sensor can respond selective to a particular single gas. Fig. 2(a) shows the selectivity of CeO_2 based gas sensors to different oxidizing and reducing gases. It can be seen that CeO_2 NPs gas sensors are much more response to NO_2 and very few response to the other possible interferential gases, showing more selectivity toward NO_2 gas. The strong interaction between electron-donating groups of CeO_2 and electron-withdrawing NO_2 molecules can enhance the response of CeO_2 NPs-based sensor.

The sensing response (S) is defined as the total change in sensor resistance when it exposed to gas to the original resistance when it was in air as eq. (1),

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100 \qquad (1)$$

Fig. 2(b) shows the dynamic response of CeO_2 NPs thin film sensors toward NO_2 gas in the concentration range 5-200 ppm at 200°C. The response increased from 5 to 44% with increasing the gas concentration of NO_2 from 5 to 200 ppm. Above 100 ppm, the CeO_2 film showed the maximum response of 44%. Such a maximum response is due to interactions between the NO_2 gas and the n-type CeO_2 surface. The reproducibility of the CeO_2 thin films sensor response toward 100 ppm NO_2 gas was measured for three continuous gas in and out cycles are shown in Fig. 2(c). After each gas in and out cycle, the sensor almost restore to its initial value, which indicates the sensor has excellent reproducibility. The stability of the CeO_2 NPs thin films sensor studied for 100 ppm of NO_2 at 200°C temperature over a period of 45 days at intervals of 5 days is shown in Fig. 2(d). It is observed that, initially CeO_2 sensor shows maximum response and it was dropped from 44% to 39% and stable response was obtained after 15 days with 39% stability.

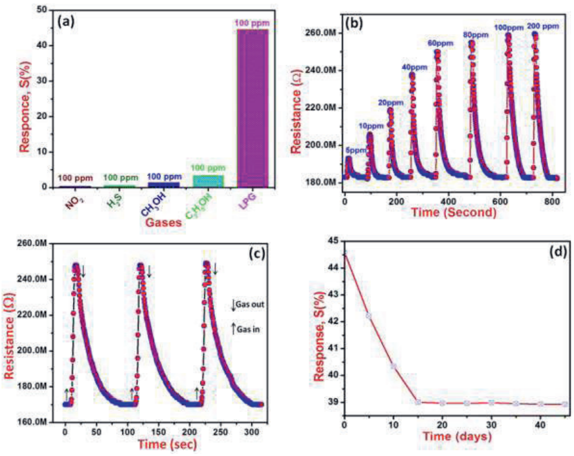

Fig.2. (a) Selectivity of CeO_2 based gas sensors to different oxidizing and reducing gases, (b) Dynamic response of CeO_2 NPs thin film sensors toward NO_2 gas in the concentration range 5-200 ppm at 200°C, (c) Reproducibility and (d) Stability of CeO_2 NP film sensor to NO_2 for 100 ppm concentration at 200°C.

Conclusion

The porous morphologies of CeO_2 NPs thin films was successfully fabricated through sol-gel method. Morphological and structure analysis of the prepared samples confirmed the purity and crystallinity of CeO_2 NPs thin films. The gas-sensing tests exhibited that the CeO_2(700°C) NPs thin film possessed high sensitivity, excellent repeatability and good selectivity to 100 ppm level of NO_2 at 200°C, which is mainly attributed to their morphology and particle size. The prepared CeO_2 NPs thin films with excellent surface morphology are a promising candidate for good performance NO_2 gas sensor.

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