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$^\circ$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$^\circ$C, leading to the formation of yellow color powder. The dried powder was thermally treated at temperature 700$^\circ$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$^\circ$C temperatures. The diffraction peaks are indexed to the cubic phase structure of CeO$_2$ with lattice parameters, $a=b=c=5.4137\AA$. The average crystallite size of CeO$_2$ NPs was 20nm at the processing temperature 700$^\circ$C.

Composition analysis
Fig. 1(b) shows the FTIR spectra of CeO$_2$ synthesized nanoparticles processed at 700$^\circ$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$_3^-$ 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$^\circ$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.

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),

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

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.

References

