International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.5, pp 46-53, 2015

National conference on Nanomaterials for Environmental [NCNER-2015]
19th & 20th of March 2015

Synthesis of CeO_2 Nanoparticles via Solvothermal Route and Their Application in Sensors

Dhananjay Shukla[1], K Himabindu[2], K Chidambaram[1], Kalim Deshmukh[3], M. Basheer Ahamed[3], SK Khadeer Pasha[1*]

[1]Sensors Laboratory, Material Physics Division, School of Advanced SciencesVIT University, Vellore – 632014, TN, India
[2]School of Electronics Engineering, VIT University, Vellore – 632014, TN, India
[3]Department of Physics, B.S. Abdur Rahman University, Chennai-600048, TN, India

Abstract : In the present investigation we have reported solvothermal method to synthesize cerium oxide nanoparticles having modified parameters with a comprehensive overview of their structural and morphological study. To explore its electrical, structural and optical properties as synthesized particles were characterized by X-ray diffraction (XRD), Fourier transform Infrared spectroscopy (FTIR), UV-Vis-NIR spectroscopy, Scanning Electron Microscopy (SEM), and Particle size analysis. These crystalline size nanoparticles were utilized in sensors to detect volatile organic compound (Ethanol, Methanol and Formaldehyde) and was found to have high sensitivity and quick response time.
Keywords : CeO_2 nanoparticles, Solvothermal rout, structural and morphological.

1. Introduction

Cerium oxide is a member of lanthanide group and has been identified as rare earth material. It has abundant applications as catalyst, UV preventing material, mechanical polishing, optical electrochemical, magnetic data storage, energy storage, electrolyte, gas sensors etc. Out of those applications gas sensing is an indispensible application because pollutant gases (flammable and toxic compound) in the environment released by industries and factories have harmful effect on living organism, human health and causes many genetic disease[1, 2]. Taking all these in to consideration it is a vital need to come up with an effective, reliable, efficient and inexpensive sensing technique, so that they can be easily deployed wherever needed. In this connection after a long investigation it has been concluded that cerium oxide can be the best sensing material because of its good structural stability, large surface area and capacity of storing and releasing oxygen. Cerium oxide has cubic fluorite structure and it accommodates a large number of oxygen defects in form of vacancy[1, 3]. Due to this defect it has inherent property to adsorption of ion species, particularly oxygen ion, on the surface of semiconducting oxide and consequent formation of energy barrier. From previous study now it has been confirmed that the particle size of oxide material has direct impact on its characteristics and various properties. Hence to meet our growing needs for particular application it is needed to modify the particle dimension that in turn change in active surface area of nano-materials. The lower the particle size more

the active surface area will be and it causes to enhance the conductivity, sensing and catalytic properties of the nano-material[6, 7, 9].In this paper we have reported solvothermal method of synthesis of cerium oxide nanoparticles, its characterization and its utilization in sensors to detect harmful gases even in very low range of concentration.

There were many methods to synthesize CeO_2 but we preferred solvothermal method because, it was easy to use, able to reduce the temperature and time without using any catalyst. Whereas hydrothermal method needs expensive autoclaves and sol-gel can change the functionality of molecule at local environment.

2. Experimental Section of Synthesis of Cerium Oxide

The materials used to synthesize cerium oxide nanoparticles were Ammonium Ceric Nitrate ($[(NH_4)_2Ce(NO_3)_6]$), Sodium Hydroxide(NaOH) and Ethylene glycol used as a capping agent[4].The source material ammonium Ce(IV) Nitrate and Sodium Hydroxide have been taken in the molar ratio of 1:5 and both were dissolved in distilled water completely. When those solutions were mixed a white precipitate solution was formed and same was stirred for 8 hours upon magnetic stirrer with 350 rpm [4]. The stirred solution was then kept in microwave oven for 20 minutes at 65°C [4, 8]. Under the influence of microwave radiation in the oven, the H^+ proton was removed from the cerium hydroxide and all particles settled down.

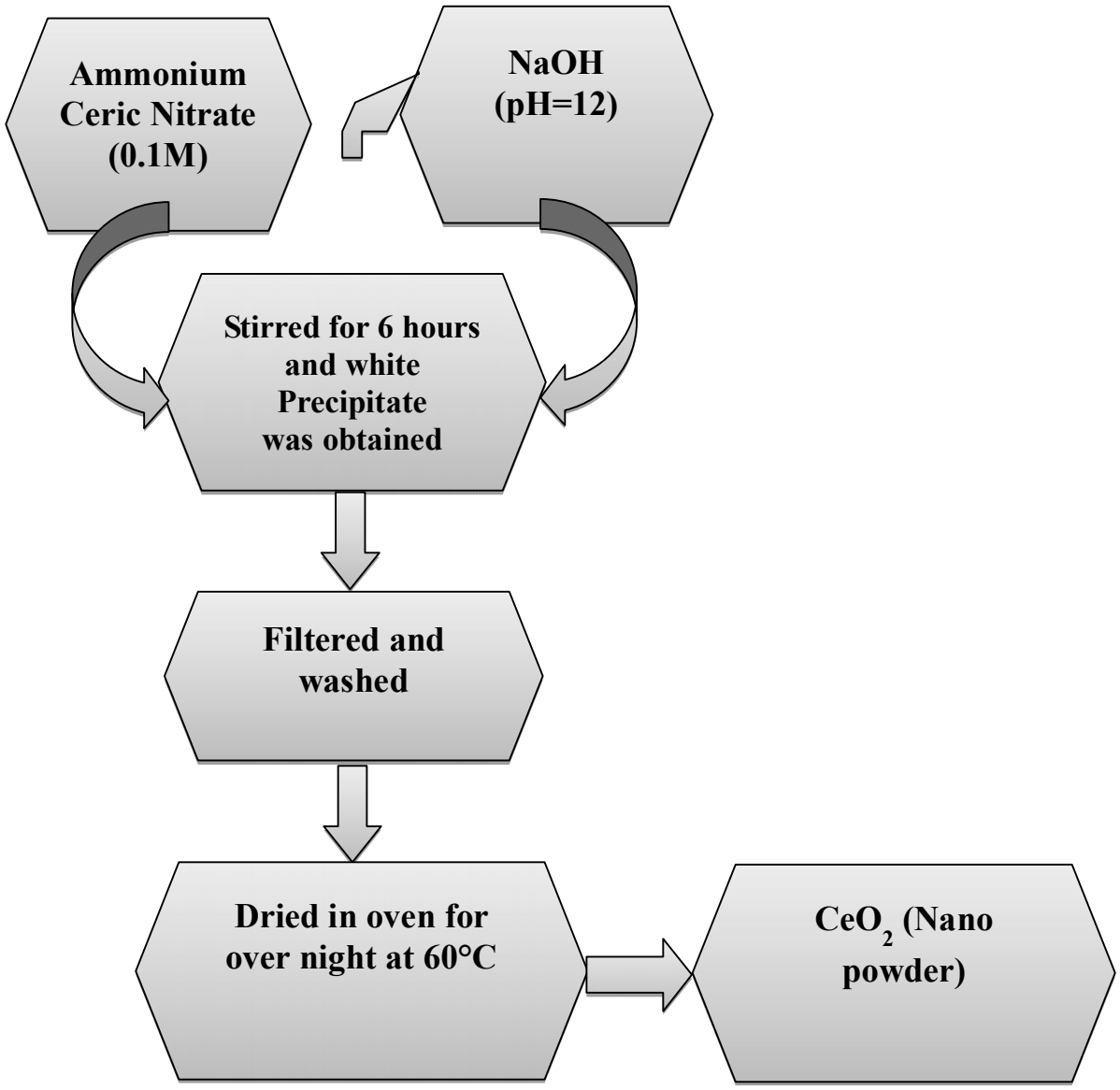

Fig.1. Flow chart for preparation of Ceria NPs

2.1.1. Instrumentation and Characterization

X-ray diffraction of synthesized $CeO_2$was recorded using Cu Ka radiation of wavelength λ=1.54060 Å with a graphite monochromator produced by a Bruker AXS D8 focus advanced X-ray diffraction meter (Rigaku, Japan, Tokyo) with 'Ni-filtered'. The scans were taken in the 2θ (diffraction angle) range from 10–80º with a scanning speed and step size of 1^o/mm and 0.01^o, respectively. FTIR spectroscopy of CeO_2 sample was carried out with Fourier Transform Infrared Spectrophotometer (Shimadzu, IRAffinity-1, and Japan) in the range of wave number 400–4000 cm^{-1} in the transmittance mode. The optical spectra (UV-vis absorption spectroscopy) of the CeO_2 sample were recorded with a Shimadzu UV-2401PC, UV-vis spectrophotometer in the range of 190–900 nm. The SEM images of as synthesized CeO_2 NPs were recorded using a Hitachi Quanta 200 FE Scanning Electron Microscope (SEM) of flexible high resolution. EDAX spectra were taken to confirm the composition of the synthesized sample.

3. Results and Discussion

Fig. 2 Shows the exhibited peaks in XRD pattern corresponds to Miller indices of (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) demonstrating the formation of crystalline with cubic fluorite structure of nanoceria[4, 8].

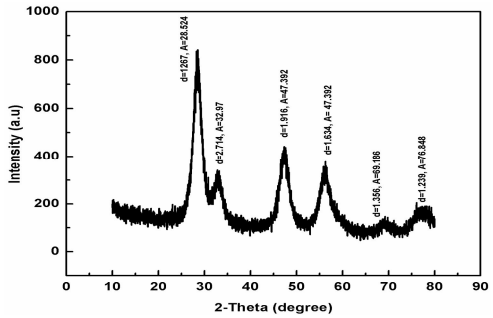

Fig. 2. XRD pattern of as synthesized Ceria NPs

The crystal structure was determined from X-Ray diffraction using Cu radiation and the phase identification was also verified from observed XRD pattern. The XRD plots indicate that the prepared nanoparticles are crystallite in nature. In order to confirm the prepared sample and its structure the peaks observed in XRD were matched with cubic structure of CeO_2 (JCPDS No. 65-0692). The average crystallite size was calculated using Debye Scherer's formula.

$D = 0.9 \lambda / (\beta \cos\theta)$

Whereas D is the average crystallite size of the particles, β is the full width at half maximum (FWHM), λ is the wavelength of the X-Ray light (1.54060Å), θ is the diffraction peak angle. The average crystallite size was obtained to be around 12nm.

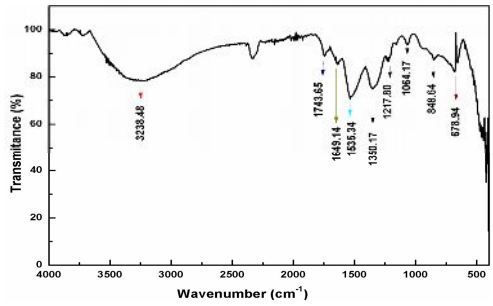

Fig. 3. FTIR spectra of Ceria NPs

Fig.3 illustrating the FTIR spectra of prepared sample, exhibiting the absorption peaks at distinct wave numbers and exemplify its chemical texture that reveals the information about the functional group. From above figure it is evident that the broad absorption band located around 3238cm^{-1} corresponds to the O-H stretching vibration of hydroxyl group. In association to the bands in the range of 848-1664cm^{-1} the stretching frequency band of ceria-oxygen (Ce-O) can be perceived below 848 cm^{-1}.It also exhibited absorption peaks around 1743

cm^{-1}, 1535 cm^{-1} and 1350 cm^{-1} that are held responsible for water and carbon dioxide. The absorption peak near 678 cm^{-1} is typical peak for Ce-O stretching bond vibration.

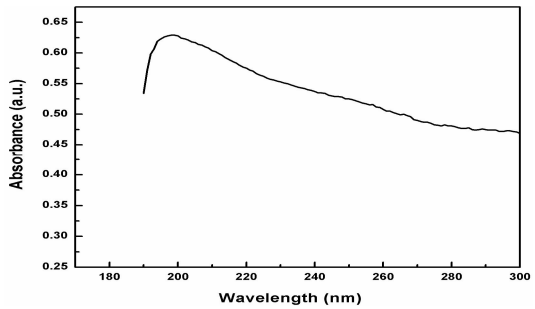

Fig . 4. UV-Vis spectra of Ceria NPs

Ultraviolet (UV) Visible spectroscopy was used to find the optical band gap of the material. Fig. 4 shows a well defined and sharp absorption peak at 198nm. On comparing with previously reported results of UV spectra of cerium oxide nanoparticles, the synthesized CeO_2 peak was moved towards lower wavelength i.e. blue shift. Based on size and morphology of cerium oxide the absorbance positions were indicated[11, 14].

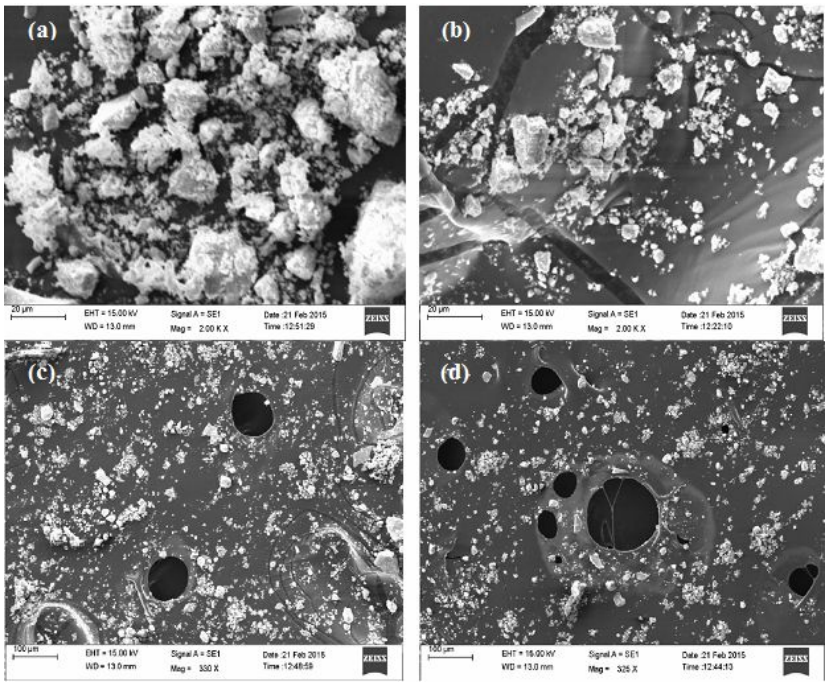

Fig. 5. SEM images of Ceria NPs with different resolutions

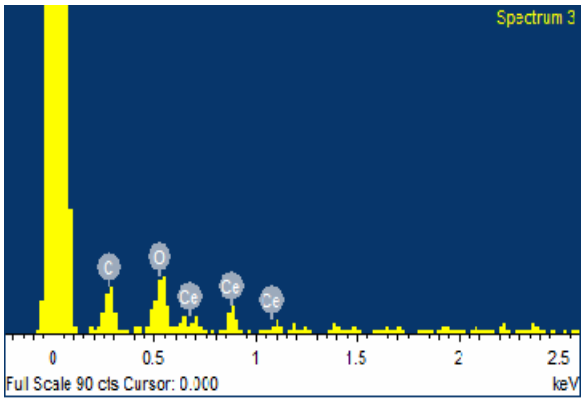

Fig. 6. EDAX Spectrum of Ceria NPs

To understand morphology SEM image (Fig. 5)of the CeO_2sample was recorded and were found to be almost spherical with some of them prolonged in shape. It was a porous like structure and perceived like an agglomerated form. The Cerium Oxide nanoparticles were also tested by EDAX and obtained spectra revealed the peaks of Cerium, Oxygen and Carbon. From Fig. 6EDAX result confirms the composition of the element present and it was found to be 55.76 % of Cerium, 21.05 % of Oxygen, and 23.19 %Carbon.

3.1. Chemical Sensing Mechanism and its realization on Volatile Organic Compounds (VOCs)

The CeO_2 nanoparticles were utilized as sensing material to detect some harmful gasses like ethanol, acetone and formaldehyde by coating on substrate surface of the ceramic tube with two electrodes.

Enhancement in Sensitivity and control of response are the major challenges in gas sensors made of metal oxide semiconductor. Sensing mechanism is based on the drastic change of its conductivity/resistivity. When sensor was exposed to air then the conduction band of cerium oxide will give electrons to the oxygen molecules and convert into O^- or O^{2-} or O_{2-} species [14] so there will be change in the potential barrier. Based on detection principle of metal oxide gas sensors when the sensor is exposed to oxidizing gases the resistivity increases and resistivity decreases when it is exposed to reducing gases [11].

3.1.1 Sensor Fabrication

The experimental setup of sensor was suitably made and it was constructed within a glass chamber having provision of inlet and outlet with a semiconducting alumina ceramic tube and heating coil.To produce and maintain temperature in surrounding ambient of sensor a temperature controller, connected properly with power supply and voltage supplier, was utilized. The dimension of the tube was taken as 5-6 mm in length and 2-3 mm in radius. Initially the synthesized nano particle was coated on the surface of tube after making the solution with polyvinyl alcohol (PVA) as a binder. The thickness of coated film was kept around 25-35 µm.

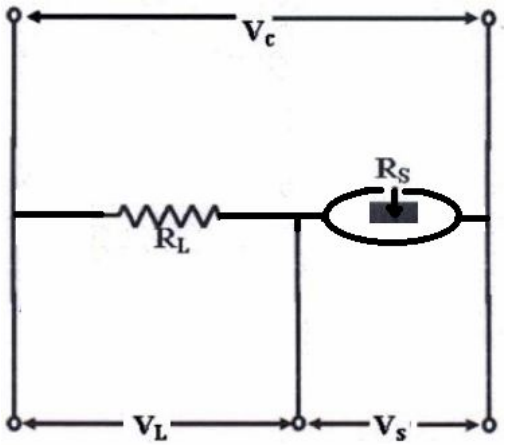

Fig. 7.Circuit diagram of the resistance of the gas sensor

A close circuit was made with the sensor, load resistance and power supply. Sensor consists of two electrodes tied over its surface and one heating coil placed inside the tube. To calculate sensor resistance (Rs) that in turn relates to sensitivity of the sensor (S), the voltage drop across load resistance (V_{out}) was measured up on injection of gases.

$R_s = R_L[(V_c / V_L) -1)]$ …… (1)

$$= \frac{\Delta R}{R}$$ ….. (2)

By making use of obtained value of Rs from equation (1) in equation (2) the sensitivity of the sensor was calculated.

The electrical responses in terms of sensitivity were measured for given three different Volatile Organic gases (VOCs) different temperature ranging from 50°C to 300°C.

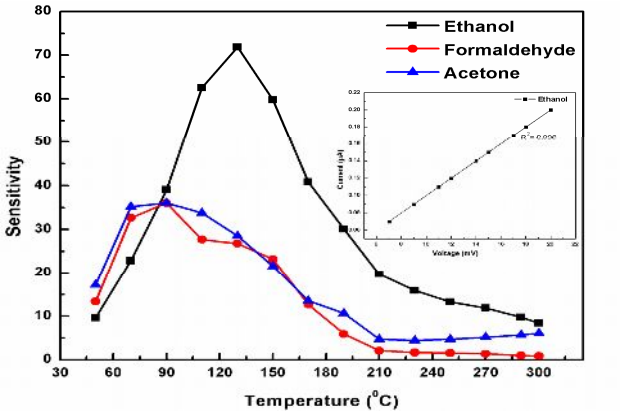

Fig .8. Temperature *Vs* Sensitivity of as synthesized CeO_2NPs(Inset I-V Characteristics of Ethanol)

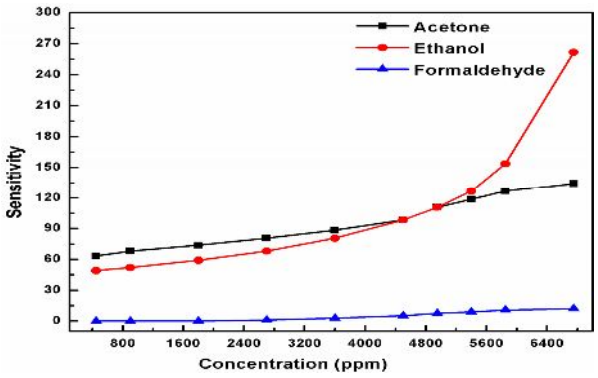

Fig. 9.Sensitivity variation of the gases atdifferent concentration in ppm range

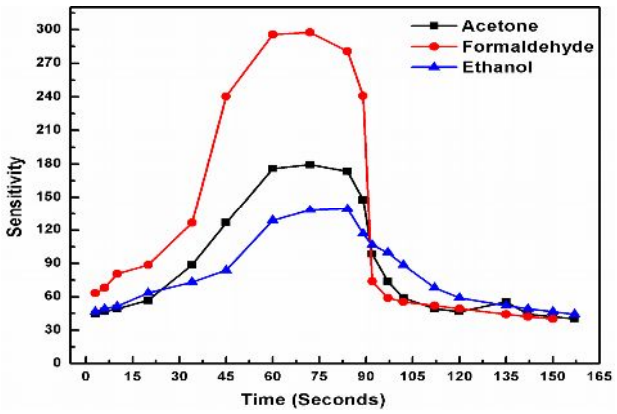

Fig. 10. Transient characteristics of analyzing gases at constant temperature

Table 1.Sensor properties for different gases corresponding to their operating temperature

S.N.	Analyzing Gas	Operating Temperature (°C)	Sensitivity	Response Time (sec.)	Recovery Time (sec.)
1.	Ethanol	130	73.851	28	12
2.	Formaldehyde	80	36.127	20	12
3.	Acetone	90	36.024	43	27

Fig. 8 shows the sensitivity of cerium oxide sensor at different temperatures for different Volatile Organic gases (VOCs). It can be observed that the maximum sensitivity for different gases is found at different temperatures, like for ethanol the highest sensitivity is at 130°C and for acetone and formaldehyde it showed highest sensitivity at 90°C and 80°C respectively as demonstrated in table 1. Based on nature of the gases also (oxidizing or reducing) the sensitivity will vary. If the grain size is less then sensitivity will be high i.e. more number of grains can occupy the surface area then the potential will increase[12,15].

4. Conclusions

Cerium oxide nanoparticles have been successfully prepared by solvothermal method and were found to be crystalline in nature having approximately 12nm of grain size with cubic fluorite structure. The structural and morphological properties were explored with the help of XRD, FTIR and SEM, whereas its composition was confirmed from EDAX analysis having with 55.76 % of Cerium, 21.05 % of Oxygen, and 23.19 % Carbon. A strong UV absorption was observed below 450nm and a well defined peak was obtained at 198 nm, the band gap energy was found to be 3.42eV. By using these NPs a sensitive gas sensor for recognition of volatile organic compound has been successfully developed and was effectively tested for ethanol, acetone and formaldehyde as target gases by varying concentration and operating temperature. The developedmetal oxide semiconductor gas sensor was found possessing highest sensitivity for ethanol at 130°C. Further, on comparing the obtained result with previously reported research results one can be precisely affirmed that large surface area can provide good reaction contact between target gas and sensing material. Hence the materials having porous structure are known to be better for sensing response. Hence this in turn it relates to its grain size and it is found that lower grain size of material was responsible for showing high sensitivity.

Acknowledgment

We are highly obliged for this opportunity to thank VIT University for providing us XRD and SEM characterizations facilities of sample through DST-FIST scheme.

References

1. N.Masson, R. Piedrahita, M. Hannigan; “Approach for Quantification Of Metal Oxide Type Semiconductor Gas Sensors Used For Ambient Air Quality Monitoring”; Sensors and Actuators B 208(2015) 339-345.
2. G. Korotcenkov, B.K Cho; “Engineering Approaches To Improvement of Conductometric Gas Sensor Parameters Part 2: Decrease Of Dissipated Power And Improvement Stability And Reliability”; Sensors and Actuators B 198(2014) 316-341.
3. R. Suresh, V. Ponnuswamy, R. Marippan; “Nanostructured Cerium Oxide Thin Films By Nebulized Spray Pyrolysis (NSP) Technique: Impact Of Surfactants On The Structural, Optical and Compositional Properties”;; Ceramics International Journal 40(2014) 13515-13527.
4. E. Kumar, P. Selvarajan, D. MuthurajE. Kumar, P. Selvarajan, D. Muthuraj; “Synthesis And Characterization Of CeO_2 Nanoparticles By Solvothermal Route”; Materials Reasearch 2013;vol 16; 269-276.
5. Noriya Izu, Ichiro Matsubara, Toshio Itoh, Takafumi Akamatsu and Woosuck Shin; “CO Responses Of Sensors Based On Cerium Oxide Thick Films Prepared From Clustered Sperical Nanoparticles”; Sensors 2013, 13, 3252-3261.
6. Parastoo Jamshidi, Masoud Salavati-Niasari, Davood Ghanbari, Hamid Reza Shams; “Synthesis, Characterization, Photoluminescence and Photocatalytic Properties Of CeO_2 Nanoparticles By Sonochemical Method”; J Clist Sci (2013) 24;1151-1162.
7. Yu-Feng Sun, Shao-Bo Liu, Fan-Li Meng, Jin-Yun Liu, Zhen Jin, Ling- Tao Kong and Jin- Huai Liu; “Metal Oxide Nanostructures and Their Gas Sensing Properties: A Review”; Sensors 2012, 12, 2610-2631.
8. Richard I. Walton; “Solvothermal Synthesis Of Cerium Oxides”; Progress in Crystal Growth and Characterization Of Material 57(2011) 93-108.
9. Elaheh K. Goharshadi, Sara Samiee, Paul Nancarrow; “Fabrication Of Cerium Oxide Nanoparticles: Characterization and Optical Properties” ; Journal Of Colloid and Interface Science 356(2011)473-480.
10. Hongyun Jin, Ning Wang, Liang Xu, Shuen Hou; “Synthesis and Conductivity Of Cerium Oxide Nano Particles” Materials Letters 64 (2010) 1254-1256.
11. George F. Fine, Leon M. Cavanagh, Ayo Afonja and Russell Binions; “Metal Oxide Semi- Conductor Gas Sensors in Environmental Monitoring”; Sensors 2010, 10, 5469-5502.
12. Noriya Izu, Sayaka Nishizaki, Toshio Itoh, Maiko Nishibori, Woosuck Shin, Ichiro Matsubara; “Gas Response, Response Time and Selectivity Of a Resistive CO Sensor Based On Two Connected CeO_2 Thick Films With Various Particles Sizes”; Sensors and Actuators B 136(2009) 364-370.
13. Bahcine Bakiz, Frederic Guinneton, Jean-Pierre Dallas, Sylvie Villain, Jean-Raymond Gavarri; “From Cerium Oxycarbonate to Nanostructured Ceria: Relations Between Snthesis, Thermal Process and Morphologies”; Journal Of Crystal Growth 310(2008) 3055-3061.

14. Amnat Reungchaiwat, Teerapol Wongchanapiboon, Saisunee Liawruangrath and sukon Phanichphant; "Home Made Detection Device for the Mixture of Ethanol and Acetone"; Sensors, 2007, 7, 202-213.
15. Noriya Izu, Woosuck, Shin, Ichiro Matsubara, Norimitsu Murayama; "The Effects Of The Particle Size and Crystallite Size On The Response Time For Resistive Oxygen Sensor Using Cerium Oxide Thick Film"; Sensors and Actuators B 94 (2003) 222-227.

*****