https://doi.org/10.30799/jnst.S10.19050305 J. Nanosci. Tech. - Volume 5 Issue 3 (2019) 725–726

ISSN: 2455-0191

Share Your Innovations through JACS Directory

Journal of Nanoscience and Technology

Visit Journal at http://www.jacsdirectory.com/jnst

Special Issue on "International Conference on Advanced Materials and Their Applications" *Issue Editor:* Dr. C. Vedhi

Synthesis and Characterization of Pure and Gd-Doped CeO_2 Nanoparticles

M. Sridaran, K. Dhanasekar, M. Arivanandhan*

Centre for Nanoscience and Technology, Anna University, Chennai – 600 025, Tamilnadu, India.

ARTICLE DETAILS

Article history:
Received 20 March 2019
Accepted 29 April 2019
Available online 04 June 2019

Keywords:
CeO_2
Microwave
Raman Spectroscopy

ABSTRACT

CeO_2 and Gd-doped CeO_2 nanoparticles were synthesized by microwave-assisted method. The structural properties of cerium oxide were analyzed by XRD. The XRD pattern confirmed the cubic structure of cerium oxide. The morphology and size of the CeO_2 and Gd-doped CeO_2 nanoparticles were analyzed by SEM and TEM analysis. From the SEM and TEM images it was confirmed that the pure cerium oxide exhibited the spherical morphology whereas Gd-doped CeO_2 shows rod like morphology as it was confirmed by SEM and TEM images. Raman spectra confirm the F2g mode of vibration of cerium oxide and it was slightly shifted in the Gd-doped cerium oxide sample due to incorporation of Gd.

1. Introduction

The nanomaterials are highly useful as a catalyst for toxic dye degradation and biodiesel production due to their high surface activity originated from high surface to volume ratio. Therefore, the nanomaterials with controlled morphology is imperative to improve the surface activity. Cerium oxide is one of the promising rare earth oxides and very much useful for photocatalytic and energy storage applications [1-3]. Moreover, the multi valence state of cerium leads to interesting properties of the material such as oxygen storage and releasing capacity [4,5]. The cerium oxide has the ability to shift easily between reduced and oxidized states. The fluorite structure of cerium oxide can withstand high levels of oxygen non-stoichiometry without changing its structural type [6]. Further, treating at different atmosphere and doping with different elements can tune the oxygen storage and releasing capacity of cerium oxide.

Cerium oxide can be synthesized by various methods such as sol-gel, co-precipitation and hydrothermal methods [4-7]. However, these methods offer limited controllability over size and morphology of the material. Whereas microwave assisted synthesis method is highly useful for synthesizing mono dispersed nanoparticles due to its direct and drastic heating process. Therefore, the aim of the present work is to synthesis pure and Gd doped cerium oxide nanoparticles by microwave assisted synthesis method. The physicochemical properties of the prepared nanoparticles were studied by XRD, SEM, TEM and Raman analysis.

2. Experimental Methods

Cerium nitrate hexahydrate (Alfa aesar, 99.5%) was used as precursor for synthesizing cerium oxide. 0.3 M of cerium nitrate hexa hydrate was dissolved in de-ionized water under stirring condition. 0.5 mL of PEG was added as a capping agent to control the agglomeration. After that, ammonium hydroxide (NH_4OH) was added to the obtained solution and system was brought to a higher pH value under the stirring for half an hour. The solution was placed in the microwave oven of 850 watts in 60s. The solution was transformed into yellow color. After the reaction, the precipitates were collected by centrifugation at 4000 rpm for 15 min. The CeO_2 powder was obtained by drying the collected product at 80 °C in an oven for 24 hours and the resulted product was pale yellow powder. The final product was treated at 350 °C for 3 hours to remove the unreacted residuals. Gadolinium nitrate hexa hydrate was used as a source material for the preparation of Gd-doped cerium oxide. The similar procedure was followed for the synthesis of Gd doped cerium oxide by changing the molar concentrations cerium precursor as 0.27 M and gadolinium precursor as 0.03 M. The prepared pure and Gd-doped cerium oxide materials were analyzed by XRD, SEM, TEM and Raman analysis for studying their structural and morphological properties.

The structural properties of the samples were analyzed using Bruker D8 advance X-ray diffractometer with Cu Kα (1.54 Å) radiation. The X-ray diffraction patterns were recorded in the range of 2Θ from 20 to 80 with a stepwise increment of 0.02. Morphology of the samples was investigated by scanning electron microscopy (TESCAN VEGA3 scanning electron microscope) and transmission electron microscopy (JEOL 3100 TEM). The Raman spectra of the samples were recorded using L-PeakSeeker Raman spectroscopy, Agiltron.

3. Results and Discussion

3.1 Structural Analysis

Fig. 1 shows the XRD pattern of the prepared cerium oxide sample. All the diffraction peaks of (111), (200), (220), (311), (222) and (400) were indexed and well matched with standard JCPDS Card No. 65-5923. The patterns of cerium oxide samples confirmed the cubic structure of the material. The sharp and high intense peaks of XRD patterns confirm the high crystalline quality of the samples. The crystallite size of pure cerium oxide was calculated from the diffraction peaks of XRD pattern using Scherer's formula. The calculated sizes of the crystallites are shows in Table 1. From the calculated size of the crystallites, the average size of the crystals is found as 12.5 nm.

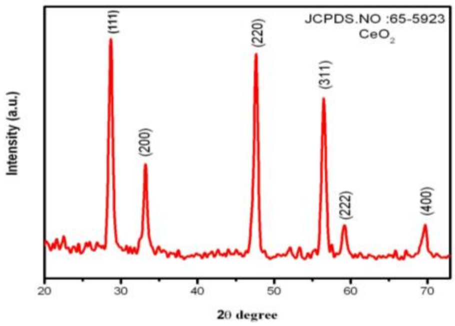

Fig. 1 XRD pattern of CeO_2 nanoparticles

*Corresponding Author:arivucz@gmail.com(M. Arivanandhan)

https://doi.org/10.30799/jnst.S10.19050305

Cite this Article as: M. Sridaran, K. Dhanasekar, M. Arivanandhan, Synthesis and characterization of pure and Gd-doped CeO_2 nanoparticles, J. Nanosci. Tech. 5(3) (2019) 725–726.

Table 1 Calculated crystallite size from the XRD pattern

Peak position 2θ (°)	(hkl)	FWHM (°)	Crystallite size (nm)
28.641	(111)	0.69	12.42
33.208	(200)	0.61	14.20
47.618	(220)	0.73	12.43
56.518	(311)	0.73	12.91
69.061	(400)	0.883	10.81

3.2 Morphological Studies

Fig. 2 shows the SEM images of pure and Gd-doped cerium oxide nanoparticles. The image of pure cerium oxide shows that the obtained particles are spherical in shape and highly mono dispersed. The SEM image of Gd-doped cerium oxide nanoparticles showed highly agglomerated particles with wide range of size distribution

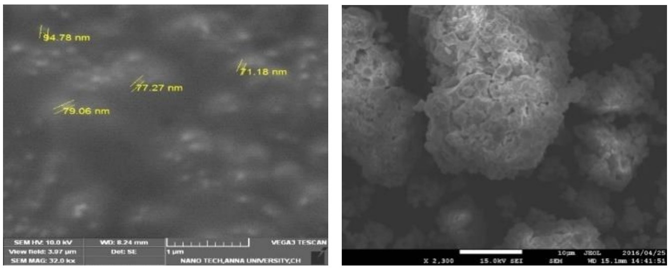

Fig. 2 SEM images of pure CeO_2(a) and CeO_2:Gd(b) nanoparticles

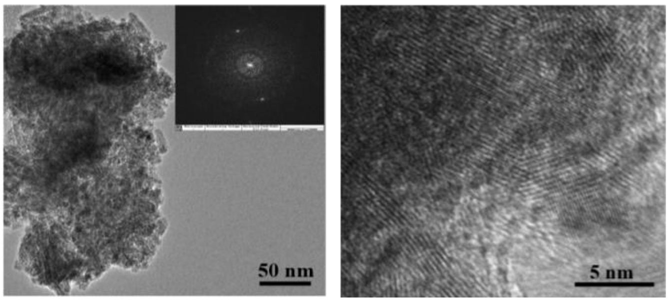

Fig. 3 TEM images of pure cerium oxide nanoparticles. Inset image shows the FFT of pure sample

Fig. 3 shows the TEM images of the pure cerium oxide nanoparticles. As can be seen from Fig. 3, the cerium oxide nanoparticles are having spherical morphology and the size of the particles is in the range of 10 nm. The HRTEM image shows the lattice fringes of the particles, which shows high crystalline nature of the sample. The inset of Fig. 3 shows the FFT pattern of the sample and it shows ring pattern, which confirms the polycrystalline nature of the sample.

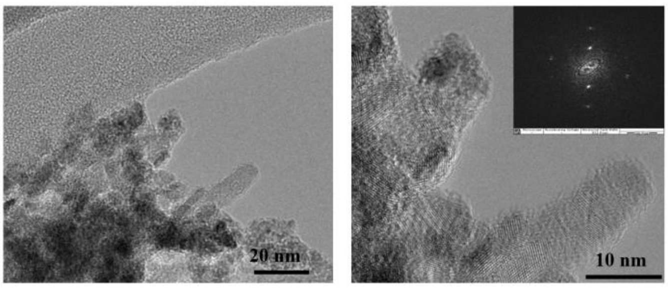

Fig. 4 TEM images of Gd-doped cerium oxide nanoparticles. Inset image shows the FFT of Gd-doped cerium oxide

Fig. 4 shows the TEM images of Gd-doped cerium oxide nanoparticles. The rod like morphology was clearly observed in the TEM images and the sizes of the rods are in the range of 10 to 20 nm diameter and 30 to 50 nm in length. The inset of Fig. 4 shows the FFT pattern of the sample, which confirms the polycrystalline nature of the sample. From the TEM images, it is obvious that the spherical morphology of the particles is changed into rod like morphology. Moreover, the similar rod like morphology for Gd-doped cerium oxide sample was reported in the literature [8, 9].

Fig. 5 shows the Raman spectra of pure and Gd-doped cerium oxide samples. In Fig. 5, the active mode of F2g vibration is observed at 458 cm^{-1} which confirms the fluorite cubic structure of the material [10, 11]. In the Raman spectrum of Gd-doped cerium oxide nanoparticles, the characteristic peak of F2g is observed at 454 cm^{-1} and the Raman shift is mainly due to the incorporation of Gd in cerium oxide lattice.

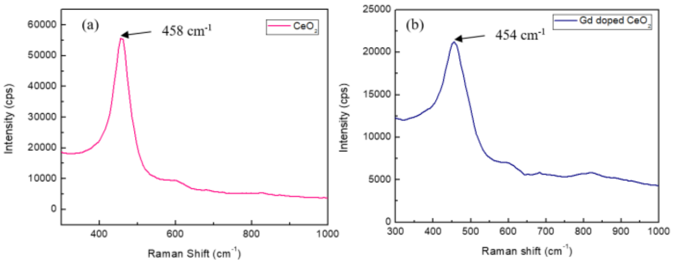

Fig. 5 Raman spectra of (a) pure CeO_2 and (b) Gd-doped CeO_2 nanoparticles

4. Conclusion

CeO_2 and Gd-doped CeO_2 nanoparticles were successfully synthesized by microwave-assisted method. The crystal structure of cerium oxide was confirmed by XRD analysis. From the SEM and TEM analysis, it was observed that the morphology and size of the cerium oxide nanoparticles are changed from spherical to rod like morphology due to the incorporation of Gd in cerium oxide. Raman spectra confirm the F2g mode of vibration of cerium oxide and it was slightly shifted in the Gd-doped cerium oxide sample due to incorporation of Gd.

References

[1] C. Hu, Z. Zhang, H. Liu, P. Gao, Z.L. Wang, Direct synthesis and structure characterization of ultrafine CeO_2 nanoparticles, Nanotechnol. 17 (2006) 5983-5987.

[2] T. Saravanan, M. Shanmugam, P. Anandan, M. Azhagurajan, K. Pazhanivel, et al., Facile synthesis of graphene-CeO_2 nanocomposites with enhanced electrochemical properties for supercapacitors, Dalton Trans. 44 (2015) 9901-9908.

[3] K. Chinnu, P. Anandan, M. Arivanandhan, A. Venkatesan, R. Mohan Kumar, R. Jayavel, Effect of rare earth doping on the enhancement of photocatalytic performance of ceria nanocrystals under natural sunlight, J. Mater. Sci.: Mater. Electron. 29 (2018) 9564-9572.

[4] Dengsong Zhang, Xianjun Du, Liyi Shi, Ruihua Gao, Shape-controlled synthesis and catalytic application of ceria nanomaterials, Dalton Trans. 41 (2012) 14455-14475.

[5] Z. Wang, Z. Quan, J. Lin, Remarkable changes in the optical properties of CeO_2 nanocrystals induced by lanthanide ions doping, Inorg. Chem. 46 (2007) 5237-5242.

[6] M. Godinho, Edson R. Leite, Rosana F. Gonclaves, et al., Gadolinium-doped cerium oxide nanorods: Novel active catalysts for ethanol reforming, J. Mater. Sci. 45 (2010) 593-598.

[7] V. Arul Mozhi Selvan, R.B. Anand, M. Udayakumar, Effect of cerium oxide nanoparticles and carbon nanotubes as fuel-borne additives in diesterol blends on the performance, combustion and emission characteristics of a variable compression ratio engine, Fuels 130 (2014) 160-167.

[8] K. Zhou, X. Wang, X. Sun, Q. Peng, Y. Li, Effects of nano-CeO_2 with different nanocrystal morphologies on cytotoxicity in HepG2 Cells, J. Catal. 229 (2005) 206-212.

[9] H.X. Mai, L.D. Sun, Y.W. Zhang, R. Si, W. Feng, et al., Shape-selective synthesis and oxygen storage behavior of ceria nanopolyhedra, nanorods nanocubes, J. Phys. Chem. B 109 (2005) 24380-24385.

[10] J.D. Yang, R.A. Rocha, R. Muccillo, E.N.S. Muccillo, Synthesis and characterization of gadolinia-doped ceria with manganese addition, Mater. Sci. Forum 727-728 (2012)1296-1301.

[11] M.F.S. Machadoa, L.P.R. Moraesa, N.K. Monteiroa, V. Espositob, D.Z. DeFlorioc, et al., Low temperature synthesis and properties of gadolinium-doped cerium oxide nanoparticles, ECS Trans. 78 (2017) 387-394.

About the Conference…

"International Conference on Advanced Materials and Their Applications" has been convened by Dr. C. Vedhi, Assistant Professor, PG and Research Department of Chemistry, V.O. Chidambaram College, Thoothukudi at his designated venue on 27th December 2018.

https://doi.org/10.30799/jnst.S10.19050305

Cite this Article as: M. Sridaran, K. Dhanasekar, M. Arivanandhan, Synthesis and characterization of pure and Gd-doped CeO_2 nanoparticles, J. Nanosci. Tech. 5(3) (2019) 725–726.