International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 04 Special Issue: 09 | Sep -2017 www.irjet.net p-ISSN: 2395-0072
One Day International Seminar on Materials Science & Technology (ISMST 2017)
4th August 2017
Organized by
Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India

ROLE OF SURFACTANT ON SYNTHESIS AND CHARACTERIZATION OF CERIUM OXIDE (CeO_2) NANO PARTICLES BY MODIFIED CO-PRECIPITATION METHOD

[1,2]M.Ramachandran, [1,3]M.Shanthi, [1]R.Subadevi,[1]M.Sivakumar*

[1] #120, Energy Materials Lab, Department of Physics, Alagappa University, Karaikudi-630003. India
[2] Department of Physics,Arumugam Pillai Seethai Ammal College, Tiruppattur 630 211.
[3] Department of Physics, Kamaraj College of Engg. And Tech, Virudhunagar 626001,
(Corresponding Author – susiva73@yahoo.co.in Mobile no: 9842954116 (M.Sivakumar))*

***

Abstract - *In this work, Cerium oxide (CeO_2) nano particles were nucleated by mixing aqueous Cerium nitrate ($(CeNO_3)_3.6H_2O$ and sodium hydroxide (NaOH) using modified co-precipitation method at room temperature. Different organic molecules such as poly (vinyl pyrrolidone) (PVP), poly (ethylene glycol) (PEG) and hexadecyl trimethyl ammonium bromide (CTAB) were chosen as surfactant and injected into the reaction medium at the beginning of the system. For comparison, surfactant free sample was also prepared. The XRD measurements show that the cubic fluorite structure having the crystallite size of 15-32 nm. The lattice strains were detected using Williamson-Hall plot method. The surface morphology and elemental analyses of the prepared nanoparticles were studied through SEM and EDX analyses. The SEM images show that the morphology mainly depends on the surfactant content added. The optimized sample towards the structure was characterized through PL analysis. The band gap of the CeO_2 nano particles was estimated as 3.37 eV, which is lower than the bulk.*

Key Words**: Cerium oxide; Poly vinyl pyrrolidone; Poly Ethylene Glycol, Hexadecyl trimethyl ammonium bromide, Williamson-Hall plot.**

1.INTRODUCTION

Ceria (Cerium oxide, CeO_2) is one of the most lavish among rare earth elements with wide energy gap (Eg=5.5 eV) and high dielectric constant(ε=26). The physical and chemical properties of Ceria nanocrystalline material often contrast from crystalline and amorphous one. Rare earth oxide nanoparticles have unique luminescence, magnetic and electronic properties due to their unfilled 4f electronic structure. Ceria was currently a subject of great interest due to its extensive array of applications, e.g., as associate materials for three way catalysis, oxygen sensors, solid oxide fuel cells that employ the oxygen storage capacity, oxygen sensors, glass-polishing, ceramics and uv absorbent [1,2]. However, the device performances are strongly influenced by the properties of CeO_2 particles. Several techniques have been proposed to synthesize nano-sized CeO_2 particles with auspicious control properties such as combustion synthesis, spray pyrolysis, micro emulsion, sonochemical, co-precipitation and sol-gel. However, it was difficult to obtain nanoparticles with low degree of agglomeration of these techniques required a very stringent control on various processing parameters together with low production yield. Therefore, simple and low cost routes to synthesize CeO_2 nanoparticles with low degree of agglomeration are still the key issues. The surfactant mediated co-precipitation method can overcome the above issues, owing to the advantages of simple process, mild synthesis condition, easy scale-up and low cost.

Somalian Prokha et.al., [3] synthesized monodisperse CeO_2 nanospheres using PVP as a surfactant. Guofeng Wang et.al., [4] reported the weakly aggregated CeO_2 nano particles has been developed using CTAB as surfactant at room temperature. Although CeO_2 nanoparticles prepared by the co-precipitation route have been extensively studied that most of the previous reports were focused on direct precipitation of ceria without using surfactant. Surfactant plays an important role in the presence of CeO_2 nanoparticles. The present investigation describes the synthesis of CeO_2 nanoparticles with low degree of agglomeration using PEG, CTAB and PVP as surfactant and Cerium nitrate hexa hydrate as starting material. The CeO_2 nanoparticles were characterized structural, morphology and optical studies. In addition, the formation mechanism of surfactant passivated CeO_2 nanoparticles was discussed.

1.1 Materials and methods:

All reagents of analytical grade were acquired from commercial sources and used without further purification. Cerium nitrate hexa hydrate ($(Ce(NO_3)_3.6H_2O$ (Alpha Aeser

>99%) as cerium salt, Sodium hydroxide (NaOH) (SRL Grade) was used as precipitation agent. Polyvinyl pyrrolidone (PVP (Mol.wt.40,000, Merck, Germany)), hexadecyl-trimethylammonium bromide, $C_{10}H_{42}BrN$ (CTAB, Acros Organics, >99 %) and PEG (Acros Organics, M.W.400) were applied as surfactants.

CeO_2 nano particles were prepared by the modified co-precipitation method. To obtain different morphology, the appropriate amount of PEG, CTAB and PVP were added separately to 0.01 M of aqueous Ce $(NO_3)_3.6H_2O$. The resulting aqueous mixture was stirred further for 10m at room temperature and then aqueous NaOH was added drop wise under vigorous stirring until pH ≈ 8. This resulted in the appearance of yellow precipitate which was further stirred for about 90min when it was converted to light yellow slurry. The precipitate was centrifuged at 200 rpm and washed with deionized water and acetone several times to ensure the complete deletion of the surfactant. Finally the precipitate was dried in an oven at 110°C for 4h, milled the sample for 30m and consequently calcined in air at 600°C for 2h to get CeO_2 material.

The X-ray diffraction pattern (XRD) was carried out on an X-ray diffractometer (X'Pert PRO) with CuKα (45KV, 50mA) radiation at room temperature in the range of $20° < 2\theta < 80°$. Fourier Transform Infrared (FTIR) study was made using Thermo Nicolet 380 Instrument Corporation and kBr in the region between 4000-400 cm^{-1}. The surface morphology of the samples was observed using a Scanning Electron Microscopy (SEM) Quanta FEG 200 Instrument with EDX facility. Photoluminescence spectroscopy was performed on Bruin omega-10 spectrometer.

2. Results and discussion:

Fig.1 shows the XRD patterns of the Ceria (CeO_2) nanoparticles using a) surfactant free b) PVP c) PEG and d) CTAB as surfactants. The diffraction peaks of all synthesized samples are labeled and can be indexed to the typical face-centered cubic phase (JCPDS.No. 81-0792, space group Fm3m). The strong and sharp diffraction peaks indicate the good crystallization of the samples. No additional peaks such as PVP, PEG, CTAB and ceria nitrate in the XRD were observed, revealing the high purity of the preparation Ceria nano particles. The crystalline size was calculated by using the Debye-Scherrer formula [5] and the micro strain was calculated using Williamson-Hall plot method [6]. The mean crystalline size is about 32.4, 15.10, 28.5, 23.02 nm and the micro strains are 0.00086, -0.0014, 0.00067, -0.0022 for a, b, c and d samples respectively. These values are comparable to the literatures [7,8].

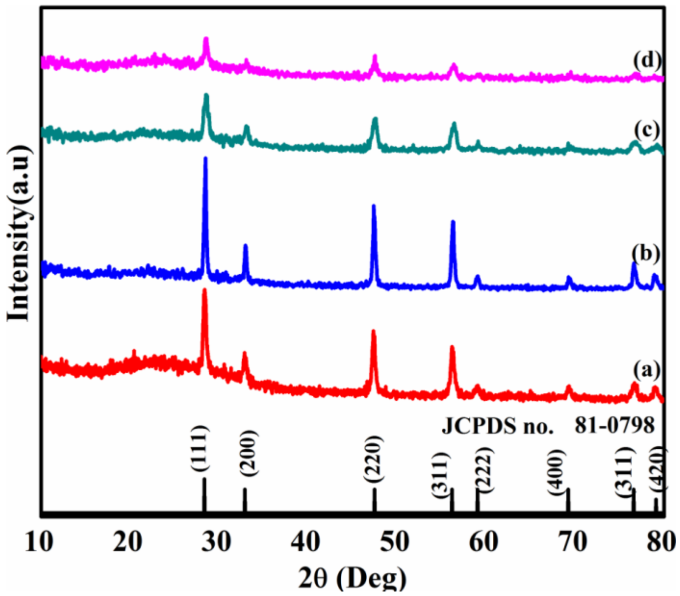

Fig -1: XRD pattern of CeO_2 nano particles a) surfactant free b) PVP c) PEG d) CTAB as a surfactant.

The FT-IR spectra of the samples (a-d) were shown in fig.2 in the frequency between 4000-400 cm^{-1}. The broad peaks around 3337 cm^{-1} and 1664 cm^{-1} correspond to the physically absorbed water and OH stretching vibration respectively.

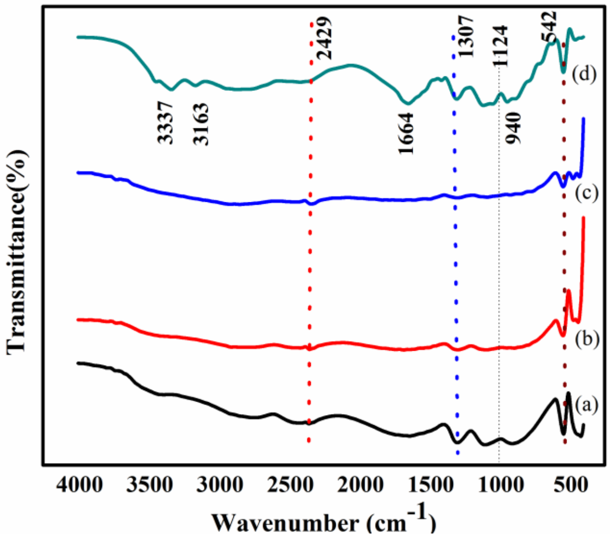

Fig -2: FTIR spectra of CeO_2 nano particles a) surfactant free b) PVP c) PEG d)CTAB as a surfactant.

The peak at 3163 cm^{-1} elucidated CH bond of the surfactant molecule. The peaks at 542cm^{-1} and 940 cm^{-1} attributed to Ce-O stretching vibration and Ce-O_2-Ce bending vibrations respectively confirms the formation of Ceria (CeO_2) nanoparticles.

It is evident from the fig 3(a-d), surfactant play vital role in the surface morphology in the prepared Ceria nanoparticles. Fig.3.a, surfactant free sample revealed that large particles are composed of small crystallites and show the particle aggregate of irregular shape. In Fig. 3.b, When PVP is added, there are two types of particles were seen such spherical (142 nm) together with needle like particles (570× 142) nm. Fig 3.c and d, uniform hexagonal particles and cauliflower like particles were observed. It is clearly evident that the surfactant plays vital role in particle morphology of the CeO_2.

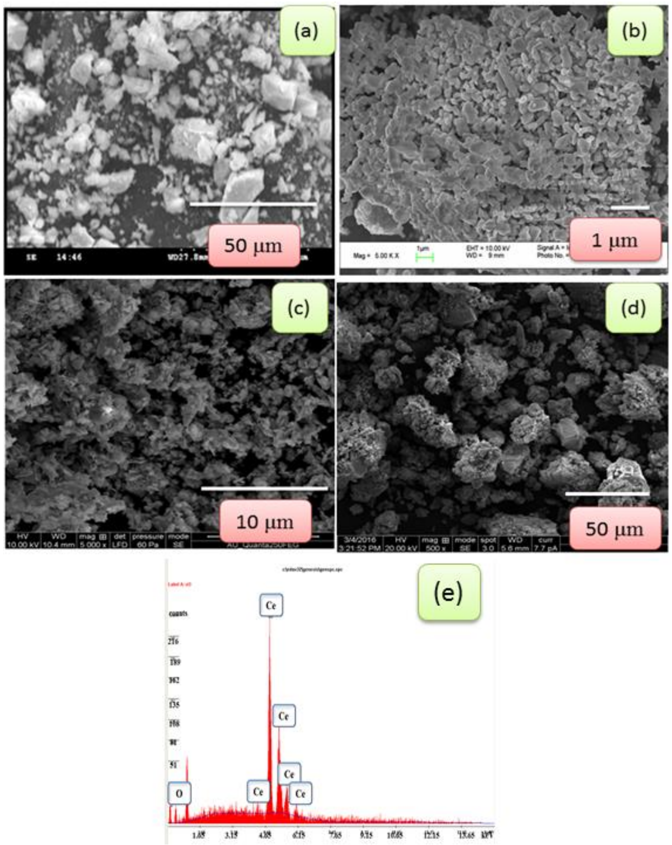

Fig -3: SEM image of CeO_2 nano particles a) surfactant free b) PVP c) PEG d)CTAB as a surfactant.e) EDX spectra of CeO_2 nano particle.

From the above structural analyses, the ceria with PVP assisted surfactant is lower particle size with homogeneous morphology than CTAB and PEG assisted ceria. It may be due to absorption of PVP molecules on various crystallographic planes of cerium source played a major role in determining the product morphology; due to the fact of supersaturation degree has substantial influence on the crystal nucleation rate and the crystal growth rate [9]. CTAB might not be absorbed at the surface. A certain repellent action occurs between the hydrophilic group of CTAB and Cerium cation at grain surface, which makes stabilizing effect of CTAB on grain become weaker. When a non-ionic surfactant (PEG) was used, the average particle size of CeO_2 was bigger than other surfactant. This result can be attributed to the stabilizing effect of non-ionic surfactant on water droplets and particles mainly derived from its hydrogen bond with water.

The energy dispersive X-ray spectrum (EDX) in Fig.3.e performed on the materials suggests the existence of Ce and O, EDX measurements on different spots of the samples always gave the same patterns, which prove the homogeneity of the samples.

The Photoluminescence spectrum of the as prepared CeO_2 is shown in Fig.4 with an excitation wavelength 290 nm. Whereas band to band transition was seen at 368nm with corresponding energy of 3.37 eV. The peaks at 434 and 524 nm correspond to blue and Green emission respectively, which can be attributed to the presence of oxygen vacancies.

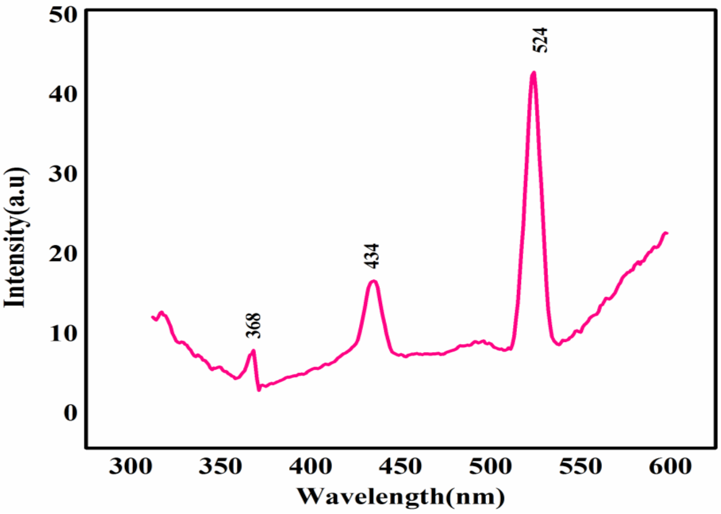

Fig -4: PL spectra of CeO_2 nano particles using PVP as surfactant.

3. Conclusion:

The Ceria (CeO$_2$) nano particles were successfully synthesized via modified co-precipitation method using PVP, PEG and CTAB as surfactants. The cubic structure with Fm3m space group (JCPDS: 81-0792) was confirmed through XRD analysis. Further, the presence of Ce,O species was investigated via FT-IR, EDX analyses. The morphology of CeO$_2$ nano particles was highly dependent on the surfactant. The well dispersed spherical together with needle morphology was observed through PVP assisted surfactant. Also, it has a band gap of 3.37 eV, which was lower than bulk. Based on the analyses, one can accomplish that the material can eventually be used as filler for Lithium polymer battery electrolyte application.

REFERENCES

[1] F-S Sangsefidia, M-S Niasaria, S. Mazaherib, M. Sabetc, "Controlled green synthesis and characterization of CeO2 nanostructures as materials for the determination of ascorbic acid"J.Mole.Liquids; (2017), 241, 772-781. doi.org/10.1016/j.molliq.2017.06.078.

[2] K-J Lee, Y. Kim, J-H Lee, S-J Cho, J-H Kwak, H-R Moon; " Facile Synthesis and Characterization of Nanostructured Transition Metal/Ceria Solid Solutions (TMxCe1–xO$_2$–δ, TM = Mn, Ni, Co, or Fe) for CO Oxidation" Chem. Mater., (2017), 29 (7), 2874–2882. DOI: 10.1021/acs.chemmater.6b05098

[3] S. Prokha, S-P Soontorn, P. Chirawatkul, Y. Poo-aporn, S.Maensiri; "Synthesis, characterization, and magnetic properties of monodisperse CeO2 nanospheres prepared by PVP-assisted hydrothermal method"Nanoscale Research Letters, 2012, 7, 425. doi:10.1186/1556-276X-7-425.

[4] H. Lia, G. Wanga, F. Zhanga, Y. Caia, Y. Wang, I. Djerdj, "Surfactant-assisted synthesis of CeO2 nanoparticles and their application in wastewater treatment" RSC Adv., (2012), 2, 12413-12423. doi: 10.1039/C2RA21590J.

[5] K.Kalishwaralal, S.Ramkumarpandian. H.Nellaiah, G.Sangiliyandi, "Extracellular biosynthesis of silver nanoparticles by the culture supernatant of Bacillus licheniformis" Materials Letters, (2008), 62(29) , 4411-4413. doi.org/10.1016/j.matlet.2008.06.051.

[6] R.Miuruganantham, M.Sivakumar, R.Subadevi, "Enhanced rate performance of multiwalled carbon nanotube encrusted olivine type composite cathode material using polyol technique" J.Power Sources, (2015), 300, 496-506. doi.org/10.1016/j.jpowsour.2015.09.103.

[7] D. Das, J. Liorca, M. Dominguez, S. Colussi, A. Trovarelli, A. Gayen; " Methanol steam reforming behavior of copper impregnated over CeO2–ZrO2 derived from a surfactant assisted coprecipitation route" J.Hydrogen Energy (2015), 40, 10463-10479. doi.org/10.1016/j.ijhydene.2015.06.130.

[8] V.Ramasamy, G.Vijayalakshmi; "Synthesis and characterization of ceria quantum dots using effective surfactants" Materials Science in Semiconductor Processing, (2016), 42(3), 334-343. doi.org/10.1016/j.mssp.2015.10.026.

[9] Y. Jiang, X. Zhang, X. Dai, W. Zhang, Q. Sheng, H. Zhuo, Y.Xiao,H. Wang; "Microwave-assisted synthesis of ultrafine Au nanoparticles immobilized on MOF-199 in high loading as efficient catalysts for a three-component coupling reaction" Nano Research, 2017, 10(3), 876–889. dx.doi.org/10.1007/s12274-016-1341-1.

BIOGRAPHIES

M.Ramachandran is working as Assistant Professor of Physics at A.P.S.A.College, Tiruppattur, Sivagangai. He is currently pursing his Ph.D under the supervision of Dr.M.Sivakumar at school of Physics, Alagappa university, Karaikudi. His research interest mainly focused on composite based polymer electrolyte design for Lithium-ion batteries.

M.Shanthi is working as Assistant Professor of Department of Physics at Kamaraj College of Engg. And Tech, Virudhunagar. She is currently doing Ph.D under the supervision of Dr.R.Subadevi at school of Physics, Alagappa university, Karaikudi. Her research interest focused on polymer electrolyte for Lithium-ion batteries.

Subadevi Rengapillai received his Ph.D. in Alagappa University, and currently she is working Assistant professor in Alagappa University, Karaikudi. Her research interests focus on rechargeable Batteries, Super capacitors, Nano materials and Bio-diesel. She has published more than 39 papers in international journals.

Sivakumar Marimuthu received his Ph.D. in Alagappa University, and then Post-Doctoral Fellow in National Taiwan University, Taipei. Currently, he is now an Assistant professor in Alagappa University, Karaikudi. His research interests are in the areas of Batteries (Li-ion, Li-S and Na-ion), Super capacitors, Bio-fuels and Nano materials. He has published more than 41 papers in international journals.