Effect of Surfactant inthe Structural, Morphological and Optical Properties of CeO_2 Nanoparticles

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***Abstract:**CeO_2nanaoparticles were synthesized in the presence of surfactants: CTAB and PEG via low temperature hydrothermal method. The structural, morphological and optical properties of pure and surfactant assisted CeO_2 nanoparticles were compared. XRD analysis confirms the formation cubic phase CeO_2 nanoparticles. The crystal size of CeO_2 nanoparticles found to be decreased in the presence of surfactants. SEM and TEM image shows the formation of well dispersed hexagonal shaped CeO_2 nanoparticles. The bonding nature and the function groups present in the pure and assisted CeO_2 nanoparticles were investigated usin FT-IR analysis.*

***IndexTerms -**CeO_2, Hydrothermal method, Surfactants, HR-TEM, Physical properties.*

I.INTRODUCTION

Cerium oxide (CeO2) is rare-earth oxide material which has wide application in the fields of fuel cells, catalysis, anti-UV radiation and photosensitive material etc. It has pulled in extensive consideration in catalysis because of its capacity to store/discharge oxygen as an oxygen supply by means of the redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reducing conditions. In the recent years, due to the excellent physical and chemical properties of nano-sized particles, which are significantly different from those of bulk particles, there is a considerable interest in enhancing solar cell activity, magnetic, and other properties by decreasing the grain size into a nanometer range [1-4]. Nanocrystalline CeO_2 powders have been considered as an important nanomaterial for applications in catalysts, fuel cells, ultraviolet absorbers, hydrogen storage materials, oxygen sensors, optical devices and polishing materials [5]. Ceria has also received much success in redox and combustion catalysts due to its ability to shift between reduced and oxidized state as a result of change in gas phase oxygen concentration [6]

Several methods were used for synthesizing nanocrystalline cerium oxide such as sol-gel [7], Spray drying system [8], Plasma spray technique [9], Thermal decomposition [10], and Hydrothermal method [11]. Among them, particularly the hydrothermal synthesis technique is a main procedure for the preparation of low-dimensional nanostructures keeping all the advantages of purity, high quality, low-cost and good homogeneity.

In the present work, CeO_2 nanoparticles were synthesized by hydrothermal method using two different surfactants PEG and CTAB. The structural, optical and morphological properties of pure and surfactant assisted CeO_2 nanoparticles were compared.

II.EXPERIMENTAL PROCEDURE

Cerium (III) Chloride, ammonium hydroxide, Polyethylene Glycol (PEG)/CTAB were used in the preparation of CeO_2 nanoparticles. All the chemicals used in the experiment were analytical grade reagent and were used without further purification. Initially 12.324g of $CeCl_3$ dissolved in 100ml of distilled water and allowed to stir in a rapid rate of 550rpm for 2hr at 60^oC using magnetic stirrer. 5ml of PEG is mixed with 50ml of 0.5N NH_3OH solution and added drop wise to the above solution with continuous stirring. The mixture is allowed to stir in room temperature for 24hr. The precipitate was filtered and washed with deionized water for three to five times and then dried in hot air oven at 80^oC for 3hr to get yellow coloured CeO_2 NPs. Similar procedure has been followed with CTAB.

III.CHARACTERIZATION TECHNIQUES

The crystalline phase and particle size of pure and surfactant assisted CeO_2 nanoparticles were analyzed by X-ray diffraction (XRD) measurement, which was carried out at room temperature by using SHIMADZU-XRD 6000 diffractometer system equipped with a Cu tube for generating Cu Kα radiation (k= 1.5406 Å). The incident beam in the 2-theta mode over the range of 10–80^o, operated at 40 kV and 30 mA. The chemical structure was

investigated by SHIMADZU-UV 1800 Fourier transform infrared spectrometer (FTIR) in which the IR spectrum was recorded by diluting the milled powder in KBr and in the wavelength between 4000 and 400 cm^{-1} was used to assess the presence of functional groups in CeO_2. The morphology of the samples was characterized by SEM (Hitachi S-4500 SEM Machine) with EDS and HR-TEM analysis was taken by TECNAI F20.

IV.RESULT AND DISCUSSION:-

A. STRUCTURAL ANALYSIS:-

Figure.1 shows the XRD spectra of the CeO_2 nanoparticles prepared with different surfactants. The diffraction peaks of spectra coincide with JCPDS card no. 34-0394 so that it is clearly indicate the presence of well crystalline and single phase of pure CeO_2 nanoparticles with cubic structure. No other peaks were detected which indicates that all the precursors have been completely decomposed and no other complex products were formed.[12]

The crystallite size has been obtained from 2θ and FWHM of the (h k l) plane using Scherrer's relation.[13]

$$\textbf{Average Crystal size } D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

where D is the average crystallite size in Å, K is the shape factor (0.9), λ is the wavelength of X-ray, θ is the Bragg angle and β is the corrected line broadening of the nanoparticles. By applying Scherrer's formula on the cubic (111) diffraction plane, the crystallite size is found to increase with increase of molarities and the results are given in Table 1

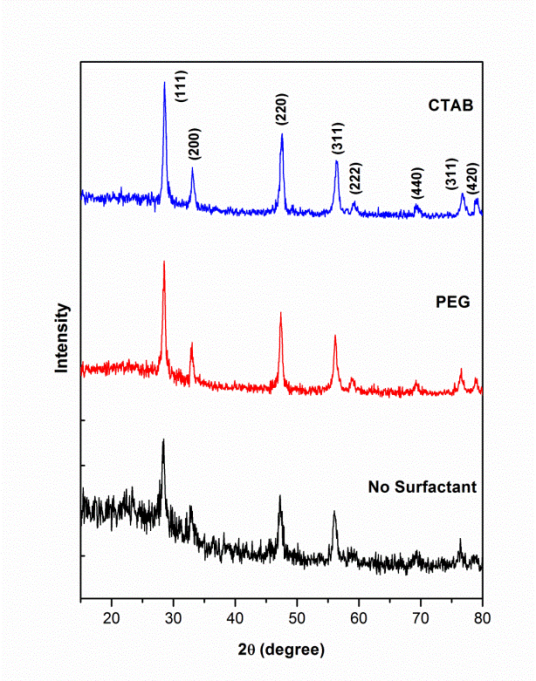

Figure.1 XRD pattern of the pure and surfactant assisted CeO_2 nanoparticles

Table.1 Structural parameters of CeO_2 nanoparticles at different molarity

Molariy (M)	Crystality size (nm)	Microstrain Ɛ ($\times 10^3$)	Dislocation density δ ($\times 10^{-15}$)
Pure	9.43	0.00415	10.7608
PEG	8.87	0.00446	12.7102
CTAB	7.92	0.00493	15.9423

The lattice constants can be evaluated from the following expression,

$$\textbf{Lattice constant, } d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

From the Table 1, the lattice parameters a=b=c are in concordance with the standard CeO_2 single crystals (a=b=c=5.412nm), which indicate that the quality of CeO_2 nanoparticles is good crystalline in nature. The values of lattice constants are higher than the bulk CeO_2, which is

strong indication of stress in the powder. The structural parameters are calculated from the following equations,[14-18]

Micro strain, $\varepsilon = \frac{\beta cos\theta}{4}$

Dislocation density, $\delta = \frac{1}{D^2}$

Stacking fault, $SF = \left[\frac{2\pi^2}{45(3tan\theta)^{\frac{1}{2}}}\right]\beta$

Texture Co-efficient, $TC_{(hkl)} = \frac{I_{(hkl)}/I_{o(hkl)}}{\sum I_{(hkl)}/I_{o(hkl)}} \times 100\%$

The structural parameters including dislocation density (δ), micro strain (ε), stacking fault (SF) and texture co-efficient (TC) of cubic CeO_2 nanoparticles are summarized in Table 1& 2.

Table.2 Structural parameters of CeO_2 nanoparticles at different molarity

Molariy (M)	Stacking fault	Texture coefficient (TC)	Lattice constant Å
Pure	0.00461	1.0109	5.443
PEG	0.00443	1.0092	5.426
CTAB	0.00411	1.0113	5.414

B. FUNCTIONAL GROUP ANALYSIS OF CeO_2

FT-IR spectrum of the synthesized CeO_2 nanoparticles showed (Figure.2) the fundamental mode of vibration at 3408.80 cm^{-1} which correspond to the O-H stretching vibration of H_2O in the sample. The sample showed a peak at 2350.00cm^{-1} which is due to the presence of dissolved or atmospheric CO_2 in the sample. The absorption band at 1626.06 cm^{-1} which is characteristic for O-H bending vibration was observed. The presence of absorption band at around 1402.25cm^{-1} can be assigned to C-O stretching vibration of acetate groups completed with CeO_2. Thus the formation of CeO_2 Cubic(fcc) structure has been further corroborated by FT-IR spectra.[19]

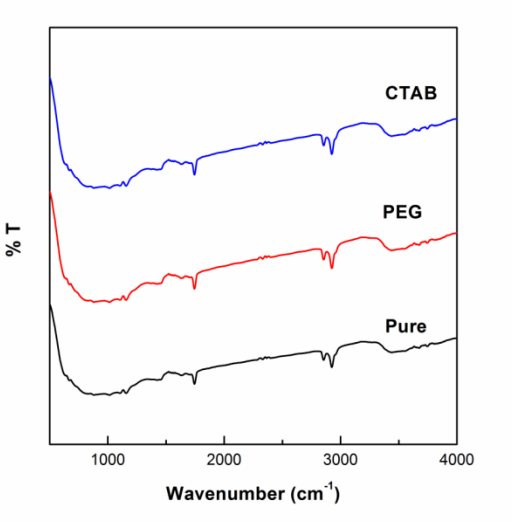

Figure.2.FT-IR spectra of pure and surfactant assisted CeO_2 nanoparticles

C. SURFACE MORPHOLOGY AND COMPOSITIONAL ANALYSIS

Figure.3 (a-c) shows the SEM images of pure, PEG and CTAB assisted CeO_2 nanoparticles respectively. In the case of pure CeO_2 nanoparticles the image shows the particles are agglomerated together as clusters. This agglomeration is may be due to Vanderwaal's force. For PEG assisted CeO_2 nanoparticles the image shows less agglomeration as compared to pure CeO_2 nanoparticles. In CTAB assisted CeO_2 nanoparticles, the particles were uniformly distributed and shows regular morphology with well crystallized cubic structure. The addition of the surfactant reduces the surface tension of the precursor and prevents the coalescence of the particles.[20]

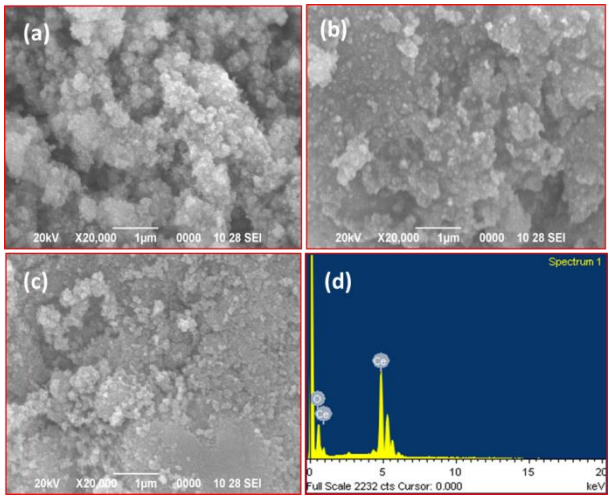

Figure 3. SEM image of a) Pure, b) PEG assisted, c) CTAB assisted CeO_2 nanoparticles and d) EDAX spectra

Figure.3 (d) shows EDAX spectra of pure, PEG and CTAB assisted CeO_2 nanoparticles. From the spectrum it is observed that the nanoparticles were only composed of cerium and oxygen in appropriate proportion. No other impurities were found.

D. HR-TEM ANALYSIS

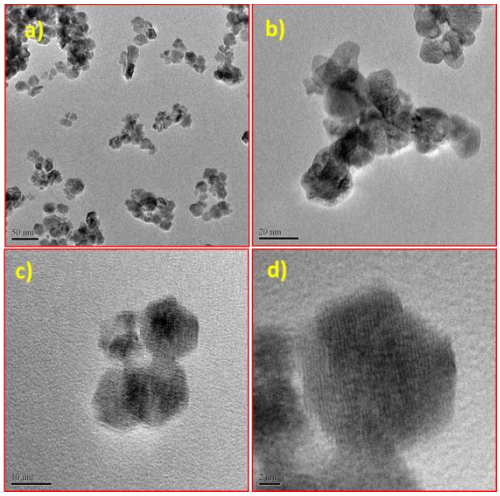

Figure 4 TEM image of CTAB assisted CeO_2 nanoparticles

Figure.4 shows the HR-TEM images of CTAB assisted CeO_2 nanoparticles. From the image it is clear that the particles have cubic morphology. The SAED patterns of Cerium oxide is shown in Fig.5f. The SAED pattern of CeO_2 phase exhibits a well defined electron diffraction spots, confirming the poly crystalline nature. The diffraction rings are indexed to (111), (200) , (220) and (311) planes, which confirms the presence of cubic CeO_2 phase. The obtained HR-TEM results are well matched with the XRD observations.[21]

V. CONCLUSION:

We have reported a hydrothermal method for the synthesis of CeO_2 nanoparticles using two different surfactants. The structural, optical and morphological properties of pure and surfactant (PEG and CTAB) assisted CeO_2 nanoparticles were compared. The role of surfactants on the characteristics of CeO_2 has been discussed. The XRD analysis reveals the formation of high purity cubic phase CeO_2 nanocrystals. The particle size of the nanoparticles found to decrease with the introduction of surfactants. Surfactant assisted CeO_2 nanoparticles show well dispersed morphology as compared to that of the pure nanoparticles. From the results it is clear that the CeO_2 nanoparticles grown with CTAB assistance shows remarkable properties as compared with pure and PEG assisted CeO_2 nanoparticles.

REFERENCES

[1] M. Mousavi-Kamazani, M. Salavati-Niasari, H. Emadi, Micro Nano Lett. 7 (2012)896.
[2] M. Mousavi-Kamazani, M. Salavati-Niasari, H. Emadi, Mater. Res. Bull. 47 (2012)3983.
[3] M. Mousavi-Kamazani, M. Salavati-Niasari, Compos. Part B: Eng. 56 (2014) 490.
[4] N. Mir, M. Salavati-Niasari, Sol. Energy 86 (2012) 3397
[5] D.G. Shchukin, R.A. Caruso, Chem. Mater. 16 (2004) 2287.
[6] A. Trovarelli, Catal. Rev. Sci. Eng. 38 (1996) 439
[7] M. Alifanti, B. Baps, N. Blangenois, Chem. Mater. 15 (2003) 395
[8] V. Sharma, K.M. Eberhardt, R. Sharma, J.B. Adams, P.A. Crozier, Chem. Phys. Lett. 495 (2010) 280–286.
[9] V. Singh, A. Karakoti, A. Kumar, A. Saha, S. Basu, S. J. Am. Ceram. Soc. 93 (2010) 3700–3708
[10]. M. Kamruddin, P.K. Ajikumar, R. Nithya, A.K. Tyagi and B. Raj, Acta Materialia, 50 (2004) 417-422.
[11]. A.I.Y. Tok, F.Y.C. Boey, Z. Dong and X.L. Sun, J. Mater. Processing Tech. 190 (2007) 217-222.
[12] J. Jasmine Ketzial and A. Samson Nesaraj, Journal of Ceramic Processing Research. Vol. 12, No. 1, pp. 74~79 (2011).
[13] M. Jothibas C. Manoharan, S. Johnson Jeyakumar, P. Praveen,J Mater Sci: Mater Electron,1-7 (2015)
[14]. Y. Zhang, T. Cheng, O. Hu, Z. Fang and K. Han, J. Mater. Res. 22 (2007) 1472-1478.
[15] C. Manoharan, M. Jothibas, S. Johnson Jeyakumar, S. Dhanapandian, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 47–53.
[16] C. Chen, P. Liu, C. Lu, Chemical Engineering Journal 144 (2008) 509-513.
[17] J.I. Pankove, Prentice-Hall Inc, Englewood Cliffs, NJ, 1971.
[18] Punithavathy, I.K., Richard, J.P., Jeyakumar, S.J. et al. J Mater Sci: Mater Electron (2016). doi:10.1007/s10854-016-5823-4
[19] Sher Bahadar Khan, M. Faisal, Mohammed M. Rahman, Aslam Jamal, Science of the Total Environment 409 (2011) 2987–2992
[20] Kang-Qiang Liu, Cheng-XiuKuang, Ming-QiangZhong, Yan-Qin Shi, Feng Chen, Optical Materials 35 (2013) 2710–2715
[21] P.J. Hay, R.L. Martin, J. Uddin, G.E. Scuseria, Journal of Chemical Physics 25 (2006) article no. 034712.