PEG-Assisted Synthesis and Characterization of Ceria Nanoparticles

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By:

Sitakanta Satapathy

Under the Guidance of

Dr. Aparna Mondal

DEPARTMENT OF CHEMISTRY

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

ORISSA-769008

CERTIFICATE

Dr. Aparna Mondal
Department Of Chemistry,
National Institute Of Technology, Rourkela

This is to certify that the dissertation entitled "***PEG-Assisted Synthesis and Characterization of Ceria Nanoparticles***" being submitted by **Sitakanta Satapathy** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela**.** **Dr. Aparna Mondal**
Date: *(Supervisor)*

DECLARATION

I Mr. Sitakanta Satapathy, National Institute of Technology, Rourkela declare that all my research works are original and no part of this thesis has been submitted for any other degree or diploma. All the given information and works done are true to my sense and knowledge.

Sitakanta Satapathy

Date:

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Department of Chemistry

NIT, Rourkela

TABLE OF CONTENTS

CONTENTS	PAGE
CERTIFICATE……..	2
DECLARATION……	3
ACKNOWLEDGEMENT…….	4
TABLE OF CONTENTS……	5
ABSTRACT ……	6
CHAPTER 1 INTRODUCTION	
1.1. Introduction……...	7
1.2. Advantage of PEG……	7
CHAPTER 2 LITERARY REVIEW	
2.1 Literature Review……	8
2.2 Objective…….	8
CHAPTER 4 EXPERIMENTAL	
3.1. Experimental procedure……	9
3.1 (a) Synthesis of ceria nanopowder	
3.1.(b) Procedure for Cr-adsorption study	9
3.2 Characterization and Measurements	
3.2.(a). X-ray Diffraction Studies……...	10
3.2.(b). FT-IR Spectra……..	11
3.2.(c). UV-Visible Spectra…….	11
3.2.(d).SEM……	11
CHAPTER-4 : RESULTS AND DISCUSSION, APPLICATION	12-19
CHAPTER-5: SUMMARY AND CONCLUSION , FUTURE WORK	20
REFERENCES……	21

ABSTRACT

Ceria nanopowders were prepared by varying surfactant (2.5%, 5% and 10% PEG) and solution concentrations (0.25M, 0.5M and 1M).The preparation of nanopowders were carried out using inorganic salts of cerium ammonium nitrate. Cerium ammonium nitrate was used as precursor. Poly ethylene glycol was used as surfactant. The characterization of samples were done by X-ray diffraction studies, UV, IR and SEM images. XRD data showed that the both the as-prepared and calcined samples have cubic fluorite structure through out and the sharp peaks indicated the higher crystallite size (~ 12 nm). FT-IR results showed that the nanopowders heated at 500^{o}C were almost free from surfactant. UV-Visible spectra showed that the ceria nanopowders prepared by varying PEG concentration exhibited a red shift in the absorption edge with increasing the surfactant concentration. From Cr-adsorption studies it was found that better results were obtained for the sample heated at 500^{0}c around pH 6 (normal).

CHAPTER-1

1.1 INTRODUCTION

Ceria (CeO_2); also known as Ceric oxide, Cerium oxide or Cerium dioxide is a rare earth oxide of Cerium that is of significant interest in the field of material science due it's unique properties and wide applications. It has fluorite structure and can be used as an additive to glass (2-4%) to protect light sensitive materials, in coating application for protecting corrosion of metals, as a catalyst in oxidation and also in electrochromic devices as a counter electrode.[1]

Besides it is currently also used in solid oxide fuel cell as an oxygen ion conductor, electrolyzers, oxygen pumps and amperometric oxygen monitors which confirms it's high oxygen ion conductivity.[2] It is also potentially applied to silicon-on-insulator structure, stable capacitor devices for large scale integration and stable buffer layers between temperatue superconducting and silicon substrate.[3]

The wide range of application of ceria ranges from heterogenous catalysis such as TWC's for automobile exhausting gas emission control, removal of SOx- NOx from fluid catalytic cracking fuel gases to catalysts used for various oxidation and hydrogenation reactions.[4,5] It is one of the most promising electrolyte materials for SOFC.[6]

1.2 ADVANTAGE OF ASSISTING PEG

Here we have carried out experiments by using PEG (poly ethylene glycol) as Surfactant. PEG is one of the widely used neutral surfactant. As other surfactants it also acts as a surface active reagent, i.e, it generally covers the surfaces of small particles of colloidal dimensions in suspension and thus stabilizing them. This property makes PEG to act as a very well known dispersion stabilizer. Being a surfactant it also helps to control the morphology and pore size of the nanoparicle. Use of PEG also gives some biological stealth to the metal oxide. The use of PEG oligomers also functionalizes the rare earth oxide CeO_2 nanoparticles.[7]

CHAPTER-2

2.1 LITERATURE REVIEW

An excellent hydrothermal has been done using cerium(III) nitrate hexahydrate and hexamethylene tetramine as starting materials. It was found that the crystallite sizes of the nanopowders ranged from 12-16 nm. with high surface area.[8]

Also another hydrothermal synthesis has been carried out using Cerium(III) nitrate hexahydrate only as the starting material in which CeO_2 crystals having uniform dimension of 40-60 nm. has been obtained [9]

A facile hybrid organic/inorganic route in which using $CeCl_3$ as starting material and $7H_2O$.CTAB as a surfactant was carried out. The surface area of the resulting nanoparticles was found in excess of $200m^2/g$. This increased surface area was found on heating the nanopowder at 723 K.[10]

A self-rising approach has been made to synthesize CeO_2 nanopowder using $Sm(NO_3)_3.6H_2O$ and $Ce(NO_3)_3.6H_2O$ in which the BET surface area was found to be $54.4m^2/g$.[11]

An electrospinning technique has been carried out using $Ce(NO_3)_3.6H_2O$ and $Y(NO_3)_3.6H_2O$ as starting material in which BET surface area of 1.4-12.7 m^2/g nanopowders were obtained.[12]

Successful synthesis of Ceria nanoparticles has been achieved by a simple and fast microwave hydrothermal method at 130^0c for 20 min. The as prepared samples were calcined at 500^0c for 1, 2 and 4 hours. It was found that synthesized ceria powders exhibited a spherical shape with particle size below 10nm., a narrow distribution exhibited weak agglomeration. The microwave hydrothermal method enabled cerium compounds to be synthesized at lower temperature and shorter time. [13]

2.2 OBJECTIVE

- Synthesis of CeO_2 nanomaterials using inorganic precursors and poly ethylene glycol (PEG) as a surfactant.
- To study the role of PEG on crystal structure of ceria.
- Effect of calcination temperatures on phase transformation of ceria.
- Structural characterization using TG, XRD, UV, IR, SEM and BET analysis.

CHAPTER-3

3.1 EXPERIMENTAL PROCEDURE

3.1 (a) Synthesis of Ceria nanopowders

Chemicals used: Cerric ammonium nitrate, Poly ethylene glycol(PEG), Ethanol, Sodium hydroxide, acetone…

The original solution was first prepared by dissolving Cerium ammonium nitrate in water. The solution was then stirred for sometime and the surfactant was then added dropwise to the solution at regular interval of time nearly for about one hour. The whole solution was then stirred for nearly about 3-4 hours for homogeneous mixing.After that the base (NaOH solution) was added to the original solution dropwise slowly untill the required pH of the solution was maintained to get the precipitate. The solution was then kept for ageing and after that it was filtered,washed several times with water and ethanol followed by drying with acetone and was then kept on water bath overnight.Finally the precipitate was collected, powdered properly and the sampling was done.In this way several precursors were prepared by varying the surfactant (PEG) concentration, Ce^{3+}/Ce^{4+} solution concentration.The samples were also calcined at different temperatures to study the effect on crystalline size and phase transformation.

3.1(b) Experimental procedure for chromium adsorption

Chemicals used: potassium dichromate solution, 500^0c calcined nanopowder (Ce2.5%PEG.500^0c, 0.1 g), dilute nitric acid (HNO_3, as acid) and dilute sodium hydroxide (NaOH, as base)

The original potassium dichromate solution was first prepared. 10 ml of this solution were taken in four different beakers. After that about 0.1 mg of the calcined sample was measured and introduced into the beakers. The normal pH (without disturbance) of the solution was found to be 6.3 while the pH of other solutions were adjusted to about 3, 5 and 9 by adding the required amount of acid and base. The solutions were kept for stirring for 4 hours. After that nearly about 5-6 ml of the solutions were withdrawn, centrifuged and finally carried out for UV-Visible absorption spectra to determine the extent of adsorption.

3.2 Characterization and Measurements

Synthesis of PEG doped CeO2 nanopowder was analyzed using X-ray diffraction, IR spectra, and SEM analysis and UV absorption spectra.

3.2(a) X-Ray Diffraction studies

X-Ray Diffraction is used to perform phase analysis. The sample for this measurement was prepared by using a glass slide with a groove as the sample holder. The powder was placed in a groove and was compressed with the help of another glass slide. The excess powder was removed. A very small amount of alcohol was used to paste it properly. The sample at the flat surface of the slide was used to measure it's characteristics X-ray Diffraction pattern by using X-ray diffraction on pattern by using X-ray diffractometer with the following set-up.

Target - CuKα of wavelength λ= 0.1540 nm.

Range of diffraction angle - 2θ (20-80)

Scanning Speed – 0.080/s

For a crystalline solid, the structure may be specific in terms of crystal unit cell and translation symmetry, the lattice leading to sharp bragg peaks which are characteristics of diffraction pattern of the crystalline solids, the structure of the amorphous solid, on the other hand, is characterized by a lack of symmetry, periodicity and long range order, resulting in a diffraction pattern. By using the XRD plots and Bragg's law the peaks were identified. Average crystallite size in the sample has been calculated from peak widths in characteristic diffraction peaks using Debye-Scherrer's formula.

$D = k \lambda / \beta \cos \theta$

Where λ is the wavelength of X-ray radiation.

K is a constant taken as 0.89.

θ is the diffraction angle and β is the full width at half maximum (fwhm).

3.2(b) FT-IR Spectra

The IR-Spectra was measured in the range of 400-4000 cm^{-1} for sample dispersed in KBr pellets (in 1:4 ratio) with IR-Spectrophotometer.

3.2(c) UV-Visible spectra

UV-Visible absorption studies were carried out in the range of 200-800 nm. to study the optical properties of the ceria nanopowders and to determine the extent of chromium (Cr) adsorption.

3.2(d) SEM

SEM measurements were carried out to investigate the detailed morphology, surface roughness, topography and structure of powders.

CHAPTER-4

4.1 RESULTS AND DISCUSSION

Figure 4.1(a) shows the X-ray diffractograms of the as prepared Ce5%PEG and the same sample calcined at different temperatures. The diffraction peaks corresponds to (111),(200),(220) and (311) planes which corresponds to non other than single phase cubic fluorite structure of CeO_2.The intensities and positions of the peaks are in perfect agreement with the literature values It is observed that with increase in calcination temperature the peaks become sharper. This indicates an increase in crystallite size with heating at higher temperatures. The crystallite size of the as-prepared sample was found to be 10.2 nm. and the same sample heated at 500^0c, 650^0c and 800^0c were found to be 12.0 nm, 15.7 nm and 26.19 nm respectively.

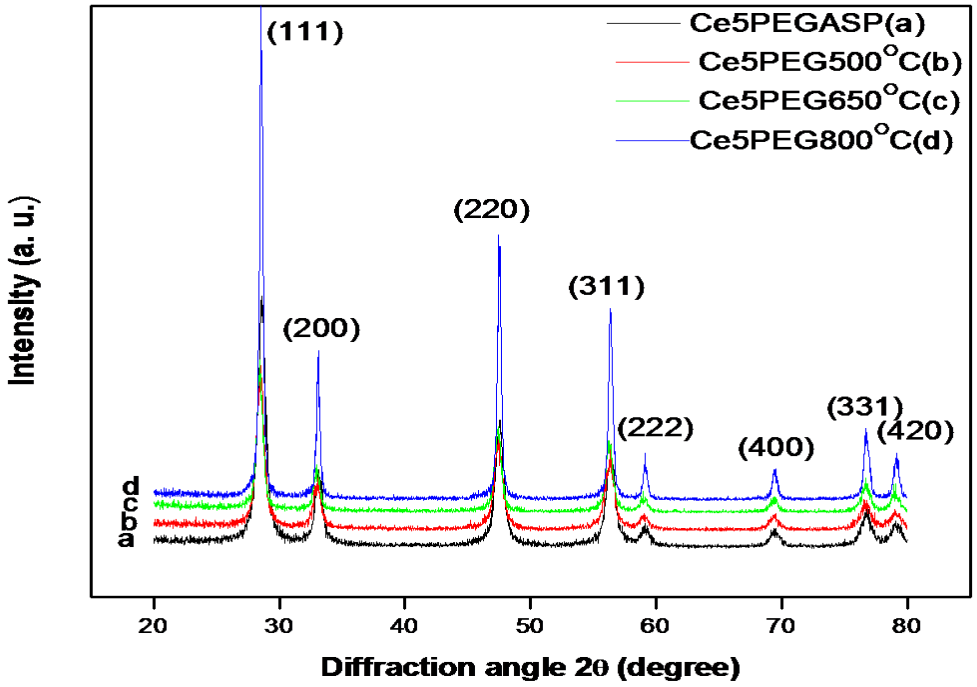
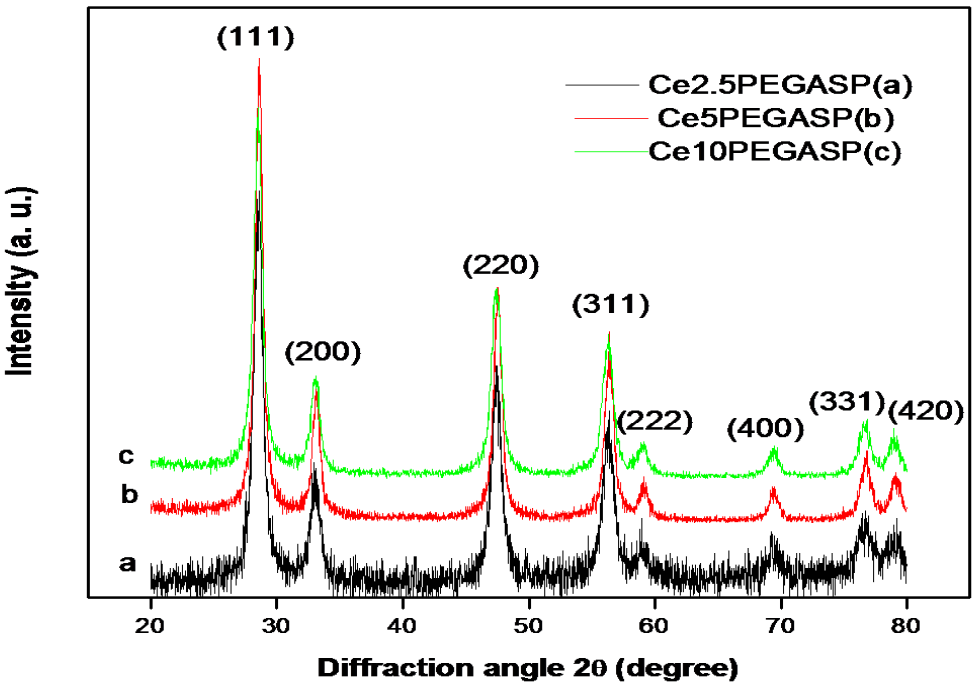


Fig 4.1(a): X-ray diffractograms of 5%PEG CeO_2 nanopowders heated at different temperatures; Ce5PEG.Asp, Ce5PEG.500^0 c, Ce5PEG.650^0c and Ce5PEG.800^0c.

Figure 4.1(b) shows the effect of varying surfactant (PEG) concentration on crystallite size. As the concentration of the surfactant is increased it is observed that the peaks becomes sharper to an extent. This suggests that with increase in PEG concentration upto 5wt% the crystallite size increases resulting in the sharpening of the peaks but further increase in PEG concentration results in a slight broadening of the peaks corresponding to a decrease in size. Hence it can be concluded that concentration of surfactant (PEG) also controls the crystallite size.The crystallite sizes were found to be 10.04 nm,11.89 nm and 10.54 nm for Ce2.5%PEG.Asp, Ce5%PEG.Asp and Ce10%PEG.Asp.Here also the diffraction peaks corresponds to (111),(200),(220) and (311) planes which corresponds to non other than single cubic flourite sttructure of CeO_2.



Diffraction angle (2ɵ,degree)

Fig 4.1(b): X-ray diffractograms of as prepared CeO_2 nanopowders with various surfactant concentrations; Ce2.5PEG.Asp, Ce5PEG.Asp andCe10PEG.Asp.

Figure 4.1(c) shows the effect of varying the original Ce^{3+}/Ce^{4+} solution concentration on crystallite size. As the concentration of the solution is increased it is observed that the peaks becomes sharper This suggests that with increase in solution concentration the crystallite size increases resulting in the sharpening of the peaks. The crystallite sizes were found to be 8.13 nm,10.00 nm and 10.67 nm for 0.25MCe10%PEG.Asp, 0.5MCe10%PEG.Asp and 1MCe10%PEG.Asp respectively. Here also the diffraction peaks corresponds to (111),(200),(220) and (311) planes which corresponds to non other than single cubic flourite sttructure of CeO_2. Average dimension of the crystals also depends on the concentration of the precipitating agent (NaOH, in this case) solution.Thus the crystal growth is not only confined to the $Ce^{3+/}Ce^{4+}$ soution concentration.

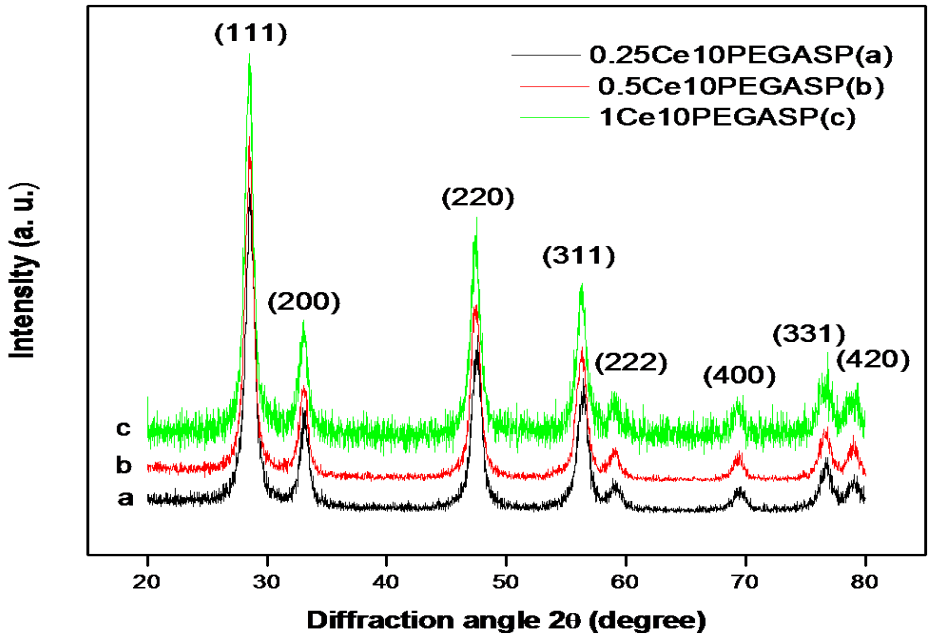


Fig 4.1(c): X-ray diffractograms of as prepared CeO_2 nanopowders with various Ce^{3+}/ Ce^{4+}concentrations; 0.25MCe10%PEG, 0.5MCe10%PEG and1MCe10%PEG

Figure 4.1(d) shows the FT-IR spectra of the as prepared Ce2.5PEG sample and the same heated at 500°C. Peaks at 589 cm-1 in the as prepared sample and 558 cm-1 in the calcined sample arises due to Ce-O vibrations of the metal oxide. Peak at 1319 cm-1 arise due to Ce-OH deformation in the as prepared sample. The peaks at 1594 cm-1 correspond to NH stretching. The peaks at 1053 cm-1 in both the as prepared and calcined samples are due to the C-O stretching of the glycol (PEG), which is very less intense in the heated sample. So we may conclude that the powder heated at 500°C is almost free from the surfactant. The less intense peak at 3566 cm-1 correspond to OH stretching. It can be clearly marked from the figure that the intensities of the peaks for the calcined sample decreases as compaired to the as prepared samples. These results demonstrates that the calcined sample has adsorbed H_2O molecules on it's surface.

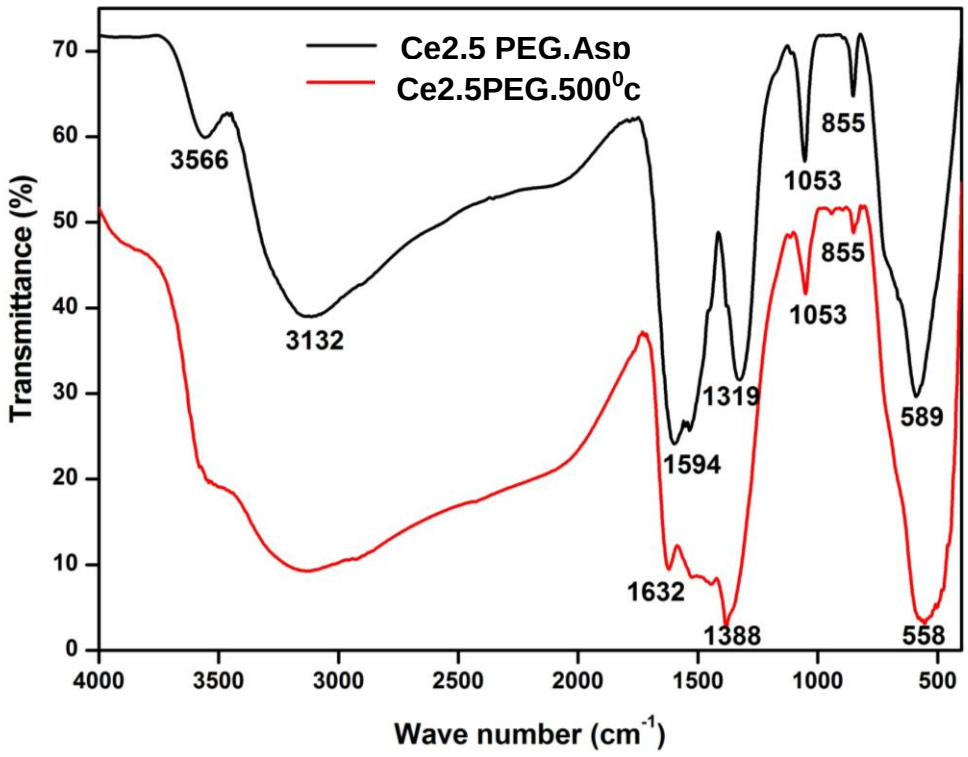


Fig. 4.1(d) FT-IR spectra of the as-prepared Ce2.5PEG.asp and the same sample calcined at 500^0C.

Fig 4.1(e) shows the UV-Visible absorption spectra for the as prepared ceria nanopowders of varying surfactant(PEG) concentration. It has been found that the original Ce^{3+}/Ce^{4+} solution with 2.5 wt%, 5 wt% and 10 wt% PEG concentration exhibited strong absorption peaks around 271 nm, 279 nm and 283 nm respectively. This corresponds to an approximate red shift in the absorption edge with increase in surfactant (PEG) concentration. This type of behavior may be attributed to a number of oxygen vacancies in CeO_2.Other factors like particle size and the presence of a small amount of Ce^{3+} ions on the surface may also be responsible for the red shift. Also it was found that the absorption edge extends upto 500 nm in wavelength and no further absorption was further detected. This property Ceria signifies it to act as a well known UV-blocking material in different applications. The strong absorption of ceria in the UV-range (200 - 400 nm) is due charge transfer transition from 2p-orbital of O^{2-} to the 4f-orbital of Ce^{4+} in CeO_2.

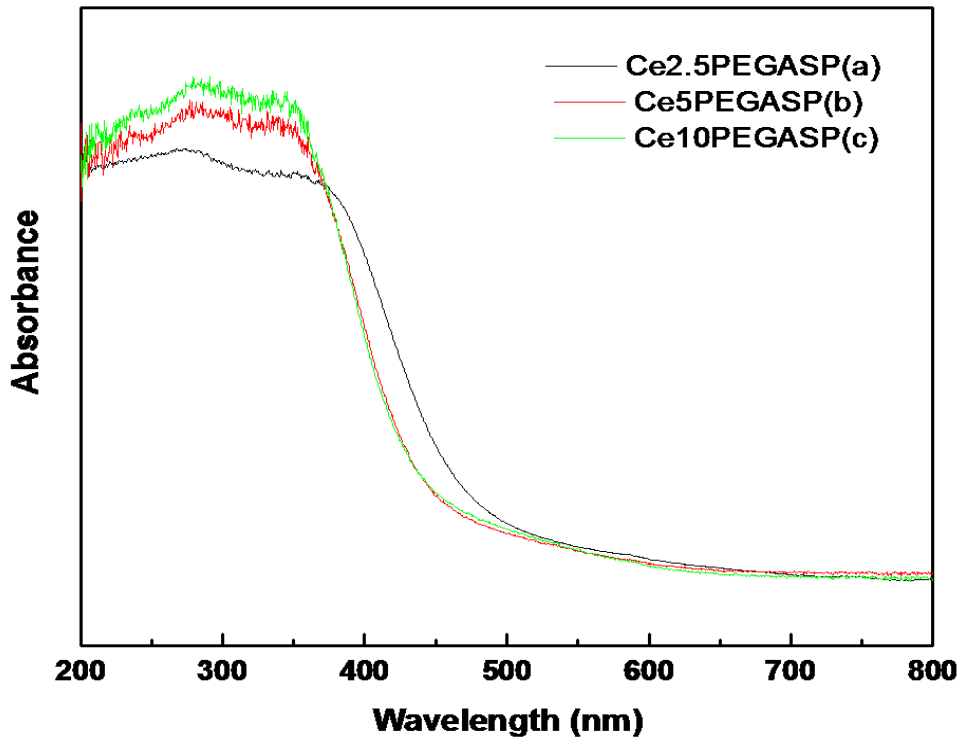


Fig 4.1(e) UV-visible absorption spectra of ceria samples with different PEG concentrations: Ce2.5%PEG, Ce5%PEG and Ce10%PEG

Fig 4.1(f) shows the UV-Visible absorption spectra for the as prepared Ceria nanopowders with 5 wt% PEG and the same sample calcined at different temperatures. A clear blue shift in the absorption spectra can be marked here with increasing the calcination temperature. The absorption peaks for both the 500^0c calcined sample and the as prepared sample were found at 278 nm. and 283 nm. respectively. The interesting phenomena which occurred here is that both the samples calcined at 650^0c and 800^0c exhibited absorption peaks at 274 nm. This type of spectral profile is due to the overlapping of charge transfer transition of Ce^{4+} with the $4f^1$-$5d^1$ transition of Ce^{3+}.This concludes the presence of some Ce^{3+} ions on the surface along with Ce^{4+} ions.

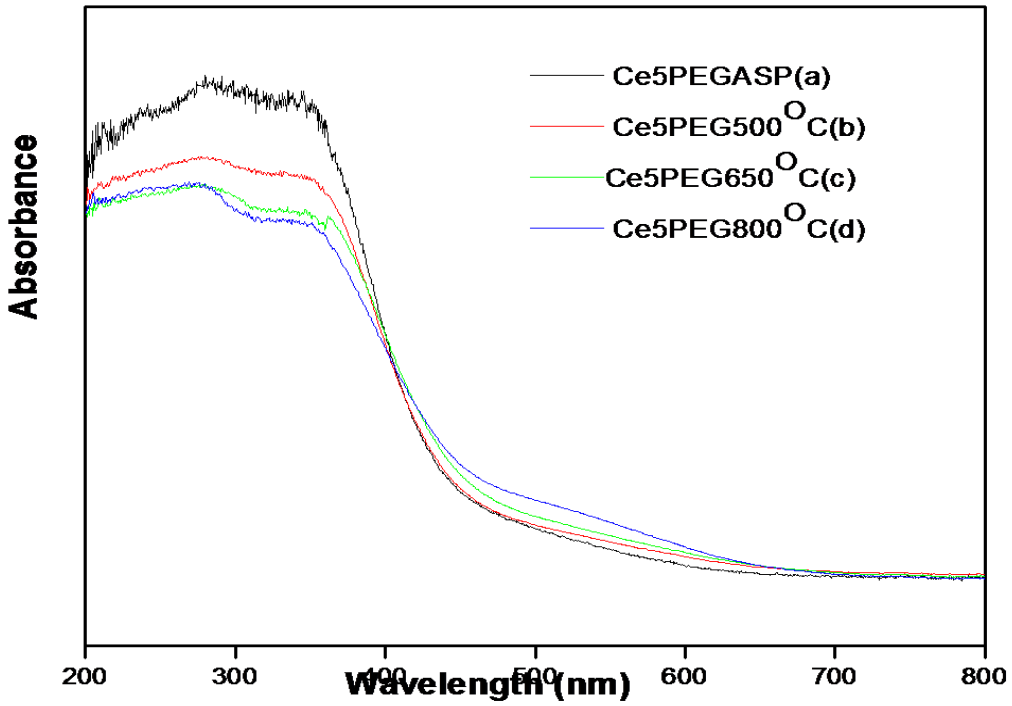


Fig 4.1(f) UV-visible absorption spectra of ceria samples heated at different temperatures: Ce5%PEG.Asp, Ce5%PEG.500^0c, Ce5%PEG.650^0c and Ce5%PEG.800^0c

The morphology of the particles were analysed by scanning electron microscopy (SEM) for the samples with varying surfactant (PEG) concentration. From the SEM images in Fig. 4.1 (g), 4.1 (h) and 4.1 (i) it can be seen that at lower PEG concentration(2.5 wt% PEG) the particles were uniformly dispersed and composed of many isolated discrete small size particles. The prepared material is not agglomerated. But agglomeration occurs on increasing the concentration of the surfactant (PEG) which can be marked from the SEM image of Ce10%PEG.Asp. The particles are not visible clearly, making it very difficult to distinguish. Not much information can be obtained from these images. It requires further investigation by transmission electron microscopy.

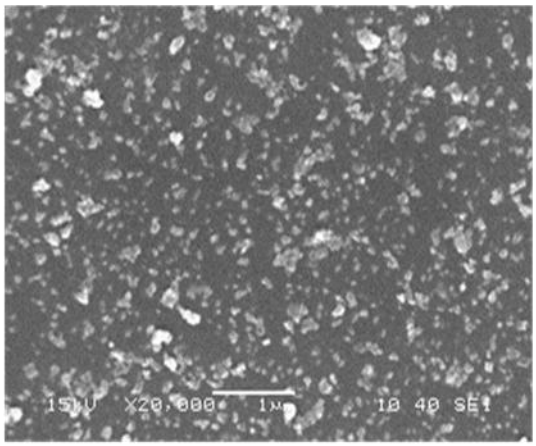


Fig 4.1 (g) Ce2.5PEGASP

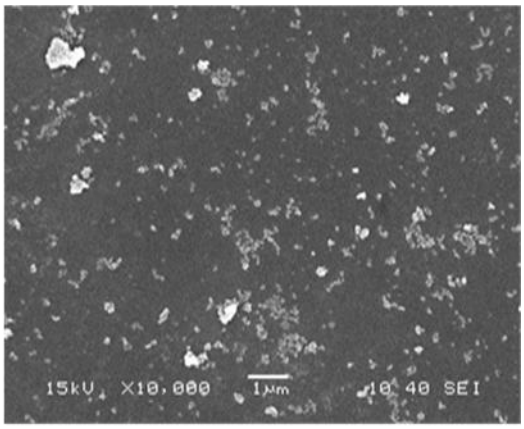


Fig 4.1 (h) Ce5PEGASP

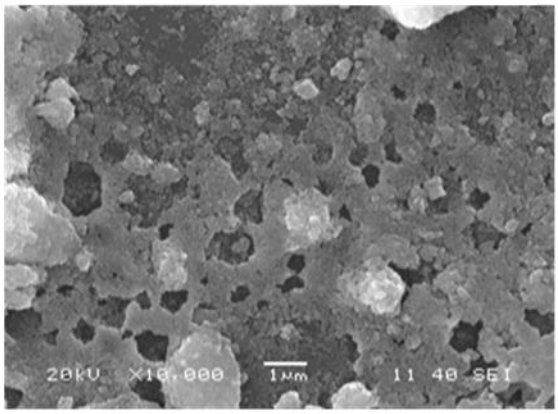


Fig 4.1 (i) Ce10PEGASP

Fig 4.1 shows the SEM images of (g) Ce2.5%PEG.Asp, (h) Ce2.5%PEG.5%PEG.Asp and (i) Ce 10% PEG. Asp

4.2 APPLICATION

The application part of the experiment was carried out by performing chromium adsorption studies. Initially the adsorption experiments were performed using the as prepared samples. But none of the samples were found to give good results. Finally the adsorption experiment was performed by using the calcined sample (Ce 2.5% PEG.500^{0}c) in which about 97% of adsorption was found after constantly stirring the solution for 4 hours at normal pH (pH-6), as indicated from Fig 4.2 (a).

Fig 4.2 (a) shows the results for Cr-adsorption studies.

.Fig 4.2 (a) shows the variation of percentage adsorption with pH of the solution. It can be clearly seen that the percentage of adsorption increases slowly with increasing pH from 3 to 5. After that there is a steep increase in the adsorption curve found with increasing the pH upto 6. Finally the percentage of adsorption decreases on further increasing the pH.

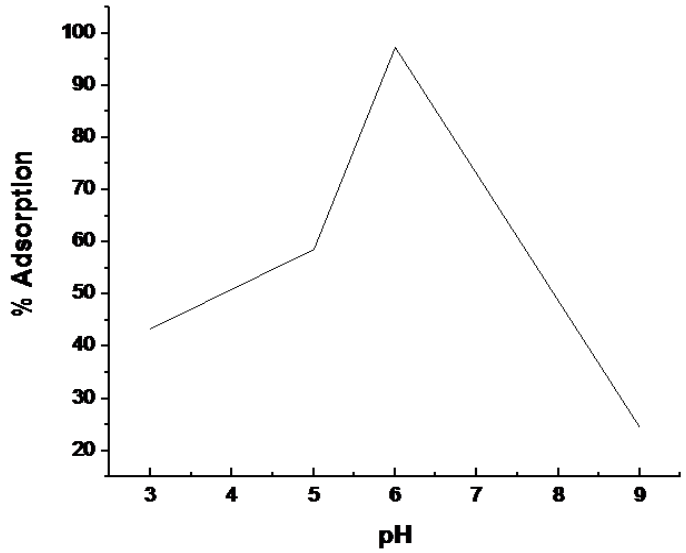


Fig 4.2 (a) Variation of adsorption (%) with pH

CHAPTER-5

5.1 SUMMARY AND CONCLUSIONS

- CeO_2 nanopowders were synthesized using inorganic salts of cerium and PEG as surfactant.
- FTIR results shows that CeO^2 nanopowders heated at 500^0c are almost free from the surfactant.
- The crystal structures of all the samples were fluorite type ceria based solid solutions.
- It is predicted that the scale up of this method used may lead to large quantities of nanosized ceria particles with wide applications.
- From the adsorption experiments we may conclude that there may be some problem that lies in the surfactant because of which initially good results were not obtained with the as prepared sample while the same sample when calcined was found to give better results.
- Also better absorption results were found at normal pH, i.e pH-6.3 while poor results were obtained in properly acidic or basic conditions.
- Thus we may conclude that the calcined sample can act as a pretty good adsorbent.

5.2 FUTURE WORK

- BET surface area of the respective samples.
- Kinetic studies involving adsorption application of the same calcined sample whose Cr-adsorption studies were performed by varying pH.
- Cr-Adsorption studies of ceria nanopowders prepared without assisting surfactant.
- Other application studies like coating, dye degradation etc.
- TG-DSC analysis of the respective samples.
- Analysis of TEM of the respective samples.

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