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ROLE OF PRECIPITATION AGENT ON FACILE SYNTHESIS OF CERIA NANO PARTICLES-POLY VINYL PYROLODIVINE ASSISTED CO-PRECIPITATION METHOD

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Abstract — *We report a facile synthesis of Poly vinyl pyrrolidene (PVP) assisted Ceria (CeO_2) nano particles by modified Co-precipitation method. The particles were nucleated by mixing aqueous solution of Ce $(NO_3)_3.6H_2O$, strong base sodium hydroxide (NaOH) and weak base ammonia (NH_3) as precipitation agent at room temperature separately. The organic molecule such as Poly vinyl pyrolodivine (PVP) was chosen as surfactant and injected into the reaction medium at the beginning of the synthesis. The thermal history of the precursor was examined using Thermo gravimetric analysis. The effect of precipitation agent is found in the synthesis of CeO_2 nano particles in the way of structure, morphology, photo luminescence studies. Consequently, Sodium hydroxide is the most effective precipitation agent on synthesis of CeO_2 and mechanism of formation CeO_2 nano particles were discussed.*

Keywords- *Ceria, ammonia, sodium hydroxide, Poly vinyl pyrolodivine*

I. INTRODUCTION

Rare-earth metals oxides receive great attention in material science, because of the existence of 4f electrons consequences in attractive optical, magnetic, chemical, gas sensing and catalytic properties. Currently Ceria (CeO_2), is a material of great improvement due to its wide range of uses, e.g., as supporting materials for three-way catalysis [1,2] oxygen sensors, solid electrolytes in solid oxide fuel cells that utilize the oxygen storage capacity [3,4]. Moreover, it is a wide band gap semiconductor with a band gap of 3.2 eV. Most of the advanced application generally depends on the nanoscale regime, in which many physical properties strongly depend on the size and show the significant quantum size effect. Generally, a series nano structure could be achieved by controlling nucleation growth, and aggregation of materials concerned. Until now there are numerous methods of synthesizing CeO_2 have been employed such as synthesis co-precipitation method[5], Sonochemical method[6], electrode deposition[7], mechano chemical processing[8], thermal decomposition[9], spray pyrolysis[10], thermal hydrolysis[11], solvo[12], and hydrothermal synthesis [13]and sol-gel methods[14].

Some conventional decomposition reagents have been used to obtain the homogeneous precipitation of the oxide nano particles such as strong base NaOH and weak base NH_3, the homogeneous precipitation is a kinetically controlled method of synthesis, where the precipitation agent is generated in the cation solution as a result of the hydrolysis of a reagent or the combination between two reagents. This process gives rise to uniform and homogenous distribution of precipitation throughout the reaction medium. This method has also been applied for the synthesis of Ceria.

However, it was difficult to obtain the monodisperse or low degree of agglomeration or require very stringent control in various processing parameters, together with low production yield, or they are not easy to obtain the high surface area powder. Therefore, the simple or low cost routes to synthesize CeO_2 nano particles with mono disperse or low degree of agglomeration are still the key issues. This paper describes the interconnectivity and agglomeration of CeO_2 particles which were drastically reduced by the inclusion of Poly vinyl pyrolodivine (PVP).

In the present work, we report a novel and very versatile synthesis of surfactant assisted (PVP) CeO_2 nano crystals by chemical precipitation at room temperature in aqueous solution containing various precipitation agents like strong base NaOH and weak base NH_3. The aim of this work was to investigate the role of precipitation agent on the size and morphology on the product obtained using the co-precipitation method under the same experimental condition. Several characteristics methods such as Thermo gravimetric analysis (TG), X-ray diffraction (XRD) analysis, Scanning electron microscopy (SEM), Fourier transform infrared analysis, Raman scattering, Photo luminescence studies were employed to correlate the structural, morphology properties of the obtained CeO_2 nanopowders with the type of precipitation agent employed in the co-precipitation synthesis performed under identical conditions.

II. MATERIALS AND METHODS

Ceria (CeO_2) was prepared by a surfactant assisted co-precipitation method. The method involves slow addition of an aqueous solution containing stoichiometric amount of Ce $(NO_3)_3.6H_2O$ (Merck, GR 99%) to an aqueous solution of the surfactant PVP (Merck, Mol.wt.40,000) under stirring condition. The resulting aqueous mixture was stirred further for 10 min at room temperature and then aqueous ammonia and aqueous NaOH was added drop wise under vigorous stirring until pH> 9. This resulted in the appearance of a yellow-precipitate which was further stirred for about 90m when it was transformed into light yellow slurry. The precipitate was centrifuged at 200 rpm and washed with deionized water and acetone several times to ensure the complete elimination of surfactant. Finally, precipitate was dried in oven at 110°C for 4h and consequently calcined in air at 600°C for 2h to get the CeO_2 material.

III. RESULTS AND DISCUSSION

TG analysis was employed for an examination of the surface hydration (Fig.1.a). According to the analysis of the precursor samples, the three steps are visible: (i) 6.67 % and 2 % mass loss up to 252°C and 111°C respectively (ii) 8.325% and 3 % mass loss up to 322°C and 184°C respectively. (iii) 13.75% and 7.5 % mass loss up to 545°C and 437°C for a and b respectively. The first loss may be corresponding to the removal of moisture, the second loss may be due to the elimination of sodium nitrate, ammonium nitrate and the decomposition of PVP respectively, and third weight loss may be due to the crystallization of CeO_2 respectively. The weight loss of as prepared CeO_2 sample corresponding to the NaOH and NH_3 as precipitation agent were 13.75 and 7.5 respectively. These values were comparable to the earlier literatures [1,15].

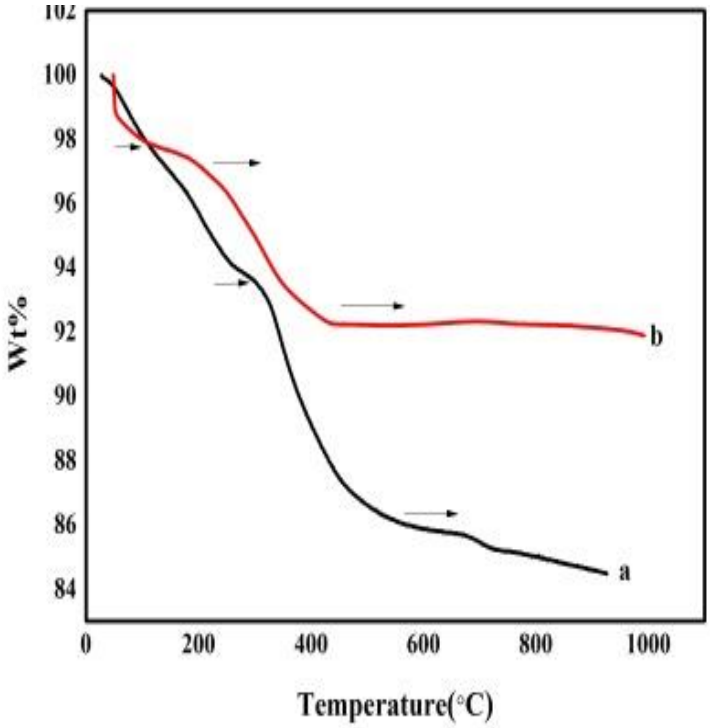

Figure.1 a) TG profile for the precursor Spectrum of Prepared PVP assisted CeO2 using a) NaOH b) NH3 as precipitation agent

X-ray powder diffraction pattern for CeO_2 nanoparticles with PVP assisted a) NaOH b) NH_3 as a precipitating agent is depicted in Fig. 2. All peaks have been indexed to pure cubic fluorite structure of CeO_2 (space group Fm-3m) which coincide with JCPDS card.no. 81-0792 for both samples. No impurity peaks were observed, revealing the high purity of the sample. The crystallite size of the nano CeO_2 powder was determined by diffraction approximation methods such as Debye-Scherrer formula. Due to presence of crystal distortion, lattice strain may be expected. So strain, dislocation density lattice parameter and volume of the cell were calculated. The calculated values are tabulated in Table.1. The calculated cell parameters were somewhat larger than the literatures values which could be explained by lattice extension due to the small particle size [16,17].

Table.1: XRD Data calculations:

Sample code	Crystalline size (nm)	Strain (no unit)	Dislocation density ($\times 10^{15}$)	Lattice parameter(Å)	Volume(Å^3)
A	17.48	-0.00269	5.779	5.4262	159.77
b	17.97	-0.00241	4.633	5.4142	158.71

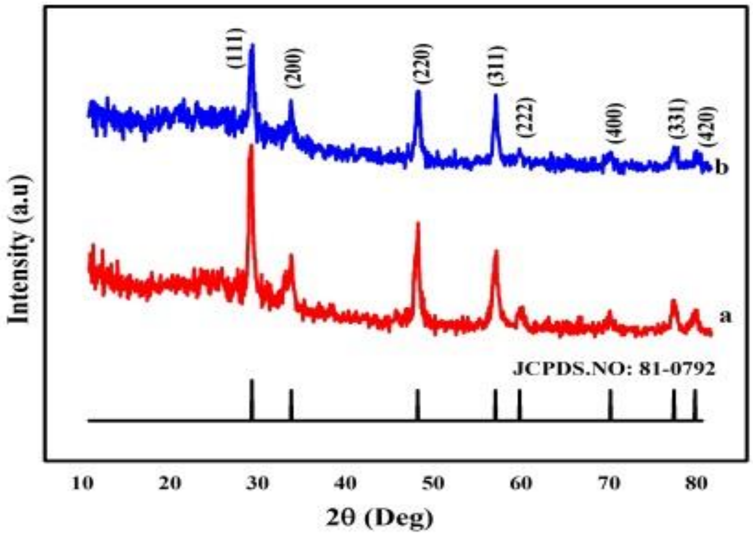

Figure.2 XRD pattern of PVP assisted CeO2 nanoparticles using a) NaOH b) NH3 as precipitation agent

The FT-IR spectra of strong base (NaOH) and weak base (NH_3) based CeO_2 nano particles are shown in fig.3. It is observed that the broad band appears at 3392cm^{-1} and 3422cm^{-1} could be assigned to the O-H stretching vibration of the observed water on Ceria surface for a and b respectively. The strong band at 1762cm^{-1} and 1696cm^{-1} can be ascribed to the bending mode of hydroxyl group of absorbed water for a and b respectively. The sharp peak at 867 cm^{-1} for a and 1621 cm^{-1} for b corresponds to the rocking mode of methylene mode and deformation of $-CH_2$ symmetric stretching vibration of surfactant (PVP) respectively. The sharp band at 1452cm^{-1} and 1370cm^{-1} are an indicative of N=O stretching vibration due to trace amount of nitrate for a and b respectively. The strong band at 473cm^{-1}, 503cm^{-1}, 688cm^{-1} and 659cm^{-1} ascribed to Ce-O stretching mode, O-Ce-O stretching mode for a and b respectively, confirms the formation CeO_2 nano particles. These results are consistent with earlier literatures [15,18].

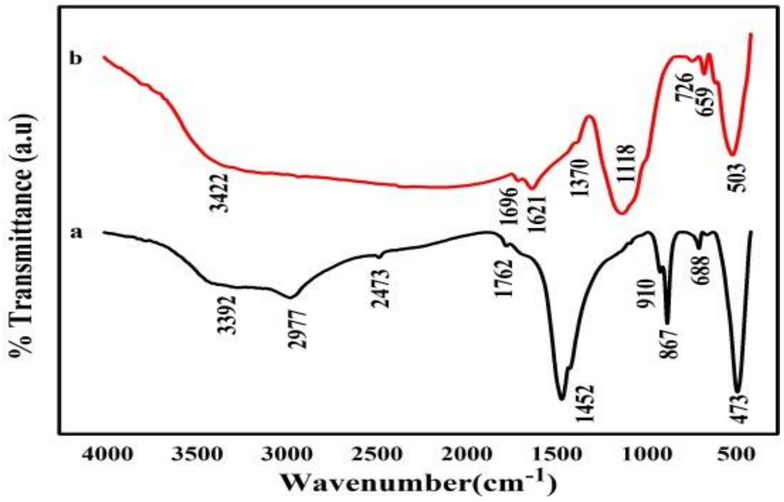

Figure.3 FTIR specrum of PVP assisted CeO2 nanoparticles using a) NaOH b) NH3 as precipitation agent

The cubic fluorite structure of CeO_2 was further confirmed by Raman spectra. Fig 4 depicted the Raman spectra of Ceria nanoparticle. Elahah K.Gohorshadi et.al [16] reported that the bulk Ceria has single broad band at 464cm^{-1}. In our study, raman band was ascertained in 462 cm^{-1} for both samples, which is assigned to triply degenerate F2g symmetry and can be viewed as a symmetric breathing mode of the O-atom around each cation. Since only the O atom move, the vibrational mode is nearly independent of the cation mass. The red shift of this main raman band is attributed to the lattice relaxation revealed by XRD, while several factors such as phonon confinement, increased lattice strain, non-uniform strain and variations in phonon relaxation may account for the broadening of the F2g band and decreased crystallite size.

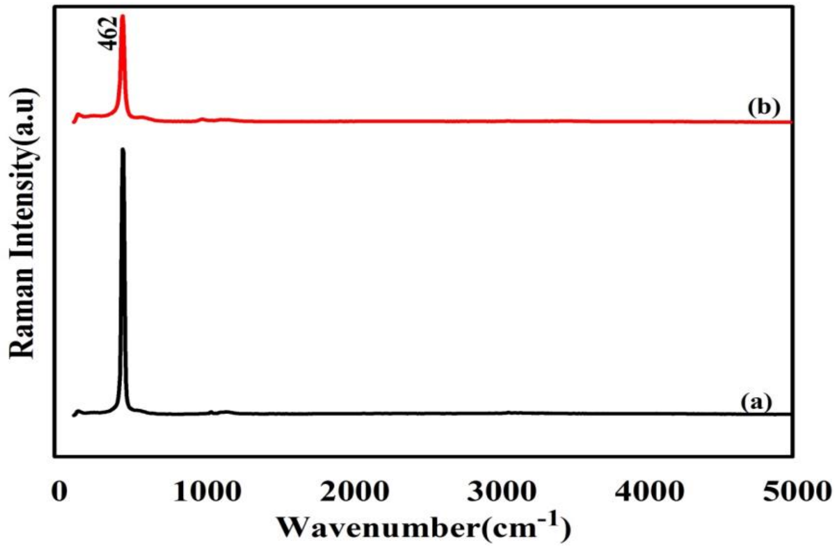

Figure.4 Raman specrum of PVP assisted CeO2 nanoparticles using a) NaOH b) NH3 as precipitation agent

The surface morphology of the nano particles has been characterized through SEM analysis. Fig. 5 (a-b) shows the SEM images of PVP assisted CeO_2 nano particles with NaOH and NH_3 as precipitation agent respectively with a magnification of 4 K. In Fig.5.a, the uniform spherical particle distribution morphology was formed, for NaOH as precipitation agent. The precipitation agent played a major role in the adiabatic temperature changes as observed in the microstructure. It must be noted that soft templates (PVP) approach is a general technique feature of chemical species that are not explicitly for a single type of structures, but final geometry rather developing by applying synthetic parameters such as temperature, reaction time, cerium precursor, surfactant/cerium ratio, pH etc., that can assertively affect the final product. In fig.5.b, it is observed that the particles consist of non-uniform distribution with single particles or with some cluster particles. It seems to be agglomerated particle that arose due to the less gas being released during the calcination process which occurred in the precipitation lean condition. Consequently, the fusing result could be reflected by Oswald ripening process for which the primary particles act as sources for the direct evolution of the ceria monomers [19].

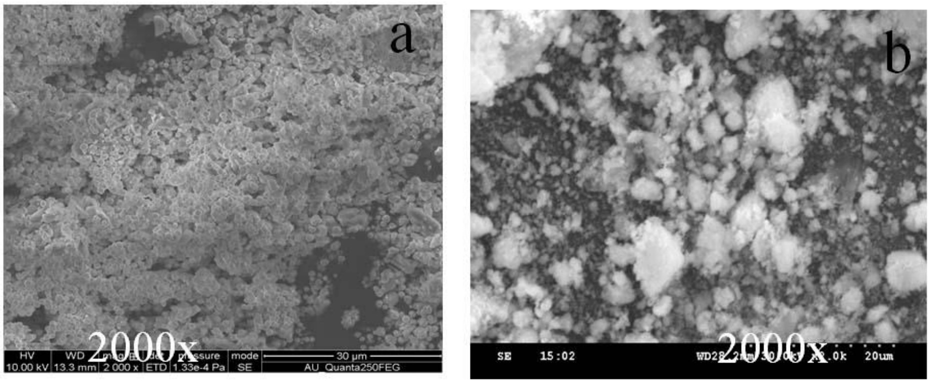

Figure.5 SEM images of PVP assisted CeO2 nanoparticles using a) NaOH b) NH3 as precipitation agent

Photoluminescence (PL) is one of the important characterization tools to study the structural defects and quality of crystalline structure which plays an essential role in the development of catalytic property in CeO_2 nano particles. The room-temperature photoluminescence spectrum of the CeO_2 nano particles measured using 325 nm excitation wavelength is shown in Fig 6 (a-b). The strong peaks are observed at 522 (2.377 eV) and 523nm (2.374 eV) for sample a and b respectively. The relative peaks 368 and 434 for sample (a) and 329, 368 and 435 for sample (b) are corresponding to the ultraviolet and blue emission attributed to the surface defect in the CeO_2 nano particles. The investigations show that emission band ranging from 400 to 500 nm for CeO_2 sample attributed to the hopping from different defect levels of range from Ce 4f to O 2P band. The band at 435nm is related to abundant defect such as dislocation which is helpful for fast oxygen transportation [20,21]. Thus the more active surface oxygen species in sample a exhibit higher oxygen mobility when compared with sample b.

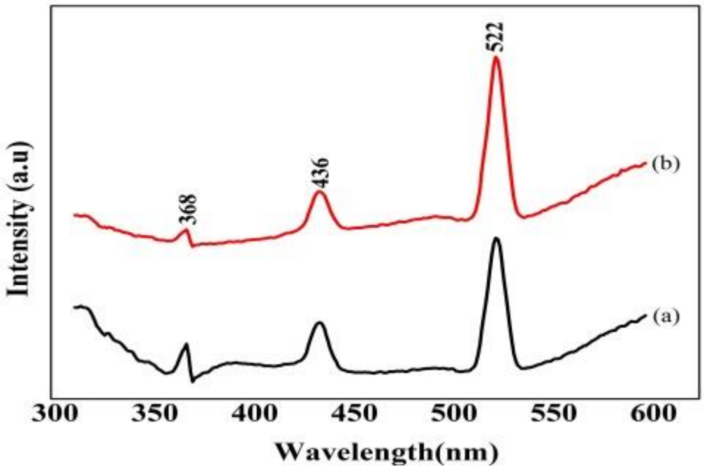

Figure.6 Photoluminescence spectrum of PVP assisted CeO_2 nanoparticles using a) NaOH b) NH3 as precipitation agent

IV. CONCLUSION

CeO_2 nanoparticles were successfully synthesized by surfactant assisted co-precipitation method using NaOH (strong base) and NH_3 (weak base) as precipitation agent at room temperature. The precursor of the samples were characterized by TG analysis. The result showed that the stable, well dispersive and crystalline pure phase CeO_2 nano particles with cubic fluorite structure and the mean grain size of 18 nm was obtained. The Ce-O stretching vibration was confirmed through FT-IR analysis. Further, Raman band was ascertained at 462 cm^{-1} for both samples, which is assigned to triply degenerate F2g symmetry and can be viewed as a symmetric breathing mode of the O-atom around each cation. The uniform spherical particle distribution morphology was formed, when NaOH acts as precipitation agent. The precipitation agent played a major role in the adiabatic temperature changes as observed in the microstructure. The sample also exhibited room temperature photoluminescence of the blue light at 435nm which is related to abundant defect such as dislocation which is helpful for fast oxygen transportation. Obviously, the prepared CeO_2 nano particles with NaOH as precipitation agent rather than NH_3 as precipition agent could be used as filler for the composite lithium polymer electrolyte fabrication.

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