



Role of pH on synthesis and characterization of cerium oxide (CeO₂) nano particles by modified co-precipitation method



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ABSTRACT

A facile synthesis has been made to prepare cerium oxide (CeO₂) nano particles via modified co-precipitation method using different pH values viz, 9 to 12 in steps of 1. The as prepared powders have been systematically studied to analyze their structure, morphology and photoluminescence properties. The representative samples have been analyzed through TEM and XPS analyses. The crystallite size has been decreased upon increasing the pH of the environment. When pH of the solute reached 12, the particle size is reached to 27 nm, which is ascertained through TEM analysis.

1. Introduction

Cerium is the most excessive among rare earth elements, occupying at about 66 parts per million of the earth crust, and also presently a subject of great care due to its multiple applications, which include materials for catalysis, gas sensors, solid oxide fuel cells, ceramics, and oxygen storage [1,2]. Nowadays, nano materials are playing vital role in many applications due to its outstanding physical and chemical properties, which are significantly different from those bulk materials. Rigorous studies have revealed that the extensive applications of Ceria are associated to its relative abundance, unique acid-base surface properties with the dynamically reversible Ce³⁺/Ce⁴⁺ redox pair. These properties also provide ceria with remarkable catalytic performance [3]. Numerous methods, including precipitation from solution [4], microwave assisted method [5], hydrothermal synthesis [6], sol-gel [7], solvo thermal method [8] and polyol method [9] have been used to prepare ceria nano particles with different morphologies and size such as nano belts, nano spheres, nano fibres and nano flower etc.

Among these, modified co-precipitation method has been an extensively proficient assembly of homogeneous high-purity and crystalline oxide at low cost, also simple procedure allows scaling up for mass production [10]. Zaravkovic et al. [11], synthesized CeO₂ nano particle with irregular morphology and soft agglomeration via chemical route. Guangyu et al. [12], reported yeast adopted CeO₂ with hollow microsphere morphology via bio-template chemical route. However, it is still a challenge to develop the efficient route for fabricating the CeO₂ nanoparticles with preferred morphology. With the specific curiosity to

overrule this issue, an attempt is made to synthesize CeO₂ using cerium nitrate as source material, PVP as surfactant by using modified co-precipitation method by varying the pH as 9, 10, 11 and 12. The as prepared powders were analyzed for their structure, morphology and photoluminescence properties.

2. Materials and methods

The CeO₂ nano particles were synthesized by the modified co-precipitation method. Cerium nitrate hexa hydrate (Ce(NO₃)₃·6H₂O) (434.8 g/mole; 99%, Alpha Aeser), sodium hydroxide (NaOH); (39.99 g/mole, SRL), polyvinyl pyrrolidone (PVP) (Mol.wt.40,000 Merck, Germany) were used as starting materials without further purification. To obtain different morphology, 2.5 wt% of PVP [13] was added separately to 0.01 M of aqueous Ce(NO₃)₃·6H₂O. The resulting aqueous mixture was stirred further for 10 min at room temperature and then the pH value has been varied to the desired value (viz, 9 (CP1), 10 (CP2), 11 (CP3), and 12 (CP4)) by adding the NaOH drop wise into the mixture. The whole mixture was further stirred for 90 min to obtain pale yellow precipitate. The precipitate has centrifuged at 200 rpm and splashed with deionized water and acetone several times to get rid of the residual surfactant. Then the precipitate was dried in vacuum oven at 110 °C for 4 h, milled the sample for 30 m and subsequently calcined in air at 600 °C for 2 h to get CeO₂ powder.

The crystalline structure of the material has been analyzed through X-ray diffraction analysis (XRD) using X-ray diffractometer (Philips X'Pert PRO) with CuKα (45 KV, 50 mA) radiation at room temperature

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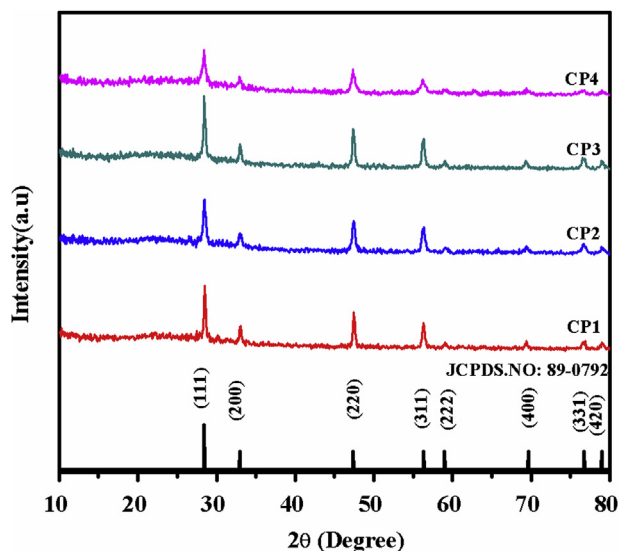


Fig. 1. XRD patterns of CeO₂ nano particles prepared by varying pH as 9(CP1), 10(CP2), 11(CP3), and 12 (CP4).

in the range of $20^\circ \leq 2\theta \leq 80^\circ$. Fourier Transform Infrared (FTIR) study was performed using Thermo Nicolet 380 spectrophotometer in the region $4000\text{--}400\text{ cm}^{-1}$. The surface morphology and size of the as-prepared samples have been observed using scanning electron microscopy (SEM) (Quanta FEG 200 Instrument with EDX) and high resolution transmission electron microscopy (HRTEM, FEI Techno F30 ST equipped with a field emission gun at 300 KV) techniques. The electronic state of the elements has been analyzed by X-ray photon electron spectroscopy (XPS, PHI model 5802). Photoluminescence spectroscopy has been performed using Bruin omega-10 spectrometer.

3. XRD analysis

The purity and crystallinity of the as-synthesized CeO₂ samples have been studied using X-ray powder analysis and Fig. 1 illustrates the X-ray diffraction patterns of CeO₂ particles prepared by varying pH such as 9 (CP1), 10 (CP2), 11 (CP3) and 12 (CP4) respectively. It can be seen from Fig. 1, the diffraction peaks at $2\theta = 28.5, 33.1, 47, 56.3, 59.1, 69.5, 76.7, \text{ and } 79.1^\circ$, which are indexed to (111), (200), (220), (311), (222), (400), (331) and (420) lattice planes of cubic phase of cerium oxide with space group Fm-3m and JCPDS(81–0792). The sharp and strong diffraction peaks in Fig. 1 reveals that the as-prepared samples are well crystallized; also, the diffraction peaks from other species could not be identified. This elucidates the purity of the obtained samples. According to the X-ray diffraction patterns, the crystallite diameters of samples CP1, CP2, CP3 and CP4 have been respectively calculated as 33, 30, 23 and 19 nm using Debye Scherrer equation [14]. The diffraction patterns reveal that the crystallite size has been decreased upon increasing pH. The OH[−] ions are highly involved in the aggregation process which would strongly affect the supersaturation degree of initial precipitate [15,16]. Henceforth, the particle size decreased upon increasing pH during the synthesis.

4. FTIR analysis

Fig. 2 shows the FT-IR spectra of the as-synthesized CeO₂ nano particles (CP1–CP4). The absorption bands at $1554, 1409 \text{ and } 730\text{ cm}^{-1}$ are ascribed to the stretching vibration of O–H absorption and non-bridging of OH groups and characteristic of cubic CeO₂ respectively. This indicates the presence of physisorbed water molecules linked to CeO₂ nanoparticles. Moreover, the lattice vibrational modes appearing at $434 \text{ and } 853\text{ cm}^{-1}$ are recognized to the Ce–O stretching vibration,

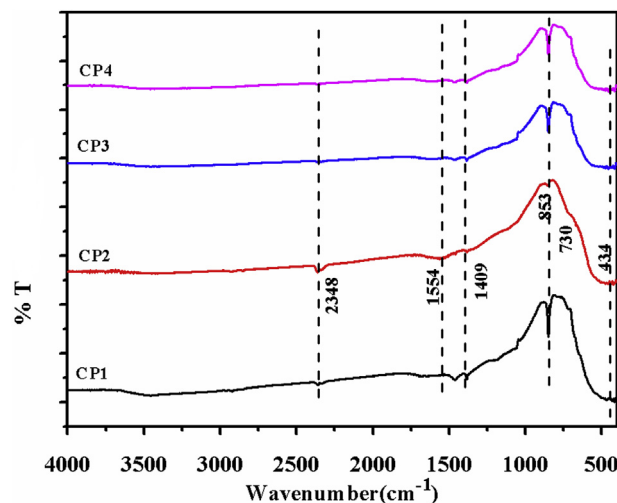


Fig. 2. FTIR spectra of CeO₂ nano particles prepared by varying pH as 9(CP1), 10(CP2), 11(CP3) and 12 (CP4).

which are the characteristic bonds of cubic CeO₂ [17]. The vibrational peak appeared at 2348 cm^{-1} is corresponding to the C=O stretching vibration of CeO₂, which appears weakly when the pH is 9 and 10 and disappears when the pH is > 10 . All the vibrational peaks assigned in the spectra are in agreement with the pure material that has been used in the present study.

5. SEM analysis

The surface morphology of all the samples has been analyzed using SEM analysis and the SEM images are shown in Fig. 3(a–d) along with the EDX spectrum (Fig. 3(inset)) of the sample CP4. It is obviously noticed from Fig. 3(a–d), that the solute environment (pH) plays a vital role in its surface morphology during the preparation of CeO₂ nanoparticles. Fig. 3 displays that the samples CP1 and CP2 are composed of small crystallites and shows the irregular particles with soft agglomeration. When the environment of the solute is highly basic i.e., (pH > 10), the small nano particles of CeO₂ aggregate and gradually evolved into spherical assembly, in which a minimum energy is required to form the ceria particle. It may be due to the nucleation effect of nano particles. It is described that the pH of the medium used in co-precipitation method has an acute and significant impact in the final product. The inset of Fig. 3(d) exhibits the typical EDX spectrum, which reveals the several well defined bands of Ce and O in the as-synthesized CeO₂ nanoparticles.

6. TEM analysis

To further examine the morphology and size of the as-synthesized sample, it has been subjected to the transmission electron microscopic (TEM) investigation with the selected area electron diffraction analysis (SAED). The TEM overview of the optimized sample (CP4) is shown in Fig. 4(a). This clearly displays the uniform distribution of the particle along with its size and shape. The particle size has been measured using Measure IT software (Olympus soft imaging solution GMBH product) to ensure a reliable representation of the actual size distribution and the estimated particle size is about 27 nm. From Fig. 4 (b), it is clearly seen that the high crystallinity of the powder leads to its respective well-pronounced diffraction rings in the SAED pattern [18,19]. Fig. 4(b) can be assigned to the reflection (111), (400), (311), and (200) planes of cubic CeO₂. There are no additional rings in the SAED pattern due to any other crystalline impurities. These entire outcomes are in accordance with the XRD results. Therefore, it can be used as suitable filler in the fabrication of composite electrolytes in Lithium secondary

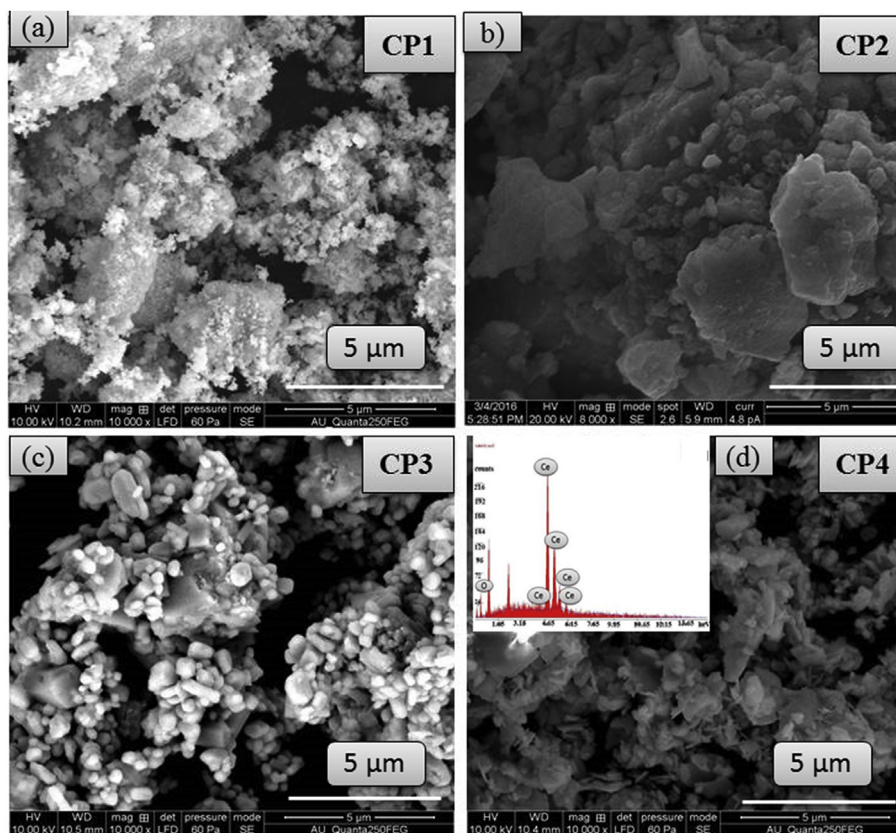


Fig. 3. SEM images of CeO_2 nano particles prepared by varying pH as a) 9(CP1), b)10(CP2), c) 11(CP3) and d) 12(CP4) (Inset: EDX spectra of CP4).

batteries.

7. XPS analysis

The chemical valence state of the prepared CeO_2 (CP4) has been examined by XPS analysis and the high resolution XPS spectra of wide, Ce 3d, O1s of CeO_2 are shown in Fig. 5(a–c). Fig. 5(a) shows the wide range scanning XPS spectrum and it reveals that the sample consists of Ce, O and C elements on the surface of the sample. Fig. 5(b) demonstrates the Ce 3d core level peak of ceria. The symmetric peaks of $\text{Ce}^{4+} 3d_{3/2}$ and $\text{Ce}^{4+} 3d_{5/2}$ have been observed at binding energies 874.42 and 880.86 eV respectively. The spin-orbit split energy is about 6.44 eV for the sample. These values are in good agreement with Ce^{4+} ion in the sample [20,21]. The binding energy of oxygen O1s is superposed around 530.24 eV with two more peaks in higher and lower sides,

which is shown in Fig. 5(c). The high binding energy is recognized to chemisorbed oxygen that is known to be the oxidation activity. The lower binding energy is analogous to the lattice oxygen in CeO_2 [12]. All perceived binding energy values are in agreement with the literature, which reveals the chemical stability of the sample.

8. PL analysis

The photoluminescence spectroscopic analysis has been performed with an excitation wavelength of 270 nm for all the samples (CP1–CP4) and the spectra are given in Fig. 6. It is noticed from the typical fluorescence spectrum of all samples (CP1–CP4) that a UV band has been occurred around 363 nm (3.4 eV). The peaks at 434 and 523 nm corresponds to energies 2.86 and 2.37 eV respectively are evidently lower than the deduced band gap. This is likely to be related with band

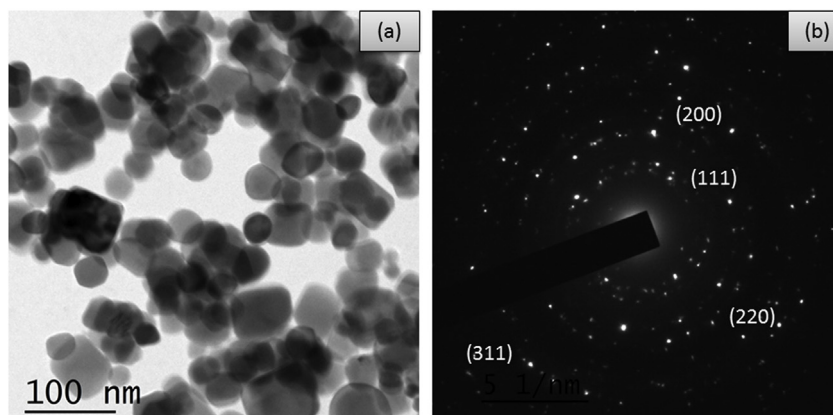


Fig. 4. a) TEM image b) SAED pattern of CP4.

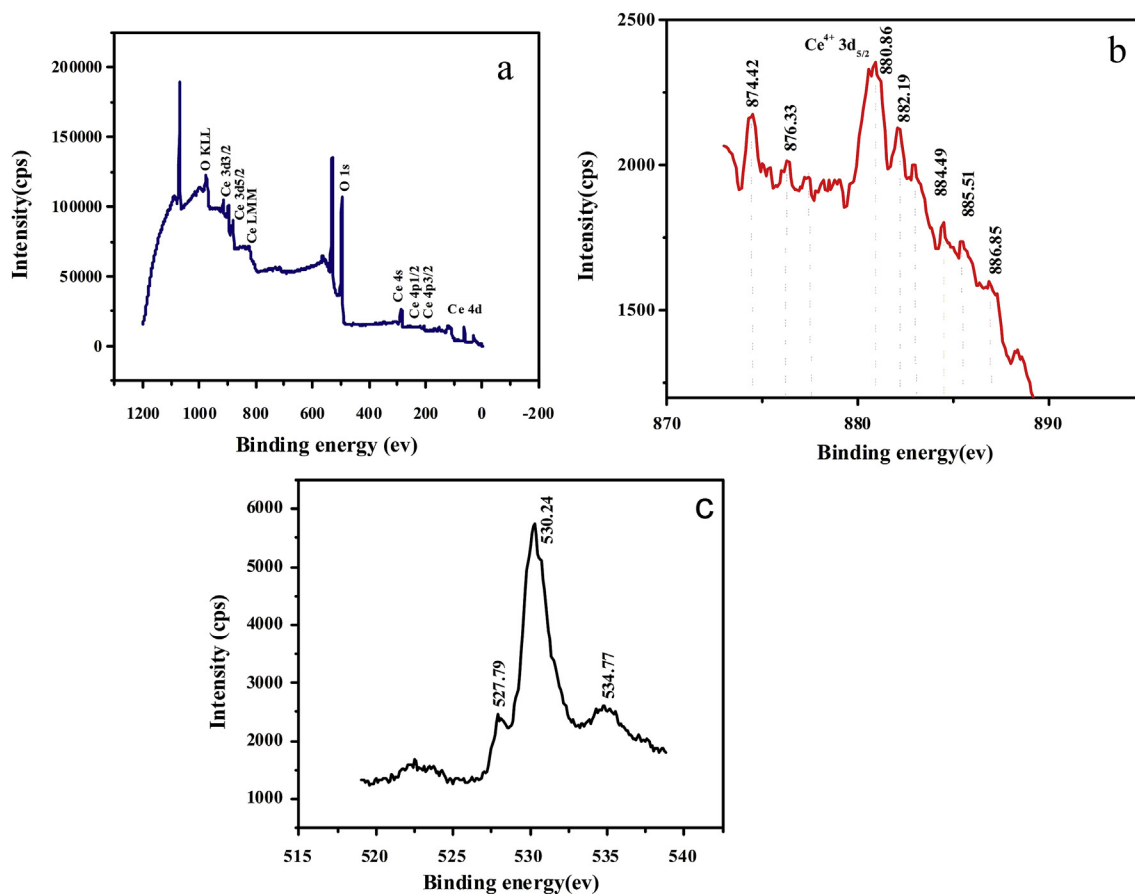


Fig. 5. XPS spectra of (a) wide b) Zr c) O1s of CP4.

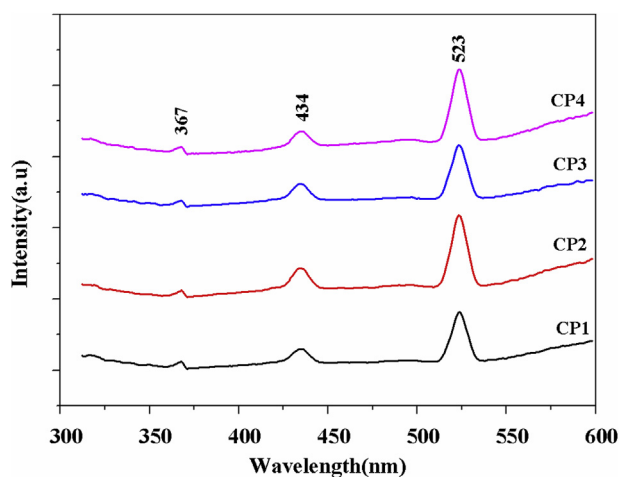


Fig. 6. Photoluminescence spectra of CeO₂ nano particles prepared by varying pH as 9 (CP1), 10 (CP2), 11 (CP3) and 12 (CP4).

to band emission which is probably involving the localized or free excitons. It reveals the mid-gap trap states such as oxygen vacancies or defect states.

9. Conclusion

The CeO₂ nano particles have been synthesized using co-precipitation method by varying pH values such as 9, 10, 11 and 12 (CP1-CP4). The cubic structure with crystallite size between 33 and 19 nm of CeO₂ has been ascertained using XRD. The functional group vibrations have been confirmed through FT-IR analysis. The aggregated spherical nano

particles are evolved when pH approaches 12. The spherical morphology with particle size 27 nm has also been confirmed through TEM analysis. The chemical stability has been affirmed using XPS analysis. The band to band transition has been observed at 3.57 eV from photoluminescence study, which is related to the mid band transition. From the above analyses, the optimized sample is believed to serve as suitable filler in the Lithium polymer electrolyte in the Li-secondary battery fabrication.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.vacuum.2018.12.002>.

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