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INVESTIGATION ON ANNEALED BEHAVIOUR IN THE POWDER OF CERIUM OXIDE NANOSTRUCTURES

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ABSTRACT

In this study, CeO_2 nanoparticles were synthesized by a microwave-assisted method. The samples were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Brunauer–Emmett–Teller method and UV- visible spectroscopy. Results show that the annealed temperature significantly affected the crystalline nature, particle size, and optical properties of the processed CeO_2 nanoparticles. The XRD spectra indicate that the CeO_2 crystal has a pure cubic structure. TEM images agreement with the XRD data shown that the average size of the nanoparticles. The optical properties of the samples are investigated by measuring the UV-VIS absorption at room temperature. With increasing annealed temperature the band gap of the samples remains almost same, and the size of the particles increases.

Keywords: Nanocrystalline materials, CeO_2, Microwave heating, XRD, BET, TEM *and UV- visible spectroscopy.*

1. INTRODUCTION

Nanocrystalline powders – due to their average particle size (below 100 nm) – can show different behaviours resulting from a higher surface energy due to the large surface area and the energy gap between the valence band and conduction band, effects characteristic of sizes close to the atoms. These phenomena may increase the potential use of the material, including optical, chemical, and electromagnetic, among other properties. Therefore, because of its exceptional physical and chemical characteristics [1-4].

Cerium oxide has attracted intense interest due to its high potential applications such as supports for catalytic processes, high temperature ceramics, for promotion of water gas shift and reforming reaction, noble metal dispersion, and solid oxide fuel cells, etc [5, 6]. Thus, for such applications, it is desirable to prepare ceria materials with enhanced textural, thermal properties,

and high surface area, in particular in the form of mesoporous frameworks. Recently, intensive research has been focused on fabricating CeO_2 nanostructures revealing their growth mechanisms, optical and electronic properties. Many techniques including microwave heating [7], chemical-precipitation [8], and hydrothermal process [9]. In this paper, we report the crystalline CeO_2nanonmaterial through a simple in situ microwave-assisted method combined with PEG surfactants.

Microwave synthesis is promising due to its unique effects such as energy saving, higher reaction rates, rapid volumetric heating, higher selectivity and higher yields of products. In the microwave heating method, energy is transferred through the material (into the bulk) electro-magnetically, and not as a thermal heat flux. Therefore, the rate of heating is not limited to the surface and the uniformity of heat distribution is greatly improved. Similarly, in the present investigation, we have obtained CeO_2 nanostructures in morphology when the precursor solution is exposed to microwave radiation for only ten min without need of a post annealing process. This should lead to potential applications in optoelectronics since size-dependent optical properties are expected as a result of quantum size effects.

2. EXPERIMENTAL TECHNIQUES

CeO_2 was prepared by microwave-assisted heating of an aqueous solution of 0.03 mol $L^{-1}Ce(NO_3)_3$. $6H_2O$ containing 0.5g poly(ethylene glycol) 200 (PEG). The solution was obtained adding drop wise ammonia solution NH_3 (AR 28%) under stirring, until pH =9. The prepared aqueous solution was put in a quartz vessel into the microwave reaction system. Then the solution was treated under microwaves for 40 min at 150ºC (800 W).The resulting precipitate, cooled to room temperature, was centrifuged, washed with distilled water several times and finally dried at 100º for 24 h. The final yellow product was annealed at different temperature, 500, 600,700,800,900, and 1000ºC for 1 h in air. The structure of the as-prepared and CeO_2 powder samples was characterized using Powder X-ray diffraction (XRD) patterns were obtained on a Rich Siefert, Model 3000 powder diffractometer operating at 40 kV and 25 mA using CuKα1 (λ = 1.54 Å) radiation. Data were collected from 10° to 70° with a sampling interval of 0.01° per step and a counting rate of 1 s per step. The lattice parameters of the samples were calculated by the help of XRD peak fit (using XRDA software) and the average crystallite size were calculated using Scherer's formula. The specific surface area of the prepared samples was calculated from the adsorption isotherm of nitrogen at 250 °C on the basis of the Brunauer–Emmett–Teller method. Band gap energies of the samples were calculated using UV–visible spectrophotometer (Lambda 20, Perkin Elmer). The size and morphology of nanocrystallites were observed through transmission electron microscopy (TEM, JEOL JEM-1200EX). Crystal lattice fringes were observed by high-resolution transmission microscope (HRTEM, JEOL 3010) with an accelerating voltage of 200 kV.

3. RESULTS AND DISCUSSIONS

3.1. Structural and Phase Studies

Fig. 1 shows the XRD patterns of the as-prepared powder and heat-treated CeO_2 nanoparticles at different temperatures. The as-prepared and annealed sample exhibits XRD peaks that correspond to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), and (4 0 0) planes for the cubic fluorite structure of CeO_2 in the standard data (JCPDS: 34-0394). It is clearly seen that the reflection peaks are broad, indicating that the crystal size is small and should be in the range of nanoscale. The average crystallite size of the sample was calculated from X-ray line broadening of the reflections of (1 1 1) using Scherrer's equation (i.e. $D = K\lambda/(\beta \cos\theta)$, where λ is the wavelength of the 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) [10]. As-prepared CeO_2 powder were annealed at 500, 600, 700, 800, 900 and 1000 ºC for 1 h, respectively, their XRD peaks became gradually sharper with increasing temperature and the average crystal size increased from 5 to 27 nm at 500–1000 ºC, indicating that the crystallinity of CeO_2 are accelerated by the annealed process. No crystallized precursor is observed in the XRD pattern, and the broadening of the reflections distinctly indicates the intrinsic nature of nanocrystals. The particle size and lattice parameter a are also summarized in Table 1. It is seen that the value of the lattice parameter a for the CeO_2 sample is close to that reported for CeO_2 (a = 0.5411 nm) in the standard data (JCPDS: 34-0394).

3.2. Morphology Studies

Figure 2 shows the typical TEM image, selected area electron diffraction (SAED) pattern and HRTEM images from annealed at 500^0C materials. Figure 2(a),(b), and (c) show the distribution of nanoparticles and from these images it is seen that average size of the nanoparticle of CeO_2 is 10 nm.The results are in well agreement for CeO_2 with the calculated size of respective nanoparticles from the XRD results using the Debye-Scherrer formula. SAED patterns taken from a single nanoparticle, shown in Fig 2(b), evidently present the well-crystalline nature. From HRTEM result it is clear that nanoparticle structure uniform, perfect, well crystalline, and growth mechanics over their entire dimension.

3.3. Growth Mechanism

First, hydrated Ce(IV) ions can form complexes with H_2O molecules or OH^- ions. Polymers of this hydroxide, $Ce(H_2O)_x(OH\text{-})_y(4\text{-}y)^+$, can then serve as a precursor of the oxide. The starting precipitate from the Ce(IV) salt may be formed by nucleation of hydrated $Ce(H_2O)_x(OH\text{-})_y(4\text{-}y)^+$, so leading to very fine precursors for the final oxide. In aqueous solution, water, as a polar molecule tends to take protons away from coordinated hydroxide and the reaction equation can be expressed by

$$Ce(H_2O)_x(OH\text{-})_y(4\text{-}y)_+ + H_2O \rightarrow CeO_2.nH_2O + H_3O^+$$

Consequently uniformly small particles can be prepared. PEG, as a dispersion stabilizer, can inhibit nonhomogeneous precipitation to obtain homogeneous precipitation. Ammonia solution is used to adjust the pH of the solution.

3.4. Bet Surface Area

In general, specific surface area is a significant microstructural parameter of nano particles, which depends on the geometrical shape and porosity.N_2 adsorption–desorption isotherms of CeO_2 after annealed. The oxide is predominantly mesoporous as evidenced by the type IV-like isotherms with H1 hysteresis, indicating the results are shown in Table 1(Figure not shown).. Surface areas of porous CeO_2 calculated by the Brunauer–Emmett–Teller (BET) method were fairly large ranging decreased from 1000 to 500, which is also an indication of the mesoporosity.

3.5. Band Gap

UV-Vis spectra of the products, which were obtained from the supernates of CeO_2 powders redispersed in ethanol solution, are shown in Fig.3. The bandgap of the CeO_2 nanoparticles estimated from the onset of the absorption spectrum was 3.0 eV. Ideally, quantum size effects arising from a reduction of the particle size predict a bandgap increase that is the opposite effect to the one observed here. However, simple quantum size effect calculations assume that no significant variation of the chemical structure of the metal oxide is occurring during the particle size reduction. In the case of our CeO_2, the presence of a significant fraction of Ce atoms (in either the 3^+ or 4^+ state) on the external surface leads to oxygen vacancies and defects whose influence on the bandgap overcomes the expected influence of the regular quantum size effect [11, 12].

4. CONCLUSION

Cerium oxide nanoparticles were synthesized through microwave-assisted method by considering different annealed temperatures. The structural and optical properties of the prepared CeO_2 nanoparticles have been confirmed using TEM, XRD and UV-VIS spectroscopy. The results of the XRD and TEM showed that the average particle size of CeO_2 particles increases with increasing annealed temperature. The band gap of the CeO_2 nanoparticles was estimated from the UV-VIS absorption. It was observed that the band gap of the samples remains almost constant i.e (3.0 eV) for different annealed temperature.

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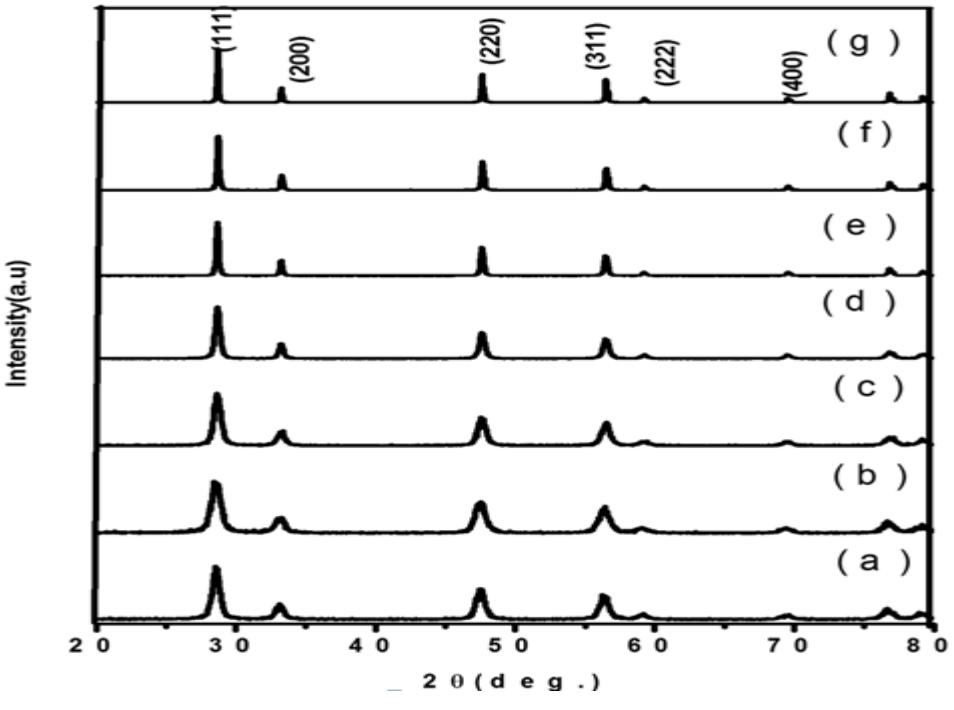

Figure-1. XRD spectra of CeO_2 nanoparticles annealed at various temperatures:(a)As-prepared,(b)500°C,(c)600°C,(d)700°C,(e)800°C,(f)900°C, and (g)1000°C for 1hrs.

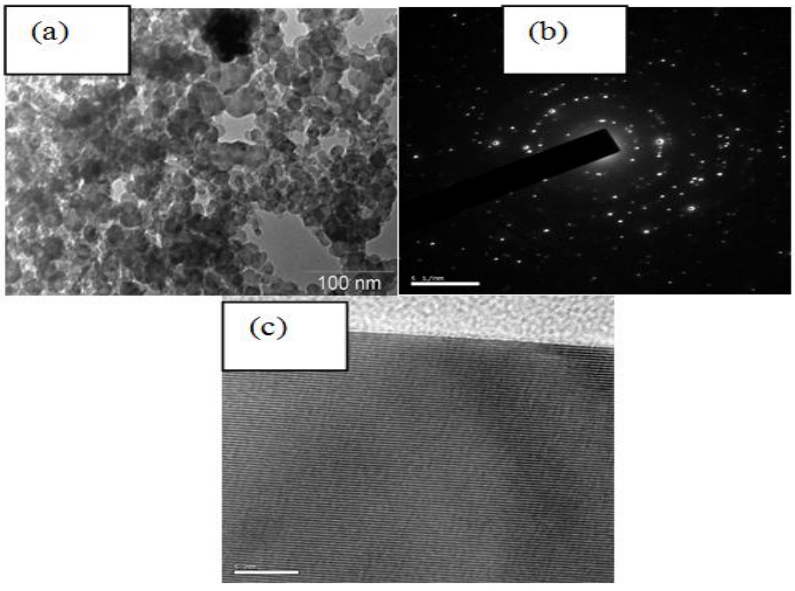

Figure-2. TEM micrographs of CeO_2 powders different annealed temperatures 500 °C: (a) TEM micrograph (b) SAED (c) HRTEM image, for 1 h.

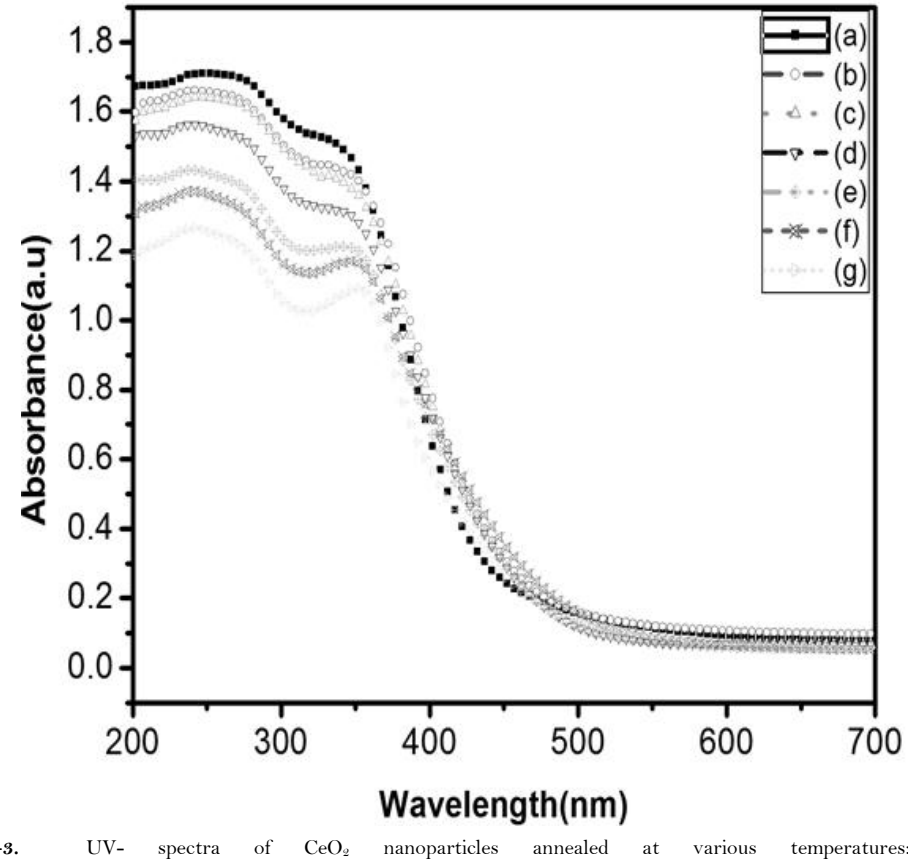

Figure-3. UV- spectra of CeO_2 nanoparticles annealed at various temperatures: (a)As-prepared,(b)500°C,(c)600°C,(d)700°C,(e)800°C,(f)900°C, and (g)1000°C for 1hrs.

Table-1. Textual properties of Annealed Ceria sample

Sample	BET surface area (m^2/g)	Pore Volumea (cm^3/g)	Poresizeb (nm)
500°C	58.14	0.0646	73.86
600°C	42.56	0.2373	71.61
700°C	23.81	0.0366	65.63
800°C	8.69	0.0079	13.39
900°C	5.04	0.0041	25.86
1000°C	2.95	0.0048	59.48

a. Total pore specific volume (at P/P0=0.95).

b. Average pore size