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Biosynthesis of Nanostructured Ceria, its Optical and Magnetic Studies for Spintronic Applications

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Abstract. Nano structured ceria or nanoceria of average crystallite size $\sim 6\,nm$ are synthesized by chemical co precipitation method using cerium nitrate hexa hydrate and sodium hydroxide as starting materials. Onion juice extract is used as biological capping agent. Structural, optical and magnetic properties of prepared samples were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman, UV-Visible spectroscopy and vibrating sample magnetometer (VSM) measurements. The increase in the value of optical band gap compared to bulk may be attributed to the quantum confinement and its band gap is well matching with that silicon. In addition to this, it also possess room temperature ferromagnetism. Thus the synthesized nanoceria have the potential to combine both semiconducting and magnetic behavior in a single system for making compatible spintronic devices.

Keywords: Nanoceria, chemical co- precipitation, Onion juice extract, RTFM

INTRODUCTION

Diluted magnetic semiconductors are currently being explored with a strong drive due to their unique property of exploiting spin of the carriers in addition to or in the place of the charge for creating new functional devices. This removes the difficulties in injecting spins into nonmagnetic semiconductors which are used in the conventional spintronic devices [1]. Spintronic devices can be used as magnetic high density data storage devices, spin based switches, transistors, diodes, modulators, etc. [2] To be commercially useful, spintronic devices have to work at room temperature and be compatible with existing semiconductor based electronic devices. Among them, nanostructured cerium oxide has attracted much attention due to its interesting characteristics such as it possess a stable cubic fluorite structure far from the stoichiometric proportion of oxygen [3]. It is one of the most important rare earth oxides which are endowed with high dielectric constant and is used as a buffer layer for silicon on insulator devices and as a high k-dielectric material in capacitors [4]. These unique and novel properties make cerium oxide a good matrix to develop compatible spintronic devices.

The properties of nano materials can be enhanced by decreasing the size and thereby increasing the active surface area. In recent years, much effort have been done for the development of new routes for the fabrication of nanostructured ceria due to wide range of applications in science and technology The large-scale manufacture need to be cost effective, simple and more eco-friendly. So chemical co-precipitation method using biological capping agent is more attractive compared to other synthesis routes such as sol-gel, sonochemical, hydrothermal, combustion and pulsed laser deposition methods [5, 6, 7].

EXPERIMENTAL

The materials used were analytical grade Cerium (III) nitrate hexa hydrate ($Ce(NO_3)_3.6H_2O$) and sodium hydroxide (NaOH) were purchased from Merck, India and were used without further purification. Cerium oxide nanoparticles were synthesized by chemical co precipitation method by taking 0.1M aqueous solution of cerium nitrate hexa hydrate and 0.4M Sodium hydroxide as starting materials and onion juice extract as capping agent. Upon adding the solutions,

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cerium hydroxide was precipitated and it was then stirred for five hours. After stirring, it was filtered, washed several times with distilled water and allowed to dry naturally. Then the dried precursor was annealed at 400° C in a muffle furnace for 3h to get nanostructured cerium oxide particles.

The XRD pattern of prepared sample was determined by Bruker AXS D8 Advance diffractometer using CuK_α radiation in the 2θ of 20° to 80° with a step size of 0.02°. The TEM analysis was done using a Jeol/ JEM 2100 instrument and the electron beam accelerating voltage was 200 kV. The optical absorbance of the sample was recorded using Cary 5000 UV-Vis-NIR spectrophotometer in the wavelength range of 200 − 800 nm. Micro-Raman spectra of the nanomaterial were recorded using Labram-HR 800 spectrometer (Horiba Jobin Yvon) using an excitation wavelength of 633nm. The magnetic hysteresis measurement was taken at room temperature from -1.5T to +1.5T using LakeshoreVSM7410 instrument.

RESULTS AND DISCUSSION

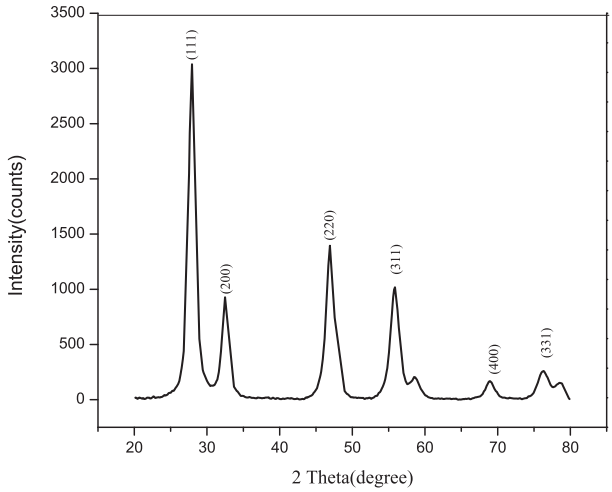

FIGURE 1. XRD pattern of the prepared sample.

The X-ray diffraction pattern of the sample is shown in Figure 1. All the peaks observed can be indexed with the respective planes corresponds to cubic fluorite structure of cerium oxide particles and also matches with the JCPDS file No. 34-0394. No additional peaks are observed indicating the purity of the sample. The broad peaks in the diffraction pattern indicates the nano crystalline nature. The average crystallite size of the sample is estimated from the Scherrer formula, $D = \frac{0.9\lambda}{\beta cos\theta}$ where β is the full width at half maximum of the (hkl) diffraction peak measured, λ is the wavelength of X-ray and θ is the Bragg angle of the (hkl) peak [8] and was calculated to be 6.7 ± 0.4nm. The value of lattice constant can be calculated using the equation, $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$ where d is the inter-planar spacing, a is the lattice constant and h, k, l are the miller indices of the plane. The lattice constant was found to be 0.5483 nm. As the size decreases to nano regime, Ce^{4+} ions reduces to Ce^{3+} ions and the number of O^{2-} anions decrease from eight to seven by creating disordered oxygen vacancies without any change in the crystal structure [9]. This induces an increase in lattice constant in order to relieve the strain. The lattice constant of nanostructured ceria is closely matching with that of silicon (0.5411 nm), which is usually used in all electronic devices.

TEM image with selected area diffraction pattern are shown in Figure 2. In the SAED pattern of the sample, Debye rings are visible because Laue spots merge into a general background due to small grain size and confirms the polycrystalline nature of the prepared sample [8]. The average particle size estimated from TEM analysis is 6 ± 1 nm which is in good agreement with XRD analysis. Furthermore, the investigation also reveals that onion juice extract is a very good capping agent for the synthesis of nanostructrured ceria of very low dimension.

The Raman spectra of cerium oxide nanoparticle sample is shown in Figure 3. The single Raman band observed at 462.6cm^{-1} in the spectrum confirms the cubic fluorite crystal structure that exhibits only one allowed Raman mode [10]. In fluorite lattice, only F_2g mode can be observed which is due to symmetric stretching band of oxygen and cerium ions [11].

The UV-Visible absorption spectrum of the prepared sample is shown in Figure 4. The spectrum shows a strong absorption below 400 *nm*. This indicates the prepared sample is a good filter of UV radiation with transparency over the visible region. This could be due to the charge transfer transition between O 2p and and Ce 4f band [12]. The direct optical band gap of the sample is measured from Tauc Plot (Figure 5) and is found to be 3.95 *eV* which is greater than bulk cerium oxide particles (Eg=3.15eV). In semiconductor nanoparticles with size smaller than the Bohr exciton radius, quantum confinement of both electrons and holes in all the three dimensions lead to an increase in effective band gap. This indicates a blue shift due to quantum confinement with decrease in crystallite size.

In order to explore the magnetic properties of the prepared samples, the magnetization measurement was carried out using vibration sample magnetometer with an applied magnetic field ranging from -1.5T to +1.5T at room temperature, and is shown in Figure 6(a). On close examination with applied field -0.3T to +0.3T, Figure 6(b), room temperature ferromagnetism can be seen which is characterized by a closed hysteresis loop. The curve exhibits magnetic hysteresis with the remanent magnetization (Mr) of $9.06\text{x}10^{-4}$emu/g and a coercivity of 65.355 *G*. It can be explained in terms of the development of more oxygen vacancies in the lattice due to the reduction of Ce^{4+} ions ($4f^0$) to Ce^{3+} ions ($4f^1$). When Ce^{4+} changes to Ce^{3+}, an unpaired spin is generated in the subshell and thereby magnetism is induced [11, 13]. So the oxygen vacancies and defects at the surface dominate the mechanism for room-temperature ferromagnetism.

The semiconducting properties well matching with that of silicon along with room temperature ferromagnetism make synthesized nanoceria suitable in the fabrication of semiconducting and magnetic behavior in a single system.

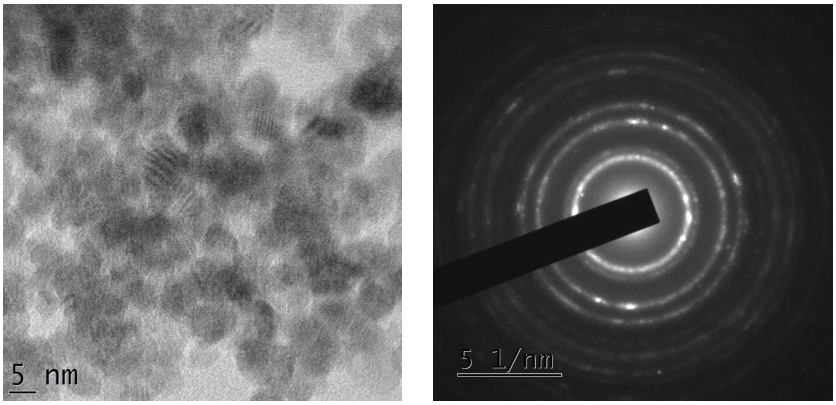

FIGURE 2. TEM images of sample with SAED pattern.

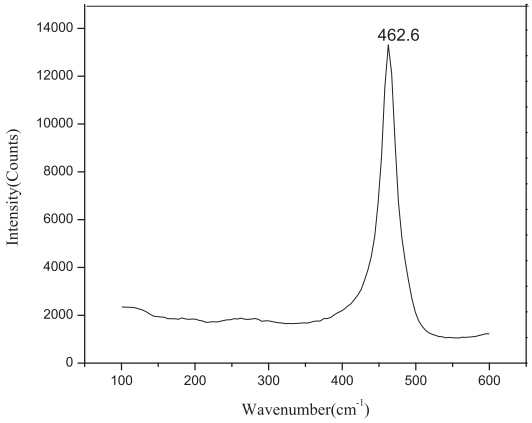

FIGURE 3. Raman spectrum of CeO_2 nanoparticles.

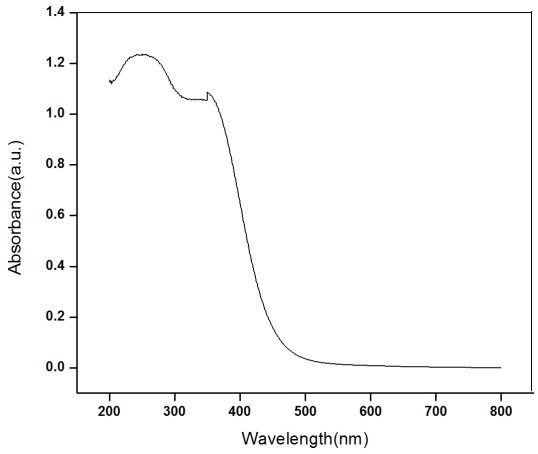

FIGURE 4. UV- Visible absorbance spectrum of CeO_2 nanoparticles.

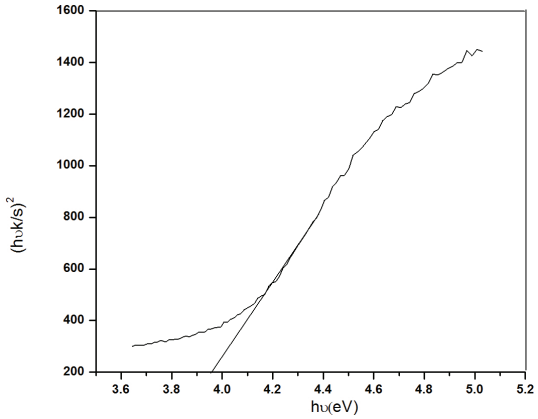

FIGURE 5. Tauc plot of the prepared cerium oxide nanoparticles.

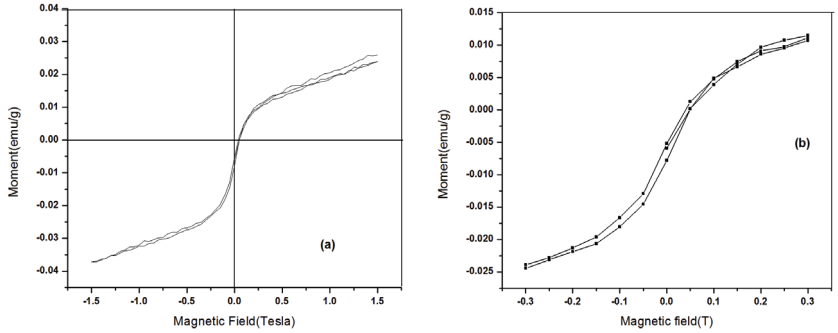

FIGURE 6. (a) M-H curve from -1.5T to +1.5T at room temp. (b). M-H curve from -0.3T to +0.3T

Conclusion

Cerium oxide nanoparticles of average crystallite size $\sim 6\,nm$ were synthesized successfully by chemical co precipitation method using onion juice extract as capping agent. The average particle size measured from the TEM analysis were found to be in agreement with result obtained from XRD analysis. The present investigation reveals the onion

juice extract is a good biological capping agent for the synthesis of nanoparticles with very low dimension. The structural, optical and magnetic properties of synthesized cerium oxide nanoparticles depends on its size and morphology. Optical studies conclude that the synthesized nanoparticle has an average crystallite size smaller than Bohr exciton radius leads to a blue shift due to quantum confinement effect. Magnetic studies shows that the synthesized nanoceria is weakly ferromagnetic in nature at room temperature. Room temperature ferromagnetism, its intimate lattice constant as well as optical band gap match with silicon, makes bio synthesized nanoceria a potential candidate for making compatible spintronic devices.

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