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Shape Controlled Synthesis, Structural and Morphological Characterization of CeO_2@ZnO@SiO_2 Core-Shell Hybrid Nanoparticles

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Abstract— **we report the fabrication of pure CeO_2, ZnO and SiO_2 deposited CeO_2 hybrid core-shell nanoparticles by simple and cost effective co precipitation method. The as synthesized samples were characterized by various experimental techniques such as XRD (X-ray diffraction), FTIR (Fourier Transform Infrared Spectroscopy) and HRTEM (High Field Transmission Tunneling Microscopy) measurements. XRD results confirm the Cubic fluorite structure for CeO_2 and hexagonal structure for ZnO nanoparticles. Functional groups present in the core-shell nanoparticles was investigated by FTIR. The formation of core-shell nanostructure was further confirmed by HRTEM studies.**

Keywords- Co precipitation; core-shell; cubic-fluorite; HRTEM.

I. INTRODUCTION

Nowadays nanosized materials plays a prominent role in the science and engineering applications due to their unusual electric, thermal, optical and magnetic properties differ from their bulk materials [1-2]. Various methods have been developed to synthesize these nanomaterials so far. Cerium oxide is one of the most reactive earth metal oxides, which has been extensively employed in various applications including oxygen storage capacitors, catalysts, UV blockers, and polishing materials [3-6]. It has a fluorite-like cubic structure in which each cerium site is surrounded by eight oxygen sites in face-centered cubic (FCC) arrangement and each oxygen site has a tetrahedron cerium site. Many synthesis methods for preparing cerium oxide nanostructures such as sonochemical and microwave assisted thermal decomposition, spray pyrolysis, gas condensation, electro synthesis , flux method , homogeneous precipitation and wet chemical methods [7-10] have been reported so far. In recent years, the development of core-shell structured materials on a nanometer scale has been receiving extensive attention [11-14]. The shell can alter functionality and reactivity of surface or improve the stability and dispersive ability of the core material. Furthermore structural, optical and magnetic functions can be imparted to the core particles by the shell material. ZnO is a well known semiconductor material with wide band gap having excellent optical features [15] which has been taken as a shell material. Doping of ZnO on the surface of CeO_2 core is expected to improve the properties of both core and shell materials. The combinations of these materials have many potential applications in catalysis, semiconductor industry, cosmetics, gas sensors and fuel cells etc.

In the present study, we have synthesized **c**ore material ceria by wet chemical method by using semi-solid low molecular weight Poly Ethylene Glycol at room temperature. The CeO_2 core was decorated with the shell ZnO layer to obtain CeO_2@ZnO core-shell nanostructures and its structural and morphological characteristics have been investigated through analytical techniques.

II. EXPERIMENTAL PROCEDURE

A. *Materials*

All the chemicals used are of analytical grade and used without further purification. Cerium Nitrate $Ce(NO_3).6H_2O$, Zinc(II)Acetate and Poly Ethylene Glycol (PEG) (~1000 MW), 1-Hexadecyltrimethyl ammonium chloride (TMAC) are purchased from Merck (Germany 99.9%).

B. *Synthesis of core ceria*

To produce pristine CeO_2 nanostructure, cost effective and simple Co-precipitation method is employed. Typical synthesis procedures should be followed; 1M of cerium nitrate and ethanol is dissolved in de-ionized water were taken in the ratio of (30mL: 20mL) and stirred for half an hour at room temperature. After 15 min 0.1 M of PEG was added to the above solution as the stabilizer. 1M of NH_4OH solution is added drop-wise to the solution over a period of 20 min for complete precipitation. The stirring is continued for further 4h at room temperature and followed by ageing process for 12 h. Finally, the solid product was separated through centrifugation, and washed several times with de-ionized water, ethanol and acetone consecutively. As obtained pale white color Ceria is dried at 60˚C under vacuum for 12h and finally the powder was calcined at 300˚C for 5h and used for analytical measurements.

C. Synthesis of CeO_2@ZnO Core-Shell nanostructures

To modify the surface of the core CeO_2, ZnO nanocrystals are grown on its surface by adding 1-Hexadecyltrimethyl ammonium chloride (TMAC) as surfactant by chemical precipitation method. Here, TMAC is used to stabilize the core and to deposit ZnO nanocrystals on it. Briefly, 1g of TMAC is dissolved in 40mL of de-ionized water under constant stirring for 15 min, 0.5g of CeO_2 is dispersed uniformly on the above solution by ultrasonication process. After 1h ultrasonication process, 1g of Zinc(II)Acetate solution is added drop-wise to the CeO_2 solution over a period of 5-10 min under vigorous stirring. Finally, 1M NH_4OH solution is added to the above solution until the complete $Zn(OH)_2$ formation over the surface of pristine ceria. The stirring is continued for another 8 h at ambient room temperature followed by 12 h ageing process. The end product is washed several times with de-ionized water, acetone and ethanol followed by the process of calcination temperature at 120˚C for 12 h.

D. Synthesis of CeO_2@ZnO@SiO_2 Core-shell nanostructures

To cover SiO_2 on the surface of CeO_2@ZnO, Stober method is employed which is reported in earlier [16]. 0.25g of CeO_2@ZnO nanostructures is dispersed in 100ml of de-ionized water under constant stirring and the solution is further processed to ultrasonication for complete dispersion of the particles. Required amount of Tetra Ethyl Ortho Silicate (TEOS) and NH_4OH is added in the ratio of 1:4 to the above solution. Initially TEOS is dropped in to the solution under stirring followed by the drop wise addition of Ammonia solution. The second shell silica is grown on CeO_2@ZnO surface is carried out by continuous stirring for 24 h. The end product is separated by centrifugation and washed several times with de-ionized water, ethanol and acetone to remove the untreated secondary silica particles. Finally, it is dried at 80˚ C for 12h

III. CHARACTERIZATION

Crystalline phase and structure of the core-shell nanostructures are analyzed from the BRUKER D5 Phaser model powder X-ray diffractometer (XRD). FTIR spectra of the samples are obtained from the Perkin FTIR spectrophotometer over the range of 400-4000 cm^{-1}.To analyses the nanostructures and morphological features High Resolution Transmission Electron Microscope (HRTEM) (HITACHI H-7650-80KV) are directly used with Energy Dispersive Spectroscopy attachment

IV. RESULT AND DISCUSSION

A. Phase Analysis

Powder X-Ray diffraction pattern of pristine and the core-shell nanostructures are shown in Fig.1. Crystalline phases of pristine Ceria and typical core-shell nanostructures are investigated. Observed diffraction peaks of the pristine Ceria nanostructures are well indexed to the cubic fluorite structure and matched with the corresponding JCPDS (#81-07902) card number [17]. ZnO coated CeO_2 nanostructure shows the additional diffraction peaks which are attributed to the hexagonal ZnO crystal structure. The peaks due to CeO_2 and SiO_2 are overlapped in the typical core-shell nanostructures. From the fig.1, strong and intense characteristic diffraction peaks conclude that a well crystalline ZnO layer is deposited on the surface of the core Ceria. After the coating of second shell SiO_2, the XRD pattern drastically changes and exhibits only the cubic fluorite structure of pristine CeO_2 phase with reduced intensity. It confirms a dense SiO_2 is covered on the CeO_2 surface and it suppresses the ZnO peaks. Further, no peaks due to any solid-solution between Ce and Zn or other related oxides are observed in the XRD pattern which confirms the formation of pure core-shell nanostructures.

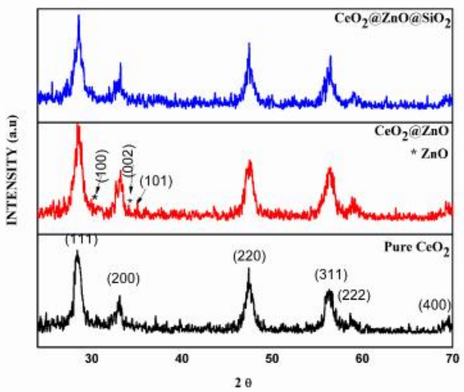

Figure 1 XRD of pure CeO2, CeO2@ZnO, CeO2@ZnO@SiO2

B. FTIR Analysis

Fig. 2 shows the FTIR characteristic studies of pristine CeO2 and ZnO coated CeO2 core-shell nanostructures are recorded in KBr medium at room temperature in the region of 400-4000cm-1. This technique is used to identify the functional groups present in the synthesized material. For pristine CeO2, the bands observed at 3400 cm-1 which corresponds to the O–H stretching vibration of residual water and hydroxyl groups. Also the band at 1630cm1 is due to the scissor bending mode of associated water. The complex bands observed at about 1518, 1350, 1053 cm-1 are due to unwanted residues in the sample. The band at 645 cm-1 corresponds to metal–oxygen bond. In the case of CeO2@ZnO core-shell nanostructures the additional peaks positioned at a lower wave-number region corresponds to the Zn-O absorption bond. The second shell silica over the surface of CeO2@ZnO exhibits the strong characteristic bands at 1090 and 460 cm-1 which was produced by the vibration of Si–O–Si bonds and the absorption at 804 cm-1 comes from the [SiO4] tetrahedron [18]. Coating of silica over CeO2@ZnO completely suppresses the Zn-O band. Thus this confirms the coating of silica over the surface of CeO2@ZnO core shell nanostructures

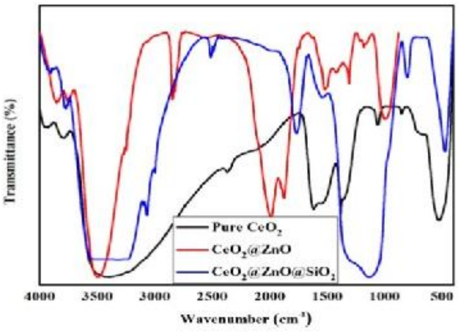

Figure 2.FTIR of pure CeO2, CeO2@ZnO, CeO2@ZnO2@SiO2

C. Morphological analysis

More details about the structure of pristine CeO2, CeO2@ZnO and CeO2@ZnO@SiO2 core-shell spherical crystallites are investigated by the High Resolution Transmission Electron Microscopy (HRTEM), which were shown in Fig.3(a,b). Low magnification HRTEM images indicate that well-developed spherical CeO2 crystallites are obtained with the size range of 5-100nm, which agrees well with the results of XRD. High magnification images reveals that the pristine CeO2 composed of small CeO2 nano-particles with diameter of 15-20nm. From this analysis it is observed that the well crystalline ZnO nanoparticles around thickness of ~15nm and SiO2 shells have been successfully covered over Ceria core-shell nanostructures. After the coating of SiO2 over the surface of CeO2@ZnO is also having the same spherical morphology. From the images it is clearly observed that the shell ZnO and SiO2 has covered the surface of core CeO2. Overall, the results indicate that the core-shell nanostructure consists of spherical crystallites with smooth and little rough surfaces.

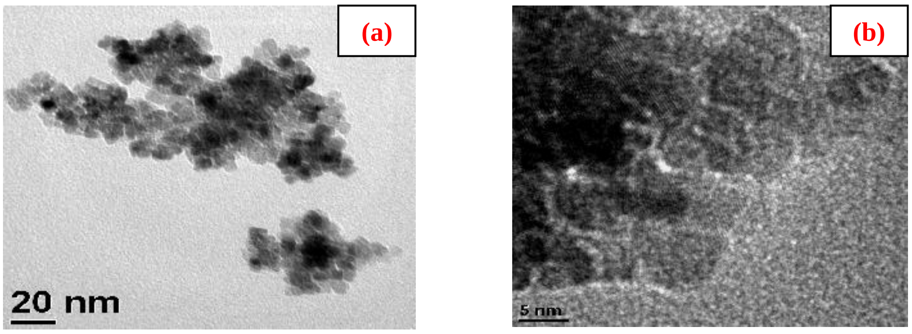

Figure 3a. HRTEM image of Pure Ceria and fig.3b. HRTEM image of ZnO and SiO2 coated CeO2 core-shell nanoparticles

V. CONCLUSIONS

In summary, we reported the synthesis of well crystalline CeO_2, ZnO and SiO_2 coated CeO_2 core-shell nanostructures by simple wet chemical precipitation method. From the XRD pattern polycrystalline natures with cubic fluorite phase of pure Ceria and hexagonal phase of ZnO core-shell nanostructures are confirmed. Core-shell nanostructures of the samples are obtained from HRTEM analysis. This study concludes, the surface modification with insulating oxide layer coating can tune the structural and morphological features of the CeO_2. Thus induces the multi-functionality of these core-shell nanostructures. However, it needs further investigations with the desired structural features could be the better choice of materials for various technological applications.

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