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Composite ceria nanofiber with different copper loading using electrospinning method

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ABSTRACT

Nanofibers of CeO_2 and CuO/CeO_2 were prepared using electrospinning method. Known volumes of aqueous solutions of copper acetate monohydrate and cerium nitrate hexahydrate were mixed with a fixed volume of aqueous polyvinyl pyrrolidone and electrospinning was carried out at 12 kV DC by maintaining the tip to collector distance as 10 cm. The green nanofibers thus obtained were calcined at 500 °C for 3 h. The morphology of the synthesized nanofibers (both green and calcined) was determined by SEM analysis and their elemental composition was verified using XPS and EDX spectroscopy. Green ceria nanofibers had an average diameter of about 130 nm, and the average diameter of the green nanofibers containing 10, 20, 30, 40 and 50 mol. % Cu in ceria were found to be approximately of 124, 117, 114, 108 and 98 nm, respectively. The crystal structure of nanofibers was determined by X-ray diffraction (XRD) which showed the peaks of CeO_2 appearing at 2θ of 28.83° and those for CuO at 47.45°. The average crystallite size of CeO_2 and CuO/CeO_2 were calculated by Debye-Scherer formula and found to be 14 nm for CeO_2 and 9–12 nm for CuO/CeO_2composites of different copper loadings.

1. Introduction

Cerium (Ce) is the most abundant rare-earth element. Its electronic configuration is [Xe] $4f^2 6s^2$ and it has two common valence states: Cerium (III) and Cerium (IV) [1]. Cerium (IV) oxide (CeO_2) or ceria has been extensively researched in the field of catalysis due to its abundance and desirable set of chemical and physical properties. Ceria and ceria-based materials have high oxygen transport capacity along with the unique ability to switch easily between the reduced and oxidized states (i.e. Ce^{3+}-Ce^{4+}) and this property can be further improved with the addition of transition metal ions (such as copper) in the ceria lattice [2]. As a result ceria-based materials have found wide applications in three-way catalytic converters for CO, HC and NO_x removal from automobile exhausts [3,4], water gas-shift (WGS) reaction [5], VOC oxidation [6], photocatalysis [7] and electro-catalysis [8]. These materials have also been employed in oxygen sensors [9], fuel cells [10] and as abrasive [11] and oxygen storage materials [12] and also in optical and ultraviolet adsorbents films [13,14].

It is well documented that nano-structured materials have better catalytic activity than conventional materials due to their higher surface area-to-volume ratio. It has been shown that nanostructured ceria has improved oxidizing ability, specific surface area and oxygen storage capacity [15]. Hence, in recent years, one-dimensional (1-D) ceria nanomaterials such as nanorods, nanotubes, nanowires, nanobelts, nanoribbons and nanofibers have been fabricated and studied in detail [16]. The 1-D ceria nanomaterials have lower tendency for agglomeration, possess high porosity and have exceptionally high specific surface area.

Nanofibers can be synthesized using various methods such as phase separation [17], template synthesis [18], electrospinning [19,20] etc. The electro-spinning, however, is considered to be the most suitable method for fabrication of nanofibers. Electrospinning is quite versatile and produces continuous nanofibers at low cost and permits ease of production and flexibility [21,22] and better control over fiber diameter, microstructure and fiber arrangement [22,23]. Different fiber assemblies such as random mats, aligned fibers, patterned fibers, etc. can be easily fabricated through this technique [21]. The three basic units of the electrospinning setup are high voltage supply, a programmable syringe pump (syringe included), and a metallic collector plate [24]. The electrospinning process is influenced by the properties of the polymeric solution and various process and ambient parameters [25].

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The aim of the present work is to fabricate pure ceria and CuO/CeO_2 composite nanofibers having varying mol. % Cu (copper-cerium basis) loading using electrospinning method. The influence of copper loading on the nanofiber characteristics has been investigated using Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Fourier Transforms Infrared Spectroscopy (FTIR) and Energy Dispersive X-Ray (EDX) Spectroscopy techniques.

2. Experimental

2.1. Preparation of the spinning solution

Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$; Sigma-Aldrich) and cupric acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$; SDFCL) precursors were used as received. Polyvinyl pyrrolidone (PVP; Sigma-Aldrich) was used as the base polymer because it has a remarkably large molecular weight and high solubility in polar solvents. Ethanol (Merck) and de-ionized water were selected as the solvent and co-solvent, respectively. Aqueous solutions with 10, 20, 30, 40 and 50 mol. % Cu were prepared by dissolving appropriate amounts of $Cu(CH_3COO)_2 \cdot H_2O$ in a solution of 0.434 g cerium nitrate hexahydrate prepared in 4 ml of deionized water and kept in five different vials. In another set of five vials 10% (w/v) solution of PVP in 8 ml ethanol was prepared by adding appropriate amount of PVP and stirring with magnetic stirrer to ensure complete dissolution. For preparing the spinning solution the contents of the first set of five vials were added separately to the vials containing ethanol solution of PVP [26]. The contents of the vials were mixed together and acetic acid was added drop-wise (2–3 drops) to each vial to get the final solution. The mixed solutions were then magnetically stirred for 3 h at room temperature to form a homogeneous solution.

2.2. Preparation of electrospun nanofiber

The precursor solution was drawn in a 6 ml plastic syringe equipped with a stainless steel flat-tip needle (21 gauges). The syringe was mounted vertically and attached to a syringe pump. The flow rate from the syringe was set at 1 ml/h. The metallic collector plate was covered with aluminium foil and kept directly under the needle tip to collect the nanofibers. The distance between the syringe tip and the collector plate was maintained at 10 cm. The syringe, stainless steel needle and solution delivery tube were washed thoroughly with ethanol each time before casting fibres from a new solution. Further details of the procedure used are available elsewhere [27].

2.3. Characterization

X-ray analysis of the nanofibers was carried out using Rigaku Ultima IVX-ray diffractometer (Germany) for phase identification. The patterns were run with Cu-Kα radiation at 40 kV and 40 mA. The mean crystallite size (d) of the phase was calculated from the line broadening of the most intense reflection using the Debye-Scherer Equation (1).

$$d = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

Where d is the mean crystallite diameter, 0.89 is the Debye-Scherer constant, λ is the X-ray wave length (1.54056 Å), and β is the effective line width of the observed X-ray reflection, calculated by the expression $\beta_2 = B_2 - b_2$ (where B is the full width at half maximum (FWHM), and b is the instrumental broadening) determined through the FWHM of the X-ray reflection at 2θ of crystalline SiO_2.

Fourier transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm^{-1} using Shimadzu 8400 FTIR spectrometer with KBr pellets at room temperature. Scanning electron micrographs (SEM) and SEM-EDX finger prints were recorded on Zeiss EVO 18 scanning electron microscope. An accelerating voltage of 15 kV was applied and a magnification of 1000× was used.

X-ray photoelectron spectroscopy (XPS) was carried to determine the surface compositions and chemical states of the constituent elements using an Amicus Kratos Analytical unit equipped with Mg Kα X-ray radiation. For typical analysis, the source was operated at a voltage of 15 kV and current of 12 mA. The binding energy scale was calibrated by setting the main C 1s line of adventitious impurities at 284.7eV, giving an uncertainty in peak positions of ±0.2 eV.

3. Results and discussion

3.1. Scanning electron microscopic (SEM) analysis

The SEM analysis confirmed the formation of cylindrical nanofibers of varying diameters. Fig. 1 (a–f) show the microphotographs of ceria nanofibers having varying copper loadings (0–50 mol. % Cu) prior to calcinations. Green ceria nanofibers had an average diameter of about 130 nm (Fig. 1a), whereas the average diameters of the green nanofibers containing 10,20, 30, 40 and 50 mol. % Cu were found to be 124 (Fig. 1b), 117 (Fig. 1c), 114 (Fig. 1d), 40 108 (Fig. 1e) and 98 nm (Fig. 1f), respectively. It is seen that after calcination, the average fiber diameter has reduced by about 20–30% of the green fiber diameter. Shan Xu and other have reported an average diameter of green nanofiber as around 200 nm [28]. The reduction in diameter takes place due to the loss of PVP and other organic compounds during calcination [32].

3.2. X-ray diffraction analysis

The diffraction patterns have been indexed by comparison with the JCPDS files. The XRD patterns of the CeO_2 and CuO/CeO_2 nanofibers with different copper loadings (10–50mol. %Cu) are depicted in Fig. 2. The graphs exhibit characteristic peaks of a fluorite-like cubic phase. The most intense reflection of CeO_2 at 2θ values of 28.83° is clearly visible. The average crystallite size of CeO_2 (14 nm) and CuO/CeO_2 (9–12 nm) were calculated by Debye-Scherer formula. For ceria catalyst with Cu incorporation it has been reported that Cu impregnation influences the ceria lattice parameter marginally [29]. Competing effects are at play when doping the fluorite like lattice of ceria with the divalent Cu^{2+} cations. The smaller ionic radii of both Cu and Cu^{2+} suggest that doping will lower the lattice parameter, but the increased vacancies and lattice distortion due to doping will increase the lattice parameter [29].

3.3. Fourier transforms infrared (FTIR) analysis

The FTIR spectra of CeO_2 and CuO/CeO_2 nanofibers are given in Fig. 3. The broad bands (3700–3000 cm^{-1}) are present due to the stretching vibration of hydroxyl (OH) group of chemisorbed water. The disappearance of peak (900–1630 cm^{-1}) after calcination of CeO_2 at 500 °C indicates removal of most of the organic materials present in the sample. The significant enhancement in the absorption band (500–1060 cm^{-1}) represents formation of CeO_2 nanofiber. Some authors [30,31] have reported that these stretches may be assigned to the O–H from the residual water, the C–C and C–H to residual polymer, and stretches below 1200 cm^{-1} to the