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A Novel Process for Preparation of Hybrid Nanosized Neodymium Oxybromide and Neodymium Oxide[1]

Verma Sarika and S. S. Amritphalae

CSIR-Advanced Materials and Processes Research Institute,
Hoshangabad Road, Bhopal (M.P.), 462064 India
e-mail: drsarikaverma@hotmail.com

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Abstract—A novel process to prepare hybrid nanosized neodymium oxybromide and neodymium oxide from neodymium(III) nitrate hexahydrate has been developed. The simultaneous use of two capping agents (cytosine and cetyltrimethylammonium bromide) in the process allows for efficient control of properties of the so synthesized nanoparticles. The product has been characterized by means of X-ray diffraction, infrared spectroscopy, field emission scanning electron microscopy, differential scanning calorimetry, and thermogravimetric analysis. The nanoparticles size ranges from 17.0 to 64.2 nm.

Keywords: nanoparticle, neodymium oxybromide, neodymium oxide

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The interest in synthesis and study of lanthanide-containing nanoparticles has emerged over the recent years due to special set of properties arising from the small size and large specific surface area of the nanoparticles. These peculiar properties form a basement of a wide range of applications.

The contraction of lanthanides due to their 4f orbitals shielded by the 5*s* and 5*p* shells directly impacts on their physical and chemical properties. Lanthanide materials are among most common phosphors for solid state lighting and medical imaging. Lanthanide oxyhalides, especially the oxybromides, have received considerable attention because of their application as luminescent substances. Neodymium oxybromide (usually doped with the trivalent thulium and/or terbium ions) have been used as commercial X-ray phosphors since mid-1970s [1–4]. On top of that, neodymium oxide has been recognized as a promising dopant to improve phosphorescence properties of neodymium oxybromide materials.

Recent applications of neodymium-containing nanoparticles have been directed to the areas of material science, medicine, and electronics. The interaction of poly(methyl methacrylate) with neodymium oxide as dopant have been reported in [5]. Moreover, neodymium oxide nanoparticles have been found to be cytotoxic and induce apoptosis of certain tumor cells [6–8] and have been recognized as dopant improving properties of lasers, lamps, sunglasses, and colored glasses [9–11].

Neodymium oxide nanoparticles can be prepared via direct precipitation [12], sol-gel synthesis [13, 14], solvothermal synthesis [15], combustion process [16, 17], inverse microemulsion technique [18], and reverse micelle method [19]. The reported methods generally yield single-component nanoparticles; therefore, novel methods are required to prepare hybrid phases of different materials. In particular, this can be achieved by using a pair of capping agents (dual capping) instead of a single surfactant (for instance, lauryl-ammonium chloride). Moreover, when a single surfactant is used, mesoporous and/or microporous structures are formed instead of the target solid nanoparticles of neodymium oxide.

Here we report a novel process for synthesis of hybrid nanosized neodymium oxybromide/neodymium oxide material. Two different capping agents were used, cytosine and cetyltrimethylammonium bromide. Cytosine was expected to impart the additional surface modification rather than to alter the nanoparticles size as reported earlier [20]. Cetyltrimethylammonium bromide played dual role reducing the particles size down to the nanometer range as well as stabilizing the formed particles [21]. The use of two different capping

[1] The text was submitted by the authors in English.

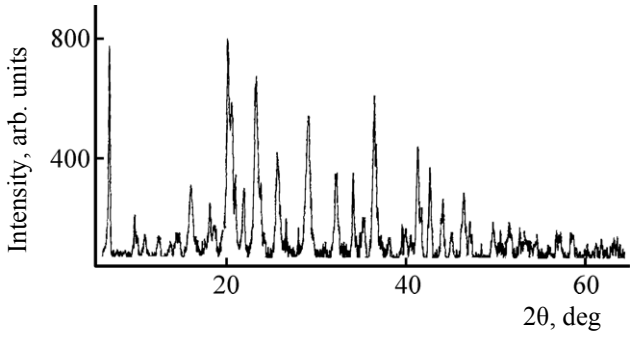

Fig. 1. X-ray diffraction pattern of the product.

agents allowed for simultaneous fine tuning of the properties of hybrid nanosized neodymium oxybromide/oxide particles. The used salt precursor was readily soluble in the polar high-boiling solvent (ethylene glycol) used in this work; moreover, the solvent could act as weak reducing and stabilizing agent preventing aggregation of the nanoparticles.

X-ray diffraction (XRD) pattern of the synthesized hybrid nanosized neodymium oxybromide/oxide is shown in Fig. 1. The XRD peaks were sharp thus confirming the fine crystalline structure of the sample. The observed *d* values were compared with the reference JCPDS data [22–23]. In detail, the XRD data evidenced about formation of neodymium oxide as the one of the phase (*d* = 3.20, 1.96, and 1.67 Å; JCPDS file number 21-579) along with neodymium oxybromide (2.75, 2.83, and 1.63 Å; JCPDS file number 16-781), and isocytosine (*d* = 4.26, and 5.59 Å; JCPDS file number 39-1753) as minor phases. The peaks for sodium ammonium nitrate (*d* = 3.03, 2.68, and 2.22 Å; JCPDS file number 28-490), sodium bromate (*d* = 3.00, 1.79, and 4.74 Å; JCPDS file number 6-377), and sodium oxalate (*d* = 2.83, 2.60, and 2.33 Å; JCPDS file number 20-1149) were observed in the XRD pattern as well. The semi quantitative analysis revealed the following composition of the product: neodymium oxide 20%, neodymium oxybromide 15%, isocytosine 20%, sodium ammonium nitrate 20%, sodium bromate 15%, and sodium oxalate 10%.

Field emission scanning electron microscopy image of the prepared product is shown in Fig. 2. It is to be seen that the particles were well dispersed and almost spherical in shape. The size of the nanoparticles ranged from 17 to 64 nm.

FTIR spectrum of the prepared product is shown in Fig. 3; the observed vibration bands were in accordance with those of the expected components. In particular, a

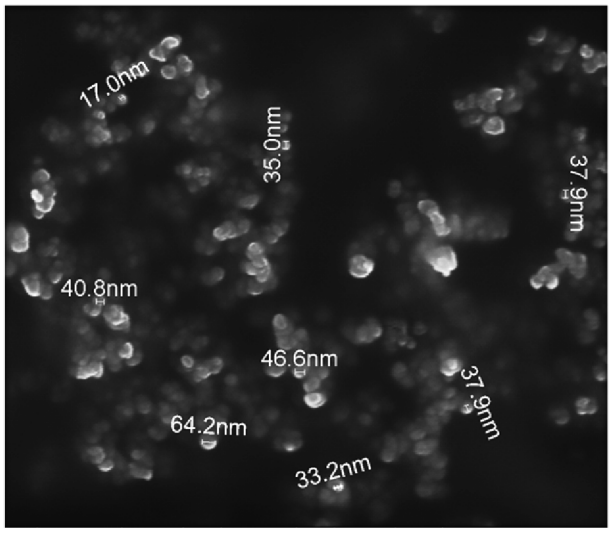

Fig. 2. Field emission scanning electron microscopy image of the product.

broad band at 1045.5 cm^{-1} was assigned to Nd_2O_3 [24]; broad strong bands at 3419–3042 cm^{-1} and a band at 1613 cm^{-1} were assigned to (NH + NH_2) stretching and NH_2 deformation of isocytosine, respectively; ring and C–N stretching bands were observed at 1470 and 1600 cm^{-1}, respectively; the band assigned to C=N stretching and N–H bending vibrations appeared at 1442 cm^{-1}; the strong peak at 1384 cm^{-1} was attributed to the presence of nitrate anion; the peak at 726 cm^{-1} was assigned to out-of-plane ring and COO rocking; a peak at 1317 cm^{-1} was assigned to (C–O) + (OCO) stretching; finally, a peak at 822 cm^{-1} was assigned to (C–C) + (OCO) stretching of sodium oxalate. In general, the FTIR results were in accordance with the above-described XRD data.

Results of TGA and DSC studies of the synthesized product are shown in Fig. 4. The weight loss observed

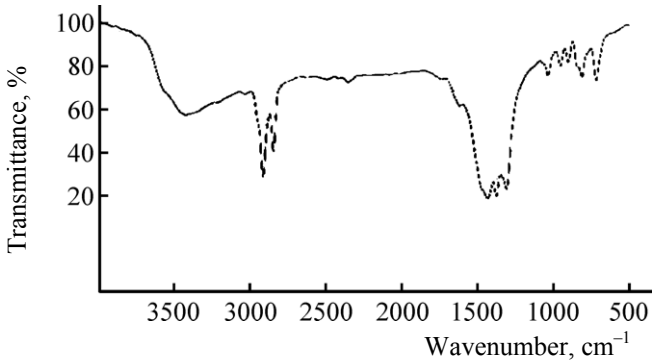

Fig. 3. FTIR spectrum of the product.

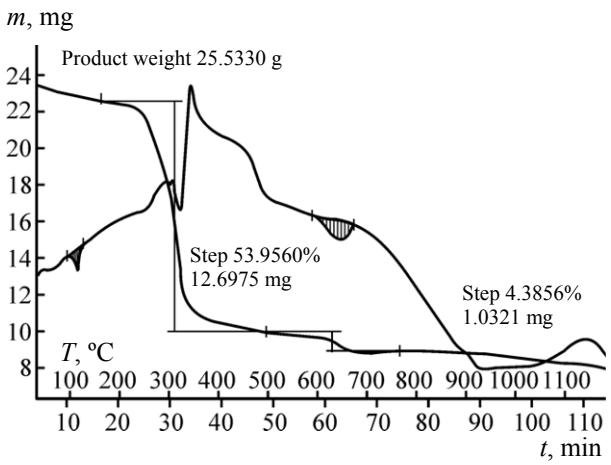

Fig. 4. TG/DSC data for the product.

in the TGA experiment occurred in two stages (53.95% at 300–400°C and 4.85% at 600–680°C. It should be noted that decomposition of neodymium oxybromide occurs at 880–1180°C [25], sodium oxalate decomposes into sodium carbonate and carbon monoxide at 750–800°C, further decomposition of sodium carbonate starts at above 880°C [26], and isocytosine decomposes into carbon and nitrogen oxides at 900–1000°C. It is evident that the only component that decomposes at 300–400°C is sodium and ammonium nitrates. Thus, results of TGA were in general in accordance with the XRD and IR spectroscopy data.

The proposed process mechanism is as follows. Under the reaction conditions, neodymium nitrate dissociates to give neodymium ions that react with sodium hydroxide in the presence of ethylene glycol to form neodymium oxide along with sodium oxalate. Cytosine is simultaneously converted into isocytosine and contributes to the particles surface modification. The products are coagulated and precipitated with ammonium nitrate owing to the electrolyte effect. Neodymium oxybromide is formed via the in situ reaction of neodymium oxide with bromide salts [27].

EXPERIMENTAL

Neodymium(III) nitrate hexahydrate, cytosine, sodium hydroxide, cetyltrimethylammonium bromide, ammonium nitrate (all from Rankem), and ethylene glycol (Merck) were used as received.

Synthesis of hybrid nanosized neodymium oxybromide/oxide was carried out by refluxing a mixture of 8.76 g of neodymium(III) nitrate hexahydrate, 2.2 g of cytosine, 14.65 g of cetyltrimethylammonium bromide, and 20 g of sodium hydroxide in 400 mL of ethylene glycol during 2 h. The product was then precipitated with 30 mL of aqueous ammonium nitrate solution (25 wt %), and washed with the same solution to ensure complete precipitation. The precipitate was dried in air at 110°C during 2 h. Yield 16. g of light-purple powder.

X-ray diffraction pattern was obtained with a D8 advance X-ray diffractometer using CuK_α radiation at 2θ range of 5°–70°. IR spectra was recorded using a Bruker alpha FTIR spectrometer at 500–4000 cm^{-1}. A NOVA NANOSEM-430 (COMFEI) field emission scanning electron microscope was used to visualize the morphology of synthesized nanoparticles. The specimen was sonicated during 15 min in acetone prior to the microscopic study. Thermal analysis was performed using a Toledo TGA/DSC-1 (Mettler) at a heating rate of 10°C/min over the 30–1200°C range under nitrogen atmosphere.

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