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Synthesis and characterization of neodymium oxide nanoparticles

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Abstract

The nanometric precursors of neodymium oxide of various morphology from fibrous to well-dispersed spheroidal were prepared via a solvothermal reaction routes. The precursors and their thermal evolution to neodymium oxide phase were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). It was found that the reaction parameters, kind of solvent as well as neodymium salt used played a key role for the product formation of desired morphology and structure. Similarly, kind of neodymium oxide precursor determined the morphology and the crystal structure (haxagonal or cubic) of the final oxide. The potential application of Nd_2O_3 precursors prepared by solvothermal method as convenient material for preparation of homogeneous thin coatings on planar substrates is shown.

Keywords: Nanostructures; Scanning and transmission electron microscopy

1. Introduction

Neodymium oxides are widely used in photonic applications (e.g. as phosphors providing yellow-to-violet upconversion emission [1]), as components for advanced materials (e.g. high temperature ceramics and superconductors) [2,3], as components of catalytic systems (oxidative coupling of methane, N_2 decomposition, dehydrogenation of alcohols, high-temperature processes) [4–6] and in many special applications (among others, to simulate the actinide oxides during testing the new materials as a host matrix for long life nuclear wastes [7]). Moreover, thin films of Nd_2O_3 are of interest for many other purposes such as optical antireflection coatings, gate insulators and protective coatings. For most of these applications the ultrafine (in nanometric scale) neodymium oxide with well-defined particle morphology is the most interesting material.

Neodymium oxide is usually prepared by the well-known chemical synthesis including sol–gels process with alkoxides as precursors. Because of the difficulties in the synthesis of rare earth alkoxides their usage as precursors is, however, unfavourable. We propose therefore, a modified sol–gel method using solvothermal treatment and simple neodymium salts. Solvothermal technique is also advantageous because it enables better control of the particle size distribution and morphology.

In this work, nanocrystalline neodymium oxide as well as it precursors were prepared by solvothermal treatment using alcohol or water as solvent and neodymium acetate or nitrate as raw material. The main purpose was to obtain Nd_2O_3 nanoparticles with various morphology.

2. Experimental

Neodymium nitrate and acetate, both prepared at our Institute, were used as starting materials. Other reagents were of analytical grade. The neodymium nitrate was prepared by dissolving the oxide in the concentrated nitric acid at room temperature and further evaporation of the excess acid in the water bath. The neodymium acetate was prepared by slow dissolution of the oxide in a hot acetic acid (glacial) and then vacuum evaporation of the excess acid at room temperature.

An appropriate amount of the neodymium salt (nitrate or acetate) was added into 300 ml distilled water (previously degassed at boiling temperature in order to remove CO_2) or alcohol (ethanol, butanol or methanol) with continuous stirring until it was completely dissolved. After that, a stainless steel autoclave equipped with glass vessel of 300 ml capacity was filled with prepared solution up to 80% of the total volume. The autoclave was sealed and maintained at temperature from the range 140–220 °C for 4–8 h with continuous

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stirring and then cooled to room temperature naturally. The light violet precipitate or sol was obtained. The former was filtered and washed with solvent used during synthesis (water or alcohol). The nanoparticles in the sol were concentrated and separated from the solvent by centrifugation. The products were dried in vacuum at ambient temperature for several hours and then heat treated at temperatures up to 800 °C to obtain the well-crystallized neodymium oxide.

Neodymium coatings were deposited on two different substrates: glass slide and stainless steel plate. The substrates were ultrasonically cleaned in an alcohol and then annealed at 140 °C for 1 h. The cleaned substrates were immersed lengthwise in the neodymium oxide sol, then taken out from the solution and left at ambient temperature until transparent gel film was formed. The coated substrates were heated in air at the rate of 5 °C/min from room temperature to 600 or 1100 °C in the case of glass and steel substrate, respectively. The procedures were repeated until Nd_2O_3 coatings of desired thickness (~5 μm) were obtained.

X-ray diffraction (XRD) measurements were performed on fresh and calcined samples for phase identification. Transmission electron microscopy (TEM) images were taken for

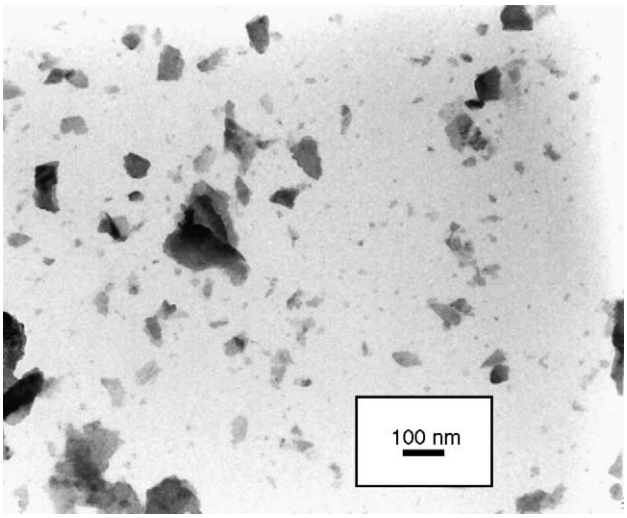

Fig. 2. TEM image of solvothermally prepared nanoparticles at 160 °C for 4 h using ethanol as solvent and neodymium nitrate as raw material.

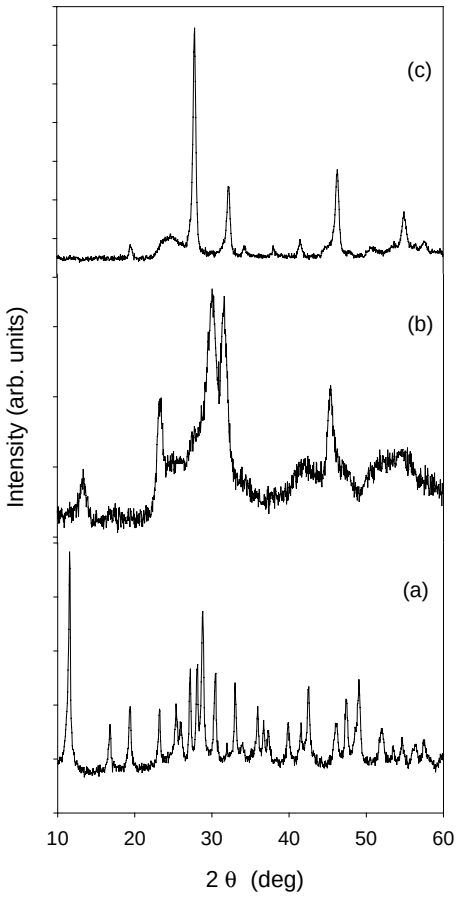

Fig. 1. XRD diffraction patterns of the sample prepared under solvothermal conditions ($T = 160$ °C, $t = 4$ h) using ethanol as solvent and neodymium nitrate as starting material: (a) as-prepared, (b) heated at 500 °C, (c) heated at 800 °C.

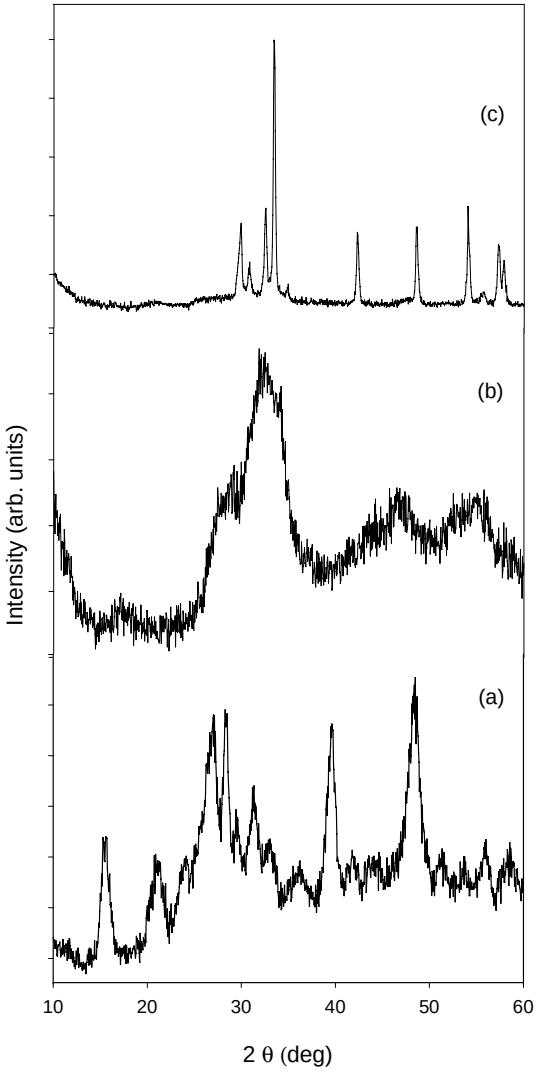

Fig. 3. XRD patterns of the sample synthesized under hydrothermal conditions ($T = 140$ °C, $t = 4$ h) using neodymium acetate as starting material: (a) as-prepared, (b) heated at 500 °C, (c) heated at 800 °C.

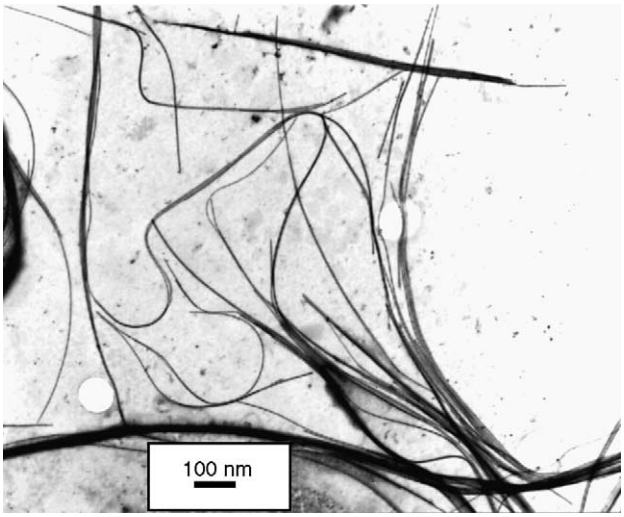

Fig. 4. TEM image of hydrothermally prepared fibrous nanoparticles at 140 °C for 4 h using neodymium acetate as precursor.

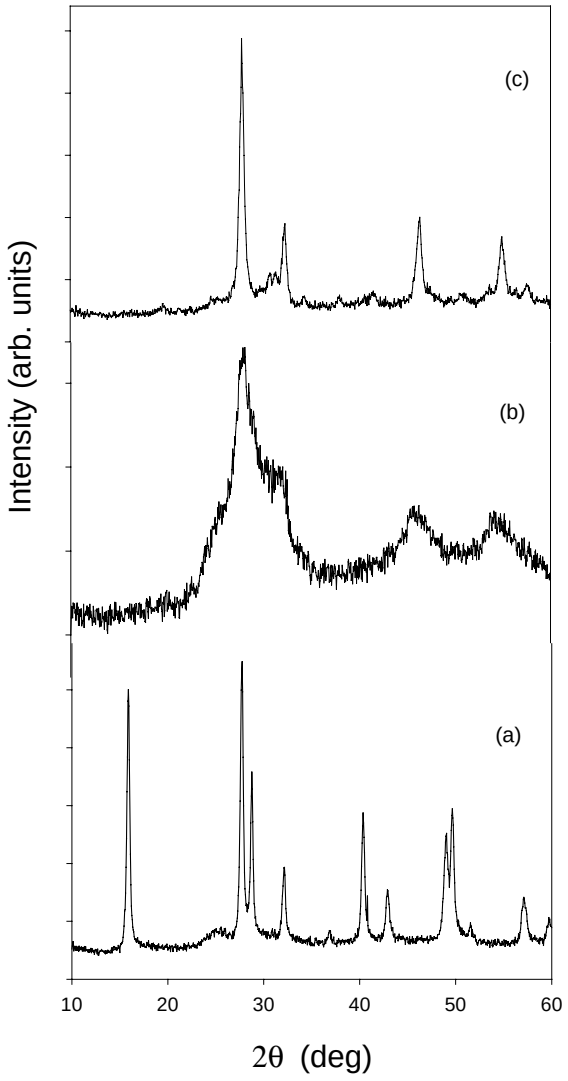

Fig. 5. XRD patterns of the sample synthesized under hydrothermal conditions ($T = 160\,^{\circ}C$, $t = 4\,h$) using neodymium acetate as starting material: (a) as-prepared, (b) heated at 500 °C, (c) heated at 800 °C.

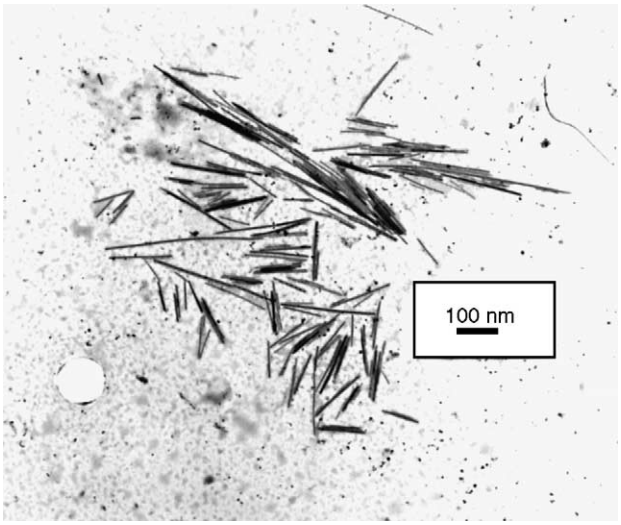

Fig. 6. TEM image of hydrothermally prepared needle-like nanoparticles at 160 °C for 4 h using neodymium acetate as precursor.

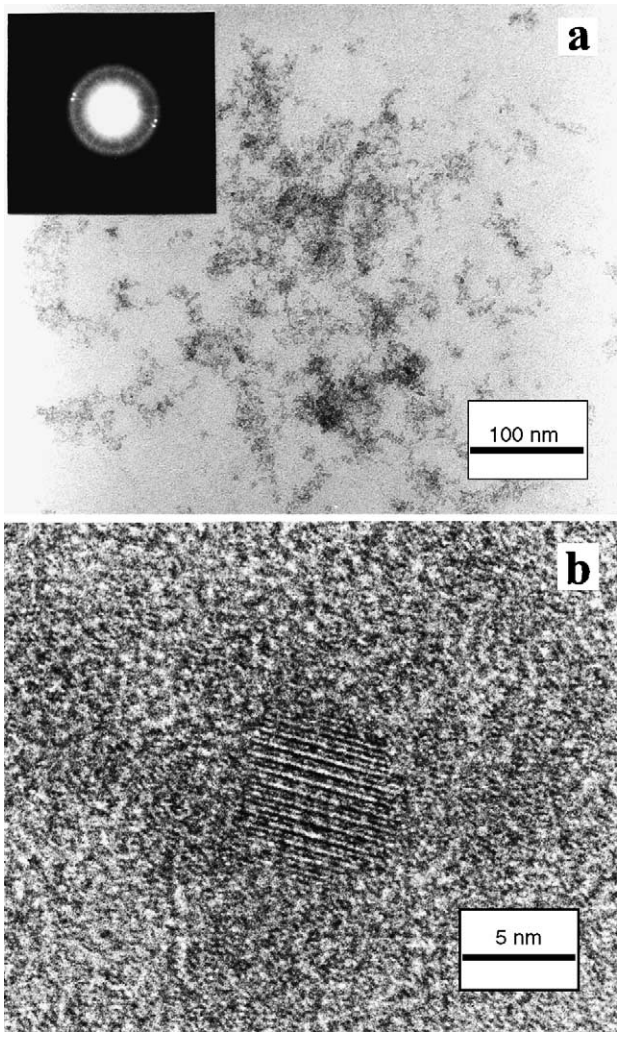

Fig. 7. TEM images of hydrothermally prepared spheroidal nanoparticles at 180 °C for 8 h using neodymium acetate as precursor ((a) low and (b) high magnification) with SAED pattern showing rings that match *d*-spacings for the structure of C-type neodymium oxide.

morphology determination of sol and powder particles. The average particle sizes of the samples were measured from TEM micrographs. The morphology of the Nd_2O_3 thin films coatings were observed in a scanning electron microscope and EDS analysis was used to check the surface composition of the films.

3. Results and discussion

Typical XRD patterns of the samples prepared by alcohothermal synthesis using ethanol as solvent and neodymium nitrate as raw material and calcined at various temperatures are shown in Fig. 1. The analysis of the XRD patterns indicates that as-prepared sample is neodymium dihydroxy-nitrate $Nd(OH)_2NO_3$ ([8], Fig. 1a) which decomposes after heat treatment at 800 °C to cubic Nd_2O_3 (JCPDS no. 21-0579, Fig. 1c) via the intermediate formation of neodymium oxicarbonate $Nd_2O_2CO_3$ (JCPDS no. 25-0567, Fig. 1b). Obtained C-type of neodymium oxide is probably stabilized by water and can be consider as a hydrate of the composition $Nd_2O_3 \cdot 0.3H_2O$ [9]. The morphology of as-prepared sample is shown in Fig. 2. It consists of irregular nanoparticles with various sizes. Similar results were obtained using another alcohol (methanol, propanol) and neodymium acetate as starting material.

The most interesting results were obtained during hydrothermal treatment of neodymium acetate. Fig. 3 presents XRD patterns of the sample prepared at 140 °C for 4 h and calcined at various temperatures. It appears that pure hexagonal phase of neodymium oxide was obtained after treatment at above 500 °C. TEM image in Fig. 4 shows that the as-prepared sample is composed of bunches up to several micrometers long each of them consisting of individual fibrous particles with diameter about 3 nm. The fibrous morphology

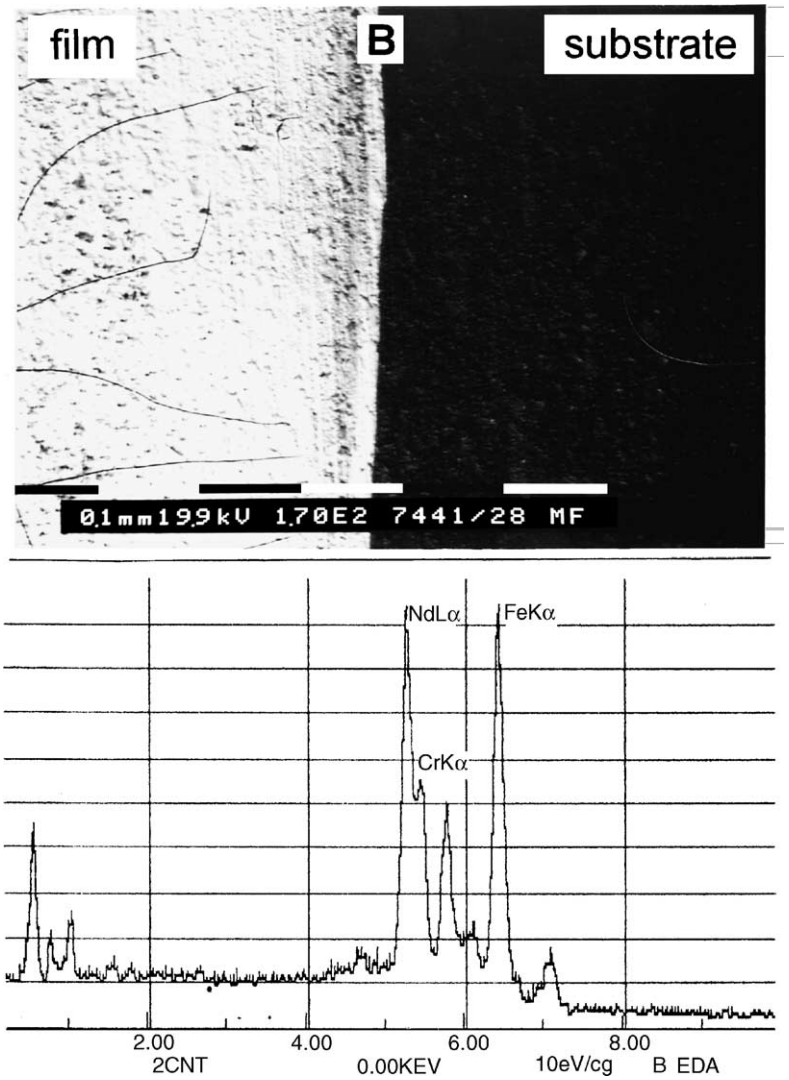

Fig. 8. SEM image of neodymium oxide thin film deposited on stainless steel substrate (prepared from fibrous precursor) and heated at 1100 °C. EDS analysis confirmed the presence of Nd_2O_3 film.

was preserved after heating to temperature when neodymium oxide was formed.

XRD patterns of the product obtained under hydrothermal treatment at 180 °C for 6 h and then calcined up to 800 °C are presented in Fig. 5. It appears that the as-prepared sample is well-crystallized $Nd(OH)_3$, which upon further heat treatment transformed into cubic neodymium oxide. The particles of neodymium hydroxide (seen in Fig. 6) were uniform exhibiting rod-like shape with an average diameter 4 and 200 nm long. At higher temperatures, aggregation of particles occurs and an increase in the particle size is readily noticeable.

TEM micrographs of typical product prepared under hydrothermal treatment of neodymium acetate at 220 °C for 8 h are shown in Fig. 7 (a: low, b: high magnification). From this figure, it is clear that obtained sol is composed of well-dispersed tiny particles. Corresponding selected area electron diffraction (SAED) pattern (Fig. 7a) exhibits two broad rings with *d*-spacings 0.315 and 0.196 nm, which could be attributed to (2 2 2) and (4 4 0) reflections of the cubic neodymium oxide structure, respectively ($a = 1.108$ nm, JCPDS no. 21-0579). The broadening of the diffraction rings suggests that the particles are small and/or are of low crystallinity. The average diameter of the as-prepared Nd_2O_3 particles estimated from TEM is about 8 nm and does not change upon heat treatment up to ∼500 °C. However, an increase of crystallinity and size of the particles was observed at temperatures higher than 500 °C. These results have been confirmed by XRD analysis.

Homogeneous and transparent neodymium oxide thin films with a good reproducibility were prepared on glass and stainless steel substrates by dip-coating process using hydrothermally prepared neodymium sols. Thin oxide films of Nd_2O_3 on glass substrates are interesting for optical applications and those deposited on steel are very useful for protection against corrosion at high temperature. Though stainless steels usually develop protective oxide layers in high temperature oxidation conditions they are often poorly adherent and destroy for a short time. Deposition of Nd_2O_3 thin film on stainless steel surface drastically improves the oxidation resistance of the metallic substrate under such conditions.

It was found that both coatings (prepared on glass or steel substrates) exhibit good adherence but the best result was obtained when fibrous precursor was used. A liquid film attached to the substrate becomes a gel film as a result of the gelling reaction in the ambient atmosphere after withdrawal from the coating solution. The substrate with a gel film is then heated in order to produce chemical bonding between the film and the substrate. This bonding is usually formed as a result of dehydration. SEM and EDS data shown in Fig. 8 indicate that neodymium oxide film on stainless steel substrate sustains as rather smooth and continuous coating with only small cracks, even after heat treatment at temperatures up to 1100 °C.

4. Conclusions

The nanometric precursors of neodymium oxide of fibrous or rod-like particle morphology were successfully obtained under hydrothermal conditions at relatively low temperature using simple neodymium salts as starting material. It was found that kind of the neodymium precursor determined the morphology, as well as the crystal structure (hexagonal or cubic) of the final oxide. Nd_2O_3 spheroidal nanoparticles <10 nm in diameter were directly prepared using the same synthesis method but at higher temperature and for a longer time. The dip-coating procedure was used for preparing thermally stable neodymium oxide thin films coatings on different substrates.

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