Research Article

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Novel Synthesis and Characterization of Lanthanum oxide Nanoparticles from Nano-sized Lanthanum(III) Compound

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ABSTRACT

A new nano-sized La (III) compound, La[$(N_2H_4)_2${$C_{10}H_6$(3-O)(2-COO)}$_{1.5}$].H_2O (X), was synthesized by the sonochemical method and characterized by field emission scanning electron microscope (FESEM), X-ray powder diffraction (XRD) and elemental analyses. Lanthanum oxide nanoparticles were prepared by direct thermal decomposition of nanostructures in a programmable furnace up to 800 °C in ambient atmosphere. The structural characterization was done by powder XRD, and morphological observations by FESEM revealed that the quasi-spherical La_2O_3 nanoparticles obtained are well crystallized and uniform in both morphology and particle size. The study demonstrates that supramolecular compounds may be suitable precursors for the simple one-pot preparation of nanoscale metal oxide materials with different morphologies.

Keywords: Nanoparticle; Supramolecule; Novel precursor; Lanthanum oxide; Sonochemical method.

1. INTRODUCTION

Inorganic materials have become more significant as a result of the wide range of intriguing and practical uses they offer in the materials sciences. The fact that properties of nanomaterials differ from those of bulk morphological forms is widely established. For the synthesis of nanostructural materials with various morphological shapes and size distributions, several techniques have been devised (Yazdan Parast *et al*. 2011). Because metal-coordinated supramolecular compounds have numerous potential uses in molecular adsorption, catalysis, magnetism, luminescence, nonlinear optics, and molecular sensing, chemists and material scientists have extensively researched them. (Safarifard *et al*. 2012).

Numerous scientific domains have conducted extensive research into the possible applications of one-dimensional nano-scale materials. The peculiar configuration of their 4f electrons gives lanthanides their distinctive optical, catalytic, and magnetic capabilities, making them an attractive class of elements. Due to its uses as a hydrogen storage material, an electrode, a sorbent, and a gate insulator among other lanthanum-based compounds, lanthanum oxide is of particular research interest (Ersoy *et al*. 2004; Chen *et al*. 2005). La_2O_3 has also drawn more attention as a result of its widespread use in thermoelectricity, galvanothermy, piezoelectricity, light-emitting phosphors, catalyst supports, and vehicle exhaust gas convector parts. (Rambabu *et al*. 2013; Long *et al*. 2013; Lu and Wanjun, 2012; Mao *et al*. 2012; Rocha *et al*. 2012).Rare earth oxides can now be prepared using a variety of methods to form ultrafine nanopowders. High-energy ball milling, sonochemical, hydrothermal, sol-gel, and spray deposition methods are a few of these (Soofivand *et al*. 2013; Abed *et al*. 2013; Wu *et al*. 2013; Ranjbar *et al*. 2012). This paper describes a simple calcination method for the preparation of La_2O_3 nanoparticles from a compound, La[$(N_2H_4)_2${$C_{10}H_6$(3-O)(2-COO)}$_{1.5}$].H_2O, where in nanostructured compound was synthesized by the reaction of lanthanum(III)hydroxy naphthoate and hydrazine.

2. EXPERIMENTAL SECTION

2.1 Materials and Physical Techniques

All of the chemicals used in this study were of analytical reagent grade. All solutions were prepared using double distilled water. A multiwave ultrasonic generator, equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for ultrasonic irradiation. Melting points were measured with a Thermo Scientific 9200 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus rapid analyzer. The La content in the complex was determined by EDTA

complexometric titration. X-ray powder diffraction (XRD) measurements were performed using an INEL Equinox 3000 diffractometer with monochromated CuKα (K = 1.5418 A˚) radiation at room temperature from 2θ =10°-60°.The crystallite sizes of selected samples were estimated using the Scherrer formula. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software. Field emission scanning electron microscope (FESEM) photographs were taken on a ZEISS PIGMA VP apparatus equipped with an energy dispersive X-ray (EDAX) microanalysis with gold coating.

2.2 Synthesis of Nano-sized La[$(N_2H_4)_2${$C_{10}H_6$(3-O)(2-COO)}$_{1.5}$].H_2O by the Sonochemical Method

To prepare the nanoparticles of X, lanthanum(III) nitrate hexahydrate (0.389 g, 0.9 mmol) was dissolved in water (20 ml) and placed in a vessel of a high-density ultrasonicprobe running at 20 kHz with a maximum power output of 600 W. Into this solution, a proper volume of ligand N_2H_4 (0.5 g, 1.8 mmol) in water was added dropwise. After 1hour, a light-yellow precipitate was formed, which was isolated by centrifugation (4,000 rpm, 15 min), washed with water and acetone to remove residual impurities and dried in air (0.55 g, yield = 62 %). d.p.250 ℃. Anal. Calc. (%) for La[$(N_2H_4)_2${$C_{10}H_6$(3-O)(2-COO)}$_{1.5}$].H_2O: C, 36.00; H, 3.15; N, 11.05; La, 21.93 found (%): C, 35.94; H, 3.18; N, 10.97; La, 22.02. For the preparation of lanthanum oxide nanoparticle, calcination of (X) was carried out at 800℃ at a heating rate of 5℃/min in air. After cooling, a white precipitate was obtained. All the organic components were volatilized and La_2O_3 nanostructures were produced. The XRD pattern (Fig. 1) shows that the product is La_2O_3 nanoparticle.

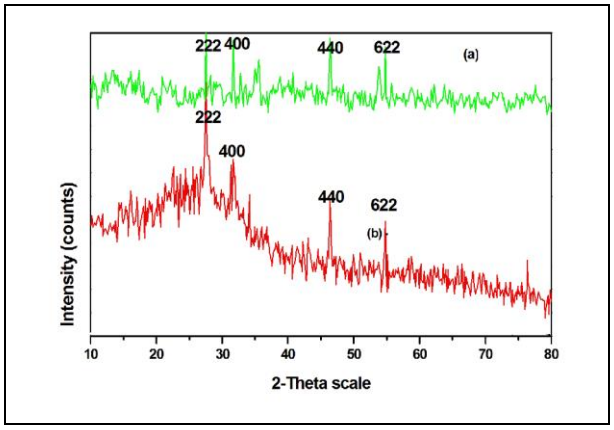
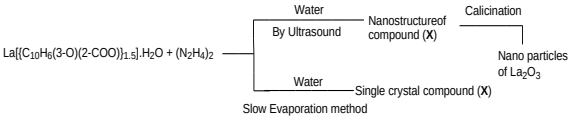


Fig. 1: XRD patterns; a stimulated pattern based on Single crystal data(a) and (b) nano structure of (X) prepared by Sonochemical method

3. RESULTS AND DISCUSSION

The reaction of ligand (N_2H_4) with La{$C_{10}H_6$(3-O)(2-COO)}$_{1.5}$].H_2O in water using the ultrasonic method at ambient temperature and atmospheric pressure leads to the formation of a nano-sized La(III) supramolecular compound.The complex displayed a distinct melting point and the elemental analysis is consistent with the formula La$_2$[$(N_2H_4)_2${$C_{10}H_6$(3-O)(2-COO)}$_{1.5}$].H_2O (X). Scheme .1 provides an overview of the synthesis using two different routes. Figure 1 shows the simulated XRD pattern of the single crystal X-ray data of (X) (Fig.1a) compared to the XRD pattern of a sample (X) prepared by the sonochemical method (Fig.1b). Acceptable matches are seen between the simulated and experimental powder XRD patterns, with only minor deviations in 2θ. This indicates that the substance produced by the sonochemical process has a single crystalline phase.



Scheme 1: Compound preparation methods

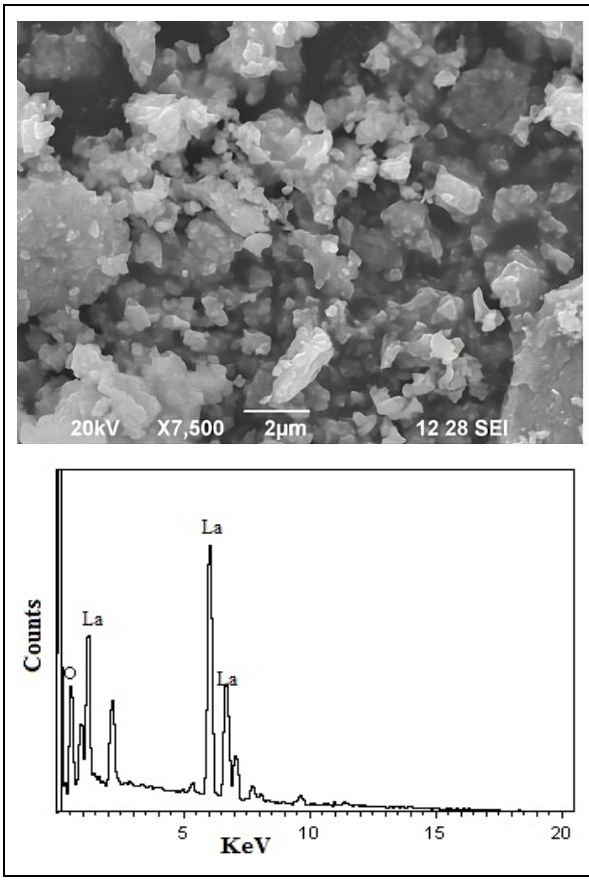


Fig. 2: FESEM photograph and EDAX analysis of La_2O_3

The notable widening of the peaks suggests that the particles are nanometer-sized (Moghimi *et al*. 2002). Calculating particle sizes from the XRD peaks (D = 0.891 λ/βcosθ, where D is the average grain size, λ is the X-ray

wavelength (1.5418 Å), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively (Jenkins *et al*. 1996). The average size of the particles, estimated from Scherrer formula is 60 nm. This size is in agreement with the value obtained from the FESEM image (Fig. 2). The structures (X) consist of six-membered 3-hydroxy – 2 - naphoate ring and hydrazine connects to the one metal fragment. Each La atom is surrounded by nine coordinated atoms in a geometry known as the bicapped square antiprismatic geometry. Six O- and four N-donor atoms surround by each La atom (Fig. 3).

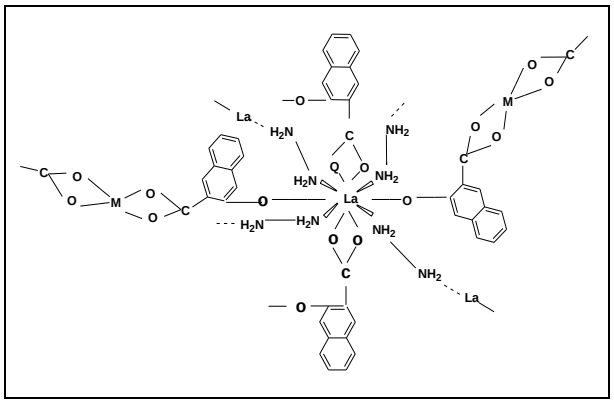


Fig. 3: Structure of $La[(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}_{1.5}].H_2O$

XRD was used to study the composition and phase data of the final calcination product. The XRD pattern of the lanthanum oxide obtained from calcination La compoundat 800℃. It is concluded that La_2O_3 nanoparticle is obtained in high purity; i.e., the pattern matches that of La_2O_3 with a hexagonal structure (space group P3-m1 with lattice parameters a = 3.9471 A˚, b = 3.9470 A˚, and c = 6.1299 A˚, JCPDS No. 05-0602). The strong diffraction peaks reveal thatwell-crystallized lanthanum oxide may be produced using this synthetic method. The FESEM pictures and the widening of the peaks show that the particles are on the nanometer scale. According to the Scherrer equation, the average particle size is 60 nm. The morphology and size of the lanthanum oxide nanoparticles revealed homogenous, quasi-spherical La_2O_3 nanoparticles at the nanometer scale. The particle separation and size distribution are good. The size distribution histogram of La_2O_3 nanoparticles (100–120 nm) shows a largely uniform distribution. EDAX analysis of the La_2O_3 nanoparticles (Fig. 2) reveals that lanthanum is the only fundamental component present. This demonstrates that the end result of direct calcination La compoundwas made entirely of pure La_2O_3 nanoparticles.

4. CONCLUSION

The sonochemical approach was used to successfully synthesise a nano-sized La(III) $La_2[(N_2H_4)_2\{C_{10}H_6(3\text{-}O)(2\text{-}COO)\}_{1.5}].H_2O$, and its crystalline structure was compared. At 800℃, the compound broke down in air to form La_2O_3 nanoparticles. FESEM, EDAX, and XRD methods were used to characterise La_2O_3 nanoparticles. The XRD pattern confirms theformations of well-crystallized lanthanum oxide nanoparticles are formed. The sonochemical process is quick, and the final product has consistent nanometer-sized particles that are well separated. In this method, no additives are necessary to produce nanoparticles. This study demonstrates that supramolecular compounds might be appropriate precursors for the production of metal oxide nanoparticles with unique morphologies.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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