Synthesis and Characterization of Lanthanum Oxide \( \text{La}_2\text{O}_3 \) Net-like Nanoparticles By New Combustion Method

Waleed Madhloom Khalaf 1*, Mohammed H. Al-Mashhadani 2*

1 Ministry of Interior, Iraqi Police College, Baghdad, Iraq; waleedalogedy@yahoo.com (W.M.K.);
2 Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq; mashhadani@ced.nahrainuniv.edu.iq (M.H.A.-M.);
* Correspondence: mo_chemical@yahoo.com (M.H.A.-M.);

Abstract: Herein is a new procedure to synthesize lanthanum oxide \( \text{La}_2\text{O}_3 \) nanoparticles, which is eco-friendly and simple. The \( \text{La}_2\text{O}_3 \) nanoparticles were prepared by sol-gel method using modification in time of stirring, type of PEG, and temperature of the reaction. Scherer’s formula was used to estimate the average crystallite of \( \text{La}_2\text{O}_3 \) nanoparticle size from X-ray diffraction peaks of powder. The measured average particle size of \( \text{La}_2\text{O}_3 \) nanoparticles using the major signals of the X-ray diffraction spectrum after calcination was 37 nm. Fourier Transform Infrared Spectroscopy technique was done to analyze the chemical structure of synthesized materials. The surface morphology of obtained nanoparticles was also studied by SEM and AFM techniques. Thermal gravimetric analysis was investigated by Thermogravimetric analysis (TGA) to confirm the thermal stability of synthesized nanoparticles.

Keywords: lanthanum oxide \( \text{La}_2\text{O}_3 \), combustion method; nanoparticles; X-ray diffraction films;

© 2021 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

In this century, Nano-materials science is considered one of the major promising and attractive subjects in the developed technology. Different terms of Nanomaterials can be found in the literature, such as nanoparticles, nanocrystals, nano-composites, nanotubes, etc. In general, all these terms are related to the materials’ nanostructure that is worth highlighting, and their structural features are well-defined in the scientific literature [1-5]. Nanomaterials usually demonstrate different features compare to other materials on bigger scales. In fact, the most common nanoscales that researchers have studied are in the range of 1-100 nm. Several important organic and inorganic materials have been synthesized in nanoparticle scale, and one of these compounds is complex oxides [6-9]. Lanthanum oxide \( \text{La}_2\text{O}_3 \) and other metallic oxide have very attractive properties, which make them suitable for a lot of applications such as catalysts [10], optical filters [11], metal support [12, 13], water treatment [14-17], and dielectric material [18, 19]. Last decades, the synthesis of novel nano complex oxides with uniform crystalline nano size, high purity, and homogeneity had brought much attention by researchers [20]. Nowadays, many approaches have been followed to synthesize them, for example, hydrothermal microwave synthesis [21, 22], Solution combustion method [23], reverse micelle approach [24], sol-gel processing [25], Pechini procedure [26], precipitation from aqueous solution method [27] and solution combustion approach utilizing altered fuel and a chelating agent such as glutaric acid and propylene glycol [28]. This work demonstrated the synthesis of \( \text{La}_2\text{O}_3 \) nanoparticles utilizing the combustion method by dissolving bulk \( \text{La}_2\text{O}_3 \) in nitric acid to
form lanthanum oxide, which is converted to nanoparticles of La₂O₃ after calcination step at 850 °C. This is a very simple and cheap method to synthesize nanoparticles of La₂O₃.

2. Materials and Methods

2.1. Instrumentation.

X-Ray Diffraction (XRD) technique was utilized to record the XRD of synthesized nanoparticle materials using the SHIMADZU 6000 machine. A high-intensity Cu Kα radiation (λ=1.54060 Å) was applied; furthermore, the graphite monochromatic source was also used to radiate and generate at 40 kV and 30 mA. Fourier transfer infrared (FTIR) technique was also exhibited using a range between 400 cm⁻¹ to 4000 cm⁻¹ wavenumbers. Scanning electron microscope (SEM) Inspect S50 (FEI, Czech Republic) and AFM (Atomic Force Microscope) techniques were utilized to exam the surface morphology of synthesized nanoparticles. TGA technique was used to examine lanthanum carbonate's thermal stability by combustion way and after converted to La₂O₃ NPs.

2.2. Synthesis La₂O₃ by combustion method

The synthesis of La₂O₃ dissolve 1.4 g of lanthanum oxide bulk powder in 16 ml 23% HNO₃ and filter the solution using vacuum filtration 450 nm filter paper, dissolve 1.09 g of PEG in the filtered solution, and heat the mixture at 90 °C for 170 minutes in a water bath with the steering to forming the "gel" after this dry the gel at 92 °C for 86 hours and 15 minutes, forming the lanthanum nitrate, yellowish is then milled the product using a mortar, and the lanthanum nitrate is burnt at 300 °C in an oven for forming lanthanum carbonate gray color after this calcination at 850 °C for 3h to forming La₂O₃ nanoparticles, the weighing before calcination was 0.0658gm and after the calcination was 0.0562gm the diagram of this procedure can be schematic flowed Scheme 1 and characterization by XRD, FTIR, SEM, TGA, AFM Techniques.

3. Results and Discussion

3.1. Synthesis La₂O₃ net-like nanoparticles by combustion method

Xingang Wang et al. [29] was prepared La₂O₃ NPs by sol-gel method were used PEG (Mwt 20000) with a reaction time of 80 h, but in this work, we synthesized La₂O₃ with modification in time of stirring, type of PEG, and temperature of the reaction. To synthesis of La₂O₃ NPs dissolve 1.4 g (4.29X10⁻³ mol) of lanthanum oxide bulk powder in 16 ml 23% HNO₃ and filter the solution using vacuum filtration 450 nm filter paper, for 30 min then dissolve (0.27 mmol, 1.09 g) of (PEG4000 Mwt) polyethylene glycol in the filtered solution. After that, the mixture was heated at 90 °C for 170 minutes in a water bath with steering for 3h to form the "gel". Then the mixture was left to dry in an electric oven at 90 °C for 90 hours, forming lanthanum nitrate, yellowish. Then milled the product by mortar and burned at 300 °C for 30 min in an electric oven to form a lanthanum carbonate gray color. After that, calcination lanthanum carbonate at 850 °C for 3 h to be converted into the corresponding La₂O₃ nanopowder. The weighing before calcination was (0.0658 g), and after calcination was (0.0562 g). The characterization by XRD, FTIR, SEM, TGA, AFM techniques as will discuss in the next sections. This procedure can describe by Scheme 1.
3.2. X-ray diffract analysis (XRD)

Powder X-ray diffraction (XRD) patterns of La$_2$O$_3$ prepared by combustion method are shown in Figure 1. The main peaks observed at peak 2Ө (deg) 28.1°, 30.1°, 40°, and 48.2°, ° correspond respectively, to the planes(100,101, 102, and 110,) this results in agreement with the JCPDS card Nos 05-0602 [8,15,16,17, 18,19,20,21 La$_2$O$_3$] which corresponds to the hexagonal phase of La$_2$O$_3$ calcination at 850 C. The peaks observed at 2Ө around 16.0° and
42.1° to the planes (100 and 201) correspond, respectively; this refers to La$_2$O$_2$CO$_3$ compound [17 and 27 La$_2$O$_3$]. These patterns are in agreement with card Nos (JCPDS 84-1963). Scherer's Formula 1 was used to propose the average crystallite sizes (d) of synthesized La$_2$O$_3$ compounds.

$$d = \frac{K \lambda}{\beta \cos \theta}$$

Hence $K$ is a constant usually 0.9, and it belongs to the crystallite shape of prepared materials, $\lambda$ is the wavelength of X-ray in nanometer, $\theta$ is theta or the diffraction angle, and $\beta$ is the peak width at half maximum height obtaining from small crystallite size in radians. All data obtained from the main signals of XRD of La$_2$O$_3$ were summarized in Table 1. The measured average particle size of La$_2$O$_3$ nanoparticles using the major signals of the X-ray diffraction spectrum after calcination was 37 nm.

![Figure 1. XRD patterns of L$_2$O$_3$ obtained by combustion method calcination at 850 °C.](image)

<table>
<thead>
<tr>
<th>Peak (deg)</th>
<th>2θ</th>
<th>d(Å)</th>
<th>FWHM</th>
<th>Size diameter (nm)</th>
<th>Average size diameter (nm)</th>
<th>Morphology (SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28°</td>
<td>3.17</td>
<td>0.364</td>
<td>23</td>
<td></td>
<td>37</td>
<td>Net-like</td>
</tr>
<tr>
<td>30°</td>
<td>2.96</td>
<td>0.280</td>
<td>34.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40°</td>
<td>2.27</td>
<td>0.280</td>
<td>30.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48°</td>
<td>1.84</td>
<td>0.15</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3. Fourier-transform infrared (FTIR).

FTIR approach demonstrated the chemical structure of synthesized materials using a wavenumber range between 400–4000 cm$^{-1}$. The FTIR spectrum of La$_2$O$_3$ obtained from the combustion process is shown in Figure 2. The peaks observed in the region 3398.34–3336.62 cm$^{-1}$ are related to the stretching of the hydroxyl group, and at 1541.02 cm$^{-1}$ is belonged to the bending vibration of the same group due to the strongly adsorbed molecular water in the crystal lattice of La$_2$O$_3$ [30]. The peaks around 1541 cm$^{-1}$, 1419.51 cm$^{-1}$ and 1386.7 cm$^{-1}$ belong to asymmetric stretching of the C–O bond from La$_2$O$_2$CO$_3$. In addition, the medium band at 852 cm$^{-1}$ is related to CO$_3^{2-}$ stretching vibration that approves the formation of the carbonate. The peak observed at 563 cm$^{-1}$ belongs to the stretching of La–O, and this peak has demonstrated the formation of La$_2$O$_3$ after annealing at 850 °C.
3.4. Scanning electron microscope (SEM).

SEM technique was exhibited to study the synthesized La₂O₃ nanoparticles' surface morphology resulting from combustion methods at 92 °C in an electric oven and calcination at 850 °C, two typical SEM images of La₂O₃ powders. Figure 3 shows SEM images of synthesized La₂O₃ nanoparticles in different magnifications: (a) 2µm and (b) 500 nm. From images, many pores of different sizes can be seen, which could make these materials suitable for different adsorption applications such as gas storage. It also shows the formation of net-like shapes obtained with a size diameter range (26.4) nm, but Xingang Wang [29] was obtained Nano-sphere. These results agree with the calculations of Scherrer’s equation.
3.4. Atomic force microscope (AFM).

The AFM images of lanthanum oxide nanoparticles were obtained by adding 2 or 3 drops of synthesized La$_2$O$_3$ nanoparticles to acetone and sonicated for 30 minutes, then spell onto a glass slide. Then it was left to dry at room temperature. After that, the AFM images were taken. Figure 4 shows the AFM images of lanthanum oxide nanoparticles obtained from the combustion method at 90 °C in an electric oven and calcination at 850 °C. The results obtained by this technique are in agreement with the results obtained by SEM and Scherrer's equation. The average sizes of nanoparticles were about 56.54 nm.

3.5. Thermal gravimetric analysis.

The TGA was determined for prepared Lanthanum carbonate crystal by combustion method burn at 300 °C. In thermogravimetric analysis, the mass of a given material was measured as a temperature function by heating the material at a constant rate. The prepared
sample was heated at a rate of 20 °C per minute for this analysis. The variation of weight loss of the sample as a function of temperature is shown in Figure 5a. This figure shows three-step weight loss transitions. The weight loss was 2% at first at a temperature of about 110 °C due to the evaporation of water molecules within the crystal lattice of the particles, as shown by the TGA curve. The second step took place at a temperature of about 332.85 °C at a peak temperature 332.85 °C. Another weight loss of about 6.3% was observed at this temperature. The two steps may be attributed to the evaporation of water residue components from the complex, respectively. The final step happened at a temperature of about 671.2 °C at TGA temperature 671.2 °C by a weight loss of 15%. This step is attributed to the removal of carbonate molecules and was attributed to the complete transformation of lanthanum carbonate to needed stable lanthanum oxide nanocrystals. The TGA curve of La2O3 was got on combustion at 850 °C for 3h, as shown in Figure 5b. This figure shows three steps of weight loss transitions; in the first step, a weight loss of about 0.5% happened at range 30–88.4°C at a peak 88.9°C, as is demonstrated by the DTG curve. This step is due to the removal of residue water molecules embedded in the crystal lattice of the compound. The second step took place at a temperature range 88.9–313.2 °C at a peak temperature of 313.2 °C. Another weight loss of about 3.5 % was observed at temperature 313.2 °C at peak temperature 313.2°C. The two steps may be attributed to the evaporation of water residue components from the complex, respectively.

The final thermal decomposition step happened at range 313.2–626.2 °C at DTG 626.2°C with a weight loss of 4.5 %. This step is attributed to removing residue carbonate molecules and was attributed to the complete transformation of lanthanum carbonate to wanted stable lanthanum oxide nanocrystals. This smallest loss refers to the stability of lanthanum oxide calcination at 850 °C.
Figure 5. TGA and DTG of. (a) Lanthanum carbonate by combustion method; (b) La$_2$O$_3$ nanoparticles by combustion method.

4. Conclusions

To conclude, lanthanum oxide (La$_2$O$_3$) nanoparticles have been successfully synthesized utilizing a new combustion method considered an easy and eco-friendly method. The La$_2$O$_3$ nanoparticles were prepared by sol-gel method using modification in time of stirring, type of PEG, and reaction temperature. Different techniques were used to confirm the chemical structure and estimate the particle size of synthesized materials, such as X-ray diffraction and FTIR. SEM and AFM techniques were also done to study the surface morphology. Thus it was demonstrated the formation of net-like shapes with nanoparticle size 26.4 nm. Synthesized lanthanum oxide (La$_2$O$_3$) nanoparticles show excellent thermal stability by thermogravimetric analysis.

Funding

This research received no external funding.

Acknowledgments

We want to thank Baghdad University/College of Science for their technical support.

Conflicts of Interest

The authors declare no conflict of interest.

References


