Synthesis and Characterization of Lanthanum Oxide La$_2$O$_3$ Net-like Nanoparticles By New Combustion Method

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Abstract: Herein is a new procedure to synthesize lanthanum oxide (La$_2$O$_3$) nanoparticles, which is eco-friendly and simple. The La$_2$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 La$_2$O$_3$ nanoparticle size from X-ray diffraction peaks of powder. 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. 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 (La$_2$O$_3$), combustion method; nanoparticles; X-ray diffraction films;

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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 La$_2$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 La$_2$O$_3$ nanoparticles utilizing the combustion method by dissolving bulk La$_2$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=1.5406Å) 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 examine 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 (4.29×10⁻³ 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 mimed 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 20 (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 20 around 16.0° and
42.1° to the planes (100 and 201) correspond, respectively; this refers to La$_2$O$_3$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 1. Data obtained from main peaks of XRD pattern.

| Peak (deg) | 2θ | d(Å) | FWHM | Size diameter (nm) | Average size diameter (nm) | Morphology (SEM) |
|------------|----|------|------|-------------------|---------------------------|------------------|
| 28°        |    | 3.17 | 0.364| 23                | 37                        | Net-like         |
| 30°        |    | 2.96 | 0.280| 34.5              |                           |                  |
| 40°        |    | 2.27 | 0.280| 30.6              |                           |                  |
| 48°        |    | 1.84 | 0.15 | 60                |                           |                  |

### 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$_3$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.
Figure 2. FTIR spectra of La$_2$O$_3$ produced by combustion method calcination at 850 °C.

3.4. Scanning electron microscope (SEM).

SEM technique was exhibited to study the synthesized La$_2$O$_3$ nanoparticles' surface morphology resulting from combustion methods at 92 °C in an electric oven and calcination at 850 °C, two typical SEM images of La$_2$O$_3$ powders. Figure 3 shows SEM images of synthesized La$_2$O$_3$ 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.

![TGA and DTG curve for sam G](https://biointerfaceresearch.com/)

Onset Y = 99.0698 %
Onset X = 92.54 °C

Onset Y = 88.7442 %
Onset X = 297.22 °C
Onset Y = 74.5116 %
Onset X = 600.39 °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.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Yıldız, A.; Kara, A.A.; Acartürk, F. Peptide-protein based nanofibers in pharmaceutical and biomedical applications. *Int. J. Biol. Macromol.* 2020, 148, 1084–1097, https://doi.org/10.1016/j.ijbiomac.2019.12.275.
2. Taslak, H.D.; Gurel, G.B.; Ozcan, O.; Tunali-Akbay, T. Usage of bioactivated PCL nanofiber as a fluoxetine capturing matrix in milk. *Sep. Sci. Technol.* 2019, 55, 828–834, https://doi.org/10.1080/01496395.2019.1574829.
3. Tunali-Akbay T.; Vezir Kahraman M.; Oktay, B.; İpekci, H.; Kayaman-Aphoon, N. Bioactivated poly (vinyl alcohol) /poly(acrylic acid) based nanofiber for high-performance membrane techniques. Letters in Applied NanoBioScience. 2020. 9, 819–823, https://doi.org/10.33263/LIANBS91.819823.

4. Pradhan, S.; Biswas, S.; Das, D.K.; Bhar, R.; Bandyopahdyay, R.; Pramanik, P. An efficient electrode for simultaneous determination of guanine and adenine using nano-sized lead telluride with graphene. New J. Chem. 2018, 42, 564–573, https://doi.org/10.1039/C7NJ03308G.

5. Kumar, Y.; Kumar Vashishta, V.; Kumar Das D. Synthesis of perovskite type NdFeO3 nanoparticles and used as electrochemical sensor for detection of paracetamol. Letters in Applied NanoBioScience. 2020. 9, 866–869, https://doi.org/10.33263/LIANBS91.866869.

6. Khanna, P.; Kaur, A.; Goyal, D. Algae-based metallic nanoparticles: Synthesis, characterization and applications. Journal of Microbiological Methods 2019, 163, 105656, https://doi.org/10.1016/j.mimet.2019.105656.

7. Pathak, J.; Ahmed, H.; Singh, D.K.; Pandey, A.; Singh, S.P.; Sinha, R.P. Recent developments in green synthesis of metal nanoparticles utilizing cyanobacterial cell factories. Nanomaterials in Plants, Algae and Microorganisms: Elsevier. 2019, 237-65, http://dx.doi.org/10.1016/B978-0-12-811488-9.00012-3.

8. Khosravi-Darani K.; Gomes da Cruz, A.; Shamloo, E.; Abdimoghaddam Z.; Mozafari, M. R.; Green synthesis of metallic nanoparticles using algae and microalgae. Letters in Applied NanoBioScience. 2019, 8, 666–670, https://doi.org/10.33263/LIANBS83.666670.

9. Ezzat, H. A.; Gomaa, I.; Gavad, A-E. A.; Osman, O.; Mahmoud, A.; Abdel-Aal, M. S.; Elhaes, H.; Ibrahem, M. A. Semiempirical Molecular Modeling Analyses for Graphene/Nickel Oxide Nanocomposite. Letters in Applied NanoBioScience. 2020. 9, 1459–1466, https://doi.org/10.33263/LIANBS94.14591466.

10. Ghiasi, M.; Malekzadeh, A. Synthesis, characterization and photocatalytic properties of lanthanum oxy-carbonate, lanthanum oxide and lanthanum hydroxide nanoparticles. Superlattices Microstruct. 2015, 77, 295–304, https://doi.org/10.1016/j.spmi.2014.09.027.

11. Shinde, V.G.; Gaikwad, V.B.; Deore, M.K. Synthesis of Lanthanum Oxide (La2O3) Nanoparticles by Hydrothermal method and studies its Physical Properties. International Journal of Chemical and Physical Sciences. 2018. 7, 669–74.

12. Hereijgers, BP.; Weckhuysen, BM. Selective oxidation of methanol to hydrogen over gold catalysts promoted by alkaline-earth-metal and lanthanum oxides. ChemSusChem. 2009. 2, 743–748, https://doi.org/10.1002/cssc.200900108.

13. Nowicki, W.; Gąsowska, A.; Kirszenstztein, P. Investigation of interaction between the Pt(II) ions and aminosilane-modified silica surface in heterogeneous system. Appl Surf Sci. 2016. 371, 294–503, https://doi.org/10.1016/j.apsusc.2016.03.006.

14. Joshi, N.C.; Singh, A. Adsorptive performances and characterisations of biologically synthesised zinc oxide based nanosorbent (ZOB). Groundwater for Sustainable Development 2020, 10, https://doi.org/10.1016/j.gsd.2019.100325.

15. Joshi, N.C.; Malik, N.; Singh, A. Synthesis and Characterizations of Polythiophene–Al 2 O 3 Based Nanosorbent and Its Applications in the Removal of Pb 2+, Cd 2+ and Zn 2+ Ions. Journal of Inorganic and Organometallic Polymers and Materials 2020. 30, 1438-1447, https://doi.org/10.1007/s10904-019-01252-7.

16. Joshi, N.C.; Chodhary, A.; Prakash, Y.; Singh, A. Green synthesis and characterization of α-Fe2O3 nanoparticles using Leaf Extract of Syzygium cumini and their suitability for adsorption of Cu(II) and Pb(II) ions. Asian Journal of Pharmaceutical and Clinical Research 2019, 31, 809-1814, https://doi.org/10.14233/ajphcr.2019.22024.

17. Joshi, N.C.; Malik, S.; Gururani, P. Utilization of Polyppyrole/ZnO Nanocomposite in the Adsorptive Removal of Cu2+, Pb2+ and Cd2+ Ions from Wastewater. Letters in Applied NanoBioScience. 2021, 10, 2339–2351, https://doi.org/10.33263/LIANBS103.23392351.

18. Wong, H.; Zhou, J.; Zhang, J.; Jin, H.; Kakushima, K.; Iwai, H. The interfaces of lanthanum oxide-based subnanometer EOT gate dielectrics. Nanoscale Res Lett. 2014, 9, 472–477, https://doi.org/10.1186/1556-276X-9-472.

19. Zhao, Y. Design of higher-k and more stable rare earth oxides as gate dielectrics for advanced CMOS devices. Materials 2012, 5, 1413–1438, https://doi.org/10.3390/ma5081413.

20. Pathan, A.A.; Desai, K.R.; Bhasin, C.P. Synthesis of La2O3 Nanoparticles Using Glutaric Acid and Propylene Glycol for Future CMOS Applications. International journal of Nanomaterials and Chemistry 2017, 3, 21–25, http://dx.doi.org/10.18576/ijnc/030201.

21. Bikshalu, K.; Reddy, V.S.K.; Reddy, P.C.S.; Rao, K.V. Synthesis of La2O3 Nanoparticles by Pechini Method for Future CMOS Applications. International Journal of Education and Applied Research 2014, 4, 12–15.

22. Krishnaveni, T.; Murthy, S.R.; Gao, F.; Lu, Q.; Komarneni, S. Microwave Hydrothermal Synthesis of Nanosize Ta2O5 Added Mg-Cu-Zn Ferrites. Journal of Materials Science 2006, 41, 1471–1474, https://doi.org/10.1117/12.598201.

23. Kalantari, Z.; Bolaghi, S.; Masoudpanah M.; Hasheminiasari, M. Photocatalytic activity of ZnO/RGO composite synthesized by one-pot solution combustion method. Material Research Bulletin 2019, 115, 191–195, https://doi.org/10.1016/j.materresbull.2019.03.024.
24. Li, H.; Xue, J.; Liu, Z.; Wang, Y.; Lv, Z.-G.; Jian Zhou, X.; Wang, W.-C.; Liu J.; Tang J. Reversible phase-transfer mediated single reverse micelle towards synthesis of silver nanocrystals. *Sci. China Technol. Sci.* 2020, 63, 1–5. https://doi.org/10.1007/s11431-020-1572-3.

25. Kim, W.C.; Kim, S.J.; Lee, S.W.; Kim, C.S. Growth of Ultrafine NiZnCu Ferrite and Magnetic Properties by a Sol-Gel Method. *Journal of Magnetism and Magnetic Materials* 2001, 226, 1418-1420.

26. Rodrigues, E.S.; Silva, M.S.; Azevedo, W.M.; Feitosa, S. S.; Stingl, A.; Farias, P. M. A. ZnO nanoparticles with tunable bandgap obtained by modified Pechini method. *Appl. Phys. A*. 2019, 125, 504. https://doi.org/10.1007/s00339-019-2805-4.

27. Ghosh Chaudhuri, R.; Paria, S. Core/shell nanoparticles: Classes, properties, synthesis mechanisms, characterization, and applications. *Chem Rev* 2011, 111, 2373–2433.

28. Pathan, A.A.; Desai, K.R.; Bhasin, C.P. Synthesis of La₂O₃ Nanoparticles Using Glutaric Acid and Propylene Glycol for Future CMOS Applications. *International journal of Nanomaterials and Chemistry* 2017, 3, 21–25, http://dx.doi.org/10.18576/ijnc/030201.

29. Wang, X.; Wang, M.; Song, H.; Ding, B. A simple sol–gel technique for preparing lanthanum oxide nanopowders. *Materials Letters* 2006, 60, 2261–2265, http://dx.doi.org/10.1016/j.matlet.2005.12.142.

30. Verma, N. K. Study on the controlled growth of lanthanum hydroxide and manganese oxide nano composite under the presence of cationic surfactant. *Advances in Materials* 2015, 4, 11–15, http://dx.doi.org/10.11648/j.am.20150401.13.