Structural characterization of LaCoO₃ perovskite nanoparticles synthesized by sol–gel autocombustion method

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Abstract
Nanostructure perovskites such as LaMO₃ (where M = transition metal such as Mn, Co, Ni, and Fe) have captured attention in materials science fields due to their promising catalytic properties. In this study, the LaCoO₃ perovskite nanoparticles were synthesized by a two-step route via the sol–gel autocombustion method. In this method, lanthanum nitrate and cobalt nitrate were used as metal sources, after dissolving in distilled water. PVP was used as a surfactant, while urea and glycine were applied as fuel. The sol was formed at the stirring stage at 60°C, and then continued to gelation through water evaporation at 90°C, to end up in the autocombustion state. The product of combustion was washed, centrifuged three times, and heat-treated at 600°C for 2 h. Synthesized nanoparticles were characterized by scanning electron microscopy, X-ray powder diffraction (XRD), and particle size analyzer. Characterization results show that nanoparticles were synthesized in a narrow size range, below 100 nm, with perovskite structure using sol–gel autocombustion method; these particles were spherical in shape and without visible porosity on the surface. The purity and crystalline size of nanoparticles were studied through XRD analysis indicating that variation in these parameters depends on the fuel and fuel-to-oxidizer ratio, as impurities decreased by increasing the fuel ratio, for both glycine and urea. In addition, using glycine is demonstrated to result in better purity as compared with urea as fuel.

KEYWORDS
autocombustion, LaCoO₃, nanoparticle, nanostructure, perovskite, sol–gel, structural characterization

1 | INTRODUCTION

Metal oxide nanoparticles have certain properties that include optical, magnetic, electrical, catalytic, mechanical strength, thermal stability, and chemical properties which make them attractive for industrial use. The production of metal oxide...
nanoparticles is carried out through diverse chemical methods, including sol–gel, reduction–oxidation, hydrothermal hydroxide oxidation, and metal-salts decomposition. In order to find the most attractive method of synthesis, parameters such as production cost, ability to operate continuously, and production rate are considered. The solution combustion synthesis (SCS) or sol–gel auto combustion method appears to be a promising method due to its low production cost since it requires low-cost precursor materials and equipment. This method allows synthesis of a wider range of metal oxides nanoparticles, and also shows to be more efficient compared with other methods.1-5

The perovskite oxides are mixed metal oxides with the general formula AMO₃, where A is a larger cation (usually an alkaline-earth or rare-earth metal cation) and M is the smaller cation (usually a transition metal cation: e.g., Mn, Co, Fe, Ni) surrounded by six oxygen atoms in an octahedral coordination.6 However, perovskite oxides of the form LaMO₃, where M is a transition metal, containing Mn, Co, Fe, and Ni have been synthesized in different structures such as nanostructured films, hollow spheres, and mesoporous nanowires, nanoparticles, porous, and fibrous structures,7-12 and have been used in variety of applications, including gas sensors (CO, propane, and ethanol sensing), photocatalytic reduction of CO₂ with visible light, electronic devices, electrochemical systems, solid oxide fuel cell, solar cells, and catalysts.11,13-21 Similarly, to synthesize and develop the perovskite phase of LaCoO₃ as nanoparticles and nanowires, different methods have been used. These methods include thermal decomposition, hydrothermal decomposition, microwave-assisted coprecipitation, coprecipitation, spray-flame, sol–gel, and combustion methods. With the exception of sol–gel and combustion, these methods need different facilities and precursors that make the processes to be time-consuming and costly.10,18,21-29

LaCoO₃ perovskite nanoparticle as a catalyst for NOₓ gas reduction is a promising substitute of three-way catalysts (TWCs) based on noble metals. Narrow size distribution of catalysts particles are vital characteristics. This study aims to synthesize spherical solid nanoparticles of perovskite phase of LaCoO₃ in a two-step by combining the sol–gel and auto combustion methods in narrow size distribution. The influence of fuel ratio and different fuels on nanoparticles’ characteristics is also addressed in this research work since such particles can be used as a catalyst in the reduction of nitrogen oxide gases (NOₓ).

2 | EXPERIMENTAL

The following materials were used as precursors for the synthesis of perovskite particles: Lanthanum Nitrate (La(NO₃)₃·6H₂O) and Cobalt Nitrate (Co(NO₃)₂·6H₂O) as a supplier of metal elements, and glycine (C₂H₅NO₂) and urea (CH₄N₂O) as fuel, PVP as a surfactant. All of the precursor materials were obtained from Merck-Germany and used in the experiments without further purification.

Step 1: A 0.1M solution of lanthanum nitrate and cobalt nitrate was prepared in 100 ml of distilled water, using a 250 ml beaker. The solution was stirred on a magnetic stirrer for 15 min until the material was completely dissolved, forming a uniform pink solution.

Step 2: Four different samples were prepared, as shown in Table 1. An appropriate amount of glycine and urea was slowly added to the solutions. The glycine/total metals and urea/total metals ratios were kept as 1 and 2 in this experiment (F/O = 1 and 2). The temperature of the solutions was increased to 60°C. Five weight percent PVP of the available metals was added. PVP played the role of surfactant in the experiment to obtain a uniform shape and narrow size distribution. Solutions were vigorously mixed on a magnetic stirrer for 30 min.

Step 3: The temperature of the solutions was increased to 90°C to gradually evaporate water. The solutions were stirred using a magnetic stirrer until gelation and combustion occurred. The powders were rinsed using distilled water and centrifuged at 2000 RPM for 15 min, three times. The collected nanoparticles were heat treatment in a furnace at 600°C for 2 h.

| Sample no. | Fuel  | F/O ratio | Metal solution molarity (M) | PVP (wt%) |
|------------|-------|-----------|-----------------------------|-----------|
| LCG 1      | Glycine | 1         | 0.1                         | 5         |
| LCG 2      | Glycine | 2         | 0.1                         | 5         |
| LCU 1      | Urea   | 1         | 0.1                         | 5         |
| LCU 2      | Urea   | 2         | 0.1                         | 5         |

TABLE 1 | Experimental conditions of sol–gel auto combustion method
FIGURE 1  Schematic of LaCoO$_3$ nanoparticles using sol–gel autocombustion method

Equation (1) provides the overall combustion reaction for the preparation of lanthanum cobalt oxide during combustion stage, using different fuels.$^{30}$

$$
\text{La(NO}_3\text{)}_3\text{.6H}_2\text{O} + \text{Co(NO}_3\text{)}_2\text{.6H}_2\text{O} + n\text{fuel} + 6 \left( \frac{R_v}{R_o} n - 1 \right) \text{O}_2 \rightarrow \text{LaCoO}_3 + \text{gas (CO}_2\text{, H}_2\text{O, N}_2\text{).} \quad (1)
$$

During the experiment, all parameters that influence the properties of nanoparticles such as heating rate, exposure to air, and stirring speed were kept constant. The variable parameters were fuel and fuel-to-oxidizer (F/O) ratio.

The following figure represent the schematic process of preparation method (Figure 1).

3 | RESULTS

X-ray powder diffraction (XRD) patterns were recorded by a D8 Advance (Bruker) with Cu K$_\alpha$ (wavelength 1.54 Å) after nanoparticles were heat treated at 600°C for 2 h. Scanning electron microscopy (SEM; FEI Company, USA-Quanta 200) was used to investigate the morphology, size, and uniformity of the products. A particle size analyzer (PSA) was used to determine the size distribution. During the PSA test, the ethanol was used as a dispersant, and the temperature was set at 25°C. The duration of the test was 50 s.

The powder XRD data shown in Figure 2(A,B) and Figure 3(A,B), indicates the crystalline structure of the as-synthesized perovskite-type oxide nanoparticles obtained using the sol–gel autocombustion method. The ratio of F/O and different fuel tested in this method had an effect on the crystalline properties and purity of the final product. However, XRD patterns of all samples exhibited diffraction peaks of LaCoO$_3$ (PDF No.-01-084-0848), irrespective of the F/O ratio and fuel. Some impurities were observed in the samples (Co$_3$O$_4$, La$_2$O$_2$(CO$_3$)). Figure 2(A,B) shows the XRD patterns

FIGURE 2  X-Ray powder diffraction patterns of LaCoO$_3$ nanoparticles, using glycine as fuel and calcined at 600°C in air (A) sample LCG1 F/O = 1, (B) sample LCG2 F/O = 2
of sample LCG1 and LCG2, respectively. As shown in Figure 2(A), by using glycine in the ratio F/O = 1, the mixture of the cobalt oxide (Co$_3$O$_4$-PDF No.: 00-009-0418), lanthanum oxide-carbonate (La$_2$O$_2$(CO$_3$)-PDF No.: 00-048-1113 and 01-070-5546), and perovskite phase obtained, but Figure 2(B), shows the purity of perovskite phase. Strong peaks at 32.9° (110) and 33.3° (104), and the peaks observed around 32°, 60°, and 70° were bifurcated, which is the characteristic peak of the rhombohedral structure. No trace of CoO, La(OH)$_3$, or La$_2$O$_3$ was observed, which corresponds to the high degree of incorporation of La and Co into the perovskite structure. In this case, glycine was used as fuel and F/O = 2. Figure 3(A,B) shows that using urea as fuel may cause changes in purity and crystalline properties of the final product. Production of LaCoO$_3$ nanoparticles, with Co$_3$O$_4$, La$_2$O$_3$, and La$_2$O$_2$(CO$_3$) as impurities, was obtained by using urea in both F/O = 1 and F/O = 2 ratios. It can be concluded that a higher ratio of glycine causes complete oxidation, while low and high ratios of urea cause partial oxidation and lower degrees of incorporation of La and Co oxide into the perovskite structure. Because combustion enthalpy of fuel molecule in glycine is higher than the urea and it may cause complete oxidation of metals.

Finally, crystallite size and the average crystallite size was estimated according to the Debye and Scherrer formula from the (110), (024), and (214) reflection of the LaCoO$_3$ phase at 2θ ≈ 32.9°, 47.5°, and 58.9°, respectively, and is presented in Table 2.

\[
D = \frac{0.94\lambda}{\beta \cos \theta},
\]

where:
- $D$ is the crystallite size
- $\lambda$ is the X-ray wavelength (1.5418 Å)
- $\beta$ is the full width of the half maximum of the diffraction peak
- $\theta$ is the Bragg diffraction angle

Table 2 shows that LaCoO$_3$ synthesized with glycine exhibited the lowest crystallite size (~14.9 and 28.1 nm) compared with the synthesis with urea (~41.6 and 25.7 nm). This result reveals that glycine and urea act in the opposite manner; while increasing fuel ratio in glycine increase the crystallite size and purity, increasing urea decreases crystallite size and improves purity.

| Sample no. | LCG1 | LCG2 | LCU1 | LCU2 |
|------------|------|------|------|------|
| Crystallite size $D_{110}$ (nm) | 15.9 | 18 | 36.7 | 31.4 |
| Crystallite size $D_{024}$ (nm) | 18.9 | 37.8 | 57.7 | 25.6 |
| Crystallite size $D_{214}$ (nm) | 9.9 | 28.4 | 30.3 | 20.2 |
| Crystallite size $D_{ave}$ (nm) | 14.9 | 28.1 | 41.6 | 25.7 |
| PSA-average (d.nm) | 72.2 | 70.2 | 72.0 | 72.8 |
| Z-average (d.nm) | 104.1 | 97.9 | 101.9 | 106.5 |

**Abbreviations:** d.nm, diameter size in nanometer; PSA, particle size analyzer.
Results from particle size analyses show the narrow size distribution as illustrated by Figures 4 and 5, and the SEM micrograph indicates that.

Particle size analysis confirms the SEM result, which increasing the glycine ratio causes increasing particle size, while urea acts oppositely.

The morphologies of LaCoO$_3$ synthesized with the sol–gel auto-combustion method using glycine and urea as fuel are presented in Figures 6(A,B) and 7(A,B), respectively. The SEM images show the non-porous nature of the synthesized perovskite particles with spherical shape in all samples. The porous nature can be due to the nitrate precursors because burning of the nitrates at a higher temperature may lead to porous structures.

A comparison of these micrographs reveals that the glycine in the ratio of 2 resulted in a lower particle size and greater homogeneity, while the powder prepared by the urea showed a relatively bigger particle size. Some agglomeration and inhomogeneity in shape and size are also observed. The average particle size of LaCoO$_3$ synthesized by glycine is below 70 nm with a spherical shape; whereas the powder obtained using urea has a broader particle size distribution and inhomogeneity in shape. However, SEM results of particle size are different from the results of crystallite size estimation (see Table 2). Particle size is different from crystallite size suggesting that individual particles have several crystallites. It would seem a particle is made up of several different crystallites.
4 | CONCLUSION

LaCoO₃ perovskite nanoparticles can be synthesized using sol–gel auto combustion, two-step method. This method is low-cost, efficient, and does not require advanced equipment for synthesis. Investigation of the lattice structure, morphology, and particle size by XRD, SEM, and PSA analysis methods indicate that particles are uniform in shape and size. These characteristics will play an important role in the use of perovskite nanoparticles as catalysts and lead to uniformity in the properties of the catalyst. The uniform size nanoparticles produced through this method is a result of the use of surfactants in the synthesis process. The results confirm the successful synthesis of LaCoO₃ nanoparticles of spherical shape and narrow size distribution, below 100 nm in size.

LaCoO₃ perovskite nanoparticle as an excellent catalyst for CH₄ oxidation, CO oxidation, and NO reduction, is a promising substitute for TWCs based on noble metals, as they are limited by restricted resources, high price, and particle growth at high temperatures.

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CONFLICT OF INTEREST

Authors have no conflict of interest relevant to this article.

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DATA AVAILABILITY STATEMENT

Research data are not shared.

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