

RESEARCH PAPER

Synthesis, Characterization and Electrochemical properties of Lanthanum Oxysulfate Nanoceramic

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ABSTRACT

La₂O₂SO₄ nanoceramic was synthesized via sol-gel method using lanthanum nitrate and thioacetamid as precursors and stearic acid as polymeric precursor. The characterization studies were conducted by X-ray diffraction, energy dispersive X-ray spectroscopy and scanning electron microscopy. The result showed that the synthesized sample belongs to monoclinic structure with the average sizes between 70-80 nm. Further, the electrochemical behavior of La₂O₂SO₄ nanoceramic was investigated by cyclic voltammetry using [Fe(CN)₆]^{3-/4-} redox couple. These results suggest that the La₂O₂SO₄ nanoceramic is a highly promising candidate for electrochemical sensing of analytes.

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INTRODUCTION

Lanthanum oxysulfate belongs to the family of rare-erth oxysulfate compounds, Ln₂O₂SO₄ (Ln: La, Pr, Nd, Eu, Gd, Tb) that are the subject of interest because of its application on preparation of magnetic gigante resistance compounds (manganites) and oxide fuel cell [1,2]. Several methods can be employed for the synthesis of oxide-based systems. The most common methods are: solid state reaction, sol-gel, micro-emulsion, co-precipitation, hydrothermal and polymeric precursor method [3-5]. This latter method should be emphasized as it offers important advantages in relation to other chemical methods, such as: low cost, as the reagents used in large scale are relatively cheap, good chemical homogeneity at the molecular level of all the components and accurate stoichiometric control, even in complex

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systems [6-8]. In this paper, we focus on a sol-gel synthesis method of La₂O₂SO₄ nanoceramic based on a metal-stearic complex system reported recently [9]. This method offers an easy route to control the final stoichiometry of lanthanum oxysulfate composition and lead to the uniform nanopowders. The electrochemical properties of the obtained nanopowders were evaluated by the cyclic voltammetry (CV) technique. La₂O₂SO₄ nanoparticles were used to design a nanostructured modified carbon paste electrode (La₂O₂SO₄/CPE) and enhance electronic transmission rate between the electrode and [Fe(CN)₆]^{3-/4-} redox couple.

MATERIALS AND METHODS

All the chemicals were analytical grade and were used without further purification. For the

gel synthesis the following materials and reagents were used: stearic acid, lanthanum nitrate and thioacetamid. The crystal phase of the product was determined by a Philips X-pert diffractometer using Cu K α radiation as the X-ray source in the 2 θ range of 10–80°. The crystal morphology of the nanopowders was investigated using scanning electron microscopy (SEM) (Philips XL-30ESM) equipped with an energy dispersive X-ray (EDX).

Electrochemical measurements were carried out using an electroanalyzer system; SAMA 500 (Islamic Republic of Iran) equipped with SAMA software. The electrochemical cell was equipped with a CPE as the working, a platinum electrode (Metrohm, Switzerland) as the counter and an Ag/AgCl (KCl 3.0 M, Metrohm, Switzerland) as the reference electrode. Cyclic voltammetric spectra were recorded in a background solution of 5.0 mM K₃Fe(CN)₆ + K₄Fe(CN)₆ in 0.2 M phosphate buffer (PB) solution (pH 7.0) at a formal potential. All experiments were carried out at room temperature.

Preparation of lanthanum oxysulfate Nanoceramic

In this synthesis, La₂O₂SO₄ were prepared via sol-gel method, using polymeric precursor. The appropriate amounts of lanthanum nitrate and thioacetamid were dissolved in distilled water, separately. Then, two mixtures were added to the melted stearic acid, stirred to form a dark homogeneous mixture and heated in an oven

at 120 °C for 3 h. During this time, diffusion of metallic cations from aqueous to organic phase was occurred and homogeneous sol consists of stearic acid and metallic cations was obtained. The product was cooled to room temperature and drying in an oven for 10 hours to obtain dried gel. Finally, the gel was calcined at 700 °C for 2 h to obtain La₂O₂SO₄ nanopowder.

RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns of sample. According to the XRD analysis, a single-phase oxide La₂O₂SO₄ with well pronounced monoclinic structure (JCPDS card No. 85-1535) has formed. No any impurity phases in the sample have been detected. The most intensive lines (-3 1 1), (-4 0 2) and (-1 1 2) are observed at 2 θ \approx 28.50 (100 %), 28.86 (91.5 %) and 29.77 (81.1 %), respectively.

Fig. 2 illustrates the EDX spectrum of La₂O₂SO₄ sample. Energy dispersive X-ray spectroscopy (EDX) confirms the existence of lanthanum and sulfur in the samples. The molar ratio of the metals can be calculated using such technique.

The molar ratio of lanthanum to sulfur in the sample is 2:1 (Table 1.).

This can demonstrate the fact that lanthanum manganite was synthesized with high purity.

Fig. 3 is a typical scanning electron microscopy (SEM) image of La₂O₂SO₄ sample, from which a large number of spheres with average diameter of 70-80 nm can be observed. High-magnification

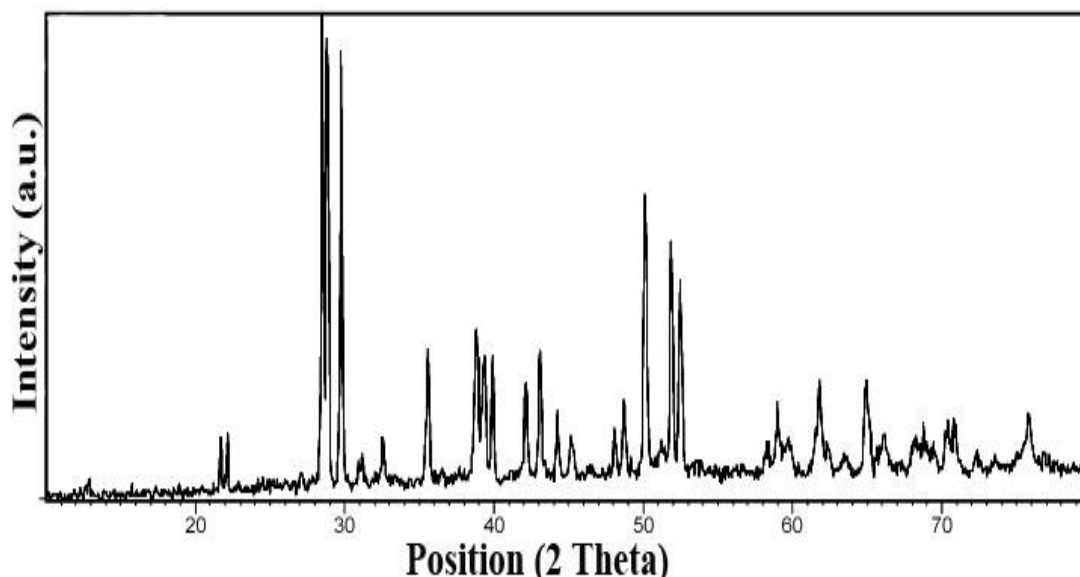


Fig. 1. XRD pattern of as- synthesized sample.

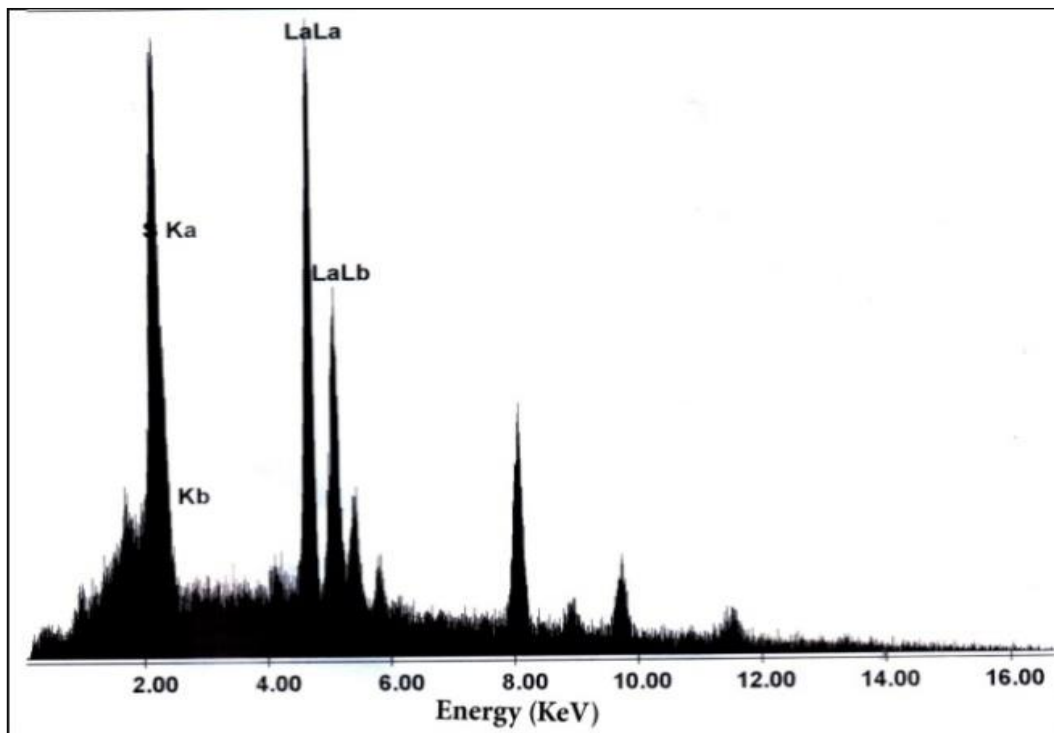


Fig. 2. EDX spectrum of La₂O₂SO₄ nanoceramic.

Table 1. Elemental analysis results of the La₂O₂SO₄ nanoceramic.

Element	Wt%	At%
S K	8.35	28.31
La L	91.65	71.69
Total	100.00	100.00

SEM image shows that the surface of the spheres is not smooth and the spheres are constructed of numerous nanoparticles.

Electrocatalytic activity of La₂O₂SO₄ nanoceramic was investigated by cyclic voltammetry (CV) technique. The cyclic voltammetric experiments were performed in a 5.0 mM redox probe K₃Fe(CN)₆ + K₄Fe(CN)₆ PB solution (0.2 M, pH 7.0) at a scanning rate of 100.0 mVs⁻¹. Fig. 4 shows the CV responses of the bare carbon paste electrode (CPE) and nanostructured modified electrode. It is clear that the La₂O₂SO₄/CPE shows well defined redox peaks with improved current response and decrease in ΔE_p than the CPE. It demonstrates the strong electrocatalytic ability of the La₂O₂SO₄/CPE. This electrocatalytic effect was mainly ascribed to the excess available surface area of the modified sensor due to the nanometer size of the sample

[10,11].

Also the effect of scan rate (v) on the electrochemical response of 5.0 mM [Fe(CN)₆]^{3-/4-} redox couple in 0.2 M PB solution (pH 7.0) at the surface of La₂O₂SO₄/CPE is shown in Fig. 5. As can be observed, the anodic peak potential with increasing the scan rates moved positively and the cathodic peak potential moved negatively, confirming the kinetic limitation of the electrochemical reaction. Fig. 6 shows that the oxidation peak current (I_{pa}) of 5.0 mM [Fe(CN)₆]^{3-/4-} were linearly proportional to the square-root of the scan rate (v^{1/2}). This result indicated that the La₂O₂SO₄ layer has good electrochemical activity and also the oxidation was controlled by diffusion process [12]. The electrochemical results demonstrate that catalytic reaction occurred between the La₂O₂SO₄ nanoparticles and [Fe(CN)₆]^{3-/4-} which

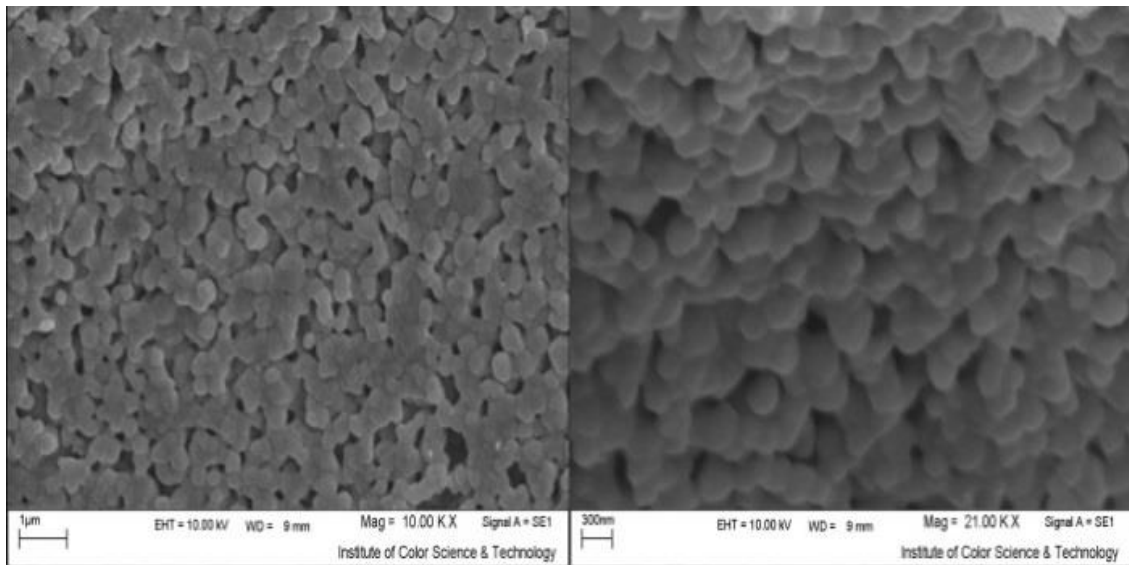


Fig. 3. SEM micrographs of as-synthesized sample.

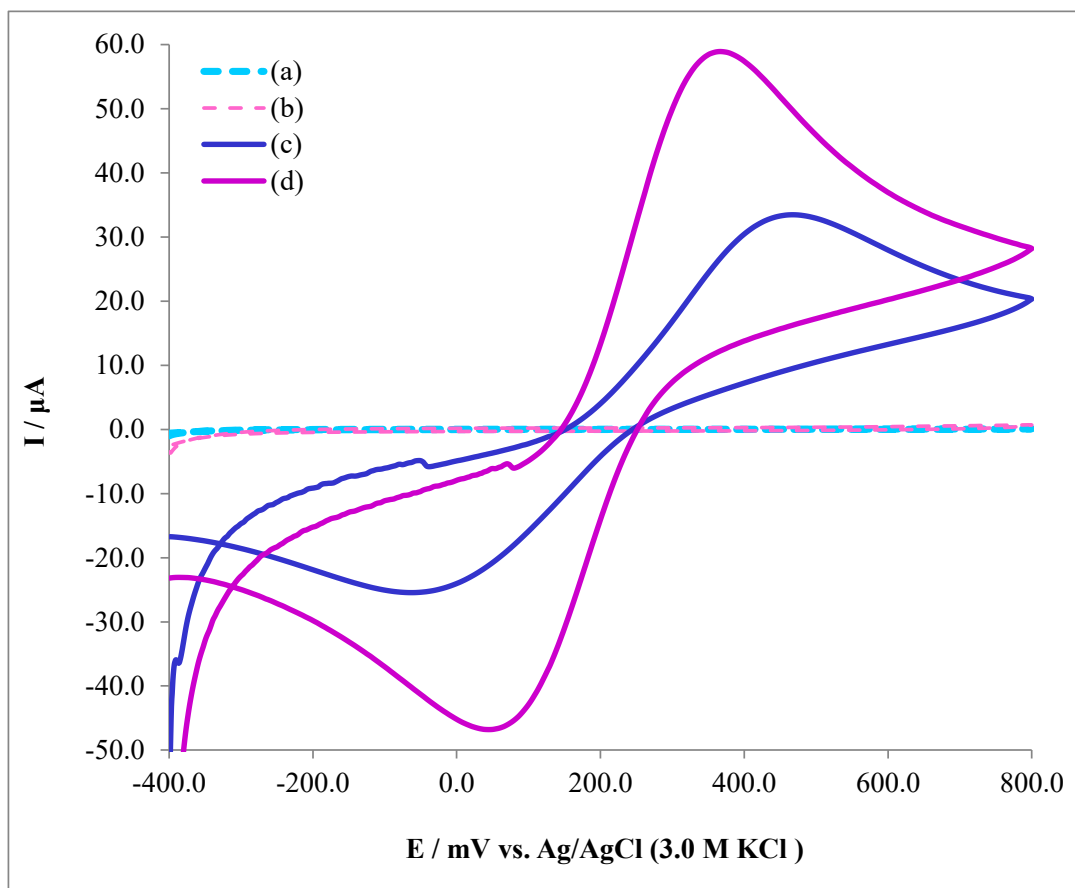


Fig. 4. Cyclic voltammograms of the bare CPE electrode in the absence (curve a) and presence (curve c) of 5.0 mM $[\text{Fe}(\text{CN})_6]^{3/4-}$ in PB solution; the $\text{La}_2\text{O}_2\text{SO}_4/\text{CPE}$ in the absence (curve b) and presence (curve d) of 5.0 mM $[\text{Fe}(\text{CN})_6]^{3/4-}$ in PB solution, scan rate 100.0 mVs⁻¹.

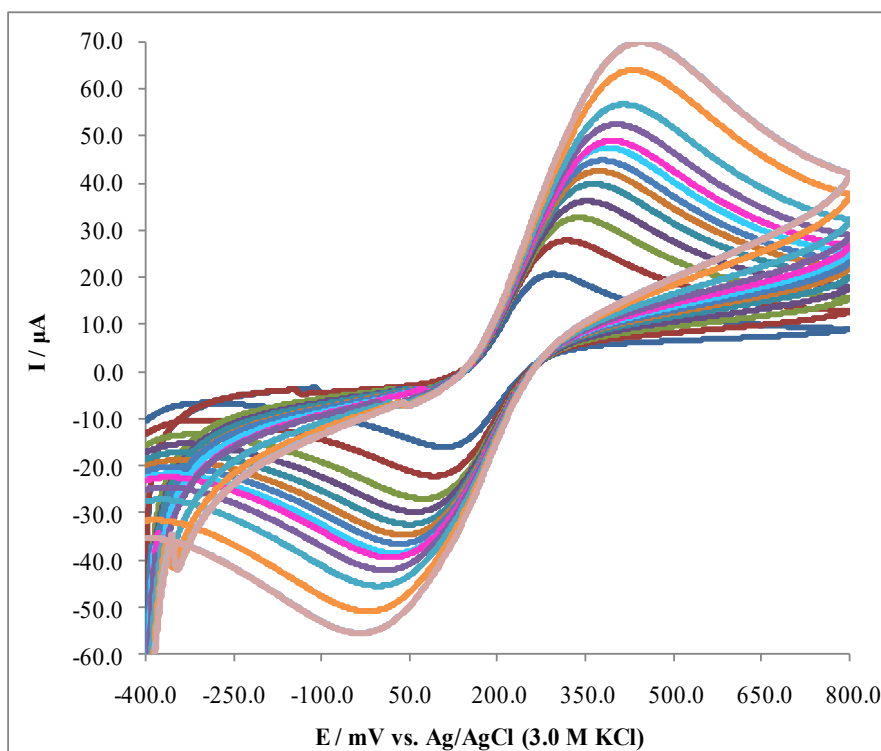


Fig. 5. Cyclic voltammetric responses of La₂O₂SO₄/CPE for 5.0 mM [Fe(CN)₆]^{3-/4-} in PB solution (0.2 M, pH 7.0) with scan rates of 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0, 125.0, 150.0, 175.0 and 200.0 mVs⁻¹.

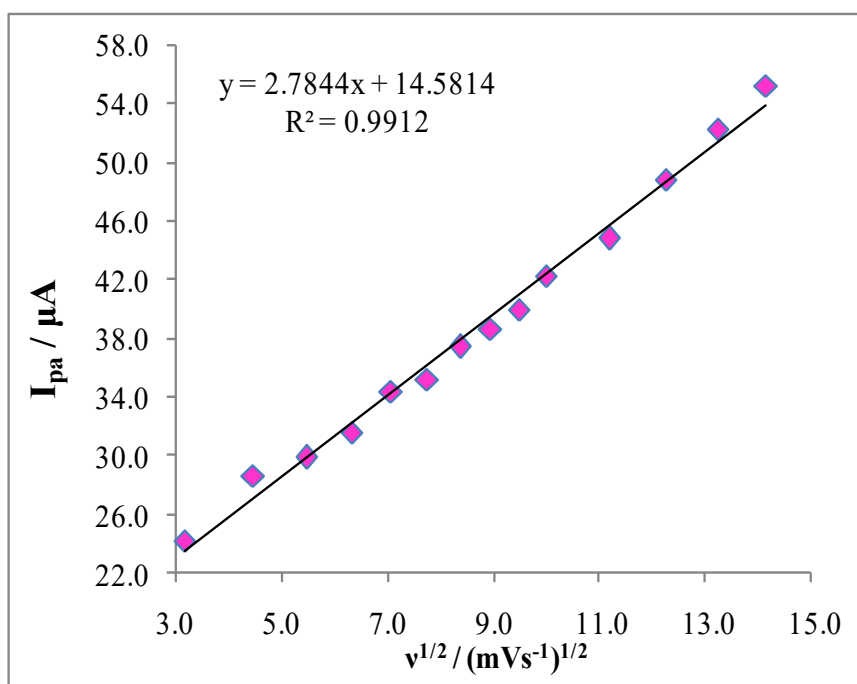


Fig. 6. Plot of anodic peak current (I_{pa}) versus the square-root of scan rate, (v/mVs⁻¹)^{1/2}.

facilitates electron transfer between $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and the modified electrode. The reason is that the synthesized $\text{La}_2\text{O}_2\text{SO}_4$ nanoparticles can act as a catalyst for the electrochemical sensing of analytes.

CONCLUSION

Lanthanum oxysulfate nanoceramic has been synthesised via sol-gel method, using stearic acid as complexing reagent. The as-synthesised sample showed pure monoclinic structure with average particle sizes of 70-80 nm. Moreover, this system could also be used in electrochemical applications. The $\text{La}_2\text{O}_2\text{SO}_4$ nanoparticles were applied for modification of the CPE and could raise electronic transmission rate between the electrode and $[\text{Fe}(\text{CN})_6]^{3-/4-}$.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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