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Synthesis and Characterization of Lanthanum Oxide and Lanthanumoxid Carbonate Nanoparticles from Thermalizes of [La(acacen)(NO_3)(H_2O) Complex

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ABSTRACT

In this investigation, we report facile synthesis of transition metal oxides ($La_2C_2O_5$ and La_2O_3) as nanoparticles. The process contained two steps: first preparation of complex [La(acacen)(NO_3)(H_2O)]**(1)** where acacen= acetylacetonatoethylenediamine. Then the precursors were calcination. In first step, complex **(1)** synthesized using a methanolic solution of La (NO_3) $_3$and acetylacetonatoethylenediamine. Then desired product was collected by suction filtration and characterized using Fourier transform infrared (FT-IR), Ultra Violet-Visible (UV-vis) spectroscopy and cyclic voltammetry (CV) method for electrochemical studies. The next step to prepare nanoparticles, amount of compound **(1)** put in silica gel and oleic acid solution for 4-hours. Then compound **(1)** was placed in a furnace with a temperature of 600, 700, 800 and 900°C. After calcination of title compound, this sample studied using XRD (X-ray Diffraction)and SEM (Scanning Electron Microscopy)techniques. Particle size for several diffraction and average crystallite size were measured from the XRD data based on Debye- Scherrer equation. The X-ray diffraction patterns at room temperature revealed that, highly pure and crystallized Lanthanum oxide nanoparticles as $La_2C_2O_5$and La_2O_3formula with orthorhombic phases in 600°C and 900°C respectively, with an average particle size of about less than 100nm for both nano-oxide. SEM figure show that the particles have same morphology with a uniform porous surface.

Key words: Nanoparticle, X-ray Diffraction, Morphology, Orthorhombic. (Footnotes).

INTRODUCTION

In recent years, the synthesis of inorganic materials with specific size and morphology has attracted considerable attention. Their excellent physical and chemical properties in various fields, such as solar cells, catalysis, photo detectors, sensors, light emitting diodes and laser communication, have made them attractive[1-4] and promising materials. It is well documented that materials with nano-scale grain

size show different properties relative to the same material in bulk form [5-7]. Preparation of various nano-materials have many different synthetic approaches such as chemical vapor deposition (CVD), thermal evaporation, chemical bath deposition,laser ablation, hydrothermal, homogeneous precipitation in an organic matrix,sonochemical and sol–gel method [8-15].The synthesis, production and manipulation of materials on the Nano scale is one of the favorite areas of research which also attracts the industrialists for designing and fabricating new functional materials with novel special properties [1,2]. Among the lanthanides, lanthanum has been extensively examined for its unique properties[7–12] and lanthanum has been synthesized in various compositions such as $La(OH)_3$[13], LaF_3[5],$La_2(CO_3)_3$[14], $LaPO_4$[15–17], $LaBO_3$[18], LaOF[19],$La_2Sn_2O_7$[20],La_2O_3[21] nanoparticles.

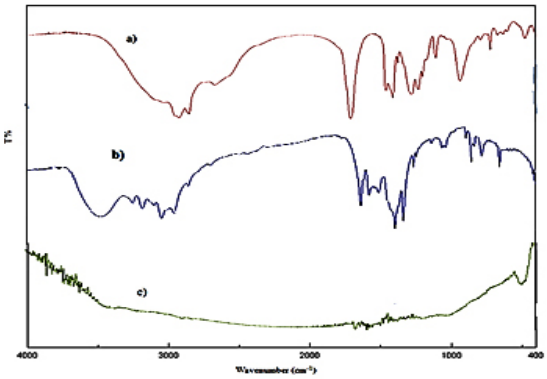

Fig. 1: FT-IR spectra of a) oleic acid b) [La (acacen) (H2O) (NO3)] (1) c) La2O3 (3) in KBrpellets

Lanthanum oxide (La_2O_3) powders have a lot of attractive properties for industrial and technological applications such as: 1- Nanometer lanthanum oxide can be used in piezoelectric materials to increase product piezoelectric coefficients and improve product energy conversion efficiency; 2- Nano-lanthanum oxide can be used for the manufacture of precision optical glass, high-refraction optical fiber, all kinds of alloy materials; 3- Nano-lanthanum oxide can be used for the preparation of organic chemical products catalysts, and in automobile exhaust catalyst; Nanometer Lanthanum oxide can improve the burning rate of propellant, is a promising catalyst; 4-As regards the photoelectric conversion efficiency of nano-lanthanum oxide is high, it can be used in light-converting agricultural film; 5- Also, nano-lanthanum oxide can be used in electrode materials and in light-emitting material (blue powder), hydrogen storage materials, laser materials etc.

In the present work, we report the synthesis of [La(acacen)(NO_3)(H_2O)]**(1)**, then this compound has beenconvert to Lanthanum oxides nanoparticle as La_2CO_5 at 600°C and La_2O_3 at 900°C.

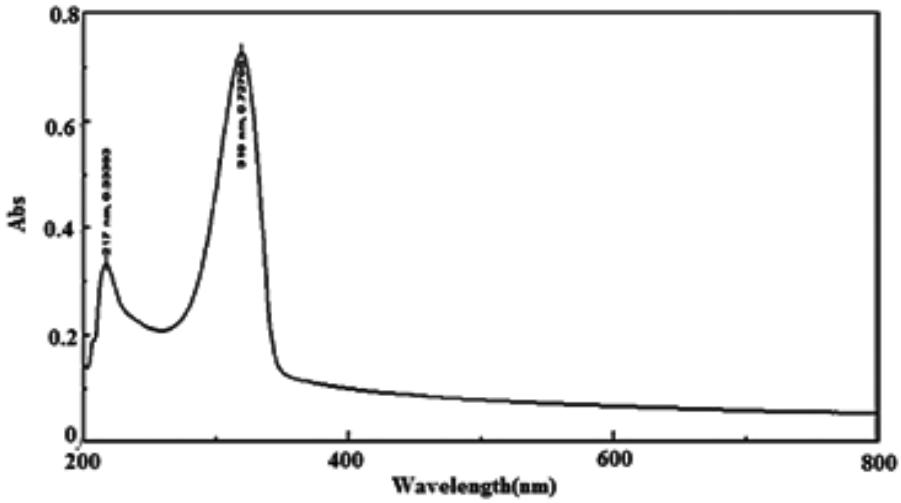

Fig. 2: UV-vis absorption spectra of [La(acacen)(H2O)(NO3)](5×10-5M) in DMF(1)

EXPERIMENTAL

Material and Characterization

All chemicals and solvents were reagent grade or better, obtained from Merck, and used without further purification.

Infrared spectra (4000–250 cm^{-1}) of solid samples were taken as 1% dispersion in KBr pellets using a JASCO FT-IR 460 PLUS. Electronic absorption spectra in DMF solution were taken at room temperature on a JASCO 7850 spectrometer. Cyclic voltammograms were recorded using a SAMA500. Three electrodes were utilized in this system: a glassy carbon working electrode, a platinum wire auxiliary electrode and an Ag wire reference electrode. The glassy carbon working electrode was manually cleaned with 1-*i*m diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammoniumhexafluorophosphate (TBAH), was recrystallized twice from ethanol-water (1/1) and vacuum-dried at 110%C overnight. A sweep rate of 100–500 mVs^{-1} was used for all the scans. Ferrocene was used as an internal standard to compensate for the junction potential variability among experiments.

The thermal behavior was measured with a PL-STA 1500 apparatus. XRD analysis was conducted on a Philips diffractometer of X'pert

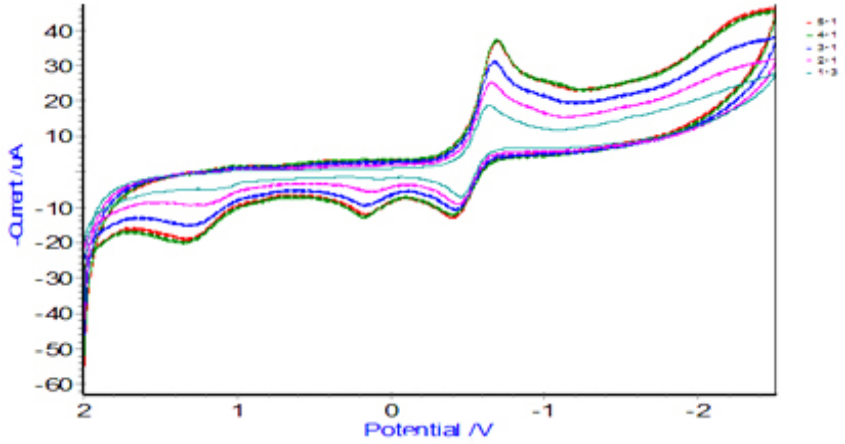

Fig. 3: Cyclic voltammogram of [La(acacen)(H2O)(NO3)](1) in DMF, 0.1 M TBAH as a supporting electrolyte

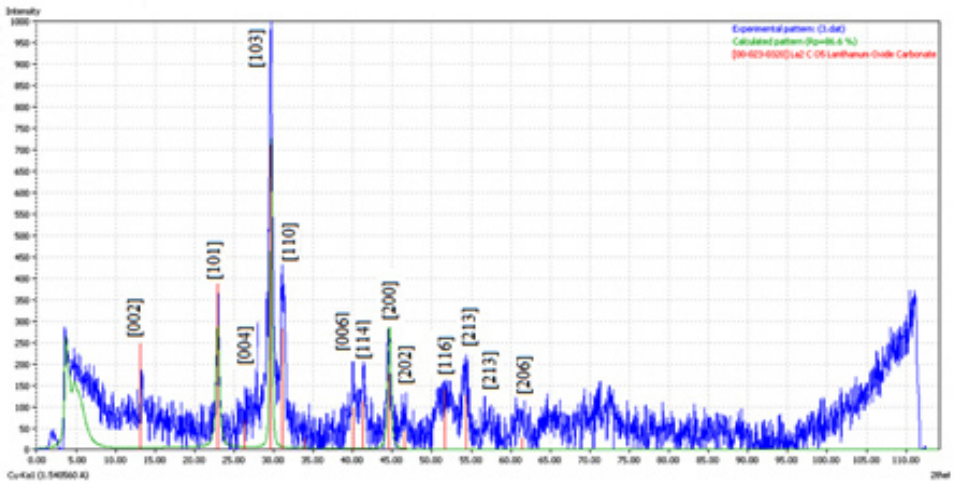

Fig. 4: XRD pattern of La2CO5 at 600°C, compared with standard sample

company with graphite monochromatic Cu Ká radiation (λ= 1.54056 Å). The crystallite sizes of selected samples were estimated using the Scherrer method.

SEM images of the samples were collected on Philips XL30 equipped with an EDX microanalysis (TarbiatModares Uni.).

Synthesis of [La (acacen) (H_2O) (NO_3)]

To a methanolicsolution (10 ml) of La (NO_3)$_3$ (0.1 M) was added dropwiseaqueous solution acetylacetonatoethylenediamine (0.1 M). The resulting solution was stirred at 55–60%C for 2h. The solid (desired product) was collected by suction filtration, washed with MeOHsolution, then air dried (Yield %34). Anal.Calc: C, %32. 22; H, %5.86,; N, %9. 4). Found: C, 32.12; H, 5.73; N, 9.54.IR (KBr, cm^{-1}): 3419 and 2928 *ν*(CH), 1644 *ν*(N-O), 1530- *ν*(C=C) and í(C=N),3454 *ν*(O-H), 1303 *ν*(conjugated NO_3^-), 900*ν*(C-O)

Synthesis of nanoparticles (La_2CO_5 (2) and La_2O_3 (3))

Lanthanum oxide nanoparticles were prepared from [La (acacen) (H_2O) (NO_3)] **(1)** using the physical method. First 1.0 g of compound **(1)** dissolved in oleic acid solution (5mL) as a surfactant, then calcinated at 600 C and 900 C for 4h,to get La_2CO_5 and La_2O_3nanoparticlesrespectively. The

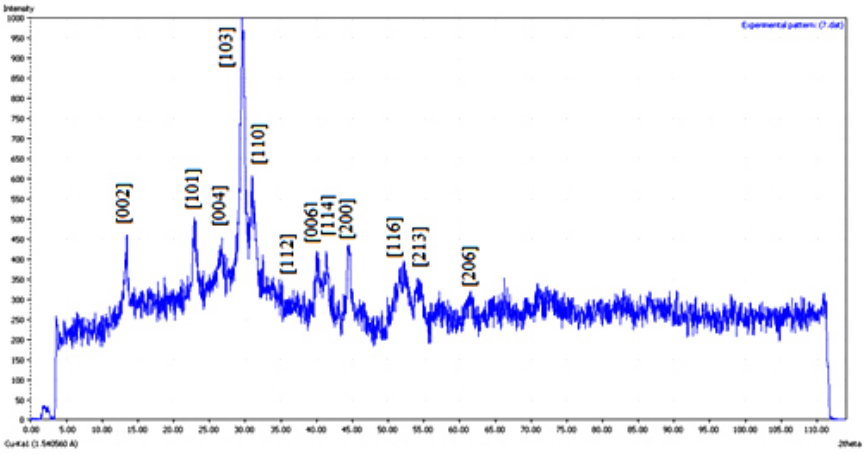

Fig. 5: XRD pattern of La2CO5 in presence of oleic acid at 600°C, compared with standard sample

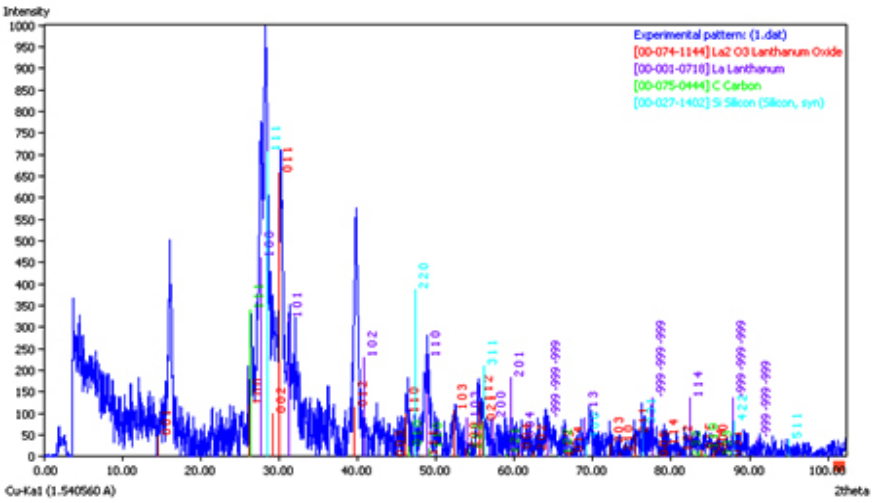

Fig. 6. XRD pattern of La2O3 at 900°C, compared with standard sample

final productswere collected and washed with distilled water and absolute ethanol several times, dried in air and kept for further characterization.

RESULTS AND DISCUSSION

FT-IR spectroscopy

The broadbands at 2600-3000 $cm^{-1}$and 1712 cm^{-1} assigned to stretching vibration of O-H and C=O groupsin oleic acid respectively (Fig 1a). As it can be observed in Fig.1 all the bands of the oleic acid and [La (acacen) (H_2O) (NO_3)](1) were disappeared when the product wascalcinatedin 900 °C (Fig1c) and only broad band was appeared that attributed to lanthanum oxide (Fig1c). The strong band at 500 cm^{-1} is assigned to the *v*(La-O), indicating formation of La_2O_3(3).

Strong bandsat1585,1505 and 1625cm^{-1}, related to thestretchingvibrations ofC = C, C = N, C = Ocanbeshared onacacenligand. Andstretchingfrequencyobservedin the1374 cm^{-1}at attributed to NO_3^-group[22]. Weakabsorptionsin theregion3158and 3226cm^{-1}assigned to N-Hvibrationsoftheacacen ligand[22,23].

FT-IRspectra ofoleic acidshowed in theFig1b.The broadbandobservedat2925-2000 cm^{-1}, attributedtooverlap of stretching vibrationfrequency of theacidicOHscrewwithCH bands. The bonds observed at3006 cm^{-1},1711cm^{-1}, 1378 cm^{-1} and 1465 cm^{-1}assign to CH, C=O, CH_2andCH_3groups, respectively.

Table 1: Particle and average crystallite size of La2CO5in absence of oleic acid at 600°C

2θ	B	Size (nm)	Average size(nm)
3.71	0.006	23.1	
22.92	0.009	17.32	25.02
29.67	0.005	34.65	

Table 2: Particle and average crystallite size of La2CO5in presence of oleic acid at 600°C

2θ	B	Size (nm)	Average size(nm)
3.77	0.007	19.8	
22.95	0.013	11.55	15.58
29.90	0.010	15.4	

Electronic Excitation Study

The electronic spectrum of the [La (acacen) (H_2O) (NO_3)] **(1)**showed in Fig2. Absorption bands in 217 and 319 nm can be assigned to the intraligand $\pi\rightarrow\pi$ transition of the aromatic ring and $\pi\rightarrow\pi$ transition of the acacen and nitrate ligands, respectively. There was any transition in visible region due to Lanthanum (III) has d^0 electron configurations.

Electrochemical Studies

Cyclic voltammetry was performed in an DMF solution of [La(acacen)(H_2O)(NO_3)]**(1)** with 0.1M TBAH as a supporting electrolyte at scan rate 100-500 mV s^{-1} (Fig. 3). In this voltammogram, two quasi-reversible reduction couples at -0.458 and -0.690 V are assigned to the reduction of acacen ligand, by analogy to other acacen complexes[24]. In comparison with free acacen, the reduction couples shift to more positive potentials due to the coordination of acacen ligand to the La(III) center.

X-ray diffraction

Fig 4 and 5 show the representative XRD pattern of La_2CO_5in the absence and presence of oleic acid at 600°C respectively. It is obvious that all the diffraction peaks can be indexed to orthorhombic phase La_2CO_5 (LCSD Card Number 4242).Compared with the standard diffraction pattern. Maximum diffraction observedat 2θ=29.67° and (103) as miller indices, Fig 4. In addition, the distance between crystalline planes is d=3Å[25]. Also the intense and sharp diffraction peaks with any signals of impurities were attributed to high purity of the product.As can be seenin Fig 5.maximum

Table 3: Particle and average crystallite size of La2O3at 900°C

2θ	B	Size (nm)	Average size(nm)
15.94	0.015	86.62	
28.68	0.019	36.47	56.43
39.80	0.006	46.2	

diffraction is in 2θ=29.90° with (103) as miller indices and d=3.1 Å, with addition of oleic acid.

Also particle size for several diffraction and average crystallite size that were measured from the XRD data based on Debye- Scherrer equation for La_2CO_5 in absence and presence of oleic acid at 600°C show in Table **1** and **2** respectively. As can be seen in Table **1**, the compound has nano-sized in the range of nanoparticles (below 100 nm)[25].

[La(acacen)(H_2O)(NO_3)]calcinatedto La_2O_3 in a furnace at 900C°.Fig **6.**Show XRD pattern of La_2O_3at 900°C.Nano lanthanum oxide

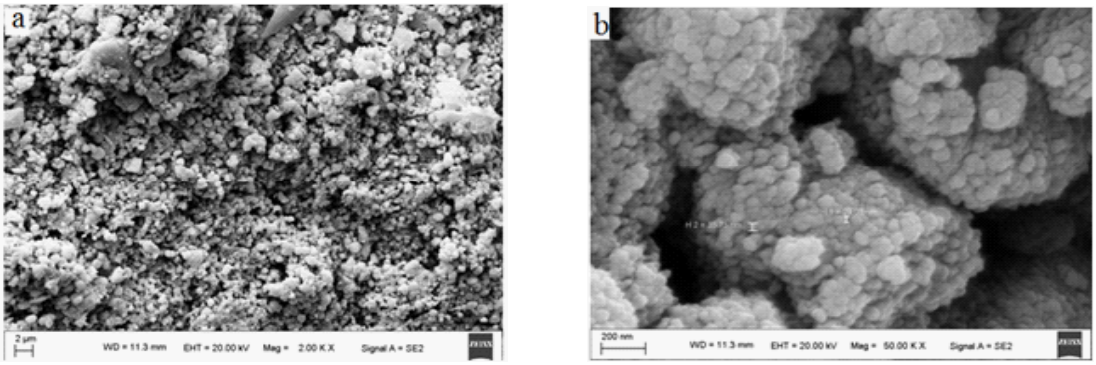

Fig. 7: SEM images of La2CO5 at 600°C

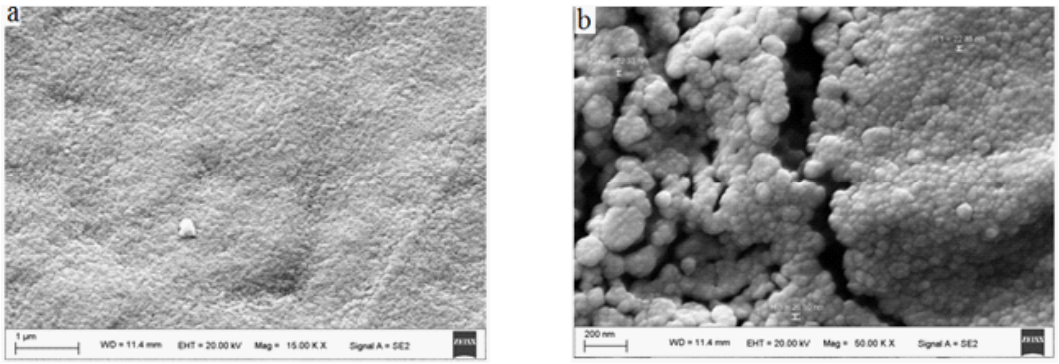

Fig. 8: SEM images of La2CO5in presence of oleic acid at 600°C

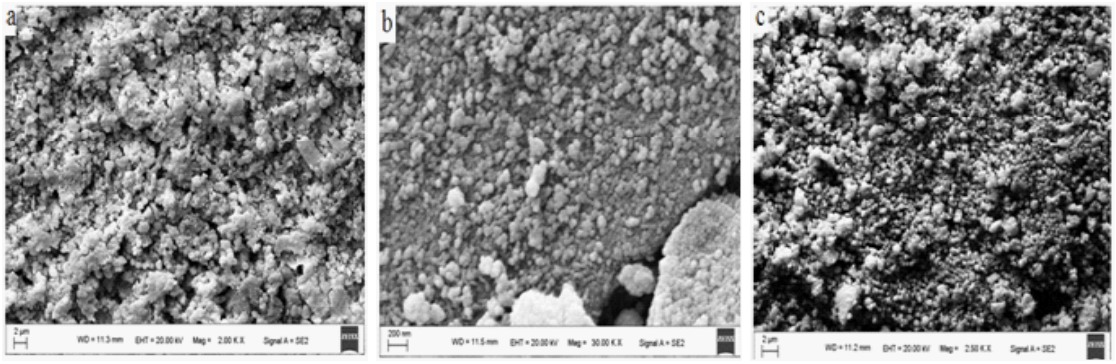

Fig. 9: SEM imagesLa2O3 at a=700, b=800, c=900˚C

has orthorhombic system with diffraction maximum intensity at 2è =39.80and Miller indices (1 1 1) with distance between the plates d= 2.98Å (Table **3**).

Surface morphology

The morphology of the La_2CO_5 nanoparticles was characterized using scanning electron microscope (SEM) at 600°C. Fig. **7** and**8** show the SEM images of La_2CO_5 in absence and presence of oleic acid respectively. As can be seenthe images are clear examples and nano-carbonateoxiderelatively spherical, porous and beneath the high porosity for use as a catalyst for much is suitable. So that the particle size is found 29.0-35.73nm and 22.33-26.89nm respectively that in orderto the effect of surfactants on the image more uniform and stronger link between particle surface area that can provide a better view.

La_2O_3 have spherical shape with porous surface and particle size 24.56- 13.40nm. Fig 9.

CONCLUSION

Metals,rare earths,has a strong tendencyto combinewithnon-metallic elementsuch asoxygen, nitrogen, carbonandhydrogen, and various factors such as geometry and central atom, the structural features ofthe ligandmolecules, witha solvent can play key rolesin the formation of structures them.

The nano-sized particles have different properties than the bulk material can be explained by the factthatthe smaller the particle size, the number of at swill be a higher. As a result,the surface energy of atoms with in a material volume with a different energy and this will cause different properties. The uniqueproperties of nanometer particles, not only because of their high level, but alsofor other reasons such as changes in the crystal lattice, the link between nuclearenergy and soisals orelevant.Its hould be noted that the production of nano-materials and the geometric arrangement ofatoms is consistent with the changes in particle size,particle size reduction increases the effect of the level. Increased surface to volume ratioof nanoparticlesca uses the atoms in the surface atoms than the particle size, the particles have physical properties. This feature greatly increases the reactivityof nanoparticles.

In summary, we prepared Lanthanum oxide nanoparticles in the presence and absence Oleic acid as a surfactant. The size of these nanoparticles was measured using XRD and SEM. Theimagesof nanolanthanum oxide at elevated temperatures (600,700, 800 and900ºC)observed that in all the images of the particles are almost spherical, with uniform and porous orphology and particle size are almost identical.

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