JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 17, No. 9-10, September – October 2015, p. 1458 - 1463

Effects of ultrasound irradiation time on the synthesis of lead oxide nanoparticles by sonochemical method

M. R. VAEZI[a*], S. M. KAZEMZADEH[a], A. HASSANJANI[a], A. KAZEMZADEH[b]
[a]*Department of Nanotechnology and Advanced Materials, Materials and Energy Research Center, Karaj, Iran*
[b]*Deapartment of Semiconductors, Materials and Energy Research Center, Karaj, Iran*

In this paper, lead oxide (PbO) nanoparticles were synthesized by sonochemical processing. Lead chloride ($PbCl_2.6H_2O$), ethanol (C_2H_5OH), sodium hydroxide (NaOH) and deionized water were used as the initial materials. The ultrasonic irradiation time plays the most important role in the size and morphology of the final products. Sonochemical processes at different sonication time were carried out at synthesis temperature (25 °C) and then the materials were washed and dried at room temperature for 48 h. To determine the crystallite size and particle size, also evaluation of the crystal structure and morphological properties, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used. The results show that the size of the particles is ranged from 28-43 nm and the average size of the crystallite for two stable phases detected by XRD (Litharge and lead monoxide) is about 6-10 nm. The morphology of particles is spherical and semi spherical.

(Received February 18, 2015; accepted September 9, 2015)

Keywords: Lead Oxide, Nanoparticles, Sonochemical, Ultrasound Irradiation Time

1. Introduction

Nowadays nano-semiconductors have become one of the most attractive aspects of materials research. Among these nano materials, Lead oxide has become the most interesting material due to its physical and chemical properties. PbO powders remain widely used because they are cheap and reliable materials for battery applications, gas sensors, pigments and paints [1-4]. PbO has two polymorphic forms and a wide band gap: red α-PbO, stable at low temperature, and yellow β-PbO, stable at high temperature [5].

The control of morphology, particle size, particle size distribution, phase composition and the amount of porosity of PbO nanoparticles are vital factors in determining the properties of the final material [6].

In recent years, nano PbO has been synthesized via different methods [1-7]. Among these synthesis methods which have been used by several researchers, the direct chemical method has some advantages including easy operation, being fast, low cost and highly efficient. In addition, this method has been also successfully applied for the synthesis of several other types of nanostructured materials [8-13].

Recently, sonochemical methods, a chemical reaction of the starting materials in the presence of applied high frequency ultrasonic waves, has been employed for several purposes and the effect of ultrasound on chemical reactions is not well understood, however, it is mostly believed that a sonication acoustic cavitation phenomenon generates cavities in the liquid solution of the reactants. The cavitation processes consist of the creation, growth and implosive collapse of gas bubbles in the solution. According to the ‘‘hot-spot’’ theory, extreme temperatures (> 5000 K) and high pressures (> 1000 atm) occur within the bubbles during cavitational collapse [14-17]. Under such extreme conditions the solvent molecules undergo hemolytic bond breakage to generate radicals, H+ and OH− when H_2O is sonicated for example. The liberated radicals therefore, may lead to various chemical and physical effects in reaction pathways and mechanisms. Moreover, the other benefit in using ultrasonic waves in reactions is believed to be providing highly-intensive mixing especially in viscous media. This would lead to an acceleration effect in chemical dynamics and rates of the reactions. Therefore, by this circumstance, different properties of the final products such as particle size, shape and its purity would be controlled by as sonication output power, temperature, the solvent, the chemical species and their concentrations in the reaction mixture. Using ultrasonic wave to synthesize as an external source of energy, affects the final properties of products. As mentioned before, this energy even can change the chemical route of synthesized particles. Due to the mentioned phenomena and by considering the reduction in size by increasing sonication power, the whole optical properties of synthesized nano particles could change. This can cause several differences in the nature of the materials obtained. In semiconductors, the reduction in size can influence the wavelength of optical absorption edge and consequently the band gap energy [18]. Thus besides the differences in morphology and particles size of synthesized particle, the band gap energy which acts as a main character ofsemiconductors in all aspects, should be investigatedcarefully [19].

In the present paper, PbO nanoparticles were synthesized via a sonochemical method. ultrasound irradiation time was investigated as a variable. TEM, SEM and XRD analysis were used to study the morphological and structural characteristics of nanomaterials.

2. Experimental

2-1. Materials and equipments

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. An amount of lead chloride ($PbCl_2.6H_2O$, Merck), sodium hydroxide (NaOH, Merck), ethanol (C_2H_5OH) and deionized water were used to synthesize the pure nanosized PbO particles. **S**onication of the solution was performed by **a** sonicator, Missonix model S4000. The solution was directly irradiated with ultrasonic waves by immersing a Ti alloy ultrasonic horn (12.7×3.8 cm^2, 20 kHz, 1000W/cm2, USA) in the solution and a flat-bottomed Pyrex glass beaker (total volume of 150 ml) were used for the ultrasound irradiation. After preparation of PbO nanopowders, they were heat treated at 600 ºC for 1 hour to obtain crystalline nanoparticles.

2-2. Synthesis of nano PbO via sonochemical method

To prepare PbO nanoparticles, NaOH was dissolved in deionized water and the solution (1M, 50ml) was added drop-wise to an aqueous $PbCl_2.6H_2O$ solution that was dissolved in deionized water (0.2 M, 50 ml) within about 30 minutes. During this process, a high-density ultrasonic probe, operating at 20 kHz with an ultrasonic horn was positioned in the solution for different sonication times. The solution was irradiated with ultrasonic radiation of sonication power and for synthesis times and at the temperature listed in Table 1. The power (W) given by the operation and the ultrasound intensity (W/cm^2) was set at the sonicator. The different PbO samples were prepared by this procedure under otherwise the same conditions. Finally, precipitated particles were collected, washed carefully with ethanol and double distilled water and then were centrifuged to remove by-products. All the prepared samples were dried in air at room temperature for 48 h.

Table 1. The sonication experimental conditions

Sampels	I	II	III	IV
ultrasound irradiation time (min)	45	60	75	90
synthesis temperature (^oC)	25	25	25	25
Initial sonication power (W)	10	10	10	10
Ultrasound intensity (W/cm^2)	41	56	68	79

2-3. Characterization

The PbO nanoparticles were characterized by different techniques. The evaluation of crystal structure and determination of the crystallite size were performed by X-ray powder diffraction (XRD) (SIEMENS, D5000) with monochromatized Cu-Kα radiation source. The crystallite sizes of the selected samples were estimated using the Scherer's equation. An acceleration voltage of 30 kV with a 25 mA current flux and an angular speed of 2^o/minute were used to record the patterns in the 2θ range of 20^o-70^o. The XRD analysis was done on powders before and after the calcination steps. The morphology and size of the particles was determined, using transmission and scanning electron microscopy (TEM; ZEISS, Germany and SEM; VEGA TESCAN Czech Republic). TEM samples were prepared by dispersing a few drops of PbO on carbon films supported by copper grids, and SEM samples were prepared by a dispersing thin layer of the powders on aluminum grids while the surface of each specimen was coated with a thin layer of gold before SEM examination. The SEM analysis was performed at 15 kV. Particle size measurements were carried out by using an Able Image Analyzer v3.6.

3. Results and Discussion

3-1. X-Ray Diffraction analysis

Fig. 1 shows the XRD patterns of PbO nanoparticles prepared via a sonochemical method. Fig. 1(a) show the X-ray diffraction pattern of Pbo sample obtained at 25^oC. The XRD results showed that the initial product had amorphous characteristics.

Fig. 1(b) shows the XRD pattern of PbO nanoparticle calcined at 600 ^oC for 1h. As it can be shown the calcined sample has crystalline structure [4, 6].

Figs. 1(b) show the XRD pattern of PbO nanoparticle synthesized at different times and calcined at 600 ^oC for 1h. It can be seen that Litharge (JCPDS. Pattern 00-005-0561) and lead monoxide (JCPDS.Pattern 00-038-1477) phases exist in the diffractograms.

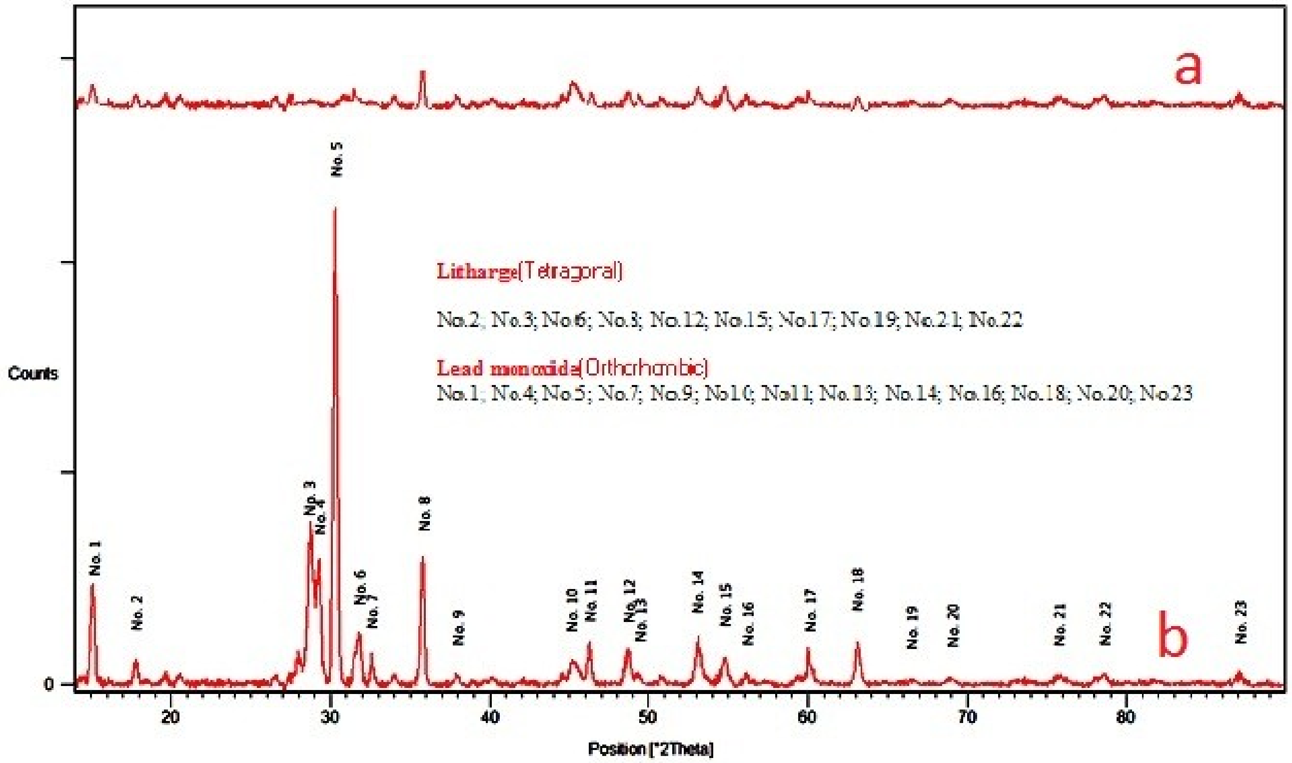

Fig.1. XRD patterns of PbO nanoparticles (sample I) prepared by a sonochemical method at (a) 25°C and (b) calcined at 600 °C for 1 h.

In the X-ray diffractogram of all samples, the characteristic peaks of Litharge and lead monoxide at (2θ = 17.8033°, 28.6828°, 31.8175°, 35.8257°, 48.7677°, 54.8107°, 60.1485°, 66.4839°,75.7419°, 78.6027°) and (2θ =15.1797°, 29.2800°, 30.3039°, 32.5695°, 37.9474°, 45.1320°, 46.2688°, 49.4596°, 53.0953°, 56.1977°, 63.1134°, 69.0690°, 87.1030°) were observed, respectively. The peak broadening of an XRD reflection can be used to estimate the crystallite size based on Scherer's equation as follows [20]:

$$D_{hkl} = \frac{k.\lambda}{\beta.Cos\theta} \qquad (1)$$

Where D is the crystallite size (nm), k is a shape-sensitive coefficient (0.9, assuming spherical spheres), λ the wavelength of the X-ray beam (λ = 0.15406 nm for Cu-Kα radiation), β the full width at half maximum (FWHM) for the diffraction peak under consideration and θ the diffraction angle. Table 2 shows the average crystallite sizes of the Litharge and lead monoxide phases determined from Scherer'sequation.

Table 2. The average crystallite sizes of the Litharge and lead monoxide phases of the samples

Sample	**2 (max)**	**d_{hkl}(nm)**	**D_{hkl}(nm)**	**Phase**
I	30.3039	0.287	10	lead monoxide
	35.8257	0.251	9.5	Litharge
II	30.3039	0.287	8.5	lead monoxide
	35.8257	0.251	9	Litharge
III	30.3039	0.287	7	lead monoxide
	35.8257	0.251	8	Litharge
IV	30.3039	0.287	6	lead monoxide
	35.8257	0.251	7	Litharge

The crystallite sizes of the Litharge and lead monoxide phases determined from Scherer's equation are ranged from 6-10 nm.

3-2. SEM analysis

SEM images of the samples are shown in Fig. 2. These images depict that the morphology of all samples after calcination at 600°C were spherical and semispherical. Also, it is shown that the particle size of the nanoparticles were approximately in the range of 20-70 nm.

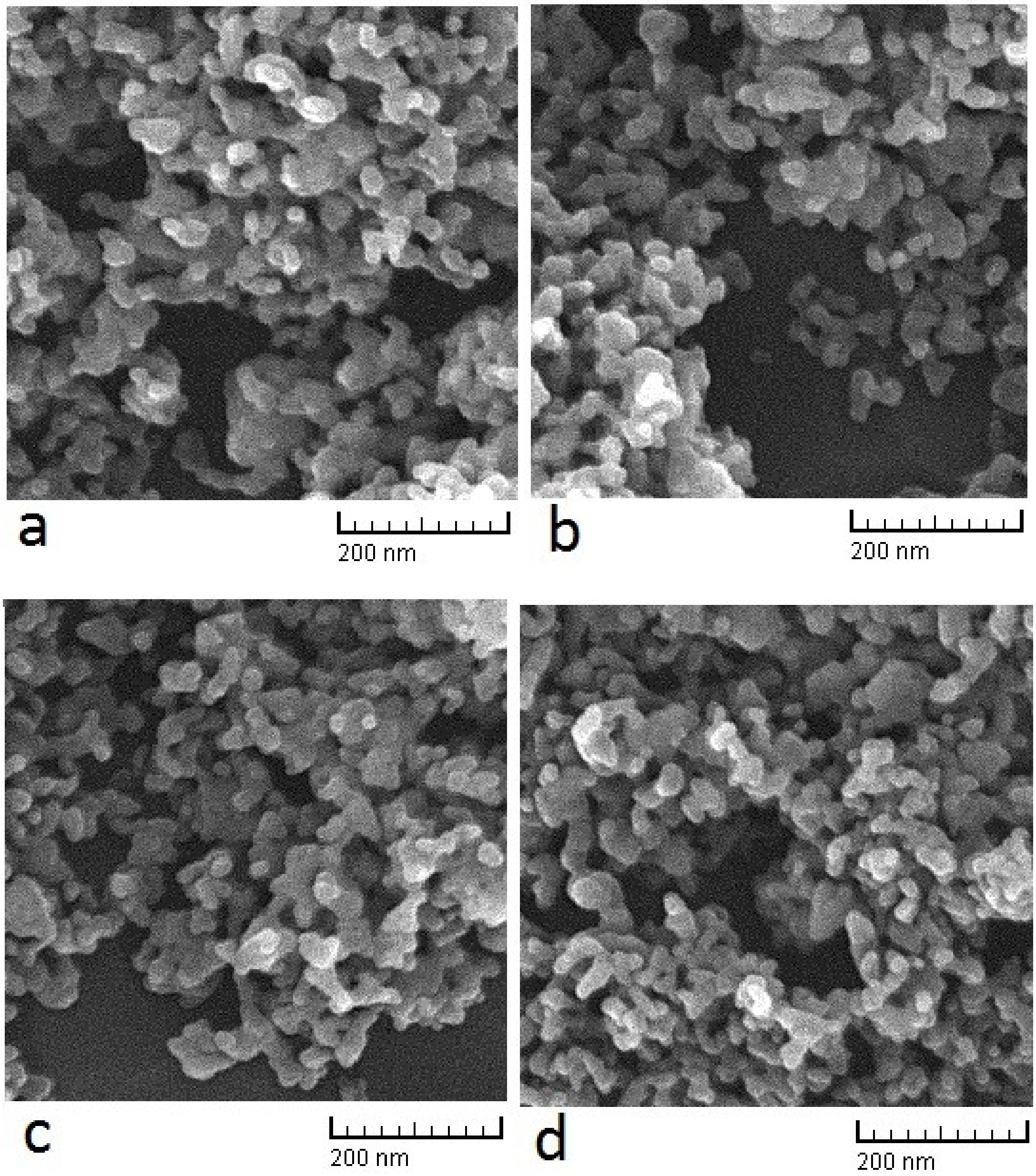

Fig. 2. Scanning electron microscopy (SEM) images of PbO nanoparticles calcined at 600^{oC} and synthesized at (a) 45 min (b) 60 min (c) 75 min (d) 90 min.

3-3. TEM analysis

TEM was used to examine and estimate the Lead Oxide crystallites. Fig. 3 shows TEM images of PbO nanopowders prepared with different ultrasound irradiation time. The images indicate that the samples have nearly spherical and semi spherical grains with a smooth geometry and their sizes do not exceed 70 nm, confirming the SEM findings.

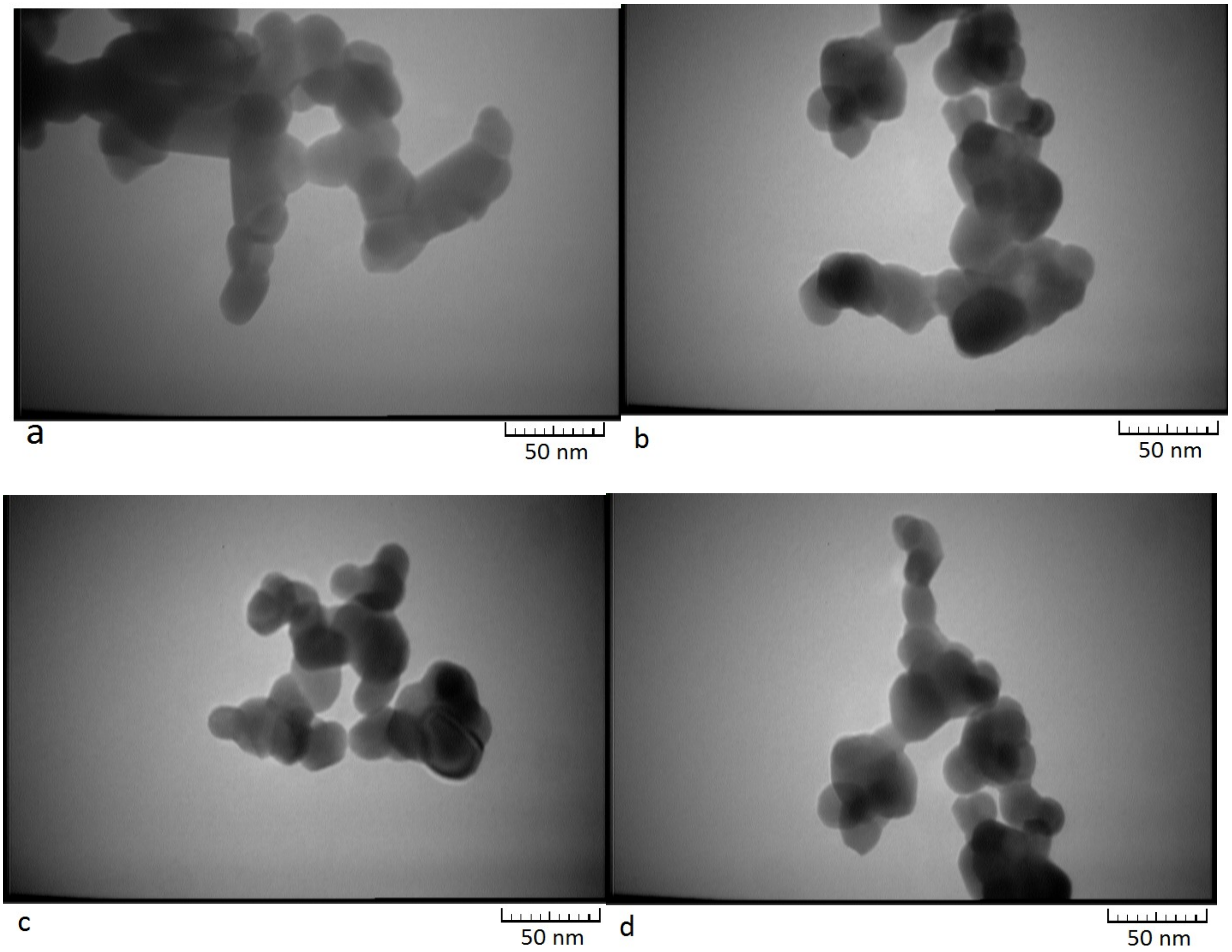

Fig. 3. Transmission electron microscopy (TEM) images of PbO nanoparticles calcined at 600^{oC} and synthesized at (a) 45 min (b) 60 min (c) 75 min (d) 90 min

The average particles sizes of PbO nanoparticles from the TEM images are listed in Table 3. The average size of PbO nanoparticles was decreased from 43 to 28 nm when the ultrasound irradiation time was increased from 45 min to 90 min in this process. From TEM images of these nanoparticles, it can be clearly seen that the nanoparticles have some aggregation.

Table 3. AverageParticles size of synthesized samples from TEM images

Sample	average Particles size
I	43
II	38
III	33
IV	28

4. Conclusions

In this paper, PbO nanopowders were synthsized via sonochemical method successfully. The ultrasound irradiation time has important effects on the particle size and the formation of a stable phase. Also, increasing the ultrasound irradiation time decreases the particle size of the PbO. According to the results, the average size of the particles is ranged from 28-43 nm and the size of the crystallite for two stable phases (Litharge and lead monoxide) in this process is about 6-10 nm. The morphology of particles is spherical and semi spherical.

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*Corresponding author: m_r_vaezi@merc.ac.ir