

# Sonochemical Synthesis and Characterization of a Nano-Sized Lead (II) Coordination Polymer; A New Precursor for the Preparation of PbO Nanoparticles

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## Abstract

Development of components that can form large molecular aggregates through non-covalent interactions, in nano size structures, has been an active area of research. In current study, a nano-sized Pb(II) coordination polymer,  $\{[Pb(pydc)(pydc.H_2)(H_2O)_2]_2\}_n$  (**1**), where  $[pydc.H_2 = 2,6$ -pyridinedicarboxylic acid), were synthesized by sonochemical method and characterized by field emission scanning electron microscope (FESEM), X-ray powder diffraction (XRD), FT-IR spectroscopy and elemental analyses. The sizes of the nano-structures were approximately 90 nm. The thermal stability of compound **1** has been studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The crystal structure of compound **1**, based on an X-ray structural analysis has been reported before, in which the crystal dimensions was in millimeter range. Pure phase PbO nanoparticles were simply obtained by calcination of nano-sized compound **1** at 600 °C under argon atmosphere and the particles size of the PbO were about 26 nm. This study demonstrates that the coordination polymers may be suitable precursors for the simple one-pot preparation of nanoscale metal oxide materials with different and interesting morphologies.

**Keywords:** Lead (II) oxide nanoparticles, Nano-sized coordination polymer, Sonochemical method.

## 1. INTRODUCTION

Nanoparticles are a class of materials with properties distinctively different from their bulk and molecular counterparts and find use in a variety of different areas, such as electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic, and materials applications. Because of the potential of this technology, there has been a worldwide increase in investment in nanotechnology research and development [1, 2]. Although extensive effort has been done for the synthesis of metals, oxides, sulfides, and ceramic materials with nanoscale dimension, little attention has

given to date on supramolecular compounds such as coordination polymers. The size and shape of solid materials influence on the chemical and physical properties. By decreasing the size of coordination polymers as in nano-size, surface area would be increase. Hence making coordination polymers in any form in nano-scale is certainly a major step forward toward the technological applications of these new materials [3, 4].

Design and synthesis of metal-coordination polymers are of great interest due to the special properties of these compounds and their potential applications in sorption,

electrical conductivity and catalysis [5-8]. In the past decade, their fascinating properties have prompted studies on the architectures of many such metal-coordination polymers. The structure of coordination polymers may be influenced by such factors as the typical coordination of the metal ions, the structural characteristics of polydentate organic ligands, the metal to ligand ratio, the counter ions and many other contributions. Alteration of any of these factors can lead to the formation of new structures or extended frameworks [7, 8].

From synthetic point of view, several different synthetic approaches have been offered for the preparation of coordination polymers. Some of them are such as: slow diffusion of the reactants into a polymeric matrix, diffusion from the gas phase, evaporation of the solvent at ambient or under reduced temperatures, precipitation or recrystallization from a mixture of solvents, temperature controlled cooling and hydrothermal synthetic methods [9]. The synthesis of lead (II) coordination polymers is an increasingly active area due to presence of a  $6s^2$  electron configuration and stereoactivity of the valence shell lone electron pair and according to directed ligands classify as holodirected and hemidirected [10]. In this paper we would like to describe a simple synthetic sonochemical preparation of nano-structured lead(II) coordination polymer,  $\{[\text{Pb}(\text{pydc})(\text{pydc}.\text{H}_2)(\text{H}_2\text{O})_2]_2\}_n$  (**1**), by the reaction of lead(II) nitrate and  $\text{LH}_2$ ,  $[\text{pyda}.\text{H}_2]^{2+}[\text{pydc}]^{2-}$ , (pyda= 2,6-pyridinediamine and pydc. $\text{H}_2$ = 2,6-pyridinedicarboxylic acid). The  $\text{LH}_2$  ligand acts as a flat system with the ability of proton transfer from its pydc $\text{H}_2$  fragment as a proton donor to pyda fragment as a proton acceptor. Its synthetic procedure, characterization and crystal structure determination has been performed by Moghimi et al. [11]. The results reveal that compared with traditional synthetic techniques, such as solvent diffusion technique, hydrothermal and solvothermal

methods, ultrasonic synthesis is a simple, efficient, low cost, and environmentally friendly approach to nanoscale coordination polymers [12]. Sonochemical method can lead to homogeneous nucleation and a substantial reduction in crystallization time compared with conventional oven heating when nanomaterials are prepared [13]. Many researchers have investigated the effect of ultrasound on chemical reactions, and most theories imply that the chemical or physical effects of ultrasound originated from acoustic cavitation within collapsing bubbles, which generates extremely localized hot spots having temperatures of roughly 5000 K, pressures of about 500 atm, and a lifetime of a few microseconds. Between the microbubble and the bulk solution, the interfacial region around the bubble has very large gradients of temperature, pressure, and the rapid motion of molecules leading to the production of excited states, bond breakage, the formation of free radicals, mechanical shocks, and high shear gradients [14]. The use of high-intensity ultrasound to enhance the reactivity of metals as a stoichiometric reagent has become a synthetic technique for many heterogeneous organic and organometallic reactions such as: Pb(II)-Minoxidil [15], La(III)- $\text{LH}_2$  [16], Zr(IV)-Neocuproine [17], Cu(I)-Neocuproine [18], Zr(IV)-Isophthalic acid [19], and Cd(II)-Thioacetamide [20].

Lead oxide (PbO), is an important industrial compound which has been widely applied in storage batteries, gas sensors, pigments and paints [21, 22]. Lead oxide has two polymorphic forms and a wide band gap: red  $\alpha$ -PbO and yellow  $\beta$ -PbO which is stable at low and high temperatures, respectively [23], and the  $\alpha$ -PbO  $\rightarrow$   $\beta$ -PbO phase transition occurs at about 490 °C. However, the high temperature yellow form can exist even at room temperature. Till now, many methods have been developed to synthesize PbO nanoparticles including vapor phase growth [24], vapor-liquid-solid process [25], electrophoretic deposition [26], sol-gel process [27], homogeneous

precipitation [28], and so on. The use of metal-coordination polymers as precursors for the preparation of inorganic nanomaterials such as lead(II) oxide has not yet been investigated thoroughly [29]. To proceed, we report the facile synthesis of lead(II) oxide nano-structures by thermal decomposition of nano-sized compound **1** as a new precursor at 600 °C under argon atmosphere and without any surfactant or capping molecules.

## 2. EXPERIMENTAL

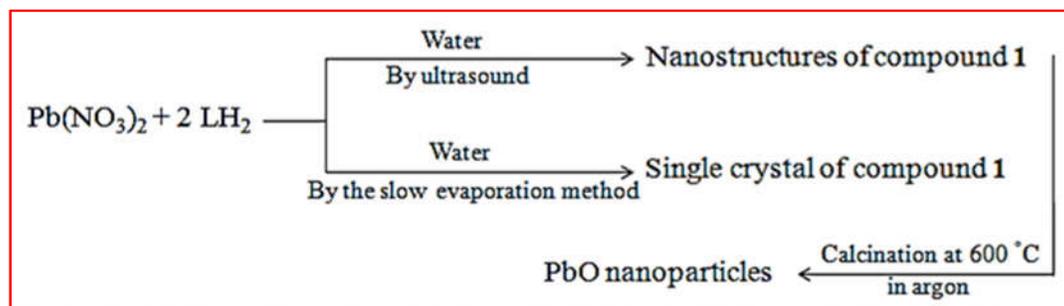
### 2.1. Materials and Physical Techniques

The LH<sub>2</sub> ligand, [pyda.H<sub>2</sub>]<sup>2+</sup>[pydc]<sup>2-</sup> was prepared according to the literature procedure [11]. All reagents for the synthesis and analysis were purchased from Merck Company and used as received. A multiwave ultrasonic generator (Sonicator-4000; Misonix, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 KHz with a maximum power output of 600 W, was used for ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. Melting points were measured with a Thermo Scientific 9200 apparatus and are uncorrected. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Heraeus CHN–O–Rapid analyzer. FT-IR spectra were recorded on a Bruker tensor 27 spectrophotometer in the range 400–4000 cm<sup>-1</sup> using the KBr disk technique.

Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) of the title compound were performed on a computer-controlled PL-STA 1500 apparatus. Powder sample of **1** was loaded into alumina pans and heated with a ramp rate of 10 °C/min from room temperature to 1400 °C under argon atmosphere. X-ray powder diffraction (XRD) measurements were performed using an INEL Equinox 3000 diffractometer with monochromated Cu-K<sub>α</sub> (λ= 1.5418 Å) radiation at room temperature in the 2θ range of 10–70°. The crystallite sizes of selected samples were estimated using the Scherrer formula. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software [30]. Field emission scanning electron microscope (FESEM) photographs were taken on a ZEISS ΣIGMA/VP apparatus equipped with an energy dispersive X-ray (EDAX) microanalysis with gold coating.

### 2.2. Preparation of Nano-Structured {[Pb(pydc)(pydc.H<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>]<sub>n</sub> (**1**) by the Sonochemical Method

To prepare the nano-structure of compound **1**, lead(II) nitrate (0.3 g, 0.9 mmol) was dissolved in 20 ml water and was placed in a vessel of the high-density ultrasonic probe, operating at 20 kHz with a maximum power output of 600 W. Then into this solution, a



*Scheme 1. Materials produced and synthetic methods.*

proper volume of LH<sub>2</sub> ligand (0.5 g, 1.8 mmol) in water was added dropwise. After 1 hour a light green precipitate was formed.

It was isolated by centrifugation (4000 rpm, 15 min), washed with water and acetone added to remove residual impurities and

finally dried in air (0.59 g, yield: 74%). Dec. p. ~ 250 °C. Anal. Calc. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>11</sub>Pb (%): C, 28.30; H, 2.35; N, 4.71. Found (%): C, 28.70; H, 2.30; N, 4.76. FT-IR (cm<sup>-1</sup>) selected bands: 423(vs), 509(s), 663(m), 692(m), 728(vs), 766(vs), 824(m), 913(vs), 1017(vs), 1069(vs), 1142(s), 1180(m), 1271(m), 1379(s), 1422(vs), 1610(s), and 3348(br).

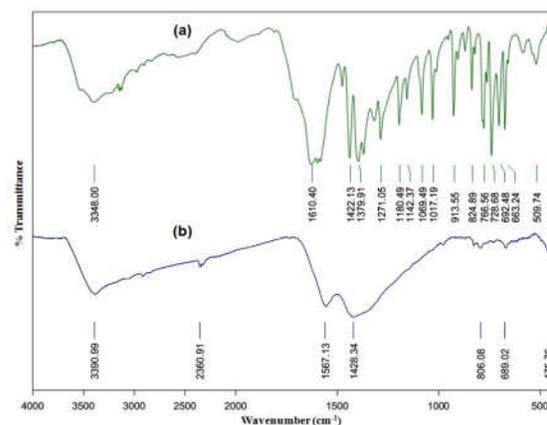
### 2.3. Preparation of PbO Nanoparticles by Thermal Decomposition of Compound 1

For preparation of PbO nanoparticles, calcination of the compound **1** was done at 600 °C under argon atmosphere. After cooling, black precipitate was obtained. The FT-IR spectrum and powder XRD diffraction shows that calcination was completed and the entire organic compound were decomposed. The XRD pattern shows the product is PbO.

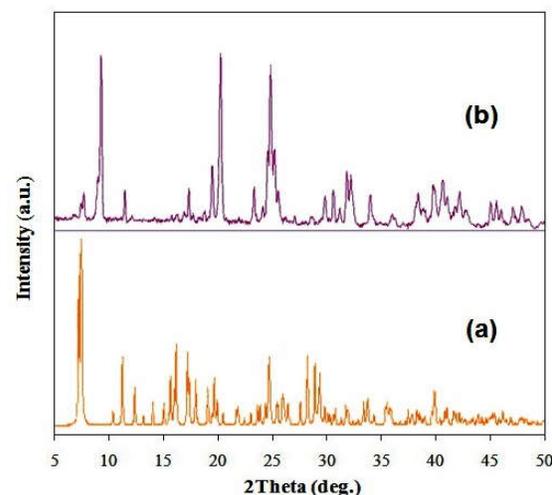
## 3. RESULTS AND DISCUSSION

The reaction of LH<sub>2</sub> ligand with lead(II) nitrate in water using the ultrasonic method at an ambient temperature and atmospheric pressure leads to the formation of a nano-sized lead(II) 3D coordination polymer, {[Pb(pydc)(pydc.H<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>}<sub>n</sub> (**1**). Scheme 1 gives an overview of the synthetic methods of compound **1** using two different routes. This complex displayed distinct melting point and elemental analysis consistent with the formula C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>11</sub>Pb. The FT-IR spectra of the lead(II) coordination polymer produced by the sonochemical method and the as-prepared PbO nanoparticles in the frequency range from 400-4000 cm<sup>-1</sup> are shown in the Figure 1. In Figure 1a, the symmetric and asymmetric vibrations of the carboxylate group are observed as two strong bands at 1422 and 1610 cm<sup>-1</sup>, respectively. The corresponding bands in the free ligand are at 1340 and 1700 cm<sup>-1</sup>. The shifts in position and the shapes of these bands suggest that both carboxylate groups of [pydc]<sup>2-</sup> are coordinated to lead(II) atom. The broad band near 3450 cm<sup>-1</sup> shows the existence of water molecule

[31]. The FT-IR spectrum of PbO (Figure 1b) shows a broad band with very low intensity at 3390 cm<sup>-1</sup> corresponding to the vibration mode of OH group indicating the presence of small amount of water adsorbed on the PbO nanoparticle surface and the water bending vibration appears at 1428 cm<sup>-1</sup>. Bands at 475, 689, and 806 cm<sup>-1</sup> are attributed to the Pb-O vibrations. This indicated that the calcination temperature was suitable to form PbO nanoparticles.



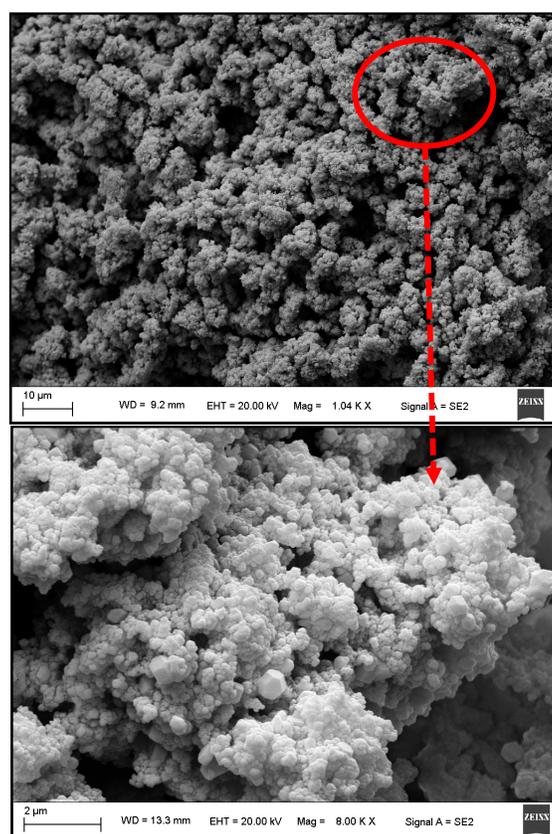
**Figure 1.** FT-IR spectra of (a) nanoparticles of compound **1** produced by sonochemical method, (b) PbO nanoparticles produced by calcination of compound **1** at 600 °C.



**Figure 2.** XRD patterns; (a) simulated pattern based on single crystal data of compound **1**, and (b) nanoparticles of compound **1** produced by sonochemical method.

Figure 2 shows the simulated XRD pattern from single crystal X-ray data of compound **1** (Figure 2a) in comparison with the XRD pattern of the typical sample of compound **1** prepared by the sonochemical method (Figure 2b). Acceptable matches, with slight differences in  $2\theta$ , were observed between the simulated and experimental powder XRD patterns. This suggests that the compound obtained by sonochemical method has a single crystalline phase and that this phase is identical to that reported by Aghabozorg and coworkers [32].

The significant broadening of the peaks indicates that the particles are of nanometer dimensions. Estimated from the Scherrer formula, calculation of particle sizes from the broadening of the XRD peaks ( $D=0.891\lambda/\beta\cos\theta$ , where  $D$  is the average grain size,  $\lambda$  is the X-ray wavelength (1.5418 Å), and  $\theta$  and  $\beta$  are the diffraction angle and full-width at half maximum of an observed peak, respectively [33]) was found to be around 90 nm, which was in agreement with the value obtained from the FESEM images, as shown in Figure 3.



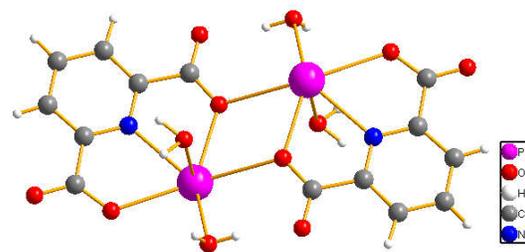
**Figure 3.** FESEM photographs of compound **1** nanostructure produced by sonochemical method.

The structure of compound **1** has been reported by Aghabozorg et al. [32]. The molecular structure of dimeric polymeric Pb(II) complex,  $\{[\text{Pb}(\text{pydc})(\text{pydc}.\text{H}_2)(\text{H}_2\text{O})_2]_2\}_n$  (**1**),

consists of two metal fragments linked via the central four-membered  $\text{Pb}_2\text{O}_2$  ring. In compound **1**, the lead atom is surrounded by nine ligating atoms involving one nitrogen atom from the  $[\text{pydc}]^{2-}$  ligand, two

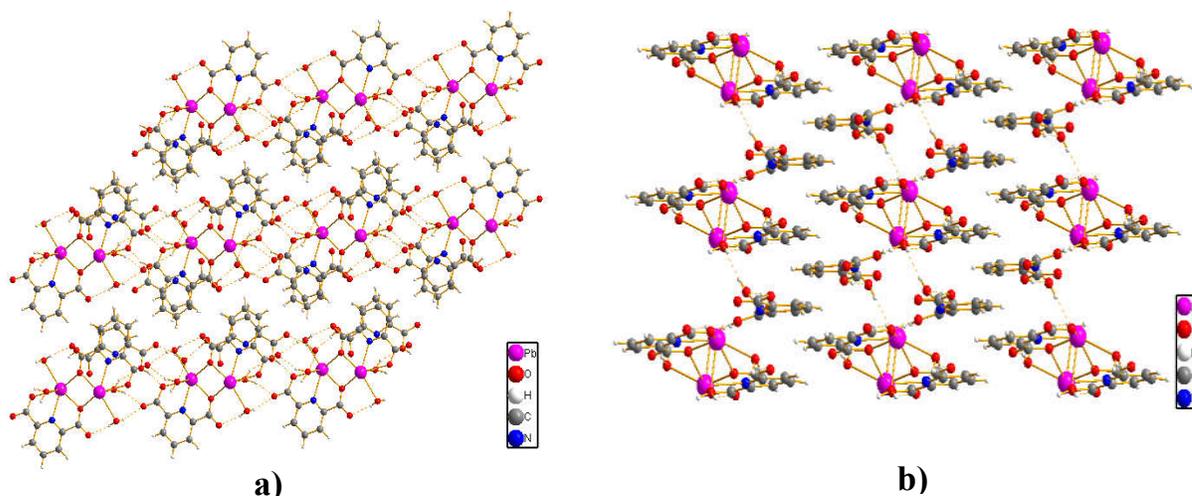
carboxylate oxygen atoms from a  $[\text{pydc}]^{2-}$ , two carboxylate oxygen atom from  $[\text{pydc.H}_2]$ , three oxygen from three water molecules, and one carboxylate oxygen atom from two neighboring  $[\text{pydc}]^{2-}$  units. A view of the coordination environment around the lead(II) ion of compound **1** is shown in Figure 4.

The crystal also contains a neutral  $[\text{pydc.H}_2]$  molecule, that form hydrogen and coordination bonds that dominate the crystal packing, by forming layers of molecules. The packing of compound **1**, viewed approximately along  $a$  and  $c$  axes, is shown in Figure 5.

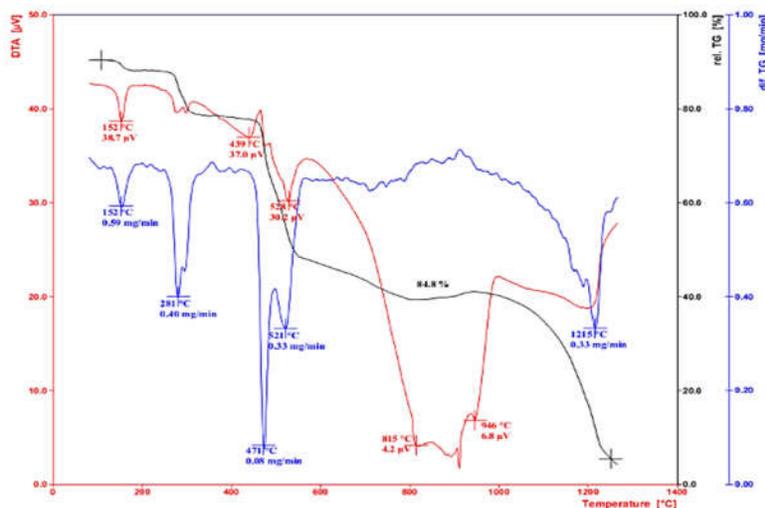


**Figure 4.** The coordination environment of the compound  $\{[\text{Pb}(\text{pydc})(\text{pydc.H}_2)(\text{H}_2\text{O})_2]_2\}_n$  (**1**).

The title complex crystallizes in the triclinic space group  $P\bar{1}$  and two molecules per unit cell [32].



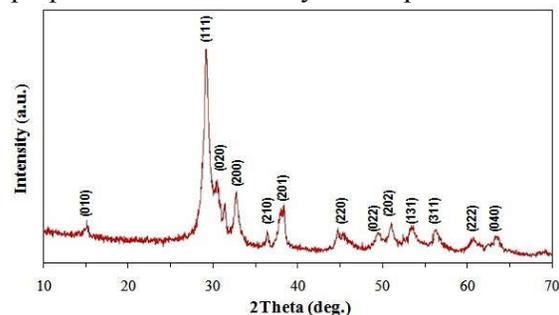
**Figure 5.** A fragment of the 3D coordination polymer **1**, viewed along (a) the  $a$  direction, and (b) the  $c$  direction.



**Figure 6.** Thermal behaviour of compound **1** nanoparticles produced by sonochemical method.

To examine the thermal stability of the nano-sized compound **1** that were obtained from sonochemical method, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between room temperature and 1400 °C under an argon flow (Figure 6). The compound **1** is stable up to 152 °C, at this temperature the coordinated water molecule begins to be removed. Decomposition of compound **1** occurs between 152 and 521 °C with a mass loss of 84.8 %. The weight loss between 281 °C to 521 °C may be ascribed to the removal of [pyda.H<sub>2</sub>]<sup>2+</sup>[pydc]<sup>2-</sup> ligand. Mass loss calculations of the end residue and the XRD pattern of the final decomposition product (Figure 7) show the formation of PbO. The DTA curve of compound **1** indicates the decomposition of the compound takes place with three endothermic events at 152 °C, 439 °C, and 528 °C (Figure 6).

To investigate the composition and phase information of the final calcination product, XRD was carried out. Figure 7 provides the XRD pattern of lead(II) oxide obtained from calcination of compound **1** at 600 °C under argon atmosphere, from which we concluded that the PbO with high purity obtained and the pattern matches with PbO with a orthorhombic structure (space group *Pcam* (57) with lattice parameters *a* = 5.4903 Å, *b* = 5.8920 Å, and *c* = 4.7520 Å, JCPDS No. 038-1477), the sharp diffraction peaks of the sample indicated that well crystallized lead oxide crystals can be prepared under current synthetic procedure.



**Figure 7.** XRD pattern of PbO nanoparticles.

The broadening of the peaks indicated that the particles were at the nanometer scale, which is in agreement with that observed

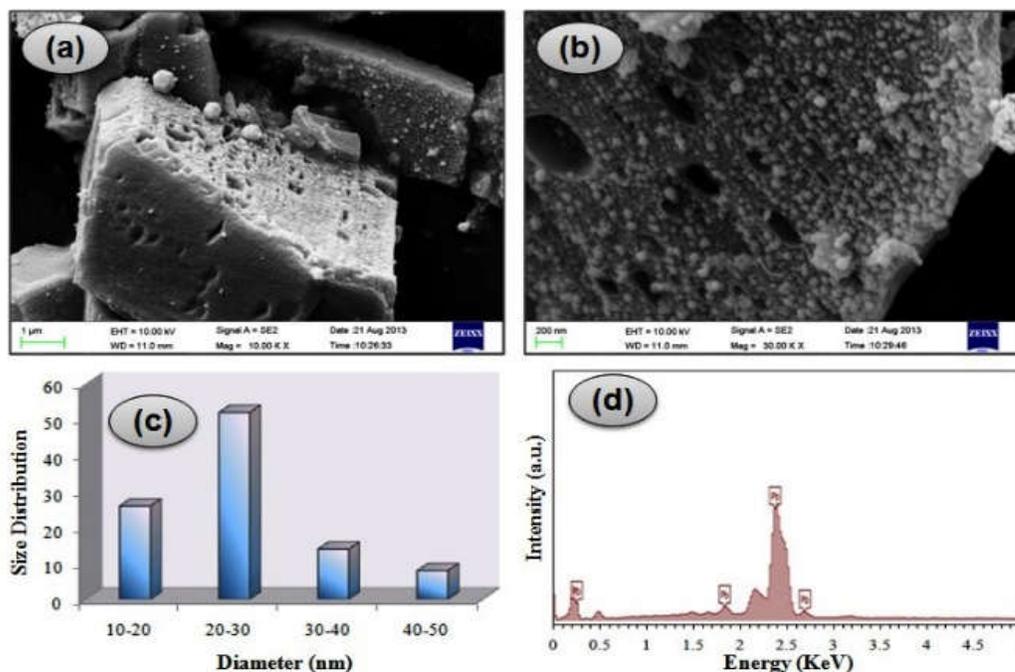
from FESEM images (Figures 8a and 8b). Average size of the particles was estimated from Scherrer equation, average particles size of the product was 26 nm.

The morphology and size of the lead(II) oxide nanoparticles were studied by FESEM (Figures 8a and 8b), which shows porous and spherical PbO nanoparticles. The particles have a good size distribution and good particle separation. The size distribution histogram of PbO nanoparticles (20-30 nm) is shown in Figure 8c and indicates a relatively uniform distribution. Furthermore, EDAX was performed on the PbO nanoparticles (Figure 8d). The EDAX spectrum shows the presence of lead as the only elementary component. This indicates that the product from direct calcination of compound **1** is pure PbO nanoparticles.

The morphology of the PbO particles is different from compound **1**. This point may be due to complete decomposition and break up of the compound with change of morphology of nano-structure. The morphology variation is also evidenced with some other similar compounds [34]. It is noteworthy to mention that in some cases, however, calcination gives rise to metal oxide nano-structures with morphology similar to the parent polymer structure [35]. From this perspective, further systematic studies of other coordination polymers with different metal ions and ligands via different procedures are ongoing in our laboratory. These investigations may offer new insights into metal-organic supramolecular assembly and nanochemistry.

#### 4. CONCLUSION

In this study we have successfully demonstrated the synthesis of a porous nano-sized Pb(II) 3D coordination polymer, {[Pb(pydc)(pydc.H<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>]<sub>n</sub> (**1**) by sonochemical method. To proceed, compound **1** was decomposed at 600 °C under argon atmosphere to produce PbO nanoparticles and characterized by FESEM, EDAX, FT-IR, and XRD analyses. The XRD pattern indicates that the



**Figure 8.** (a,b) FESEM photographs, (c) particle size distribution histogram, and (d) EDAX analysis of PbO nanoparticles.

well-crystallized lead (II) oxide nanoparticles can be easily obtained under the current synthetic conditions. However this method is fast and the product has a good separation with uniform nanometer scale particles and it does not need any additive and yields smaller particles. This study shows that the coordination polymers may be suitable precursors for the preparation of nanoscale metal oxide materials with different and interesting morphologies. To the best of our knowledge, this is the first report on the synthesis of PbO porous nanoparticles with this precursor. The study also establishes that sonochemical method can be employed

successfully as a simple, efficient, low cost, environmentally friendly and very promising method for the fabrication of nanoscale coordination polymers with tunable size and morphology by varying the reaction conditions.

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