

Sonochemical syntheses of nano lead(II) coordination polymer; precursor for preparation of lead(II) oxide/iodide nano-structures

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ABSTRACT

Nanoparticles of a one-dimensional coordination polymer $[\text{Pb}(\text{L})(\mu_2\text{-I})]_n$ (**1**), ($\text{L}^- = 1\text{H-1,2,4-triazole-3-carboxylate}$), have been synthesized by a sonochemical process and characterized by field emission scanning electron microscopy (FESEM), X-ray powder diffraction (XRPD), FT-IR spectroscopy and elemental analyses. The thermal stability of compound **1** both its bulk and nano-size has been studied by thermal gravimetric (TG) and compared each other. Concentration of initial reagents effects and the role of power ultrasound irradiation on size and morphology of nano-structured compound **1** have been studied and show that low concentrations of initial reagents and also high power of ultrasound irradiation decreased particles size and led to uniform nanoparticles morphology. PbO nano-structures were simply synthesized by solid-state transformation of compound **1** at 630 °C under air atmosphere whereas thermal decomposition of compound **1** in oleic acid as surfactant at 200 °C yield PbI_2 nanoparticles.

1. INTRODUCTION

During the last two decades, the rational design and syntheses of novel metal coordination polymers with multi-dimensional networks, which involves self-assembly of organic multitopic ligands with appropriate functional groups and metallic centres, with potentially useful applications as functional materials, ion exchange, catalysis, luminescence, magnetism, nonlinear optics, and molecular sensing, have made considerable progress in the field of coordination chemistry and crystal engineering (Almeida Paz 2012). 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 increased. Hence making coordination polymers in any form in nano-scale is certainly a major step forward toward the technological applications of these new materials (Lu 2008).

In this paper we would like to describe a simple synthetic sonochemical preparation of nano-structured lead(II) 1D coordination polymer, $[\text{Pb}(\text{L})(\mu_2\text{-I})]_n$ (**1**), ($\text{L}^- = 1\text{H-1,2,4-triazole-3-carboxylate}$). Sonochemistry is the research area in which molecules

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undergo a reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz) (Bang 2010).

Lead oxides are very fascinating because several compounds exist, with a variety of oxidation states and mixed-valence species (Aslani 2009). Till now, many methods have been developed to synthesize PbO nanocrystals including vapor phase growth, vapor–liquid–solid process, electrophoretic deposition, sol–gel process, homogeneous precipitation, etc. To proceed, we report the facile synthesis of lead(II) oxide nanostructures by solid-state transformation of compound **1** calcined at 630 °C in air and without any surfactant or capping molecules as well as synthesis of lead(II) iodide nanoparticles by thermal decomposition of compound **1** in oleic acid as a surfactant at 200 °C.

2. EXPERIMENTAL SECTION

Syntheses of [Pb(L)(μ_2 -I)]_n (1**).** Compound **1** was prepared using the branched tube method: 1H-1,2,4-triazole-3-carboxylic acid (0.117 g, 1 mmol), potassium iodide (0.166 g, 1 mmol) and lead(II) nitrate (0.331 g, 1 mmol) were placed in the arm to be heated. Water was carefully added to fill both arms, and then the arm to be heated was placed in a bath at 60 °C. After 10 days, yellow crystals were deposited in the cooler arm which were filtered off, washed with water and air dried. (0.28 g, yield 63%), m.p. > 300 °C. (Anal. calc. for C₃H₂IN₃O₂Pb: C 8.07, H 0.45, N 9.41%; found: C 8.15, H 0.43, N 9.63%). IR (cm⁻¹) selected bands: 810(m), 981(m), 1280(m), 1453(vs), 1622(vs), 3102(br) and 3444(br).

Synthesis of [Pb(L)(μ_2 -I)]_n (1**) nanostructure by a sonochemical process.** To prepare nano-sized [Pb(L)(μ_2 -I)]_n (**1**), 50 ml solution of lead(II) nitrate (0.1 M) in water was positioned in a high-density ultrasonic probe, operating at 50 Hz with a maximum power output of 138 W. Into this solution water a 50 ml solution of the ligand 1H-1,2,4-triazole-3-carboxylic acid (0.1 M) and sodium hydroxide (0.1 M) and potassium iodide (0.1 M) were added dropwise. The obtained precipitates were filtered off, washed with water and then dried in air. m.p. > 300 °C. (Found C, 8.32; H, 0.51; N, 9.22%). IR bands: 819(m), 995(m), 1286(m), 1457(vs), 1626(vs), 3113(br) and 3422(br).

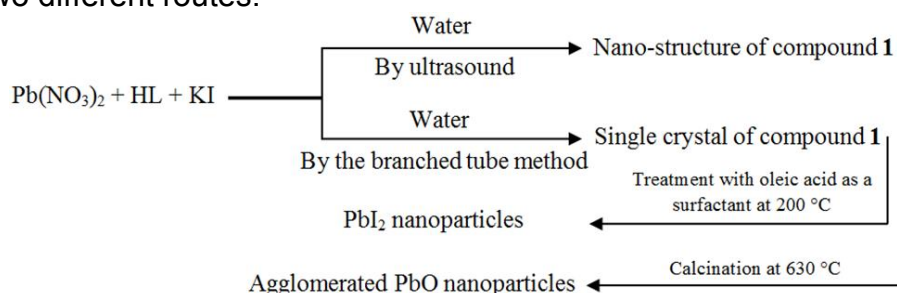
For study of the effect of concentration the initial reagents and the role of power ultrasound irradiation on size and morphology of nano-structured compound **1**, the above processes were done with concentrations of 0.05 and 0.01 M and electrical powers of 138 and 305 W from the ultrasonic generators.

Synthesis of PbO nanostructures by thermal decomposition of compound 1. Nanoparticles of compound **1** (446 mg, 1 mmol) transferred to a crucible (10 mL capacity). The crucible was transferred to furnace and heated at 630 °C under static atmosphere of air for 4 h. The furnace was cooled to 35 °C. The organic components were combusted and PbO nanostructures were produced. The XRD pattern shows the product is PbO.

Synthesis of PbI_2 nanoparticles by thermal decomposition of compound 1 in oleic acid as a surfactant. The 0.446 g of the yellow single crystals of compound 1 were dispersed in oleic acid, (8 mL, 25 mmol) to form a homogenous emulsion solution. This solution was stirring for 15 min at mild heating (60 °C) and then heated to 200 °C in an electric furnace under air atmosphere for 2 h. Two milliliter of toluene and a large excess of EtOH (20 ml) were added to the reaction solution. Nanoparticles of lead(II) iodide was separated after washing with ethanol. The solid was washed with EtOH and dried.

3. RESULTS AND DISCUSSION

Reaction of 1H-1,2,4-triazole-3-carboxylate (L^-) and potassium iodide with lead(II) nitrate leads to formation of a 1D coordination polymer $[\text{Pb}(\text{L})(\mu_2\text{-I})]_n$ (**1**). Nano-structure of compound **1** were obtained in aqueous solution by ultrasonic irradiation, while single crystals of compound **1** were prepared by a heat gradient applied to a aqueous solution of the reagents (the “branched tube method”) (Morsali 2009). Scheme 1 gives an overview of the methods used for the synthesis of $[\text{Pb}(\text{L})(\mu_2\text{-I})]_n$ using the two different routes.



Scheme 1. Materials produced and synthetic methods.

The elemental analysis and IR spectra of the nano-structure produced by the sonochemical method and of the bulk material produced by the branched tube method are indistinguishable (Fig. 1). The triazole out of plane rings absorption can be observed $\sim 655\text{ cm}^{-1}$. The symmetric and asymmetric vibrations of the carboxylate group are observed as two strong bands at 1453 and 1622 cm^{-1} , respectively. The $\Delta(u_{\text{as}} - u_{\text{sym}})$ values indicate that the carboxylate anions coordinate to the Pb(II) center in bridging mode.

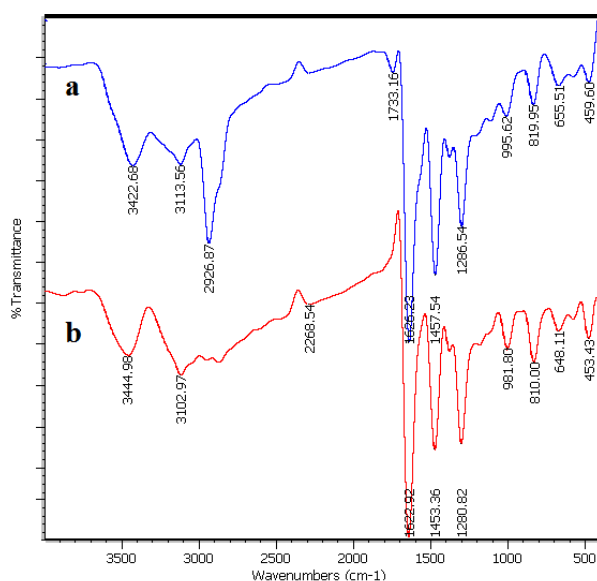


Fig. 1. IR spectra of (a) nanoparticles of compound **1** produced by sonochemical method, (b) bulk materials as synthesized of **1**.

Fig. 2 shows the simulated XRD pattern from single crystal X-ray data of compound **1** (Fig. 2a) in comparison with the XRD pattern of the single crystals compound **1** as synthesized (Fig. 2b) and a typical sample of compound **1** prepared by the sonochemical process (Fig. 2c). Acceptable matches, with slight differences in 2θ , were observed between the simulated and experimental powder X-ray diffraction patterns. This indicates that the compound obtained by the sonochemical process as nano-structures is identical to that obtained by single crystal diffraction. The significant broadening of the peaks indicates that the particles are of nanometer dimensions.

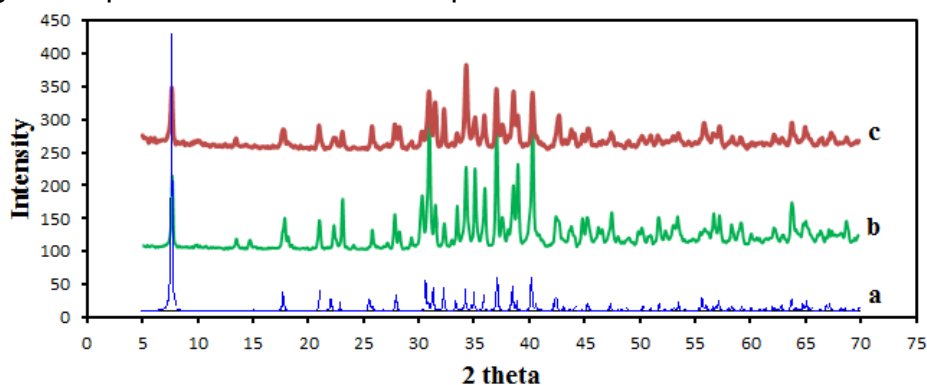


Fig. 2. XRD patterns; (a) simulated pattern based on single crystal data of compound **1**, (b) as synthesized and (c) nanostructure of compound **1** prepared by sonochemical process.

The morphology and size of compound **1** prepared by the sonochemical method was characterized by field emission scanning electron microscopy (FESEM). Fig. 3a shows the field emission scanning electron microscopy (FESEM) of the compound **1** prepared by ultrasonic generator 138 W in concentration of initial reagents $[Pb^{2+}] = [L^-] = [I^-] = 0.1$ M. Another high-density ultrasonic probe, operating at 35 kHz with a maximum power output of 305 W and different concentrations of lead(II) nitrate and

ligands 1H-1,2,4-triazole-3-carboxylate (L^-) and potassium iodide solution (0.05 and 0.01 M) were tested (Fig. 3b,c).

Appropriate nano-sized particles of compound **1** were obtained at a concentration of 0.01 M and with electrical power of 305 W from the ultrasonic generator (Fig.3c). Morphology and particle sizes of the nanostructures depend on the concentration of initial reagents and also power of ultrasound irradiation. In order to investigate the role of concentration of initial reagents and power ultrasound irradiation on the nature of products, reactions were performed under two different powers of ultrasound irradiation with three different concentrations of initial reagents. Comparison between the samples with different concentrations and different electrical powers from the ultrasonic generators shows that reduction of concentrations of initial reagents and simultaneously increasing the electrical power of ultrasonic generator decrease the particles size and also lead to uniform nanoparticles morphology. Thus, particles sizes produced using lower concentrations of initial reagents and higher ultrasound irradiation (0.01 M with 305 W, Fig. 3c) are smaller than particles size produced using higher concentrations and lower irradiation (0.1 and 0.05 M with 138 W, Fig. 3a 3b, respectively).



Fig. 3. FESEM photograph of compound **1** nanoparticles prepared by (a) ultrasonic generator 138 W in concentration of initial reagents $[Pb^{2+}] = [L^-] = [I^-] = 0.1$ M, (b) ultrasonic generator 138 W in concentration of initial reagents $[Pb^{2+}] = [L^-] = [I^-] = 0.05$ M and (c) ultrasonic generator 305 W in concentration of initial reagents $[Pb^{2+}] = [L^-] = [I^-] = 0.01$.

In **1**, the Pb^{II} ion is in the hemidirected geometry and five-coordinated with one nitrogen atom, two oxygen atoms from the L^- anions and two iodide ions. One $\mu_{1,1}-I^-$ ligand and the L^- anions act as bridging ligands to join neighboring lead(II) centers to form a 1D linear chain. The subtle combination of $Pb...I$ interactions and hydrogen bonding serves to connect these 1D coordination chains to 2D layered networks, and then a 3D framework. A view of the coordination environment around the lead(II) ion and packing of compound **1** is shown in Fig. 4. The title complex crystallizes in the orthorhombic space group $Pbca$.

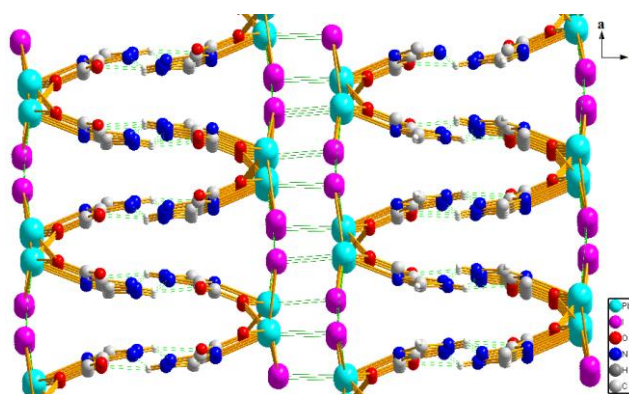


Fig. 4. A fragment of the 3D framework in compound **1**, viewed along b direction.

To examine the thermal stability of the nanoparticles and the single crystals of compound $[\text{Pb}(\text{L})(\mu_2\text{-I})]_n$ (**1**), thermal gravimetric analyses (TGA) were carried out between 25 and 600 °C under argon flow (Fig. 5). The compound **1** is stable up to 210 °C and decomposition takes places between 210-652 °C with a mass loss ~54.5%. The solid residue formed at around 652 °C is suggested to be PbO (observed: 45.5, calcd: 50.1%). Nano-sized compound **1** is less stable and starts to decompose at 187 °C. Detectable decomposition of the nanoparticles of **1** thus starts about 23 degree earlier than that of its bulk counterparts, probably due to the much higher surface to volume ratio of the nanoparticles, as more heat is needed to annihilate the lattices of the bulk materials.

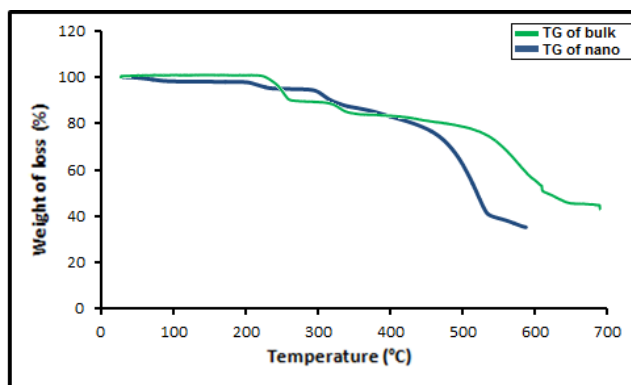


Fig. 5. Thermal behaviour of compound **1** as bulk and nanoparticle.

Ligand-free PbO nano-structure was simply synthesized by solid-state transformation of compound **1** at 630 °C under air atmosphere for 4 h. Fig. 6 provides the XRD pattern of the residue obtained from the calcination of compound **1**. The obtained pattern matches with the standard pattern of PbO with the lattice parameters ($a = 3.9729 \text{ \AA}$, $c = 5.0217 \text{ \AA}$, S.G. = P4/nmm and $z = 2$) which is the same as the reported values (JCPDS card number 05-0561)

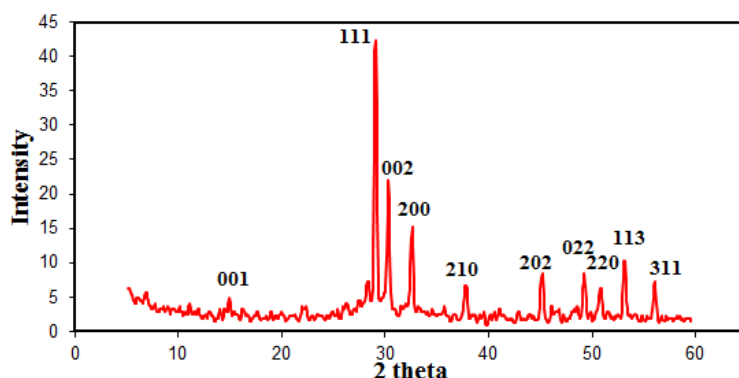


Fig. 6. XRD pattern of PbO nanostructure prepared by calcination of compound **1** at 630 °C

As the calcination process was successful for the preparation of PbO, we used the nano-sized compound **1** prepared by the sonochemical process at a concentration of 0.1 M and 138 W power of ultrasonic irradiation for the preparation of PbO nanoparticles. The SEM image of the resulting residue shows the formation of agglomerated PbO nanoparticles (Fig. 7).

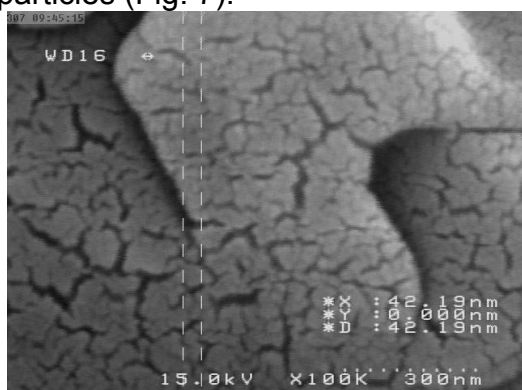


Fig. 7. FESEM image of agglomerated PbO nanoparticles prepared by calcination of compound **1** nanoparticles at 630 °C.

Nanoparticles PbI_2 have been generated by thermal decomposition of compound **1** in oleic acid as surfactant at 200 °C under air atmosphere for 2 h. The final product upon calcination of compound **1** is, based on their XRD pattern, hexagonal PbI_2 (Fig. 8). The phase purity of the as-prepared hexagonal PbI_2 nanoparticles are completely obvious and all diffraction peaks are perfectly indexed to the hexagonal PbI_2 structure with the lattice parameters of $a = 4.557 \text{ \AA}$, $c = 6.979 \text{ \AA}$, $Z = 1$ and S.G = P-3m1 which are in JCPDS card file No. 73-1750. No characteristic peaks of impurities are detected in the XRD pattern.

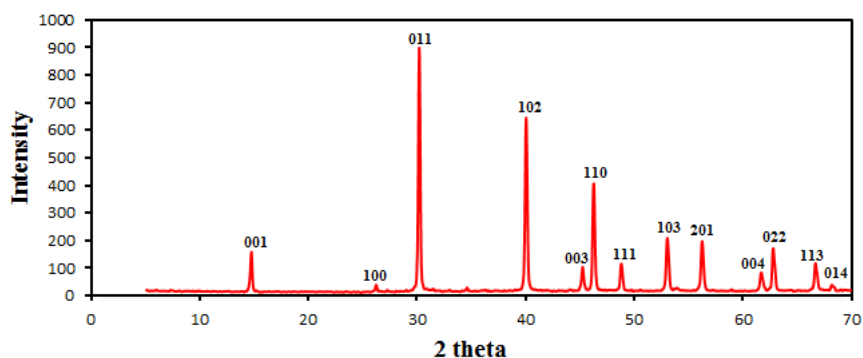


Fig. 8. XRD pattern of PbI_2 nanoparticles prepared by treatment with oleic acid as a surfactant at 200 °C.

Fig. 9 shows the SEM image of the PbI_2 nanoparticles obtained from calcination of compound **1** in oleic acid as a surfactant at 200 °C for 2 h.

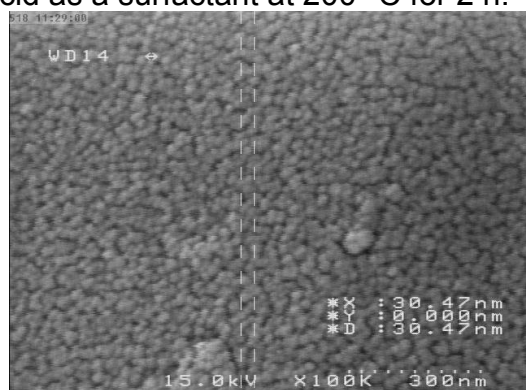


Fig. 9. FESEM image of PbI_2 nanoparticles prepared by treatment with oleic acid as a surfactant at 200 °C.

CONCLUSION

A nano-sized Pb(II) coordination polymer, $\{[\text{Pb(L)}(\mu_2\text{-I})]_n$ (**1**), $\text{L}^- = 1\text{H-}1,2,4\text{-triazole-}3\text{-carboxylate}\}$ was synthesized by sonochemical irradiation and compared with its crystalline structure. Compound **1** was characterized by X-ray powder diffraction (XRD), IR spectroscopy and thermal gravimetric (TG). To prepare the nanostructure of compound **1**, three different concentrations of initial reagents, 0.1, 0.05 and 0.01 M, and different power ultrasound irradiation, 138 and 305 W, were tested. Appropriate nano-sized compound **1** were obtained at concentration of 0.01 M and power ultrasound irradiation 305 W. Morphology and particle sizes of the nanostructures depend on the concentrations of initial reagents and power ultrasound irradiation. Results show a decrease in the particles size and also uniformed nanoparticles morphology as the concentration of initial reagents is decreased and simultaneously the electrical power of ultrasonic generator is increased. Calcination of the nano-sized

compound **1** at 630 °C in a furnace and static atmosphere of air for 4 h yields agglomerated PbO nanoparticles whereas PbI₂ nanoparticles were prepared by thermal decomposition of compound **1** in oleic acid as a surfactant at 200 °C.

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