IRREVERSIBLE TRANSFORMATIONS OF 3D LEAD(II) COORDINATION POLYMERS via MECHANOCHEMISTRY; PRECURSORS FOR THE PREPARATION OF LEAD(II) CHLORIDE/ SULFIDE/BROMIDE NANOPARTICLES

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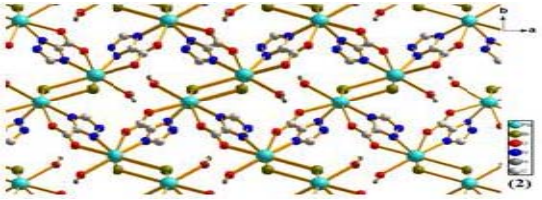
Abstract - Irreversible crystal-to-crystal transformations of 3D lead(II) coordination polymers with the ligand 1H-1,2,4-triazole-3-carboxylic acid (HL), from [Pb(L)(μ2-Cl)(H2O)]n (1) to [Pb(L)(μ2-Br)(H2O)]n (2) and [Pb(L)(μ1,1-NCS)(H2O)]n (3) by solid-state anion-replacement processes under mechanochemical reactions, have been studied. These irreversible solidstate structural transformations of compound 1 to compounds 2 and 3, have been verified by PXRD measurements. PbCl2, PbBr2 and PbS nanoparticles were obtained by thermal decomposition of compounds 1, 2 and 3 in oleic acid as surfactant at 200 °C under air atmosphere, respectively.

I. INTRODUCTION

Coordination polymers are a class of materials composed of metals or metal clusters (the ‘‘node’’) coordinated to multi-functional organic ligands (the ‘‘linker’’) [1].During the last two decades, design and synthesis of novel metal–organic coordination polymers are attracting more attention, not only for their interesting molecular topologiesbut also for their potential applications as functional materials, ions exchange, catalysis, molecular recognition, nonlinear optics, molecular magnetic materials, electrical conductivity, separation and gas storage [2]. Solidstate crystal-to-crystal transformations involving coordination polymers induced by light, heat, guest removal, uptake or exchange, expansion of coordination numbers, oxidation of metal centers, condensation, or reactions between the ligands are very fascinating and one of the hot topics in solidstate chemistry [3]. Solid state reactions by manual or mechanical grinding solid reactants together with either no added solvent or only nominal amounts for molecular synthesis have triggered lots of attention. Mechanochemical synthesis, a burgeoning field in coordination polymers, has been utilized to synthesize various coordination polymers from the reactants without solvents [4]. In this work we report the crystal-to-crystal conversions of 3D lead(II) coordination polymers by solid-state irreversible anion-replacement, [Pb(L)(μ2-Cl)(H2O)]n (1) to [Pb(L)(μ2-Br)(H2O)]n (2) and [Pb(L)(μ1,1-NCS)(H2O)]n(3)L = 1H-1,2,4-triazole-3-carboxylate (Fig. 1).



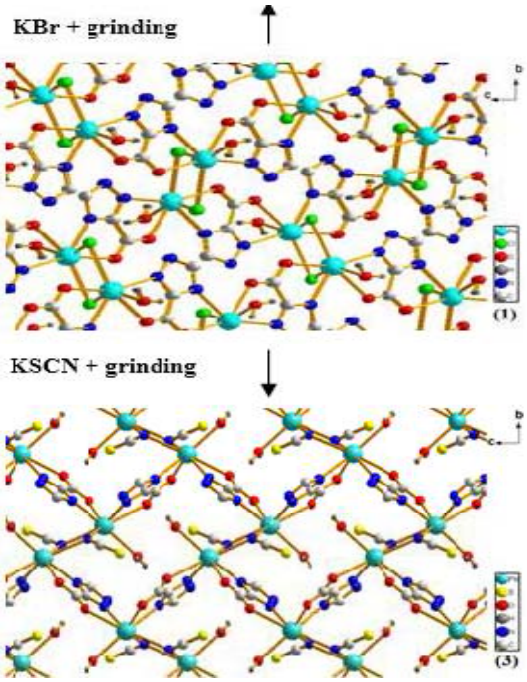


Figure 1A schematic diagram illustrating the structural conversions from 3D coordination polymer 1 (middle) to 3D coordination polymers 2 (up) and 3 (bottom) by solid state irreversible anion-replacement.

II. DETAILS EXPERIMENTAL

2.1. Synthesis of coordination polymers 1, 2 and 3

Crystals of 1 were prepared by a branched tubemethod,20 1H-1,2,4-triazole-3-carboxylic acid (0.117g, 1 mmol), potassium chloride (0.074 g, 1 mmol)and lead(II) nitrate (0.331 g, 1 mmol) were placed in the arm to be heated. Water was carefully added tofill both arms, and then the arm to be heated was placed in a bath at 60°C. After 3 days, colorless crystals were deposited in the cooler arm which were filtered off, washed with water and air dried. (0.21 g, yield 57%), m.p. >300 °C. (Found C, 9.88; H, 1.12; N, 11.47. calculated for C3H4ClN3O3Pb; C: 9.67, H:

1.08, N: 11.27%). IR (cm-1) selected bands: 560(s), 663(s), 1094(s), 1302(m), 1468(m), 1595(vs), and 3407(br). The 3D [Pb(L)(μ2-Cl)(H2O)]n(1) polymerizes on grinding the solid with KBr and KSCN for 20 min in an agate mortar and pestle to form 3D coordination polymers, [Pb(L)(μ2-Br)(H2O)]n(2)19a and [Pb(L)(μ1,1-NCS)(H2O)]n(3),21 respectively. These powder samples separated by washing. In the case of 2, yield: 70% (m.p> 300 □C).

Found C, 8.55; H, 0.99; N, 10.43. calculated for C3H4BrN3O3Pb; C: 8.63, H: 0.96, N: 10.07%. In 3, yield: 64% (m.p> 300 □C). Found; (C, 12.22; H, 0.79;N, 14.25%. calcd. for C4H4N4O3PbS; C, 12.19; H,0.77; N, 14.21%).

2.2. Synthesis of PbCl2, PbBr2 and PbS nanoparticles

Precursors 1-3 (0.1 mmol) were dispersed in oleic acid (1.35 ml) to form homogenous emulsion solutions. These solutions were degassed for 20 min and then heated to 200 °C for 2 h. At the end of the reaction, white precipitates for precursor 1-2 and black precipitates for precursor 3 were formed. A small amount of toluene and a large excess of MeOH were added to the all of three reaction solutions and PbCl2, PbBr2 and PbS nanoparticles were separated by centrifugation for the precursors 1, 2 and 3, respectively.

The solids were washed with EtOH and dried under air atmosphere. PbCl2 with the lattice parameters (a = 7.6222(5) Å, b= 9.0448(7) Å, c = 4.5348(4) Å, S.G. = Pnam (62) and z = 4); PbBr2 with the lattice parameters (a =8.062 Å, b = 9.5393 Å, c = 4.7348 Å, S.G. = Pnam (62) and z = 4); PbSwith the lattice parameters (a =5.9362 Å, S.G. = Fm3m (225) and z = 4)

III. RESULTS AND DISCUSSION

The [Pb(L)(μ2-Cl)(H2O)]n (1) was prepared by a branched tube method and this compound polymerizes by grinding the solid with KBr and KSCN for 20 minutes in an agate mortar and pestle undergo irreversible transformations, to form [Pb(L)(μ2-Br)(H2O)]n (2) and [Pb(L)(μ1,1-NCS)(H2O)]n (3), respectively. Irreversible crystal-to-crystal conversions along with anion-replacement from compound 1 to 2 and 3 were confirmed by powder X-ray diffraction patterns, IR spectroscopy and thermogravimetric and differential thermal analyses. To study the sufficiency of coordination polymers as suitable precursors for the syntheses of metal nanostructures materials, 3D coordination polymers, [Pb(L)(μ2-Cl)(H2O)]n (1) and the same samples after rinding with KBr and KSCN, [Pb(L)(μ2-Br)(H2O)]n (2) and [Pb(L)(μ1,1-NCS)(H2O)]n(3), respectively, used as precursors to preparation of lead(II) chloride, lead(II) bromide and lead(II) sulfide nanostructures by thermal decomposition in oleic acid as a surfactant at 200 °C under air atmosphere for 2h, respectively (Fig. 2).

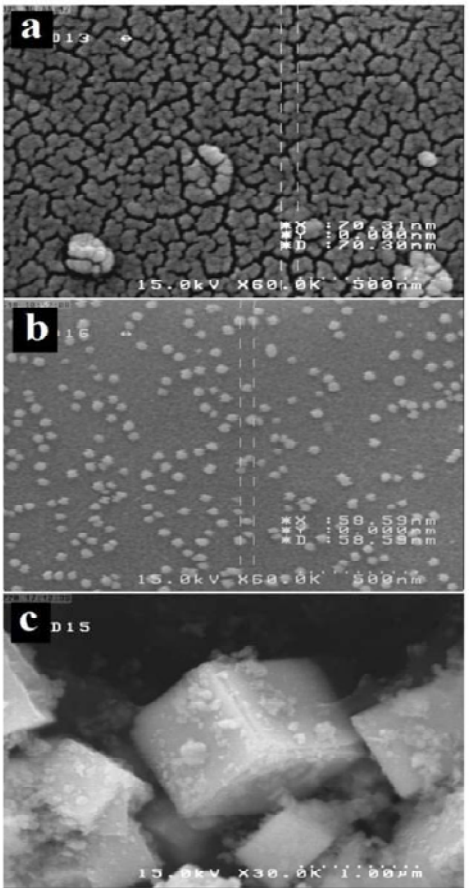


Figure 2The SEM images of (a) PbCl2, (b) PbBr2 and (c) cubicshaped PbS nanoparticles prepared by thermolysis of compounds 1, 2 and 3 in oleic acid at 200 °C under air atmosphere for 2 h, respectively

CONCLUSIONS

In summary, a3D lead(II) coordination polymer [Pb(L)(μ2- Cl)(H2O)]n (1) polymerize on grinding thesolid with KBr and KSCN to form the 3D coordination polymers, [Pb(L)(μ2-Br)(H2O)]n (2) and [Pb(L)(μ1,1-NCS)(H2O)]n(3), respectively. PbCl2, PbBr2 and cubic-shaped PbS nanoparticles were obtained by thermolysis of compounds 1, 2 and 3 in oleic acid as surfactant at 200 °C under air atmosphere, respectively.

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