

Synthesis and Characterization of α - and β -HgS nanoparticles from Hg(II) dithiocarbamate Complexes

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Abstract

Bis(N-(pyrrol-2-ylmethyl)-N-butylthiocarbamate-S,S')mercury(II) (**1**) and bis(N-(pyrrol-2-ylmethyl)-N-(2-phenylethyl)dithiocarbamate-S,S')mercury(II)(**2**) were used as single source precursors for the preparation of mercury sulfide nanoparticles. Mercury sulfides were characterized by XRD, TEM, EDAX, IR, UV and fluorescence spectra. Solvothermal decomposition of **1** yielded three different morphological (hexagonal, cube and spherical) α - mercury sulfide nanoparticles and **2** gave only spherical β - mercury sulfide nanoparticles.

Keywords: Nanoparticle, mercury, dithiocarbamate and hexagonal.

Introduction

Mercury(II) dithiocarbamate complexes have been extensively studied because of their wide biological, industrial, agricultural and chemical applications [1-5]. Dithiocarbamate ligands display a variety of coordination patterns such as monodentate, bidentate (isobidentate or anisobidentate in chelating and bridging situations), triconnective etc., leading to a great diversity of molecular and supramolecular structures [6]. Particularly, six

different coordination motifs have been observed for mercury (II) dithiocarbamates [7]. There are two mononuclear motifs (I and II). Motifs I and II feature a grossly distorted tetrahedral geometry [8] and a square planar geometry [9], respectively about the central atom. Dimeric motifs fall in to two distinct classes (motifs III and IV). These motifs are found that feature two chelating and two bridging dithiocarbamate ligands. The only difference between the motifs III and IV relates to the relative disposition of the bridging dithiocarbamate ligands i.e., in motif III they lie to the same side of the dimer [10] but for motif IV they lie in opposite sides [11]. The eight membered ring in structural motifs III and IV can be described as a saddle and twisted chair conformations, respectively. Trimeric motif (V) is found in [Hg₃(thqdtc)₆].py (thqdtc=1,2,3,4-tetrahydroquinoline carbodithioate)[12]. In this motif the environments of two mercury atoms are similar (five coordinated) but their environments are different from another mercury atom (four coordinated). Finally, there is one example of motif VI (layer structure) i.e. for Hg(S₂CNH₂)₂ [13]. In this case all dithiocarbamate ligands are bridging and each

mercury atom exists in a distorted tetrahedral geometry. Based on systematic studies of series of structures where the only difference between them is in the nature of N-bound organic moiety, it has been concluded that the actual structure adopted in Hg(II) dithiocarbamate complexes is dependant of the N-bound organic moiety. This may be utilized as a design element in crystal engineering especially in main group elements [6]. In addition to the structural properties, mercury(II) dithiocarbamate complexes have been used as single source precursors for the preparation of mercury sulfide nanoparticles [14-16]. Suitable changes in the organic moiety of dithiocarbamate ligands can affect the phase and morphology of the metal sulfide nanoparticles [17]. Various size and shape of mercury sulfide nanoparticles have a wide range of applications such as ultrasonic transducers, image sensor, electrostatic image materials, flat-panel devices, photoelectric conversion devices, non-linear optical material and solar cells [18-24]. Due to the interesting structural variations of Hg(II) dithiocarbamate complexes and their utilization to prepare various size and shape of mercury sulfide nanoparticles, herein we report synthesis, spectral and structural studies on complexes **1** and **2** and preparation of mercury sulfide nanoparticles from both the complexes.

Experimental

Materials and techniques : All chemicals were of analytical grade obtained from commercial sources and used without further purification. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer (range: 4000–400 cm^{-1}) as KBr pellets. PXRD and TEM images were performed using EQUINX 1000 and TECNAI T2 G2 make-FEI, respectively. EDS were performed by SUPRA 55VP CARL. A Shimadzu UV-1650 PC double-beam UV-vis spectrophotometer was used for recording the electronic spectra. Fluorescence

spectra were recorded using Perkin Elmer 1555 fluorescence spectrophotometer at room temperature.

Preparation of complexes

Preparation of amines : N-(pyrrol-2-ylmethyl)-N-butylamine and N-(pyrrol-2-ylmethyl)-N-(2-phenylethyl) amine were prepared by general methods reported earlier [28].

Preparation of mercury sulfides: 0.5 g of **1** was mixed with 15 ml triethylenetetraamine in a round bottom flask and then the content of the flask was refluxed for 15 minutes. The dark red color precipitate was filtered off and washed with methanol several times to remove the excess triethylenetetraamine .

Similar procedure was adopted to prepare mercury sulfide from complex **2**.

Result and discussion

Characterization of metal sulfide nanoparticles:

Mercury sulfide nanoparticles from complexes **1** and **2** are represented as samples **1** and **2**, respectively. Powder X-ray diffraction patterns of the samples **1** and **2** displayed in **Fig 1**. All the diffractions peaks in powder X-ray diffraction patterns of samples **1** and **2** could be indexed to be hexagonal phase (α -HgS, cinnabar) and cubic phase (β -HgS, meta cinnabar). These are in good agreement with standard data from the JCPDS card No. 89-7103 and 89-0432 for sample **1** and **2**, respectively. In both the cases, no peaks due to any impurities were detected, revealing the presence of single phase in the product.

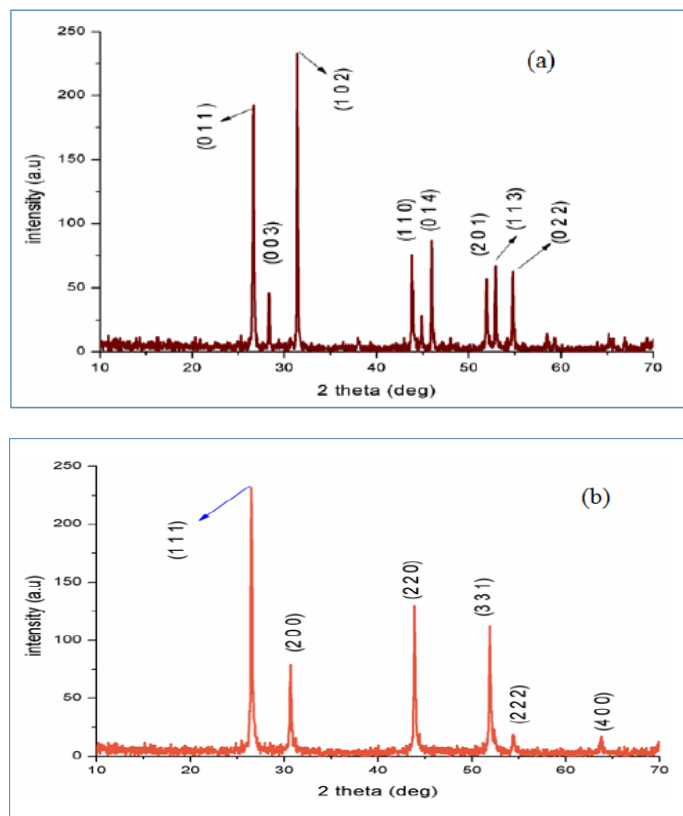


Figure 1

TEM images of samples **1** and **2** are shown in **Fig 2**. TEM images of sample **1**(**Fig.2 (a)** and **(b)**) reveal that most of the particles are spherical with diameter in the range 14-36 nm. A few hexagonal and cubic particles are also present in the sample **1**. In the case of sample **2**, all the particles are spherical with diameter in the range 20-30nm.

Powder X-ray diffraction and TEM studies support that the different phases, shape and size of HgS nanoparticles can be prepared using mercury(II) dithiocarbamate complexes containing various N-bound organic moiety of dithiocarbamate.

Energy dispersive X-ray spectra of both the samples exhibit strong signals for mercury and sulfur. This confirms that the solvothermal decomposition of both the complexes **1** and **2** yield mercury sulfide. Elemental analytical data obtained from EDS of sample **1** reveal that the atomic percentage of Hg and S are 43.68 and 56.32 (ratio: 1:1.29), respectively. This reveals that a higher

number of sulfur atoms present in the products compared to mercury. This may be due to the presence of some vacant sites of Hg 2+ or sulfur dangling bonds in the sample **1**. In the case sample of **2**, the atomic percentage of mercury and sulfur [53.15:46.85; ratio: 1:0.88] indicate the presence of excess Hg 2+ in the sample **2**.

UV-vis absorption spectra of sample **1** and **2** are respectively. An absorption maximum is appeared at 220 nm in the UV-Vis absorption spectra of both the samples. A blue shift is observed in the absorption maxima relative to the bulk HgS (620 nm) [29]. Generally, the absorption maxima (λ max) decreases with a decreasing size of the nanoparticles as a

Photoluminescence spectra of samples **1** and **2**are respectively. The spectra of samples **1** and **2** exhibit a broad emission peak at 364 and 340 nm, respectively on excitation at 265 and 270 nm, respectively. These peaks are due to the core state radioactive decay from CB to VB and the blue shift of the emission peak compared to those of bulk HgS (588 nm) [31] is attributed to the quantum confinement effect.

Consequences of quantum confinement of the photogenerated electron-hole carriers [30].

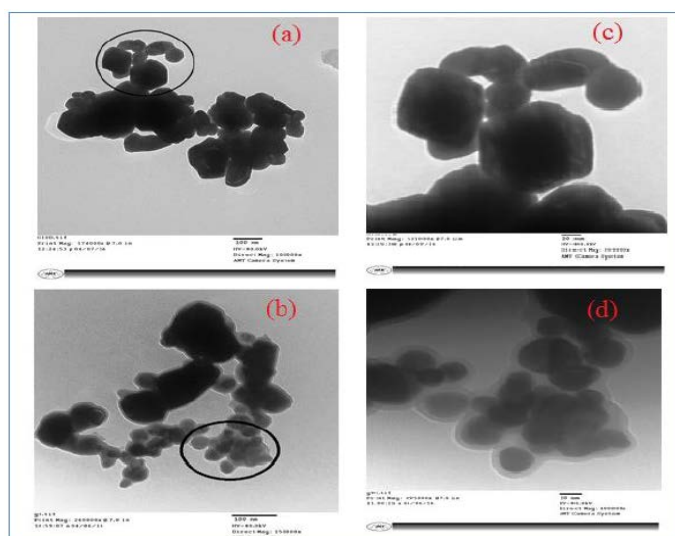


Figure 2

The FTIR spectra of samples **1** and **2**. In the spectra of both samples, a broad band around 3400 cm⁻¹ for samples **1** and **2** correspond to the stretching vibration of N–H and the peaks in the region 2851-2959 cm⁻¹ are assigned to the stretching vibrations of aliphatic C–H. No peaks observed due to the stretching vibrations of C–N (thioureide), C–S and aromatic C–H indicate the absence of dithiocarbamate ligands in the samples **1** and **2**.

Conclusion

Three different morphological α -HgS and spherical β -HgS nanoparticles were obtained from **1** and **2**, respectively. This study also shows that various morphological and phase (α and β) HgS nanoparticles can be prepared from different mercury (II) dithiocarbamate complexes.

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