

Synthesis and Characterization of Nano Structured Zinc(II) Cysteine Complex Under Ultrasound Irradiation

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ABSTRACT

Cysteine and zinc oxides are important materials that have a wide range of applications especially in biomedical sciences. In this study, synthesis and characterization of nano structured Zn(II) complex of cysteine, (cysteine = 2-Amino-3-mercaptopropanoic acid), in two different particle sizes, has been investigated. The reaction of Zinc(II) acetate and KI with cysteine ligand under ultrasonic irradiation, leads to the formation of nano sized Zn(II) cysteine complex. Particle sizes of the product have been decreased after thermal treatments in an autoclave. The hexagonal micro crystalline zinc oxide, has been prepared using Zn(II) cysteine complex as precursor. Characterization of the Zn(II) complex, has been performed using elemental analysis, FTIR spectroscopy, energy dispersed X-ray analysis (EDAX), scanning electron microscopy (SEM), thermal analysis (TG/DTA) and gel-permeation chromatography (GPC). Based on the results, chemical formula for the Zn(II) cysteine complex is proposed as $[ZnI_2(C_3H_5NO_2S)]_n$. Scanning electron microscopy (SEM) analysis has demonstrated nano particles Zn(II) complex with average diameter of about 38-54 nm. Hexagonal ZnO micro structures were characterized by FTIR, X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) techniques.

Keywords: Zn(II) complex, zinc oxide, sonochemical method, cysteine ligand

1. INTRODUCTION

Cysteine is known to act as an active site in bio performance of the enzymes known as cysteine protease. Many cysteine containing natural products exhibit important biological activities, Cakir, S., et al. (2009). It is used in some antibiotics for the treatment of skin damages and as a radio protective agent. It is also involved in the structure of vasopressin as anti diuretic hormone, Wring, S., et al. (1989). Metal complexes continue to find applications in the treatment of a wide variety of human ailments. For example, in medical imaging, Gd(III) complexes are used in MRI as contrast agents while Technetium-99 complexes are employed as cardiovascular imaging dyes, Wring, M., Hell, R. (2003, 2006). Recently mercury(II) complex with L-Cysteine in alkaline aqueous solutions have been structurally characterized by means of extended XRD absorption fine structure

spectroscopy, Jalilehvand, F., et al., (2006). Transition metal-cysteine complexes have considerable biological activities, Sallmann, M., et al., (2012); some of their antitumor properties show promise in therapeutic applications, Masond, M.S., Abd El-Hamid, O.H. (1990). Formation of the stable complexes with [S,O] coordination mode of Ala-Cys, Phe-Cys, and Ala-Ala-Cys were studied by potentiometric and spectroscopic methods, that has been characteristic for cobalt(II), zinc(II), and cadmium(II) ions Cherifi, K., et al., (1990).

In recent years, nano structured compounds have witnessed an increasing interest in both fundamental and technological applications, Yin. Y., Alivisatos, A.P. (2005); Duan, X., et al., (2003). Considerable efforts have been dedicated to the controlled synthesis of metal oxides, sulfides and ceramic materials with micron and nano scale dimensions. A review in the literature showed that among various methods for preparing nano scale materials, sonochemistry has attracted much attention Ranjbar, Z.R., Morsali A. (2011); Haddadian, H., et al., (2008); Aslani, A., et al., (2008); Yadav, R.S., Mishra, p. (2008); Kristl, M., Drofenik, M. (2008); Peng, C., et al., (2012); Suslick, K.S., et al., (1996); Gedanken, A. (2004). A. Morsali's research team has succeeded in preparing different kinds of metal oxides such as PbO, Mn₃O₄, MgO, HgO, BaCO₃ under ultrasonic irradiation and or using metal complexes, as precursors Mousavi, R., et al., (2012); Safarifard, V., Morsali, A. (2012); Alavi, M.A., Morsali, A. (2010); Khanjani, S., et al., (2010); Monfared, H.H., Morsali, A. (2009); Askarinejad, A., Morsali, A. (2009); Alavi, M.A., Morsali, A. (2008). Recently, zinc oxide (ZnO) has attracted much attention within the scientific community as a future material. ZnO is a unique material that exhibits exceptional semiconducting, piezoelectric, and pyroelectric properties and its large-scale, low-cost, patterned, and designed growth as well as self-organization, makes it good candidate for future applications, Zhong L. W. (2008). ZnO has been widely studied since 1935, Xu, F., et al., (2009). The renewed interest in this material has arisen out of the development of growth technologies for the fabrication of high quality single crystal and epitaxial layers, allowing for the realization of ZnO-based electronic and optoelectronic devices Gupta, T.K. (1990). Coordination polymers have been good candidate for preparation of metal oxides Ranjbar, Z.R., Morsali A. (2011); Hosseini, A., et al., (2012); Ranjbar, M., et al., (2012).

In this paper we report a sonochemical synthesis of a new nano structured Zn(II) cysteine coordination polymer from the methanolic solution of some simple metallic salts. In this method, we also describe the synthesis of ZnO micro structure with hexagonal morphology from thermal decomposition of Zn(II) cysteine coordination polymer as precursor.

2. EXPERIMENTAL DETAILS

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. A multiwave ultrasonic generator (UP 400 Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 24 kHz with a maximum power output of 400 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. FTIR spectra (400-4000 cm⁻¹) were recorded on a Bruker tensor 27 spectrometer in a KBr matrix. Elemental analyses were performed with a Heraeus CHN-O-rapid analyzer apparatus. A Pye-Unicam Spa Philips atomic absorption was used to determine the percentage of Zn(II) in the complex. A Jenway ion analyzer 3045 was applied for quantitative analysis of the I⁻ anion.

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. X-ray powder diffraction (XRD) measurements were performed with monochromatized CuK_α radiation using a Philips diffractometer manufactured by X'pert. Crystallite sizes of selected samples were estimated using the Sherrer method. The samples were gold coated for

characterization with a scanning electron microscope. Thermo gravimetric analysis was carried out using a pyres diamond instrument. The compound was heated in a static atmosphere of nitrogen from 10-600 °C, with a heating rate of 10 °C/min. Gel permeation chromatograms were measured on a waters GPC system consisting of an isocratic pump, solvent degasser, column oven, 2996 photo diode array (PDA) detector, 2414, refractive index detector, 717plus autosampler and a Styragel HT 4 GPC column with precolumn installed. Linear PMMA standards were used for calibration. The solvent was DMF containing 5 mmol/L NH_4PF_6 . The flow speed was 0.5 mL/min.

2.1 Synthesis of nano-structured Zn(II) cysteine complex

Zinc acetate (0.109 g, 0.5 mmol) and cysteine ligand (0.06 g, 0.5 mmol) were mixed in double distilled water (10ml) and the mixture was stirred at 80 °C for 5 min, then with solid KI (0.116 g, 1mmol) were placed in an ultrasound vessel with the rated output power of 400 W and frequency 24kHz. After one hour a white powder was obtained. The product was filtered by centrifuging at 4000 rpm for 15 min and washed with double distilled water and acetone respectively. The resulting white powder Zn(II) cysteine complex (0.167 g) was prepared in 77% yield. Decomd. at: 230-232 °C. Anal. Calcd for $(\text{ZnI}_2 \text{C}_3\text{H}_5\text{NO}_2\text{S})_n$: Zn, 14.92; C, 8.21; H, 1.14; N, 3.19; I, 57.92. Found: Zn, 14.6; C, 8.14; H, 1.24; N, 3.17; I, 58.12. FTIR (KBr) 3247(b), 1596(s), 1401(w), 1304(w), 1110(w), 984(w), 643(w), 575(w). M_n (GPC) = 19400 g.mol⁻¹, PDI (GPC) = 1.15; M_w = 22500 g.mol⁻¹.

0.14 g of the product and 15 ml double distilled water was placed in 50 ml stainless-steel Parr bomb container (autoclave). After 48 h at 150°C, the autoclave was immersed in 4°C water. The suspension formed was centrifuged at 4000 rpm for 15 min. The precipitate was washed and dried at room temperature. Based on elemental analysis, FTIR, melting point and GPC results, the product was the same as Zn(II) cysteine complex, with smaller particle sizes (as shown in Figures 1 and 2, particle sizes decreased from about 24 nm to 14 nm).

To isolate single crystal of $[\text{ZnI}_2(\text{C}_3\text{H}_5\text{NO}_2\text{S})]_n$, cystein (0.5 mmol, 0.06g), zinc (II) acetate (0.5 mmol, 0.109 g) and potassium iodide (1mmol, 0.116g) were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the main arm was immersed in an oil bath at 60 °C, while the other arm was kept at room temperature. After 15 days clear solution was obtained.

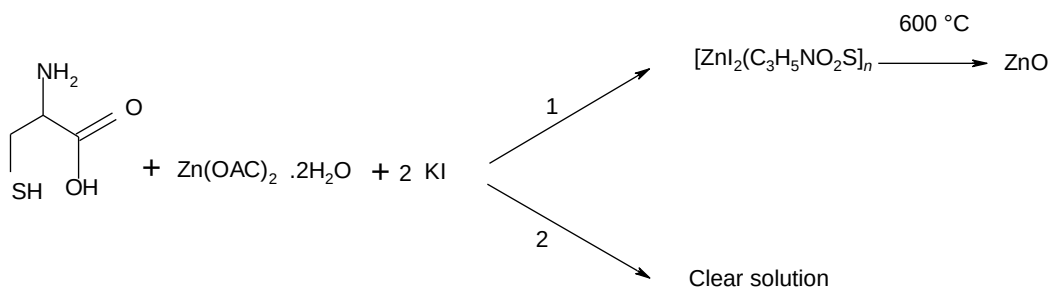
2.2 Synthesis of ZnO micro particles

In order to prepare the ZnO micro particles, the white powders of the Zn(II) cysteine complex was calcinated at 600 °C for 2 hours, under ambient atmospheric condition. The product was separated by centrifuging at 4000 rpm for 15 min and was washed with double distilled water and acetone respectively. The product was characterized with FTIR, UV-Vis spectroscopy, scanning electron microscopy (SEM), energy dispersive X-Ray (EDAX) and X-Ray powder diffraction (XRD).

3. RESULTS AND DISCUSSION

Reaction between cysteine ligand, 2-amino 3-mercuptonoic acid, with mixture of Zn(II) acetate and potassium iodide under ultrasonic irradiation, leads to the formation of the new

Zn(II) cysteine complex (Scheme 1) in 77% yield. The resulting cysteine complex was insoluble in H₂O and DMSO.



1: under ultrasonic irradiation

2: Branched Tube technique absence of ultrasonic irradiation

Scheme 1. Materials produced and synthetic methods.

On the other hand we run the same reaction via a common method for preparing coordination polymers, named branched tube Mahmoudi, G., et al., (2007); Aslani, A. et al., (2008); Ranjbar, M. et al., (2012), but no solid product obtained. The first step to check the purity of the new cysteine complex was a melting point measurement, which was quite different from starting materials indicating a new product formation. Elemental analysis for Zn, I, C, N, H and O values and GPC results indicated that the chemical formula of the product can be [ZnI₂(C₃H₅NO₂S)]_n. A comparison between FTIR spectrum of free cysteine ligand and its Zn(II) complex, revealed that a distinct carbonyl peak $\nu(\text{COOH})$ around 1608 cm⁻¹ in free cysteine, has been shifted to 1595 cm⁻¹ and the weak vibration mode due to $\nu(\text{SH})$ at 2547 cm⁻¹ disappeared. It is quite likely to be due to the coordination link of O and S atoms to Zn(II) metal ion. The IR spectra of ZnO showed characteristic bands in the region from 680 up to 434 cm⁻¹, Yadav, R.S. (2008). The morphology of the Zn(II) cysteine complex was examined by SEM. Typical SEM image is shown in Fig. 1 shows nano crystals with particle sizes about 54 nm. After hydrothermal treatment in an autoclave the particle size reduced up to about 38 nm (Fig 2). In our previous work, hydrothermal treatments causes to prepare PbOHBr from [Pb(minoxidil)Br]_n, Ranjbar, M., et al., (2012).

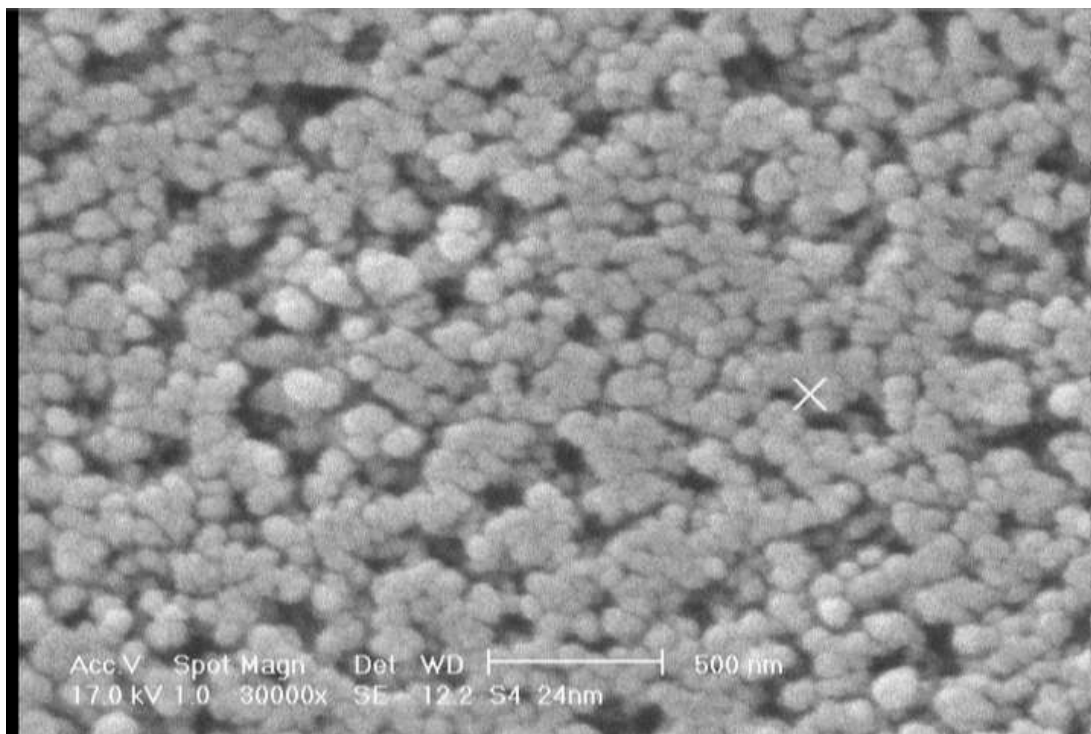


Fig. 1 SEM photograph of Zn(II) cysteine complex.

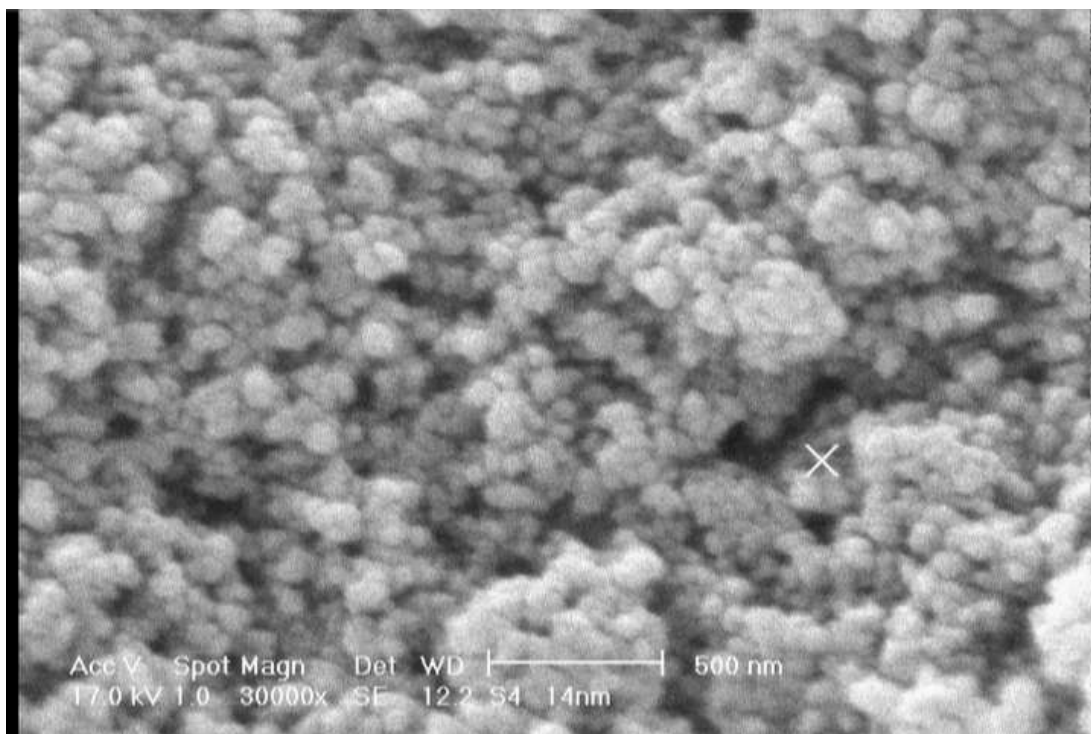
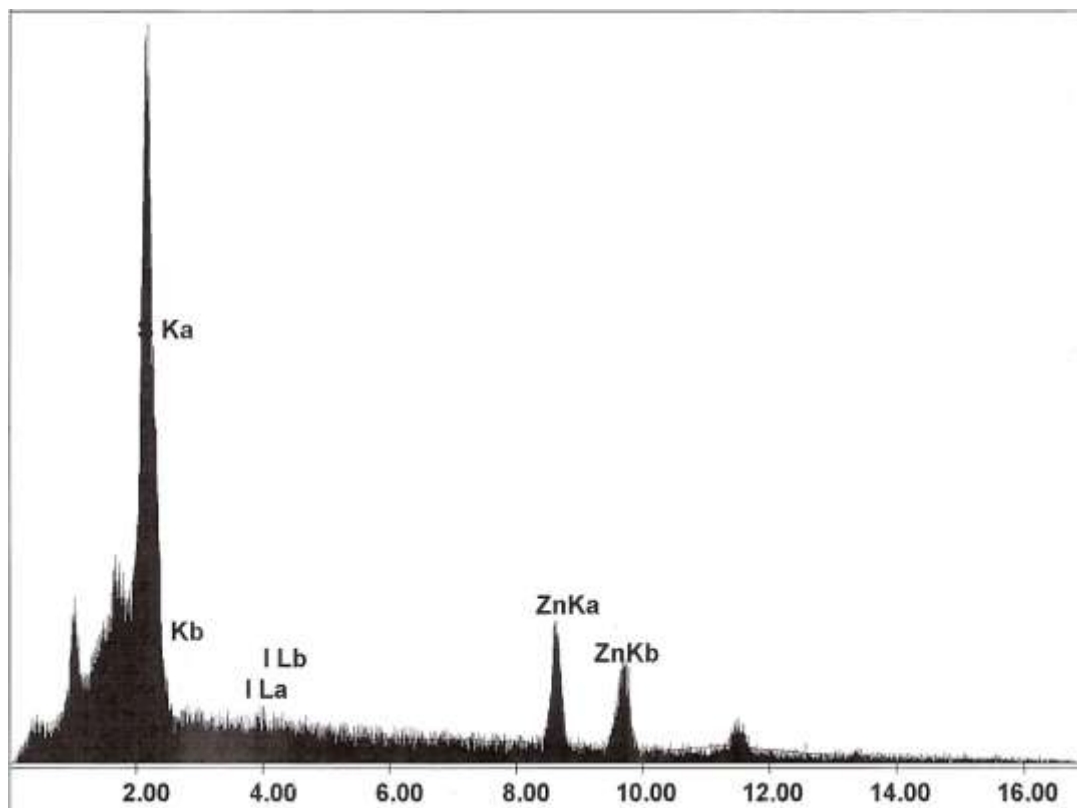
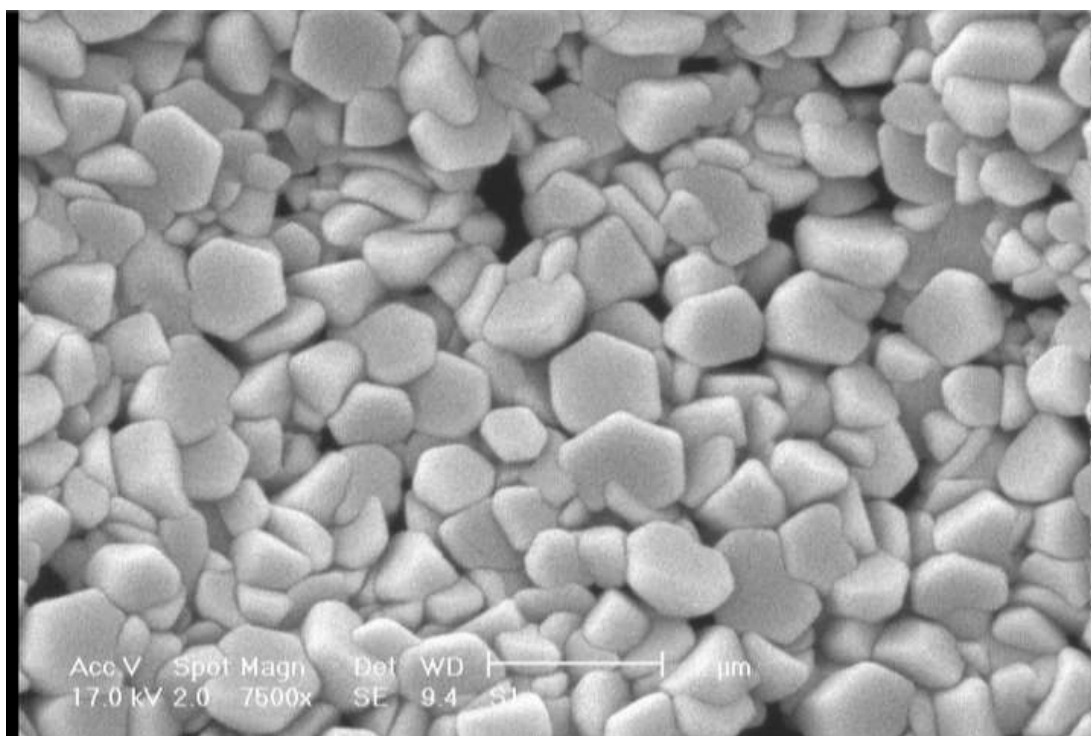


Fig. 2 SEM photograph of Zn(II) cysteine complex after hydrothermal treatment.

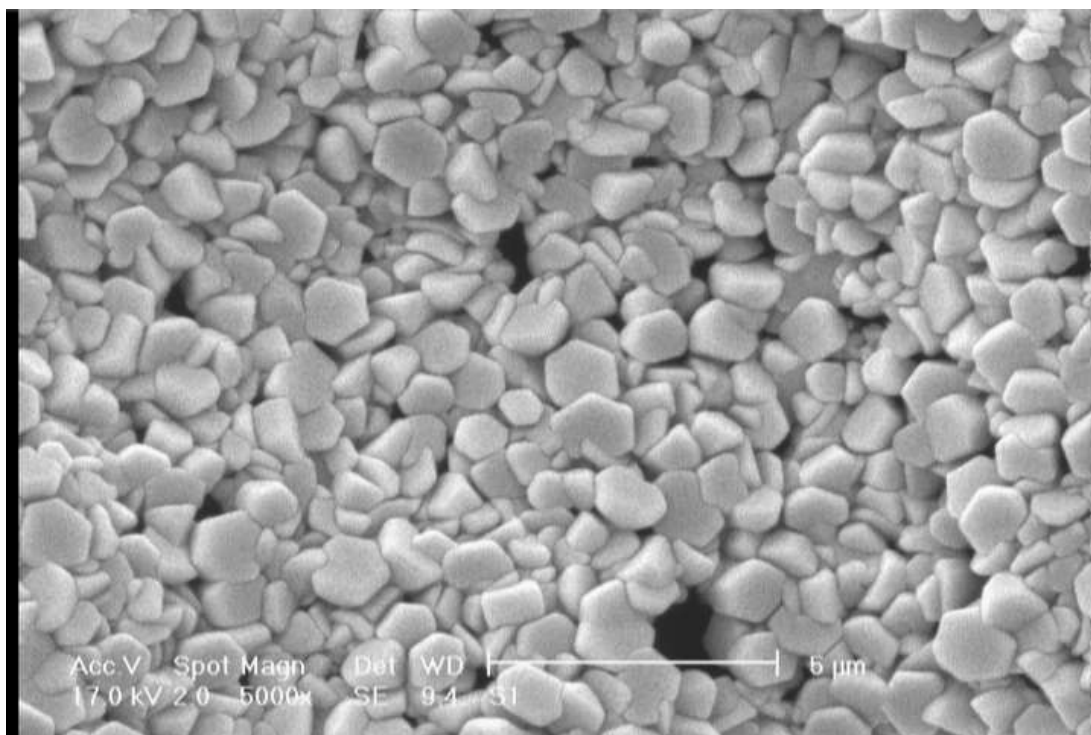
190 FTIR, elemental analysis and GPC analysis showed that the product obtained after thermal
191 treatments in an autoclave, is the same as the product obtained by sonochemical method.
192 Of substantial significance is the fact that the results show that the product is stable in
193 aqueous solution under super critical condition. The energy dispersive X-ray analysis
194 (EDAX) both of the Zn(II) cysteine complexes, confirm the existence of zinc and iodide (Fig
195 3) . Zinc oxide hexagonal particles has been prepared from the calcination of the polymeric
196 Zinc(II) complex at 600 °C under ambient air atmosphere after 2 hours, Fig. 4 shows the
197 SEM photograph of ZnO. Elemental analysis were tested by EDAX, energy dispersive X-ray
198 analysis showed that produced ZnO micro crystals is pure as shown in Figure 5.
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Fig. 3 Energy-dispersive X-ray analysis of Zn(II) cysteine complex.



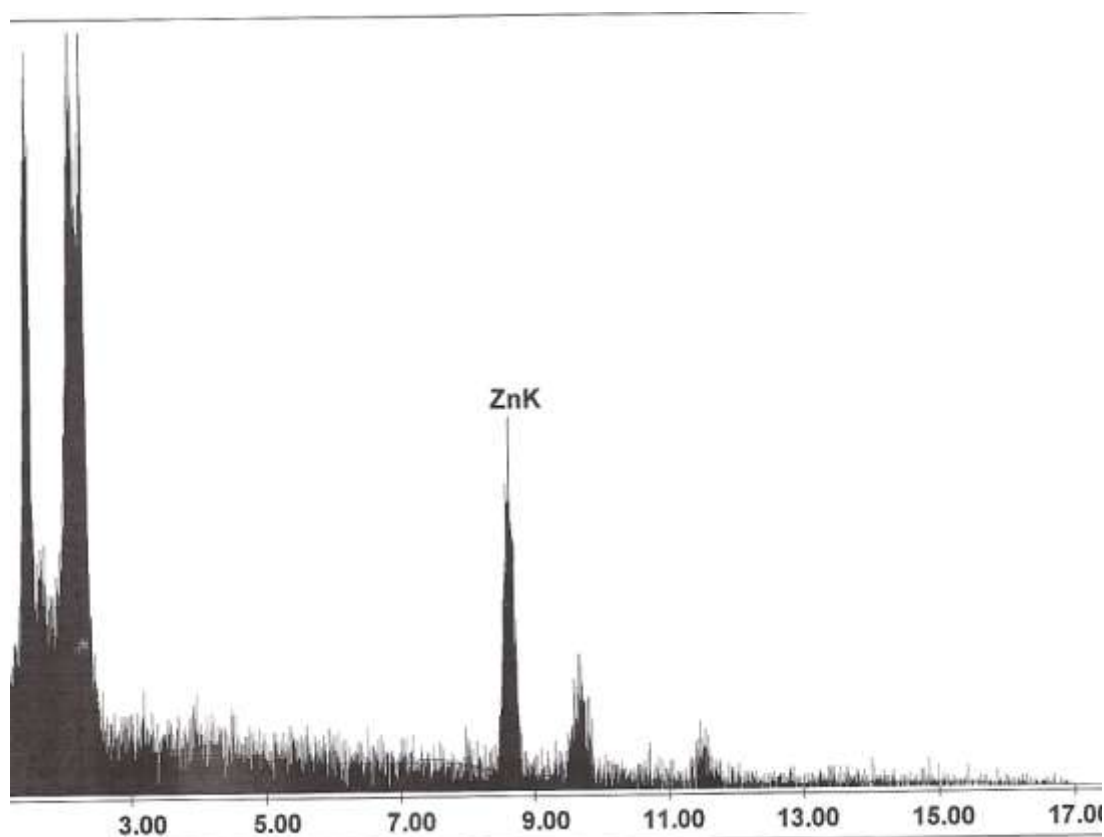
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Fig. 4 SEM photograph of ZnO (produced by calcination of the Zn(II) cysteine complex in air atmosphere).

213 The XRD pattern of the prepared ZnO microcrystals, using Cu-K α radiation source of
214 $\lambda=1.5406$ Å, is shown in Fig. 6. The spectrum shows sharp peak at 36.492° corresponding
215 to hkl (101). The reflections can be indexed well to hexagonal wurtzite ZnO diffraction (space
216 group $P6_3mc$; JCPDS No. 36-1451, cell constants $a = 3.294$ Å and $c = 5.206$ Å) the sharp
217 diffraction peaks are due to high crystallinity of ZnO obtained.
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222 **Fig. 5 Energy-dispersive X-ray analysis of hexagonal ZnO micro particles.**
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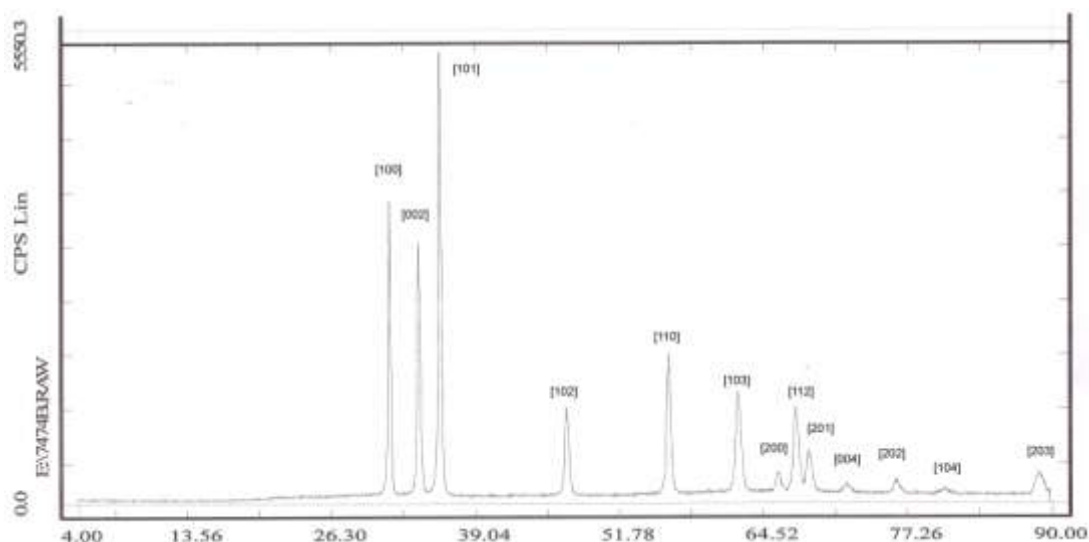


Fig. 6 XRD pattern of the ZnO.

Thermal gravimetric (TG) and differential thermal analysis (DTA) were carried out between 10 to 600 °C in a static atmosphere of nitrogen (Fig. 7). Decomposition of the compound starts from 231 up to 500 °C. Between this temperatures may be removal of the ligands occurs. At higher temperature more than 550 °C residue compound, probably ZnO, crystallizes and particle sizes increases and crystals growth. TG curve exhibits two distinct decomposition stages between 231 to 372 °C with a mass loss of about 55%. Based on TG/DTA analysis, production of ZnO probably occurs after 550 °C. As thermal decomposition was take placed during 2 h at 600 °C, the ZnO nano particles have been grown, and the particle sizes increased to micron sizes.

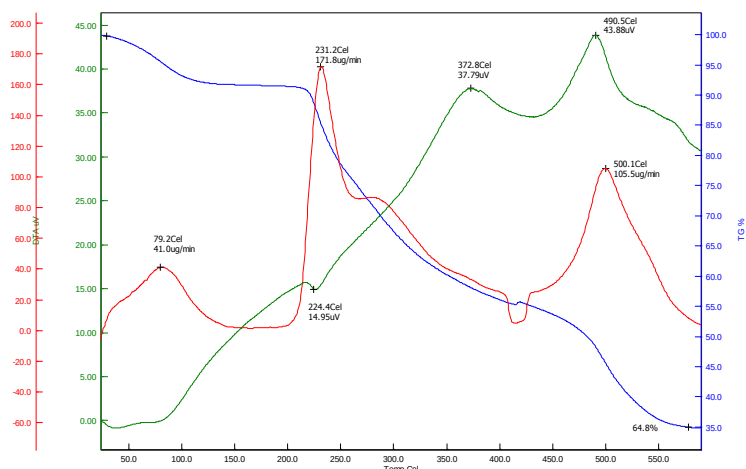


Fig. 7 TG/DTA diagrams of Zn(II) cysteine complex.

4. CONCLUSION

A new nano structured Zn(II) cysteine and iodide complex, has been synthesized by sonochemical method and the complex has been found to be stable under hydrothermal treatment in an autoclave. Based on the results the proposed chemical formula is $[ZnI_2(C_3H_5NO_2S)]_n$. The complex has been characterized by elemental analysis, FTIR, scanning electron microscopy (SEM) and EDAX and thermal analysis (TG/DTA). Calcination of the complex was produced hexagonal ZnO micro structures. This study demonstrates that the Zn(II) cysteine and iodide type of nano-sized polymeric complex may be a suitable precursor for preparation of zinc oxides with interesting morphologies. The importance of this method of synthesis is that it not only produces good yield but also it does not require high temperatures or high pressures. The products obtained by this synthetic method may turn out to be good candidates for specific industrial and biomedical applications.

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