

Synthesis of Zinc (II) Oxide Wurtzite Nano Crystals Via Zn (II) Minoxidil Nanocomposite As a New Precursor

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Abstract:

The study describes the synthesis and characterization of zinc(II) minoxidil nanocomposite (1). The reaction between zinc(II) acetate, minoxidil, $\{C_9H_{15}N_5O = \text{minoxidil} = (2,4\text{-diamino-6-piperidine-1-yl}) \text{ pyrimidine N-oxide}\}$ as a ligand and KI as bridging agent, in methanol at 60°C leads to the formation of nano-sized Zn(II) minoxidil nanocomposite, 1. Characterization of (1) was carried out by elemental analysis, FTIR, scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), and gel-permeation chromatography analysis (GPC). The result showed that nanocomposite (1) has polymeric structure with spherical morphology and particle size of about 77 nm. Wurtzite (hexagonal) nanocrystals of zinc oxide were prepared from decomposition of the coordination polymer (1) at 400°C. Characterization of zinc oxide nanocrystals was performed by FTIR spectroscopy, scanning electron microscopy (SEM), EDAX and X-ray powder diffraction XRD. The results showed that the product has spherical morphology with particle size of about 34 nm.

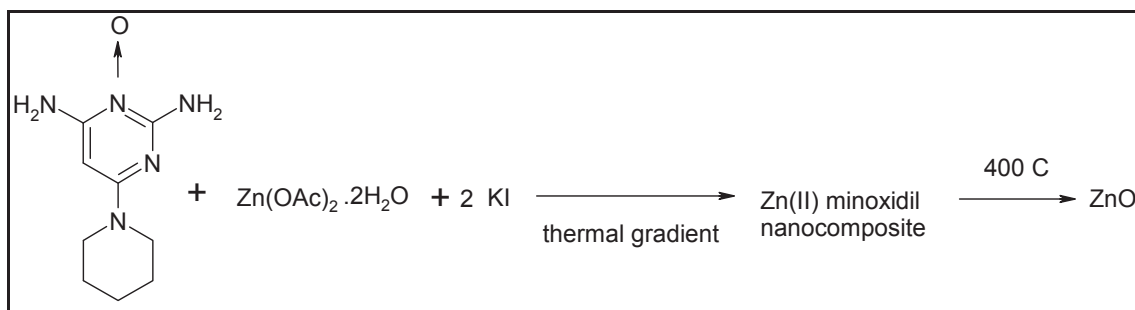
Keywords: Minoxidil, zinc oxide, nanocrystals, thermal gradient method.

1. INTRODUCTION

Zinc has been shown to be a cofactor of over 300 metalloenzymes [1] and over 2000 transcription factors [2]. For example, zinc constitutes an essential prosthetic group in zinc/copper superoxide dismutase, thereby affecting cellular reduction/oxidation status. Another example of the importance of zinc is its involvement in the gene transcription on several levels, via participation in histone deacetylation reactions [3]. Recently, zinc oxide has attracted much attention within the scientific community as a future material. ZnO has been widely studied since 1935 [4]. 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 [5].

Minoxidil [2,4-diamino-6-piperidine-1-yl) pyrimidine N-oxide] is a potent vasodilator and is used therapeutically as a hypotensive agent. A common side effect observed in patients following the use of orally administered minoxidil is an increased incidence of hypertrichosis, (hair growth) [6,7]. It has been exploited as an anti-aloplectic agent since the late 1980s, and has become one of the most popular medicaments in the world, with a market of more than \$100 million per year in the 80s and 90s in the United States alone. Just in 1995, the world market



Scheme 1: Synthesis methods.

was 125 million USD [8]. A review in the literature showed that very few metal complexes of minoxidil have been yet reported. We have succeeded however, to make a coordination polymer of minoxidil and Pb(II) in presence of KI and KBr [9, 10].

Recently, the introduction of inorganic nanoparticles to organic polymers has attracted much attention because organic-inorganic nanocomposites offer an effective way to improve the physical properties of conventional polymers such as mechanical properties, thermal stability, flame retardancy, low vapor permeability, and chemical reagent resistant [11].

In recent years, nano-structured compounds have witnessed an increasing interest in both fundamental and technological applications [12-14]. Considerable

efforts have been dedicated to the controlled synthesis of metal oxides, sulfides and ceramic materials with micro and nano-scale dimensions. Recently, the nano-structured polymeric coordination compound, when used as a precursor, showed to drive chemical reactions to form micro- and nano-sized particles in the polymeric framework [10,15-19]. Two new coordination polymers of Zn(II) have been synthesized with 1, 6-bis(2-methyl-imidazole-1-yl)-hexane (bimh), namely $\{[\text{Zn}_3(\text{BTC})_2(\text{bimh})] \cdot (\text{bimh})\}_n$ and $\{[\text{Zn}(\text{IPA})(\text{bimh})] \cdot (\text{CH}_3\text{CH}_2\text{OH})_{0.5}\}_n$ (H_3BTC =trimesic acid, H_2IPA = isophthalic acid), via hydrothermal reactions [20].

ZnO nanostructures have been prepared by different methods such as thermal decomposition of a metal

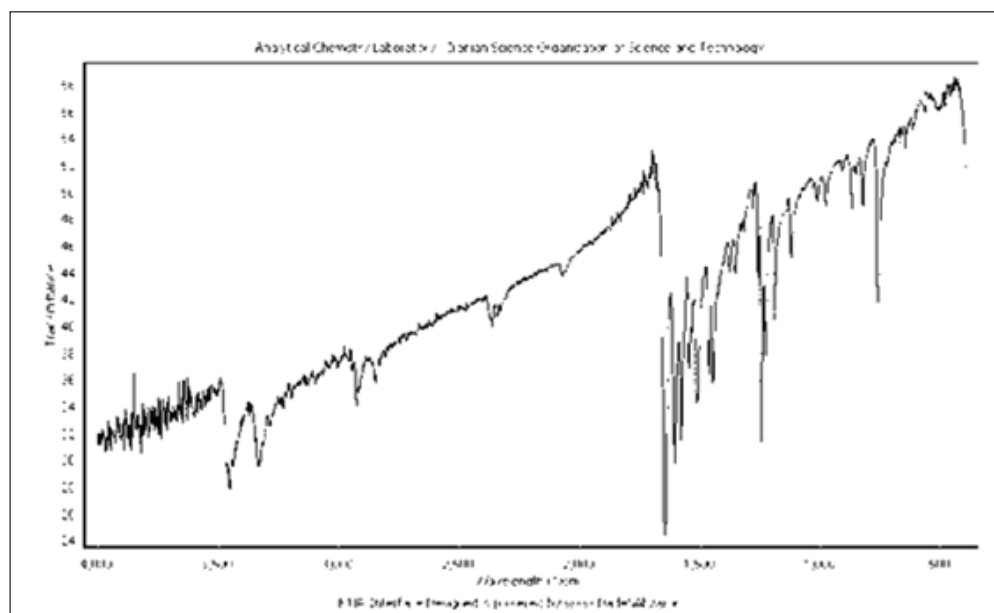


Figure 1: FTIR spectrum of Zn(II) minoxidil coordination polymer.

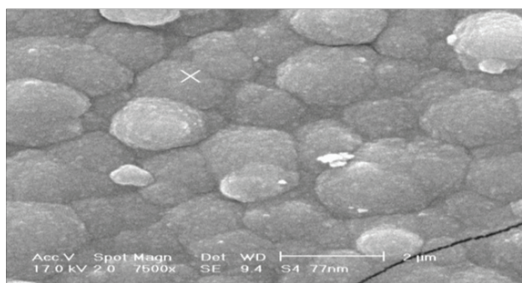


Figure 2: SEM image of the polymeric nanocomposite 1 prepared by thermal gradient method in branched tube.

precursor in presence of a surfactant [21], thermolysis of Zn-oleate complex [22], and sonochemical method, by aqueous-alcoholic-ethylendiamin solutions of zinc nitrate and sodium hydroxide [23]. Here we prepared ZnO nanocrystals by thermal decomposition of minoxidil Zn(II) coordination polymer. In the present paper, we describe synthesis of a new Zn(II) minoxidil nanocomposite (1), because of its potential important application in biomedical field. Application of this nano-structured polymeric compound (1), as precursor for preparation of nano zinc oxide, can drive chemical reactions to formation of nano-sized particles, in the polymeric framework of starting material. The ZnO nano crystals were prepared by thermal decomposition of the nano-composite 1 as starting materials.

2. EXPERIMENTAL

All reagents and solvents for the synthesis and analysis were commercially available and were used as received.

FTIR spectra ($400\text{-}4000\text{ cm}^{-1}$) were recorded on a Bruker tensor 27 spectrometer in a KBr matrix. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer and Atomic absorption, Py unican Philips, Ion Analyzer Jenway, for I⁻ measurement. Melting points were measured on an Electrothermal 9100 apparatus and X-ray powder diffraction (XRD) measurements were performed with monochromatized $\text{CuK}\alpha$ radiation using a Philips diffractometer manufactured by X'pert. Crystallite sizes of selected samples were estimated using the Sherrer method. The samples were coated with gold for characterization with a scanning electron microscope.

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, 717 plus auto sampler and a Styragel HT 4 GPC column with installed precolumn. Linear PMMA standards were used for calibration. The solvent was DMF containing 5 mmol/L NH_4PF_6 . The flow rate was 0.5 mL/min.

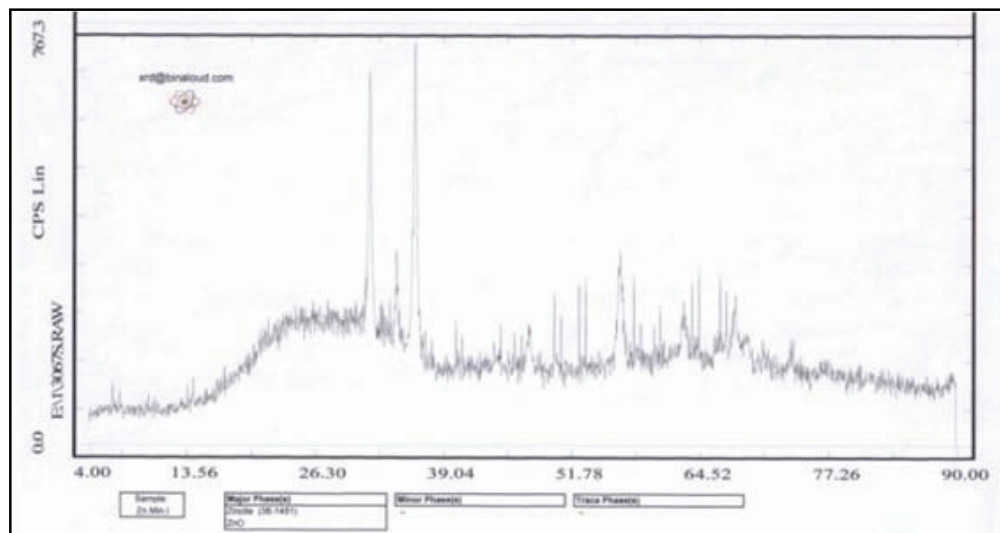


Figure 3: XRD pattern of ZnO nano crystals.

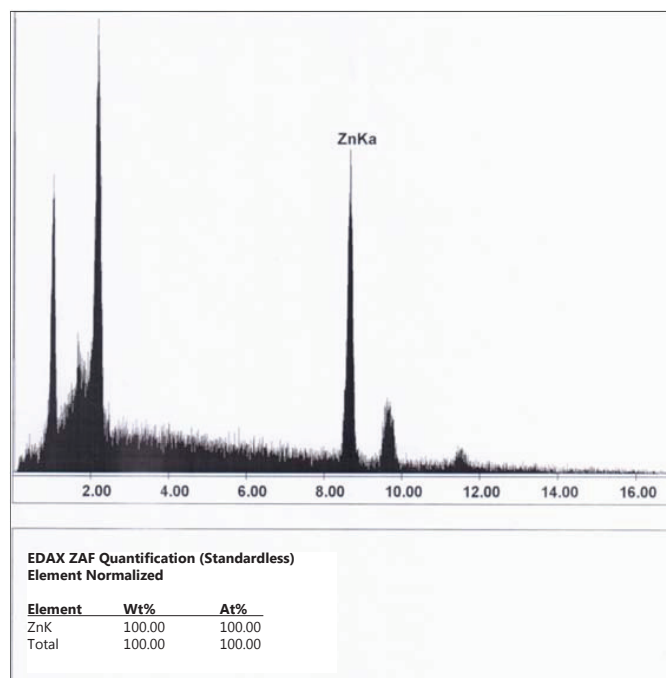


Figure 4: EDX spectrum of ZnO prepared by calcinations of the compound 1.

2.1 Synthesis of Zn(II) minoxidil nanocomposite (1)

Zinc acetate dihydrate (0.109 g, 0.5 mmol) and minoxidil (0.104 g, 0.5 mmol) were mixed in methanol (10 ml) and the mixture was stirred at 80°C for 5 min and the solid KI (0.16 g, 1mmol) was placed into the branch tube. Then, the mixture was added in to the branch tube kept in oil bath with constant temperature at 60°C. After 26 days the yellow thin layered shape appeared in the bottom of the main branch. The product was washed with methanol and acetone, and dried at room temperature. The resulting yellow product, indicated a 72% yield of the compound 1, Dec.p > 300°C. Elemental analysis showed the following results: Zn, 12.57 and I, 47.40. FTIR (KBr): 3439(m), 3300(sh), 2922(w), 2361(w), 1626(w), 1610(w), 1563(w), 1426(w), 1250(s), 1180(m), 673(w), 420(w). Mn (GPC) = 19300 g.mol⁻¹, PDI (GPC) = 1.19; Mw = 23000 g.mol⁻¹.

2.2 Preparation of ZnO nano crystals

In order to prepare the ZnO nanoparticles, the yellow thin film of the compound (1) was calcinated at 400°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, successively. The resulting white powder indicated a 99% yield of ZnO Anal. Calcd for Zn 80.33; Found: Zn, 80.25. FTIR (KBr): 3490(w), 1629(w), 500(s).

3. RESULTS AND DISCUSSION

The Zn(II)-minoxidil nano composite (1) has been synthesized by the reaction between zinc(II) acetate, minoxidil ligand and KI in 1:1:2 mole ratio in methanol by thermal gradient method (as shown in Scheme 1). The yellow compound was isolated and characterized by elemental analysis, FTIR, GPC and SEM methods. In spite of much unsuccessful effort for preparation of single crystals of the product, recently we succeeded however, to prepare Pb(II)-minoxidil coordination polymer, [PbBr₂(C₉H₁₅N₅O)]_n, as single crystal via sonochemical and thermal gradient methods [10]. The structure is containing lead(II) ion in which

coordinated by two O-atoms of minoxidil and four Br⁻ ligands, which results in a six-coordinate complex with a PbO₂Br₄ core. Also the structure consists of asymmetric units of [Pb(minoxidil)(μ-Br)₂]_n chain. In the reaction presented in Scheme 1, GPC results showed that the compound 1 has polymeric structure with a molecular weight of 23000 g.mol⁻¹. The presence of I⁻ was established by ion metric method. But we could not suggest the exact chemical formulas of the compound 1.

As shown in Figure 1, FTIR absorption bands around 3439cm⁻¹ are due to the N-H stretching modes of diamino groups on the pyrimidine. The absorption band at 2922 cm⁻¹ indicates the presence of aliphatic C-H bonds in piperidine ring. The peaks with different densities appeared in frequency range of 1426-1626 cm⁻¹ correspond to vibrational modes of aromatic C=C and C=N bonds in aromatic pyrimidine ring. There is a characteristic absorption mode at 1250 cm⁻¹ which relates to the N-O stretching vibrations. New vibration bands appeared in 421, 450 and 470 cm⁻¹ may be due to Zn-O and Zn-I [24].

The morphology of compound 1 is examined by SEM. This micrograph reveals that nanocomposite 1 is uniform in shape and size. Also, spherical shaped morphology have been observed for the nanoparticles. As a result, the nano particles aggregate randomly to form almost spherical shape. It seems that the chemical structure of the polymeric nano composite can play a critical role for the morphology control. The average particle size of the polymeric compound 1 prepared by the thermal gradient method is about 77 nm, as shown in scanning electron microscopy image (Figure 2).

The current synthetic procedure for preparation of ZnO nanocrystals, is a new method developed by Morsali group for the synthesis of various nanoparticles of metal oxides and metal halides, which employ the thermal decomposition of coordination polymers under different atmospheres [15-19]. The synthetic pathway is shown in Scheme 1. The yellow thin layered shaped nanocomposite 1, was put in a furnace at 400 °C, in 2h under ambient atmosphere, the white powder was washed by acetone and methanol, followed by centrifugation. In fact, thermal decomposition of nano-sized coordination polymer 1, produced ZnO

nanocrystals. The powder X-ray diffraction (XRD) of ZnO consists of the crystal data for zincite, (JCPDS card no: 36-1451) as shown in Figure 3.

The broadening of the peaks is shown in Figure 3, indicates that the particles are of nanometer dimensions. Estimated by the Sherrer formula, $D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ the X-ray wavelength (0.15405 nm), and θ and β the diffraction angle and full-width at half maximum of an observed peak, respectively. The average size of the particles is 30 nm, which is in agreement with which was observed by scanning electron microscopy.

Elemental analysis were tested by EDAX, energy dispersive X-ray analysis showed that produced ZnO nanocrystals is pure as shown in Figure 4.

The morphology of the product is examined by SEM. Typical SEM image of wurtzite ZnO nanocrystals is shown in Figure 5. It represents that the obtained nanocrystals has spherical shape. The diameters of the particles are about 34 to 50 nm. The diameters of the products are in good agreement with those calculated by XRD pattern.

The growth mechanism could be assumed to be the basis of the following reactions and the crystal habits of hexagonal ZnO. In the presence of minoxidil and iodide as bridging ligand, polymeric nano composite were synthesized. By putting the produced nanocomposite 1, under thermal degradation, it will be decomposed at high temperature. The framework of the nanocomposite 1, can provide great steric hindrance to control

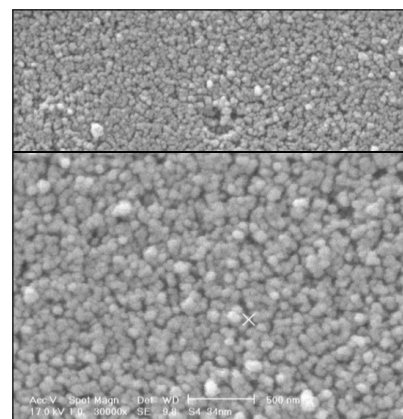


Figure 5: SEM image of ZnO nano crystals (prepared by calcination of compound 1).

the size of metal nanoparticles [10,15-19]. In fact, the polymeric nanocomposite, acts as template for preparation of ZnO nanocrystals. Minoxidil ligand is coordinated to Zn(II) atom from oxygen site, then these polymeric complexes transform to ZnO.

4. CONCLUSIONS

In this work, we synthesized a new polymeric Zn(II) minoxidil nanocomposite 1, by thermal gradient method, in a branched tube. The yellow thin layer shaped nanocomposite 1 produced with about 77 nm diameters, as spherical shaped aggregated particles. Then we synthesized pure crystalline ZnO nanocrystals by thermal decomposition of zinc(II) minoxidil nanocomposite, as template, under mild conditions. The particle size of the nanocrystals estimated between 34-50 nm by Debye-Scherrer equation and SEM methods. The precursor 1 is produced under ambient conditions. It is air-stable, environmentally friendly and potentially can be used in medical applications. This procedure can be generally approached to synthesis many other metal oxide nanoparticles.

5. ACKNOWLEDGEMENT

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REFERENCES

1. J. Coleman, *Annu Rev Biochem*, 1992, 61, 897.
2. A.S. Prasad, *Biochemistry of Zinc*, New York: Plenum Press, 1993, 14-17.
3. M. Hernick, C. Fierke, *Arch Biochem Biophys*. 2005, 433, 71.
4. F. Xu, Y. Lu, Y. Xie, Y. Liu, *Materials & Design* 2009, 30,1704.
5. T.K. Gupta, *J. Am. Ceram. Soc.* 1990, 73, 1817.
6. S. P. Clissold , R. C. Heel , *Drugs*, 1987, 33, 107.

7. A. P. Martin-Islan, D. Martin-Ramos, C. I. Sainz-Diaz, *J. Pharm. Sci.*, 2008, 97, 815.
8. History of Minoxidil, <http://crownhairloss.org/history-minoxidil.html>, available in 30 Apr 2011
9. M. Ranjbar, S. H. Mahmoudi Najafi, , S. W. Ng, *Acta Cryst.* 2009, E65, m749.
10. M. Ranjbar, O. Celik, S. H. Mahmoudi Najafi, S. Sheshmani, N. Akbari Mobarakeh, *J Inorg Organomet Polym.*, 2012, DOI 10.1007/s10904-011-9648-6.
11. U. Díaz, Á. Cantín, A. Corma, *Chemistry of Materials*, 2007, 19, 3686.
12. A. Aslani, A. Morsali, M. Zeller, *Solid State Sciences*, 2008, 10, 1591.
13. Y. Yin, A. P. Alivisatos, *Nature*, 2005, 437, 664.
14. M. Salavati-Niasari, F. Davar, Z. Fereshteh, *Chem. Eng. J.* 2009, 146, 498.
15. H. Haddadian, A. Aslani, A. Morsali, *Inorg. Chim. Acta.* 2009, 362, 1805-1809.
16. K. Akhbari, A. Morsali, *Cryst. Eng. Comm.* 2011, 13, 2047–2053.
17. L. Hashemi, A. Morsali, P. Retailleau, *Inorg Chim Acta* 2011, 367, 207–211.
18. M.J. Soltanian fard, A. Morsali, *J. Inorg. Organomet. Polym.*, 2010, 20,727–732.
19. L. Hashemi, A. Morsali, *J. Inorg. Polym.*, 2010, 20, 856–861.
20. L.-L. Xu, J.-G. Cheng, K.-F. Yue, Y.-L. Liu, C.-J. Wang, Y.-Y. Wang, *Z. Anorg. Allg. Chem.*, 2012, 638, 366–371.
21. K. Simeonidis, S. Mourdikoudis, M. Moulla, I. Tsiaoussis, C.M. Boubeta, M. Angelakeris, C.D. Samara, O. Kalogirou, *J. Magn. Magn. Mater.* 2007, 316, e1-e4.
22. S.-H. Choi, E.-G. Kim, J. Park, K. An, N. Lee, S.C. Kim, T. Hyeon, *J. Phys. Chem.* 2005, B109, 14792-14794.
23. R.S. Yadav, P. Mishra, A.C. Pandey, *Ultrason. Sonochem.* 2008, 15, 863-868.
24. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 5th ed., New York, (1997).