



Preparation of zinc oxide (ZnO) and zinc cobaltite spinel (ZnCo₂O₄) nanoparticles by thermal decomposition of inorganic precursors

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ABSTRACT

Zinc oxide (ZnO) and spinel-type ZnCo-mixed oxide (ZnCo₂O₄) nanoparticles were prepared by thermal decomposition of (NH₄)₂[Zn(dipic)₂]. H₂O and [Zn(H₂O)₅Co(dipic)₂]. 2H₂O inorganic precursors, respectively. Thermal gravimetric analysis (TGA) was applied to determine the thermal behavior of the complexes. Characterization of products was carried out using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR). The crystallite size of prepared ZnCo₂O₄ is smaller than those of the samples prepared by conventional methods.

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KEYWORDS

Nanoparticles;
ZnO;
ZnCo₂O₄;
Inorganic precursor;
Thermal decomposition.

INTRODUCTION

Nanosized zinc oxide (ZnO) has been extensively studied owing to great potential in applications such as semiconductor chemical sensors^[1], field effect transistor (FETs)^[2] gas sensors^[3], chemical absorbent^[4], electrostatic dissipative coating^[5], catalysts for liquid phase hydrogenation^[6], catalysts for photo-catalytic degradation^[7], and ultraviolet light emitting devices^[8]. Nanocrystalline zinc cobaltite spinel (ZnCo₂O₄) has also been applied as electrocatalyst for many anodic processes such as oxygen evolution^[9], photocatalyst^[10] and semiconductor gas sensor^[11]. Both zinc oxide and zinc cobaltite have been employed in solar energy conversion due to their stability against photocorrosion and

similar photochemical properties as of titania^[12].

Conventional semiconducting oxides have been prepared by a variety of methods such as Czochralski method^[13], solid state synthesis^[14], sol gel^[15], co-precipitation^[16], combustion^[17], hydrothermal^[18], microemulsion^[19], solvothermal^[20] and sonochemical^[21].

In this work, the Zinc oxide and spinel-type ZnCo-mixed oxide nanoparticles were prepared via thermal decomposition of (NH₄)₂[Zn(dipic)₂]. H₂O and [Zn(H₂O)₅Co(dipic)₂]. 2H₂O as new inorganic precursors. This procedure is a suitable method for large-scale production of oxide nanocrystals, because it is relatively simple, low-cost, facile and reproducible process. Furthermore, using of novel inorganic compound for preparing nanomaterials provides many advantages as a

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preparative route since: control of process conditions, nanocrystal size, particle crystal structure, purity and distribution size^[22].

EXPERIMENTAL

Materials and general methods

All the chemicals were purchased from Merck and used without further purification. For synthesis of Ammonium 2, 6-pyridinedicarboxylate, 2, 6-pyridinedicarboxylic acid (10000 mg, 60 mmol) and ammonia (200 mL) were reacted at 70 °C. Infrared spectra were recorded as KBr discs using JASCO FT-IR spectrometer (4000-400 cm⁻¹). Thermal analysis was performed on a NETZSCH TG model of (F1 Iris) thermal analyzer under air from 30 to 600 °C at heating rate of 10 °C/min. XRD patterns were recorded on a (Rigaku) diffractometer (SIEMENS, D5000 (GERMANY)) using Cu Kα (λ = 1.5418 Å) as incident radiation. Size and morphology of the nanoparticles were evaluated by (Philips, EM-2085) Transmission Electron Microscopy under maximum acceleration voltage of 100 kV. The BET Surface areas and pore volumes were measured by using BELSORB mini model apparatus. Scanning Electron microscopy (SEM) of the nanoparticles was studied by using the (Philips, XL30) with an accelerating voltage of 30 kV.

Preparation of (NH₄)₂[Zn(dipic)₂]. H₂O

To an aqueous solution (600 mL) of ammonium 2, 6-pyridinedicarboxylate (5000 mg, 25 mmol) was added a solution of Zn(NO₃)₂.6H₂O (3700 mg, 12.5 mmol) in water (100 mL), and the mixture was stirred at room temperature for 5 h. Finally, the solvent separated by rotary evaporator and a white solid obtained in ca. 65 %. Anal. Calcd. for C₁₄H₁₆N₄O₉Zn (449.7): C, 37.39; H, 3.59; N, 12.46. Found: C, 37.28; H, 3.62; N, 12.42.

Preparation of ZnO nanoparticles

The (NH₄)₂[Zn(dipic)₂]. H₂O precursor was heated to 450, 550 and 650 °C in the electric furnace by rate of heating 10° C/min and kept at those temperatures for 4 hours.

Preparation of [Zn(H₂O)₅Co(dipic)₂]. 2H₂O

The precursor complex was synthesized by a pre-

cise variation of the synthesis method of the literature^[23] and the detailed procedure is as following: to an aqueous solution containing an equimolar mixture of two metal nitrates [10 mL of Zn(NO₃)₂.6H₂O (1 mmol) + 10 mL of Co(NO₃)₂.6H₂O (1 mmol)] of was added an aqueous solution (20mL) of ammonium 2, 6-Pyridinedicarboxylate (429 mg, 2 mmol) with continuous stirring at room temperature. The resulting mixture was stirred for 3 h, filtered off and then left to evaporate in a beaker in air at ambient temperature. Air-stable, water-soluble, Light-pink crystals were formed within 1–3 days, then collected and dried in air to give the compound in ca. 60% yield. Anal. Calc. for C₁₄H₂₀CoN₂O₁₅Zn (580.6): C, 28.96; H, 3.47; N, 4.82. Found: C, 28.88; H, 3.42; N, 4.76%. UV-Vis (H₂O): no band of [Co(H₂O)₅]²⁺.

Preparation of ZnCo₂O₄ spinel nanoparticles

The [Zn(H₂O)₅Co(dipic)₂]. 2H₂O precursor was heat-treated at 400 °C in static air in the electric furnace for 2 h. The black powder, ZnCo₂O₄ was formed and kept in desiccator.

RESULTS AND DISCUSSION

Characterization of (NH₄)₂[Zn(dipic)₂]. H₂O precursor and ZnO nanoparticles

TGA curve of the (NH₄)₂[Zn(dipic)₂]. H₂O precursor is shown in Figure 1. The thermal treatment of the precursor resulted in the following three processes: (i) The first stage that occurs in temperature range 26–139 °C corresponds to the loss of the crystal water molecules and the complex loses 4% of its weight. (ii) The second stage, abrupt weight loss in the region 139 – 375 °C, is due to the decomposition of dipic ligands and ammonium and 41% of precursor remained in this stage. (iii) The third stage that occurs at 375 – 500 °C is related to decomposition of remainder composition and causes to preparation of the ZnO and at last 19.26% of precursor remained when the heating continued to 600°C.

The FT-IR spectra of precursor and products are shown in Figure 2. (NH₄)₂[Zn(dipic)₂]. H₂O complex exhibits strong bands in the range 3450–3325 cm⁻¹ due to O–H vibrations which indicate the presence of crystallization water molecules in the crystal lattice. The

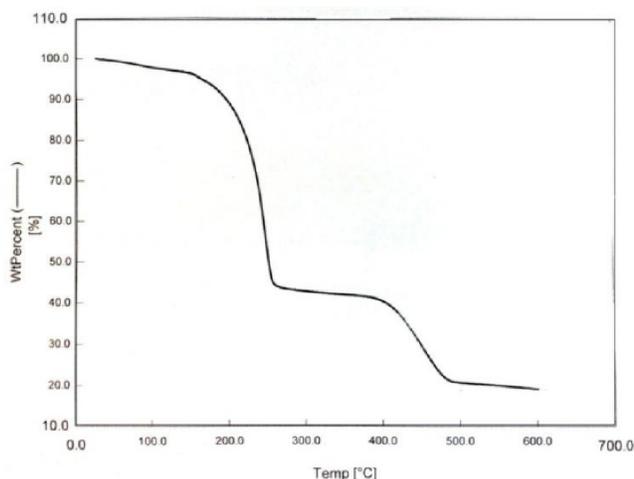


Figure 1 : Thermogram of $(\text{NH}_4)_2[\text{Zn}(\text{dipic})_2]$ precursor

absorption bands at 1615 and 1382 cm^{-1} are assigned to the asymmetric, $\nu_{\text{as}}(\text{COO})$, and symmetric, $\nu_{\text{s}}(\text{COO})$, stretching vibrations, respectively. The frequency difference between these bands, " $\nu(\text{COO}) = 179\text{ cm}^{-1}$ ", suggests a unidentate coordination of the carboxylate group to the $\text{Zn}(\text{II})$ ion^[24]. ZnO nanoparticles have bands

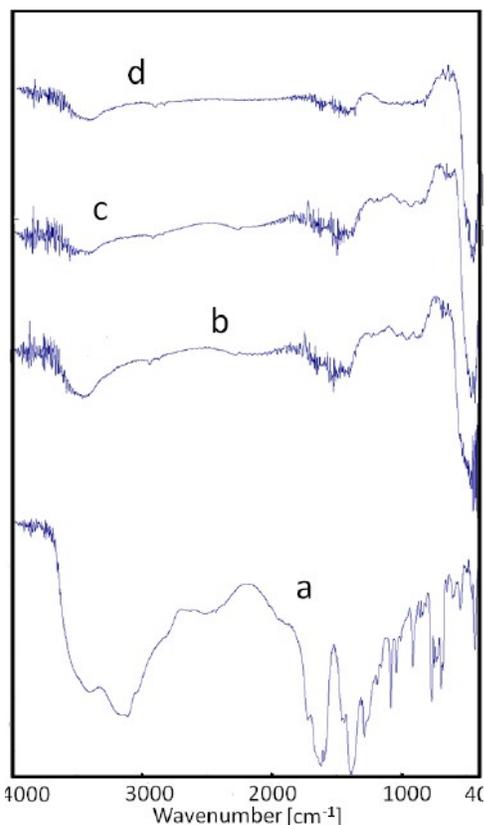


Figure 2 : FT-IR spectra of $(\text{NH}_4)_2[\text{Zn}(\text{dipic})_2] \cdot \text{H}_2\text{O}$ precursor (a) and ZnO nanoparticles prepared at 450°C (b), 550°C (c) and 650°C (d)

in 480 , 1629 and 3437 cm^{-1} . The weak band at 1628 cm^{-1} is corresponding to the OH bending of water. The strong band at 480 cm^{-1} is ascribed to Zn-O stretching band.

Figure 3 shows the XRD patterns of the ZnO nanopowders prepared via thermal decomposition of $(\text{NH}_4)_2[\text{Zn}(\text{dipic})_2] \cdot \text{H}_2\text{O}$ precursor at several temperatures for 4 hours. Distinguished diffraction peaks at 2θ values of 31.9 , 34.5 , 36.4 , 47.6 , 56.7 , 62.9 , 66.4 , 68.0 and 69.2° correspond to the crystal planes of (100), (002), (101), (102), (110), (103), (200), (112) and (201), indicating that the particles have hexagonal crystal system with wurtzite structure of ZnO . The average sizes of the ZnO nanocrystals at calcination temperatures of 450 , 550 , and 650°C calculated from the all diffraction peaks using Scherrer equation are about 27 , 29 and 31 nm , respectively. The XRD patterns of the ZnO nanoparticles prepared at different temperatures show that the size of nanocrystals grows with increasing the temperature of calcination.

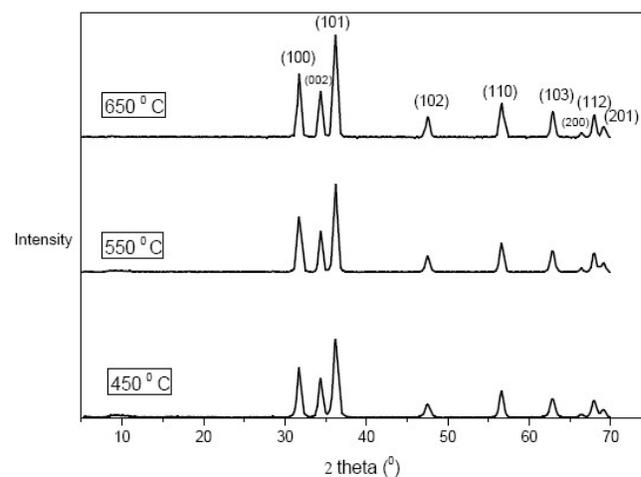


Figure 3 : XRD patterns of ZnO nanoparticles prepared by thermal decomposition of precursor at several temperatures.

The TEM image of the ZnO nanoparticles prepared at 550°C is shown in Figure 4A, from which it can be seen that the ZnO is composed of some agglomerated particles with an average size of about $30\text{--}40\text{ nm}$. The TEM image shows hemispherical nanoparticles. The size of the nanoparticles obtained from the XRD diffraction pattern is in close agreement with the TEM studies, which show sizes of $30\text{--}40\text{ nm}$. Diffraction Pattern (DP) imaging of the nanoparticles indicates that the nanoparticles have crystal structure and aren't amorphous. Furthermore, diffraction pattern shows that each

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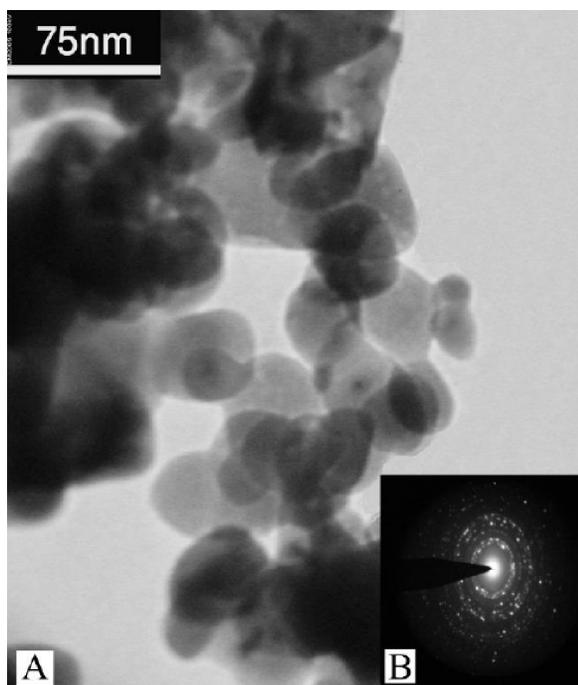


Figure 4 : TEM image of ZnO nanoparticles prepared at 550 °C (A) and diffraction pattern of nanoparticles (B)

particle is accumulation of several single crystals by different direction and thermal shock during the calcination causes to porosity in nanoparticles (Figure 4 B).

Morphology of the ZnO nanoparticles prepared at 550 °C has been examined by SEM image (Figure 5). It can be seen that the products are tiny, aggregated nanoparticles with hemispherical shapes.

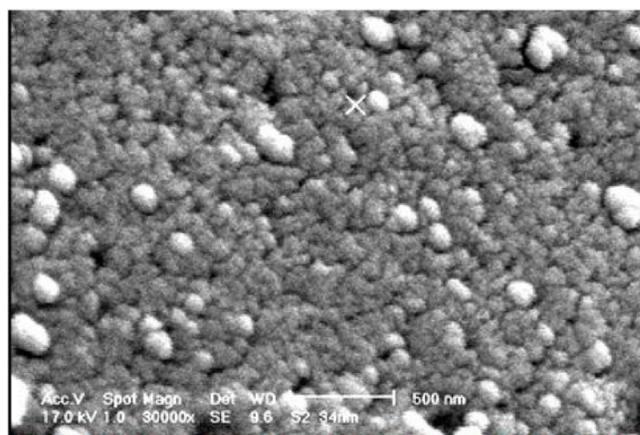


Figure 5 : SEM image of ZnO nanoparticles prepared at 550 °C

Characterization of [Zn(H₂O)₅Co(dipic)₂].2H₂O precursor and ZnCo₂O₄ spinel nanoparticles

FT-IR of [Zn(H₂O)₅Co(dipic)₂].2H₂O complex (Figure 6) has characteristic absorption bands at 400-4000 cm⁻¹. The broad band at 3500 cm⁻¹ is associated to the ν(OH) stretching vibrations of coordinated water. The sharp absorption bands at 3200 and 1635 cm⁻¹ are assigned to lattice water molecules. Characteristic bands at 1639 and 1579 cm⁻¹ are attributed to asymmetric stretching of dipicolinate carboxylate groups and bands associated with ν_s of the COO groups are observed at 1383 and 1456 cm⁻¹.

Four weight loss peaks in the temperature range of 30–520 °C are observed in the thermogram of pre-

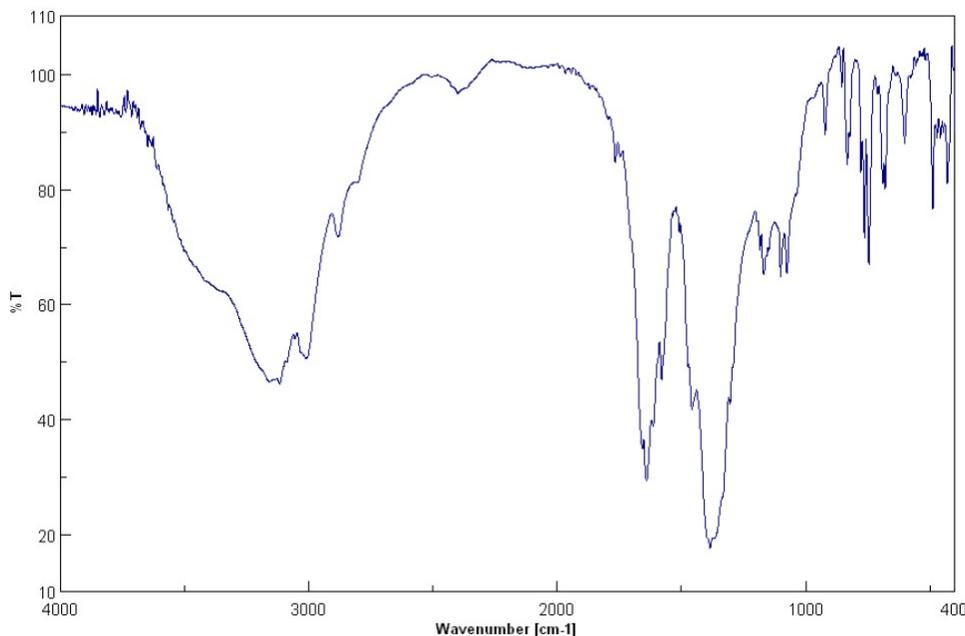


Figure 6 : FT-IR spectrum of [Zn(H₂O)₅Co(dipic)₂].2H₂O

cursor (Figure 7). The first weight loss peak is attributed to the removal of the physically adsorbed and lattice water molecules. The subsequent weight loss peak is due to the loss of coordinated water molecules. Loss in weight due to dipic decomposition could give rise to the other two high temperature peaks. The final decomposition products were the zinc cobaltite spinel and zinc oxide, identified by IR spectroscopy.

In the IR spectrum of the product, absorption bands at $637\text{-}454\text{ cm}^{-1}$ are assigned to Co–O and Zn–O vibrations, which indicate the presence of the ZnCo_2O_4 .

XRD pattern of sample heat-treated at $400\text{ }^\circ\text{C}$ (Figure 8) shows characteristic peaks at $2\theta = 31.3, 37, 44.8, 59.3$ and 65.2° , where confirm existing the spinel-type ZnCo_2O_4 as the single phase. Average crystallite size of ZnCo_2O_4 nanoparticles calculated by Scherrer equation is about 10 nm.

TEM image of the obtained product by thermal decomposition of $[\text{Zn}(\text{H}_2\text{O})_5\text{Co}(\text{dipic})_2] \cdot 2\text{H}_2\text{O}$ precursor (Figure 9) shows quasi-spherical shape and average crystallite size of about 10–15 nm for nanoparticles. The size of the nanoparticles obtained from the XRD diffraction pattern is in close agreement with the TEM studies, which show sizes of 10–15 nm.

The crystallite size of prepared ZnCo_2O_4 is smaller than those of the samples prepared by co-precipitation^[25], hydroxide decomposition^[26], oxalate decom-

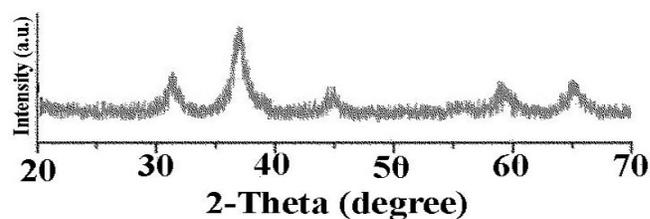


Figure 8 : XRD pattern of ZnCo_2O_4 spinel nanoparticles prepared by thermolysis of $[\text{Zn}(\text{H}_2\text{O})_5\text{Co}(\text{dipic})_2] \cdot 2\text{H}_2\text{O}$ at $400\text{ }^\circ\text{C}$

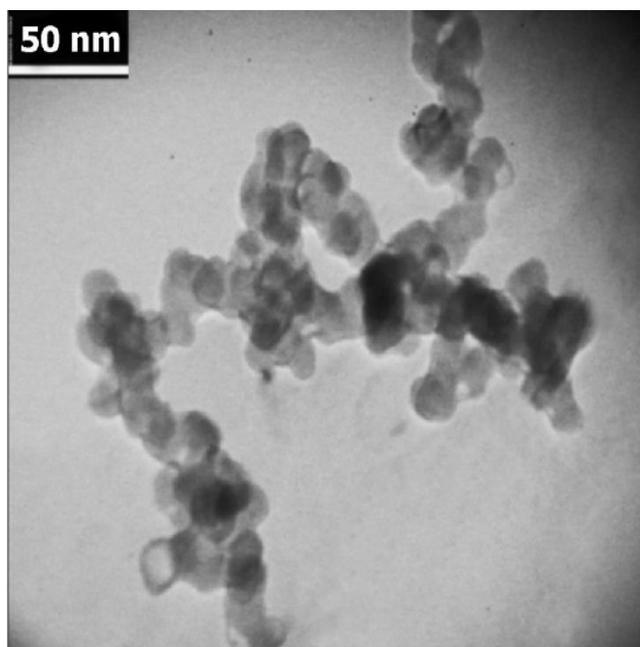


Figure 9 : TEM image of ZnCo_2O_4 nanoparticles

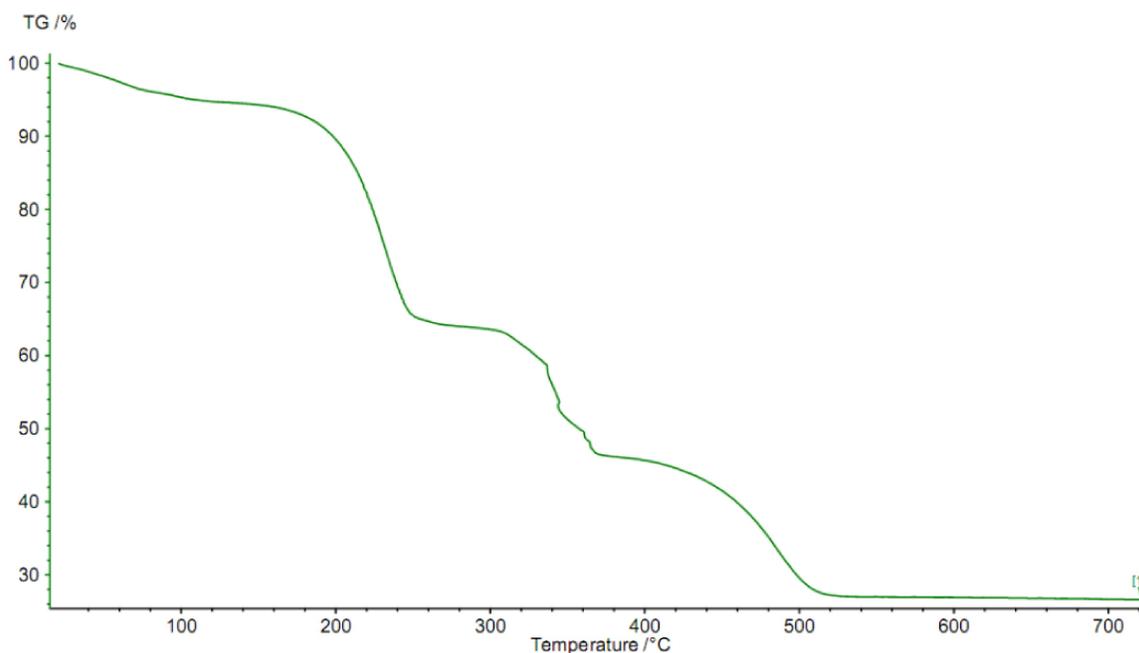


Figure 7 : Thermogram of $[\text{Zn}(\text{H}_2\text{O})_5\text{Co}(\text{dipic})_2] \cdot 2\text{H}_2\text{O}$ complex

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position^[27], urea combustion^[28], W/O microemulsion^[11] methods. The smaller crystallite size of prepared ZnCo₂O₄ can be attributed to the adopted preparation method and preparation parameters.

CONCLUSIONS

The ZnO and spinel-type ZnCo₂O₄ nanoparticles were synthesized by thermolysis of (NH₄)₂[Zn(dipic)₂]. H₂O and [Zn(H₂O)₅Co(dipic)₂]. 2H₂O precursors, respectively. Thermal decomposition method is a suitable inexpensive way for the large-scale preparation of zinc oxide and zinc cobaltite nanoparticles. Furthermore, used inorganic complexes can be applied for synthesis of many other metal oxide nanocrystals, because they are cheap, air-stable, and available. The crystallite size of the prepared ZnCo₂O₄ nanocrystals is smaller in compared to the samples prepared by conventional methods.

ACKNOWLEDGEMENT

The authors are grateful to the USB for financial support.

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