Synthesis and Characterization of Ferromagnetic CoBaO$_{2.70}$ Nanoparticle with Ferromagnetic Properties

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In this research we report synthesis of a new Barium-Cobalt precursor complex with 2,6-pyridine dicarboxylic acid (dipic). The complex $[Ba(H_2O)_6][Co(dipic)_2]$ (1) has been characterized using spectral methods (FT-IR, UV-Vis), elemental analysis and Cyclic voltammetry (CV). We also report thermal decomposition of inorganic precursor complex (1). Characterization of the binary oxide nanoparticlewas carried out using Fourier Transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), Vibrating sample maghetometer (VSM) and energy dispersive X-ray analysis (EDX). The X-ray diffraction pattern at room temperature revealed that, highly pure and crystallized BaCoO$_{2.70}$ in orthorhombic structure with a = 4.2300 Å, b = 4.3500 Å and c = 11.3200 Å.

Keywords: X-ray diffraction, Cyclic voltammetry, Scanning electron microscopy

INTRODUCTION

Oxide structures with nanometric dimensions exhibit novel physical and chemical properties, with respect to bulk oxide materials, due to the spatial confinement and the proximity of the substrate [1-5]. In recent years, there have been increasing interest in the synthesis of nanosized crystalline metal oxides because of their large surface areas, unusual adsorptive properties, surface defects and fast diffusivities [6-8]. Cobalt, on the other hand, is earth-abundant and Co$_3$O$_4$ shows good activit [9]. For this cause, considerable effort has been devoted to the understanding of the changes in composition and structure of cobalt anodes as a function of applied potential. Now, cobalt oxide has been extensively involved in many applications such as heterogeneous catalysts, electrode materials, high density magnetic recording media, ink printing, pigments, adsorbents, magnetic resonance lithium rechargeable batteries, imaging and gas sensors because they possess outstanding characteristics such as toxicity, high resistance to corrosion, durability and low cost [10-12].

Due to their small size, nanoparticles exhibit novel material properties that are significantly different from those of their bulk counterparts [13].

Albeit modified electrodes have displaied very high capability toward detection, they also show problems related to the immobility of the mediator and mediator leakage, stability, down sensitivity and its toxicity. Moreover, heavy cost, poor reproducibility and down repeatability are also disadvantageous of these sensors. Cobalt oxide nanopowders are known to be highly reactive and they have been used in heterogeneous catalysis, magnetoresistive devices electrochromic thin films and energy storage system. Cobalt-based oxides have considerable interest, mainly due to their excellent electrocatalytic activity [13]. Cobalt metal has known as an interesting non-noble metal. Important research works have been devoted to synthesis Co-based compounds as homogenous molecular catalysts and several excellent reviews relevant to this topic are available.

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In this research we report preparation of the Barium-Cobalt nanoparticle oxide *via* synthesis of precursor complex with organic ligand. The precursor complex was characterized using spectroscopic studies (FT-IR, UV-Vis) and elemental analysis. Also cyclic voltammetric (CV) method was used to investigate the electrochemical behavior of the complex (1). Characterization of the binary oxide nanoparticle was carried out using Fourier Transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), Vibrating sample maghetometer (VSM) and energy dispersive X-ray analysis (EDX). The X-ray diffraction pattern at room temperature revealed highly pure and crystallized $BaCoO_{2.70}$ in orthorhombic structure.

EXPERIMENTAL

Materials and Physical Measurements

The raw materials used in this work were of purities above 99%, therefore no further purification was required. All solutions were prepared with double distilled water. Elemental analysis (CHN) was determined on a Heraeus rapid analyzer. Fourier transform infrared (FT-IR) spectra were recorded using JASCO 460 FT-IR spectrophotometer in a KBr matrix. UV-Vis spectra were recorded on a JASCO 7850 spectrophotometer. The redox properties of the complex were studied by cyclic voltammetric method. Cyclic voltammogram was recorded by using a SAMA 500 Electro Analyzer. X-ray powder diffraction (XRD) measurement was performed using an X'pertdiffractometer of Philips Company with graphite monochromatic Cu K_α (λ = 0.1540 nm) radiation at room temperature in the 2θ range of 0-90°. The sample was characterized by using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques (Philips XL30) with gold coating.

Preparation of [Ba(H₂O)₆][Co(dipic)₂] (1)

For the synthesis of this complex, the cationic and anionic parts were prepared separately, then added together and the final product was obtained.

Prepare cationic part. Barium Chloride (0.244 g, 1 mmol) was added to double distilled water (20 ml) and the mixture was stirred for 2 h at room temperature to give a clear solution.

Prepare anionic part. To an aqueous solution (15 ml) of $CoCl_2.6H_2O$ (0.238 g, 1 mmol) was added an aqueous solution (10 ml) of $(NH_4)_2(dipic)$ (0.408 g, 2 mmol) and the mixture was refluxed for 2 h to give a clear solution.

Then the mixture of cationic and anionic parts have been refluxed for 24 h. Crystals of complex (1) were obtained by slow evaporation of solvents and kept for further characterization. Yield 69%. Anal. Calcd. for $C_{14}H_{18}BaCoN_2O_{14}$: C, 26.50; H, 2.86; N, 4.41. Found: C, 26.52; H, 2.88; N, 4.45%. FT-IR (KBr, cm^{-1}) ν_{max}: 2600-3000 ν(O-H), 1331, 1619 ν (-COO$^-$), 1530-1384 ν(C=C) and ν (C=N), 428 ν(Co-O), 358 ν(Co-N), 542 ν(Ba-O) (Scheme 1).

RESULTS AND DISCUSSION

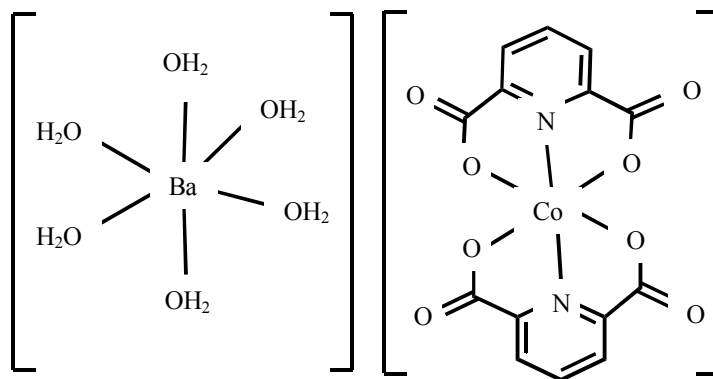### Characterization of [Ba(H₂O)₆][Co(dipic)₂] (1)
IR spectra

Figure 1 show FT-IR spectrum of complex (1) before thermal decomposition. The FT-IR spectrum of precursor complex (1) show the broad absorption band at 3200-3500 cm^{-1} related to stretching vibrations of O-H group. The absorption bands at 1300 cm^{-1} and 1530 cm^{-1} belong to stretching vibrations of C=N and C=C groups, respectively. Also the bands at 428 cm^{-1} and 542 cm^{-1} are assigned to stretching vibrations of Co-O and Ba-O bands, respectively [14-19].

Electronic Excitation Study

The UV-Vis spectrum of the complex acquired in aqueous solution. Several absorption bands in the UV and a band in visible region have been observed. In the visible region, the band at 466 nm is ascribed to LMCT transition for complex (1) [20]. Absorption bands in the UV regions have been observed at approximately 220 nm for compound (1) attributed to intra-ligand transitions [21]. The bands at 260-280 nm are assigned to both d-d transitions and intra-ligand transitions that overlap with each other [22,23] (Fig. 2).

Electrochemical Studies

Cyclic voltammograms (CV) were performed in a

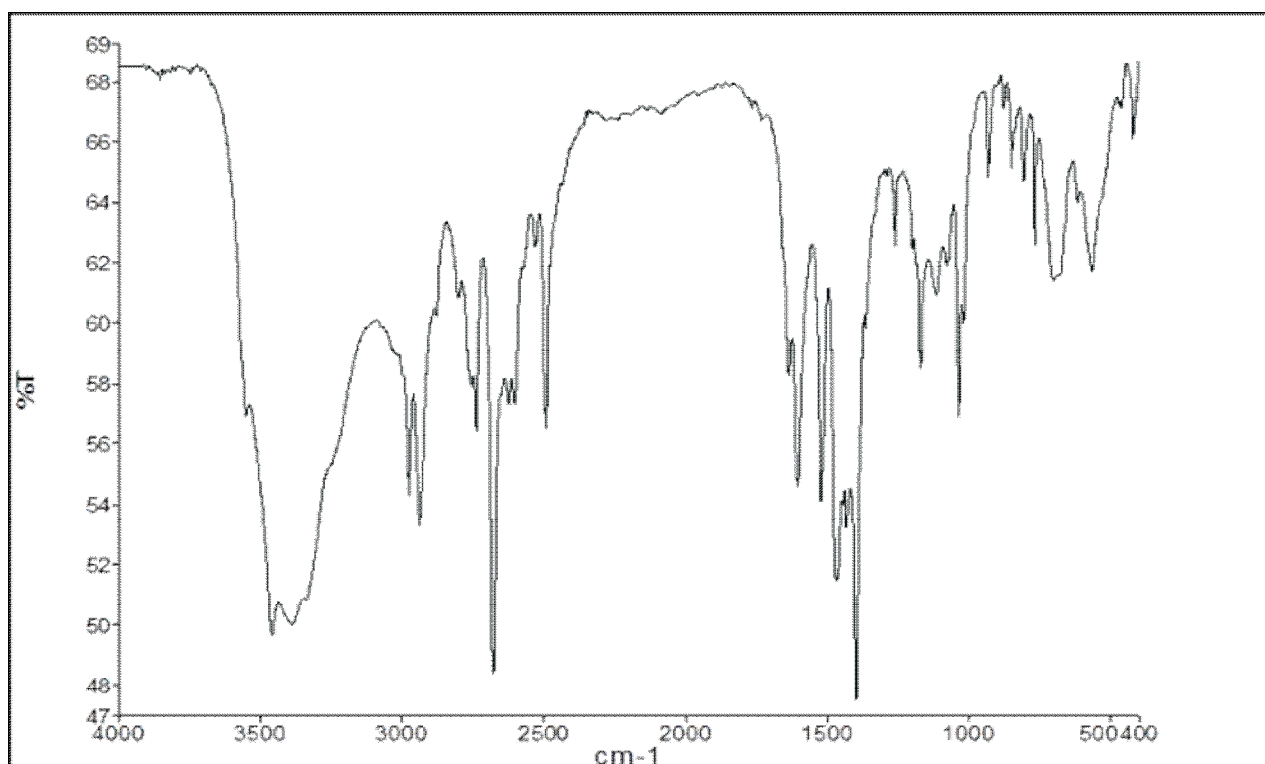*Scheme 1*. Suggested structure for precursor complex (1)

Fig. 1. FT-IR spectrum of complex (1) before thermal decomposition.

DMF solution of [Ba(H$_2$O)$_6$][Co(dipic)$_2$] (1) with 0.1 M TBAH as a supporting electrolyte at scan rate 100-500 mV s^{-1}. Complex (1) shows two quasi reversible reduction waves at approximately 0.69 V and 0.13V *versus* the Fc/Fc$^+$ couple attributed to reduction of Co(III)/Co(II) and Co(II)/Co(I), respectively [24-27] (Fig. 3).

Preparation of Barium-Cobalt Nanoparticle (BaCoO$_{2.70}$)

Barium-Cobalt nanoparticle oxide was prepared from compound (1) using the physical method. First 1.0 g of compound dissolved in oleic acid solution (5 ml) as a surfactant. Then precursor complex was calcinated at 1100 °C
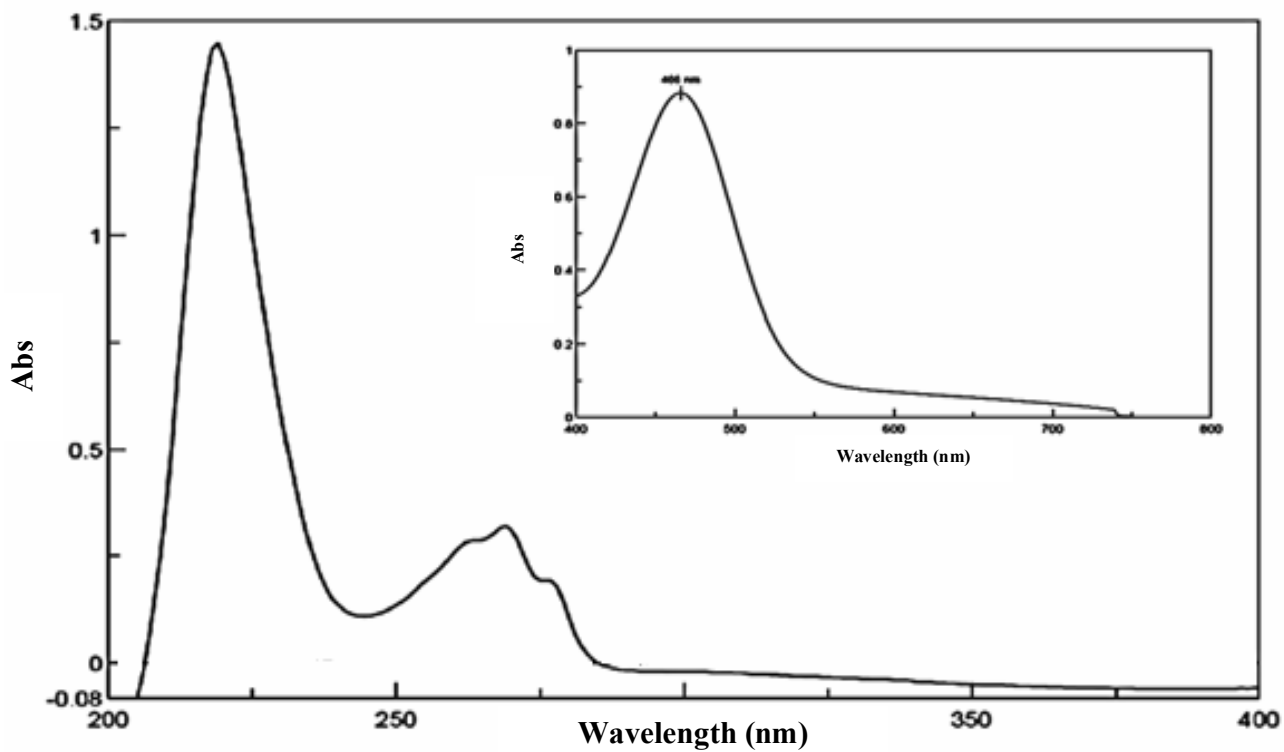
Fig. 2. UV-Vis absorption spectrum of $[Ba(H_2O)_6][Co(dipic)_2]$ (1).

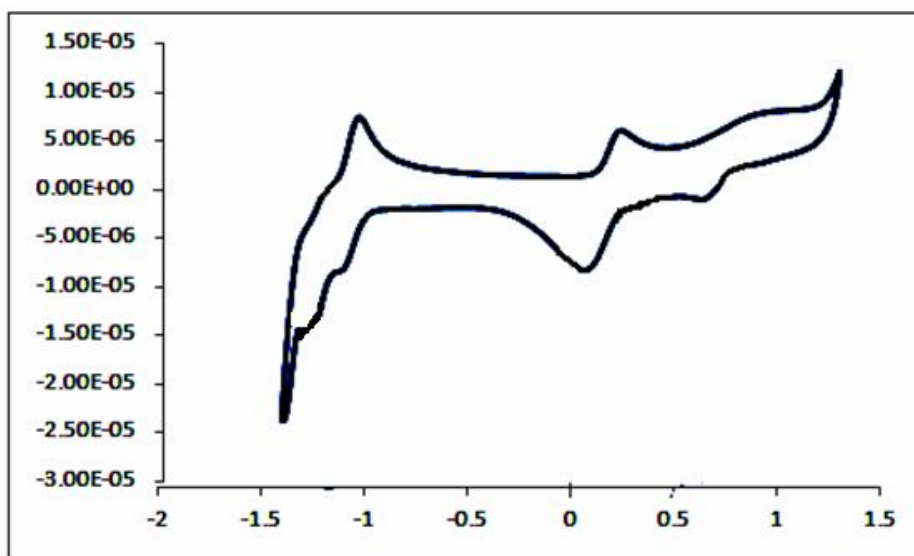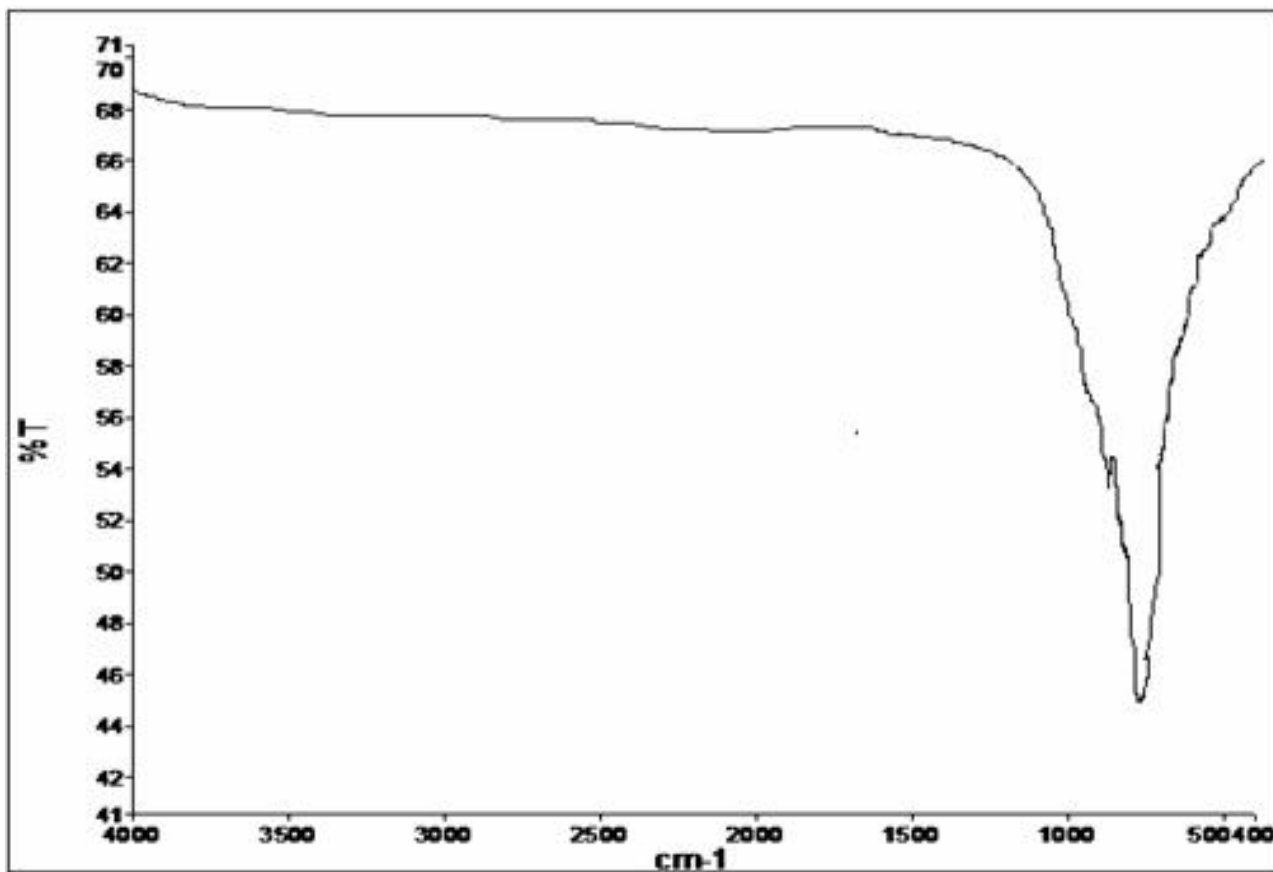**Fig. 3.** Cyclic voltammogram of $[Ba(H_2O)_6][Co(dipic)_2]$ (1).

Fig. 4. FT-IR spectrum of BaCoO$_{2.70}$ after calcined of complex (1) in 1100 °C.
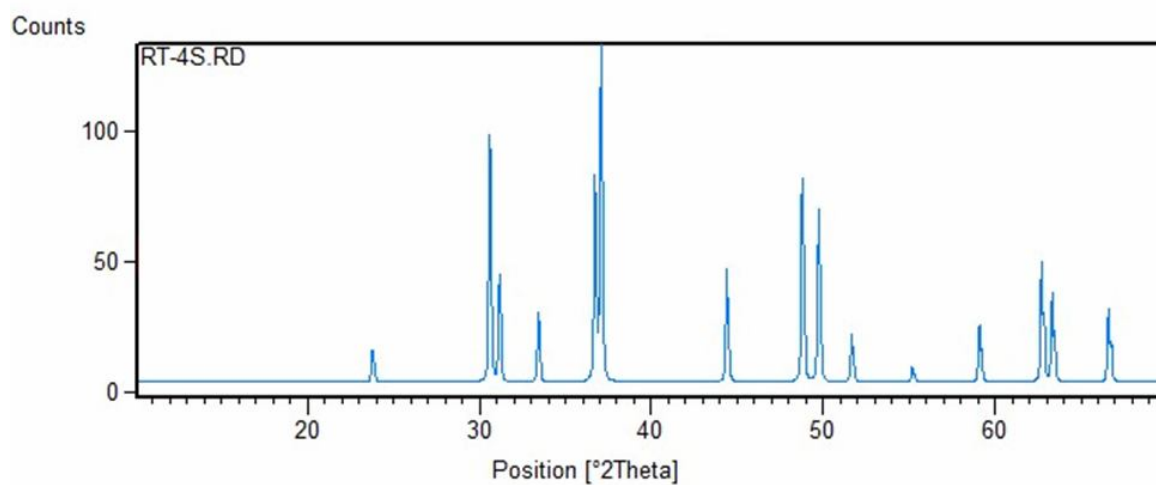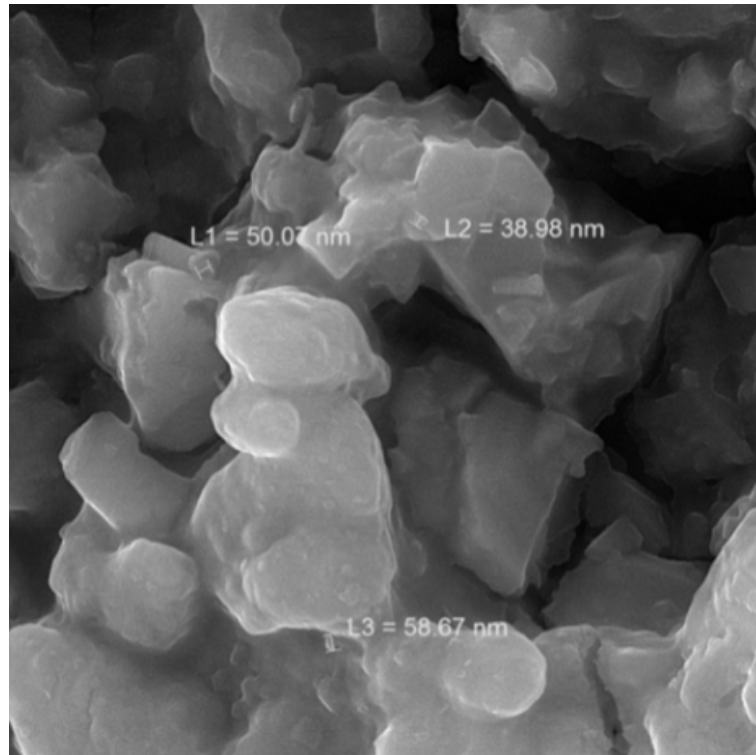

Fig. 5. XRD pattern of BaCoO$_{2.70}$.
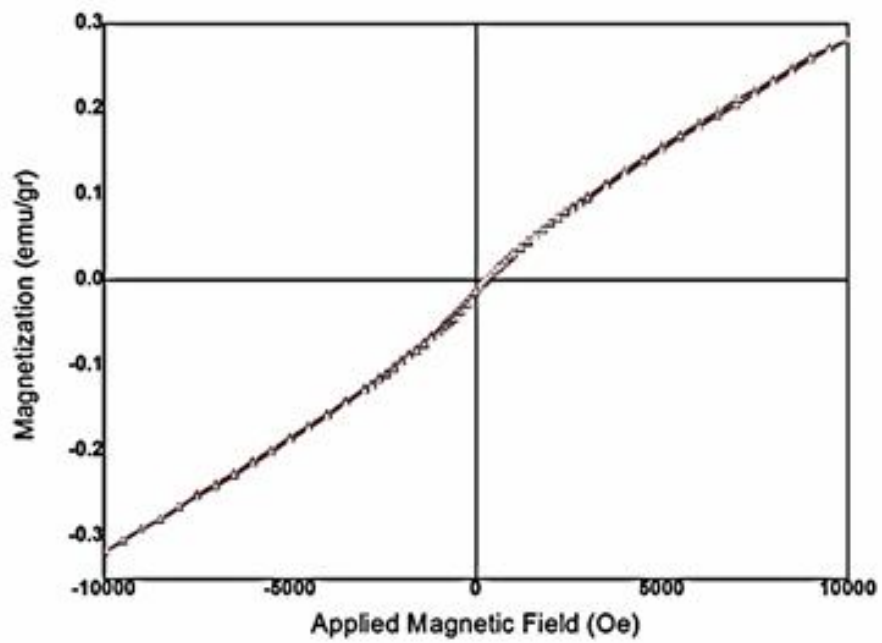
Fig. 6. SEM images of BaCoO$_{2.70}$.

Fig. 7. VSM image from CoBaO$_{2.70}$.

Fig. 8. EDX pattern of the nanocrystalline CoBaO$_{2.70}$.

Table 1. EDX Data of CoBaO$_{2.70}$

El	W%	A%
O	36.10	11.81
Co	33.27	31.93
Ba	29.75	52.62
Au	0.87	3.52

for 4 h in the furnace. Nano oxide (BaCoO$_{2.70}$) was obtained by thermal decomposition [28,29]. The final product was collected and washed with distilled water and absolute ethanol several times, dried in air and kept for further characterization.

RESULTS AND DISCUSSION

FT-IR spectrum of nanoparticle oxides (BaCoO$_{2.70}$) obtained *via* solid state thermal decomposition showed a reduce of mentioned peaks in spectrum. The intense peak approximately at 400-500 cm^{-1} assign to stretching mode of Barium-Cobalt oxide obtained from (1), that gave clear evidence about the presence of the metal oxide structure [30]. Figure 4 shows FT-IR spectrum of BaCoO$_{2.70}$.

Figure 5 shows the XRD pattern of the BaCoO$_{2.70}$. The diffraction peaks in Fig. 5 can be indexed to pure nanoparticle with orthorhombic phase. The crystallite size

of the title nanoparticle, was calculated using the Debye-Scherre formula from the major diffraction peak of the corresponding particle [31]. Specifically the position and relative intensities of all peaks confirm well with standard XRD pattern of $BaCoO_{2.70}$ (JCPDS card No.00-047-0211). Maximum diffraction is $2\theta = 37.07$ and (103) as miller indices. The distance between crystalline planes is $d = 2.8$ Å.

The surface morphology, structure and size of the nanoparticle were studied using SEM image. The SEM image of title nanoparticle is clear, providing in the form of nanoparticle. Therefore the morphology and uniformity of them, relatively spherical and porous and beneath the high porosity as a catalyst is suitable. Figure 6 shows the SEM image of the prepared $BaCoO_{2.70}$ nanoparticle.

The magnetic properties of $CoBaO_{2.70}$ have been measured using VSM technique. The graph of hysteresis loop at room temperature (Fig. 7) indicates soft ferromagnetic feature of the $CoBaO_{2.70}$ [32].

The EDX analysis was performed to further confirm the composition of the obtained product (Fig. 8). The strong peaks related to Co, Ba and O are found and no impurity was detected. This method was also verified the formation of title nanoparticle by measuring of ingredient atoms which can be observed in percent of them (Table 1).

CONCLUSIONS

In summary, we have successfully synthesized precursor Barium-Cobalt complex with 2,6-pyridinedi-carboxylic acid (dipic) ligand. $BaCoO_{2.70}$ nanoparticle prepared from that complex using thermal decomposition method. The size of the $BaCoO_{2.70}$ nanoparticle was measured using XRD and SEM. The results were in good agreement with each other. XRD reveals the pure phase formation of title nanoparticle, which is further confirmed by FT-IRspectra. All results reveal that thermal decomposition method can be employed successfully as a simple, efficient, low cost, environmentally friendly and very promising method for the synthesis of nanoscale materials without special conditions, such as long reaction times, and high pressure. This method may be extended to synthesize other metal oxide nanoparticles, nanowires, nanodisks and even nanotubes.

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