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RESEARCH ARTICLE

Ultrasound-assisted synthesis of Co(II) nanoparticles using novel nano-structure cobalt coordination polymer

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ABSTRACT

In this paper, a new method for the synthesis of spherical CoO nanoparticles using a new metal-organic framework of Co(II) is reported. Nanoparticles of a coordination polyaned nanoparticles. Scanning electron microscopy (SEM), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering (DLS), and IR spectroscopy were used to characterize the CoO nano-structures. Experimental results showed that the morphology of the CoO nanoparticles is spherical and the size of the nanoparticles is dependent on the particle size of compound 1.

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INTRODUCTION

Recent years, have witnessed the growing interest in the design and construction of coordination polymers or CP. (1) Mainly, the previous decade saw the pronounced interest in new coordination polymers based on polydentate organic ligands owing to their novel structural characteristics and potential uses in sensing, catalysis, ion exchange, separations, or gas storage. (2) Recently, CP nanocrystals, nano-sized coordination polymers with finite repetitions up to the point that they aroused a growing interest in their unique properties that are different from conventional bulk CP (3-5). So far, many interesting molecular frameworks have been designed and synthesized through the direct chemical combination of the selected essential components while taking into account variables such as the coordination composition of metal cations, the binding site in donating atoms, and also the length and shape of spacers (6-13). Besides, features of counter-ions including charge, size, arrangement as well as solvent template effects play important roles in the way functional molecular complexes assemble themselves. Many kinds of nanomaterials have been prepared using sonochemical and hydrothermal methods in recent years. Sonochemistry refers to a study field through which a chemical reaction occurs between molecules, due to using powerful ultrasonic radiation (20 kHz to 10MHz)(14-17). Ultrasonic procedures lead to chemical reactions thanks to cavitation procedures that include bubble formation, growth, and quick collapse in liquid resulting in local hot spots with 500 C temperature and 500 atm pressure (18). Because of involving large surface area, adsorptive characteristics, surface defects and fast diffusivities, synthesis of nano-sized crystalline metal oxides has recently drawn the attention of numerous researchers. Co_3O_4 is one of the most critical materials used in catalysis, gas sensors, electrochromic films, battery cathodes, heterogeneous catalytic materials and magnetic

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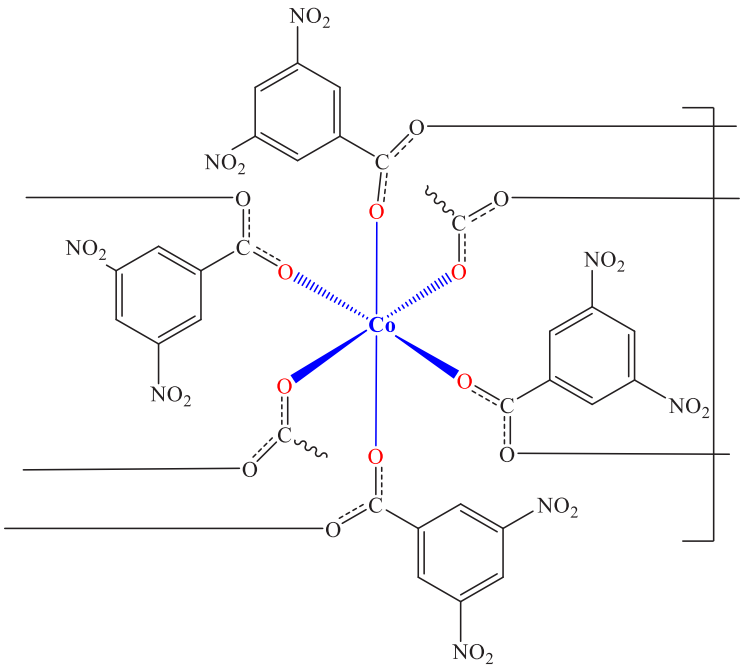
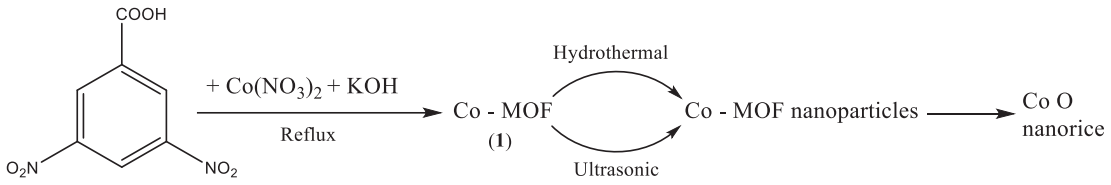


Scheme 1. Proposed Molecular Structure of $[Co(3,5\text{-}DNBA)]_n$ compound **1**.



Scheme 2. Reaction steps for synthesis Co-MOF and CoO nanorice

materials (19, 20).

Hydrothermal synthesis is generally used to define nanomaterial synthesis or crystal growth at an ambient temperature. The product obtained through this method is characterized by high purity and greater regularity(21).

Many kinds of nanomaterials have been prepared by sonochemical and hydrothermal methods in recent years. Ultrasonic and hydrothermal irradiations are understood as green energy source techniques since they offer shorter reaction times and higher yields when compared with thermal energy sources [22].

In this paper, we have synthesized and identified a new coordination polymer $[Co(3,5\text{-}DNBA)]_n$ **(1)** (L^- = 3,5-dinitro benzoic acid) (Scheme 1) which is resulted from the reaction of cobalt(II) nitrate afterward preparation of nanoparticles using the ultrasonic and hydrothermal methods at an ambient temperature (Scheme 2).

Finally, we could use two different and easy methods to achieve a morphologically uniform and homogenous product.

EXPERIMENTAL SECTION

Materials and methods

All reagents and solvents for the synthesis and analysis were commercially available and used as received. Melting points were measured with an Electrothermal 9100 apparatus. X-ray powder diffraction (XRD) measurements were performed with a Philips X'pert diffractometer with monochromatized Cu-Kα radiation. The crystallite sizes of selected samples were estimated using the Scherrer formula. TGA and DTA curves were recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating and also a transmission electron

microscope (TEM) (EM 900) at an accelerating voltage of 120kV. The DLS experiments were carried out using a Malvern ZEN3600 zeta sizer (Nano Zn). IR spectra were recorded on a SHIMADZU-IR460 spectrometer in a KBr matrix. All UV-Vis spectra were recorded on a computerized double-beam Shimadzu 255o spectrophotometer using two matched 10-mm quartz cells.

Synthesis of $[Co(3,5\text{-}DNBA)]_n$ (1)

A water solution containing ligand 3, potassium hydroxide (0.05 g, one mmol), and 3,5-dinitro benzoic acid (0.211 g, one mmol) were added dropwise to a water solution of cobalt(II) nitrate (0.183 g, 0.5 mmol) and the mixture was refluxed during the reaction. The produced dark precipitates were sieved, washed with water, and finally dried.

d.p. >300°C, yield: 0.258 g (80%). Anal.Calc. IR (KBr, cm^{-1}) selected bands: 576 (m), 1060 (m), 1139 (m), 1340 (vs),1531 (m), 1599 (vs), 3105 (w), 3228 (m), and 3672 (w).

Synthesis of $[Co(3,5\text{-}DNBA)]_n$ nano structures by sonochemical process

Preparation of nanosized $[Co(3,5\text{-}DNBA)]_n$ (1) involved positioning 50 ml solution of 3,5-dinitro benzoic acid (0.1 $mol.L^{-1}$) in water in a high-density ultrasonic probe which operated at 50 Hz with a maximum power output of 305 W. A 50 ml solution of the ligand 3,5-dinitro benzoic acid (0.01 M) and potassium hydroxide (0.01 M) were added dropwise into the water solution. The resulting precipitates were filtered off, washed with water, and then dried in air. m.p. > 300 °C. IR bands: 834(w), 1038(w), 1383(vs), 1635(m) and 3444(m).

Synthesis of $[Co(3,5\text{-}DNBA)]_n$ nano structures by hydrothermal process

The mixture of cobalt(II) nitrate (3 mmol), KOH (2.5 mmol), and 3,5-dinitro benzoic acid (3 mmol) in 60 ml of DMF was stirred in a conical flask at room temperature for 20 min before going through sonication. The mixture was transferred into a Teflon-coated autoclave and then heated up to 110°C for 24 h. Subsequently, the mixture was cooled down to room temperature. The solid black product was then filtered and washed entirely with DMF to remove unreacted reagents, followed by drying at room temperature (25–30 °C) under vacuum overnight. Then the dried material was transferred into a vacuum desiccator. m.p. > 300 °C. IR bands: 880(m), 1384(vs), 1631(w) and 3443(m).

RESULT AND DISCUSSION

The reaction between ligand 3,5-dinitro benzoic acid (L^-) and cobalt(II) nitrate led to the formation of the complex $[Co(3,4\text{-}DCBA)]_n$ (**1**). The IR spectrum shows characteristic absorption bands for complex **1**. Fig.1. shows the IR absorption bands for aromatic CH vibrations that are found at approximately 300 cm^{-1}. The IR spectra of the nano-structure of the compound **1** by sonochemical method resemble the IR spectra produced in a hydrothermal method (Fig 2(a) and (b)). Also, the symmetric and asymmetric vibrations of the carboxylate group can be seen in two strong bands at 1383 and 1635 cm^{-1}, respectively [24]. A broad band of about 3443 cm^{-1} indicates the presence of water molecules.

Fig 3. shows the XRD pattern of (a) compound $[Co(3,5\text{-}DNBA)]_n$ one, and Figs. 3 (b, c) show XRD patterns of synthesized products in sonochemical and hydrothermal method (with $[Co(3,5\text{-}DNBA)]_n$ as the precursor). Accepted matches observed for both compounds show the presence of only one nanoparticle. All highest diffraction value can be attributed to the crystalline CoO in structure (JCPDS card no. 43-1003). No peak from impurities is observed in the XRPD pattern, showing a high purity of CoO products and also, that the sample is changed completely into CoO after sonochemical and hydrothermal under air atmosphere. The sharp diffraction peaks of the sample showed that thoroughly crystallized CoO crystals could be easily obtained under current synthetic conditions. They are estimated from the Sherrer formula for the calculation of particle sizes from the broadening of the XRD peaks ($D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.22007nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively, the average size of the particles was found to be around 50 nm, a value that

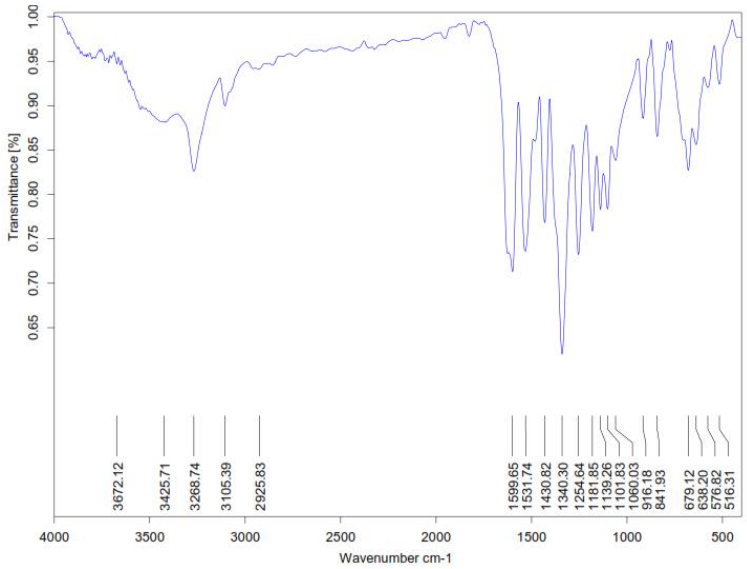


Fig. 1. IR spectra of $[Co(3,5\text{-}DNBA)]_n$ compound 1

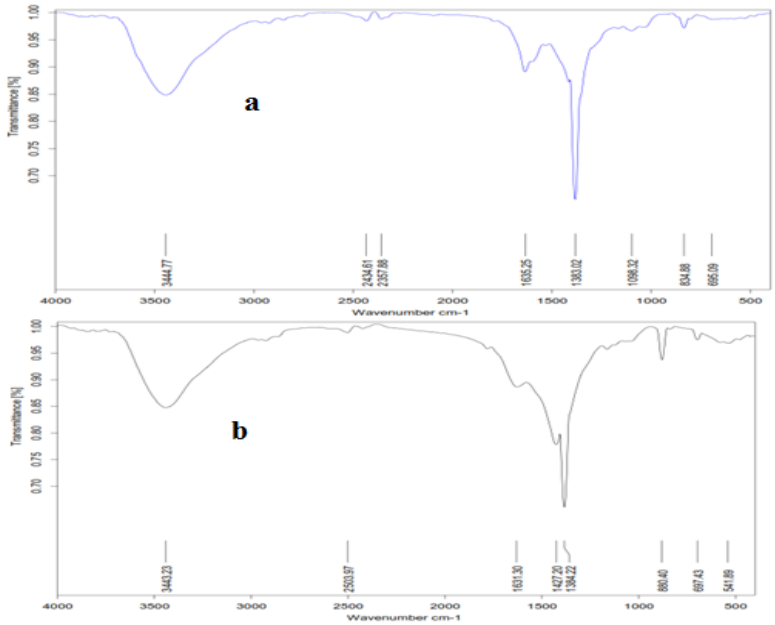


Fig. 2. IR spectra of (a) nano structure of compound **1** by sonochemical method(b) nano structure of compound **1** by hydrothermal method

agrees with the value obtained from the SEM images (Fig. 6).

Thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 25 and 900°C under argon flow with a slope of 15°C per minute (Fig. 4). The compound $[Co(3,5\text{-}DNBA)]_n$ 1 is stable up to 110°C. Decomposition of compound $[Co(3,5\text{-}DNBA)]_n$ 1 occurs between 110 and 590°C with a mass loss of 8.7% (calc. 8.2%). The DTA curve displays two exothermic effects at 110 and 799°C for the $[Co(3,5\text{-}DNBA)]_n$ 1.

The electronic absorption spectra of the ligand [3, 5-$DNBA^-$] in the presence of an increasing concentration of cobalt(II) ion in DMF at home

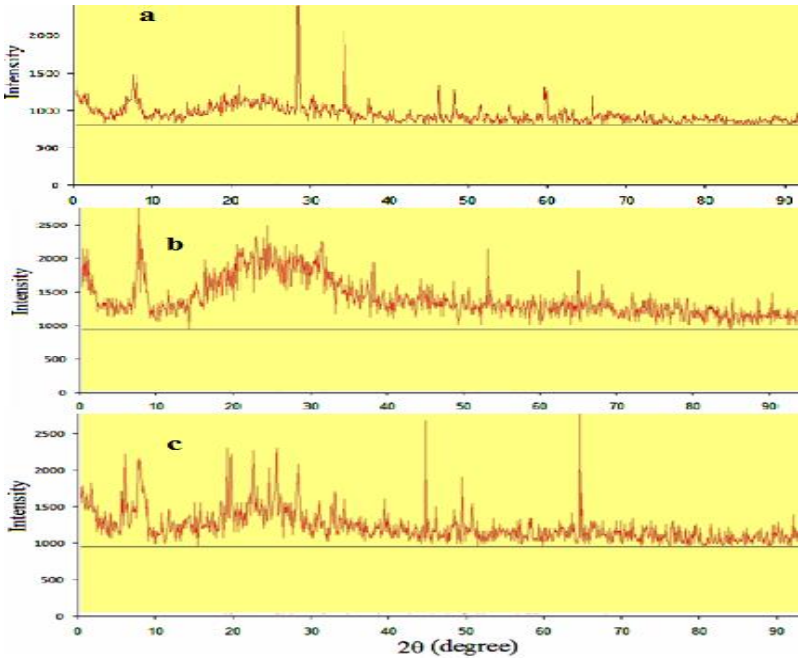


Fig. 3.(a) XRD parrern of compound $[Co(3,5\text{-}DNBA)]_n$ **1** (b) XRD sonochemical and (c) hydrothermal method

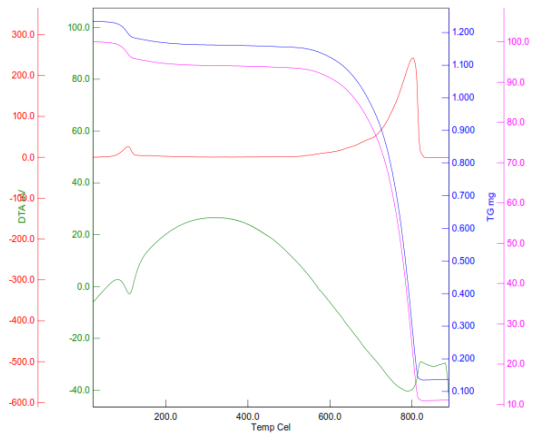


Fig. 4.Thermal behavior of $[Co(3,5\text{-}DNBA)]_n$.

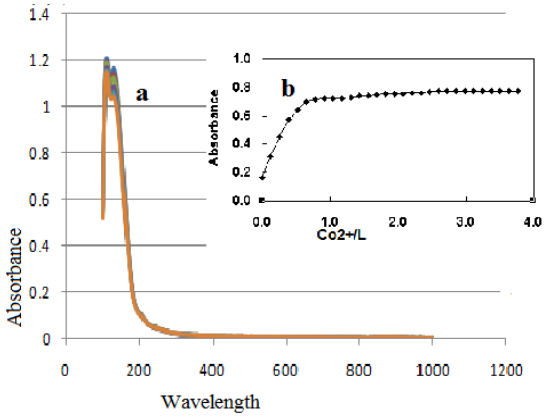


Fig. 5. (a) Electroni c absorption spectra of ligand in DMF(1.4×10^{-4}M) in the presence of increasing concentration of cobalt(II) ion at room temperature. (b) Correspounding mole ratio plot at 110 and 114 nm.

temperature are shown in Fig. 5(a). The strong absorption of the ligand at 110 nm and 114 nm increases with increasing concentration of the metal ion. The resulting absorbance against $[Co^{2+}]$/ $[3,5\text{-}DNBA^{-}]$ mole ratio plot shown in Fig. 5(b) revealed an indistinct inflection point at metal-to-ligand molar ratios of about 1, emphasizing the formation of a 1:1 complex in solution.

Figs. 6 (a) and (b) are the SEM images of nanosized particles exposed to ultrasonic waves demonstrated that nanospheres are 54 nm. The ultrasonic method has created uniform spheres while particles have more traditional forms and are more distinct.

Also, nanoparticles obtained with the hydrothermal method show that they are uniformly homogeneous spheres of 45 nm. Figs. 6 (c), (d) and (f).

The preparation of nano-cobalt (II) oxide is pretty simple in both methods. SEM images indicate that nano-spheres have empty holes responsible for the gap between the constituting

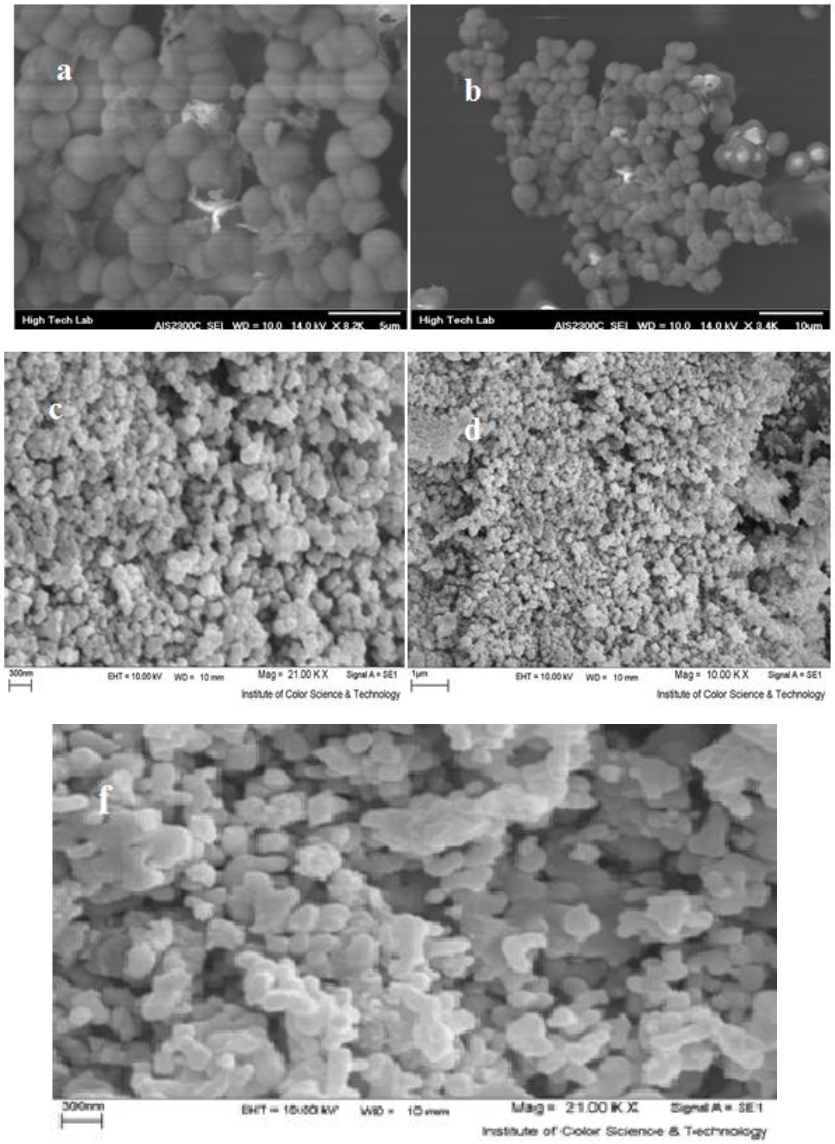


Fig. 6.(a,b) Scanning electron microscopy (SEM) photograph of CoO nanorice prepared by sonochemical method (c,b and f) CoO nanorice prepared by hydrothermal method

metal centers and these compounds can be used as a unique precursor for the supply of various gases.

According to the TEM images (Fig. 7), spherical nano-particles have an average particle size of 50 nm. DLS measurements are shown in Fig. 8. The results show two peaks with different altitudes. The first peak with a higher altitude indicates that the size of most particles is in the range of 52 nm and the second peak is related to the nanoparticles that are in the agglomerate solution. It should be noted that the SEM images (Fig. 6) indicate a considerably smaller size than the nanoparticles.

CONCLUSION

In this study, a new coordination polymer $[Co(3,5\text{-}DNBA)]_n$ (1) was synthesized and used as the precursor for the preparation of CoO nanoparticles with similar morphology. The average size of nanospheres diameters on the SEM, and TEM were 50 nm and DLS measurement showed that the average diameter was 52 nm.

We of ultrasonic and hydrothermal methods in the same conditions led to the formation of nanoparticle

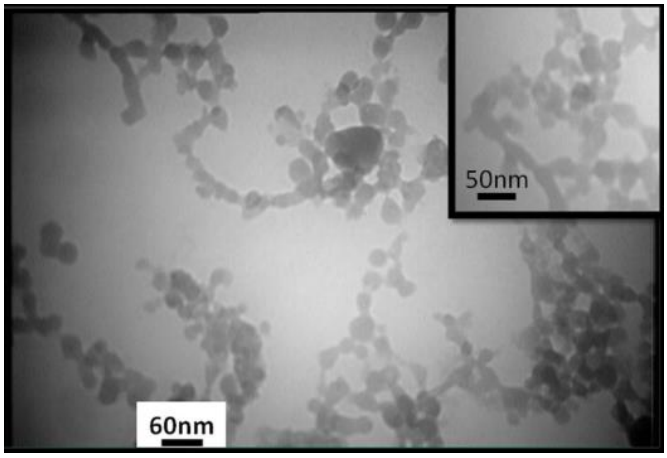


Fig. 7. TEM image of compound CoO

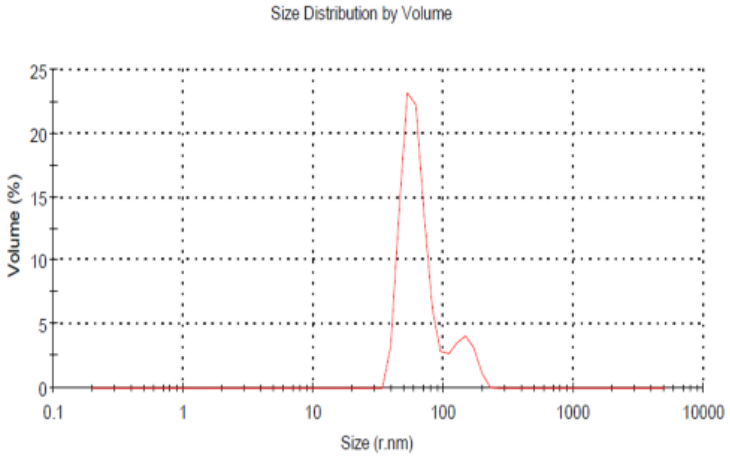


Fig. 8. DLS characterization of CoO nano-particle in ethanol.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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