

Bis(2-hydroxy-1-naphthalenehydrato) Metal Complexes as Source of Face-Centered-Cubic Trioctylphosphine Oxide-Capped ZnO and CdO Nanoparticles Using Oleylamine as Dispersion Medium

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[Bis(2-hydroxy-1-naphthaldehydato)zinc(II)] and cadmium(II) complexes were prepared, characterized to confirm the bidentate bonding to metal centre by aldehyde ligand through the two oxygen atoms. The complexes used as precursors for the synthesis of zinc and cadmium oxide nanoparticles *via* thermal decomposition method using oleylamine as a dispersion medium of the complexes prior to injection into trioctylphosphine oxide as a capping agent at 210 °C. The 4-coordinate complexes were confirmed by FTIR spectroscopy, elemental analysis and thermogravimetric analysis. The synthesized metal oxide nanoparticles gave the face-centered cubic phase of materials with average particle sizes of 4.12 (\pm 1.23) and 7.02 (\pm 2.57) nm for zinc and cadmium oxide nanoparticles, respectively.

Keywords: Naphthaldehyde ligand, Metal oxide, Nanoparticles, Oleylamine, Trioctylphosphine oxide.

INTRODUCTION

Recently, 2-hydroxy-1-naphthaldehyde has been treated as the most important ligand during the synthesis of Schiff base molecules which are very important class of organic compounds due to their ability to form complexes with metal ions. The complexes of transition metals have been investigated extensively for many years due to their importance in many applications such as in catalytic processes, materials synthesis, photochemistry and biological systems. They also show various chemical, optical and magnetic properties [1,2].

Researchers have developed a great interest in the synthesis of metal oxide nanoparticles due to their potential applications in various fields of science and industry, especially in catalysis due to their high surface activity. The metal oxide nanomaterials such as ZnO and CdO are extensively used as catalysts and supports [3], gas sensors [4,5], solar cells [6,7], in paint pigments, cosmetics, pharmaceuticals, medical diagnostics, membranes and filters, batteries and fuel cells, electronics, magnetic and optical devices, flat panel displays, biomaterials, structured materials and protective coatings [8]. Nanostructures based on zinc oxide and cadmium oxide are particularly interesting because of their n-type conductivity with the wide band gaps of 3.3 and 2.2 eV, with indirect band gaps of 2.30 and 1.36 eV, respectively, which makes these materials more suitable for modern technologies [9,10].

The greatest challenge in the synthesis of nanomaterials is their agglomeration. To prevent this problem, researchers have used various types of stabilizers such as long-chain fatty acids (stearic acid, palmitic acid and lauric acid) [11], polyvinyl pyrrolidone [12], soluble starch [13], gelatin [14], *etc.* Various synthetic methods have been developed to synthesize ZnO and CdO nanoparticles such as sol-gel method [15,16], micro-emulsion method [17,18], precipitation method, hydro-thermal method [19,20], chemical co-precipitation method [21] and thermal evaporation [22]. In this paper, the synthesis of ZnO and CdO nanoparticles using the thermal decomposition of the metal complexes based on the naphthaldehydato ligand in an organic surfactant at high temperature is reported. The bis(2-hydroxy-1-naphthaldehydato)metal(II) complexes were prepared from the reaction of the metal acetate with 2-hydroxy-1-naphthaldehyde. Each complex was then dissolved in oleylamine which served as a solvent and the mixture was injected into a hot trioctylphosphine oxide at 210 °C.

EXPERIMENTAL

Cadmium acetate dihydrate, 2-hydroxy-1-naphthaldehyde (Sigma, Aldrich), zinc acetate dihydrate, oleylamine, trioctylphosphine oxide, methanol, ethanol and toluene were reagents purchased from Merck chemicals and were all used without further purification.

The C, H, N and S elemental analysis were obtained through Leco-CHNS 932 analyzer. About 2 mg of sample was introduced into Ag capsule and was placed in a furnace maintained at 800 °C. The FTIR spectrum of the nanoparticles was recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer. Thermal gravimetric analysis/differential thermogravimetric (TGA/DTG) were performed with the TA instruments-SDT-2960 simultaneous analyzer. Samples were placed in an alumina cup and heated from 30 to 700 °C at a heating rate of 5 °C min⁻¹ in a nitrogen atmosphere. A purge gas was flowing dry nitrogen at a rate of 100 mL min⁻¹. The optical measurements were carried out using an Analytikjena Specord 50 UV-visible spectrophotometer. The particles were dissolved in toluene and solution was placed in a quartz cuvettes with 1 cm path length. A Perkin Elmer, LS 5 Luminescence spectrometer was used to measure the photoluminescence of the particles. Transmission electron microscopy was acquired on the Hitachi Jeol 100S operated at 80 keV. A drop of nanoparticles dissolved in toluene was placed on a copper grid. XRD patterns of the powdered samples were obtained on a Phillips X'Pert materials research diffractometer using secondary monochromated CuK_α radiation ($\lambda = 1.54060 \text{ \AA}$) at 40 Kv/50 mA. Measurements were taken using a glancing angle of incidence detector at an angle of 2 for 2 θ values over 10 to 80 in steps of 0.05 with a scan speed of 0.012.

Preparation of bis(2-hydroxy-1-naphthaldehydato)-metal(II), [M(HNA)₂] complex: In a typical experiment, a 20 mL methanol solution of Cd(CH₃COO)₂·2H₂O (5 mmol) was added into a 20 mL methanolic solution of 2-hydroxy-1-naphthaldehyde (HNA) (10 mmol) to form a homogeneous solution. The solution was stirred and refluxed at 60 °C for about 1 h. The precipitate that settled from the solution was centrifuged and washed with ethanol three times. The product was dried at 50 °C, weighed and characterized.

Zn(C₁₁H₆O₂)₂ complex: The complex was obtained as a dark green solid. Percentage yield: 72 %. m.p. 110.6 °C. Anal for C₂₂H₁₂O₄Zn calcd.: C, 65.01; H, 3.15. Found: C, 64.81; H, 2.97 %. Significant FTIR spectral bands: $\nu(\text{C}=\text{O})$: 1647 cm⁻¹, $\nu(\text{Zn}-\text{O})$: 494 cm⁻¹.

Cd(C₁₁H₆O₂)₂ complex: The complex was obtained as a light yellow solid. Percentage yield: 69 %. m.p. 180.4 °C. Anal for C₂₂H₁₂O₄Cd calcd.: C, 58.10; H, 2.66. Found: C, 57.97; H, 2.62 %. Significant FTIR spectral bands: $\nu(\text{C}=\text{O})$: 1647 cm⁻¹, $\nu(\text{Cd}-\text{O})$: 540 cm⁻¹.

Synthesis of trioctylphosphine oxide (TOPO) capped metal oxide nanoparticles: The MO-TOPO capped nanoparticles were synthesized by the thermal decomposition of [M(HNA)₂]-oleylamine complex. Firstly, the M(HNA)₂ complex (0.5 g) was dissolved in 5 mL oleylamine. The mixture was then placed in a 50 mL two-necked flask with a stopper and stirred for 1 h at 100 °C. This M(HNA)₂-oleylamine complex solution was then injected into a 5 g of hot TOPO in a three necked flask which was placed in an oil bath. The solution was stirred and refluxed at 210 °C under nitrogen gas environment for 1 h. The solution was then allowed to cool to about 70 °C and methanol was added. The product was separated by centrifugation and washed three times with methanol. The resulting TOPO capped metal nanoparticles were dispersed in toluene for further analysis.

RESULTS AND DISCUSSION

An efficient approach to the synthesis of spherical metal oxide nanoparticles using thermal decomposition is reported. In this work the metal complexes of zinc and cadmium were obtained by the reaction of the metal acetate with a hydroxy naphthaldehyde. The solid products were obtained in high yield and were reasonably stable at room temperature. These metal complexes were then used to synthesize trioctylphosphine oxide (TOPO) capped metal oxide nanoparticles *via* the thermal decomposition method by firstly dissolving each metal complex in oleylamine and inject the mixture into a hot trioctylphosphine oxide which was serving as a capping molecule. The metal oxide nanoparticles were dispersed in toluene for further characterization. The overall synthetic procedure is shown in **Scheme-I**.

Infrared spectral analysis of the complexes: The FTIR spectra (Fig. 1) of Zn(HNA)₂ and Cd(HNA)₂ complexes were recorded along with that of the free ligand. A significant feature in the spectra of Zn(HNA)₂ [Fig. 1(b)] and Cd(HNA)₂ [Fig. 1(c)] complexes was the absence of $\nu(\text{OH})$ broad band of the phenolic groups which is present in 3066 cm⁻¹ in the FTIR spectrum of the 2-hydroxy-1-naphthaldehyde (HNA) at 3066 cm⁻¹ which is similar to the reported by Yearwood [23]. This is an indication of an oxygen bonding to a metal ion after the replacement of the phenolic hydrogen from 2-hydroxy-1-naphthaldehyde. The FTIR spectra of 2-hydroxy-1-naphthaldehyde and its metal complexes showed the similar absorption peaks including the C-H stretching vibrations at 2888 cm⁻¹ and the absorption band at 1623 cm⁻¹ that corresponds to C=O symmetric stretching vibration which seem to be weakened in the FTIR spectra of both [Fig. 1(a) & 1(b)] due to the bonding of oxygen in the carbonyl group with the metal ion. The new absorption peaks that are shown in Fig. 1(b) and 1c at 3182, 3281 and 3365 cm⁻¹ which are absent from the FTIR spectra of 2-hydroxy-1-naphthaldehyde are attributed to the presence of O-H residue due to moisture [24]. The absorption bands at 494 and 541 cm⁻¹ were assigned to the coordination of the metal with oxygen from 2-hydroxy-1-naphthaldehyde (*i.e.* M-O).

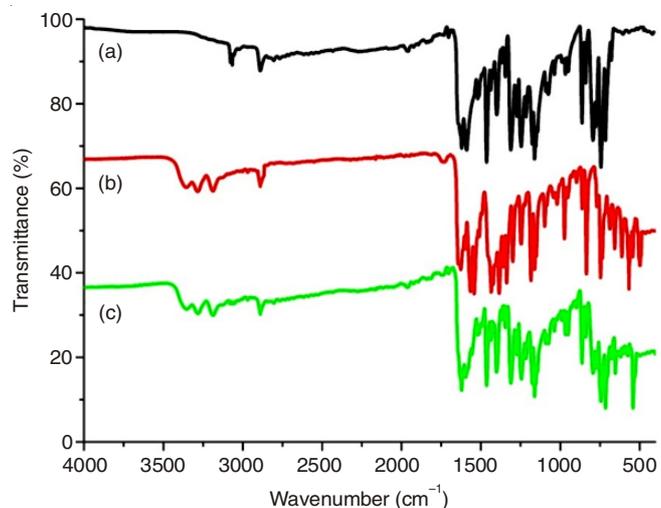
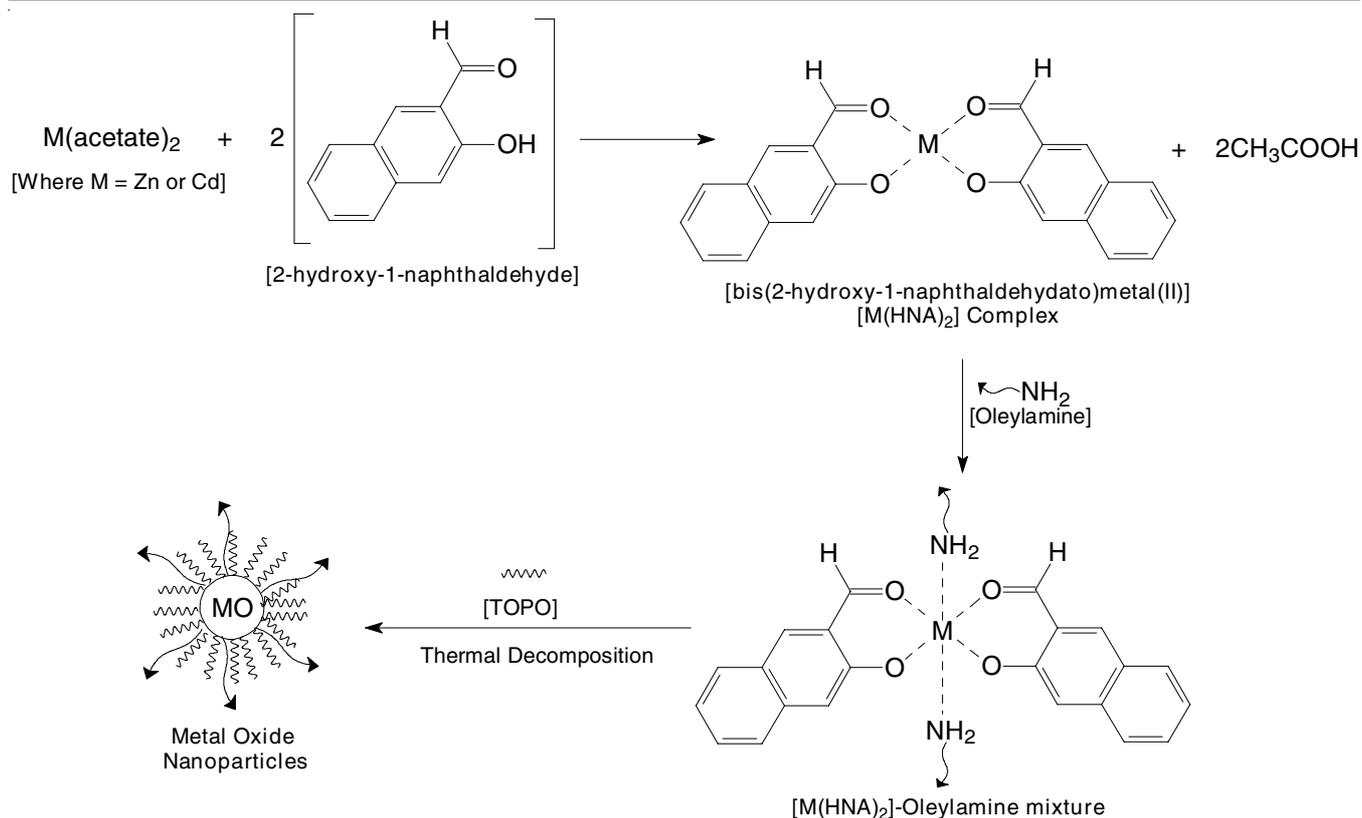


Fig. 1. FTIR spectra of the 2-hydroxy-1-naphthaldehyde (HNA) (a) Zn-HNA (b) and Cd-HNA (c)



Scheme-I: Preparation of *bis*(2-hydroxy-1-naphthaldehydato)metal(II) [M(HNA)₂] complexes and synthesis of TOPO capped metal oxide nanoparticles

Thermal analysis: In order to evaluate the potentials of the complexes as precursors for the synthesis of metal oxide nanoparticles, the thermal properties of *bis*(2-hydroxy-1-naphthaldehydato)metal(II) complexes were studied by thermogravimetric analysis/differential thermogravimetric (TGA/DTG) at the temperature ranging from 20 to 900 °C under nitrogen atmosphere. The TGA in Fig. 2(a) reveals a very strong endothermic peak at about 200–379 °C for the zinc complex. Differential thermogravimetric curve illustrates that most of the weight loss occurred at 313 °C. This sharp decomposition period brings about 63 % of the weight loss of Zn(HNA)₂ complex. Fig. 2(b) shows that Cd(HNA)₂ complex remained stable until a temperature of 117 °C. The decompo-

sition of this complex continued until about 235 °C. The DTG curve confirms that the main mass loss occurred at 234 °C. The latest results serve as an indication that it is not advisable to utilize this type of complex at higher temperatures (*i.e.* at temperature above 235 °C). Even the amount of the product after the thermolysis process during the synthesis of cadmium nanoparticles confirmed this phenomenon since the yield that was found was too small compare to the zinc nanoparticles.

Characterization of ZnO and CdO nanoparticles: During the synthesis of metal oxide nanoparticles, the oleylamine has been selected and used as a solvent to dissolve metal complexes. It is a much lower cost solvent compared to the commonly used alkylamines. It is also a liquid in room

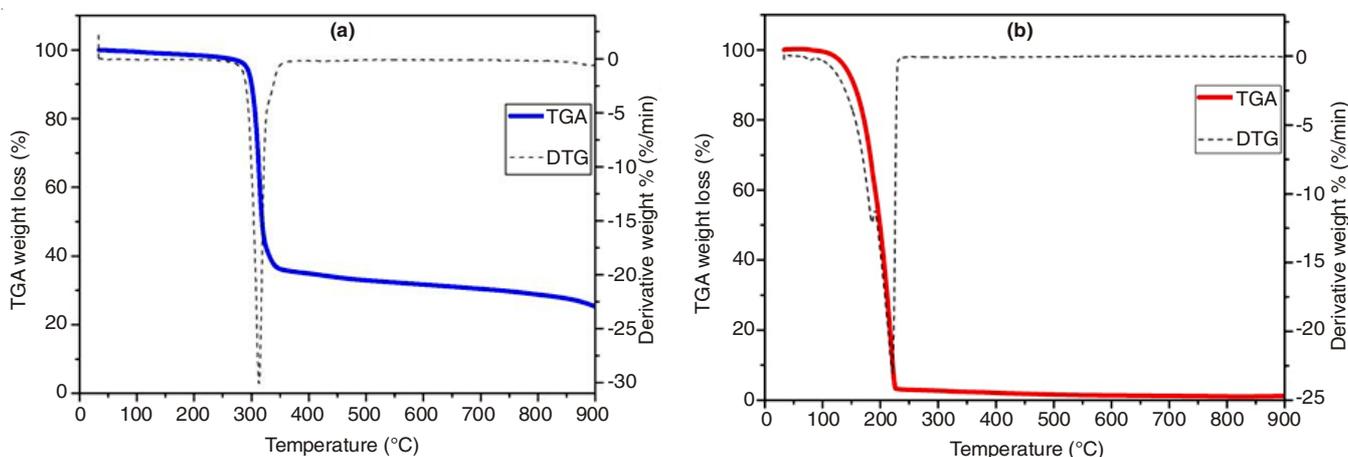


Fig. 2. TGA/DTG curves of the zinc (a) and cadmium (b) complexes

temperature with a high boiling point (348–350 °C) that allows a high temperature wet route to be carried out [25]. The trioctylphosphine oxide was used as a capping molecule since it is also a high-boiling point surfactant with a patulous long chain structure which provides a greater steric hindrance. Trioctylphosphine oxide is an agent that slow the addition rate of materials to the nanoparticles during their growth, resulting in much smaller nanoparticles. With oleylamine as a solvent and TOPO as a capping reagent, spherical and well dispersed ZnO and CdO nanoparticles were synthesized.

Optical properties: The most influential property of nanoparticles is the size advancement of the optical absorption spectra. The absorption and emission spectra of ZnO and CdO are shown in Figs. 3 and 4. The energy band gabs for bulk materials, nanomaterials as well as their emission peaks are represented in Table-1. The photoluminescence (PL) properties of TOPO capped ZnO and CdO nanoparticles at 210 °C were studied at room temperature by exciting the nanoparticles at 260 nm (4.77 eV) excitation wavelength.

Sample	Band gap (eV) (bulk)	Band edge (eV) (nanomaterial)	Emission peaks (eV)
ZnO	3.37	3.38 & 3.58	2.43 & 2.67
CdO	2.30	3.02	2.62

The absorption spectrum of ZnO nanoparticles [Fig. 3(a)] shows two absorption peaks at 346 and 367 nm, which are significantly blue-shifted relative to the bulk ZnO materials [26,27]. While the band gap increases, the particle size decreases which makes the electron hole states increases [28]. As expected, the ZnO nanoparticles exhibits two emission peaks [Fig. 3(b)], one is a narrow intensive peak at 465 nm which is due to the exciton recombination related near the band edge emission and the other one is a broad emission peak which is at 510 nm that is due to the vacancy of oxygen in the green region.

The absorption spectrum of CdO nanoparticles [Fig. 4(a)] exhibits the well-defined absorption peak at 438 nm. Fig. 4(b) shows a broad emission peak at 474 nm which is also blue shifted compared to the bulk CdO nanoparticles.

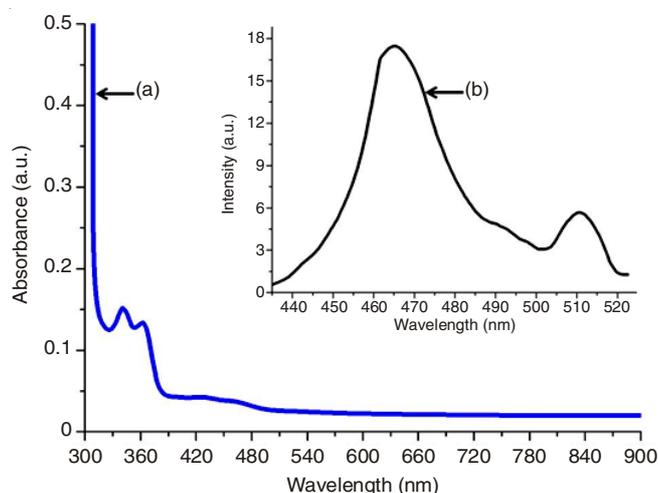


Fig. 3. Absorption (a) and emission (b) spectra of TOPO capped zinc oxide nanoparticles

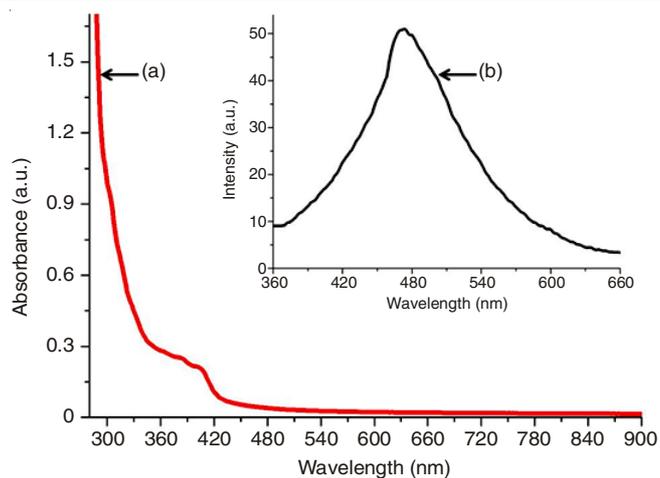


Fig. 4. Absorption (a) and emission (b) spectra of TOPO capped cadmium oxide nanoparticles

FTIR spectra (Fig. 5) of TOPO capped ZnO, CdO nanoparticles and pure TOPO were investigated. Most of the absorption peaks from the spectra of ZnO and CdO nanoparticles were similar to the peaks that were revealed by the pure TOPO including the strong absorption bands at 2919 and 2850 cm^{-1} which are attributed to the symmetric and asymmetric CH_2 stretching modes respectively [29]. The strong absorption peak at 1144 cm^{-1} is assigned to P=O group from the TOPO which is seen to be weakened in the FTIR spectra of the metal oxides nanoparticles. The absorption band that are located at 1305 and 1314 cm^{-1} which are attributed to CH_3 bonding mode from the TOPO tends to the slightly strengthened. This is evidence that the nanoparticles have attached themselves into the surface of the capping reagent through CH_3 and P=O groups. Furthermore, there were a number of new peaks that were observed in Fig. 5(b) and 5(c) that were not appearing in pure TOPO. Both spectra showed typical modes of amine groups. The absorption peaks at 3322 and 3320 cm^{-1} were assigned to the N-H stretching mode from the oleylamine which was used as a solvent [30] and the peaks between 1524 and 1649 cm^{-1} were due to the NH_2 scissoring modes. The peaks at 649 and 615 cm^{-1} are related to the stretching vibrations of the (Zn-O) and (Cd-O) bonds [31].

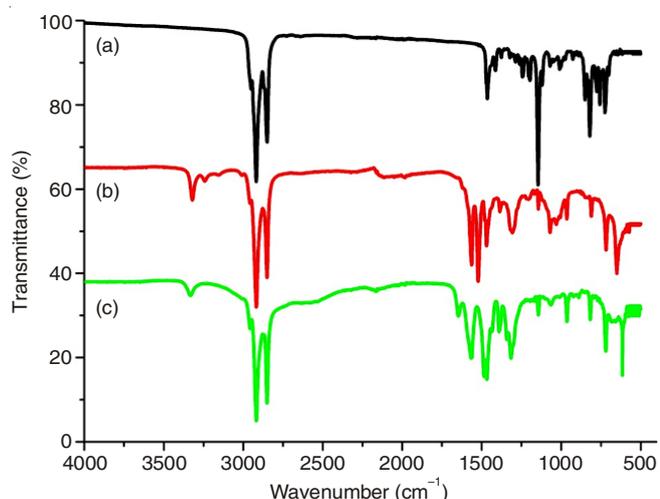


Fig. 5. FTIR spectra of the pure TOPO (a), TOPO-capped ZnO (b) and CdO (c) nanoparticles

Structural properties: The typical XRD patterns of both TOPO capped zinc oxide and cadmium oxide nanoparticles are represented in Fig. 6. CdO nanoparticles in Fig. 6(a) shows peaks at 2θ values of 37.74° , 43.94° , 64.34° , 77.44° and 81.78° , which conforms to the cubic phase [indices: (111), (200), (220), (311) and (222)]. ZnO nanoparticles in Fig. 6(b) gave the 2θ

values of 37.78° , 44.00° , 64.32° , 77.48° and 81.70° indexed to (111), (200), (220), (311) and (222) of the face-centred cubic (fcc) structures, which were in good agreement with the reported data [32]. The diffraction peaks were broad around their bases which are the indications of the particles that are in nanosize regime [33].

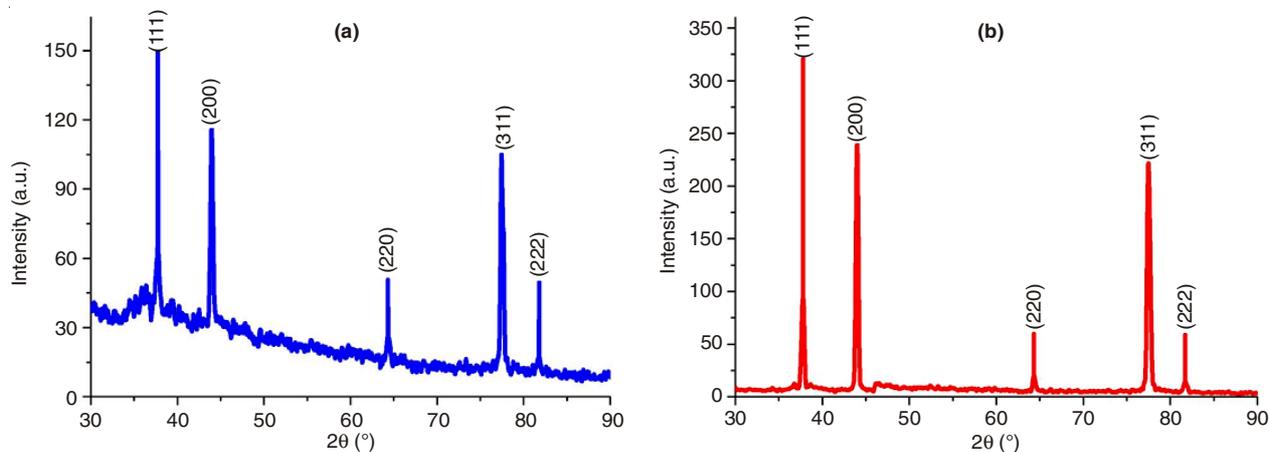


Fig. 6. X-ray diffraction patterns of TOPO capped ZnO (a) and CdO (b) nanoparticles

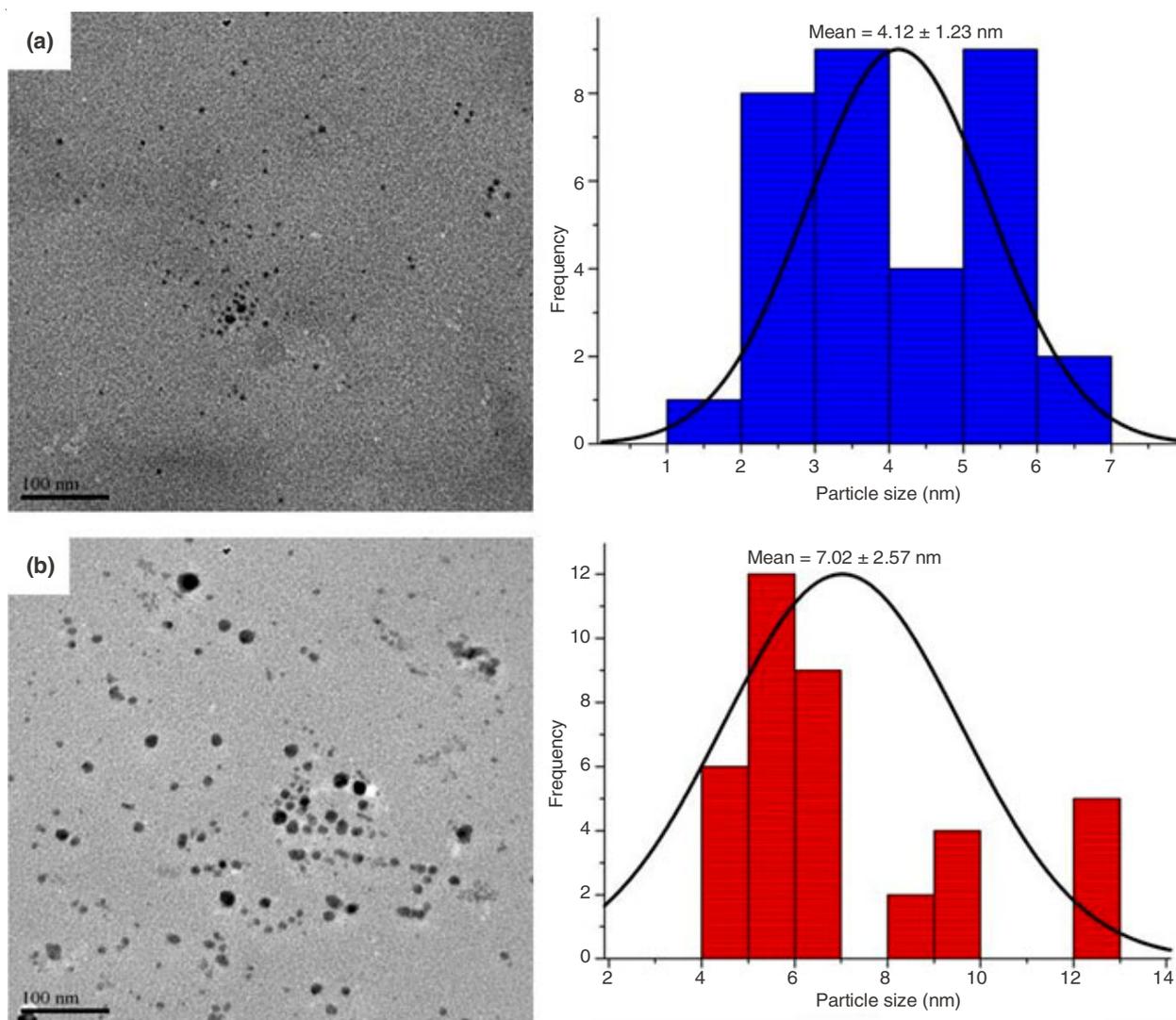


Fig. 7. TEM images of TOPO capped ZnO (a) and CdO (b) nanoparticles

Transmission electron microscopy (TEM) is a technique that can reveal information such as particle size, size distribution and morphology of the nano-particles. In particle size measurements, only the microscopic methods that are used to measured and observed the individual particles in the material [34]. Transmission electron microscopy images can also be utilized to judge whether good dispersion has been accomplished or whether agglomeration is present in the system. The TEM images of TOPO capped ZnO and CdO nanoparticles are shown in Fig. 7. Both ZnO and CdO nanoparticles [Fig. 7(a) and (b)] gave spherically shaped particles with average size distributions of $4.12 (\pm 1.23)$ and $7.02 (\pm 2.57)$ nm, respectively which is in good agreement with the UV-visible and XRD spectral analyses.

Conclusion

The study shows that the preparation of the metal complexes and the TOPO capped ZnO and CdO nanoparticles were successfully synthesized through thermal decomposition technique. The average particle sizes of ZnO and CdO nanoparticles determined from TEM are about 4.12 and 7.02 nm, respectively. The XRD patterns of both metal oxide nanoparticles show the face-centred cubic structure. The UV-visible and photoluminescence spectroscopy reveal the blue shift in their absorption band edges and emissions spectra are red shifted compared to their absorption spectra.

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