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Synthesis and Characterization of Nano Sized ZnO and CdO by Direct Thermal Decomposition of Their Nano Sized Metal Schiff base Complexes

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ABSTRACT

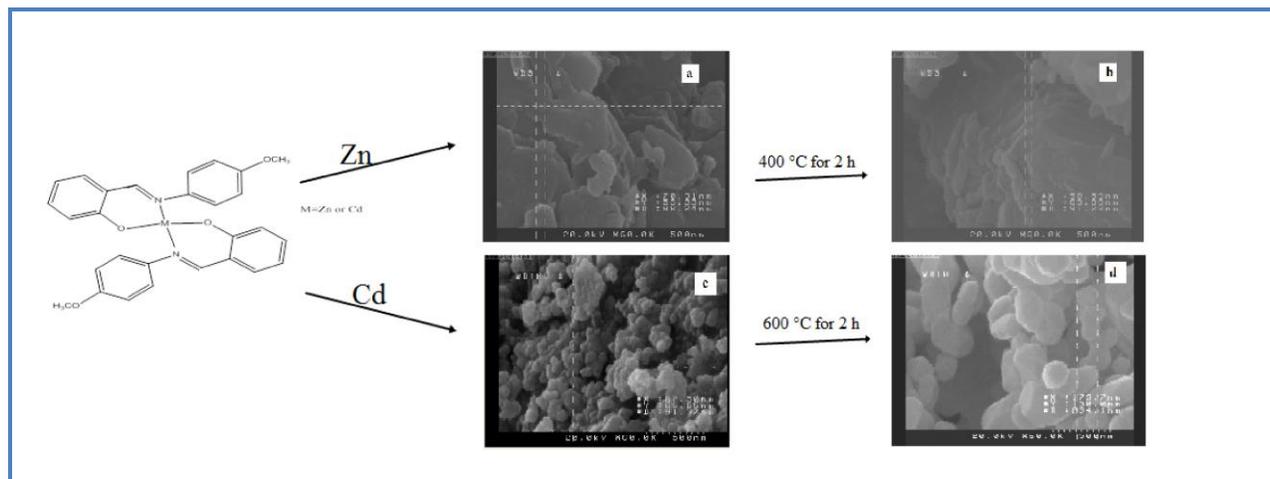
Nano sized metal oxide; ZnO and CdO have been synthesized by the thermal decomposition of two Schiff base complexes. Zinc and cadmium Schiff base complexes have been synthesized at reflux condition by the reaction between bidentate Schiff base ligand (E)-2-((4-methoxyphenylimino) methyl) phenol and nitrate salts of Zn or Cd in acetonitrile as a solvent. The nanoparticles of the title complexes were obtained using the ultrasonic irradiation method in acetonitrile as an anti-solvent of the Zn and Cd metal complexes, and also using spectroscopy and physicochemical methods including FT-IR, UV-Vis, elemental analysis, X-ray powder diffraction (XRD) and scanning electron spectroscopy (SEM). The nanoparticles (NPs) of ZnO and CdO with the average size of 27 and 32 nm were prepared by thermal decomposition of the title nano metal complexes. The metal oxide was identified by XRD pattern and SEM images.

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Graphical Abstract



Introduction

Metal complexes have quickly stabilized their position in various scientific and industrial fields such as inorganic mineralogy [1, 2], homogeneous catalysts [3-5], heterogeneous catalysts [6], biological activities [7], and sensors [8]. Moreover, metal elements can create various metal oxides under specific conditions. Almost all the catalysts were used in the chemical and petrochemical industries and environmental pollution control contain an oxide as an active phase, amplifier or support [9-11].

On the other hand, nano metal oxides have a key role in the chemistry, physics, and bioengineering technology [12-14]. ZnO is a well-known semiconductor with a wide direct band gap (3.37 eV) at room temperature and because of its low cost is widely applied as luminescence, gas sensor, photocatalysts and as Antibacterial materials [15-17]. Cadmium oxide is an n-type semiconductor, its band gap is 2.27 eV and it is used as an excellent optoelectronic material with high refractive index (2.49). Cadmium oxide has a wide range of applications such as luminescent, gas sensors, catalysts, antibacterial and biomedical applications [18-20]. Besides, nano zinc oxide and nano cadmium oxide are widely used in the fabrication of gas sensors [13, 14].

Zinc oxide and cadmium oxide nanoparticles are synthesized by different methods such as direct deposition [21], Hydrothermal [22], microwave radiation [23], sol-gel [24], and sonochemical method [25].

In this work, we have synthesized zinc and cadmium Schiff base complexes at reflux condition. Sonochemical method was applied to prepare the complexes in nanoscale. We have also synthesized nanosize metal oxide; ZnO and CdO, by the thermal decomposition of two nano Schiff base complexes.

Experimental

Chemicals and Apparatus

Zinc nitrate, tetrahydrate, cadmium nitrate.tetrahydrate, methanol, acetonitrile and dimethyl sulphoxide were purchased from Merck Company. All the chemical reagents used in experiments were of spectroscopic grade and used as received without further purification. Melting points were determined by the help of an Electrothermal Apparatus-9200. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu system FT-IR 8400 spectrophotometer using KBr pellets in the range of 400-4000 cm^{-1} . A Rigaku D-max C III, X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation, recorded product X-ray diffraction (XRD) data. The sample was characterized with a field emission scanning electron microscope (FESEM) (Hitachi S-4160) with gold coating and energy dispersive spectroscopy (EDS) was recorded on Oxford instrument. UV-Vis spectra of complexes, which were well dispersed in dimethyl sulphoxide, were recorded using Cary 50 spectrophotometer at room temperature. An ultrasonic bath (WUCAOZH, 50–60 Hz, and 0.14 kW) was used for the ultrasonic irradiation. Microanalysis for C, H, N were performed using the Thermo Finnigan Flash Elemental Analyzer 1112EA.

Synthesis of Schiff Base ligands E-2-2(((4-methoxyphenyl)imino)methyl)phenol

To synthesize the title ligand, 0.01 mol salicylaldehyde was added to 15 mL methanolic solution of 4-methoxy aniline (1.22g, 0.01 mol). The mixture was, then, refluxed for 2 hours to complete the reaction. Afterward, the formed green-gold precipitate was filtered off, washed by a 5 mL cold methanol and dried at room temperature (mp: 82 °C, yield: 51% Anal. calc. for $\text{C}_{14}\text{H}_{13}\text{NO}_2$ (227 g mol^{-1}): C, 74.00; H, 5.42 and N, 6.16%. Found C, 73.53; H, 5.34 and N, 6.02%.).

Synthesis of Zn and Cd Schiff base complexes in bulk scale

To prepare Schiff base complexes in bulk scale: 0.005 mol of synthesized ligand (1.135g) was solved in 10 mL acetonitrile. After that 0.0035 mol of metal nitrate (0.652g of Zinc nitrate. tetrahydrate or 0.625g cadmium nitrate. tetrahydrate) was added to the above solution. Each mixture was refluxed for 2 hours separately. The orange precipitates which were then separated by filtering, washed with cold acetonitrile and dried at room temperature for one day. Synthesis process is depicted in Figure 1.

Synthesis of Zn and Cd Schiff base complexes in nano scale

To prepare the Schiff base complex in nano scale: a reaction flask containing bulk Schiff base complexes in acetonitrile as an anti-solvent was placed in an ultrasonic bath. The mixture was

exposed to ultrasonic irradiation at room temperature for 40 min. Then, the dispersed products were separated by centrifuge. The precipitates were filtered off, washed with cold acetonitrile and dried at room temperature. (Anal. calc. for $C_{28}H_{24}N_2O_4Zn$ (517 g mol⁻¹): C, 64.99; H, 4.64 and N, 5.41%. Found: C, 64.50; H, 4.38 and N, 5./23. Yeild: 72%.) (Anal. calc. for $C_{28}H_{24}N_2O_4 Cd$ (565 g mol⁻¹): C, 59.46, H, 4.24, N, 5.41. Found C, 59.52, H, 4.34, N, 6/02. Yield: 78%).

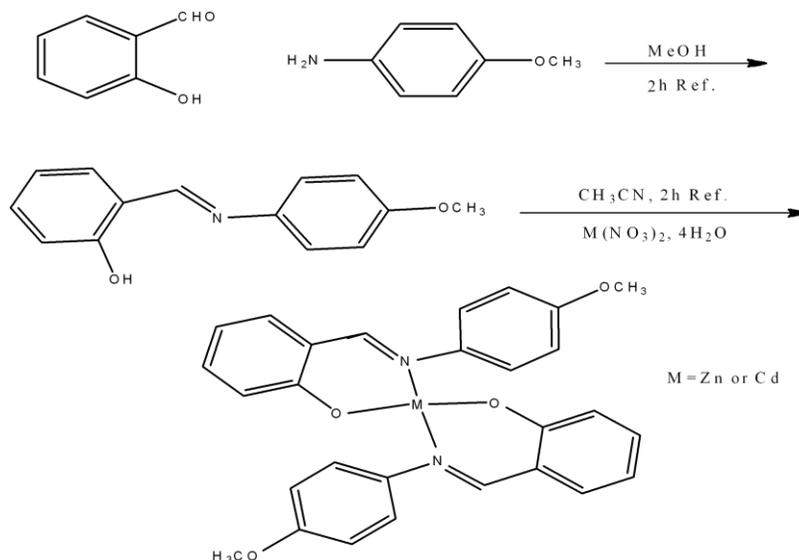


Figure 1. Schematic diagram for complexation process.

Synthesis of ZnO and CdO nanoparticles

The Zn complex was calcinated at 400 °C for 2 h. under air atmosphere leading to red-brown powder s of nanosized ZnO. By the nearly same procedure, the Cd complex was calcinated at 600 °C for 2 h under air atmosphere leading to white powders of nanosized CdO.

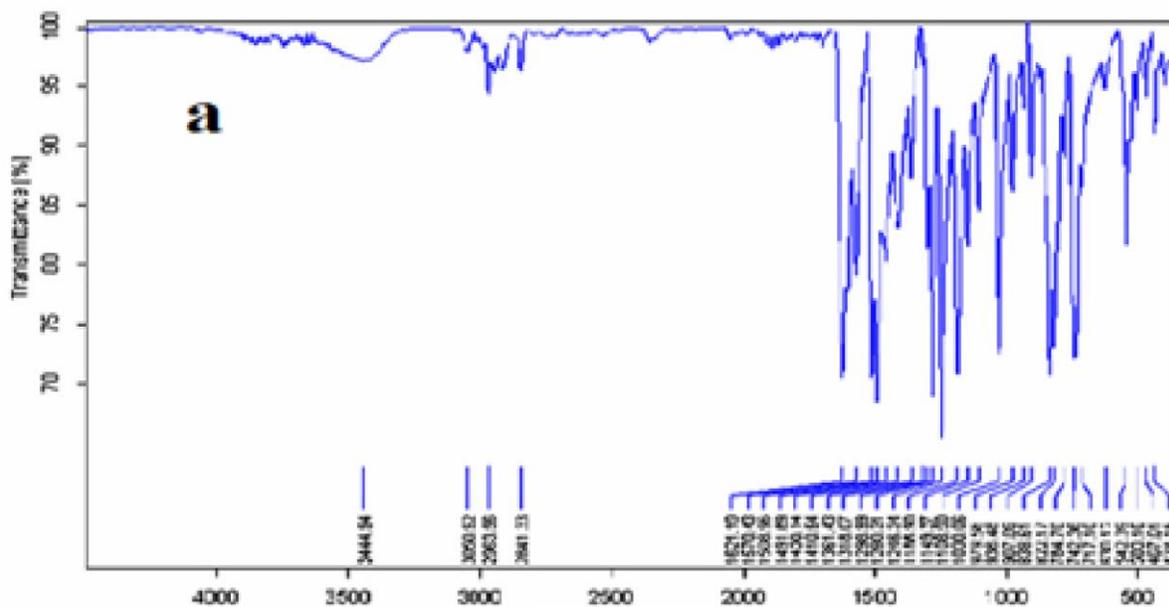
Results and discussion

IR study

The strong peak which was presented at $\nu(C=N)$ 1621 cm⁻¹ was assigned to azomethinic nitrogen in the synthesized ligand structure [26]. Moreover, the absence of NH₂ vibration proves that the Schiff base ligand is synthesized properly. Phenolic OH vibration is observable at 3444 cm⁻¹ [27]. The band observed at 1298.99 is associated to C-O bonds. The bands appeared at 1456 and 1570 cm⁻¹, are related to C=C vibration of aromatic bonds while the peaks appeared at 3050 are related to aromatic C-H bonds [28]. The red shift of $\nu(C=N)$ from 1621 cm⁻¹ of the ligand which is

observable to the 1608 and 1617 cm^{-1} regions for the Zn and Cd complexes respectively, suggests the coordination of the azomethinic nitrogen to the metal ions. In addition, the red shift of ν (C-O) from 1298 cm^{-1} in ligand to 1282 cm^{-1} for Zn and 1281 cm^{-1} for Cd complex proves the coordination of metal ions to phenolic oxygen. The vibrations ν (Zn-N) and ν (Zn-O) in Zn complex are assigned to bands occurring at 515 and 493 cm^{-1} , respectively. These bands in Cd complex appear at 574 and 543 cm^{-1} , respectively [29, 30].

The results of FT-IR spectra successfully exhibit formation of the ligand and two complexes.



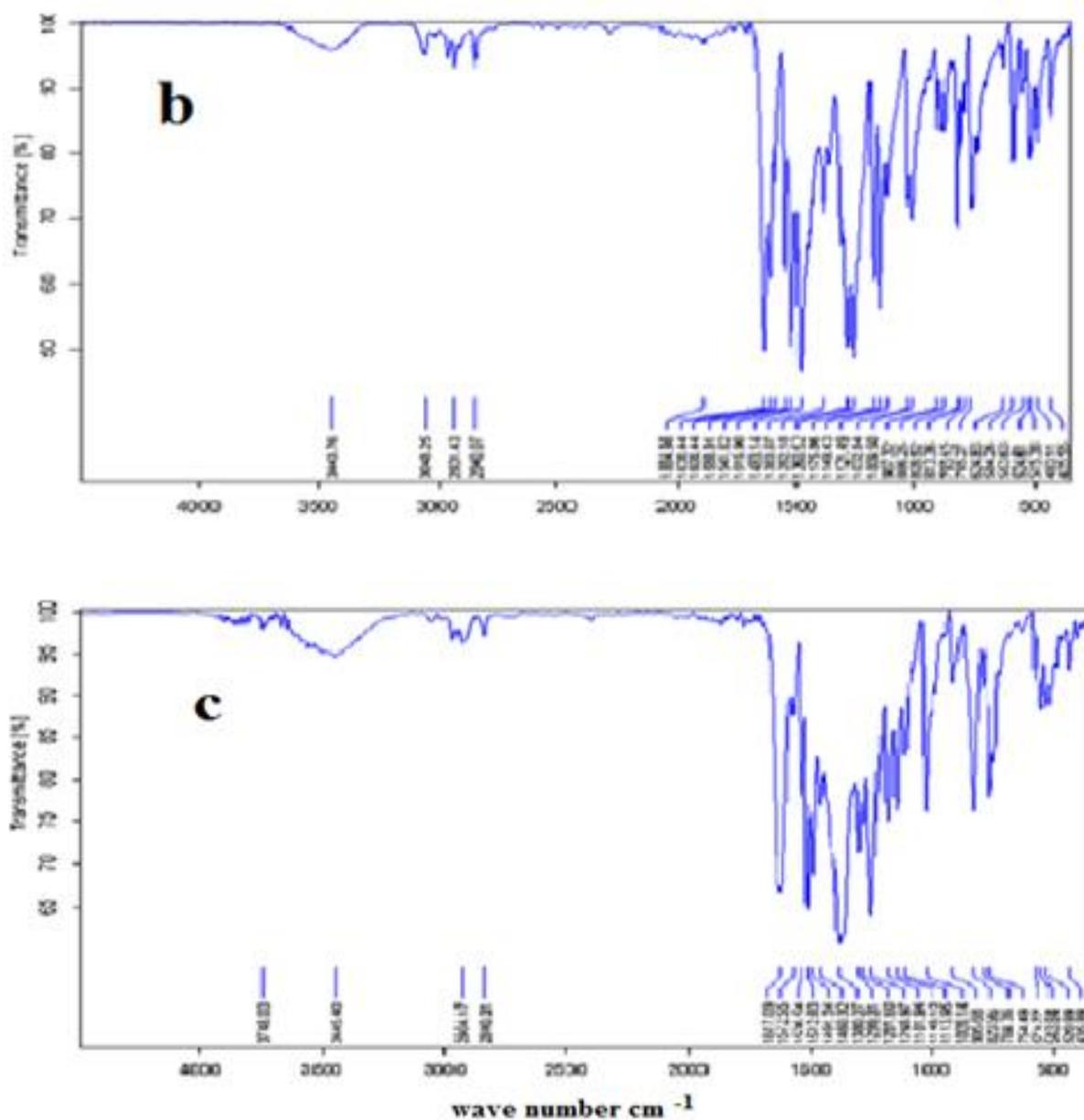


Figure 2. The infrared spectra of the (a) as-synthesized ligand (b) Zinc (II) Schiff base complex and (c) Cadmium (II) Schiff base complex

Electronic Spectra

The electronic spectrum of the title ligand was recorded in DMSO (2×10^{-5} M). The electronic spectra of the Schiff base and its Zinc (II) and Cadmium (II) complexes are shown in Figure 3. The spectra of the ligand exhibit bands at 274 and 350.94 nm attributable to the $n-\pi^*$ and $\pi-\pi^*$

transitions, respectively. In the complexes, $\pi-\pi^*$ transition has some shifts. In addition, two new bands at approximately 373 and 360 nm, probably a CT band, are observed [12].

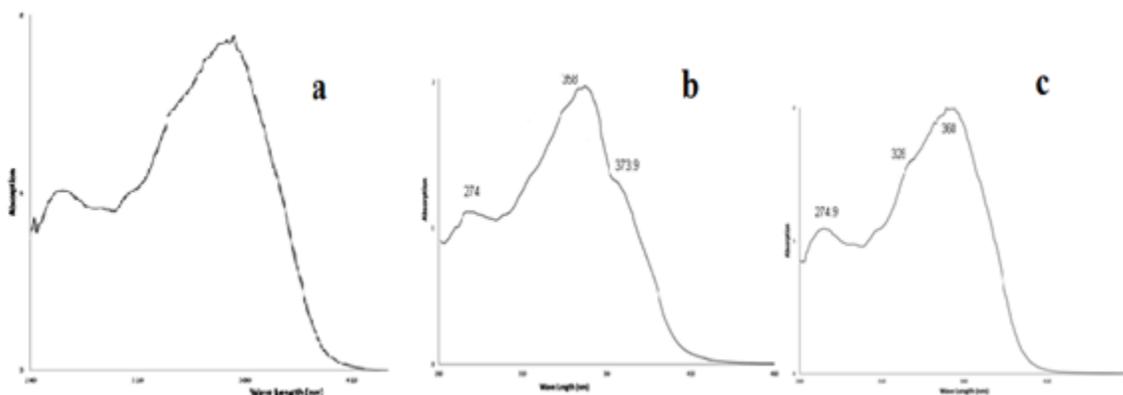


Figure 3. UV-Vis spectra of (a) the ligand, (b) nano sized Zinc (II) complex and (c) nano sized Cadmium (II) complex in DMSO

XRD Pattern

The particle size of Zn and Cd complexes in nano scale was investigated by XRD pattern (Figure 4). The broadening of the sharp diffraction peaks in Fig. 4a and 4b manifested that the particles were in nanometer scale. The average particles size were calculated 27.72 and 31.18 nm, respectively, for complexes by applying a full width at half maximum (FWHM) and the value of 2θ of the characteristic peak of the XRD pattern using the Debye–Scherer equation (Klug and Alexander 1964).

$$D = k\lambda/\beta \cos \theta$$

Where D is the average size, K is a constant (ca. 0.9), k is the wavelength of Cu K α , β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg's angle [31, 32].

Figure 4c and 4d show the XRD patterns of the as-synthesized ZnO and CdO nanoparticles. The sharp and intense peaks in the patterns indicate the good crystallinity of the materials. The broadening of the peaks in the XRD patterns indicates that the products have nano scale dimensions. The characteristic signals of ZnO which were found at $2\theta = 31.864, 34.509, 36.34, 47.636, 56.705, 62.972$ and 68.036 reveal the presence of ZnO structure (JCPDS cards Nos. 79-0206). In these patterns sharp peaks which can be well assigned to (100), (002), (101), (102), (110), (103), and (112) planes match well with ZnO structure [33]. The characteristic signals of CdO which were found at $2\theta = 33.071, 38.368, 55.362, 66.001,$ and 69.313 reveal the presence of CdO structure (JCPDS cards Nos. 73-2245). In these patterns sharp peaks which can be well assigned to (111),

(200), (220), (311), and (222) planes match well with CdO structure [34]. Using the Debye-Scherrer equation, the average particles size for ZnO and CdO were calculated 27 and 35 nm, respectively.

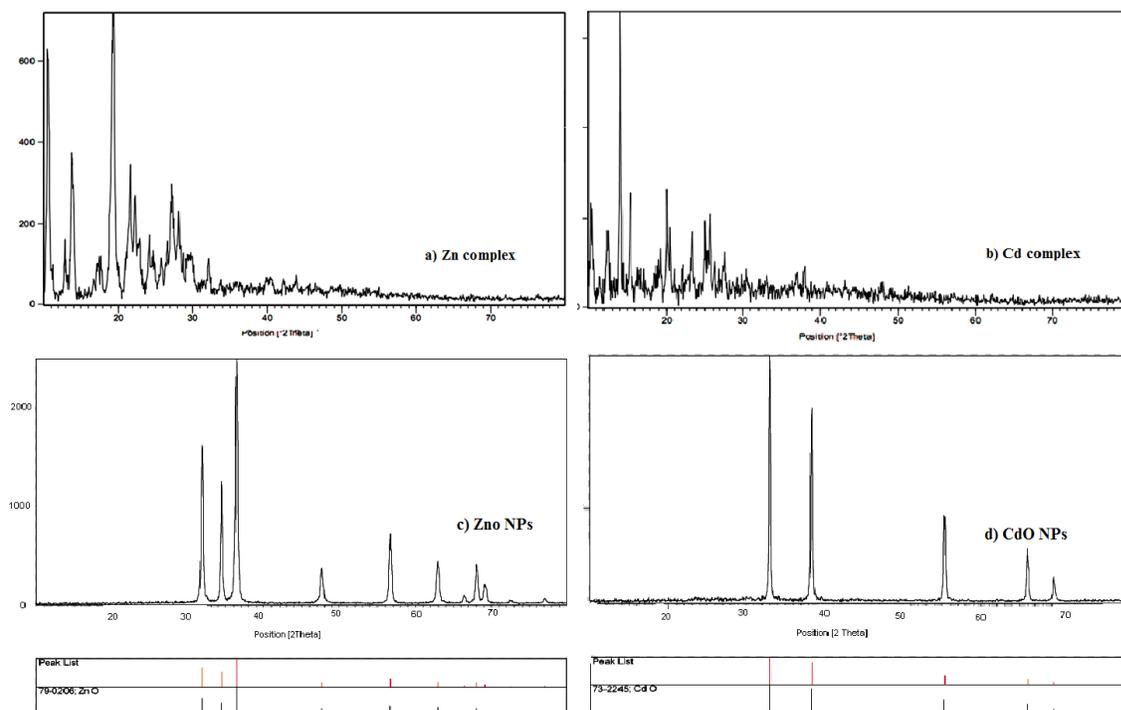


Figure 4. XRD patterns of the (a) zinc (II) complex (b) cadmium (II) complex (c) ZnO nanoparticles and (d) CdO nanoparticles

SEM Analysis

The morphology and particle size distribution of nano-sized of cadmium (II) and zinc (II) Schiff base complexes were investigated by the field emission scanning electron spectroscopy (FESEM). The FESEM micrographs of the zinc (II) Schiff base complex in Figure 5a and Figure 5c clearly shows that the morphology of the complex is spherical shape with the particle size about 70 nm (Figure 5a). Figure 5b and 5d give an overall view of the cadmium (II) Schiff base complex, revealing that its morphology is nano grains with the particle size about 60 nm (Figure 5b).

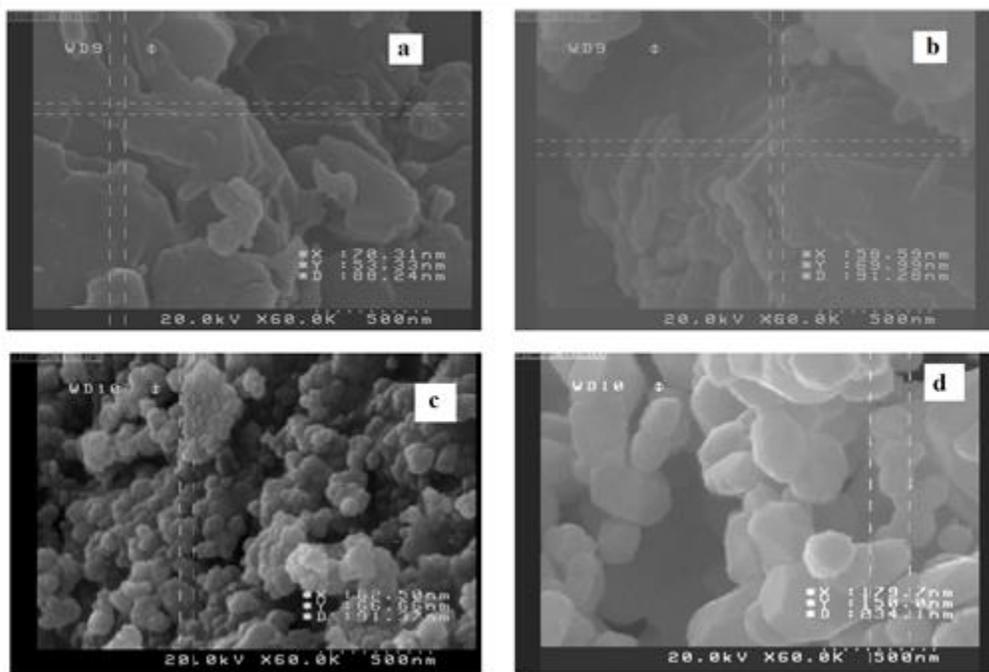


Figure 5. SEM images of (a) zinc (II) complex (b) cadmium (II) complex (c) ZnO nanoparticles and (d) CdO nanoparticles

Conclusion

Zinc and cadmium Schiff base complexes have been synthesized at reflux condition by the reaction between bidentate Schiff base ligand (E)-2-((4-methoxyphenylimino) methyl) phenol and nitrate salts of Zn or Cd in acetonitrile as a solvent. Sonochemical method was applied to prepare the complexes in nano scale. ZnO and CdO nanoparticles were synthesized via a simple method by thermal decomposition of Schiff base complexes. FT-IR, XRD, SEM, and UV-vis techniques were used to characterize the synthesized samples. XRD analysis confirmed that the samples were crystallized. Using Scherer equation, the size of ZnO and CdO were calculated 27 and 35 nm, respectively. SEM images showed that the morphology of particles is sphere, and the size of the particles is within the nano scale.

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