



Original Research article

A Novel Facile Synthesis Route for Nano-sized Zn(II) Schiff base Complex and Nano-sized ZnSe/ZnO

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ARTICLE INFORMATION

Received: 16 April 2018

Received in revised: 10 August 2018

Accepted: 08 August 2018

Available online: 01 January 2018

DOI: [10.22034/CHEMM.2018.66970](https://doi.org/10.22034/CHEMM.2018.66970)

KEYWORDS

Schiff base complex

Nano

ZnSe/ZnO

Ultrasonic

FESEM

ABSTRACT

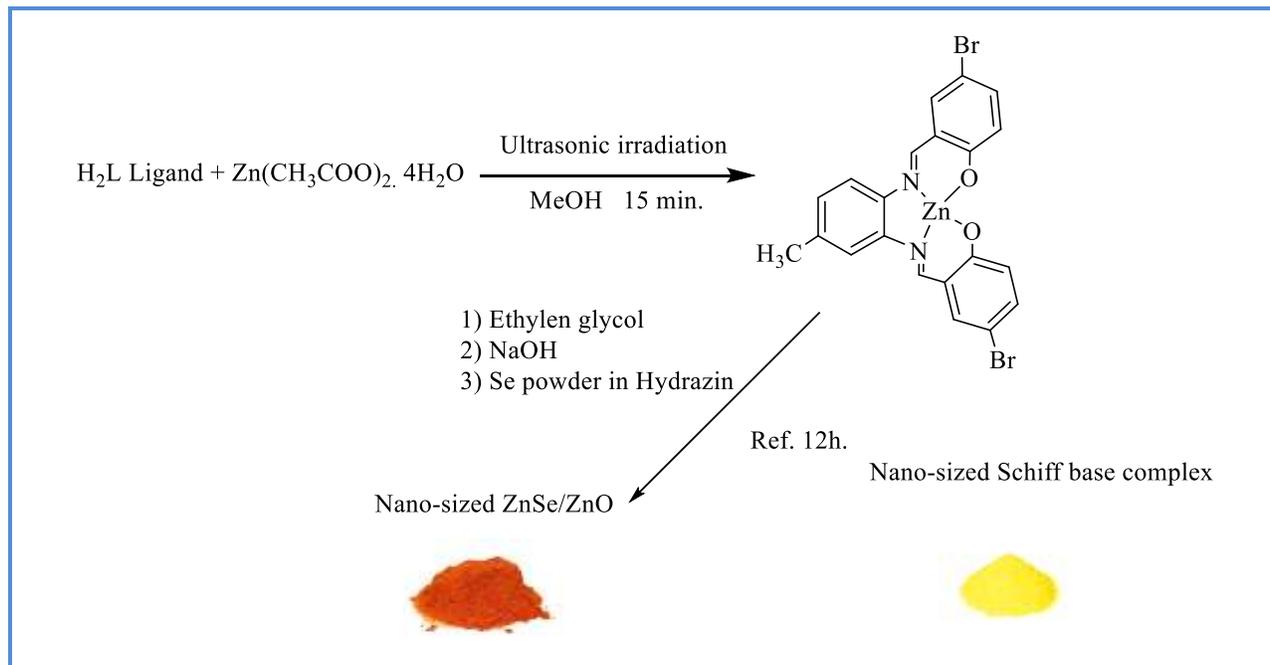
Nano- sized of 2,2'-((1E, 1E')-(1, 2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) Zn (II) Schiff base complex was quickly synthesized in mild condition by ultrasonic irradiation. The Zn (II) complex was characterized by FT-IR, ¹HNMR, FESEM as well as electronic and fluorescence property measurements. Based on the results of these analyses, the geometry of Zinc (II) Schiff base complex suggested a square-planar geometry. Antimicrobial activities of the ligand and Zinc (II) complexes were also investigated. The electronic and fluorescence bands of nano complex show a shift in comparison to the bulk sample analogue, duo to the reduction of particle size in nano scale. In continuation of our study, ZnSe/ZnO nano sized with 30 nm in average sizes was prepared, by reflux condensation method, using this complex as a new precursor.

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Graphical Abstract



Introduction

Zinc, which is always present in the +2 oxidation state, has a significant role in biochemistry, involving a large number of enzymatic and anticancer functions [1, 2]. The importance of zinc compounds as catalysis is due to the appropriate substrate formation, generation of a reactive nucleophile (Zn-OH) and stabilization of the leaving group [3]. Besides, zinc compounds have been widely studied in proteins chemistry; including the interaction of the thiol group of peptides such as cysteine (Cys) residues with Zn^{2+} in various metallothioneins and zinc fingers [4, 5].

In addition to, zinc compounds based on Schiff base ligands have played essential role in extension of coordination chemistry. Zinc Schiff base complexes were investigated increasingly as corrosion [6], antimicrobial [7], nonlinear optics [8], and molecular sensing [9] reagents. In some Schiff base metal complexes, it has been illustrated that the minor modification in the structure of the ligands containing hard soft donor atoms (N, O and/or S) markedly affected the properties of the compounds [10-13].

In recent years, luminescent properties of Zn (II) Schiff base complexes have attracted considerable attention [14, 15]. Zn (II) ion which possesses closed-shell $3d^{10}$ configuration has no optical spectroscopic signature, but that can be enhanced by ligand luminescence upon coordination (chelation-enhanced fluorescence effect) [16, 17]. Therefore, synthesis of zinc coordination

compounds with different properties based on novel structures has received considerable attention.

Recently, synthesis of materials in nano scale has been increased based on the fact that the reduction in particle size to nanometer scale results in high surface to volume ratio, changes in electronic structure of materials that shows fascinating physical and chemical properties that are different from the bulk materials such as the mechanical, optical, and magnetic properties [18, 19]. During the past several years, various synthetic techniques have been developed for synthesizing metallic nanosized materials, including microemulsions [20], chemical vapor deposition [21], sonochemical method [22] and so forth. In addition, sonochemical method has more advantages, such as environment-friendly, simplicity, safety and fast of process.

For these seasons, we succeeded in preparing a nano zinc complex, based on N_2O_2 donor Schiff base ligand, named $[Zn(L)]$ where $L = 2,2'-((1E,1E')-((4\text{-methyl-1,2-phenylene})\text{ bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenol)$. The structure and morphology of the synthesized complex were investigated by means of Fourier transformed infrared (FT-IR), Nuclear magnetic resonance (1H NMR), field emission scanning electron microscopy (FESEM) as well as electronic and fluorescence property measurements. Moreover, this complex was used as a new precursor for nano sized ZnSe/ZnO. The average crystallite size of the nano sized ZnSe/ZnO is about 30 nm as determined by the Debye Scherrer equation.

Experimental

Chemicals and apparatus

All the chemical reagents used in experiments were of spectroscopic grade and used as received without further purification.

An ultrasonic bath (WUC AOZH, 50–60 HZ, and 0.14 kW) was used for the ultrasonic irradiation. The experimental parameters were performed with output power of 0.14 kW. Melting points were measured on an Electrothermal 9100 apparatus. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu system FT-IR 8400 spectrophotometer using KBr pellets. Nuclear magnetic resonance spectra were recorded on Bruker Avance-400 MHz. spectrometer. 1H NMR chemical shifts were reported using tetramethylsilane (TMS) as the internal standard. The samples were characterized with a field emission scanning electron microscope (FESEM) (Hitachi S-4160) with gold coating. Product X-ray diffraction (XRD) data were recorded by a Rigaku D-max C III, X-ray diffract meter using Ni-filtered $Cu\ K\alpha$ radiation. Electronic spectra of the complexes were

recorded in ethanol using Cary 50 spectrophotometer. Fluorescence experiment was carried out on a Cary eclipse spectro fluorometer at room temperature.

Synthesis of 2,2'-((1E,1E')-((4-methyl-1,2 phenylene)bis(azanylylidene)) bis (methanylylidene))bis(4-bromo phenol), (H₂L)

4-Methyle 1, 2-diaminobanzen (0.1 g, 0.001 mmol) and 5-bromosalicylaldehyde (0.2 g, 0.002 mmol) in MeOH (20 mL) were refluxed for 15 min; the orange's formed precipitate was separated by filtration, washed with ether, and dried under vacuum over anhydrous CaCl₂.

M.p. = 125 °C, Yield: 40%. ¹H NMR (DMSO-d₆, d ppm): 2.4 (s, 3H, CH₃); 5.2– 8.8 (m, 10H, ArH) 10-12 (d, 1H, C=N). IR (ν_{max}; cm⁻¹, KBr): 3500 (ν OH), 2925 (ν_{as} C–H), CH₃), 2821(ν_{as} C–H in CH₂), 1589 (ν C=N), 1349 (ν C–O). UV-Vis (nm) (λ (nm) /log ε (mol⁻¹ cm⁻¹) (EtOH): 397 (3.35), 456 (4.15), 470 (4.16), 522 (4.68).

Synthesis of nano sized of 2,2'-((1E,1E')-((4-methyl-1,2 phenylene)bis(methanylylidene))bis (4-bromo phenolato) Zinc (II) complex, [Zn (L)] by ultrasonic method

In order to prepare the nano- sized of 2,2'-((1E,1E')-(1,2 phenylen bis (azanylylidene)) bis (methanylylidene)) bis (4-bromo phenolato) zinc (II) complex, a reaction flask containing H₂L (0.2 g, 0.0004 mol) in MeOH (10 ml) was placed in an ultrasonic bath with output power of 0.14 kW. The solution was exposed to ultrasonic irradiation at room temperature, then, 10 ml methanolic solution of (CH₃COO)₂Zn.4H₂O (0.2 g, 0.0004 mol) was added to the mixture in dropwise manner for 15 min. The dark yellow precipitate is filtered off, washed with cold methanol and diethyl ether, and dried under vacuum over anhydrous CaCl₂. Yield: 60%; m.p. >300 °C .¹H NMR (DMSO-d₆, d ppm): 2.3 (s, 3H, CH₃); 6.95– 8.003 (m, 10H, ArH) 8.95, 8.98 (d, 1H, C=N). IR (ν_{max}; cm⁻¹, KBr): 2919 (ν_{as}C–H in CH₃), 1617 (ν_{C=N}). UV/Vis (EtOH) λ_{max} nm (log ε, L mol⁻¹ cm⁻¹): 253 (4.19), 303 (4.08), 410 (4.07).

Synthesis of nano sized of ZnSe/ZnO by condensation method

ZnSe/ZnO was synthesized according to the experimental procedure [23]. 0.1 mol of [Zn (L)] complex was mixed with 20 mL of ethylene glycol under vigorous stirring. The pH of the solution was set to 12 by adding several drops of aqueous solution of NaOH (1M). Then 0.1 mol of selenium metal powder that was dissolved in 10 mL of hydrazine hydrate was mixed to this solution with drop wise manner. The hydrazine hydrate is solvent for selenium metal meanwhile acted as a good reducing. The resultant solution was refluxed in an atmospheric condition for 12 h. The obtained precipitate was washed three times with distilled water and several times with ethanol and

chloroform solution (1:1). Afterwards, it was dried under vacuum over anhydrous CaCl_2 . The orange powder was obtained and used for further investigation.

Results and discussion

Nano-sized 2, 2'-((1E, 1E')-((4-methyl-1, 2 phenylene) bis (methanylylidene)) bis (4-bromo phenolato) zinc (II) complex was synthesized in mild conditions by ultrasonic method in short time with improved yields. Then, the complex was used as a new precursor for preparing nano-sized ZnSe/ZnO. The reflux condensation method is a novel appropriate method for the synthesis of nano materials such as selenite metal from coordination compounds because the sufficient temperature was provided for breaking coordination bonds resided in the structure of precursor complexes. In this work, ultrasonic method was applied for preparing nano-sized ZnSe/ZnO but the precursor complex was not decomposed in different condition and ZnSe/ZnO not synthesis.

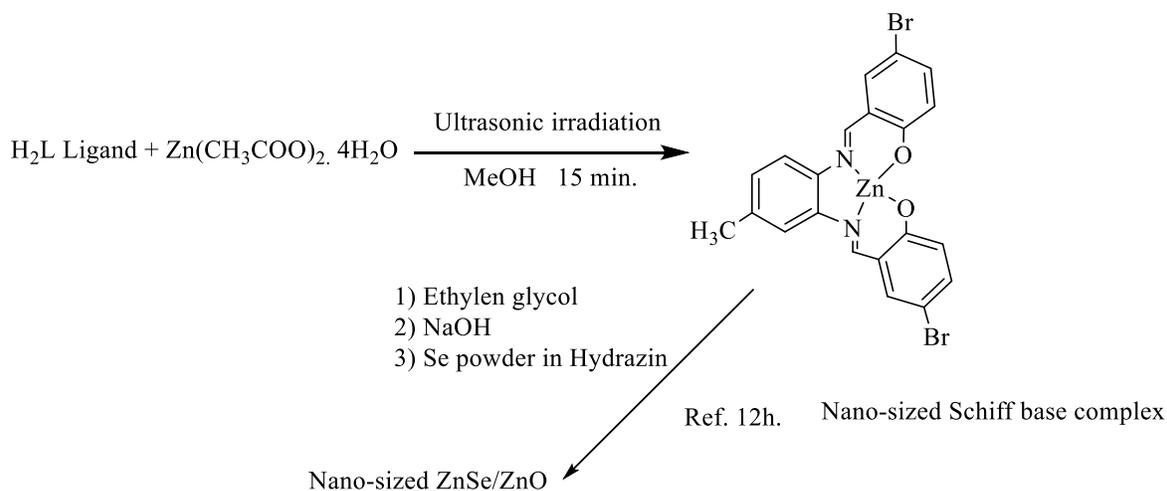


Figure 1. The experimental procedure of nano sized of $[\text{Zn}(\text{L})]$ complex and nano sized of ZnSe/ZnO

FT-IR of zinc (II) Schiff base complex study

The infrared spectra of the ligand (H_2L) and nano-sized zinc (II) Schiff base complex are shown in figure 2. According to $\nu(\text{C}=\text{N})$ of the H_2L ligand to the 1617 cm^{-1} region of the IR spectrum of the zinc (II) complex, the red shift from 1589 cm^{-1} suggests the coordination of the azomethinic nitrogens to the zinc (II) ion. Moreover, the disappearance of a broad band characteristic of the OH group in the 3417 cm^{-1} region in the FT-IR spectrum of the complex is indicative of the fact that the tetradentate N_2O_2 ligand is coordinated to Zn (II) ion. The phenolic C-O stretching vibration, which appeared at 1372 cm^{-1} in the zinc (II) Schiff base complex, undergoes a shift towards lower frequency in the ligand (1349 cm^{-1}). This shift confirms the participation of oxygen in the C-O-M

bond. The stretching C-H group, in-plane bending and out-of-plane bending occurring in 2919, 1075-1307 and 761-867 cm^{-1} respectively for Zn (II) complex, 2925, 1070-1160, 557-678 cm^{-1} respectively for H_2L ligand. The aromatic C=C bond was demonstrated by the stretching vibration at 1425 and 1589 cm^{-1} for H_2L ligand, whereas these bonds are shifted at 1461, 1515 cm^{-1} for zinc(II) complex that was confirmed by complexation. In addition, the Zn-N and Zn-O bands for zinc (II) complex were also predicted by the bands observed at around of 500-800 cm^{-1} [24, 25].

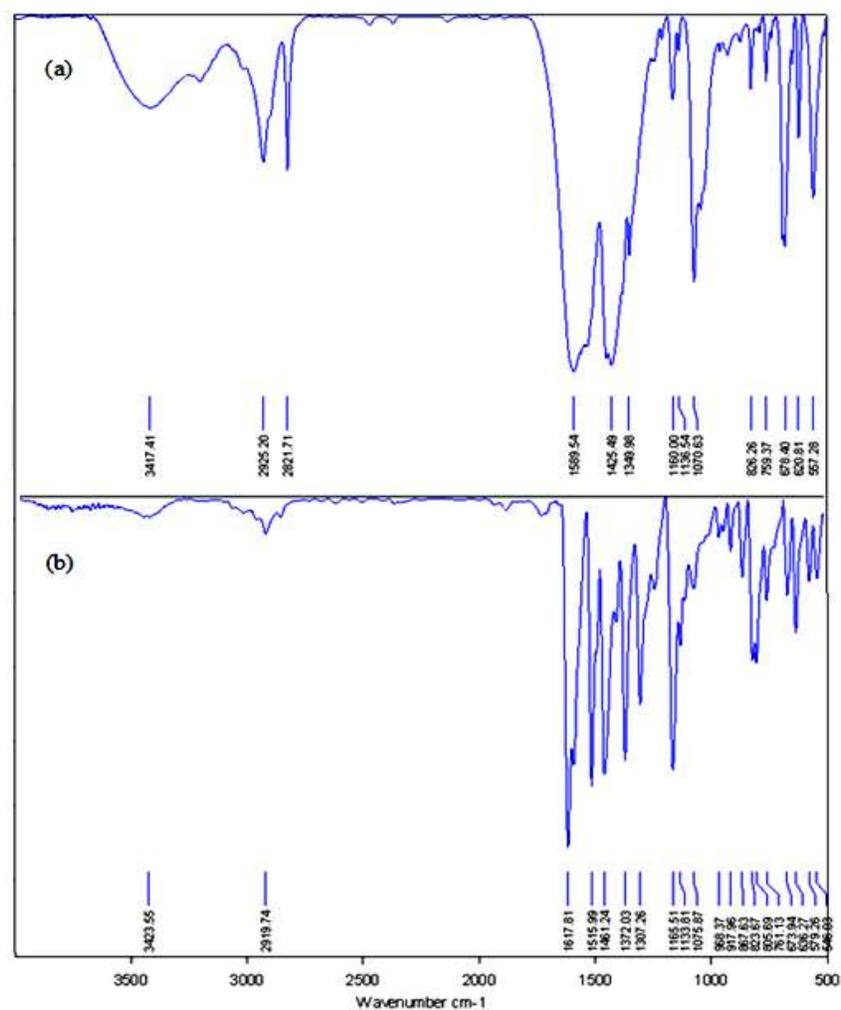


Figure 2. The infrared spectra of the H_2L ligand (a) and Zn (II) Schiff base complex (b)

$^1\text{H-NMR}$ of Zn (II) Schiff base complex study

$^1\text{H-NMR}$ spectrum of nano-sized Zn (II) complex showed disappearance of the two phenolic protons signals which were assigned at 12-14 ppm as compared to that of $^1\text{H-NMR}$ spectrum of H_2L ligand

(Figure 3a) due to the deprotonating of the phenolic groups and subsequently the replacement of the protons by Zn ion. The azomethine proton exhibited a singlet at 10-12 ppm. The signals of Zn (II) complex (Figure 2b) shift due to complexation of the Zn (II) ion by the azomethine groups. In the spectrum of H₂L ligand; the methyl protons and the aromatic protons of the phenyl group exhibited a singlet at 2.40 ppm and a multiple within the region 5.2–8.8 ppm, respectively. The corresponding peaks of these proton groups for Zn (II) complex are revealed at 2.36 and 6.6–7.7 ppm. The downfield shielding is due to the formation of Zn (II) complex with N₂O₂ Schiff base ligand. Because DMSO is coordinated to the central zinc (¹H-NMR spectrum of complex monitored in DMSO d₆ solvent), the peaks corresponding to DMSO are observed at 2.47, 3.32 ppm [26].

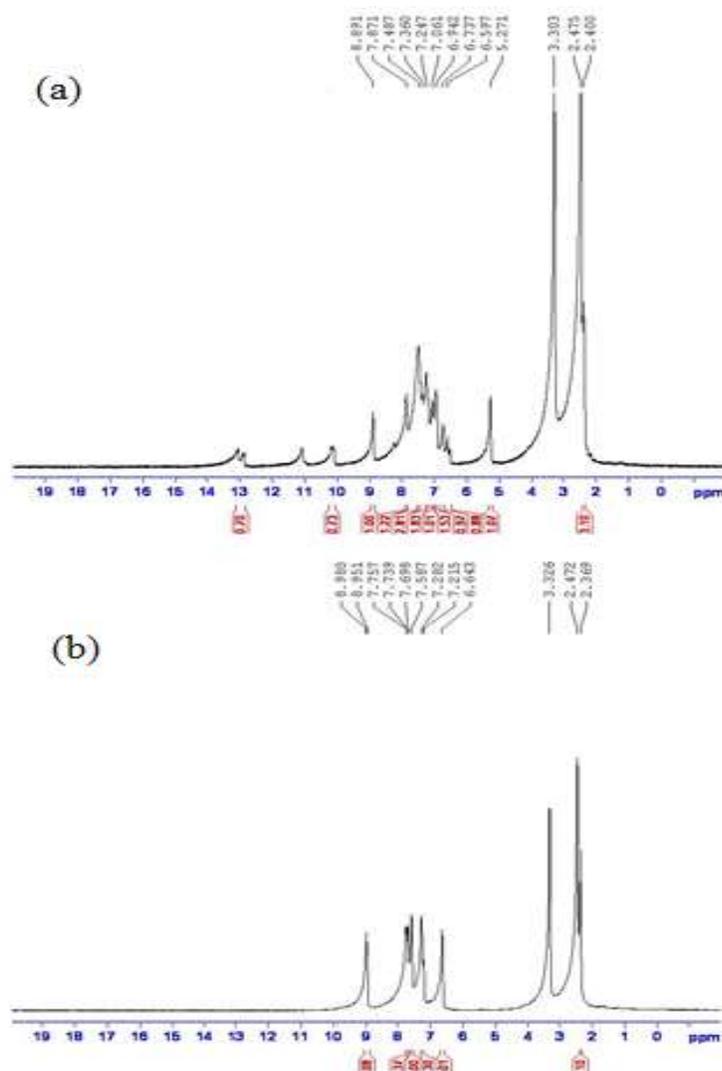


Figure 3. ¹H-NMR spectrum of the H₂L ligand (a), and Zn (II) complex (b)

Electronic of zinc (II) Schiff base complex study

The electronic absorption spectra of H₂L ligand and zinc (II) Schiff base complex are shown in Figure 5. The electronic absorption spectrum of H₂L ligand (4×10⁻⁵ M, EtOH), (Figure 2a), which consists of the bands at 300-500 nm is attributed to intraligand and π-π* transition localized on the benzene rings, whereas the band at 522 nm is due to the n-π* excitation of the lone pair on the imine nitrogen atom to the π* orbital on the C=N fragment. In Figure 2b the bands at 200-300 nm are attributed to intraligand π-π* transition of the benzene rings that shifted toward the ligand. The band in the region at about 303 nm assigned to ²B_{1g} ²E_g transition suggesting a square-planar geometry for zinc (II) Schiff base complex. A band at 410 nm can be assigned to spin-allowed metal-to-ligand charge transfer (MLCT) transition for zinc (II) complex [25-27, 28].

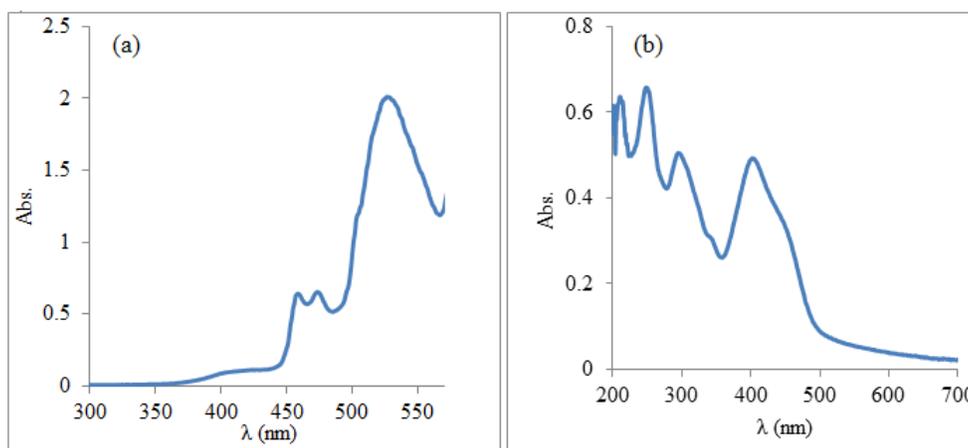


Figure 5. Electronic spectra of H₂L ligand (a) and nano-sized of Zn (II) Schiff base complex (b)

Fluorescence of Zn (II) Schiff base complex study

The fluorescence property of the nano-sized zinc (II) Schiff base complex was investigated at room temperature (298 K). The fluorescence spectra of the H₂L ligand and zinc (II) complex (2×10⁻⁵ M; EtOH) are shown in Figure 5. The emission bands are located at 472 and 514 nm for the H₂L ligand and zinc (II) complexes, respectively. The shift of emission band was due to complexation. The emission bands are assigned as intraligand fluorescence (ILCT charge transfer). These bands are due to energy transfer between the HOMO (π, bonding) and LUMO (π*, antibonding) of the ligand [29, 30].

Comparing the absorption and emission bands of zinc (II) complex in bulk scale and nano complex analog reveals that nano complex has more intensity and a shift due to the reduction particle size to nano scale [27-30].

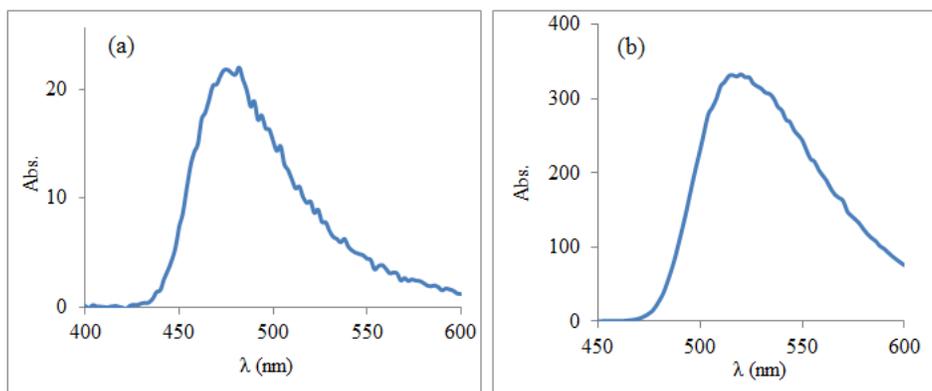


Figure 5. Fluorescent spectra of H₂L ligand (a) and Zn(II) Schiff base complex (b)

Morphology and particle size distribution of Zn (II) Schiff base complex study

The morphology and particle size distribution of Zn (II) Schiff base complex was investigated by FESEM images in different magnification (Figure 5a and b). The FESEM images of the Zn (II) complex clearly show that the morphology of the complex is rod-like shape with the particle size distribution of about 50-60 nm (Figure 6).

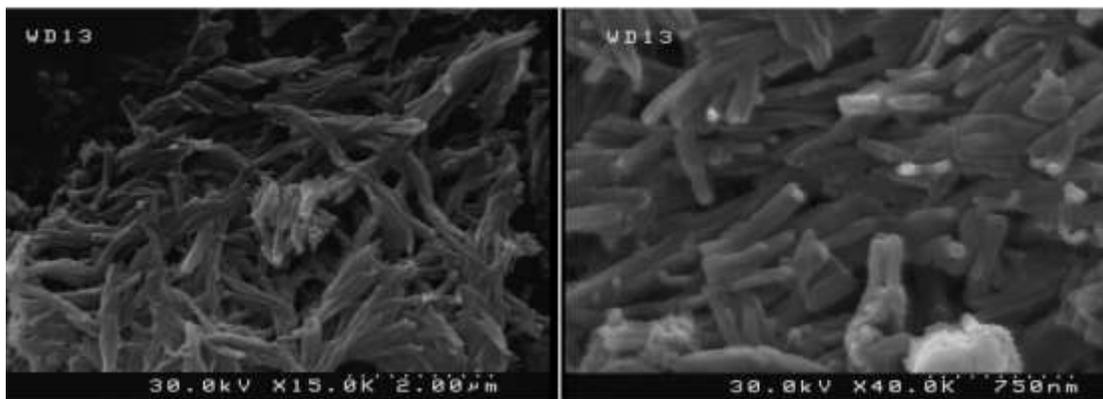


Figure 5a and b. FESEM images of nano-sized of Zn (II) Schiff base complex in different magnification

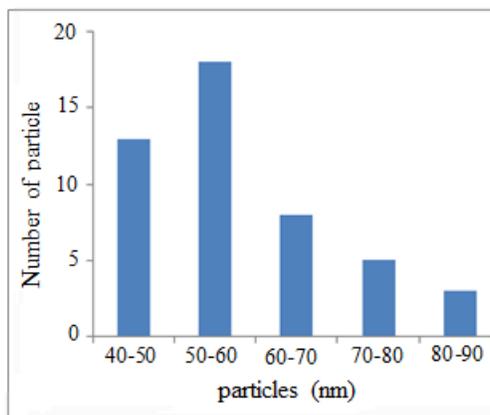


Figure 6. Particle size distribution of nano-sized of Zn(II) Schiff base complex

XRD pattern of ZnSe/ZnO study

Figure 7 shows the XRD pattern of the nano-sized of ZnSe/ZnO that was prepared by reflux condensation method. The XRD pattern reveals the diffraction peaks attributable to ZnSe with cubic phase at the main of $2\theta=27.25^\circ$ and 53.85° , which can be related to (1 1 1), and (3 1 1) crystal planes, respectively (JCPDS Card No. 01-0690). Besides, the XRD pattern has with accepted match with ZnO phase in hexagonal crystal phase (74-0534 JCPDS Card No.) For ZnO phase, the main diffraction peaks of $2\theta=31.34^\circ$, 34.44° , and 47.24° which can be related to (1 0 0), and (0 0 2), and (1 0 2) crystal planes, respectively. The broadening of the diffraction peaks in Figure 7 manifested that the particles were in nanometer scale. The average size of particles were calculated to be about 30 nm by applying full width at half maximum (FWHM) and the value of 2θ of characteristic peaks of the XRD pattern using the Debye-Scherrer equation [31].

$$D = k\lambda / \beta \cos \theta \quad (1)$$

Where D is the average size, K is a constant (ca. 0.9), λ 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.

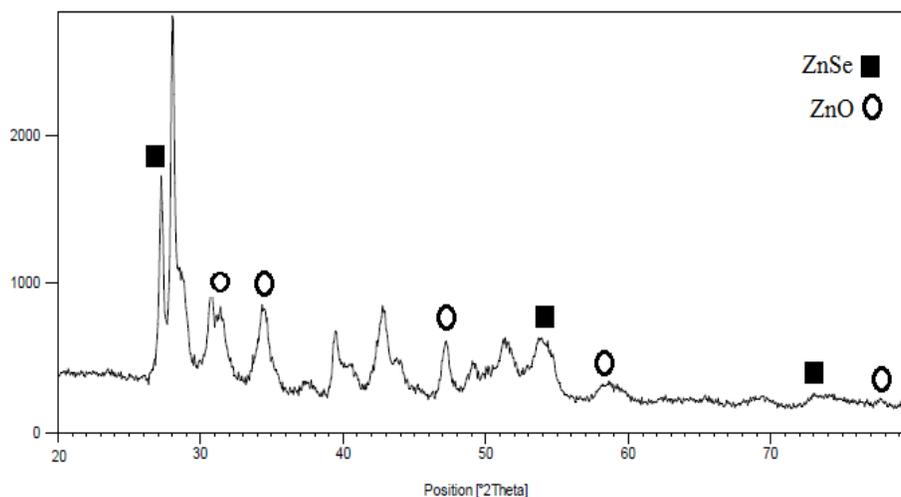


Figure 7. XRD pattern of the nano-sized of ZnSe/ZnO

Morphology and particle size distribution of ZnSe/ZnO study

The FESEM images of ZnSe/ZnO in different magnification were shown in Figure 8. The images show that the morphology of ZnSe/ZnO is semi-spherical shape with the particle size distribution of about 30-40 nm (Figure 9). Clearly, shape and morphology of ZnSe/ZnO are quite different from that of the zinc (II) Schiff base complex precursor.

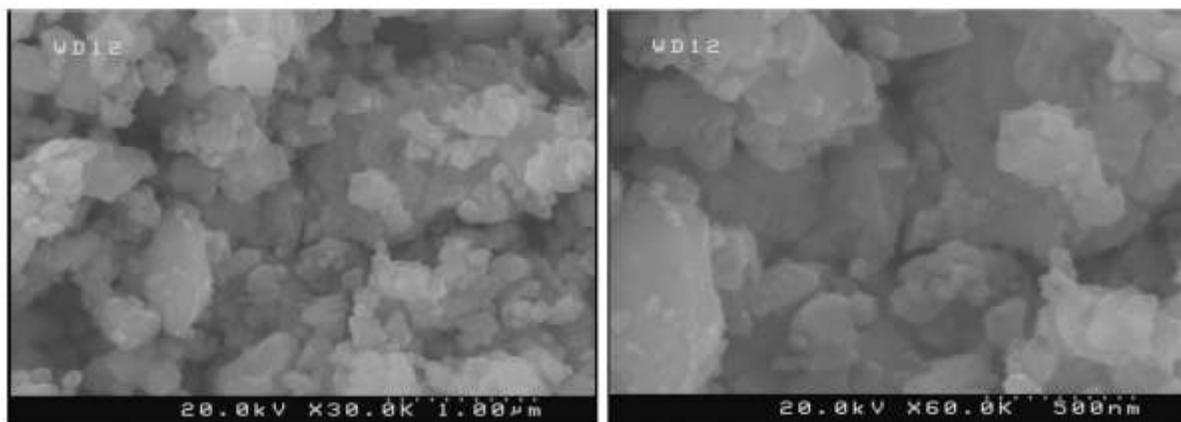


Figure 8. FESEM images of the nano-sized of ZnSe/ZnO

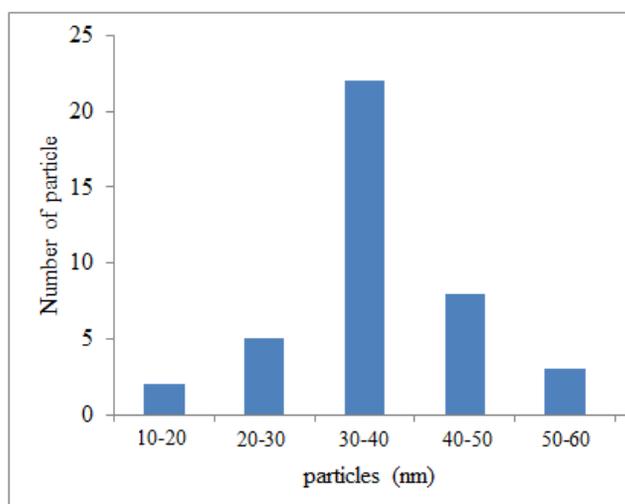


Figure 9. Particle size distribution of nano-sized of ZnSe/ZnO

Conclusion

A nano rod-like shape Zn (II) complex of N_2O_2 donor Schiff base has been successfully synthesized by ultrasonic method. The particle size distribution of the nano Zn (II) complex is 50-60 nm. Ultrasonic method is simple, fast, safe, low-cost, and suitable for industrial production of high purity. The electronic and fluorescence bands of nano Zn (II) complex shows a shift in comparison to the similar bulk samples in bulk scale, due to the reduction particle size to nano scale. This complex was used as a new precursor for preparing nano-sized ZnSe/ZnO (30 nm in average size) by reflux condensation method. The reflux condensation method is an appropriate method for synthesis of nano selenids from coordination compounds. We hope this method extends for preparing various nano materials in accordance to coordination compounds.

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How to cite this manuscript: Iran Sheikhshoaie*, Zeinab Tohidian. A Novel Facile Synthesis Route for Nano-sized Zn (II) Schiff base Complex and Nano-sized ZnSe/ZnO. *Chemical Methodologies* 3(1), 2019, 30-42. DOI: [10.22034/CHEMM.2018.66970](https://doi.org/10.22034/CHEMM.2018.66970).