

## Microwave-assisted Decomposition of two Simple Zinc(II) Schiff Base Complexes: A Facile and Fast Route to Synthesize ZnO Nanostructures

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### Abstract

ZnO nanorods and nanoparticles have been easily prepared via the decomposition of two simple Schiff base zinc (II) complexes, namely (N,N'-disalicylalethylenediamine)zinc(II) and (N,N'-disalicylphenylenediamine)zinc(II) under microwave irradiation. The decomposition products of the complexes were characterized by FT-IR, XRD, SEM, EDX and UV-visible spectroscopy. FT-IR, XRD and EDX results confirmed that as-prepared products are pure and single-phase ZnO. SEM images show that the product of each complex was made up of ZnO nanoparticles average diameter size of 50 nm and ZnO nanorods with diameter of 70–100 nm and length up to 3.5  $\mu\text{m}$ . ZnO nanostructures prepared by present method could be appropriate photocatalytic materials due to a red shift in their band gaps (2.80 and 2.95 eV) compared with the bulk sample (3.37 eV). This method is simple, fast, safe, low-cost and also it is suitable for large-scale preparation of high purity ZnO nanostructures for applied purposes.

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## 1. Introduction

One-dimensional transition metal oxides nanostructures are a large group of nanomaterials. They are now receiving much attention because of their promising and fascinating applications in optics, optoelectronics, catalysis, gas sensing, thermoelectricity, and piezoelectricity and

photovoltaic devices that differ from those of bulk materials [1-3]. Among various transition metal oxides, zinc oxide (ZnO) has attracted considerable interest in many areas of chemistry, physics and material science [4]. Bulk ZnO is an important n-type semiconductor with a wide direct band gap of 3.37 eV and high exciton energy of 60 meV at room

temperature which allows it to act as an efficient semiconducting and piezoelectric material [5]. Due to excellent chemical and thermal stability of ZnO semiconductor and its specific optoelectronic properties, a broad wide of applications, ranging from photonic crystals, photodetectors, photodiodes, light emitting diodes, varistors, solar cells, catalysts, display windows, field emission, to photocatalytic agents have been reported [6–26]. ZnO is also used in sensors and actuators due to its piezoelectric and pyroelectric properties [27,28]. At the nanometer scale, ZnO is expected to possess more interesting physical properties, and profound coupling effect compared to the respective bulk counterpart [29,30].

In recent years, the synthesis of one-dimensional ZnO nanostructures such as nanoparticles, nanorods, nanowires, nanoplates and nanotubes has acquired considerable interest due to their potential importance in nanodevice fabrication [31-34]. One-dimensional ZnO nanostructures have been successfully synthesized by various soft chemical techniques such as coprecipitation [35,36], sol–gel process [37], sol–gel combustion method [38], microwave assisted combustion method [39-41], thermal decomposition [42-46], hydrothermal/solvothermal method [47-52], sonochemical method [53-56], polymerization method [57], mechanochemical technique [58] and thermal oxidation [59,60]. However, most methods employed organic solvents or required rigorous reaction conditions, complicated procedures and specific apparatus.

Microwave-assisted synthesis is a novel method to produce various inorganic nanomaterials. The microwave heating process is fundamentally different from conventional heating processes. This method is an in situ mode of energy conversion, and heat is generated internally within the material, instead of originating from external sources. In the last two decades, numerous applications of microwave

irradiation to prepare nanostructured materials have been reported [61-63]. Compared to conventional methods, microwave-assisted synthesis is generally faster, cleaner, and more economical. Further, it gives products with smaller particle size, narrow size distribution and high purity.

In this paper, we report a novel method for the preparation of ZnO nanostructures by microwave irradiation. ZnO nanostructures were prepared via decomposition of two simple Schiff base complexes of Zn(II), namely (N,N'-disalicylalethylenediamine)zinc(II) (abbreviated as Zn(Salen)) and (N,N'-disalicylalphenylenediamine)zinc(II), (abbreviated as Zn(Salophen)) under microwave irradiation. The method is a fast, mild, energy-efficient and environmentally friendly route to produce ZnO nanostructures in only one step. The products have regular shape, small size, narrow size distribution and high purity.

## 2. Experimental

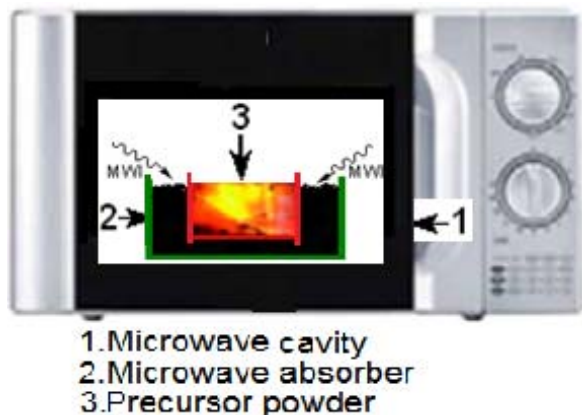
### 2.1. Materials

All materials were of commercial reagent grade and obtained from Merck chemical company. Precursor complexes, Zn(salen) and Zn(Salophen) were prepared according to the reported method [45].

### 2.2. Characterization techniques

XRD patterns were recorded on an X-pert MPD, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) to determine the phases present in decomposed samples. Infrared spectra were recorded on a Shimadzu system FT-IR 160 spectrophotometer using KBr pellets. The powder morphology was observed by a scanning electron microscope (SEM, Philips XL30) equipped with a link energy-dispersive X-ray (EDX) analyzer. Optical absorption spectra were recorded at room temperature on a Shimadzu 1650PC UV-vis spectrophotometer with the

wavelength range of 320-700 nm. The sample for UV-vis studies was well dispersed in distilled water to form a homogeneous suspension by sonicating for 30 min. In our experiments, a modified domestic microwave oven (LG-intellrowave, 900 W 2.45 GHz) working at a fixed power of 900 W was used. A schematic diagram of the system is shown in Fig. 1.



**Fig. 1.** A Schematic diagram of microwave irradiation system

### 2.3. Preparation of ZnO nanostructures

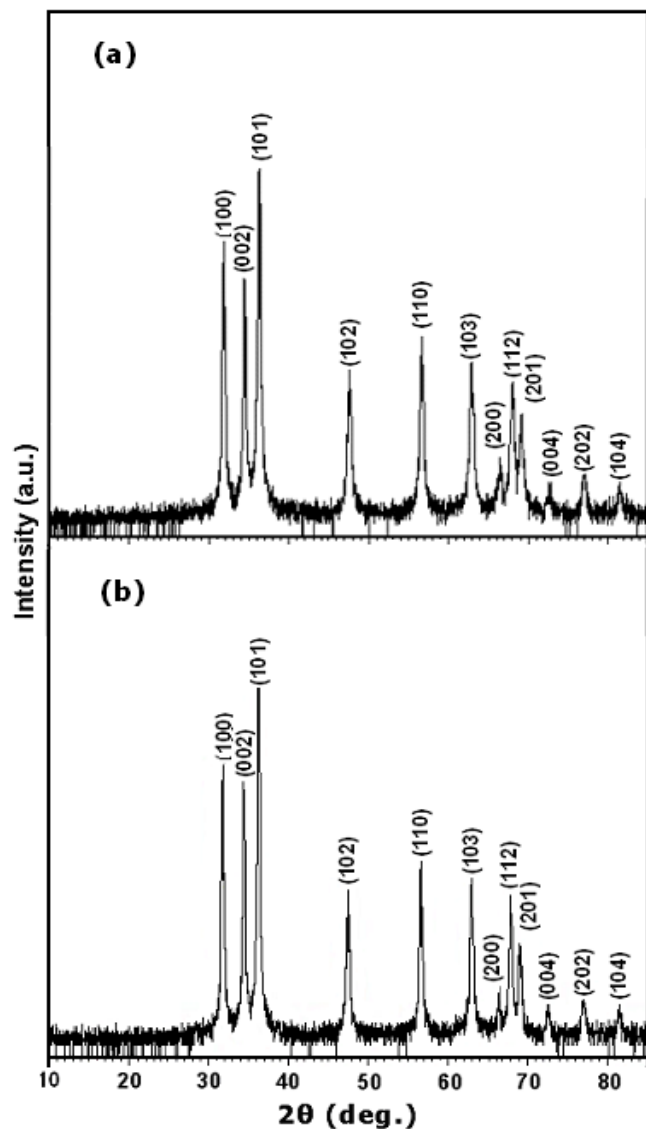
In order to prepare ZnO nanostructures via microwave-assisted decomposition of Zn(salen) and Zn(salophen) complexes, 2 g of each complex was taken in a small porcelain crucible and it was placed in the middle of a larger porcelain crucible filled with CuO powder as a secondary microwave absorber. This assembly was then irradiated at a 900W power and a frequency of 2.45 GHz. During microwave irradiation, CuO powder became fully red hot and its temperature was elevated quickly. At the same time, the decomposition of precursor complex occurs which completed after an irradiation time of 8 min. The decomposition product of each complex was cooled to room temperature and collected for the characterization.

### 3. Results and discussion

In this study, ZnO nanostructures have been prepared from decomposition of two simple Schiff base complexes: Zn(Salen) and Zn(Salophen), under microwave irradiation in the presence of CuO powder. It is known that in microwave assisted synthesis of materials at least one of reactants should be a good microwave absorber. When reactants are poor absorbers, hybrid method in the presence of a secondary absorber should be used. The Schiff base complexes used in this study do not absorb microwaves and remained unchanged without the assistance of secondary absorbers. Then, CuO powder was used as a secondary absorber. At the initial stage, the microwave radiation is mainly absorbed by CuO powder and its temperature increases very quickly. Subsequently, the precursor is decomposed by hot heating medium of CuO which resulted in a fine powder as the final product and various gases such as CO<sub>2</sub>, NO<sub>x</sub> and water vapor.

First, the crystal structure and phase compositions of the products of two complexes were investigated by XRD. Fig. 2 (a and b) shows the XRD patterns of decomposition products of the Zn(salen) and Zn(salophen) complex under microwave irradiation, respectively. XRD patterns of the decomposed samples reveal only the diffraction peaks attributable to the ZnO with hexagonal wurtzite phase at  $2\theta = 31.50, 34.40, 36.26, 47.65, 56.82, 62.90, 66.65, 68.25, 69.20, 72.90, 77.10$  and  $80.15^\circ$  which can be perfectly related to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202) and (104) crystal planes, respectively (JCPDS Card No. 5-0664). This finding confirms that precursor complexes were completely decomposed to the ZnO phase under microwave irradiation. Diffraction peaks related to the impurities were not observed in the patterns, confirming the high purity of the synthesized products. Furthermore, the diffraction peaks are

markedly broadened due to small size effect of particles.



**Fig. 2.** XRD patterns of the ZnO nanostructures prepared via microwave-assisted decomposition of: (a) Zn(salen) and (b) Zn(Salophen) complexes.

The average size of the ZnO particles was calculated by Debye–Scherrer equation [64]:  $D_{\text{XRD}} = 0.9\lambda/(\beta\cos\theta)$ , where  $D_{\text{XRD}}$  is the average crystalline size,  $\lambda$  is the wavelength of  $\text{CuK}\alpha$ ,  $\beta$  is the full width at half maximum (FWHM) of the diffraction peak and  $\theta$  is Bragg's angle. For two samples, the average size

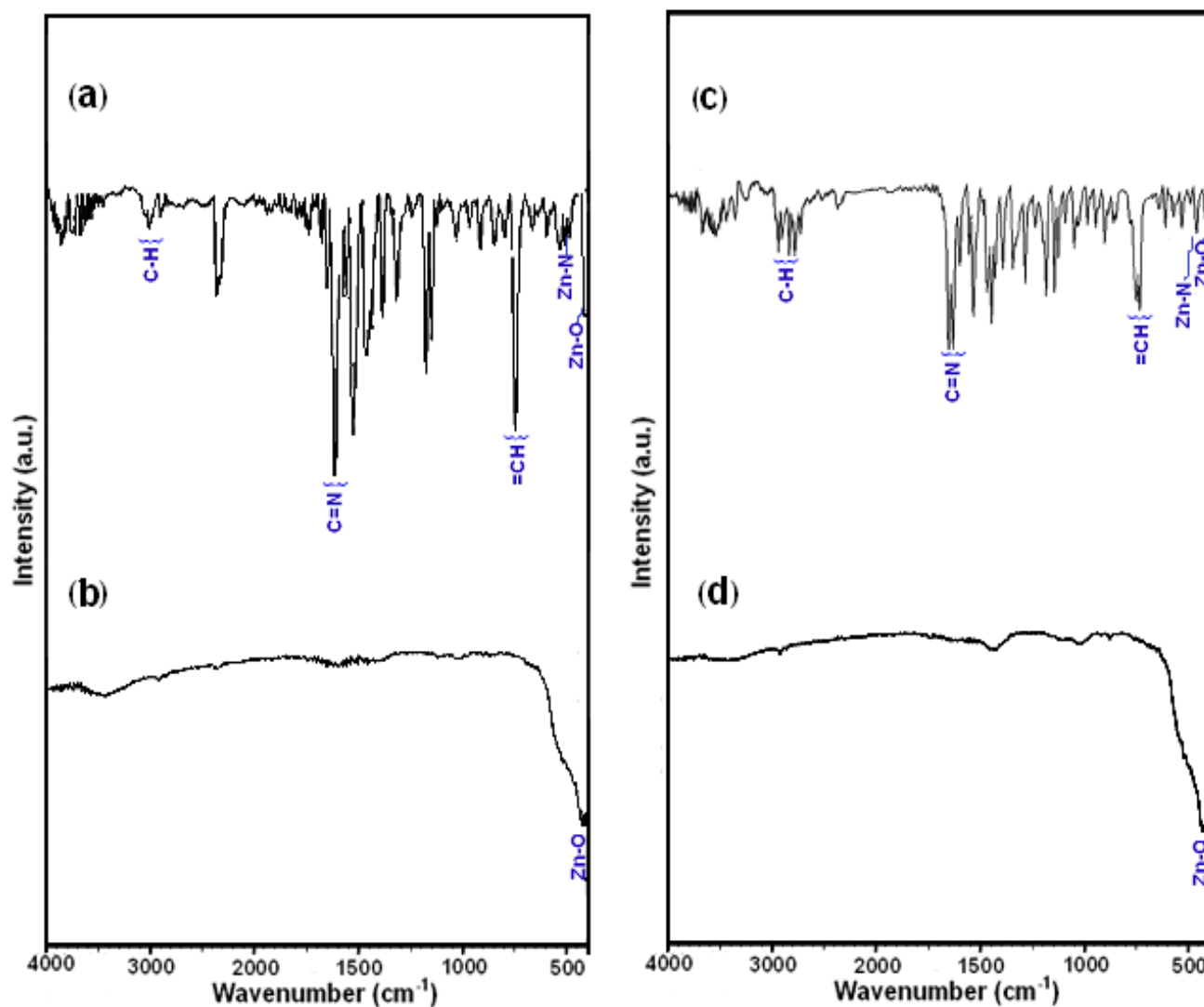
of nanoparticles calculated based on the most intense peak (101) at  $2\theta = 36.26^\circ$  is approximately 50 nm. This value is in accordance with SEM observations (discussed below).

FT-IR spectra of Zn(salen) and Zn(salophen) complexes and their decomposition products are shown in Fig. 3. Among many absorption bands appeared in the IR spectra of the complexes (Fig. 3a and c), three characteristic bands at about 2850, 1630 and  $750\text{ cm}^{-1}$  are attributed to stretching vibrations of the C–H, C=N and =C–H bonds of Schiff base ligands, respectively [65]. Also, the bands at about 490 and  $435\text{ cm}^{-1}$  can be assigned to the stretching vibrations of Zn–N and Zn–O bonds [65]. As it can be seen in Fig. 3b and d, all of these bands are eliminated after decomposition under microwave irradiation. The FT-IR spectra of products show only a relatively strong band around  $430\text{ cm}^{-1}$  which is related to the Zn–O stretching mode. This result confirms formation of the crystalline ZnO phase. Characteristic bands of the complexes are not detected, suggesting that they are decomposed completely into ZnO phase without impurities residue.

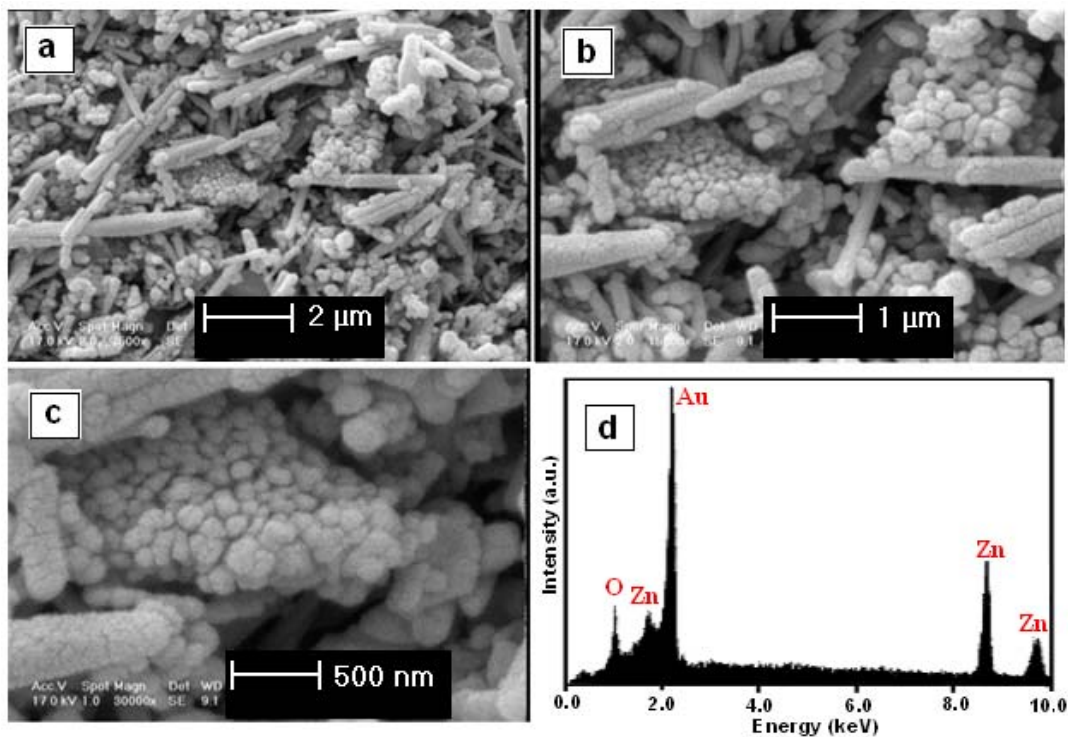
Morphology and particles size of products were investigated by SEM. Figs. 4 and 5 show SEM images of decomposition products of Zn(salen) and Zn(salophen) complexes with different magnification respectively. From the images, it is obvious that as-prepared ZnO products were made of nanoparticles and nanorods which loosely aggregated. It can be seen that ZnO nanorods are in the size with length up to  $3.5\text{ }\mu\text{m}$  and diameters of about 70–100 nm. The SEM images in high magnification exhibit that the nanorods comprised of nanoparticles self-assembled as one-dimensional rod-like shapes. The observed average particle size of the ZnO nanoparticles is approximately 50 nm which is consistent with XRD results (discussed above). To further check the composition and purity of synthesized products, EDX

studies were done on samples. As shown in Figs. 4d and 5d, EDX spectra of the products show only signals of Zn and O. The peak of Au was observed at 2.2 keV, due to the gold sputtering of instrument. In both cases, atomic percentages of Zn and O are about 50.45% and

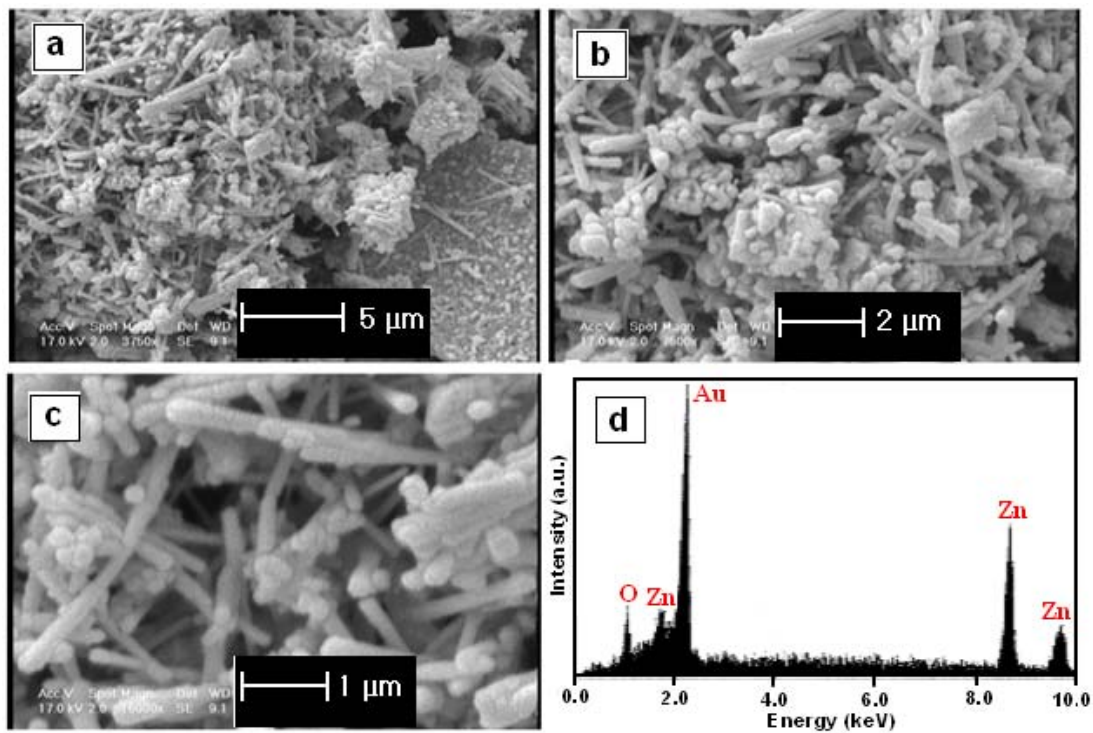
49.55%, respectively. The ratio of Zn to O is almost 1:1, further confirming that the pure ZnO phase was synthesized successfully.



**Fig. 3.** FT-IR spectra of the Zn(salen) and Zn(Salophen) complexes (a and c) and their decomposition products (b and d), respectively, under microwave irradiation.



**Fig. 4.** SEM micrographs of the ZnO nanostructures prepared from the Zn(salen) complex (a,b,c). (d) The EDX analysis of the product.

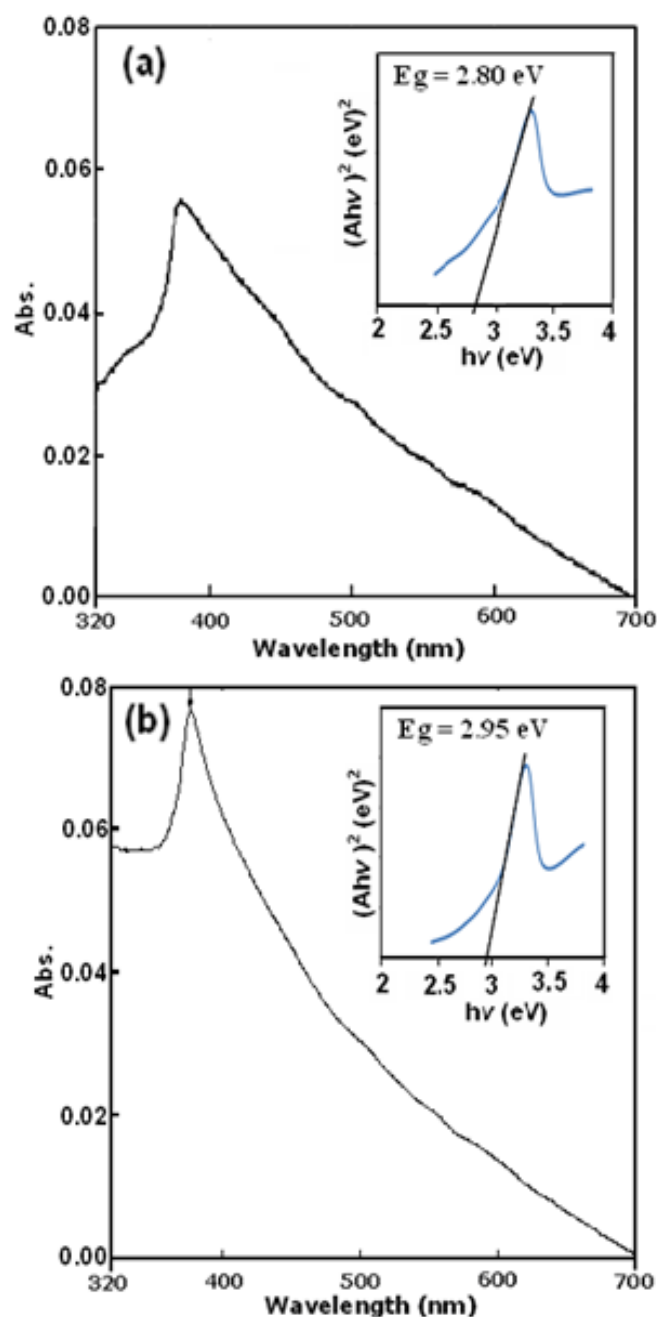


**Fig. 5.** SEM micrographs of the ZnO nanostructures prepared from the Zn(salophen) complex (a,b,c). (d) The EDX analysis of the product.

Optical properties of the as-prepared ZnO nanostructures were investigated by UV-Vis spectroscopy at room temperature, as shown in Fig. 6. In the UV-Vis spectrum of each product a relatively strong band centered at about 380 nm appeared which is characteristic of ZnO nanostructures. The appeared absorption bands are attributed to the electronic transition from valence band to conduction band in n-type ZnO semiconductor. The direct optical band gap ( $E_g$ ) of ZnO nanostructures can be calculated by  $(Ah\nu)^2 = B(h\nu - E_g)$  equation, where  $h\nu$  is photon energy,  $A$  is absorption coefficient,  $B$  is a constant relative to the material. The insets of Fig. 6(a and b) show the plot of  $(Ah\nu)^2$  versus  $h\nu$  for the ZnO samples. The band gap of a semiconductor material can be calculated by extrapolation on linear region of this curve. As shown in insets, the band gaps of ZnO nanostructures prepared from Zn(salen) and Zn(salophen) complexes were estimated to be about 2.80 and 2.95 eV, respectively, that show some red shift in comparison with bulk sample (3.37 eV). Thus, ZnO nanostructures prepared by this method could be promising photocatalytic materials.

#### 4. Conclusions

In summary, ZnO nanostructures were successfully synthesized through the decomposition of Zn(Salen) and Zn(Salophen) complexes under microwave irradiation within a short reaction time (8 min). By this method, rod-like and sphere-like ZnO nanostructures with weak agglomeration and narrow size distribution can be obtained. The optical absorption band gaps of as-prepared ZnO nanostructures (2.80 and 2.95 eV) show some red shift in comparison with bulk sample (3.37 eV). This method is simple, inexpensive, safe and suitable for preparation of high purity ZnO nanostructures for various applications.



**Fig. 6.** UV-Vis spectrum of the ZnO nanostructures prepared from: (a) Zn(salen), and (b) Zn(Salophen). The insets show  $(Ah\nu)^2$ - $h\nu$  curve of the ZnO products.

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