Synthesis of zinc oxide and zinc oxide/zinc sulfide nano composite via solution combustion route

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Abstract
In the present study, solution combustion synthesis of ZnO and ZnO/ZnS composite nanoparticles was synthesized using zinc nitrate and thioacetamide as starting materials, and Glycine as fuel. The influence of different parameters, such as oxidizer to fuel (O:F) ratio and calcination process on the structure, microstructure, photoluminescent and optical properties was investigated. X-ray diffraction (XRD) patterns showed that different phases of wurtzite structure of zinc oxide and zinc sulfide have been obtained using different O:F ratios of 1:1 and 2:3. Scanning electron microscopy (SEM) micrographs revealed that, depending on the O:F ratio, agglomerated nano particles were synthesized and formed porous microstrutures. Fourier transformed infrared (FTIR) analysis of samples synthesized using Glycine fuel showed carbon bonds of carbonaceous matters in addition to Zn-O and Zn-S bonds due to incomplete combustion. Photoluminescence emission spectra showed that the highest intensity was obtained from the samples synthesized with using O:F ratio of 1:1, which may be due to considerable lattice defects.

1. Introduction

Synthesis of semiconductor nanomaterials has been the subject of numerous studies in the last two decades because of their interesting surface, size and morphology characteristics. Among the ionic semiconductors, nanostructured ZnO and ZnS with wide their band gap values of 3.3 and 3.7 eV, are very attractive for many researchers. Several studies have been performed on the synthesis parameters and consequently, control the characteristics for different applications [1]. These nanoparticles have been employed in different fields including; photo-catalysts [2–5], solar cell [6–9], gas sensors [10], photoluminescent materials [11] and optoelectrical applications [12]. Several methods were represented for the synthesis of ZnO, ZnS and ZnO-ZnS composite nanoparticles such as; hydrothermal [1, 13–15], precipitation [16, 17], combustion method [18–23] and facile thermal treatment [24].

Although there are a lot of open literature reports on the synthesis of ZnS and ZnO nanoparticles, to the best of authors, knowledge, a few studies on the synthesis of ZnO-ZnS composite nanoparticles phases by solution combustion route was observed.

In our previous study [25] the synthesis of ZnO/ZnS composite powders via solution combustion method using Thiourea both as the combustion fuel and sulfur source was reported. Results showed that although ZnO/ZnS composite particles were obtained, they were highly agglomerated and also in the micron size scale.

The aim of present work was the synthesis of ZnO/ZnS composite nanoparticles by solution combustion method in the presence of Glycine fuel. Effect of oxidizer to fuel (O:F) ratios and calcination process on the characteristics of nano particles such as chemical composition, structure, microstructure and photoluminescence properties were investigated.

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2. Experimental

For the synthesis of ZnO particles, Glycine fuel ($C_2H_5NO_2$, MERCK) and Zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot6H_2O$, MERCK) with different molar ratios were dissolved in 20 ml aqueous solution containing nitric acid to adjust the pH value in the range of 3−4. The solution was stirred at 80−100 °C for 2 h until a yellow gel-like participate was obtained. Further heating at 100 °C caused to the combustion of the formed participate.

$ZnO/ZnS$ nanoparticles were also synthesized using zinc nitrate, Thioacetamide ($C_2H_5NS$, MERCK) as sulfur source and Glycine fuel. Similar to zinc oxide synthesis procedure, the acidic solution containing zinc nitrate and fuel was stirred at 80−100 °C for 2 h to obtain a yellow gel. Two−three minutes before beginning of combustion, Thioacetamide was added. There was a competition between solution combustion reactions for the formation of $ZnO$ and $ZnS$. In some cases, as synthesized powders were calcined (post heated) at 400−600 °C for 1 h in an electric furnace. Heating rate from room temperature to calcination temperature was 20 °C min$^{-1}$. 

![Figure 1. XRD patterns of ZnO samples synthesized using Glycine fuel and different O:F ratios.](image1)

![Figure 2. XRD patterns of ZnO/ZnS powders synthesized using Glycine fuel with O:F ratio of 1 and Glycine fuel before and after calcination at 400, 500 and 600 °C for 1 h.](image2)
Structural characterization was performed using x-ray diffraction method (Bruker, Advance D8). Mean crystallite size of powders was determined using the Scherrer equation ($d_{\text{Scherrer}} = 0.9 \lambda / \beta \cos \theta$). Microstructural investigations were performed using scanning electron microscope (SEM, KYKY EM3900). The mean particle size of the samples was determined using Image J 1.44p, the image processing software. Luminescence properties of the synthesized samples were studied by photoluminescence (PL) spectra (Perkin-Elmer LS55) with the exciting wavelength of 360 nm. Molecular studies were performed using a fourier transform infrared spectroscopy (FTIR, Bruker TENSOR II) which was equipped with platinum ATR accessory with the robust diamond crystal. One PerkinElmer UV–Vis spectrophotometer (Lambda 25) was used for obtaining UV-visible absorption spectra. Band gaps of nanoparticles were estimated by $E = \frac{h.c}{\lambda}$ equation, where $E$, $h$, $c$ and $\lambda$ are band gap, Plank constant, light velocity and wavelength, respectively.

3. Results and discussion

3.1. Structural analysis

Initially, ZnO nanoparticles synthesized with Glycine fuel and different O:F ratios were evaluated. Figure 1 shows XRD patterns of ZnO samples synthesized using different O:F ratios. As illustrated, ZnO (card no. 01-076-0704) is the dominant phase in all samples and no other phases can be detected in the XRD patterns. In
addition, there are no significant changes in the structure of synthesized powders. Broader peaks can be observed for ZnO samples obtained using O:F ratios of 2:3 and 1:2. Because of the stoichiometric ratio between oxidizer and fuel in O:F ratio of one, the highest crystallinity and the narrowest peaks of particles is seen. Increase in the fuel content (O:F ratios of 2:3 and 1:2) caused the lack of sufficient oxygen for complete reaction. Incomplete reaction resulted in lower combustion temperature and consequently, lower crystallinity of the particles [25, 26]. On the other hand, decrease of oxygen amount (O:F ratio of 2:1) led to inadequate fuel, incomplete the combustion reaction and consequently, remaining of unreacted zinc nitrate hydrate (card no.00-052-0627) from starting materials.

Figure 2 shows XRD patterns of ZnO/ZnS powders synthesized with Glycine fuel in stoichiometric ratio in the presence of thioacetamide before and after calcination at different temperatures for 1 h. As shown, Sphalerite ZnS (00-001-0792) and hexagonal structure ZnO phases were formed. It seems that thioacetamide addition (as sulfur source) weakened the combustion reaction and lowered heat liberating from the samples. On the other hand, energy of ignition could have been consumed through two combustion paths; preparation of ZnO via combustion process and formation of ZnS via decomposition of thioacetamide. So, small and broad peaks can be related to the nanoparticles or amorphous particles. After calcination at 400 and 500 °C, 3 and 5.5 nm crystallites were obtained in both ZnO and ZnS samples, because excess carbon burns at high calcination temperatures and the released heat led to more crystalline particles. Heating up to 600 °C, completion of oxidation, phase transformation of ZnS to ZnO, and self-diffusion Zn in Zn site of ZnO structure were happened [26, 27]. According to optimization of luminescence properties, the best calcination temperature was 400 °C at which ZnO/ZnS particles in nanometer range were obtained. XRD patterns of samples synthesized with O:F ratio of 2:3 were similar to that of samples synthesized with O:F ratio of 1.

3.2. Molecular studies
FTIR spectroscopy was performed, mainly to identification of the Zn−O and Zn−S bonds. Figure 3(a) show FTIR spectra of ZnO samples synthesized using Glycine fuel with different O:F ratios. The bands at in the range of 410–430 cm⁻¹ are related to stretching vibration of Zn−O bond and the peaks in the range of 500–550 cm⁻¹ are attributed stretching vibration of Zn−O [28]. Band at 1600 cm⁻¹ is related to the surface-adsorbed water [29, 30]. Moreover, bands at 3000 to 3440 cm⁻¹ are due to related to stretching O−H bonds [31, 32]. Calcination process considerably decreased these peaks intensities because of water evaporation.

Figure 4. SEM micrographs of ZnO particles synthesized with Glycine fuel and different O:F ratios of (a) 2:1, (b) 1:1, (c) 2:3, and (d) 1:2.
bonds. Also bands at 2110 and 2351 cm\(^{-1}\) are associated to absorbance of infrared spectrum by the air molecules [33]. Band at 1400 cm\(^{-1}\) is due to N–O bond from residual nitrate sources after combustion [34]. As mentioned earlier, decrease of oxygen amount (O:F ratio of 2:1) led to remaining of unreacted zinc nitrate hydrate from starting materials. So, bands of water and N–O bond are sharper than other samples.

Figure 3(b) show FTIR spectra of ZnO/ZnS composite powders synthesized using Glycine fuel with different O:F ratios. As shown, high intensity peaks at 436, 637 and 722 cm\(^{-1}\) are related to Zn–O bond. Bands corresponding to Zn–S bonds are located at about 600, 722 and 1118 cm\(^{-1}\) \[28, 35\]. Similar to ZnO particles, bands associated to water are also observed.

### 3.3. Microstructure studies

SEM micrographs of ZnO particles synthesized with Glycine fuel and different O:F ratios of 2:1, 1:1, 2:3, and 1:2 are shown in figures 4(a)–(d), respectively. As illustrated, fine particles were highly agglomerated due to combustion reaction. Moreover, clusters of these agglomerated particles formed a porous foam microstructure due to the exhaust of gases, such as N\(_2\), NO\(_2\), CO\(_2\), during combustion reaction \[36–40\]. Furthermore, the maximum porous microstructure was obtained for powders synthesized with O:F ratio of 1. Deviation from this O:F ratio led to incomplete reaction, less gas removal and consequently, lower porosity.

Combustion heat value of Glycine at 298 K is \(-975 \pm 8\) kJ mol\(^{-1}\) \[41\]. Such considerable heat released combustion reaction may cause to the growth of very fine particles, or more agglomeration.

Figures 5(a), (b) show SEM micrographs of ZnO/ZnS particles synthesized with Glycine fuel with O:F ratios of 1 and 2:3 after calcination at 400 °C for 1 h. As illustrated, the porous microstructure of both samples is consisted of agglomerated spherical nanoparticles.
3.4. Photoluminescence properties

Photoluminescence (PL) emission spectra of ZnO and ZnO/ZnS composite particles synthesized using Glycine fuel with different O:F ratios are shown in figures 6(a) and (b), respectively. Since the powders which synthesized with O:F ratio of 2:1, has considerable unreacted remaining zinc nitrate hydrate (see figure 1), PL spectrum of the sample was not presented. As shown, in figure 6(a), two peaks at 425 and 485 nm are associated to high crystalline zinc oxide and lattice defects (such as oxygen vacancy, interstitial oxygen, interstitial zinc, etc), respectively [42–44]. Moreover, more complete and stronger combustion reaction caused to demonstrate the highest intensities for stoichiometric sample. In the other words, the stronger combustion in the sample resulted in more defects than other O:F ratios and consequently, more PL intensities. Considering figure 6(b), the samples synthesized using Glycine fuel show three peaks. Here, the peak at 425 nm is due to the zinc oxide/zinc sulfide structure which has the most intensity for O:F ratio of 1, and the peaks at 485 and 530 nm (green wavelength region) are from crystal lattice defects.

Basically, there aren’t any peaks of transitions from VO in ZnO in the visible region, but in the combustion process, the high density of surface defects changes the visible peaks in blue–green to the highest emission region. Moreover, the transition between ZnS and ZnO and emission due to self-diffusion of Zn in ZnO structure can be took placed [26].

3.5. Band gap study

The band gap of ZnO and ZnO/ZnS composite particles were estimated based on absorbance versus wavelength curves (figures 7(a) and (b)) as 3.38 (λ = 367 nm) and 3.35 eV (λ = 370), respectively. The former was calculated based on maximum intensity for ZnO, and the the change of slope for ZnO/ZnS in adsorption curve.

These values are near band gap of ZnO and ZnS powders were reported by many researchers [45–49]. Since band gap can be affected by many complicated parameters including; phase concentration of ZnS and ZnO, crystallite and particle mean size, morphology and so on, considerable variation between samples were not observed [50].
4. Conclusions

In the present study, ZnO and ZnO/ZnS composite nano particles were synthesized by solution combustion method using zinc nitrate and Glycine as starting materials. XRD results generally showed that stoichiometric ratio resulted in ZnO nano particles with the highest photoluminescent intensity. Moreover, thioacetamide addition led to formation of ZnO and ZnS phases, simultaneously. Calcination process caused to grain growth, more crystallinity of nano powders, and oxidation of ZnS to ZnO. SEM micrographs showed that all nanoparticles were highly agglomerated and porous clusters. Deviation from that caused to incomplete combustion and consequently, nano particles with less spongy-like and weaker photoluminescent intensities were obtained.

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