Journal of Solar Energy Research (JSER)

Journal homepage: jser.ut.ac.ir

Green synthesis and Photo-catalyst study of ZnS-(Ni and Li) doped nanoparticles under solar irradiation

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Received: 2021-02-05
Accepted: 2021-04-05

Abstract

It is very useful to use the solar irradiation for photocatalytic property, but need to reduce the band gap by doping the ions. In this paper ZnS (zinc sulphide) nanoparticles has been synthesized via co-precipitation and hydrothermal method. The co-precipitation and hydrothermal are simple, economical methods and they were used for a green surfactant assisted method for fabrication of ZnS and ZnS– (Ni and Li) doped nanoparticles. Glucose, sucrose or fructose were applied separately as green surfactants and capping agents. The Ni and Li ions were doped in ZnS nanocrystals for improvement of band gaps. The crystalline structure of zinc sulphide nanoparticles was investigated by X-ray diffraction (XRD) spectra and crystallite size of particles were calculated by debye-scherrer equation. The shape and morphology of ZnS particles was studied via scanning electron microscope (SEM). The Fourier-transform infrared spectroscopy (FTIR) was applied for the absorption peak of Zn-S bonding atoms. The photoluminescence (PL) measurement of the ZnS nanopowder was investigated at room temperature with an excitation wavelength around 360 nm. The photo-catalyst properties of ZnS nanoparticles were studied via ultraviolet – visible spectra (UV – Vis) of four different azo dyes acids under solar irradiation in times less than 120 min.

Keywords: Semiconductor; Azo dyes; Photoluminescence; UV irradiation; Green surfactant

Introduction

The ZnS is a II-VI type semiconductor. The ZnS have many applications in solar cells, optoelectronic devices, optical coatings and light emitting diodes [1-3]. ZnS have a broad and direct band gap energy about 3.6 eV at room temperature [4]. The several differnt techniques have been used to synthesis ZnS nanoparticles like co-precipitation, sol-gel, pulsed laser deposition and hydrothermal methods [5-7].

ZnS nanoparticles with size smaller than the Bohr excitonic radius exhibit blue shift in the UV-Vis sepectra and a high photoluminescence property [8]. The band gap of ZnS nanoparticles have increased with decreasing of its size from bulk particles. Quantum confinement effect change the band structure of the materials [9,10]. When the

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particle size decrease below the excitonic Bohr radius, the band gap energy is widened. Also the surface atoms play a more important role in the nanoparticles, because to their large surface-to-volume ratio with the decrease nanoparticle diameter.

The ZnS semiconductor nanoparticles have a high photocatalytic ability under ultraviolet visible light solar radiation [11,12].

The ZnS nanoparticles with Ni and Li doping were prepared.

In this work, ZnS and ZnS-(Ni and Li) doped nanostructures prepared by co-precipitation and hydrothermal method. The samples investigated the crystal structure, size and morphology of nanoparticles, photoluminescence, optical and photocatalytic properties of ZnS nanoparticles.

The novelty of this research is that investigated simultaneously the effect of doping of lithium and nickel ions on zinc sulphide nanoparticles synthesized by green method has been.

2. Materials and Methods

2.1. Materials and methods

Zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), thiourea ($CH_4N_2S$), thioglycolic acid ($C_2H_4O_2S$), sodium sulfate ($Na_2SO_4$), sodium hydroxid (NaOH), nickel(II) sulfate hexahydrate ($NiSO_4.6H_2O$), lithium nitrate ($LiNO_3$) and distilled water were purchased from Merck Co. glucose, sucrose or fructose were purchased from Sigma-Aldrich company.

X-ray diffraction pattern was prepared via Philips diffractometer (CuKα λ=1.54Å). SEM images were taken using a LEO Model 1455VP instrument. FTIR spectrum was recorded by Galaxy series FTIR 5000 spectrophotometer. UV-Vis spectra were taken using a Scinco SUV-2120 spectrophototometer.

2.2. Synthesis of ZnS nanoparticles

0.01 mol of zinc acetate and 0.01 mol of sulfur source (thiourea, thioglycolic acid or sodium sulfate) were dissolved in 100 ml of distilled water. 0.2 g of glucose, sucrose or fructose was applied separately as green capping agents. 10 mL sodium hydroxide (1M) was added as precipitating agents. The obtained solution was heated 80°C until forming the white powder or placed in a autoclave reactor for 3 h at 180 °C.

2.3. Synthesis of ZnS-metal doped nanoparticles

1 g of zinc acetate and 0.02 g of metal ions Ni^{2+}, Cd^{2+} and Li^{+} as a doping agent were added to 100 mL of water. After that 1 g of thiourea was added to the solution. Then 10 mL NaOH (1M) added to the solution. The final solution was heated 80°C. The result powder was washed by distilled water.

3. Results & Discussion

The XRD pattern of synthesized ZnS nanoparticles is indicated in figure 1. This pattern indicated the zinc blende phase (JCPDS No.:77-2100) with (111), (002), (022) and (113) peaks. The average size of crystallite size calculated by Debye-Scherrer formula, $D=0.9K/\beta Cos\theta$ [13,14] that, D is average crystallite size, λ is X-ray wavelength, β is peak width at half maximum in radian and θ is diffraction angle. The average crystals size of ZnS nanoparticles was computed 40 nm.

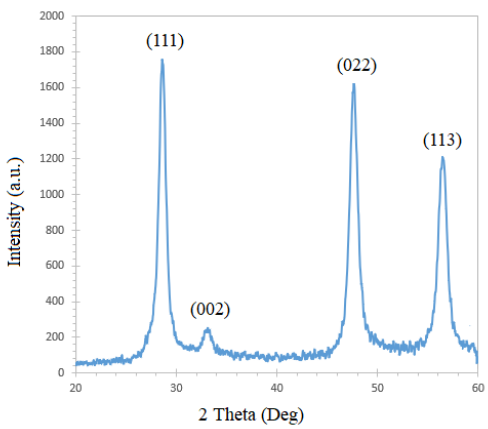

Figure 1. XRD pattern of ZnS nanoparticles.

Figure 2 indicates SEM image of produced ZnS nanoparticles fabricated via zinc acetate and thiourea

made by hydrothermal method. The ZnS nanostructures have flower-like shape.

The SEM image of ZnS nanoparticles synthesized by sodium sulfate using co-precipitation method is illustrated in figure 3. The particles have been agglomerated and average diameter size of these nanoparticles is about 45 nm. These nanoparticles have been synthesized without using any capping agents.

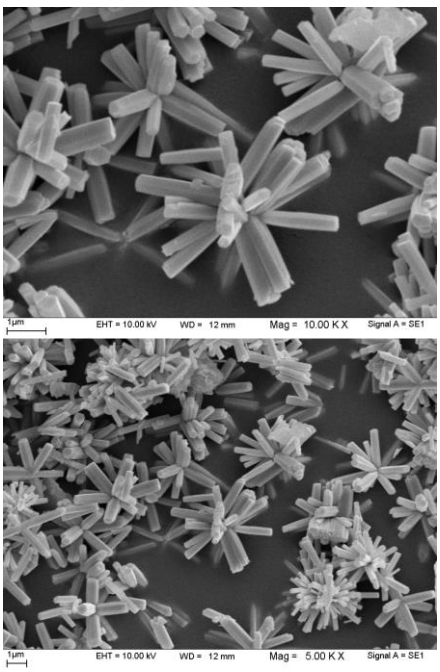

Figure 2. SEM images of ZnS nanoparticles synthesis by thiourea and hydrothermal method.

Figure 5 shows SEM image of fabricated ZnS nanoparticles using thioglycolic acid by co-precipitation method. The ZnS nanostructures have Cabbage -like shape.

The morphology ZnS nanostructures synthesis by thiourea using co-precipitation method represent in figure 4. SEM image of nanoparticles of these nanoparticles have a plane shape morphology. The thickness of planes is less than 20 nm.

SEM images of ZnS-Li doped nanoparticles synthesized by thiourea are shown figure 6. Outcomes show plane shape nanostructures like ZnS synthesis without Li but in less than particle size.

The ZnS-Ni doped nanostructures fabricated by co-precipitation method are shown in figure 7. The avrage size of Ni doped particles isabout 40 nm.

The FTIR spectrum of ZnS nanoparticles is illustrated in figure 8. The peak at 474 cm^{-1} is related to Zn–S absorption bond. The peak of 3398 cm^{-1} is for O-H peak of H_2O. The other peaks correspond to the thiourea impurities in the nanomaterials.

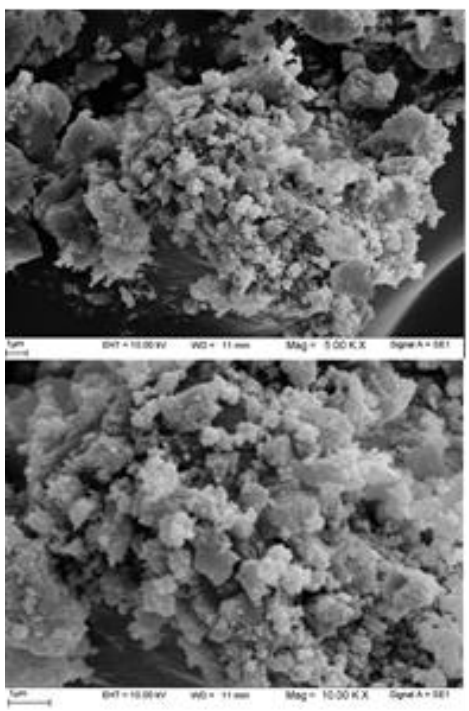

Figure 3. SEM images of ZnS nanoparticles synthesis by sodium sulfate using co-precipitation method.

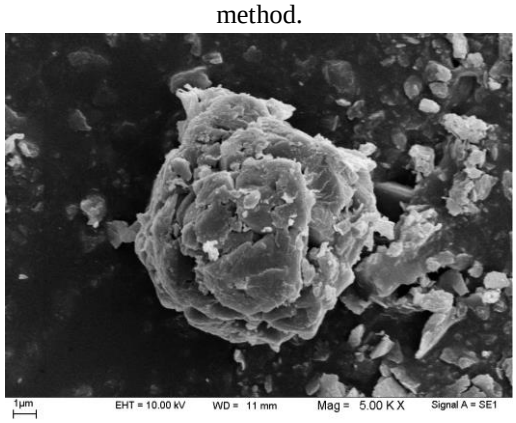

Figure 4. SEM image of ZnS nanoparticles synthesis by thioglycolic acid using co-precipitation method.

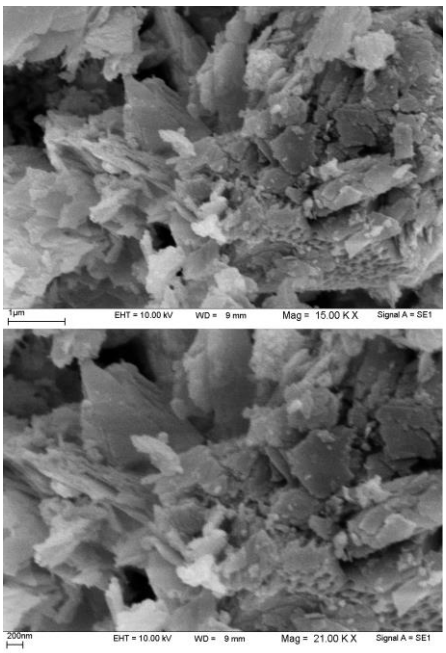

Figure 5. SEM images of ZnS nanoparticles synthesis by thiourea using co-precipitation method.

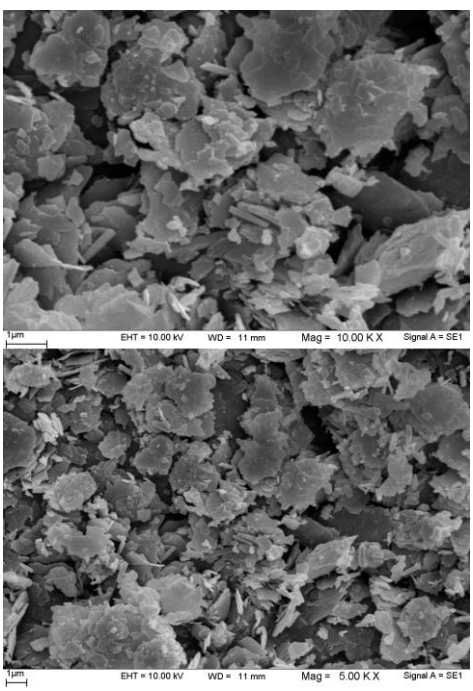

Figure 6. SEM images of ZnS- Li doped nanoparticles.

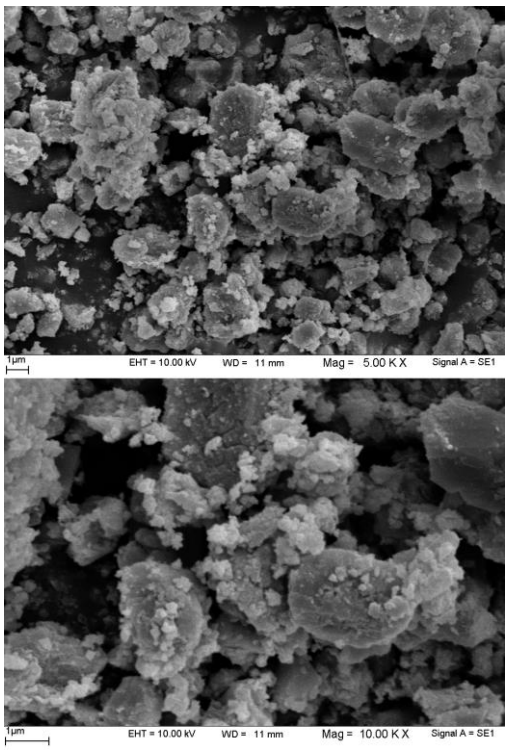

Figure 7. SEM images of ZnS- Ni doped nanoparticles.

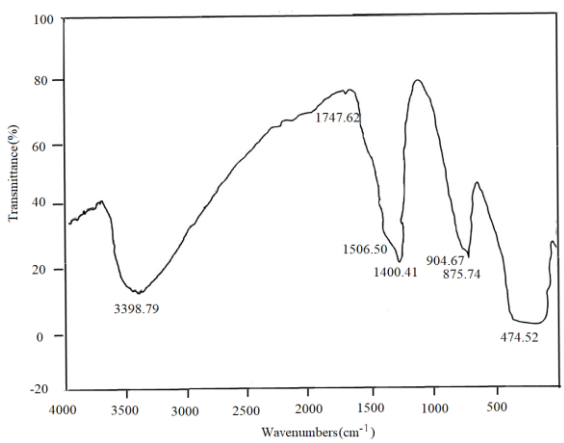

Figure 8. FTIR spectra of ZnS nanoparticles co-precipitation method.

The EDX spectra of ZnS nanoparticles synthesis by co-precipitation method shown in figure 9. The peaks of Zn Lα, Zn Kα ans S Kα indicated in this figure. The EDX of ZnS-Ni doped nanoparticles illustrated in figure 10 and the Ni Lα, Ni Kα and Ni Kβ are observed in addition to Zn Lα, Zn Kα ans S

Kα peaks. The ZnS-Li doped nanostructures shown in figure 11. As it turns out, the Li Kα peak is seen next to the Zn Lα, Zn Kα ans S Kα peaks.

The room temperature PL specta of ZnS nanoparticles was indicated in figure 12. The narrow gaussian curve fitting was applied the strong PL properties.

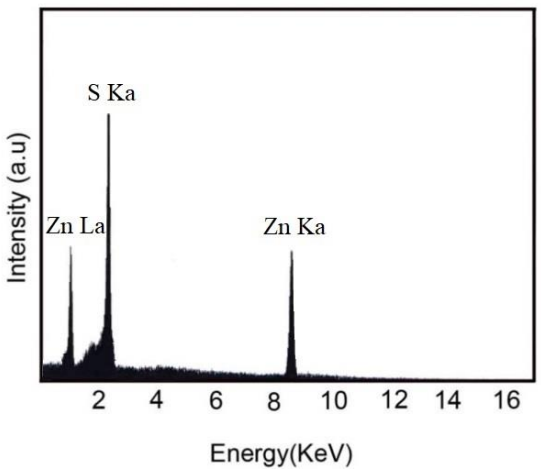

Figure 9. EDX spectra of ZnS nanoparticles by co-precipitation method.

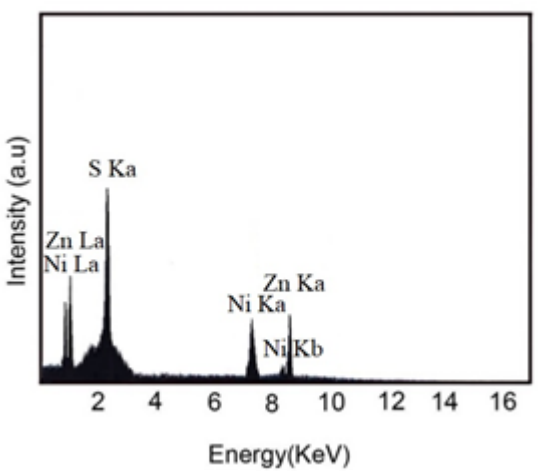

Figure 10. EDX spectra of ZnS- Ni doped nanoparticles by co-precipitation method.

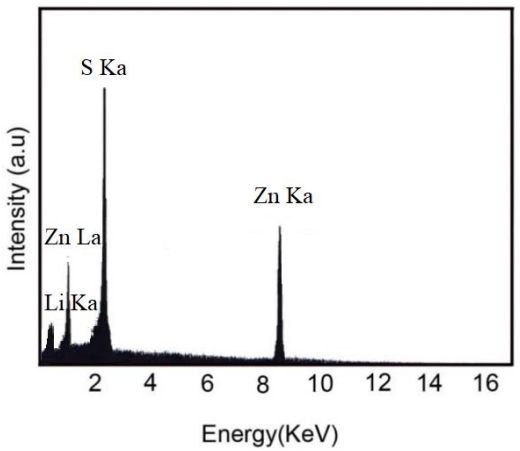

Figure 11. EDX spectra of ZnS- Li doped nanoparticles with co-precipitation method.

The room temperature photoluminescence specta of ZnS-Ni doped nanoparticles is shown in figure 13. The extra peaks compared to ZnS diagram because Ni doped observe in PL curve.

PL curve of ZnS-Li doped nanoparticles has been shown in figures 14. The PL peaks related to Li can be seen in the image.

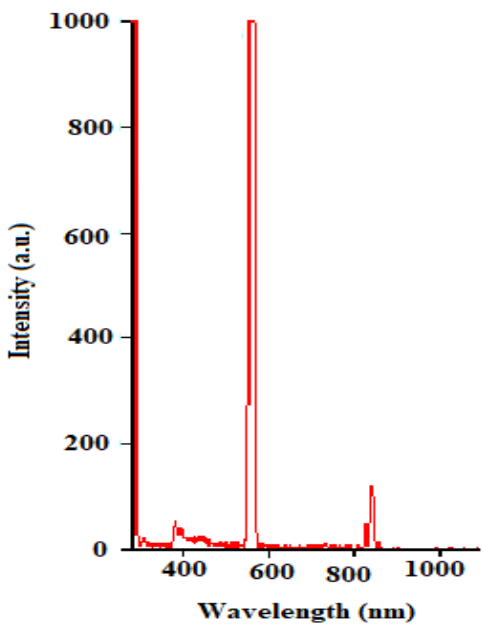

Figure 12. PL spectra of ZnS nanoparticles by co-precipitation method.

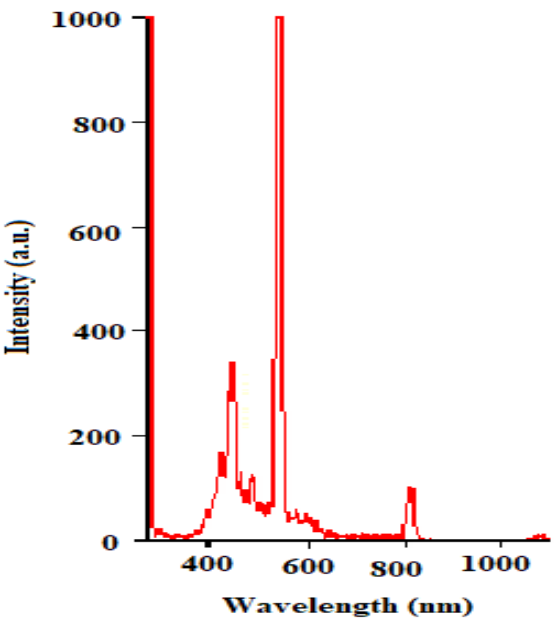

Figure 13. PL spectra of ZnS- Ni doped nanoparticles by co-precipitation method.

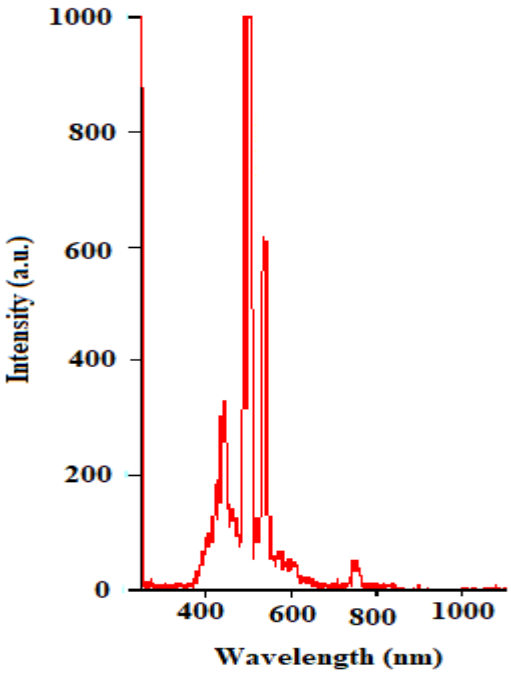

Figure 14. PL spectra of ZnS- Li doped nanoparticles with co-precipitation method.

Photocatalyst activity was examined by photo-degradation of four different azo dyes (as a blank of toxic dyes) under ultra violet irradition (Figure 15). After around 120 min all three aromatic dyes were degraded under UV and solar irradiations in the presence of nanoparticles in solvent of water and pH around 2.In this work the photo-degradation of different azo dyes under solar irradiation down about 120 min that is a beter results than other works [1,4,5].

Figure 15. Photo-degradation of toxic azo dyes under UV irradiation with the aid of nanoparticles.

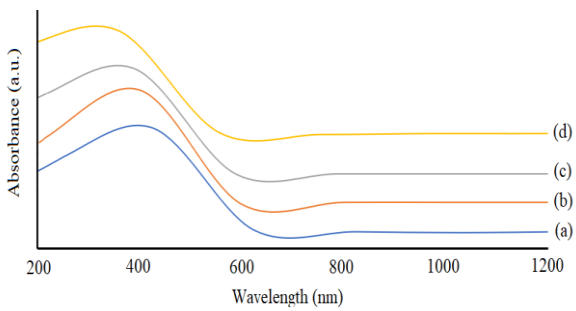

Figure 16. UV-Vis spectra of a) ZnS- Ni doped nanoparticles, b) ZnS- Li doped nanoparticles, c) ZnS nanoparticles synthesis by thiourea and hydrothermal method and d) ZnS nanoparticles synthesis by sodium sulfate using co-precipitation method.

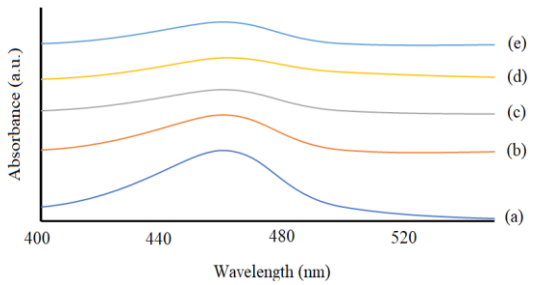

Figure 17. UV-Vis Photo-degradation spectra of methyl orange a) with out nanoparticles, b) with ZnS nanoparticles synthesis by thiourea and hydrothermal method, c) with ZnS nanoparticles synthesis by sodium sulfate using co-precipitation method, d) with ZnS- Li doped nanoparticles and e) with ZnS- Ni doped nanoparticles.

The UV-Vis spectra of ZnS- Ni doped nanoparticles, ZnS- Li doped nanoparticles, ZnS nanoparticles synthesis by thiourea and hydrothermal method and ZnS nanoparticles synthesis by sodium sulfate using co-precipitation method. shown in figure 16 (a-d) respectively. The optical energy band gap of nanostructures has been calculated using the formula $E_g=h\nu_g$ that h is plank 's constant, ν_g is absorption edge frequency and E_g is energy band gap. The balk ZnS have a band gap about 3.65 eV, because quantum confined nanostructures have a blue shift and increased band gap with decreasing particles size. ZnS nanoparticles synthesis by thiourea and hydrothermal method and ZnS nanoparticles synthesis by sodium sulfate using co-precipitation method have a band gaps about 3.94 and 4.21 eV respectively. Dop ion in semiconductors make som virtual levels and decrease the band gap. The band gap for ZnS- Ni doped nanoparticles, ZnS-Li doped nanoparticles, is abot 3.31 and 3.54 eV respectatively.

UV-Vis Photo-degradation spectra of methyl orange with out nanoparticles, with ZnS nanoparticles synthesis by thiourea and hydrothermal method, with ZnS nanoparticles synthesis by sodium sulfate using co-precipitation method, with ZnS- Li doped nanoparticles and with ZnS- Ni doped nanoparticles indicated in figure 17 respectatively. The absorption peak of methyl orange is about 460 nm. The nanoparticles with smaler than size it has a more degradation effect due to the higher surface-to-volume ratio. Also doping ion in nanoparticles because decrease the band gap and using more rang of solar irradiation have more degradation effect.

4. Conclusions

The ZnS and ZnS-(Ni and Li) doped nanoparticles was fabricated via co-precipitation and hydrothermal method. The XRD pattern illustrate the zinc blende phase for ZnS nanoparticles. The hydrothermal method synthesis a flower like shape nanoparticles. The co-precipitation method makes the plane and cabbage-like shape particles. The FTIR spectra show Zn-S peaks and confirm purity. PL spectra indicated peaks of ZnS and Ni and Li doped in particles. Photocatalyst property was examined by photo-degradation of four different azo dyes (as a blank of toxic dyes) under solar and ultra violet irradition.

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