Vázquez, A.; Aguilar-Garib, J.; López, I.; Cavazos, O.; Gómez, I.
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Revista Mexicana de Física, vol. 55, núm. 1, 2009, pp. 57-60
Sociedad Mexicana de Física A.C.
Distrito Federal, México

Available in: http://www.redalyc.org/articulo.oa?id=57030347013
Preparation of ZnS nanoparticles using microwave assisted synthesis: effects of the irradiation power and the precursors

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Recibido el 14 de agosto de 2008; aceptado el 8 de diciembre de 2008

Results of the synthesis of ZnS nanoparticles (NPs) in aqueous dispersion from ZnSO$_4$ and Zn(CH$_3$COO)$_2$, heated by means of microwaves are presented in this paper. A 1650 W oven operating at 60 and 100% of the nominal power in periods of 60 seconds was employed. The obtained dispersions where analyzed by UV-vis, X-rays diffraction, photoluminescence and transmission electron microscopy. At 100% of applied power the obtained ZnS NPs average size is 7 nm. It was estimated that concentration of NPs is affected by the applied power during synthesis, while electromagnetic properties are affected by the employed precursors.

Keywords: Nanoparticles; ZnS; microwaves; synthesis.

En este trabajo se presentan los resultados de la síntesis de nanopartículas (NPs) de ZnS en dispersión acuosa a partir de ZnSO$_4$ y Zn(CH$_3$COO)$_2$, mediante un calentamiento vía microondas. Se utilizó un horno de 1650 W operando entre al 60 y 100% de la potencia nominal en periodos de 60 segundos. Las dispersiones obtenidas fueron analizadas mediante espectrometría UV-vis, difracción de rayos-X, fotoluminiscencia y microscopía electrónica de transmisión. A 100% de potencia, las NPs de ZnS obtenidas tienen un tamaño promedio de 7 nm. Se encontró que la concentración de NPs depende de la potencia aplicada durante la síntesis, mientras que las propiedades electromagnéticas de las partículas se ven afectadas por los precursores utilizados para la misma.

Descriptores: Nanopartículas; ZnS; microondas; síntesis.

PACS: 61.46+w; 81.16.Be; 83.80 Hj

1. Introduction

Synthesis of materials at nanometrical scale has become an important research line in the last years due to the strong dependency of the size of the material particles over their properties: optical, mechanical and electrical. This knowledge has been employed in the development of new technologies in different areas such as the medicine [1], energy [2], environmental engineering [3] and biology [4].

Semiconductors deserve especial attention in a new world of functional materials and numerous research work are devoted to them; NPs of CdS, CdSe, CdTe, ZnS and ZnSe due to their potential application in photocatalytic processes [5] and solar cells [6], among others [7,8].

ZnS is one of the most applied semiconductors in optical devices due to its high refraction index and high transmission within the visible range [9].

There are several reported routes for the synthesis of semiconductors NPs, being the most common the thermal evaporation [10,11], solvothermal [5,12] and microwaves [13,14]. Thermal evaporation process is considered expensive because requires high temperature and inert gas systems or vacuum. Reaction following a solvothermal technique take long times, in the orders of several hours, while microwave irradiation technique is a promising way, which is quicker and has shown narrow size dispersion of the particles, however, despite the narrowness dispersion, its control is not as accurate in size and morphology as in the previous techniques [13,14]. This late technique was chosen in this work due to its simplicity and potentiality for being adapted to industrial synthesis of NPs, looking to identify useful relationships for having greater size control, as suggested by Tu [15].

Therefore, the objective of this work is to synthesize NPs of ZnS in aqueous dispersion using microwaves and different precursors for evaluating the effect of power.

2. Experimental procedures

A solution 30 mM of ZnSO$_4$, and a solution of thioacetamide, where stoichiometrically combined, and latter the formed solution was diluted with distilled water, adding sodium citrate for obtaining a concentration of 2 mM, while pH was adjusted to 8 with a saturated solution of KOH. The obtained solution was heated in a 2.45 GHz microwave oven...
(LG-INTELOWAVE) operating at 60% (990 W) and 100% (1650 W) power output during 60 seconds. The same procedure was followed employing a solution of Zn(CH$_3$COO)$_2$ 30 mM as cation precursor.

The obtained dispersions were characterized by means of UV–visible spectroscopy (Perkin Elmer Lambda 12), photoluminescence (Perkin Elmer Ls 55), FT-IR (Perkin Elmer Paragon 1000), X-rays diffraction (Siemens D5000, $\lambda$=1.5418 Å) and Transmission Electron Microscopy (Jeol 2010).

3. Results and discussion

The UV-vis absorption spectra for the dispersions obtained under the different conditions are shown in Fig. 1. It can be appreciated that using 100% of the power results in a greater absorption for the case of the particles synthesized as of ZnSO$_4$, however, in the case of Zn(CH$_3$COO)$_2$, the opposite effect is observed. Different reports [16,17] show that the spectrum is indeed the addition of several Gaussians curves that represent the different electronic transitions, and such transitions are more evident in the spectrum as the particle size is smaller. Moreover, the beginning of the absorption is related mainly to the $E_g$ value, which is related to the particle size, while the absorption height is related mostly to the concentration until the absorption grows exponentially.

Supported by those reports it is possible to affirm that synthesis at 100% (1650 W) of power, using ZnSO$_4$ as a precursor, allows to obtain a greater particle concentration than at 60% (990 W), this behavior is in agree with the idea of a faster temperature increase of the sample at high power, leading to decomposition of thiocetamide, promoting a greater amount of nuclei, which in turn gives a greater concentration of particles in the dispersion.

In the case of Zn (CH$_3$COO)$_2$ as precursor, a similar phenomena should occur and the result should be similar, however it is noticeable that particles obtained to 100% power exhibit an absorption spectrum with transitions which are more evident than those of the dispersion treated at 60%. As it was described above, this suggests a smaller particle size when 100% power is applied. However, the $E_g$ values calculated from these spectra are approximately 3.6 eV for any experimental condition, this value agrees with the reported in literature for the ZnS [18], meaning that $E_g$ values can not be used for estimating particle size.

The photoluminescence spectra of the synthesized dispersions is presented in Fig. 2, it can be appreciated that this spectra corroborate what was established by means of the absorption spectra, since the particles synthesized at 100% power present greater absorptions and emissions, supposing higher concentration in the dispersion. It is also noticeable that the emission of the particles synthesized from ZnSO$_4$ is more intensive than in those synthesized from Zn(CH$_3$COO)$_2$.

These results can be explained through two phenomena: first, the precipitation of ZnS is found in competition with the complex reactions of Zn$^{2+}$ with the citrate and with the anion corresponding of the source of such cation, and since the lateral equilibrium of the complex of Zn$^{2+}$ with the acetate is more favorable than those established with the sulfate ion, then it is expected that dispersions synthesized from ZnSO$_4$ would be more concentrated than those synthesized from Zn(CH$_3$COO)$_2$. The second phenomenon that explains the difference in the luminescent properties of the particles is that they are covered by the anions of the reaction media, therefore the sulfate ion could be more favorable to the electronic transitions more than the acetate ion.

Given the above arguments it is established that the synthesis of ZnS from ZnSO$_4$ at 100% applied power produce better results, both in higher concentration and luminescent properties, therefore further discussion is directed to the dissolution obtained under these conditions.

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**Figure 1.** Absorption spectra for the synthesized dispersions under different conditions, 990 W and 1560 W, 60 and 100% power output respectively.

**Figure 2.** Photoluminescence spectra for obtained dispersions at 990 W (60% power output) and 1650 W (100% power output) from both precursors.
The infrared spectrum of the particles obtained from ZnSO₄ at 100% is shown in the Fig. 3, exhibits absorption bands that demonstrate the presence of absorbed citrate in the particles.

Wide peaks in the X-rays diffraction pattern Fig. 4 suggests presence of nanometric particles, since the chosen reaction was designed to produce ZnS, then elucidated peaks in the diffraction pattern should be from ZnS. Fig. 5 presents a typical Transmission Electron Microscopy (TEM) image and the corresponding electron diffraction pattern insert in Fig. 5b, this image shows the ring pattern and confirms the peak positions than in the X-rays diffraction pattern are far less defined than those produced by bulk materials, but this evidence together is clear enough to confirm that the produced material is ZnS in cubic phase (JCPDS 75-1534). Figure 5a shows clusters of less than 20 nm made of NPs, images like this one were used for calculating the size of the particles conforming the clusters by means of image analysis, the average size was 7 ± 1.6 nm with the distribution shown in Fig. 5c, given the observed properties of the dispersion is possible that the clusters were formed during handling for characterization rather than during synthesis.

4. Conclusions

Although concentration of NPs was not actually measured and it was only sorted by the estimation from analysis of the absorption spectrum of each obtained dispersion, the results confirm that the precursors used for the synthesis ZnS NPs and the exposition power have an influence on the concentration of the obtained dispersions and its electromagnetic properties.

The amount of energy actually getting into the solution was not quantified, but higher power in synthesis produces a greater concentration of ZnS NPs. This effect is related to the decomposition of the thioacetamide, which is faster when the solution is being heated at higher power, providing S²⁻ that affects the amount of nuclei.

The dispersions synthesized from ZnSO₄ present greater emission intensity that the dispersions synthesized from Zn(CH₃COO)₂, due to the Zn²⁺ that affects electronic transitions, which modifies the luminescence of the NPs.

NPs of cubic ZnS were synthesized using ZnSO₄ as precursor and exposing the solution to 1650 W, average size was 7 nm.

Acknowledgements

The authors wish to express their grateful to the Laboratorio de Vía Húmeda y Sol-Gel at the Facultad de Ciencias Químicas UANL, as well as the Programa de Doctorado en Ingeniería de Materiales at the Facultad de Ingeniería Mecánica y Eléctrica UANL.
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