

NEW METHOD FOR PREPARING ZINC SULFIDE NANOCRYSTALLINE IN WATER AND ALCOHOL SYSTEMS: THE USE OF RADIATION TECHNOLOGY

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ABSTRACT γ -irradiation technique was used with success to prepare nanocrystalline zinc sulfide at room temperature and ambient pressure, without adding any kind of catalysts. Sodium thiosulfate and carbon disulfide were used as sulfur sources in water and absolute alcohol systems, respectively. Structure and morphology of the nanocrystallines ZnS have been characterized by XRD and TEM analysis. The product has a cubic structure and, morphologically, is in spherical shapes of 20 to 50 nanometers in size. Probable mechanisms of the nanocrystalline formation in different systems are proposed in accord with the experiment.

KEYWORDS ZnS nanocrystalline, Water system, Alcohol system, γ -irradiation

CLC O613.51, TN304.2*5, TF123, TB383

In the recent years, the synthesis and characterization of chalcogenides of different groups have attracted considerable attention due to their important non-linear properties, luminescent properties, quantum size effects and other physical and chemical properties. Among those materials, zinc sulfide is one of the most interesting materials due to its attractive application in infrared window materials and phosphors for cathode ray tubes, thin film electro luminescent devices, solar cells, and photochemical production of hydrogen. Devices based on ZnS: Mn has been produced commercially as emissive flat panel displays for a number of years. Studies of zinc sulfide are extremely active area of research^[1]. For application, it would be desirable to use particles with spherical shapes and uniform size.

Considerable progress has been made in the synthesis of zinc sulfate powders. Conventionally, zinc sulfide could be prepared by a variety of methods, including gas-phase, solid-vapor, and aqueous solutions reactions, and solvo-thermal elemental reaction^[2-5]. Usually, ZnS is prepared by passing H₂S through aqueous solution containing Zn²⁺ ions. However, ZnS, as prepared have additional disadvantages such as irregular crystallites with a wide size distribution ranging from 25—200nm. The above methods need high temperature (greater than 500°C) and the presence of H₂S a toxic gas.

Another way of synthesizing zinc sulfide is the use of organometallic precursors, but most of organometallic precursors are toxic, easy to hydrolyze, to oxidize and hard to handle.

1 Materials and methods

Nanocrystallines ZnS were prepared in water and non-water systems. Different sulfur sources such as sodium thiosulfate, Na₂S₂O₃ and carbon disulfide CS₂ were used successfully to obtain nanocrystalline ZnS in water and alcohol systems respectively. Every process was carried out in aqueous solution in the case of Na₂S₂O₃ or in absolute alcohol solution with CS₂ at room temperature and ambient pressure.

In absolute alcohol system, analytically pure zinc sulfate heptahydrate, ZnSO₄·7H₂O as Zn²⁺ source and carbon disulfide as sulfur source were dissolved into anhydrous ethanol (C₂H₅OH), glycerol (C₃H₅(OH)₃) of 1.5g/mL density was added into the solution to increase the solubility of zinc sulfate in to the solvent based in the fact that ethanol is mutually soluble with many solvents, either polar or non polar. Isopropanol (IPA) was added as scavenger for oxidative radicals O H•, sulfuric acid (H₂SO₄) of 1.84g/mL density was poured into the solution to avoid an early precipitation of zinc sulfide and then to work in an acid medium. Ethanol was selected as

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the solvent for at least two main reasons. On one hand, solvated electron can be produced in ethanol upon γ -irradiation, which is a species in the system and plays an important role in the preparation. On the other hand ethanol is a good solvent for many inorganic components. It can provide a homogeneous system, which will make sure that the reactants mix at the molecular level in the system since a good solvent is necessary for providing a homogeneous system and for preparing materials with narrow size distribution. Carbon disulfide was used as sulfur radical since it may produce sulfur radical under γ -irradiation. More importantly, it can avoid the formation of intermediate precipitates, which can reduce the purity of the products. After preparing different solutions with different concentrations, all the solutions were irradiated in the field of ^{60}Co γ -ray source of 1.2025×10^{16} Bq to different doses. After irradiation, the irradiated suspension colloids were kept for several hours to allow the precipitation of the powders. Then, the precipitates were collected and washed several times with absolute alcohol to remove the by-products. The final white precipitate was dried in vacuum oven for 4h.

In water system, zinc sulfide nanocrystalline were prepared by dissolving an appropriate amount of analytically pure zinc sulfate heptahydrate and sodium thiosulfate as sulfur source in distilled water. Isopropyl alcohol was added as scavenger for hydroxyl radicals. All the solutions were irradiated in the field of ^{60}Co γ -ray source of 1.2025×10^{16} Bq to different values of absorbed doses. The irradiated solutions were kept for several hours to precipitate powders. White precipitates of nanocrystalline zinc sulfide were collected, and washed with absolute alcohol and water in sequence to remove by-products. The final products were dried in vacuum oven for 2h.

The structure and the size of the nanocrystallines ZnS have been characterized by X-ray diffraction XRD. The morphology and particle size were determined by transmission electron microscopy, TEM. The TEM Images were taken with Hitachi model H-800 electro microscope with accelerating voltage of 200kV. The absorption wavelength were recorded by a UV-visible spectrophotometer model DMS100S.

The yield rate is defined as the molar ratio of the Zn element in the final product to that used in preparing the solution.

2 Results and discussion

The particle sizes and the shapes were investigated by TEM and XRD patterns. The results are given in Fig.1,2 and Fig.3, which one can see that the product consists of uniform spherical crystallites. The average size is about 38nm in water system and 42 nanometer in absolute alcohol system from TEM image. This is in agreement with XRD pattern as shown in Fig.3. The XRD pattern indicates that the product is β -ZnS, sphalerite phase which belongs to the cubic system crystal with a lattice parameter of $a = 0.54060\text{nm}$. Using Scherer formula $L = 0.9\lambda / B(\cos\theta)$, where B is the corrected of the diffraction peak expressed in rad, and given by the relation, $B = (\beta^2 \text{ of the sample} - \beta^2 \text{ of the reference})^{1/2}$, θ is the diffraction angle, and β the full width

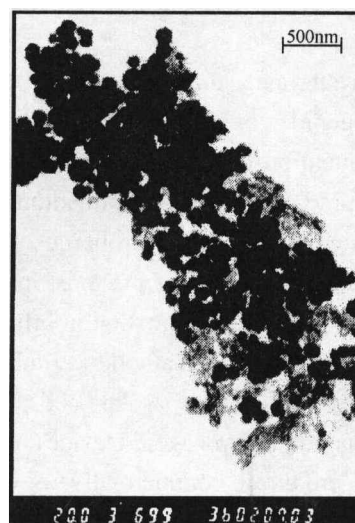


Fig.1 TEM image of ZnS in water system.

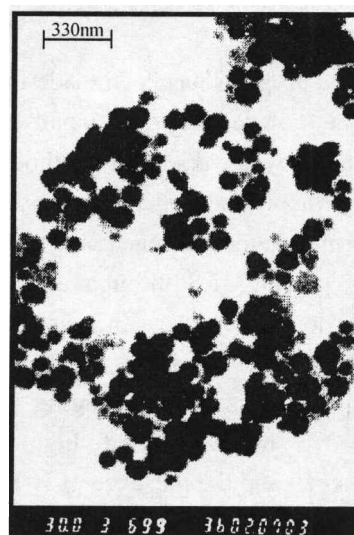


Fig.2 TEM image of ZnS in absolute ethanol system.

at the half maximum (FWHM). The average size calculated from peak 4 of (100) diffraction plane $2\theta=16.8$, is about 40.35nm in the case of absolute alcohol system and it agrees with the result of TEM. The aggregation of the products as shown in Fig.1 and Fig.2 is a common phenomenon for nanoparticles and it is due to their extremely small dimensions and high surface energy. From Tab.1 and Tab.2 it can be observed that the product has a strong absorption onset for the near ultraviolet incident light. The progressive red shift of the absorption wavelength with the increasing irradiation dose indicates that ZnS particles gradually grow larger, because it has been established that for relatively small semiconductor particles, the absorption spectrum provides a direct measure of the size of crystalline. The result is in accord with the theoretical model developed by V. Turco Liveri and col-

leagues^[6,7]. This model relates a relationship between the UV-visible wavelengths at the maximum λ_{\max} of zinc sulfide nanoparticles and the diameter d of the particles as a power law, $\lambda_{\max} = 186.7d^{0.13}$, where, λ_{\max} is expressed in nm and d in Angstrom.

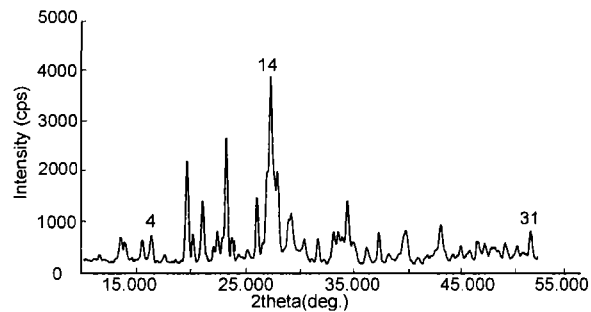


Fig.3 XRD pattern of ZnS produced by γ -irradiation in non-water system.

Tab.1 Preparation of zinc sulfide in absolute alcohol system

Sample number	[Zn ²⁺] mol/L	[CS ₂] mol/L	[IPA] mol/L	[Glycerol] mol/L	[H ₂ SO ₄] mol/L	Irradiation dose/kGy	λ_{\max} after irradiation/nm	λ_{\max} before irradiation/nm	Rate yield/%
1	0.05	0.25	1.5	0.1	0.4	30	372.3	214.6	51.4
2	0.08	0.08	1.5	0.1	0.4	30	369.2	225.6	46.2
3	0.12	0.25	1.5	0.1	0.4	30	367.2	233.8	67.6
4	0.12	0.50	1.5	0.1	0.4	11	293.1	229.2	73.1
5	0.16	0.80	0.25	0.1	0.4	11	289.9	229.2	75.3
6	0.20	0.80	0.25	0.1	0.4	30	370.7	226.5	76.0

Tab.2 Preparation of zinc sulfide in water system

Sample number	[Zn ²⁺] mol/L	[Na ₂ S ₂ O ₃] mol/L	[IPA] mol/L	Irradiation dose/kGy	λ_{\max} after irradiation/nm	λ_{\max} before irradiation/nm	Rate yield/%
1	0.05	0.25	1.5	30	347.1	216.1	57.2
2	0.08	0.25	1.5	30	346.5	227.4	62.3
3	0.12	0.25	1.5	30	347.3	226.3	70.8
4	0.12	0.50	1.5	11	299.4	229.7	74.3
5	0.16	0.50	2.5	43	372.7	227.8	76.0
6	0.20	0.30	2.5	30	347.7	215.9	73.3

From Fig. 4 and Fig. 5 relative to UV-visible spectra of ZnS in water and absolute alcohol systems respec-

tively, it can be seen that by applying this approximate formula for $\lambda_{\max} = 372.3\text{nm}$ of sample 1 of ZnS prepared in absolute alcohol system in our case, the calculated value of diameter size should be about 20.3 nm and from XRD pattern in Fig.3, the peak 31 of (221) diffraction plane of $2\theta = 51.48$, is about 22.4nm, in agreement with the theoretical approximate model. Moreover, from different values of absorption wavelength from Fig.4 and Fig.5, it can be found that all the samples could have the size below 30 nm. From Tab.1 and Tab.2 one can point out that the best conditions of obtaining a larger amount of the product should be the use of high concentrations of Zn^{2+} and sulfur sources and a lower dose of radiation.

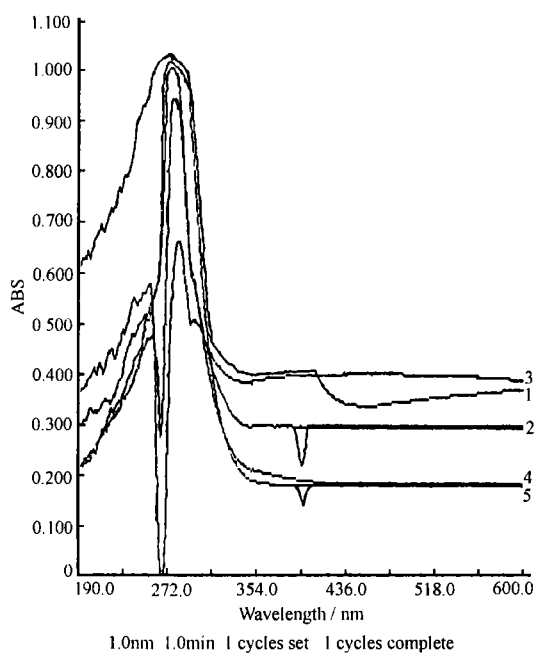


Fig. 4 UV-visible spectra of ZnS in water system.

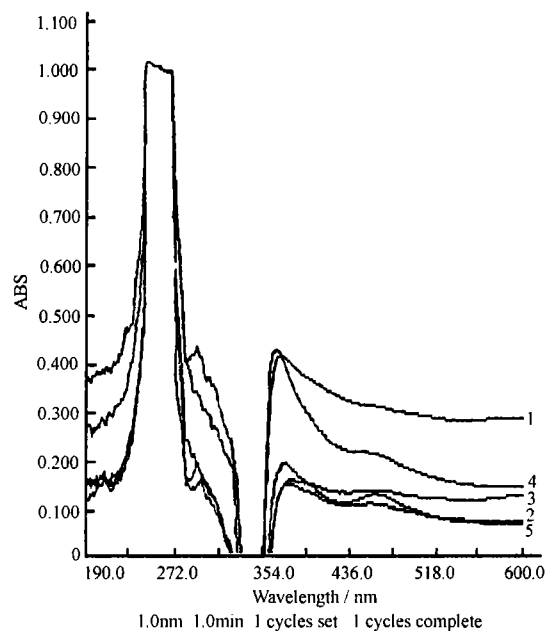
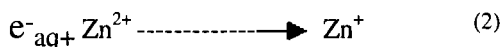
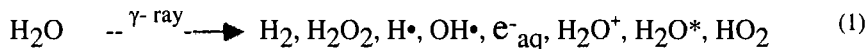


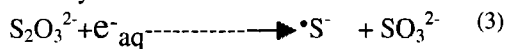
Fig.5 UV-visible spectra of ZnS.

From Tab.1 and Tab.2, it can be found that the values of absorption wavelength before and after irradiation are quite different. Probably ZnS is not produced before irradiation, it is formed as a consequence of the homogeneous mixing of $\text{S}_2\text{O}_3^{2-}$ and Zn^{2+} and the regular production of S^{2-} upon γ -irradiation.

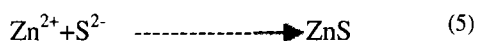
Using γ -irradiation for preparing nanoparticles, the mechanisms of the formation is not very clear up to now but however, the probable mechanism of formation of ZnS in water system could be explained as a result of reduction of zinc ions with hydrated electrons produced in solution by γ -irradiation, zinc ions in lower valence are formed [8,9]:



In the case of sodium thiosulfate as sulfur source, the mechanism may be that:

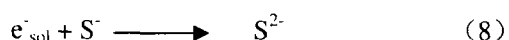
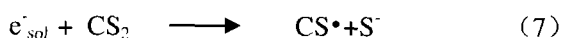


Thus, ZnS can be formed in the following way:



In order to explain the formation of nanocrystalline ZnS in alcohol system, a simple experiment was designed for this purpose; firstly, the same concentrations of CS_2 and Zn^{2+} in ethanol solution were prepared, respectively. Secondly, they were divided in to two equal parts to make easy the identification. These solutions were labeled CS_2 (1), CS_2 (2), Zn^{2+} (1) and Zn^{2+} (2). Among these solutions CS_2 (1) and Zn^{2+} (1) were irradiated while CS_2 (2) and Zn^{2+} (2) were not irradiated. After that, CS_2 (2) was added to Zn^{2+} (1), but

non-phenomenon appeared since after two weeks, the solution was still clear and transparent. However, when Zn^{2+} (2) was added into CS_2 (1), the white precipitates immediately appeared and as a result the solution became unclear and non transparent. This experiment indicated that S^{2-} ions were produced after CS_2 (1) was irradiated. Thus, when Zn^{2+} cations were introduced into the system, S^{2-} ions rapidly combined with Zn^{2+} to form ZnS. Then, the possible process could be simply described as follows:



3 Conclusions

Nanocrystalline ZnS was prepared successfully par using a new technology that is γ -radiation method at room temperature, ambient pressure and without any kind of catalysts, both in water and absolute alcohol systems. Sodium thiosulfate and carbon disulfide were used as sulfur sources in water and absolute alcohol respectively. Analysis par XRD revealed that the product has a cubic structure ZnS, sphalerite phase. The TEM images

showed that the crystallites were spherical shapes and the particles size were 38nm and 42 nm for ZnS as prepared in water or alcohol system respectively. Possible mechanisms of the formation of ZnS in both systems are proposed in accord with the experimental results.

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在水和乙醇体系中用辐射技术制备纳米 ZnS 晶体

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摘要 在水溶液体系和乙醇溶液体系中,于常温常压下不加入任何催化剂,用 γ 射线辐照技术可以成功制备出纳米 ZnS 晶体,其中硫代硫酸钠和二硫化碳分别为上述两体系的硫源。本工作利用 XRD 和 TEM 来分析观察纳米 ZnS 晶体的结构和形貌。产物具有立方体结构和球形的形貌,颗粒大小在 20—50 纳米之间。根据实验,提出了纳米 ZnS 晶体在不同体系中形成的机理。

关键词 纳米 ZnS, 水溶液体系, 乙醇溶液体系, γ 射线辐照

中图分类号 O613.51, TN304.2*5, TF123, TB383