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Research Article

Structure, morphology and luminescence properties of electrosynthesized ZnS: Cu, Cl nanoparticles

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ABSTRACT

Electrosynthesis of zinc sulfide nanoparticles doped with copper and chlorine has been investigated in this study. For the electrosynthesis of ZnS, a constant current pulse of 200 mA cm^{-2} was applied to zinc nitrate and sodium thiosulfate solution containing 1 M hydrochloric acid in an electrochemical cell. The thin film of zinc sulfide nanoparticles was placed on a graphite electrode. For doping Cl^- and Cu^+ on ZnS, the modified electrode was placed in copper sulfate solution containing 0.1 M potassium chlorate under a constant potential of -0.9 V for 3 minutes. By changing the concentration of potassium chlorate from 0.1 to 0.01 and 0.0001 M, the amount of doped Cl was variable, therefore; nanoparticles with different luminescence properties were achieved. Based on the X-ray diffraction pattern average crystallite size for nanocomposites is the same and about 34-64 nm. Using scanning electron microscopy imaging it was observed that synthesized nanocomposites have appropriate uniformity. Characterization was performed using XRD and FT-IR methods. The morphology and luminescence properties of these nanoparticles were studied using SEM and UV-Visible.

Keywords: Electrosynthesis; Zinc sulfide; Nanoparticles; Luminescence.

1. Introduction

Today, nanoparticles due to their unique properties have attracted the attention of many scientists and many attempts have been made to produce nanoparticles with multiple functions [1, 2]. Chemical and electrochemical methods are possible ways to make new nanoparticles. Among them, easier practices with less time and lower prices are in priority. Electrochemical methods provide the possibility to prepare a variety of materials with different forms in the solution [3-5].

These particles have a wide functional diversity and can live as common structural rudiments or mixes compared to bulk accouterments. The Physical-chemical properties of nanoparticles are mostly rated by the parameters like size, shape, and composition. Metallic nanoparticles of exclusive sizes and morphologies can be readily synthesized using chemical and physical methods. Most of the styles use poisonous chemicals as reducing agents, organic detergents, and non-biodegradable stabilizing agents which are potentially dangerous to the terrain and natural systems. Also, most of these styles are complicated and involve non-standard conditions making them relatively precious. Therefore, the biosynthesis of nanoparticles is being proven as a cost-effective environmentally friendly volition to the chemical and physical system). Accordingly, microorganisms and factory excerpts have been used in the conflation of nanomaterials [6].

ZnS is a well-known material used in different radiation imaging and discovery operations, as it's one of the oldest and most splendidly known marketable luminesce [7]. ZnS particles have a band gap of 3.7 eV and it is a good material as the base and can be doped with a variety of materials to improve the properties and performance, and produces nanoparticles with different [8-10]. The benefits of these nanoparticles are high stability, low cost, and low toxicity. Several metal ions, such as manganese, copper, and chlorine have been added

successfully to ZnS to produce electro-emission in different parts of the visible spectrum [7, 10, 11]. Because of the importance of phosphorus in displays, a part of this research focuses on the production of suitable phosphors for these displays. Zinc silicate doped with manganese is one of the materials used as green phosphors and in bulk in this technology. High exposure power and appropriate loss time are the most important characteristics of displays [12, 13].

In this research, ZnS: Cu, Cl nanoparticles have been synthesized by electrochemical method, and their morphology is examined by SEM. In the following, the FTIR and XRD spectrum was used to confirm the synthesis of nanocomposites. Its luminescence properties were investigated by UV spectroscopy.

2. Experimental

2.1. Materials and method

Zinc nitrate, sodium thiosulfate, HCl, copper sulfate, and potassium chlorate were purchased from Merck Company. All chemicals used had high purity and were used without purification. All aqueous solutions were made using ultra-pure water obtained by Milli Q plus machine manufactured by the American Millipore Company.

A potentiostat and galvanostat device of the Ivium model made in the Netherlands' has been used for electrosynthesis. The composite 2B pencil graphite (Staedtler Lumograph, Germany) has been used as the working electrode, and the platinum blade has been used as the counter electrode and Ag/AgCl electrode as the reference electrode in electrochemical synthesis.

FTIR device of Tensor 27 model manufactured by German Bruker Company has been used to identify electro-synthesized nanocomposite. An electron microscopy device with an

EDX (Energy Dispersive X-ray) analyzer made in England with the model of Leo Supra 50 VP has been used to study the morphology of the nanocomposite particle size. XRD test has been used by Siemens D5000 device made in Germany with Cu source with a wavelength of 1.54056 Å in the range of 2θ equal to 5 to 70 degrees at ambient temperature. The photoluminescence spectrum (PL) was measured by using the Hitachi F-4500 device at room temperature under excitation in the visible region.

2.2. Procedure

For electrosynthesis of ZnS, 0.1 M zinc nitrate and 0.12 M sodium thiosulfate were prepared in 1 M HCl, 10 ml of this solution was transferred to the electrochemical cell, and by placing graphite electrode as the working electrode, a platinum electrode as the counter electrode and Ag/AgCl electrode as the reference electrode in a solution, electrochemical synthesis was conducted with the constant current pulse of 200 mA cm^{-2}, the frequency of 18 Hz and a pulse time of 14 ms for 2 hours. Then the electrode modified with ZnS was washed in water and ethanol solution and doped with chlorine and copper on it (ZnS) and thus nanocomposite was electro-synthesized. This procedure was considered that the above-modified electrode in presence of counter and reference electrodes was placed in 10 ml of 0.1 M copper sulfate, 0.1 M potassium chlorate for 3 minutes at a constant potential of -0.9 V. It should be noted that for the preparation of nanocomposites with different luminescence properties, the concentration of potassium chlorate was changed from 0.1 M to 0.01 and 0.0001 in the next synthesis.

3. Results and discussion

3.1. Electrosynthesis of ZnS: Cu, Cl nanoparticles

First, zinc nitrate was used as the source of zinc, and sodium thiosulfate as the source of sulfur. For electrosynthesis of zinc sulfide nanoparticles, to an electrochemical three-electrode cell containing solutions of 0.1 M zinc nitrate, 0.12 M sodium thiosulfate, and 1 M hydrochloric acid, a constant current pulse of 200 mA cm^{-2} at a frequency of 18 Hz with a pulse time of 14 ms for 2 hours was applied. Then synthesized ZnS was placed in another three-electrode electrochemical cell including 10 ml of 0.1 M solutions of copper sulfate and potassium chlorate under a constant potential of -0.9 V for 3 minutes, until the nanocomposite of ZnS: Cu, Cl will be electro synthesized. By varying the concentration of potassium chlorate from 0.1 to 0.01 and 0.0001 M, Cl doped amount was varied and consequently, the nanocomposites with different luminescence properties were synthesized.

3.2. Structural Analysis of ZnS: Cu, Cl nanoparticles

3.2.1. SEM and EDX

To study the morphology of ZnS: Cu, Cl nano cylinders, scanning electron microscopy (SEM) was used (Figure 1a). The size of sample particles varies from 34.44 to 63.34 nm. EDX spectrum has appropriate results for elements with the greater atomic number because the radiation emitted by the light elements has low energy and since higher-energy X-ray is needed in the correction and interpretation of quantitative analysis models, the error will occur by using EDX in determining the elements with small atomic number. As can be seen in elemental analysis images taken (Figure 1b) the presence of the nanocomposite is confirmed.

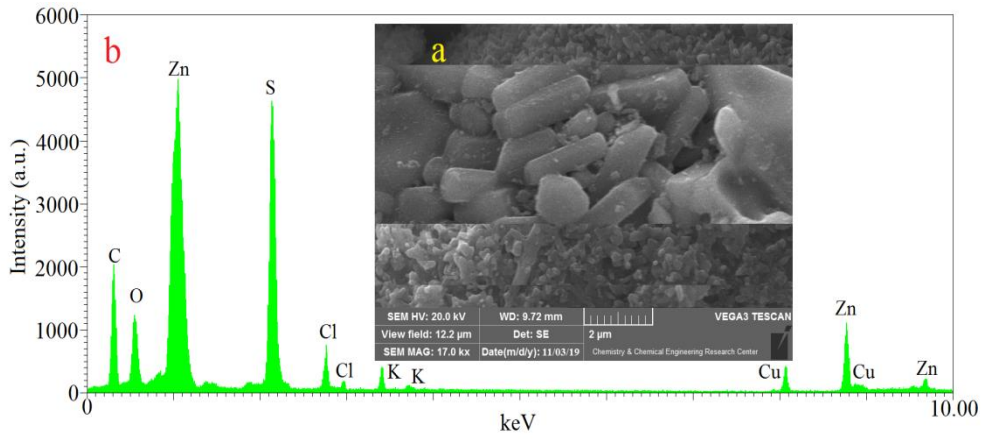

Fig. 1. SEM image of zinc sulfide nano cylinders doped with copper and chlorine (a), The EDX spectrum (b).

3.2.2. FT-IR analysis

Figure 2 shows FT-IR spectra of the ZnS: Cu, Cl nanoparticles. In this spectrum, peaks appeared in wave numbers 643 cm^{-1}, 900 $cm^{-1,}$ and 445 cm^{-1} are attributed to the bending vibrations of ZnS and wavelengths 2924 cm^{-1}, 2964 $cm^{-1,}$ and 1435 cm^{-1} due to the formation of ZnS microstructure. The observed peak in the wave number 554 cm^{-1} is probably due to the interaction between oxygen and sulfur. A very weak absorption band in the range of 3465 cm^{-1} to 3410 cm^{-1} complies with the O-H functional group that may indicate the presence of water in nanocomposites [6, 7, 12, 14].

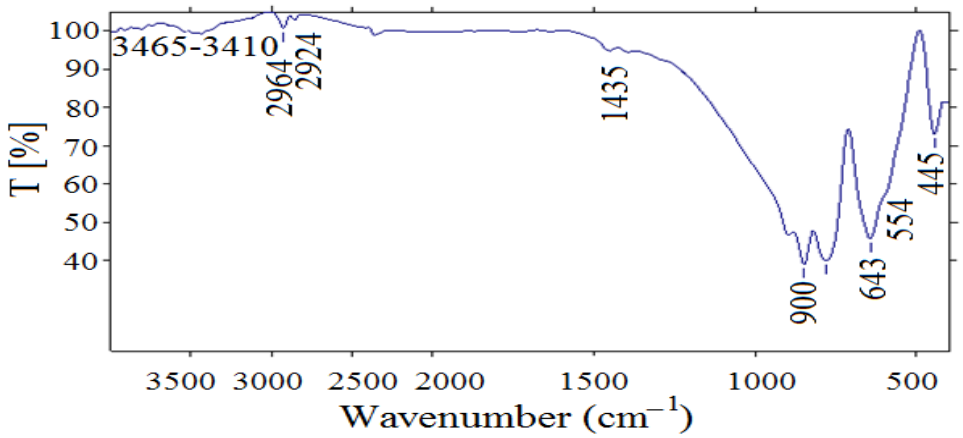

Fig. 2. FT-IR spectrum of zinc sulfide nanoparticles doped with copper and chlorine

3.2.3. XRD analysis

Figure 3 shows XRD spectra of the zinc sulfide nanoparticles doped with copper and chlorine. In this spectrum, peaks are observed at 2θ angles of 27, 45, and 56 which is fully in compliance with the spectrum obtained from the nanoparticles prepared by chemical methods and is respectively associated with crystal plates of 111, 220, and 311 which match very well with the long-cube structure of zinc (JCPDS No. 05-0566) [13, 15].

It also shows that these compounds have a zinc long-cube structure. XRD peaks have been flattened due to the nature of nano-crystalline particles and their size small. These nano-crystals compared with bulk material have fewer network plates that lead to flattening peaks in the X-ray diffraction pattern. The average crystallite size can be determined using the peak broadening method of the X-ray diffraction pattern.

Crystal size is calculated using the measurement of the peak width in the middle of the highest peak and by the Debye- Scherer formula. The formula used in this method to calculate the particle size is as follows.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, λ is the wavelength of the x-rays, β is the line broadening at half the maximum intensity (FWHM) and θ is Bragg angle in radians. The average size of crystallites calculated by the Debye-Scherrer formula was obtained at 34-64 nm (calculations have been conducted based on the feature of the main peak of zinc sulfide with an intensity of 100%).

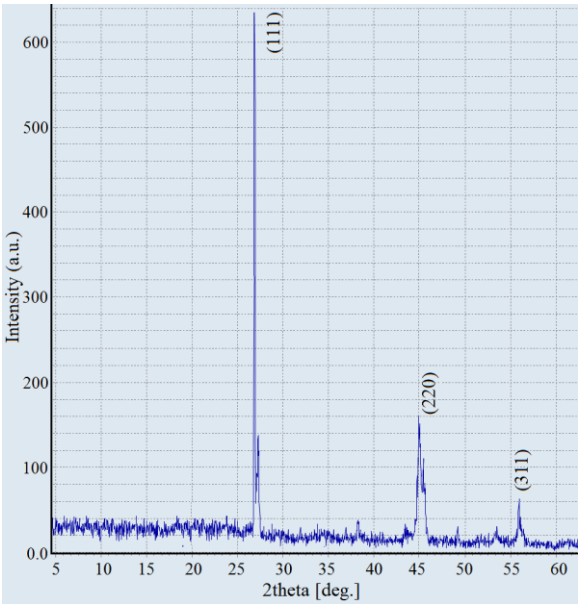

Fig. 3. XRD spectrum of the zinc sulfide nanoparticles doped with copper and chlorine.

3.3. Luminescence properties

The sample prepared was scanned in UV irradiation to determine the emission wavelength of the compound. Figure 4 shows the reflection spectrum of this sample. As can be seen, this material has luminescence at 420 to 490 nm. Luminescence wavelength is variable depending on the concentration ratio of (Activator) Cu to doped Cl (Coactivator) and these results are consistent with reports available from nanoparticles produced by chemical methods.

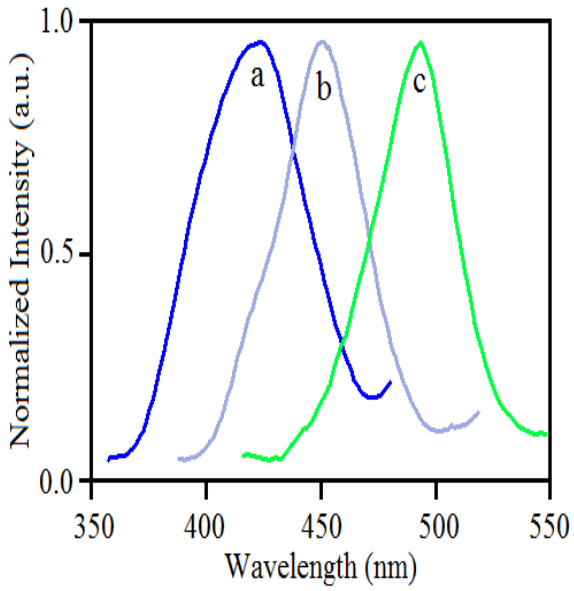

Fig. 4. Luminescence spectra of the zinc sulfide nanoparticles doped with copper and chlorine under UV-lamp irradiation, λex=300 nm, with different concentration ratios of Activator (Cu)/Coactivator (Cl): Cu/Cl=1(a), Cu/Cl=10 (b) and Cu/Cl=1000 (c).

These nanoparticles are exposed to exited visible light and lights emitted in wavelengths of 420, 450, and 490 nm as noted, this process depends on the change of the concentration ratio of Activator (Cu)/Coactivator (Cl).

4. Conclusions

In this study, zinc sulfide was synthesized by an electrochemical method doped with Cl and Cu. Based on the X-ray diffraction pattern average crystallite size for nanocomposites is the same and about 34-64 nm. Using scanning electron microscopy imaging it was observed that synthesized nanocomposites have appropriate uniformity. Samples stimulated at the wavelength of UV light at room temperature showed photoluminescence peaks at wavelengths of 420, 450, and 490 nm that which was consistent with other reports that, this

process depends to change in the concentration ratio of Activator (Cu)/Coactivator (Cl) in the nanocomposite.

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