Journal of Pharmaceutical and Applied Chemistry
An International Journal

http://dx.doi.org/10.18576/jpac/060201

Thiocarbohydrazide as a Sulfur Source for the Preparation of Nickel Sulfide Nanoparticles

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Received: 5 Feb. 2020, Revised: 6 Mar. 2020, Accepted: 7 Apr. 2020.
Published online: 1 May 2020.

Abstract: In the present work, Orthorhombic NiS nanoparticles were obtained by simple chemical method using thiocarbohydrazide as a sulfur source. X-ray diffraction (XRD) pattern was indicated the formation of orthorhombic structure of NiS, energy dispersive X-ray spectrum (EDS), Fourier Transform Infra-Red Spectroscopy (FTIR) techniques, High resolution transmission electron microscope (HRTEM), and scanning electron microscope (SEM) techniques were employed to study the chemical composition and morphology properties of the obtained sample. Crystallite size was determined by Debye—Scherrer formula and was found to be 15.76 nm. The EDS spectrum confirms the purity of the prepared nanoparticles. Optical analyses were done by UV—visible. The band gap was calculated by Tauc relation and was found to be 4.702 eV.

Keywords: Nickel sulfide, orthorhombic and thiocarbohydrazide.

1 Introduction

Nickel sulfide (NiS) is an important member of the transition metals (TM) sulphides family. Due to the various applications, different synthesis methods were employed for the preparations of NiS nanoparticles such as sol-gel, laser ablation, solvothermal process, UV irradiation and colloidal methods [1]. The chemical precipitation method is one of the most important methods for the synthesis of the nanoparticles. Nickel sulfide exhibits complicated compositional, structural, optical, electrical and magnetic phase behavior. Depending on the preparation method, Nickel sulfides can form in various phases such as NiS, $Ni_{3+x}S_2$, Ni_3S_2, Ni_7S_6, Ni_9S_8, Ni_3S_4, and NiS_2 [2]. NiS has been recently used in many applications, such as effective counter electrodes for solar cells [3, 4, 5] and cathodes for lithium batteries [6, 7, 8]. Different methods are reported for preparing metal sulphide nanoparticles [9]. The characteristics of nanomaterials are greatly influenced by the preparation methods and conditions. Consequently, synthesis of nanocrystalline substances, especially by the chemical route, is one of the most exciting fields of research where different preparation conditions can easily be controlled [10]. The used precursor is one of the magor factors that affect the prepared material properties. So the aim of the present work is to synthesis NiS nanoparticles using Thiocarbohyrazide as sulphur source and studies the effect of sulfur source on the structural and optical properties of the prepared NiS and it's the first one for prepared the NiS from Thiocarbohyrazide as sulphur source.

2 Experimental Section

2.1 Materials

The chemicals and reagents used in the experiments are high pure chemicals, Absolute Ethanol (MERCK), Hydrazine hydride (RESERCH-LAB FINE CHEM INDUSTRIES–INDIA), Carbon disulfide(ALPHA CHEMIKA–INDIA)Nickel acetate (PubChem), Potassium hydroxide (MERCK) and Potassium disulfide (MERCK) were all solutions were prepared using distiled water and used with high purity for the synthesis of NiS nanoparticles.

2.2 Synthesis of Thiocarbohydrazide (TCH) (sulfur source):

Thiocarbohyrazide was synthesized by using of 99% aqueous hydrazine hydrate and carbon disulphide according

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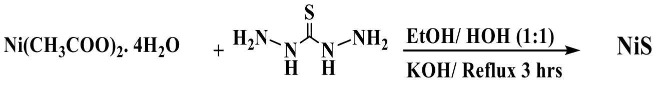
to Taguchi method [11].

2.3 Synthesis of Nickel Sulfide (NiS) Nanoparticles

A solution of Ni $(CH_3COO)_2.4H_2O$ (0.005 M) in 100 ml warm ethanol was gradually added to a warm solution of thiocarbohydrazide (0.005 M) in 100 ml distilled water with constant stirring for 30 minutes. 10 ml of an aqueous solution of potassium hydroxide (0.0125 M) was added with stirring to the reaction mixture. A brown precipitate was formed at first, which turns to black precipitate of NiS by heating under reflux for 3 hours. The formed was filtered on hot, washed with hot distilled water and dried at 100°C to give NiS as shown in scheme 1.



Scheme 1: Synthesis of Nickel Sulfide nanoparticles from thiocarbohydrazide

2.3 Characterization

The phase purity and structure of the prepared samples were characterized by X-ray powder diffraction (XRD), using PANalytical diffractometer with a Cu target and a graphite monochromator (λ= 1.54056 Å). The morphology of the obtained NiS nanoparticles was characterized with high resolution scanning electron microscope (SEM) (JOUL SEM model JSM- 5500- Japan), with accelerated voltage 10 KV. The features and shapes of the particles were also imaged by high resolution transmission electron microscope (HRTEM), model JEOL, JEM- A 2100 – Japan, performed at an accelerating voltage of 200 kV. Moreover, the functional groups in the prepared samples were evaluated using Fourier transform infra-red (FT-IR) spectra (Jasco Model 4100-Japan) with a resolution of 4 cm^{-1} at room temperature. The optical properties of the prepared NiS nanoparticles were performed by means of a computerized SPECORD 200 PLUS spectrophotometer with 1 nm step, at normal incidence at room temperature in the wavelength range 190-1100 nm.

3 Results and Discussion

3.1 X-Ray Analysis

Figure (1) shows the XRD patterns for the prepared NiS sample. The spectrum confirm the crystalline nature of the prepared sample, the spectrum were characterized by three mean peaks (220), (152), and (512) which refer to the orthorhombic NiS phase [12].

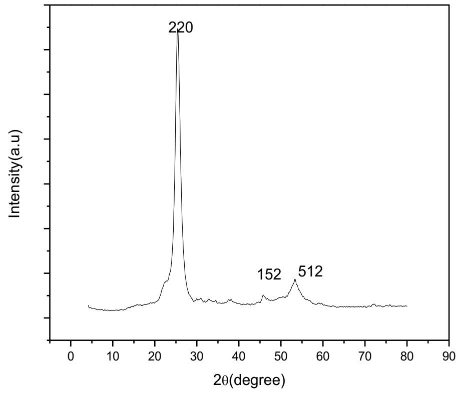


Fig. 1: XRD of NiS NPs.

3.1.1 The Lattice Parameters Calculation

The lattice parameters for the grown sample versus the angular function F(θ) are shown in figure (2). From this figure, the lattice parameters for the obtained NiS nanoparticles are a =9.33Å, b =11.21Å and c=9.43Å, The obtained lattice parameters are consistent with the lattice parameters of the standard Ni_9S_8 orthorhombic [12]. This result confirms the preparation of pure and high quality Ni_9S_8 crystals.

Crystallite size (D) of the obtained NiS nanoparticles can be estimated using Debye–Scherrer equation [13]:

$$D= nK\lambda/\beta\cos\theta \qquad (1)$$

Where, λ is the wavelength of the x-ray radiation, D is the crystallite size, θ is the incident angle (the angle between the incident ray and the scatter plane), n is an integer, β is the full width at half maximum of the diffraction peak measured at 2*θ* and K is the Sherrer constant. The average crystallite size of the obtained NiS NPs was found to be 15.67 nm.

The crystallite size (D) and the microstrain(ε) of the obtained nanoparticles can be calculated from the peak broadening in the XRD patterns using Williamson-Hall analysis. According to Wiilimson-Hall equation, the total line broadening considers two physical factors; the first one is the crystallite size (D), while the second one reflects the strain (ε) effects:

$$\beta = \beta D + \beta\varepsilon \qquad (2)$$

The Williamson-Hall equation can be written as in the following [14]:

$$\beta \cos\theta = (0.94\ \lambda)/D\ + 4\ \varepsilon \sin\theta \qquad (3)$$

The size broadening (βD) is proportional to $\cos^{-1}\theta$ and the strain broadening (βε) is proportional to tanθ.

In order to calculate the crystallite size and the microstrain of the NiS nanoparticles, a relationship between β cosθ/λ and sinθ/λ is drawn for the prepared samples and is shown in (figure 3). The average crystallite size of NiS nanoparticles is 6.17 nm, while its microstrain value is about~ 0.00811 for the prepared sample NiS.

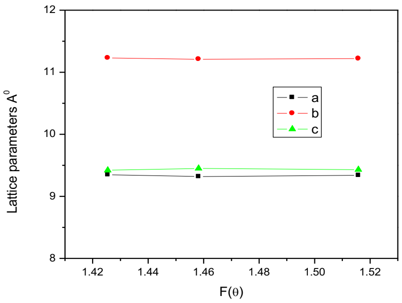


Fig. 2: The lattice parameters of NiS nanoparticles.

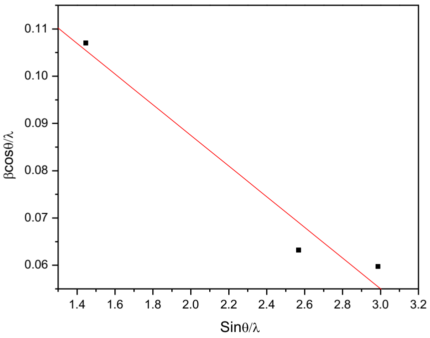


Fig. 3: Williamson-Hall plot for NiS nanoparticles.

3.2 HRTEM and FT-IR Spectra

High-resolution transmission electron microscope (HRTEM) micrograph of the prepared NiS sample are illustrated in figure (4). The HRTEM results confirm the nano size of the obtained NiS.

Figure (5) shows the FT-IR of the NiS nnopaericle prepared by the chemical method in the range of 4000- 400 cm^{-1}

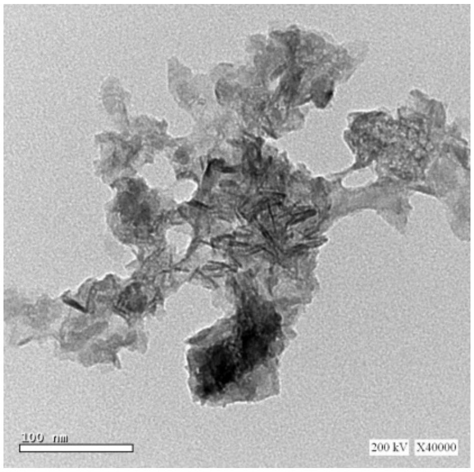


Fig. 4: TEM of NiS nanoparticles

FTIR is used to determine the functional groups and types of bonds present in the system.

showed the characteristic broad band at 3450 cm^{-1} corresponds to the lattice water (OH group) [13] indicating the presence of a small amount of water adsorbed on the sample. The absorption band located at 1112 cm^{-1} is assigned to the sulfide [16]. The band at 384 cm^{-1} is assigned for the existence of Ni-S bond (NiS nanoparticles) [17]. FTIR results indicate the structure of the pure NiS sample.

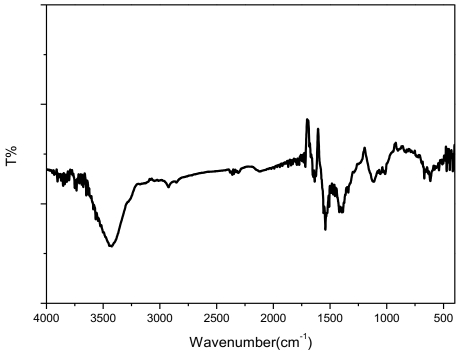


Fig. 5: FTIR of NiS nanoparticles

3.3 Optical Properties

Optical property of the nanoparticles gives specific information about size, shape, concentration, agglomeration state, etc., near the surface of the nanoparticles. These nanoparticles interact with the incident light and show a maximum absorption at a specific wavelength. Figure (6) shows the absorbance and transmittance spectra of NiS nanoparticles over a spectral ranging between 200 and 1100 nm.

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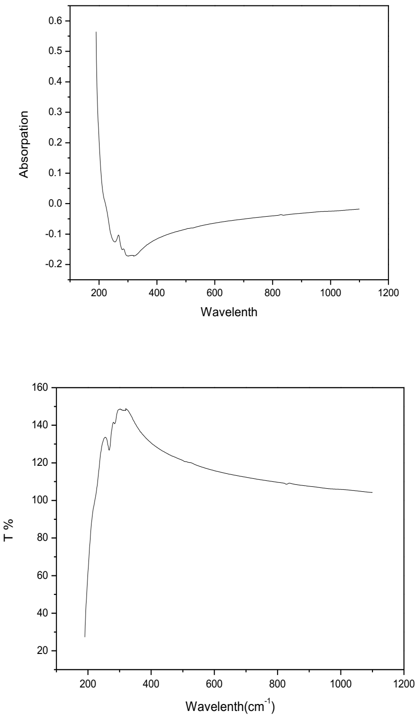

Fig. 6: The absorption and The transmission spectra for NiS nanoparticles

The optical band gap with direct transition can be calculated from the following Tauc relationship [18].

$$\alpha h\nu = B(h\nu - Eg)^n \tag{3}$$

Where hν is a photon energy, B is a parameter which depends on the transition probability, α is the absorption coefficient, Eg is the optical band gap and n is a number characterizing the transition process. Figure (7) shows plots of $(\alpha h\nu)^2$ vs hν. The values of the optical band gap Eg of NiS nanoparticles sample were determined to be 4.702 eV.

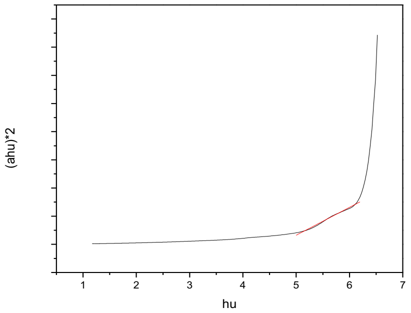

Fig. 7: The relation between $(\alpha h\nu)^2$ and hν for obtained NiS nanoparticles.

4 Conclusions

Nickel sulfide nanoparticles (Ni_9S_8) have been prepared by chemical method using TCH as a sulfur source . The XRD pattern show that the nanoparticles of NiS are in orthorhombic phase and the size estimated using Debye Scherrer equation was approximately at 15.76 nm. The characterizes of the produced nanoparticles showed the band gap found to be 4.702 eV.

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