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Synthesis By A Novel Method And Application Of Image Processing In Characterization Of Nickel Sulphide Nanoparticles

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ABSTRACT

Nanomaterials are currently gaining a lot of prominence due to their unique properties and applications in various fields .In the present paper, we report the synthesis via a simple solvothermal method using a domestic microwave oven and characterization of nickel sulphide(β-NiS-Millerite) nanoparticles. Nickel chloride hexahydrate ($NiCl_2.6H_2O$) and thiourea (NH_2-CS-NH_2) were the reactants and ethylene glycol was used as the solvent. On calcinating the sample at 500°C for one hour, β-NiS nanoparticles were obtained. The prepared sample has been characterized by powder XRD, EDX,and AFM measurements. The average particle size obtained through powder XRD analyses was 18.6nm. TheAFM image obtained were subjected to various image processing tools for analyzing the uniform size distribution of the prepared nanoparticles.

1. Introduction

Nanotechnology is the control and restructuring of matter at the level of atoms and molecules to create novel material, devices and functional system. In the past few decades, inorganic nanoparticles with controlled size and shape have drawn much attention from both fields of science and technology due to their unique properties and potential application in nanodevices.

The preparation and characterization of materials in the nanometer scale has become challenging in the field of material science. The materials in the nanoscale regime exhibit the physical and chemical properties distinctly different from that of the bulk. The new generation of nanomaterials is characterized by a high surface to volume ratio, thus allowing the development of high reactivity at the nanosized and molecular level.Nickel sulphide exists in two phases : the high temperature phase (hexagonal, α-NiS) and the low temperature phase (rhombohedralphase, β -NiS). Nickel sulphide nanoparticles has a number of application in various fields such as IR detectors, hydrogenation catalysis, battery fabrication, cathode materials for high energy density batteries, among which β-NiS have been considered as the most important ones in the terms of catalytic activity [1]. In addition, the small grain size and the large amount of grain boundaries in nickel sulphide nanoparticles leading to unique electrical, dielectric, magnetic and optical properties. β- NiS nanoparticles have been prepared already by different methods like hydrothermal method, thermal and photochemical method, homogenous sulphide precipitation method, wire electrical explosion method ,sol gel method, etc[2,3]. Recently, microwave assisted solvothermal process has been found to be simple, low cost and a potential method for large scale production.

In the present study, we have made an attempt to prepare β-NiS nanoparticles by a simple microwave assisted solvothermal method using a domestic microwave oven. The prepared nanopowders have been structurally, chemically, morphologically, and magnetically characterized. The AFM images obtained were characterized using various image processing techniques to analyze the uniform size distribution of the nanoparticles.

Edge detection is one of the fundamental operations in computer vision. Marr and Hildreth [4] introduced the theory of edge detection and described a method for determining the edges using the zero-crossings of the Laplacian of Gaussian of an image. Haralick [5] determined edges by fitting polynomial functions to local image intensities and finding the zero-crossings of the second directional derivative of the functions. Line edge where the image intensity abruptly changes value but then returns to the starting value within some short distance [6].step edge become ramp edge and line edge become roof edges, where intensity changes are not instantaneous but occur over a finite distance [7].The results obtained are reported therein.

2. Materials and methods

Analytical Reagent (AR) grade nickel chloride hexahydrate [($NiCl_2.6H_2O$)] and thiourea [(NH_2.CS.NH_2)] taken in 1:3 molar ratio were mixed and dissolved in ethylene glycol and kept in a domestic microwave oven (operated with frequency 2.45 GHz and power 800 W). Microwave irradiation was carried out until the solvent got evaporated. The colloidal precipitate obtained was cooled and washed several times with double distilled water and then with acetone to remove the organic impurities present, if any. The washed sample was then dried in atmospheric air and collected as the yield.Again the prepared sample is annealed at 500°C for one hour. The mass of the product was measured for the prepared sample in order to find the yield percentage. The yield percentage was estimated using the relation, Yield percentage = (Mass of the product/ Sum of the masses of reactants) x100.

Colour of the sample was noted. The sample was preserved and used for the X-ray powder diffraction (PXRD) and electrical measurements. The PXRD data were collected for the as-prepared sample using an automated X-ray powder diffractometer with monochromatic CuK_{α}radiation (λ = 1.54056 Å). The PXRD pattern observed was compared with the help of PXRD pattern available in the literature for NiS and the material of the sample prepared was identified.The sample prepared was characterized and studied by taking EDX and AFM measurements.

2.1 Method for Preprocessing the AFM Images

The principal source of noise in digital images arises during image acquisition (digitization) and transmission. The performance of imaging sensors is affected by a variety of factors such as environmental conditions during image acquisition and by the quality of the sensing elements themselves. For instance, in acquiring images with a CCD camera, light levels and sensor temperature are major factorsaffecting the amount of noise in the resulting image. Images are corrupted during transmission principally due to interference in the channel used for transmission [8].different types of filters are there for preprocessing.

2.1.1.Low Pass Filter

Since the energy of the typical image noise contains high frequency components compared to the true image, by reducing the high frequency components while preserving the low frequency components, low pass filtering reduces the large amount of noise. Blurring is the primary limitation of low pass filtering especially at the border of the image or area with significant change.

2.1.2.Median Filter

The best known order-statistics filter is the median filter, which replaces the value of a pixel by the median of the gray levels in the neighborhood of that pixel.

$$F(x, y) = \text{median} \{ g(s,t) \}$$

The original value of the pixel is included in the computation of the median. Median filters are quite popular because, for certain types of random noise they provide excellent noise reduction capabilities, with considerably less blurring than linear smoothing filters of similar size [9,10]

2.1.3. Wiener Filter

It is based on a statistical approach. Typical filters are designed for a desired frequency response. The Wiener filter approaches filtering from a different angle. One is assumed to have knowledge of the spectral properties of the original signal and the noise, and one seeks the LTI filter whose output would come as close to the original signal as possible.

2.1.4. Improved Median Filter

The steps in the modified median filter is as follows

Step1:The input will be a two dimensional image.
Step2: Preallocate another matrix of size (m+2 × n+2) with zero.
Step3: Copy the input matrix into the preallocated matrix.
Step4: Form a window matrix of size (3×3) with the elements of input matrix.
Step5: Copy the window matrix in to an array and sort it
Step6: Find the median element and place it in the output matrix appropriate position
Step7: Display the image without noise.

2.2 Edge Detection

Edge is a boundary between two homogeneous regions. Edge detection is a preprocessing step in image analysis. Edge is the sign of discontinuities & ending in an image. It is organized as a local change in image intensity. An image is converted into edge image using edge detection transformation techniques.

Different techniques of edge detection are there which will transform the image into edge image without any change in physical quantities [11,12].Different types of edge detection techniques are there.

2.2.1. Sobel operator

The operator consists of a pair of 3x3 convolution kernels. One kernel is simply the other rotated by 90.

These kernels are designed to respond maximally to edges running vertically and horizontally relative to the pixel grid, one kernel for each of the two perpendicular orientations. The kernel can be applied separately to the input image, to produce separate measurements of the gradient component in each orientation (call these Gx and Gy). These can then be combined together to find the absolute magnitude of the gradient at each point and the orientation of that gradient.

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2.2.2.Robert's Cross operator

The Roberts Cross operator performs a simple, quick to compute, 2-D spatial gradient measurement on an image. Pixel values at each point in the output represent the estimated absolute magnitude of the spatial gradient of the input image at that point.Theoperator consists of a pair of 2x2 convolution kernels .

These kernels are designed to respond maximally to edges running at 45° to the pixel grid, one kernel for each of the two perpendicular orientations. The kernels can be applied separately to the input image, to produce separate measurements of the gradient component in each orientation (call these *Gx*and*Gy*). These can then be combined together to find the absolute magnitude of the gradient at each point and the orientation of that gradient.

2.2.3. Prewitt's operator

Prewitt operator is similar to the Sobel operator and is used for detecting vertical and horizontal edges in images

$$h1 = \begin{bmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \\ -1 & -1 & -1 \end{bmatrix} \qquad h2 = \begin{bmatrix} -1 & 0 & 1 \\ -1 & 0 & 1 \\ -1 & 0 & 1 \end{bmatrix}$$

2.2.4Laplacian of Gaussian

The Laplacian is a 2-D isotropic measure of the 2nd spatial derivative of an image. The Lapiacian of an image highlights regions of rapid intensity change and is therefore often used for edge detection. The Laplacian is often applied to an image that has first been smoothed with something approximating a Gaussian Smoothing filter in order to reduce its sensitivity to noise. The operator normally takes a single graylevel image as input and produces another graylevel image as output.

The Laplacian L(x,y) of an image with pixel intensity values I(x,y) is given by

$$L(x,y) = \frac{\partial^2 I}{\partial x^2} + \frac{\partial^2 I}{\partial y^2}$$

2.2.5Canny edge detection algorithm

Among the edge detection methods proposed so far,the canny edge detector is the most rigorously defined operator and is widely used. The popularity of the canny edge detector can be attributed to its optimality according to the three criteria of good detection, good localization, and single response to an edge.

A typical implementation of the Canny edgedetector follows the steps below.

1. Smooth the image with an appropriate Gaussian filter to reduce desired image details.
2. Determine gradient magnitude and gradient directionat each pixel.
3. If the gradient magnitude at a pixel is larger thanthose at its two neighbors in the gradient direction,mark the pixel as an edge. Otherwise, mark the pixelas the background.
4.Remove the weak edges by hysteresis thresholding. Similar to canny edge reduction Milherdth is also one of the edge detection technique.

3.Results and Discussion:

The Nickel sulphidenanoparticles(β - NiS) prepared in the present study is found to be black in colour. The yield percentage is 38.4%. The PXRD results (Fig. 1) indicates that all the peaks can be indexed to rhombohedral structure β –NiS with space group of R3m and the cell parameters a= 9.924 Å and c=3.150 Å which is very close to the literature data (JCPDS file number 12-41).The average crystallite size was calculated by the Debye-Scherrer's formula, t=0.9λ/β cosθ, where λ is the X-ray wavelength,β is the full width at half maximum of the diffraction line, and θ is the diffraction angle of the PXRD peak. The average crystallite size of β –NiSwas calculated to be 18.6 nm.

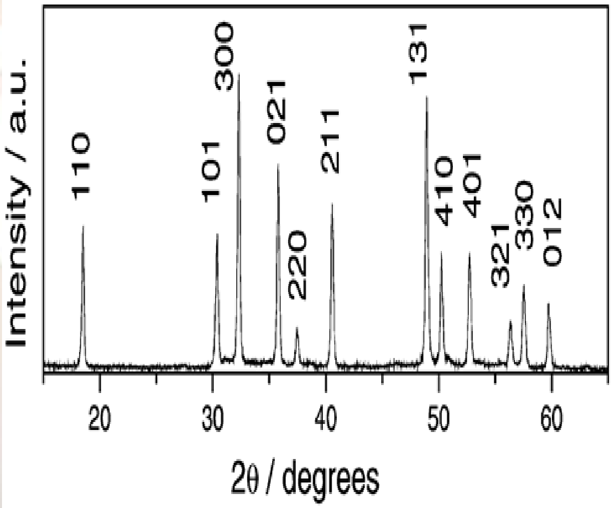


Fig 1: The PXRD pattern

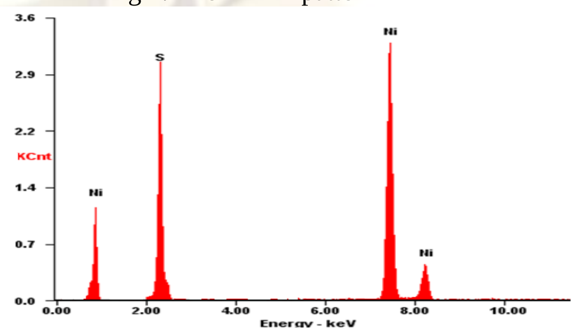


Fig 2: The EDX spectra

The EDX analysis (Fig.2) was employed to determine the chemical composition of the products. Based on the calculation of the peak areas, the atomic ratio of Ni:S for the prepared products is 49:51, which further confirmsthat the products are nickel sulphide nanoparticles..

3.1.Simulation Results

The AMF image of the nanomaterial and its gray scale image is as follows

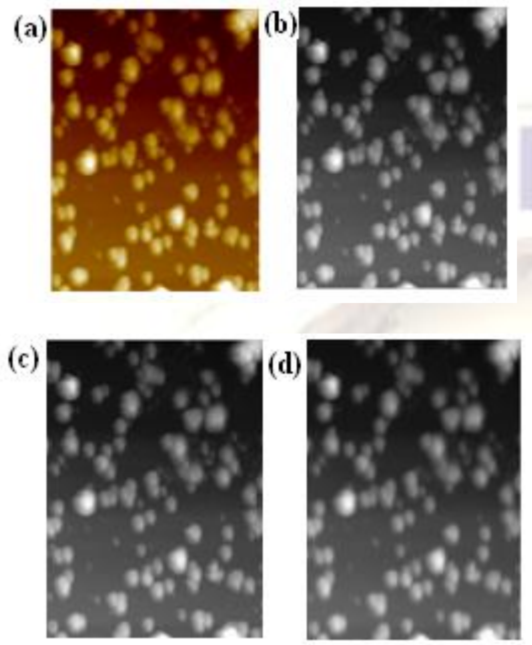


Fig 3: (a) Topography of the AFM image, (b) Gray scale image,(c) Low pass filter output (d) Median filteroutput

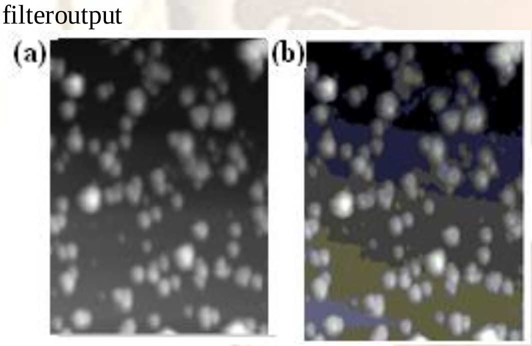
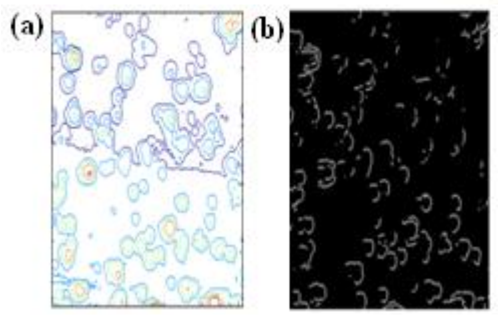


Fig 4: (a) Wiener Filter(b)Modified Median Output

The gray scale image is subjected to different edge detection techniques and the results are as follows



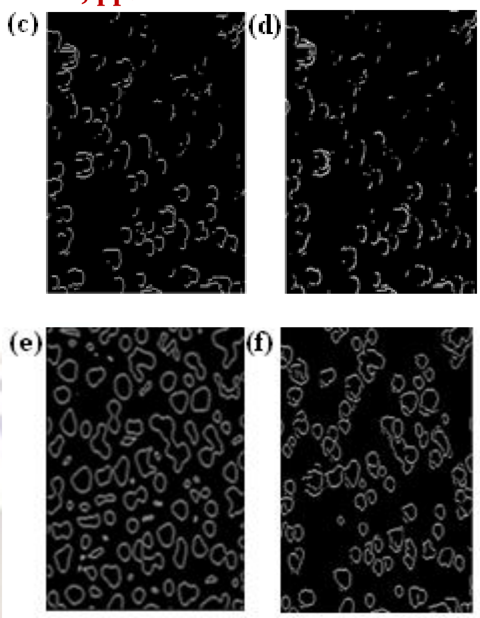


Fig 5:(a) Contour plot, (b) Sobel output(c) Perwitt output, (d) Roberts output, (e) Milherdth output, (f) canny output

Table 1:Comparison of filter output

Type of filter	PSNR	MSE
Low pass Filter	28.23	79.52
Median Filter	29.352	77.52
Wiener Filter	40.2	6.34
Modified Median Filter	42.4	4.08

A filter is said to be good if it is having high PSNR and low MSE value. The modified median filter is having high PSNR and low MSE value.

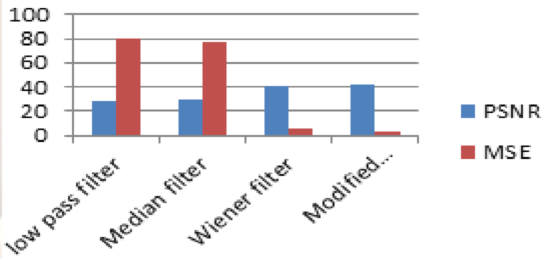


Fig 7: Plot of PSNR and MSE

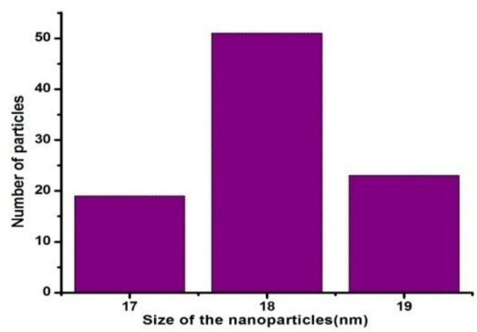


Fig 8: Size distribution of the NiS nanoparticles

Figure 8 shows the uniform size distribution of the particle obtained from the AFM images.

4. Conclusion

Nickel sulphide nanoparticles(β –NiS) have been prepared successfully by a simple solvothermal method using a domestic microwave oven. The yield percentage (38.4%) observed indicates that the solvothermal method adopted is a considerable one for the preparation of the NiS nanoparticles. The results indicate that the prepared β –NiS nanoparticles have an average crystallite size of 18nm. The size distrubition plot attained from AFM indicate that the particles are of average uniform size of 18nm. The AFM image of the nanoparticle is then subjected to image processing techniques. At first preprocessing is done and from the PSNR and MSE plot, it is clear that wiener filter is best one. The edge detection techniques shows the spherical shape of the nanoparticles prepared. The canny edge detection is found to be the best one.

References

[1] B.Viswanadh, S.Tikku and K.C.Khilar, Modeling core-shell nanoparticle formation using three reactive microemulsions, *Colloid Surf. A: Physicochem.Eng.Aspects 298*, 2007 149.

[2] Q.Z.Zhai, T.S. Jiang, W.H.Hu, X.Guan, W.Wang and S.Qiu, Preparation ,characterization ,and luminescence of host (Y zeolite)-guest(FeS,CoS,NiS) nanocomposites materials, *Mater.Res.Bull.37*, 2002,1837.

[3] W.Fu .H.Yang, L.Chang, M.Li,H.Bala, Q.Yu and G.Zou, Preparation and charecteristics of core shell structure nickel/silica nanoparticles, *Colloid Surf. A: Physicochem.Eng.Aspects 262*, 2005 ,71.

[4] D. Marr, E. Hildreth, Theory of edge detection, Proc. Roy.Soc. London B-207, 187 1980, 217.

[5] R. Haralick, Digital step edges from zero crossing of second directional derivatives, IEEE Trans. Pattern Anal.Mach. Intell.6 ,1984 ,58, 68.

[6] M. Abdulghafour, Image segmentation using Fuzzy logic and genetic algorithms, Journal of WSCG, Vol. 11, 2003.

[7] Metin Kaya, Image Clustering and Compression Using an Annealed Fuzzy Hopfield Neural Network, International Journal of Signal Processing, 2005, 80.

[8] K. S. Srinivasan and D. Ebenezer, A New Fast and EfficientDecision-Based Algorithm for Removal of High-Density Impulse Noises, IEEE Signal Processing Letters, Vol. 14, 3, 2007.

[9] R. Yang, L. Lin, M. Gabbouj, J. Astola, and Y. Neuvo, Optimal Weighted Median Filters Under Structural Constraints, IEEE Trans.Signal Processing, Vol. 43,1995, 591.

[10] Pei-Eng Ng and Kai-Kuang Ma,A Switching Median Filter with BDND for Extremely Corrupted Images, IEEE Trans Image Processing, Vol. 15, No. 6, 2006, 1506.

[11] Ibrahim M. M. El Emary, On the Application of Artificial Neural Networks in Analyzing and Classifying the Human Chromosomes, Journal of computer science. Vol 2(1), 2006,72.

[12] Senthilkumaran and R.Rajesh , A study of Edge Detection Methods for Image Segmentation , Proceedings of the International Conference on Mathematics and Computer Science (ICMS-2009), Vol 1, 255.