A Continuous Process for the Preparation, Characterization and Study Thermal Properties of Nickel Oxide Nanostructure

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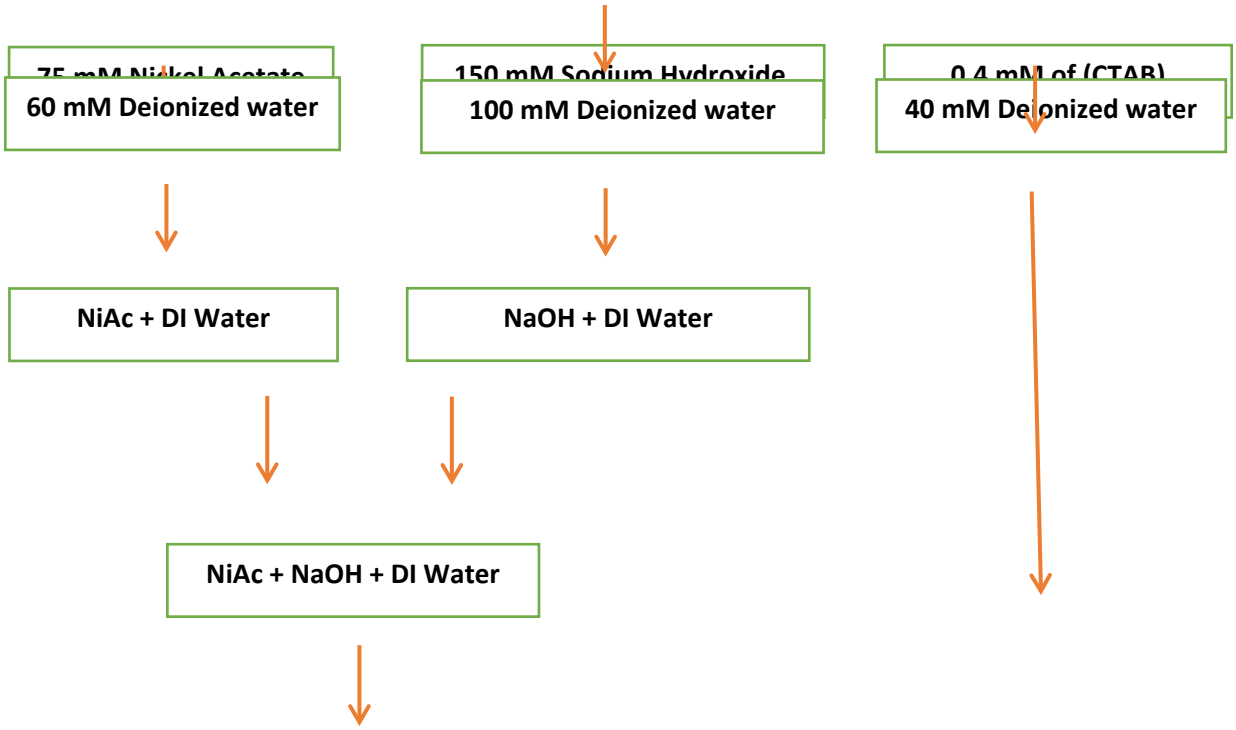
Abstract: Nickel Oxide nanoparticles prepared by sol-gel method to nanopowder, which is a bottom up way of synthesis. The main materials was sodium hydroxide (NaOH), nickel acetate and cety trimethyl ammonium bromide (CTAB), and extremely stirring until the pH becomes 7.5, and nanoparticles of (NiO) are prepared by chemical way of nickel hydroxide followed by heat treatment at 350°C. Nickel oxide is the kind of most important class of materials due to its interesting and important thermal properties and has many applications, such as in catalysis, sensors and so on. Structural properties were checked by X- Ray Diffraction (XRD) Structural and phases, transmission electron microscopy (TEM). The surface morphology of the sample was executed by scanning electron microscopy (SEM), the particle size of NiO increased with the increase in temperature. Compared with other methods, this method is simple and the materials were inexpensive. Finally our results showed that the chemical synthesis method leads to obtain nickel oxide nanoparticles with good microscopic characterization.

Keywords: - Nickel acetate, (CTAB), (NiO) NPs, (XRD), (TEM), (SEM)), chemical synthesis.

1. Introduction

Nanotechnology is revolutionizing human's life. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale. Synthesis and application of nanoparticles size (Lontio Fomekong et al., 2016) [1], at dimensions between approximately 1 and 100 nanometers (Mishra, Murugan, Kotakoski, & Adam, 2017) [2], where unique properties enable novel applications (Bera & Belhaj, 2016)[3]. Thus, a paper was conducted to create NiO Nanoparticles and successfully prepared with chemical method (sol-gel). the materials can be study of the physical, chemical, and biological properties (Skyrianou et al., 2009) [4]. To our knowledge, we have found new results about the preparation of nanomaterials using sol-gel method. In recent years, there are many who have worked on nickel oxide has been undertaken. The unique properties of nickel oxide whether physical such as magnetic properties (Jabbar, Jayapandian, & Kumar, 2015) [5] and p-type properties in solar cell (Hamzah, Jabbar, & Mesan, 2017)[6] or chemical made it interesting to researchers. NiO has been used as catalysts, electrochromic display devices, fuel cells and gas sensors. (Hassan, 2014) [7]. The characterization of (NiO) nanoparticles for structural properties were analyzed by X-Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM). The surface morphology of the sample was obtained by Scanning Electron Microscopy (SEM). Finally our results showed that the chemical synthesis method leads to obtain nickel oxide nanoparticles with good magnetic behavior. Nickel Oxide (NiO) is a p-type of semiconductor with a wide band gap (3.6-4.0 eV) and 1.8 eV of conduction band energy which has been considered as promising materials for optical, electrical [8, 9] and solid oxide fuel cells anode applications [10]. The purpose of this work is synthesis of (NiO) nanoparticales by the chemical precipitation process in the presence of sodium hydroxide, which is a simple way and low in cost since the starting materials are few and inexpensive [9-11]. The development of nanomaterials is attracting increasing attentions due to their unique physical and chemical properties that are different from conventional bulk materials.



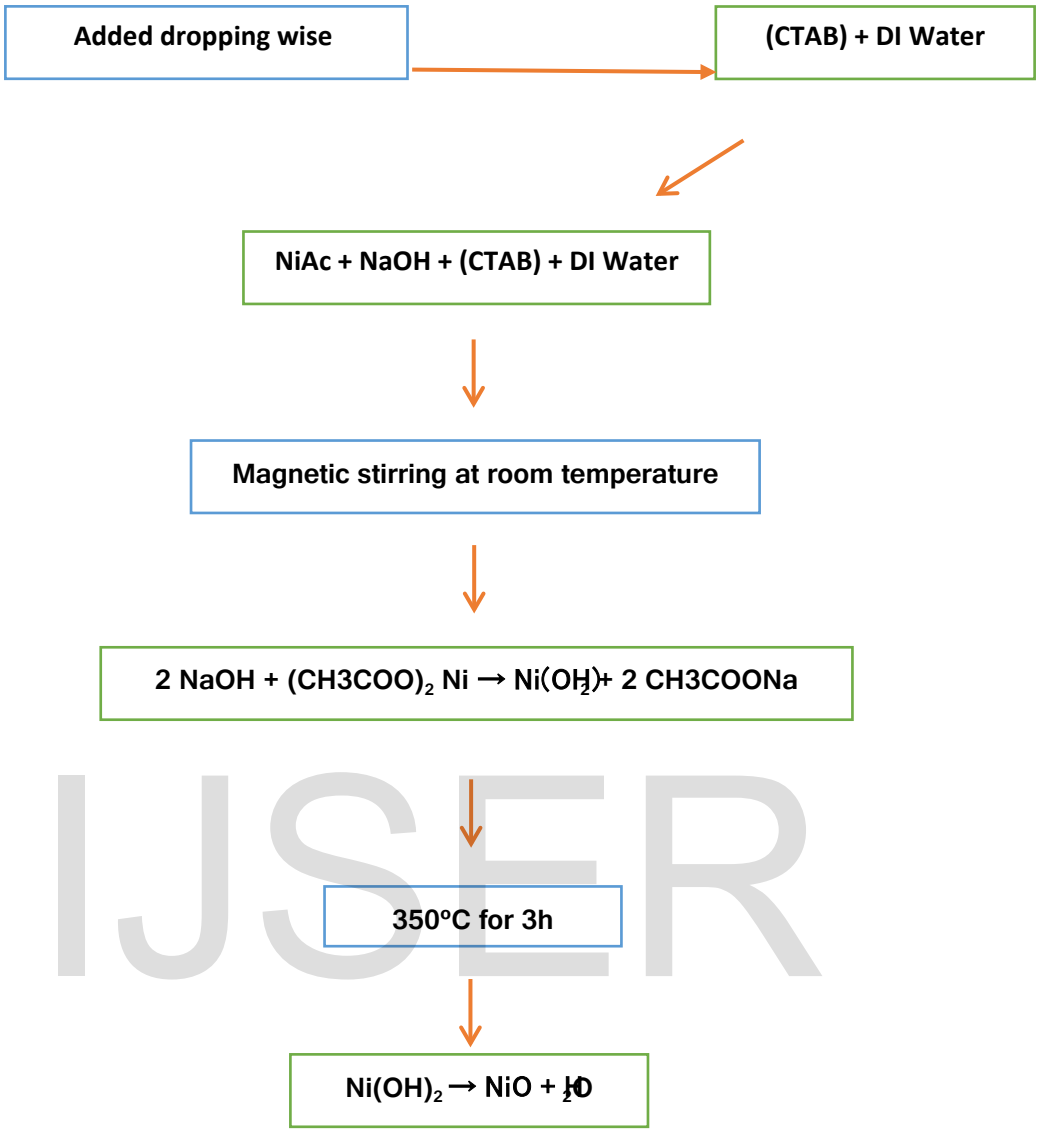


Fig. 1. Flowchart about the preparation of NiO nanoparticles.

After the process of developing the powder in the furnace becomes a Calcified Black color Nickel hydroxide decomposes into nickel oxide nanoparticles.

2- Experimentation or methodology

2.1. Preparation of NiO nanoparticles

There are various physical and chemical methods for the preparation of nanoparticles materials. In the present work nanoparticles of NiO were synthesized by Sol-gel method. The materials was Nickel (II) acetate $Ni(CH_3CO_2)_2$, sodium hydroxide (NaOH) and cety trimethy ammonium bromide (CTAB) were procured from Merk(India) Ltd India, and were used without any purification. First, we prepared two separate solutions, one of them solution of 100 mM of nickel acetate in 100 ml of deionized water and the other solution contains 200 mM sodium hydroxide in 100 ml of deionized water. An amount of 0.3 mM of (CTAB) in 50 ml was added latter to the solution. The NaOH solution added dropping into the later solution. The mixed solution was stirred by magnetic stirring at room temperature naturally. And second way used same procedure for second solution but in step magnetic stirring with heating and pH of the system reaches to 7.5, at room temperature also. In this chemical work (sol-gel method) use high frequency ultrasounds waves to remove By-products, precursor was filtered and the resultant green gel washed four times with distilled water.

2.2. Experimental Techniques

2.2.1. X- Ray Diffraction (XRD)

X-rays are electromagnetic radiation with photon energies in the field of 100 eV to 100 keV. In diffraction applications, X-ray used only with short wavelengths (X-ray harsh) in few angstrom at to 0.1 angstrom (1 keV to 120 keV). Because the wavelength of X-ray compares with the size of atoms, they theoretically appropriate in order to probe the structural arrangement of atoms and molecules in a broad spectrum of materials [11]. Powerful X-rays can penetrate deep material and provide us with information about the structure of matter. X-rays interact primarily with the electrons in the atom. When photons

collide to in X-ray electrons, deviate some photons package reaching from the original direction. If the wavelength not change of X-ray Fallen (ie X-ray photons did not lose any energy) called the process floppy Baltbosr or Thomson scattering where the momentum of the movement turns only in the process of scattering [12].

2.2.2. Transmission Electron Microscope (TEM

Transmission Electron Microscope is similar in design to an ordinary light microscope with one key difference: instead of using light, it uses electrons [13]. Using a cathode ray tube or filament (a source to generate highly excited electrons) in a vacuum, electrons are accelerated toward a given specimen by creating a potential difference. A series of magnets and metal apertures are used to focus this steam of electrons into a monochromatic beam, which then collide with the specimen and interact depending on the density and charge of the material [14]. These interactions are greatly affected by how your specimen is prepared.

2.2.3. SEM (Scanning electron microscopy)

In 1935 the original prototype of the SEM, which scans the specimen which an electron beam to obtain an image of silicon steel showing electron channeling contrast [15] Further pioneering work on the physical principles of the SEM and beam specimen interactions was performed by Manfred von Ardennes in 1937[16] who produced a British paten [17] but never made a practical instrument Scanning electron microscopy is used for inspecting topographies of specimens at very high magnifications using a piece of equipment called the scanning electron microscope[18]. "Stereoscan". The first instrument was delivered to Du Pont. The energy of the primary electrons determines the quantity of secondary electrons collected during inspection [19]. The emission of secondary electrons from the specimen increases as the energy of the primary electron beam increases, until a certain limit is reached. Beyond this limit, the collected secondary electrons diminishas

the energy of the primary beam is increased, because the primary beam is already activating electrons deepbelow the surface of the specimen [20]. Electrons coming from such depths usually recombine before reaching the surface for emission[21].

3- Result and discussion

3.1 XRD analysis

The XRD patterns of NiO are shown in Fig. 2. In the XRD pattern of the Indicator (a), no diffraction peak has appeared, so the structure of the precursor is amorphous. The diffraction peak of nickel oxide furnace at 350 °C has appeared obviously in pattern (b). It indicates that the nickel hydroxide decomposed into NiO basically at this temperature, after heating the color of this sample changes from green to black. The XRD different patterns of this sample at room temperature is shown in figure .2 from this patterns it is clear that the black colored sample is NiO.

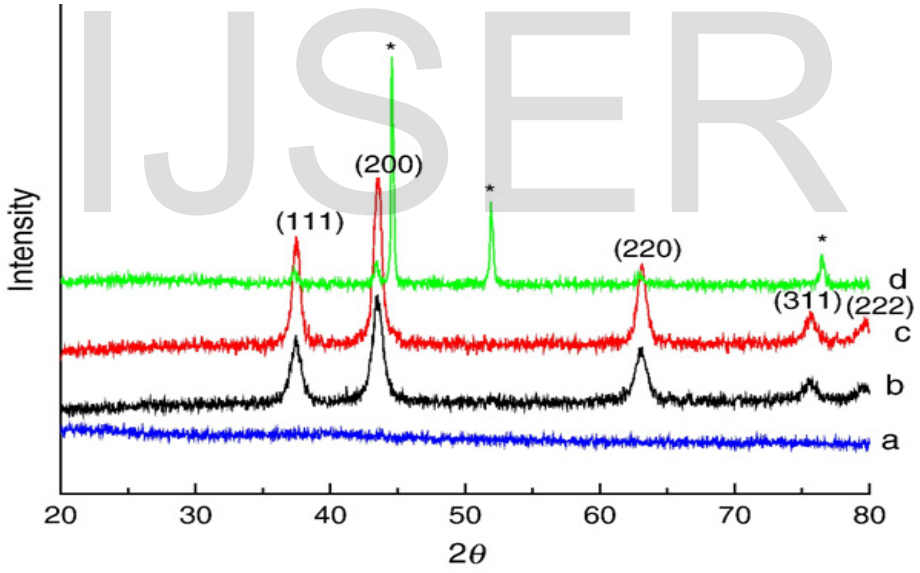


Fig.2. XRD different patterns at room temperature

Angle 2(θ)	d-value (A°)	Peak Width(2θ)	Peak Intensity (counts)	Relative Intensity (counts)	Identification (fromXRDstd Data)	Crystallite Size(nm)

37.060	2.4298	0.200	353	19.7	NiO(111)	41.77
43.095	2.1025	0.250	590	32.8	NiO(200)	34.19
62.620	1.4859	0.350	290	14.6	NiO(220)	26.60
75.090	1.2672	0.150	313	17.4	NiO(311)	60.25
79.185	1.2062	0.400	55	3.0	NiO(222)	29.70

Table .1. XRD data of NiO nanoparticles.

XRD data (table 1) shows the different peaks width 2θ. The crystallite size has been found to vary between 30 nm and 60 nm for various identified diffraction peaks (table1). The average crystallite size is calculated using the modified Scherrer formula.

$$\tau = \frac{K\lambda}{\beta\, COS\theta}$$

Where:

T is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, **K** is a dimensionless shape factor, with a value close to unity, **λ**is the X-ray wavelength, **β**is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle. The estimated grain sizes using Debye–Scherrer formula were found to be about 30 nm form XRD patterns.

3.2 Scanning Electron Microscope study (SEM)

The micrographs of the Scanning Electron Microscopy to NiO nanoparticles are shown in figure below. The cubic crystallites obtained by SEM, some of the cubic crystallites are determined by the boxes in figure 3. The micrograph also shows the conglomerate of the crystallites. The conglomerate may occur due to the crystallites being of nanodimension.

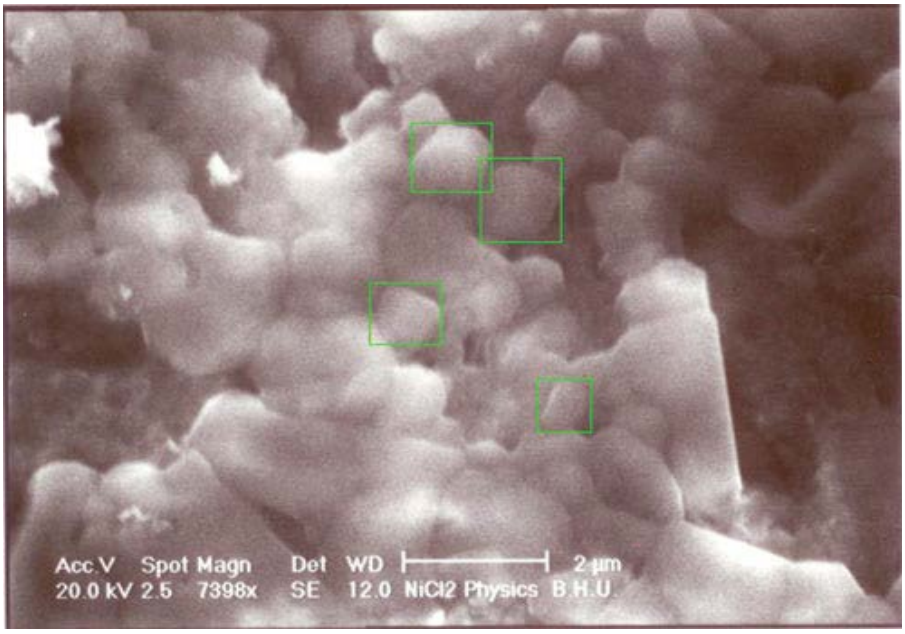


Figure 3. SEM micrograph of NiO nanoparticles prepared by heating Ni $(OH)_2$ precursor.

3.2.1 Effect of calcination temperature

Fig. 3 shows the SEM photographs of NiO samples calcinated at different temperatures. The photographs clearly show that the samples are spherical nanoparticles and the calcination temperatures have a great impact on particle size and distribution. The higher calcination temperature, the bigger the particles and the more maldistribution. The NiO sample calcinated at 350 °C has nanoscaled uniform particles with an average diameter of about 7.5 nm. Particle size increased with the increasing temperature. But the NiO sample calcinated at 350 °C is between 30–60 nm. As the calcination temperature gets higher, the particle is easy to agglomerate and the particle gets bigger.

3.2.2 Effect of pH value

As seen in Table 1, the average diameter of NiO nanoparticles is smallest and the surface area is largest when pH value is 1 and when pH is 7.5 the particle size is a little bigger. However when the pH value is higher than 1, the particle size grows bigger rapidly with solution pH value increasing. When pH is 8, the initial solution shows alkaline, and

the surface area decreases to 15 m2/g. which means they have the problem of agglomeration more or less. It is obvious that the solution pH value has more impact on average diameter: if pH value is too low, HNO3 is easy to be oxidized by citric acid during the process of evaporation, which leads to the concentration of ligand ion to decrease rapidly and coordination may be inadequate; on the contrary, if pH value is too high, the concentration of OH− is higher, the hydrolysis rate of metal ion accelerates and the obtained particles tend to agglomerate. When pH is equal to 1, the reaction of coordination rate is average and the obtained NiO nanoparticles are small and well dispersed.

3.3 Transmission electron microscopic (TEM)

In order to observe the detailed morphological differences of the NiO that exhibit drastic changes at specific calcination temperature, TEM images of nanoparticles were taken. On the other hand, the particle size of NiO is estimated by TEM images. The NiO nanoparticles obtained of [NiO] at 350^{O}C were chosen for TEM analysis, which is presented in Fig. 4. It can be observed from Fig 4, that NiO is made up of primary spherical particles which contain secondary ones with a diameter of 25nm this diameter is close to the estimated crystallite size by XRD analysis (25 nm). Fig. 2. Indicates that uniform spherical NiO nanoparticles were prepared from [NiO] 350 ^{O}C. The particle size of NiO obtained at 350 ^{O}C observes about 25–67 from TEM image.

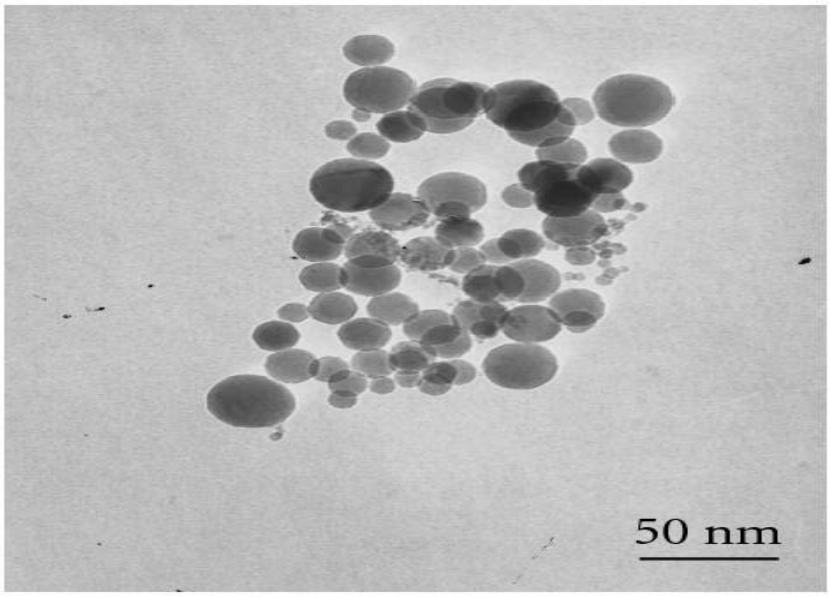


Figure 4. Transmission electron micrograph of NiO nanopowder synthesized by chemical route.

Conclusion

We have described an experimental procedure for the preparation of NiO nanoparticles based on chemical reduction of nickel acetate, sodium hydroxide (NaOH) and cety trimethy ammonium bromide (CTAB). Nanocrystalline NiO powder was synthesis by sol-gel technique, Nanoparticles prepared by the chemical decomposition of $Ni(OH)_2$ green colored sample nickel hydroxide by heating at 350°C. It's found to be antiferromagnetic at room temperature. The sample color changed from green to black. Nanoparticles of NiO are prepared by chemical way. The sample is described by X-Ray Diffraction, (SEM) and (TEM). Finally we got Nickel Oxide nanopowder black color.

Reference

[1] Skyrianou, K. C., Efthimiadou, E. K., Psycharis, V., Terzis, A., Kessissoglou, D. P., &

Psomas, G. (2009). Nickel-quinolones interaction. Part 1 - Nickel(II) complexes with the antibacterial drug sparfloxacin: Structure and biological properties. *Journal of Inorganic Biochemistry*, *103*(12), 1617–1625.

[2] Mishra, Y. K., Murugan, N. A., Kotakoski, J., & Adam, J. (2017). Progress in electronics and photonics with nanomaterials. *Vacuum*, *146*, 304–307.

[3] Lontio Fomekong, R., Ngolui Lambi, J., Ebede, G. R., Kenfack Tsobnang, P., Tedjieukeng Kamta, H. M., Ngnintedem Yonti, C., & Delcorte, A. (2016). Effective reduction in the nanoparticle sizes of NiO obtained via the pyrolysis of nickel malonate precursor modified using oleylamine surfactant. *Journal of Solid State Chemistry*, *241*, 137–142.

[4] Jabbar, A. H., Jayapandian, P. D. P., & Kumar, V. (2015). Study-Magnetic-Properties-And- Synthesis-With-Characterization-Of-Nickel-Oxide.docx, *6*(8), 94–98.

[5] Hassan, A. J. (2014). Study of Optical and Electrical Properties of Nickel Oxide (NiO) Thin Films Deposited by Using a Spray Pyrolysis Technique, (December), 2184–2191.

[6] M. Q. Hamzah, Abdullah Hasan Jabbar, Salim Oudah Mezan, "Synthesis and Characterization of Cu2ZnSnS4 (CZTS) Thin Film by Chemical Bath Deposition (CBD) for Solar Cell Applications", International Journal of Scientific Engineering and Research (IJSER), http://www.ijser.in/archives/v5i12/v5i12.php, Volume 5 Issue 12, December 2017, 35 - 37

[7] Bera, A., & Belhaj, H. (2016). Application of nanotechnology by means of nanoparticles and nanodispersions in oil recovery - A comprehensive review. *Journal of Natural Gas Science and Engineering*, *34*, 1284–1309.

[8] B. D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley Publishing Company, Inc.,

1956). Deki S, Yanagimoto H, Hiraoka S, Akamatsu K and Gotoh K 2010 Chem. Mater. 15 4916

[9] SchueleWJ and Deetscreek V D 1962 J. Appl. Phys. Suppl. 33 1136

[10] D. R. Askeland and P.P. Phulé, *"The Science and Engineering of Materials"* (4th ed., 2004).

[11] Elton J. Cairns (2010)" Electrochemical performance of TiO2 and NiO as fuel cell electrode additives". Volume 13, Issue 1, January 2011, Pages 75–77.

[12] Heh-Nan Lina. (2004) "Selective growth of vertically aligned carbon nanotubes on nickel oxide nanostructures created by atomic force microscope nano-oxidation". Chemical Physics Letters .Volume 399, Issues 4–6, 1 December 2004, Pages 422–425

[13] J. T. Richardson and W. O. Milligan, Phys. Rev. 102, 1289 (1956); J. T. Richardson, D. I. Yiagas, B. Turk, K. Foster, and M. V. Twigg, J. Appl. Phys. 70, 6977 (1991); S. A. Makhlouf, F. T. Parker, F. E. Spada, and A. E. Berkowitz, J. Appl. Phys. 81, 5561 (1997).

[14] K. Boer, ed, "Semiconductor Physics", Vols.1 and 2, Wiley, New York, 2001.

[15] Mu Y, Jia D, He Y, Miao Y, Wu HL(2010) "Nano nickel oxide modified non-enzymatic glucose sensors with enhanced sensitivity through an electrochemical process strategy at high potential". Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China.

[16] M. Sherif El-Eskandarany, Journal of Nanoparticles, Vol.2 (2009) pp14-22

[17] Prof. Dr.-Ing. Habil(2006)" Details of crystalline growth in co-deposited electroplated nickel films with hard (nano)particles". Volume 253, Issue 5, 30 December 2006, Pages 2399–2408

[18] A. Hasan, J. Working, and C. E. Techniques, “Study of Nano-Systems for Computer,” vol. 3, no. 5, pp. 63–68, 2015.

[19] I. Journal et al., “Energy Gap Investigation and Characterization of Kesterite Cu 2 Znsns 4 Thin Film for Solar ... Energy Gap Investigation and Characterization of

Kesterite Cu 2 Znsns 4 Thin Film for Solar Cell," vol. 6, no. January, pp. 4–8, 2018.

[20] Joseph Goldstein et al. "Scanning Electron Microscopy.

[21] JEOL 6700 SEM User Manual.