International Journal of Trend in Research and Development, Volume 8(5), ISSN: 2394-9333
www.ijtrd.com

Synthesis and Characterization of Nickel Nanoparticles

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Abstract-*N*ickel particles with starlike and spherical morphologies has been synthesized using nickel(II) chloride hexahydrate as a precursor andhydrazine hydrate with differnet molar ratios as a reducing agent in ethanol at 60 °C.the yield was 90 %and the as-obtained samples were characterized using X-ray diffraction (XRD),transmission electron microscopy (TEM), Thermo-gravimetry Analysis and Differential Scanning Calorimetry (TGA-DSC)andFourier Transform Infra-Red (FTIR) spectroscopy. XRDstudies confirmed that thesynthesized nickel is highly crystalline with face centered cubic structure.TEM images revealed the formation of a nickelstar-like shapewhen the molar ratio 10with an average size of 70-90 nm and a spherical particles shape with an average size of 50-80 nm when the molar ratio was 15.The nickel powders have an oxidization temperature of about 410 °C.FTIR showed only absorption band at around 550-600 cm^{-1}which confirmed the purity of synthesized nickel nanoparticles.

Keywords*—Reduction; Hydrazine; Nickel; Nanoparticles;.*

I. INTRODUCTION

Nickel metal has two manifestations of nanoparticles: nickel metal (NiNPs) and nickel oxide (NiONPs). These two classes of nanoparticles possess magnetic properties, biocompatibility, catalytic activity, antimicrobial activity and sorption nature. Further, NiONPsare semiconductor (band gap: 3.6 to 4.9 eV) with high chemical stability and electron transfer ability [1]. Hence these nanoparticles are finding wide applications in diverse fields such as electronics, energy applications, biomedicines, sensors, waste water treatment and various organic syntheses based on reduction, hydrogenation, alkylation and investigations are also being made in using these nanoparticles as adsorbents in water remediation methods [2]. Literature reports the synthesis of NiNPs using microwave assisted synthesis, micro-emulsion synthesis, chemical reduction technique using suitable reducing agents like sodium borohydride, and hydrazine hydrate, reversed micelles method, thermal decomposition of nickel (II)acetylacetonate in alkylamines and sol-gel methods [3][4][5][6][7][8][9][10][11][12][13][14].The commonly used precursors are nickel chloride, nickel sulphate, nickel acetate, nickel nitrate, nickel carboxylate etc. and the reducing agents are sodium borohydride, sodium hydride, hydrazine hydrate, organic amine (oleylamine), primary aliphatic amines (dodecylamine), sodium hypophosphite etc. and the capping agents are polyvinylpyrrolidone (PVP), sodium dodecyl sulfate, cetyltrimethylammonium bromide (CTAB) and the organic solvents used are ether, unsaturated alkynes, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, hexane, cyclohexane and octane etc[15]. Wu and Montero etal (2010)[16], synthesized pure spherical metallic NiNPs, by hydrazine reduction of Nickel chloride at room temperature without any protective agent and inert gas protection. This synthetic method is proven to be simple and very facile. In addition, it is very interesting to note that NiNPs can be isolated in stable solid state for several months in the atmosphere. The suggested mechanism for the NiNPs formation, as follows;

$$Ni^{+2} + 6C_2H_5OH \rightarrow [Ni(C_2H_5OH_6)]^{2+} (1)$$

$$[Ni(C_2H_5OH_6)]^{2+} + mN_2H_4 \rightarrow 6C_2H_5OH + [Ni(N_2H_4)_m]^{2+} (2)$$

$$[Ni(N_2H_4)_m]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + mN_2H_4\ 2\ (3)$$

$$Ni(OH)_2 + N_2H_4 \rightarrow Ni + N_2 + 2H_2O\ (4)$$

In a similar study by Elrbi and Paul (2012)[17], synthesized of NiNPs in a static microchannel T-mixer by the reduction of $NiCl_2{\cdot}6H_2O$ in the presence of ethylene glycol without a stabilizing/capping agent. In their study, Nanoparticles were formed in accordance with the modified polyol process with hydrazine used as a reducing agent and NaOH as a catalyst for nanoparticle format-ion.

II. MATERIALS

All chemicals used are of Analar grade except where stated.

III. METHODS

A. Synthesis of Nickel nanoparticles (Ni NPs)

3.0 g Nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$) were dissolved in 25 mL absolute ethanol. Solid sodium hydroxide 4.38 g (NaOH) were dissolved in 25 mL absolute ethanol, 5.4 and 8.2 g hydrazine monohydrate ($N_2H_4.H_2O$) were added to each solution. Then, (N_2H_4/NaOH) mixture was added to $NiCl_2.6H_2O$ mixture, solutions were maintained at 60 **C** with continuous stirring for 2 hours (ratio between Ni^{2+}/N_2H_4 was 10 and 15). The mixture turned blue (A) and after 2 minutes it turned to grey (B) and finally to black (C), the obtained precipitate was collected on a 0.45 μ filter, washed by absolute ethanol, deionized water and acetone and left to dry at room temperature.

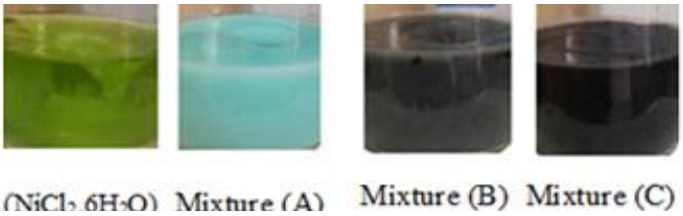


Fig. 1 Preparation of NiNPs

B. Material characterizations

XRD analysis was performed by PANalytical 3 kW X'pert Powder XRD Multifunctional diffractometer with Cu Kα radiation source (λ=0.1594 nm), and average crystal size of metallic nickel nanoparticles by applying the Scherrer equation;

$$d = \frac{K\lambda}{\beta}\cos\theta \quad (5)$$

Where; d is the grain size; K = 0.89 is the Scherrer constant related to the shape and index (h k l) of the crystal; λ is the wavelength of the X-rays; θ is the diffraction angle; and β is the corrected full width at half maximum (in radians).

The size of particles was measured by an H700H type Transmission Electron Microscope (TEM). The TGA and DSC analysis were conducted in nitrogen atmosphere on a NETZSCH STA449F3 thermal analyzer at a scanning rate of 10 **C**/min. FTIR analysis was conducted using FTIR-84005 (SHIMADZU Corporation Kyoto, Japan).

IV. Results and Discussions

Results of experiments conducted at room temperature, the reaction was not completed and no nickel was formed with both ratios. But, When the reaction temperature was raised to 60 C, the instantaneous generation of black precipitates was observed, and the reaction was completed in less than 5 min, the yield was 90 %, similar results were obtained by many researchers [8][18][19][20].

A. The X-ray Diffraction (XRD).

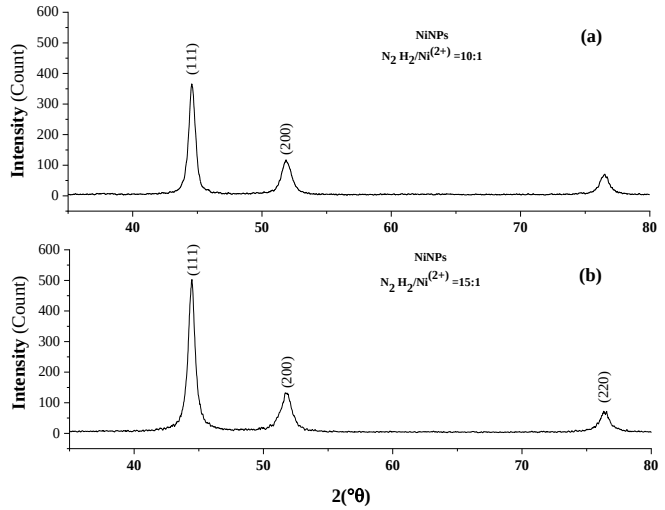
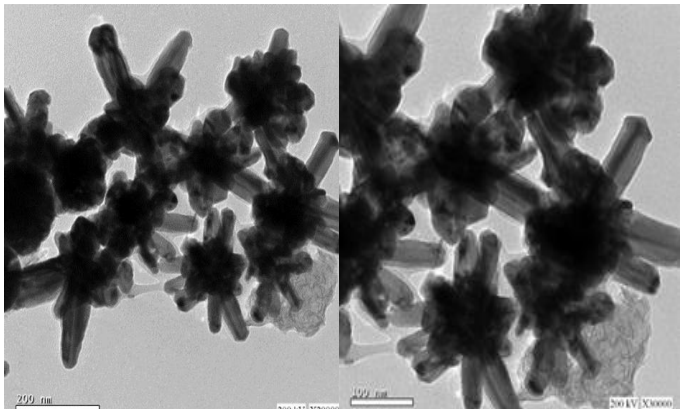


Fig. 2 XRD of NiNPs with the molar ratio(N_2H_4/Ni^{2+}) (a) 10:1 (b) 15:1.

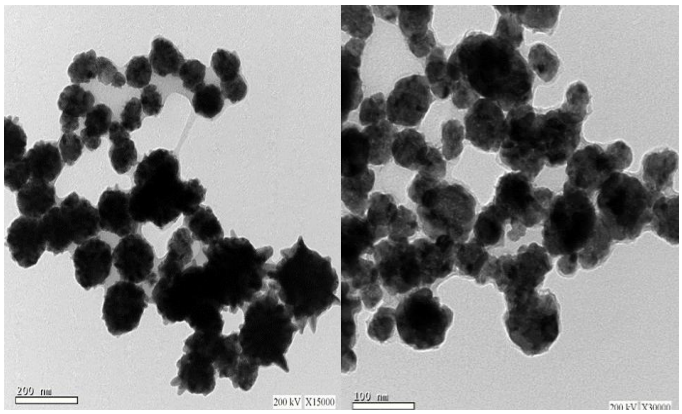
Fig.2 (a) and (b) showthe XRD pattern of NiNPs prepared with a molar ratio 10 and 15. The XRD spectrum when the ratio was 10 display three distinct diffraction peaks at 44.57°, 51.9°, and 76.4°. The highest intensity for the peak observed was at 2θ value 44.57°. Their corresponding miller indices (111) and (200) confirm that the resulting powders were face-centered-cube (fcc) nickel. the XRD spectrum when the ratio was 15, displays three distinct diffraction peaks at 44.52°, 51.70°, and 76.39°. The highest intensity for the peak observed was at 2θ value 44.52°. Their corresponding miller indices (111) and (200) confirm that the resulting crystalline particles were face-centered cube (fcc) nickel. No other species were observed in the XRD pattern, indicating that pure nickel powders. The XRD pattern matches that of the Joint Committee on Powder Diffraction Standards database (JCPDS PDF No.:04–0850) that confirms the random powdered arrangement for Nickel. Moreover, the average particle size determined using the Debye-Scherrer equation was found to be 12 nm for both ratios. The X-ray diffraction results evidenced that the nickel nanoparticles formed by the reduction of Ni2+ with hydrazine were crystalline and this is in good agreement with the earlier reports [7][8][10][18][19][20][21]. Phase analysis by XRD revealed that no oxides or hydroxide such as NiO, Ni_2O_3, and $Ni(OH)_2$ were formed.

B. Transmission Electron Microscope (TEM)



(a) (b)

Fig.3 (a-b): TEM images of 10:1 (N_2H_4/Ni^{2+}) molar ratio, (a)200 nm(b)100 nm



(a) (b)

Fig.4 (a-b): TEM images of 10:1 (N_2H_4/Ni^{2+}) molar ratio, (a)200 nm(b)100 nm

A typical TEM micrograph and the size distribution for the NiNPs are shown in Fig.3 (a-b) when the molar ratio of$N_2H_4/Ni^{2+}$was 10 and Fig.4 (a-b) when the molar ratio of$N_2H_4/Ni^{2+}$was 15. TEM images observed under low, medium, and high magnifications of the NiNPs, results when the molar ratio of$N_2H_4/Ni^{2+}$was 10 showed that the morphology is star-like with an average size 70-90nm, similar results were obtained by [20]. Fig.4 (a-b) TEM images observed under low, medium, and high magnifications of the NiNPs when the molar ratio of$N_2H_4/Ni^{2+}$was 15, results show that the morphology changed to monodispersed spherical particles with an average size of 50-80nm. It was found that, with increasing the ratio of N_2H_4/Ni^{2+}, the mean diameter decreased and the morphologies of NiNPs changed from star-like to spherical shape.

C. Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Fig.5 shows that the weight of nickel nanopowders stays constant or shows a very slight decrease (1.63% by weight) at temperatures below 270 C. This is probably caused by the absorbed residues such as water and/or carbon dioxide as the samples were exposed to the atmosphere [22]. The NiNPs begin to show weight gain at ~409 C in the thermogravimetric curve where a slight increase in the DSC curve is observed, an implication of oxidation occurs at this temperature. Comparing to the typical initial oxidation temperature of bulk nickel materials, ~ 600 C, the oxidation of NiNPs occurs at a much lower temperature. The fastest reaction occurs at ~ 410 C

where the DSC peak is detected due to the exothermic oxidationreaction.

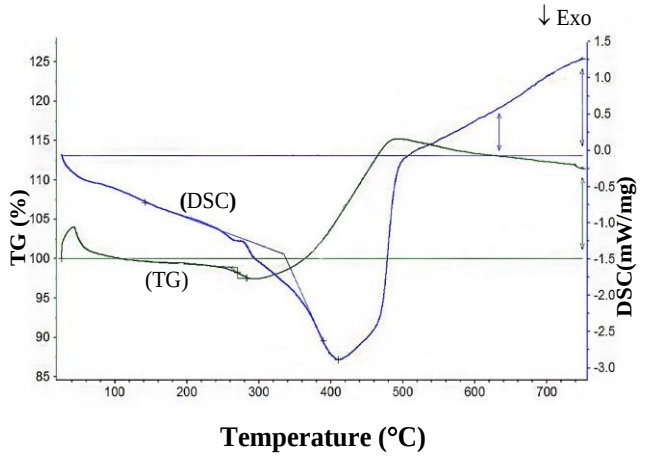


Fig.5 Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC).

D. Fourier Transform Infra-Red (FTIR) spectroscopy

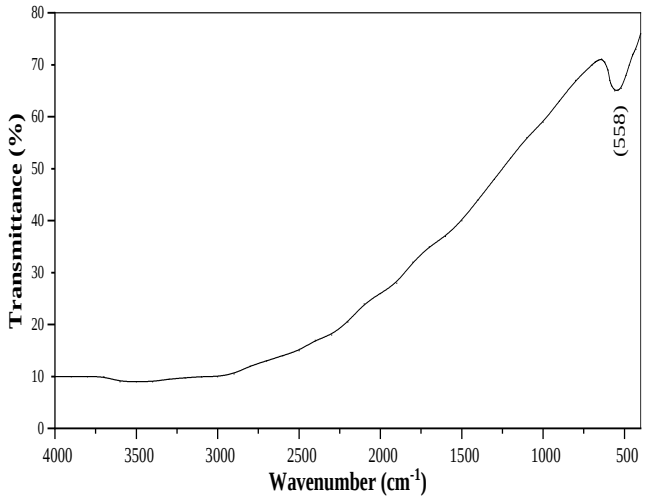


Fig. 6 FT-IR spectra of NiNPs.

Fig.6 shows the absorption band at around 550-600 cm^{-1} was the only peak observed, and it may be due to the metal nature [23].In other hand, absence of peaksin other regions demonstrates the purity of prepared NiNPs and absence of residual organic compound such as hydrazine and ethanol.

CONCLUSION

- Nickel nanoparticles (NiNPs) were synthesized using hydrazine monohydrate as a reductant of 10:1 and 15:1 (N_2H_2/N^{+2}) molar ratios in alkaline solution using ethanol as a solvent.
- No black precipitate of NiNPs were formed at room temperature
- When the molar ratio of$N_2H_4/Ni^{2+}$was 10:1, the shape of NiNPs was star-like with an average size of 70-90 nm.
- When the molare ratio was of$N_2H_4/Ni^{2+}$was 15:1, the shape of NiNPs was spherical with an average size of 50-80 nm, increasing molar ratio result in change in morphology and size of the NiNPs.

References

[1] F. Thema, E. Manikandan, A. Gurib-Fakim and M. Maaza, "Single phase BunseniteNiO nanoparticles green synthesis by Agathosmabetulina natural extract", *Journal of Alloys and Compounds*, vol. 657, pp. 655-661, 2016. Available: 10.1016/j.jallcom.2015.09.227.

[2] K. Ravindhranath and M. Ramamoorty, "Nickel Based Nano Particles as Adsorbents in Water Purification Methods - A Review", *Oriental Journal of Chemistry*, vol. 33, no. 04, pp. 1603-1613, 2017. Available: 10.13005/ojc/330403.

[3] T. LAI, C. LEE, K. WU, Y. SHU and C. WANG, "Microwave-enhanced catalytic degradation of phenol over nickel oxide", *Applied Catalysis B: Environment -al*, vol. 68, no. 3-4, pp. 147-153, 2006. Available: 10.1016/j.apcatb.2006.07.023.

[4] T. LAI, C. LEE, K. WU, Y. SHU and C. WANG, "Microwave-enhanced catalytic degradation of phenol over nickel oxide", *Applied Catalysis B: Environment -al*, vol. 68, no. 3-4, pp. 147-153, 2006. Available: 10.1016/j.apcatb.2006.07.023.

[5] R. Eluri and B. Paul, "Microwave assisted greener synthesis of nickel nanoparticles using sodium hypophosphite", *Materials Letters*, vol. 76, pp. 36-39, 2012. Available: 10.1016/j.matlet.2012.02.049.

[6] A. van Teijlingen, S. Davis and S. Hall, "Size-dependent melting point depression of nickel nanoparticles", *Nanoscale Advances*, vol. 2, no. 6, pp. 2347-2351, 2020. Available: 10.1039/d0na00153h.

[7] S. Liu, S. Tam and K. Ng, "Dual-reductant synthesis of nickel nanoparticles for use in screen-printing conductive paste", *Journal of Nanoparticle Research*, vol. 23, no. 3, 2021. Available: 10.1007/s11051-021-05191-8.

[8] S. Wu and D. Chen, "Synthesis and characterization of nickel nanoparticles by hydrazine reduction in ethylene glycol", *Journal of Colloid and Interface Science*, vol. 259, no. 2, pp. 282-286, 2003. Available: 10.1016/s0021-9797(02)00135-2.

[9] A. Ádám et al., "Ultrasound-Assisted Hydrazine Reduction Method for the Preparation of Nickel Nanoparticles, Physicochemical Characterization and Catalytic Application in Suzuki-Miyaura Cross Coupling Reaction", *Nanomateria -ls*, vol. 10, no. 4, p. 632, 2020. Available: 10.3390/nano10040632.

[10] X. Wu, W. Xing,L.Zhang, S.Zhuo, J. Zhou, G.Wang, and S.Qiao, "Nickel nanoparticles prepared by hydrazine hydrate reduction and their application in supercapacitor", *Powder Technology*, vol. 224, pp. 162-167, 2012. Available: 10.1016/j.powtec.2012.02.048.

[11] S. Sudhasree, A. ShakilaBanu, P. Brindha and G. Kurian, "Synthesis of nickel nanoparticles by chemical and green route and their comparison in respect to biological effect and toxicity", *Toxicological & Environmental Chemistry*, vol. 96, no. 5, pp. 743-754, 2014. Available: 10.1080/02772248.2014.923148.

[12] K.Harish, R.Renu, and S.Kumar,"Synthesis of Nickel Hydroxide Nanoparticles by Reverse Micelle Method and Its Antimicrobial Activity", *Research J. of Chemical Sci.*,vol. 1, pp. 42-48, 2011.

[13] Y. Chen, D. Peng, D. Lin and X. Luo, "Preparation and magnetic properties of nickel nanoparticles via the thermal decomposition of nickel organometallic precursor in alkylamines", *Nanotechnology*, vol. 18, no. 50, p. 505703, 2007. Available: 10.1088/0957-4484/18/50/505703.

[14] F. Jia, L. Zhang, X. Shang and Y. Yang, "Non-Aqueous Sol–Gel Approach towards the Controllable Synthesis of Nickel Nanospheres, Nanowires, and

Nanoflowers", *Advan -ced Materials*, vol. 20, no. 5, pp. 1050-1054, 2008. Available: 10.1002/adma.200702159.

[15] A. Pandey and R. Manivannan, "A Study on Synthesis of Nickel Nanoparticles Using Chemical Reduction Technique", *Recent Patents on Nanomedicine*, vol. 5, no. 1, pp. 33-37, 2015. Available: 10.2174/1877912305666150417232717.

[16] Z. G. Wu, M. Munoz, and O. Montero, "The synthesis of nickel nanoparticles by hydrazine reduction," *Advanced Powder Technology*, vol. 21, no. 2, pp. 165–168, 2010.

[17] R. Eluri and B. Paul, "Synthesis of nickel nanoparticles by hydrazine reduction: mechanistic study and continuous flow synthesis," *Journal of Nanoparticle Research*, vol. 14, no. 4, 2012.

[18] L. Bai, F. Yuan, and Q. Tang, "Synthesis of nickel nanoparticles with uniform size via a modified hydrazine reduction route," *Materials Letters*, vol. 62, no. 15, pp. 2267–2270, 2008.

[19] P. Khanna, P. V. More, J. P. Jawalkar, and B. Bharate, "Effect of reducing agent on the synthesis of nickel nanoparticles," *Materials Letters*, vol. 63, no. 16, pp. 1384–1386, 2009.

[20] L. Zhu, J. Cui, H. Zhang, L. Ruan, N. Ma, L. Zou, T. Deng, B. H. Chen, and Q. Xiao, "Room- Temperature Morphology- Controlled Synthesis of Nickel and Catalytic Properties of Corresponding Ru/Ni Catalysts," *ChemCatCh -em*, vol. 11, no. 13, pp. 3109–3116, 2019.

[21] H. Ghanbarabadi and B. Khoshandam, "Thermo-gravimetric synthesis of Ni nanoparticles with varied morphologies and particle sizes," *Particulate Science and Technology*, vol. 38, no. 6, pp. 685–693, 2019.

[22] P. Song, D. Wen, Z. X. Guo, and T. Korakianitis, "Oxidation investigation of nickel nanoparticles," *Physical Chemistry Chemical Physics*, vol. 10, no. 33, p. 5057, 2008.

[23] R. G. Chaudhary, "Synthesis Of Nickel Nanoparticles: Microscopic Investigation, An Efficient Catalyst And Effective Antibacterial Activity," *Advanced Materials Letters*, vol. 6, no. 11, pp. 990–998, 2015.