Synthesis and characterization of nickel nanoparticles by chemical reduction method

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Nanosized Nickel particles have been synthesized by chemical reduction method. The structure, morphology and optical properties of the as-synthesized Nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDXS) and UV-visible absorption spectrophotometer.XRD studies indicated that the as-synthesized Nanoparticles were pure crystalline nickel with a face- centered cubic (FCC) structure. SEM micrographs reveal that the Nanoparticles are mostly spherical with size around 17.97nm.EDXS analysis confirmed the presence of nickel Nanoparticles. The quantum size confinement of the crystallites is evident from the blue shift of the absorption edge in the UV-visible absorption spectrum.

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1. Introduction

When metal particles range in the size of roughly 1-50 nm, their surface area increases sharply with the decrease of particle size. The small metal crystals with high surface area are believed to be more active and have different structure and different properties different from bulk metal [1-3]. A number of methods such as photolytic reduction [4], solvent extraction reduction [5], sonochemical method [6], microemulsion technique [7], polyol process [8], and alcohol reduction [9] have been developed for the preparation of metal Nanoparticles. For the synthesis of several metal Nanoparticles, some metals such as nickel, copper, and iron are relatively difficult because they are easily oxidized. Stable Nickel Nanoparticles are promising candidates as they find applications in magnetic recording, catalysis, solid lubricants, conducting and magnetic materials, and also in pressure cells and hydrogen storage devices [10-12]. However, only a few works on the preparation of Nickel Nanoparticles have been reported until now. A suitable soluble polymer usually was added as a protective agent to produce many metal and bimetallic Nanoparticles. In the absence of soluble polymer, the resultant particles were in the micrometer or sub-micrometer size range [13-16]. However, by simple washing it was difficult to remove the soluble polymer on the surface completely. Thus, it might be an interesting challenge to prepare Nickel Nanoparticles without soluble polymer. In this work, in the absence of soluble polymer or other extra protective agents, the synthesis of Nickel Nanoparticles in ethylene glycol with hydrazine as a reducing agent was studied. The size, structure and optical features of the resultant Nanoparticles were characterized by Scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV-Vis-NIR spectrophotometer. Energy Dispersive X-ray Spectroscopy (EDXS) of Nanoparticles was performed to get information on their elemental composition.

2. Experimental

Ethylene glycol was supplied by Merck, India. Nickel chloride hexahydrate and hydrazine hydrate were obtained from Mumbai. Sodium hydroxide (NaOH) pellets was obtained from Loba Chemie. The deionized water was used throughout the experiment. Nickel sample was prepared by the methods reported earlier [17], using Nickel chloride hexahydrate as a precursor and hydrazine hydrate as reducing agent. An appropriate amount of $NiCl_2$ is dissolved in10ml Ethylene glycol. Then 15 ml hydrazine hydrate is added to above solution. NaOH, which acts as a catalyst of 10-92 μ/ml, are added in sequence and stirred well. The complete solution is kept in water bath for 1 h at 90^{o}C. During heating bluish green color precipitate slowly changed in to black color, indicating the formation of Nickel Nanoparticles. These Nanoparticles are cooled and collected, washed several times by ethanol and dried in the room temperature.

3. Results and discussion

3.1 Structural analysis

Fig. 1 shows the X-ray diffraction pattern of Nickel Nanoparticles**.** From the Fig. 1 three characteristic peaks for Nickel [2θ = 44.56˚, 51.85˚, 76.00˚] corresponding to Miller indices (111), (200), (220) are observed. This revealed that the resultant particles are pure face-centered cubic (FCC) Nickel. In Fig. 1, the intensity ratio of the peaks [111]: [200]: [220] are calculated to be [100, 26, 13] which exactly coinciding with the JCPDS [no: 040850] values. This revealed that the resultant particles are pure face-centered cubic (FCC) Nickel. This confirms the presence of Nickel particles in the sample and it is in good agreement with the earlier reports [18-20].

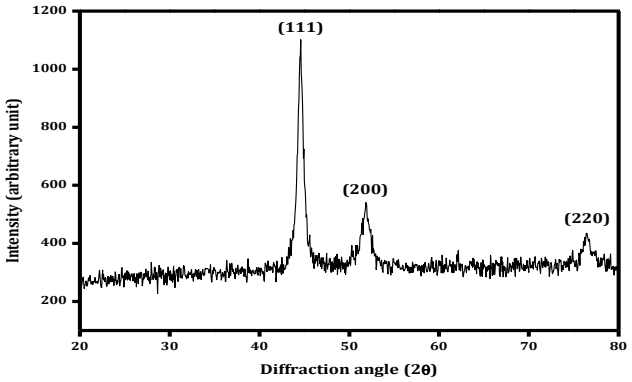

Fig. 1. XRD of Nickel nanoparticles.

From the full width at half maximum, the average grain size for the samples can be calculated. For the (111), (200), (220) diffraction peak, according to the Scherrer formula:

$$d = K\lambda / \beta \cos\theta, \quad (1)$$

where d is the grain size; K = 0.89 is the Scherrer constant related to the shape and index (hkl) 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).This calculation results in an average grain size of 17.97nm for the Nickel Nanoparticles.

No obvious peaks of Nickel oxides and hydroxides are detected, possibly it is attributed to the observed phenomenon that Nitrogen gas is produced and bubbled up continuously during the reaction. It could be suggested that the above said gas produced might auto create an inert atmosphere; hence the input of extra Nitrogen gas was not necessary for the synthesis of Nickel Nanoparticles [17]. The XRD pattern shows the presence of Ni with almost no peaks corresponding to Ni-oxide. This also indicates that the Nickel Nanoparticles prepared in this work have high purity**.**

3.2 Surface morphological studies

The particle size, shape and morphology are identified using SEM micrographs.SEM images of the obtained Nickel Nanoparticles are shown in Fig. 2. The SEM images show a typical morphology of Nickel Nanoparticles. The shape of the particles is nearly spherical with homogeneous size distribution. Nickel Nanoparticles are in the range of 17.97 nm. The crystallite size calculated from SEM analysis is quite agreement with that of crystallite size calculated from XRD analysis. In the reducing condition, the magnetic Nanoparticles are free, so that the motion or rotation of the Nanoparticle itself is easy. Because the anisotropic nature of the dipolar interaction favors the formation of the magnetic nano chains, the spontaneous self-assembly of the Nanoparticles in to unique structures such as nanochains occurs. As we know, the evolution of a solid from liquid involves two fundamental steps, i.e., nucleation and growth. The key factor for the formation of spherical Nanoparticles might be due to the difference of chemical environment of the nucleation and growth process.

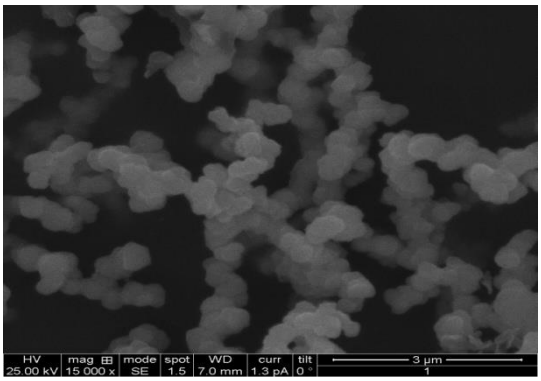

Fig. 2. SEM images of Ni nanoparticles.

3.3 EDAX

The EDAX analysis verified the composition of the small particles. EDAX analysis on various regions confirmed the presence of pure Nickel. This observation correlates with the XRD as well as the optical results. EDAX analysis is used to analyze the ingredients of its composition, indicating that the fabricated Nanoparticles contain elements of Ni and O. EDAX analysis result shows that in sample the weight percentage of O is 1.25% only, whereas that of Ni is as high as 98.75 % . Then, upon the comparison of XRD analysis, it is observed that the fabricated Nanoparticles have high percentage of pure nickel, as well as small quantities of oxides. The oxygen detected could be attributed to partial oxidation of the Nanoparticles which is due to the presence of some residual solvent or during the handling of the sample.

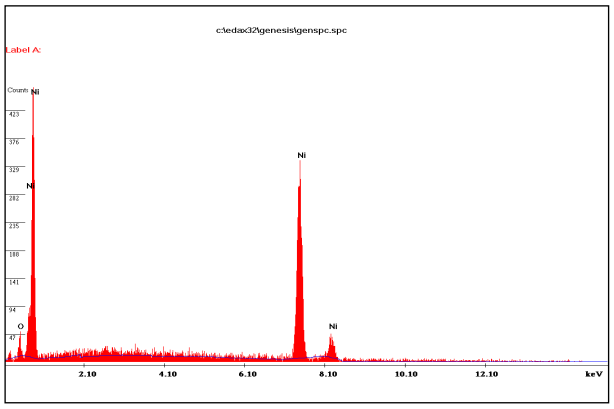

Fig. 3. Edax Spectra of Ni nanoparticles.

3.4 Optical studies

Fig. 4 is the UV- vis spectrum of the as-synthesized pure Nickel Nanoparticles. A strong absorption in the UV region is observed at wavelengths about 320 nm for the particle size of 17.97nm. Curtis et al. [21] found that Nickel bulk absorption presents, a band centered near 230nm. Galo Cardenas et al. have reported that Nickel particles of size 4.46 nm in Ni-2-propanol system shows an absorption band at 212 nm.

According to UV- vis spectroscopy, electrons are transferred from low-energy to high-energy atomic or molecular orbital's when the material is irradiated with light. Such electron transfer processes may take place in transition metal ions like nickel. The position of the absorbance maximum is not fixed but depends partially on the solvent in which the sample may be dissolved and on the molecular environment of the chemical functionalities that are responsible for absorption. So, a strong absorption in the UV region is observed at wavelengths about 320nm for the particle size of 17.97nm.The difference in position of the absorption band in the present investigation may probably due to the effect of excess addition of hydrazine which in turn increases the quantum confinement [22]. It confirms the presence of Nickel Nanoparticles. Fig. 5. shows optical transmittance spectra of the Nickel Nanoparticles. The Nickel Nanoparticles are transparent in a large range of wavelength.

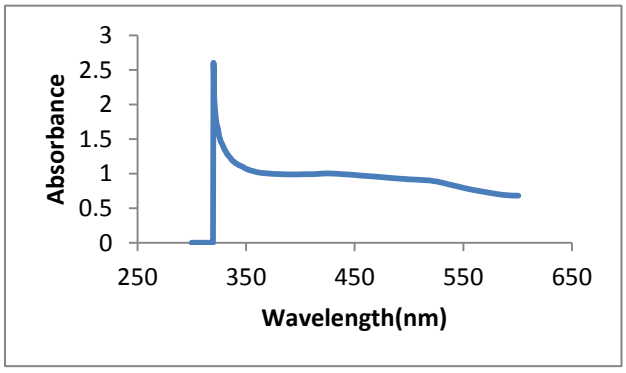

Fig. 4. Optical absorption spectra of Nickel nanoparticles.

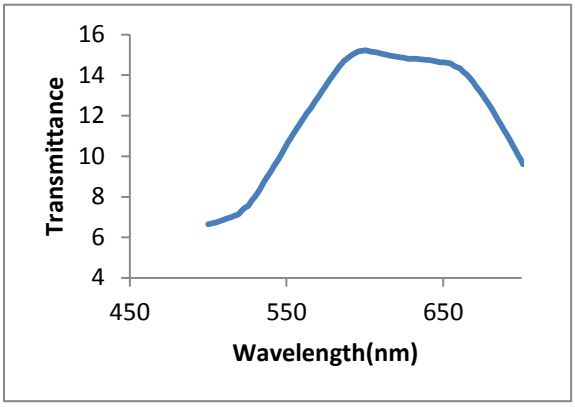

Fig. 5. Optical Transmittance spectra of Nickel nanoparticles.

3.5 PL Studies

Fig. 6 shows the photoemission characteristics of Nickel Nanoparticles at 371 nm. Two characteristic emission bands are observed at 205 nm and 215 nm with intensities 10.12 and 3.60 respectively. The PL spectrum correlates well that in these Nickel samples, the impurity state does not appear and the narrow PL lines indicates the good uniformity of nickel Nanoparticles and its high quality. The emission peaks found in the PL spectra are the characteristic features of Nickel Nanoparticles occurring due to the effect of quantum size.

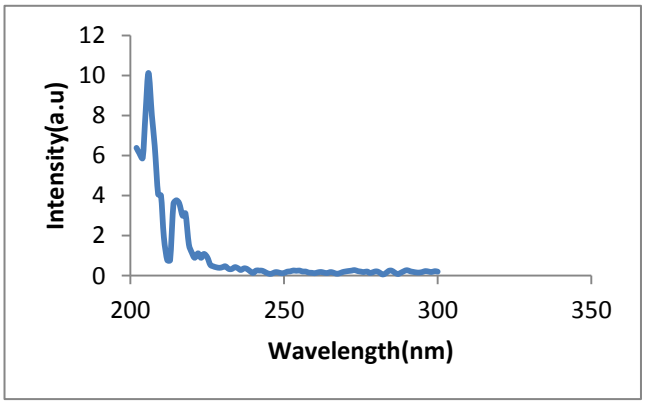

Fig. 6. Photoemission spectrum of Nickel Nanoparticles.

4. Conclusion

Nickel Nanoparticles have been synthesized by hydrazine reduction method of nickel chloride in ethylene glycol at 90^0 C without soluble polymer as a protective agent. No extra nitrogen gas was required to create an inert atmosphere due to the addition of NaOH trace. The resultant particles have been characterized and found to be pure nickel crystalline of FCC structure by XRD. UV-Visible spectroscopy curves were observed to be sensitive

to the characteristics of the Nanoparticles and the absorption spectra present an absorption edge at 320 nm. Photoluminescence characteristics strongly revealed the presence of quantum confinement effect in Nickel Nanoparticles.

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