

Two Steps Soft Chemical Method for the Synthesis of NiO Nanoparticles and its Characterization

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Abstract— A novel two steps soft chemical synthesis of defect free NiO nanoparticles has been approached. Materials mainly used in this project are nickel chloride (NiCl₂) as a basic material and sodium bicarbonate (NaHCO₃) as a precipitator material. UV-Vis, XRD and SEM were carried out to characterize the optical, structural and morphological properties of the synthesized samples respectively. Optical absorbance study in the photon wavelength range between 300 and 700nm reveals that strong absorbance peak is positioned at around 370nm (3.35eV) with corresponding band gap of 2.36eV. The observation from the XRD patterns ascertains the formation of cubic phase of NiO nanoparticles which is in accordance with that of the standard spectrum (JCP2.2CA: 47-1049) with lattice constant, $a = 4.159\text{\AA}$ and crystallite size varying between 30nm and 51nm. SEM reveals the uniformity of the average particles size and shape of the obtained NiO nanoparticles which is in good agreement with the average crystallite size calculated by the Scherrer formula from the XRD patterns.

Keywords—NiO nanoparticles, XRD, SEM, UV-Vis, Optical, structural and morphological properties of NiO nanoparticles

1. INTRODUCTION

Nanostructured metal oxides are the materials which exhibit significant electronic, magnetic, thermal and optical properties [1,2] in comparison with their bulk counterparts. NiO nanoparticles being wide band gap metal oxide act as a P-type semiconductor [3] and draw much attention due to its broad range of high technology application. It can be used in smart windows [4], electrochemical supercapacitor [5-7], as a transparent P-type semiconducting layer [8,9] and as an antiferro-magnetic film [10]. It can also be extensively used in dye sensitized photocathodes [11]. It exhibits anodic electrochromasim, excellent durability and electrochemical stability, large spin optical density and various manufacturing possibilities.

Also for low material cost as an ion storage material, NiO semiconductor becomes a motivating topic in the new era of research.

Different methods have been reported for the synthesis of NiO nanoparticles such as evaporation [12,13], magnetron sputtering [14-16] and sol-gel [17]. However, to the best of our knowledge, most of the reported synthesis techniques are still limited in laboratory scale due to special conditions, tedious procedures, complex apparatus, and high cost. Among various methods for controlled synthesis, the soft chemical route, based on solution process was used here to prepare single crystalline, defect free, cubic face shaped NiO nanoparticles.

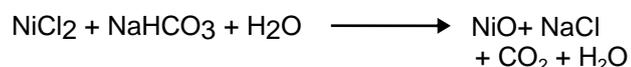
Recently, there have been reports on size induced effects in NiO nanoparticles in chemical method [18-20]. Srivastava et al. [21] have reported structural studies of NiO nanoparticles using XRD and SEM where as Chakrabarty et al. [22] have reported structural, morphological and optical studies of NiO nanoparticles using XRD, TEM, HRTEM and UV-Vis respectively. They have synthesized a series of NiO nanoparticles using chemical routes. All they have observed the strong absorption peak near about at 3.5eV and nearly transparent nature of the nanoparticles at visible region. The entire diffraction peaks from their studies are perfectly indexed to the fcc crystalline structure of NiO. They observed that nano-sized NiO nanoparticles in smaller size regime.

2. MATERIALS AND METHOD

Preparation of NiO Nanoparticles

The reagents used for the preparation of NiO nanoparticles were laboratory grade Nicle Chloride (NiCl₂) and Sodium Bicarbonate (NaHCO₃). In the synthesis shown in Fig. 1, two solutions of 2.3g NiCl₂ and 1.5g NaHCO₃ were prepared each mixing with 10ml of distilled water in glass container at room temperature. Then NaHCO₃ solution was added to the NiCl₂ solution drop wise with constant stirring. After 15

minutes of stirring the observed bluish precipitation was washed several times with distilled water in ultrasonic bath to remove NaCl and other unreacted precursors completely. The NiO nanoparticles most likely form via following reaction:



Finally the products were dried for 2 hours at 600°C which results the average composition of NiO nanoparticles.

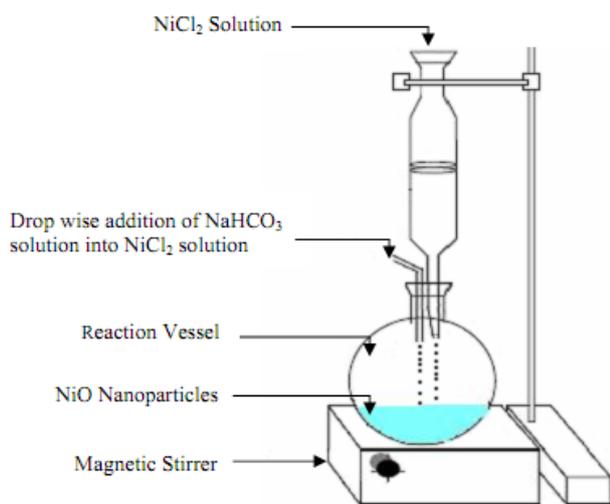


Fig. 1: Experimental setup for NiO nanoparticles synthesis.

3. RESULT AND DISCUSSIONS

UV-VIS Spectroscopy

Optical absorbance is a powerful method to determine the energy gap as well as optical properties of the samples. The UV-Vis absorption spectrum has been recorded by using a UV-Vis 1700 Shimadzu Spectrophotometer in the photon wavelength range between 300 and 700 nm. Fig.2 shows the UV-Vis absorption spectrum of chemically synthesized NiO nanoparticles dissolved with distilled water. As in Fig. 2 the optical absorption peak intensity has been found at 370nm (3.35eV).

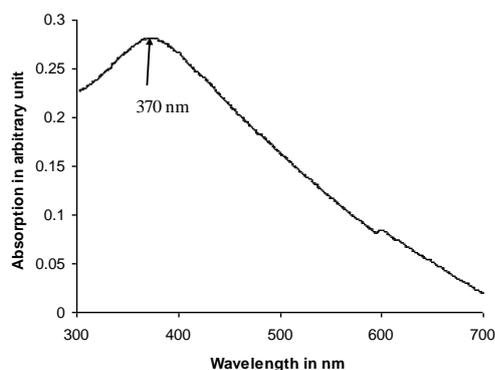


Fig. 2: UV-Vis absorbance curve of NiO

nanocrystals in the photon wavelength range between 300 and 700 nm.

From the curve we can calculate the band gap (E_g) energy of both the samples by the following equation [23]-

$$(\alpha h\nu)^n = B(h\nu - E_g) \quad (1)$$

in which $h\nu$ is photo energy, α is absorption coefficient, B is a material constant and n is either 2 for a direct band gap material or $\frac{1}{2}$ for an indirect band gap materials. Using equation (1) and taking the value $n = 2$, we can determine the corresponding band gap of the sample which have been found to be 2.36eV. It is interesting to notice that the values of band gap energy are lower than the energy reported by others [24,25]. These values also show good agreement with the reported data of Chakrabarty et al [22].

Here it is also observed that NiO nanoparticle is almost transparent in visible region and shows almost sharp absorbance peak around 3.35eV. The value $n = \frac{1}{2}$ does not produce any meaningful data for the band gap energy which corresponds that NiO is a direct band gap type semiconductor.

X-ray Diffraction

X-ray diffraction (XRD) is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials etc. The XRD of the synthesized NiO nanoparticles has been shown in Fig. 3 and the XRD data has been recorded in Table 1. This data clearly shows the distinct peaks at 2θ of 37.4°, 43.4°, 63.1° and 75.5°. The peaks have been identified as peaks of cubic NiO crystallites with various diffracting planes (111), (200), (220) and (021). The XRD patterns reveal the formation of cubic phase of NiO nanoparticles which is in accordance with that of the standard spectrum (JCP2.2CA: 47-1049) with lattice constant, $a = 4.159\text{\AA}$. The other peaks observed at an angle (2θ) of 31.9°, 56.7° and 66.7° which have been identified as Ni_2O_3 corresponds to (002), (202) and (004) crystal planes, respectively.

XRD data (Table 1) shows the peak width, 2θ , for various peaks. The broadened peak shows the nanometer-sized crystallites while the large crystallites are indicated by narrow peaks.

The average crystallite size has been estimated using the Scherrer formula [26]

$$d = K\lambda / \beta \cos \theta \quad (2)$$

where d represents the grain size, $K = 0.89$ is the Scherrer constant related to the shape and index (hkl)

of the crystals, λ is the wavelength of the X-ray (Cu Ka, 1.54056\AA), θ is the diffraction angle of the peak and β stands for the full width at half-height of the peaks (in radian) given by $\beta^2 = \beta_m^2 - \beta_s^2$, where β_m is the full width at half maximum (FWHM) of the sample and β_s is the half-width of a standard sample with a known crystal size greater than 100 nm, the effect of instrumental broadening on the reflection peaks is calibrated. The crystallite size has been found to vary between 30nm and 51nm for various identified diffraction peaks (Table 1).

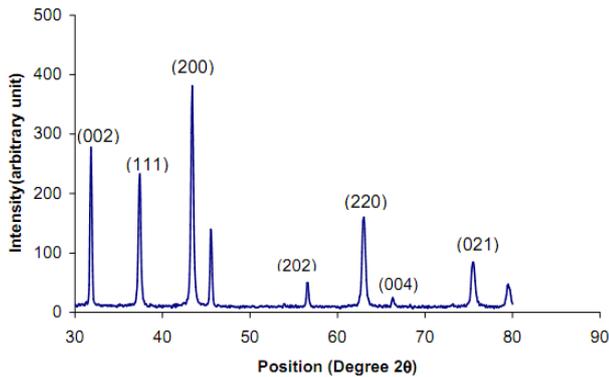


Fig. 3: XRD pattern of NiO nanoparticles. Corresponding planes are indexed within the figure.

Table 1: XRD data of NiO nanopartilces

| Angle (2θ) | d-Value (Å) | Peak Width(2θ) | Peak Intensity | Identification (from XRD std. data) | Crystal Size (nm) |
|------------|-------------|----------------|----------------|-------------------------------------|-------------------|
| 37.4° | 1.26 | 2.30 | 231.87 | NiO[111] | 36 |
| 43.4° | 1.12 | 1.7 | 381.45 | NiO[200] | 51 |
| 63.1° | 0.86 | 2.76 | 160.29 | NiO[220] | 33 |
| 75.5° | 0.79 | 3.0 | 84.576 | NiO[021] | 30 |

Scanning Electron Microscope

The Scanning Electron Microscopy (SEM) permits the observation of materials scanned over the surface of the specimen in macro and submicron ranges. The instrument is capable of generating three-dimensional images for analysis of particle size. Fig. 4 shows the SEM images of the product synthesized where the particle size was identified by measuring 100 particles.

The SEM micrographs reveal cubic crystallites of the prepared NiO nanoparticles with particle size varying between 30nm and 49nm. These sizes are probably as small as can be expected from soft chemical synthesis method. We notice that the mean particle size determined by SEM is in good agreement with the average crystallite size calculated by the Scherrer formula from the XRD patterns (as in Table 1). According to the SEM image, it could be concluded

that this preparation method had successfully overcome the problem of agglomeration and appropriate to obtain the NiO nanoparticles with smaller crystalline size.

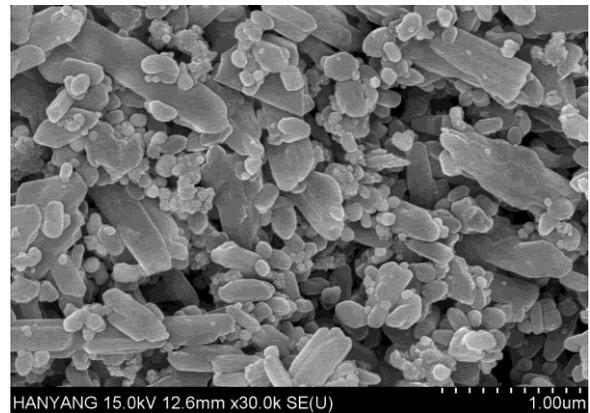


Fig. 4: SEM image of NiO nanoparticles.

For comparing the effect of surfactant on particle size distribution, however, the particle size has been identified by measuring 100 particles. Fig. 5 shows the results of such identification. The ranges of particle sizes vary between 30 nm and 49 nm. In this case, the maximum size of particles is less than 50 nm, and thus it results in small size particle. Most of the particles (about 47%) have the same and uniform size of 33 nm and near about 20 particles have less than 33 nm size.

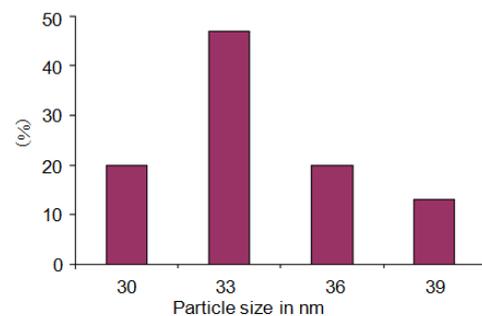


Fig. 5: Distribution of particle Sizes.

4. CONCLUSION

An efficient chemical method for the synthesis of NiO nanoparticles using nickel chloride and sodium bicarbonate as raw materials has been introduced. Different properties of the synthesized samples (dried at 600°C) have been validated on optically, structurally, compositionally, and on the basis of UV-Vis, XRD and SEM to assess the quality of synthesized nanoparticles. The majority of synthesized NiO nanoparticles have an average particle size less than 50nm.

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