Synthesis and Characterization of Nano-Dimensional Nickelous Oxide (NiO) Semiconductor

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ABSTRACT

In this work, single crystalline, defect free metal oxide (NiO) nanoparticle with diameter ~40nm was synthesized by only two steps soft chemical synthesis route. The crystalline nature of the sample was studied by X-Ray Diffraction method. TEM and HRTEM analysis was done to examine the morphology of the as prepared sample. The SAED pattern indicates the same crystal planes obtained from XRD study. The optical absorption characteristics were studied by UV-Vis Spectrophotometer and result shows the strong absorption peak at 3.75eV and nearly transparent nature of the nanoparticle at visible region. The photoluminescence properties were characterized by Fluorescence Spectrophotometer where the emission peaks was found at 3.62eV.

1. Introduction

The research in the area of nanostructured metal oxides, gradually to be interesting for their remarkable properties in electronic, magnetic, optical, thermal and mechanical fields [1]. Out of these, NiO (Nickelous oxide) nanoparticles, as an important metal oxide with a wide band gap, acts as a P-type semiconductor [2], draw much attention due to its broad range of high technology application. It can be used in smart windows [3], electrochemical supercapacitor [4-6], as a transparent P-type semiconducting layer [7, 8] and as an antiferro-magnetic film [9]. It can also be extensively used in dye sensitized photocathodes [10]. 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 [11, 12], magnetron sputtering [13-15], and sol-gel [16]. Among various methods for controlled synthesis, the soft chemical route, based on solution process was used here to prepare single crystalline, defect free, nonspherical shaped NiO nanoparticles. The crystalline phases associated with crystal planes were studied by X-ray diffraction (XRD). The structure and morphology of the samples were studied by TEM and HRTEM. Optical absorbance for the NiO was examined by

UV-Vis spectrophotometer and band gap energy was calculated from the absorbance curve. The details PL study of NiO reveals sharp emission peak at around 3.62 eV.

2. Experiment

Preparation of bare NiO nanoparticle: The synthesis process of NiO nanoparticles was done by only two steps method. Firstly 2.3gm $NiCl_2$ was dissolved in 10 ml distilled water, and 1.5gm $NaHCO_3$ was dissolved in 10ml distilled water in separate container. The $NiCl_2$ solution was stirred by a magnetic stirrer for 15minutes. Then the $NaHCO_3$ solution was added to the $NiCl_2$ solution drop wise with constant stirring. After 15 minutes the products were collected by centrifugation and thoroughly washed with distilled water. Secondly the collected product was dried at 100^oC. Then the dried sample was heated at 600^oC for 2h.

Rigaku Mini-Flex X-Ray diffractometer using Cu Kα radiation source and JEM 2010 Transmission Electron Microscope were used to characterize the structure and morphology of the samples. Optical absorption spectra of the powdered samples were recorded in a UV-VIS 1700 Shimadzu Spectrophotometer. The powdered sample were dispersed in ethyl alcohol and mounted in the sample chamber while pure ethyl alcohol was taken in the reference beam position. For photoluminescence measurement the samples were also taken in ethyl alcohol and the measurement were carried out in F-7000 Hitachi PL Spectrophotometer.

3. Result and Discussion

The details XRD patterns of the NiO nanoparticles are shown in fig 1. All the reflection peaks with relative intensities of different planes, indexed in the figure, specify the presence of NiO. The sharpness and the intensity of the peaks indicate the well crystalline nature of the prepared sample.

Size and morphology information of the samples are depicted in fig 2(a) and 2(b). The typical TEM images of NiO nanoparticles of fig 2(a) shows the nonspherical shape of NiO nanoparticles. From the image it is seen that a large number of NiO particles are present and if we consider single one of them the calculated average size is to be nearly equal to 40nm. Fig 2(b) represents the HRTEM of the sample. From HRTEM image the unidirectional fringe patterns are clearly observed which indicates single crystalline nature of NiO nanoparticle. The interplaner spacing'd' (distance of two successive lines), measured from the fringe pattern is 2.4A°, corresponds to the (101) plane which is also observed in XRD study, shown in fig1. Fig. 3 shows the selected area electron diffraction pattern (SAED) originated from the NiO nanoparticle and the planes calculated from the diffraction rings are same with the planes obtained from our XRD study.

Optical absorption spectrum of the NiO nanoparticle is represented in fig 4. The optical absorption peak intensity is found at 3.75eV (330nm). From the curve we can calculate the band gap (E_g) energy of the sample by the following equation [17]

$$(\alpha\ h\nu\ )^n = B(h\nu\ - E_g) \tag{1}$$

in which hν is photo energy, α is absorption coefficient, B is a material constant and n is either 2 for a direct band gap material or ½ 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 and the band gap energy of the NiO sample has been found to be 2.92 eV. It is interesting to notice that the value of band gap energy is lower than the energy reported by Boschloo [18] and Z Zhang [19]. Here it is also observed that NiO nanoparticle is almost transparent in visible region and shows almost sharp absorbance peak around 3.75eV. The value n = ½ does not produce any meaningful data for the band gap energy which corresponds that NiO is a direct band gap type semiconductor.

Fig. 5 shows the photoluminescence response curve of the sample. The PL characteristics was examined by exciting the sample with incident light of energy 4.12eV (300nm) and 3.99ev (310nm). The resulting emission characteristics show the origination of one main emission peak centered at around 3.62eV (341nm) with two other weak peaks at 3.77eV (328nm) and 3.46eV (357nm). The origin of the main peak associated with two feeble shoulders is attributed to the electronic transition of the Ni^{2+} ions. Optical absorption study reveals the existence of several transitions at energies below band gap in NiO [20]. Adler and Feinleib [21] reported a series of absorption peaks below 4eV as purely intraionic $3d^8$-$3d^8$ transitions of Ni^{2+}. The study of electron energy loss spectroscopy (EELS) and spin polarized electron energy loss spectroscopy (SPEELS) also confirm the existence of this kind of transition of the $3d^8$ electrons in NiO [22, 23]. Here also the luminescence peak of NiO sample is coming from the electronic transition of the cationic state and one can exploit this property of NiO nanoparticle as a good emitter of 341nm (3.62eV) wavelength.

4. Conclusions

In summery nano-dimensional NiO semiconductor was synthesized by very easy to achieve chemical route. The details of the morphology and crystal structure of the sample were characterized by XRD, TEM and HRTEM analysis. Optical absorbance study reveals that strong absorbance peak is positioned at around 330nm whereas visible energy band is almost transparent for the materials. Farther more the photoluminescence study of the sample reveals that the prepared semiconductor can successfully be used as an emitter of 341 nm (3.62eV) wavelength.
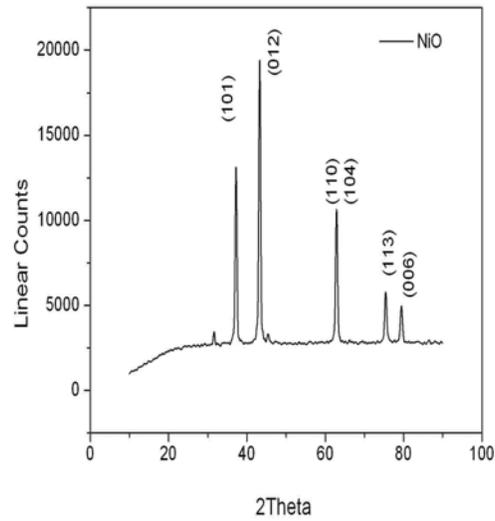
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Fig.1:   XRD pattern of NiO nanoparticles. Corresponding planes are indexed within the figure.
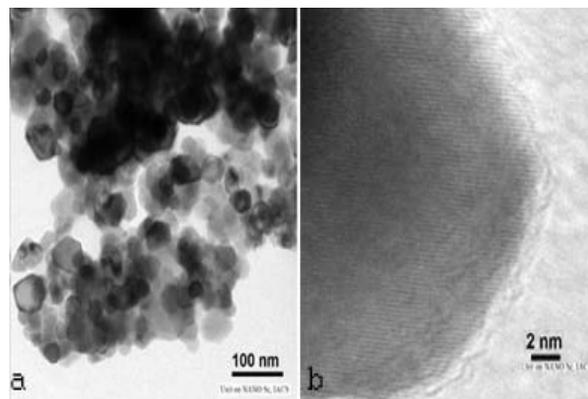

Fig.2: (a) Typical TEM image of NiO nanoparticles, (b) HRTEM image of NiO nanoparticles showing the fringe pattern of NiO crystal
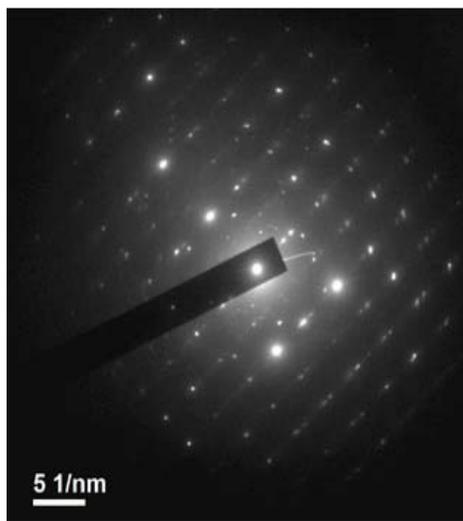
Fig.3: SAED pattern of NiO nanoparticles taken from the sample position shown in Fig. 2(b)
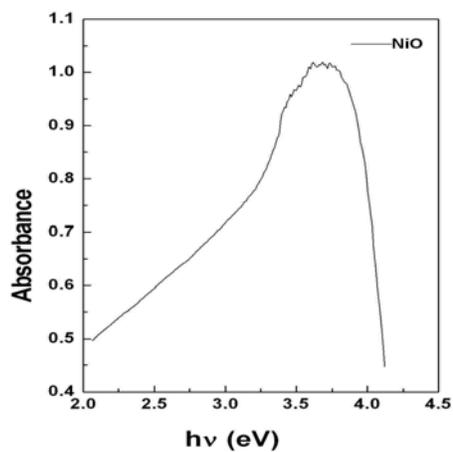
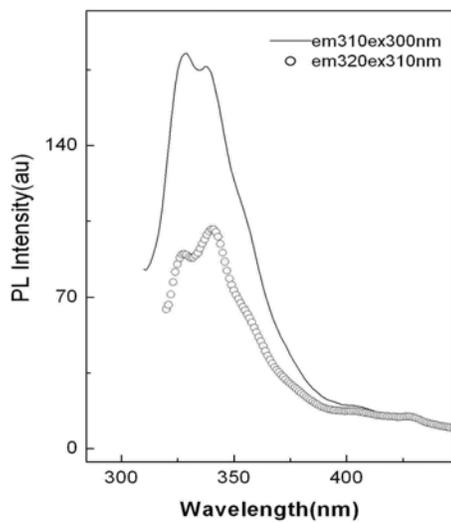Fig.4: UV-Vis absorbance curve of NiO nanoparticles

Fig.5: PL-spectra NiO nanoparticles at excitation wavelength 300nm and 310nm

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