

PL studies on NiO nanoflakes using natural Tabernaemontana Divaricata plant Leaves

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Abstract: In the present work, we have synthesized the NiO nanoflakes like structure via a complex precipitation method using $\text{NH}_3\text{H}_2\text{O}$ as a complexing agent. Structural analysis by X-ray diffraction, Fourier transform infrared spectroscopy and EDXS revealed the formation of single phase NiO with a Rhombohedral crystal structure. Morphological analysis by Field Emission scanning electron microscopy showed the formation of NiO architecture. Optical analysis by UV-Vis spectroscopy showed blue-shift in the optical band gap due to quantum confinement effect and light harvesting efficiency of NiO in dye solution of Tabernaemontana Divaricata plant leaves is also discussed. Photoluminescence spectroscopy has been employed in order to explore the optical emission properties of NiO nanoflakes.

Keywords: Complex precipitation, XRD, FESEM, UV, Natural dye.

1.Introduction

Nickel oxide (NiO) is a material that has been the subject of a considerable number of research studies, mostly on the basis of the unique electrical, optical and magnetic properties of the material [1]. NiO is considered a proto-typical p-type, wide band gap (3.6–4.0 eV) semiconductor exhibits great potential for broad applications such as anodes for lithium-ion batteries, solar cells, electro chromic coatings, anti ferro-magnetic materials, and in chemical(gas)sensing. smart windows, electrochemical super capacitors and dye sensitized photo cathodes[2]. These applications can be enhanced by decreasing the particle size and hence a precise control of the size and distribution in the nanometer region is required. Various techniques have been adopted for the synthesis of NiO nanostructures such as sol-gel [3], co-precipitation ,hydrothermal [4], Solvo-thermal [5] and chemical precipitation [6]. To some extent, all the above methods possess some disadvantages. Therefore, developing a simple, inexpensive and robust approach for the rational synthesis of NiO nanostructures under mild reaction conditions is still a challenging task and is highly desired for exploring NiO in device applications. Organic dyes resemble found in plants, fruits and other natural products and several of these have been used as the sensitizer in dye-sensitized solar cells [7]. Among the advantages of natural dyes is their easy availability, environment friendly, ease of fabrication, low process temperature and low cost of sensitization material production. Naturally most of the fruits, flowers and leaves show various colours and contain several pigments which are easily extracted and then employed as sensitizer [8].In the present work, we explore a facile and environmentally benign complex precipitation method using $\text{NH}_3\text{H}_2\text{O}$ as a complexing agent to synthesis NiO nanoflakes without using any surfactants or organic solvents. The natural dyes were extracted mostly from Tabernaemontana Divaricata (T.D) plants leaves using absolute EDTA(Ethylene di-

amine tetra acetate) solution. The structural and morphological properties of NiO nanoflakes were investigated using XRD, FTIR, FESEM and EDXS. The optical properties were investigated by UV-Vis spectroscopy and Photoluminescence measurements using T. D dye Solution.

2. Experimental

2.1 Materials

Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99 wt %), sodium hydroxide (NaOH, 96 wt%), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt%) and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) were purchased from Merck, India. All the reagents were of analytical grade and were used without further purification.

2.2 Synthesis of NiO nanoflakes and Preparation of Dye Solution

In a typical procedure, the Rod like shaped NiO nanostructure have been prepared as follows: 1.208 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added into 200 ml of distilled water under vigorous stirring to form a homogeneous solution. Then, 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added into the above solution drop by drop under vigorous stirring and kept for 30 min until a stable complex of $\text{Ni}(\text{NO}_3)_2$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ was formed ($\text{pH} = 8$). After that, 25 ml of $0.4 \text{ mol} \cdot \text{l}^{-1}$ NaOH solution was dropped slowly into the mixed solution ($\text{pH} = 11$) under vigorous stirring. After reaction, the obtained green precipitate were washed several times with distilled water and then with ethanol, and dried at 80°C for 24 hours. Finally, the product was calcimined in a furnace with an air atmosphere at 400°C for 2 hours [9]. The T.D plant leaves were collected and washed with distilled water. Washed leaves were dried and crushed in a mortar to bring them into powder form. One gram of the T.D powder was then dissolved in EDTA at room temperature in the dark for 24 hrs to extract the dyes (to liberate the dye molecules present in the sample) and the solid residues were filtered out and the UV-Vis absorption measurements were carried out using 0.5g of the annealed NiO nano flakes powder was dissolved in 10 ml of dye solution [10].

3. Result and Discussion

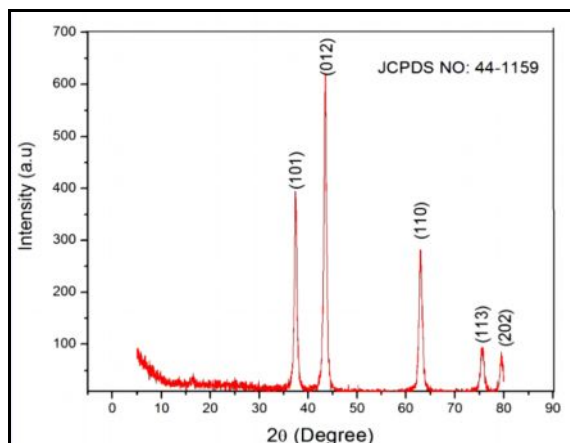


Figure 1 . XRD Pattern of NiO Nanoflakes

The crystalline and crystal phase of NiO nano flakes were examined by XRD and the result is shown in Fig. 1. All the diffraction peaks in the pattern can be indexed to the Rhombohedral structure of NiO. The sharp peaks indicate the well-crystallized single phase NiO nano crystals [11]. The crystallite size of NiO structures is determined from the reflection peak width employing Debye-Scherrer's relation given by Eq. (1),

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

Where **K** is the shape factor (0.90), λ is the wavelength of $\text{CuK}\alpha$ radiation, β is the full-width at half maximum (FWHM), and θ is the angle of reflection. The mean crystallite size was found to be 30 nm. Fig. 2 shows the FTIR spectrum of NiO nano flakes powder used to detect the possible absorbed species on the NiO nano

powder. The absorption peak in the range of $3400\text{-}3300\text{ cm}^{-1}$ corresponds to the stretching vibration of OH bond. The peaks at 765 cm^{-1} correspond to the characteristic stretching vibrations of Cu-O bond in the Rhombohedral NiO, which indicates that the products are well crystallized[5]. Energy dispersive X-ray Spectrum (EDXS) was carried out at 20KeV electron energy using SEM and is shown in Fig.3, confirms the presence of Ni and O peaks. There were two peaks relevant to Ni at about 1Kev and 7.5KeV. The atomic ratio of nickel and oxygen is 76.03 : 23.97 which can be assigned to NiO [12]. Fig. 4 shows the FESEM images of NiO nanoflakes synthesized via complex precipitation method. It can be observed that the alkaline precursors have substantial impact on the growth of NiO nanostructures. NiO synthesized using NH_4OH as complexing agent showed the formation of NiO nano structure with flake like. The nanoflakes agglomeration occurs to minimize their surface free energy.[13].

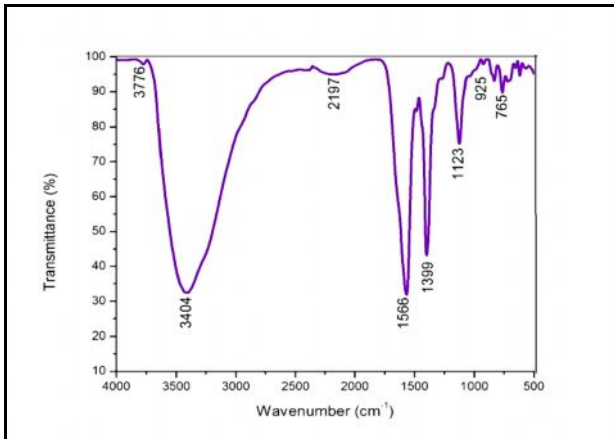


Figure 2 . FTIR Spectrum of NiO Nanoflakes

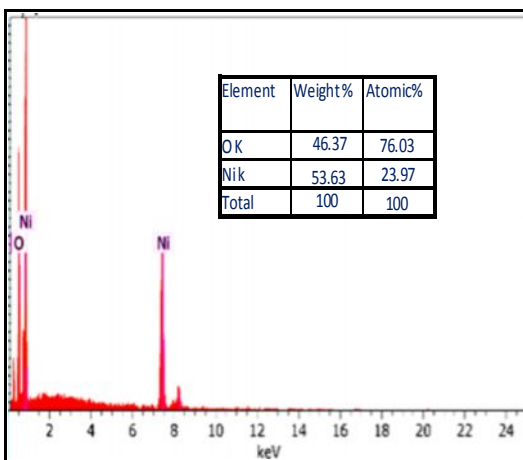


Figure 3. EDAX Spectrum of NiO nanoflakes

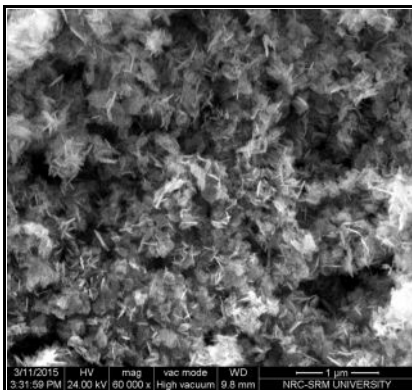


Figure 4. FESEM images of NiO nanoflakes

3.2 Optical Properties

The absorption spectrum of NiO nanoflakes, observed in the UV region, is depicted in Fig. 5. and it was used to study the optical properties of the synthesized NiO nanoflakes dissolved in T.D dye solution. The value of the band gap for the NiO nanoflakes was estimated by using Tauc equation 2.

$$\alpha h\nu = A (h\nu - E_g)^n \quad (2)$$

where α is the absorption coefficient in cm^{-1} , $h\nu$ is the photon energy, E_g is the energy gap, A is the energy

dependent constant and n is an integer that can take different values depending on the type of electronic transition, for a permitted direct transition $n=1/2$ and indirect transition $n=2$. The inset of Fig. 5 shows the plot

of $(\alpha h\nu)^2$ versus $h\nu$ for the NiO sample. From the plot, the band gap value of the NiO nano flakes by the

extrapolation was found to be = 3.30 eV, which is close to the values reported earlier [14].

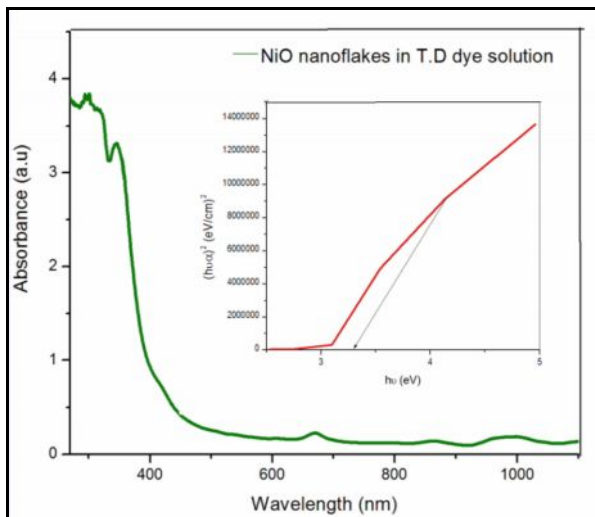


Figure 5. UV-Visible Spectrum of NiO

3.21 Dye spectral response & Light Harvesting Efficiencies (LHE)

Table 1:LHE of the NiO nanoflakes in T.D dye solution

Sample	Wavelength, λ (nm)	LHE (%)
NiO nanoflakes powders in T.D dye solution	287	99.98
	327	99.94
	643	32.50
	974	34.86

The dye spectral response & LHE were calculated from Fig.5. The small absorption peaks at 287nm and 327 nm indicate the presence of NiO in dye solution [1].The absorption peak is at 643 nm which are indicative of the presence of chlorophyll a. Besides the optical absorption spectra, LHE of the sample were calculated by using the following formula from Eq.3 [15].

$$\text{LHE} = (1 - 10^{-A(\lambda)}) \times 100 \quad (3)$$

Where $A(\lambda)$ is the absorbance at a specific wavelength. LHE is maximum at UV-Vis region and minimum at infrared region.

3.3 Luminescence spectra

The room temperature Photoluminescence spectra of NiO nanoflakes are shown in Fig.6, at the Excitation of 345nm. The strong emission peaks located at 455nm (2.73 eV) is due to the band edge emission from the new sublevels at 300 K or maybe due to the defects present in the NiO nanostructures. The emission peaks (IR band) at 704 nm (1.7 eV) ascribed to the specific surface effect, which results in the red-shift of the Fluorescence emission. [16]. Thus, considering these parameters in the design of NiO-based photo-electronic devices is important.

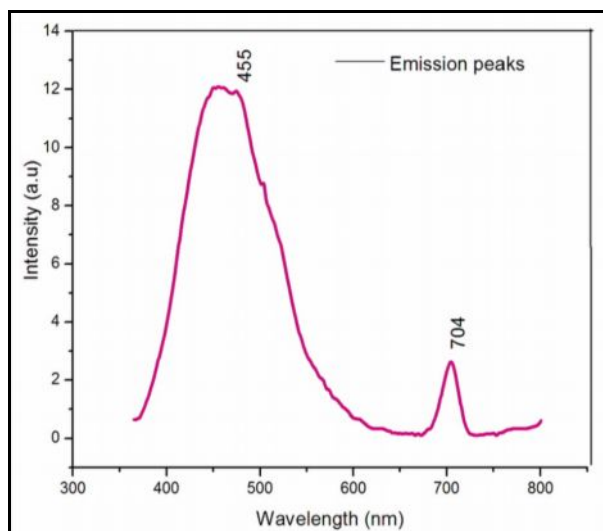


Figure 6. Luminescence Spectra for NiO nanoflakes

4. Conclusion

In this work, NiO nanoflakes have been prepared by complex precipitation method using $\text{NH}_3 \cdot \text{H}_2\text{O}$ as a complexing agent and NaOH as a precipitant. UV-Vis spectrum shows the optical properties and light harvesting efficiency of NiO in T.D dye solution and Photoluminescence spectrum revealed that this NiO nanoflakes is a good candidate for photo electronic devices in the UV-Vis-IR range and T.D dye solution plays a vital role in increasing light harvesting efficiency. So this can be used as sensitizer in DSSc applications.

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