Investigation of Structural, Morphologicaland Optical Properties of Ni Doped Cdonanoparticles for Bactericidal Applications

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Abstract

Recently in the biomedicalfield, CdO nanoparticles with novel micro or nanostructures have been at the cutting edge of research,due to their multi-drugresistant ability of several pathogenic microorganisms. Pure and Ni doped cadmium oxide nanoparticles are preparedby co-precipitation method. The change in structure and morphology of the samples while doping are studied using PXRD,FESEMand Raman analysis. The optical characteristics are found using PL andUV visiblespectroscopy. The observed PXRD spectra confirms the polycrystalline nature and cubic (fcc) structure of CdO nanoparticles.FESEM images show that Ni doped CdO nanoparticles exhibited rod-like morphology. Two optical modes in cubic CdO are detected using Raman spectrum. The blue and green emission observed in the PL spectrum indicates thatthe particles are in nano regime. The absorption bands of the pure and Ni doped CdO nanoparticles observed in UV spectrum shows a blue shift which is due to the quantum confinement of the developed nanoparticles.

Keywords -*Co-precipitation, Cadmium oxide nanoparticles, PXRD, FESEM, Raman, PL, UV spectroscopy*

I. INTRODUCTION

In recent years, much attention has been focussed on nano-crystalline oxide materials due to its wide range of applications [1-3]. CdO belongs to n-type semiconductor metal oxide with bandgap energy 2.5 eV. Large number of surface atoms is an important reason for the outstanding properties of CdO nanoparticles [4-6]. Cadmium Oxide (CdO) is a unique chemical which has both semiconductor and piezoelectric characteristics [1, 7]. Among II–VI compounds, CdO is an exceptional compound semiconductor due to its properties like wide and direct and gap, high transmission in visible region and high conductivity [7-9]. Cadmium oxide has been used in applications such as photodiodes, phototransistors, photovoltaic cells, gas sensors, liquid crystal displays, solar cells, IR detectors, and anti-reflection coatings [1-3]. The transition metal ions have different d-d transition and could split to numerous levels. Many transition metals (Cr, Fe, Co, Ni, Cu, Mg, Au, In etc.) were used as dopants in II-VI semiconducting nanoparticles [10].Nickelhasbeen used as a dopant to alter the optical properties of the nanomaterials.

There is development of rapid, simple, cost-effective and eco-friendly procedures for the synthesis of nanoparticles of different sizes, shapes and controlled dispersity [11-12]. Various chemical methods have been reported for synthesizing the nanostructure of cadmium oxide (CdO) but most of the methods are so expensive and complex, especially for controlling the size of particles and uniformity of their size. Hence co-precipitation method is chosen for its simplicity and good yield for the preparation of pure and doped CdOnanopowder samples [7,13].

In the present work, pure and Ni doped CdO nanoparticles are synthesized by simple co-precipitation method and the structural, morphological and optical properties of pure and Ni doped Cadmium oxide (CdO) nanoparticles are studied.

II. EXPERIMENTAL DETAILS

0.5 M of cadmium acetate was dissolved in 100 ml of double distilled water. Also 0.5 M of urea was dissolved in 100 ml of double distilled water. Both the solutions were stirred using magnetic stirrer for 30 minutes at room temperature. Then cadmium acetate solution was added dropwise into the urea solution. Required amount of liquid ammonia was added dropwise to the prepared solution until the pH of the solution becomes 10. During this process, precipitation was observed in the solution. Then the solution was washed using double distilled water for five times and finally it was washed using ethanol. Then the solution was dried in a hot plate at 100^0 C for 3 hours. Then it was finely ground and calcined in the muffle furnace at 300^0 C for 2 hours. Finally the reddish brown coloured pure CdOnanopowder was formed. In this work, Nickel (transition element) has been doped with CdO at a concentration of 0.01M.

For doping nickel, 0.01M of nickel acetate was dissolved in 100 ml of double distilled water. It was then added dropwise to the prepared (0.5M of cadmium acetate in 100 ml double distilled water + 0.5M of urea in 100 ml double distilled water) solution. Ammonia solution was added dropwise to the mixed solution until the pH of the solution becomes 10. And then the same procedure given above for the preparation of pure sample is followed to prepare Ni doped CdOnanopowder.

The structural analysis was carried out by recording the powder X-ray diffraction (PXRD) spectrum at room temperature using X-ray diffractometer (PANalyticalX'Pert) recorded in the 2θ range of 30^0–80^0 using Cu-K_α radiation (λ = 1.5406 Å). The morphological analysis of the prepared samples was carried out in a FESEM analysis. To get clear images and to determine the particle size of the synthesized samples Field Effect Scanning Electron Microscope (FESEM) was used. Raman spectra for the samples was carried out using Laser Raman Spectrometer. The Raman scattering (RS) technique, based on inelastic light scattering, is a well established procedure for the fast and non-destructive measurement of stress, crystal lattice disorder and homogeneity of materials with up to ~100 nm spatial resolution. Photoluminescence spectrum for the prepared nanoparticles was recorded using photoluminescence spectrophotometer (Varian Cary Eclipse) and the emission spectra were recorded at a scan rate of 600 nm/min in the range of 340 nm – 600 nm using an excitation wavelength of 320 nm. UV visible spectroscopy analysis was carried out by a computer controlled UV-vis spectrophotometer (JASCO) at the wavelength of 900–200 nm possessing a scanning speed of 400 nm/min and at a resolution of 1 nm. A small amount of the nanoparticles was dispersed by sonication process for the measurement of optical absorbance.

III. RESULTS AND DISCUSSION

A. *PXRD Analysis*

The JCPDS File No. 65-2908(a = b = c = 4.691Å; V = 103.51 $Å^3$) is used to index the PXRD spectra of pure and Ni doped CdO samples as cubic lattice. However, the diffraction peaks of doped samples are slightly shifted to lower angles when compared to the pure sample (Fig.1). This may be due to the substitution of Ni^{2+} with a smaller ionic radius of 0.69 Å to Cd^{2+} (0.97 Å) lattice sites. The average grain size of CdO nanoparticles is calculated using Scherrer's formula

$$D = \frac{0.94\,\lambda}{\beta\,\cos\theta}$$

where,λ is the wavelength of X-rays (1.5406 Å), θ is the Bragg's angle,β is the full width at half maximum [2].From the results obtained, it can be concluded that when a dopant is added to pure CdO nanoparticles, the average grain size decreases. The average grain size of pure CdO nanoparticles is 43.1198 nm, while for Ni doped sample the grain size is 38.3685 nm. Similar results are reported by Ayman M. Mostafa et al.[14] where they prepared the CdOnanopowdersamples using pulsed laser ablation in liquid environment.

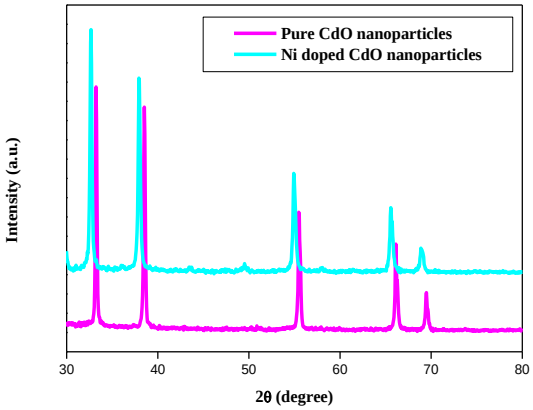

Fig.1. PXRD Pattern of Pure and Ni Doped CdO Nanoparticles

B. *SEM Analysis*

FESEM images shown in Fig.2 indicates that the produced nanoparticles exhibit uniformity. Pure CdOnanopowdersample is uniform sized with less agglomeration. This is in good agreement with SubhashKondawar et al. [6] whereCdO nanoparticles are prepared by sol-gel method and agglomerated particles are produced. The particle size is ~ 65 nm.The FESEM image of Ni doped CdO nanoparticles indicates that the synthesized nanoparticles are corn like nanorods with agglomerated structure of nanoparticles. The length of the nanorod is ~ 1 μm and the width is found as ~ 0.3 μm. Thus the particle size of the prepared undoped and doped nanoparticles ranges from 60 nm – 1 μm.

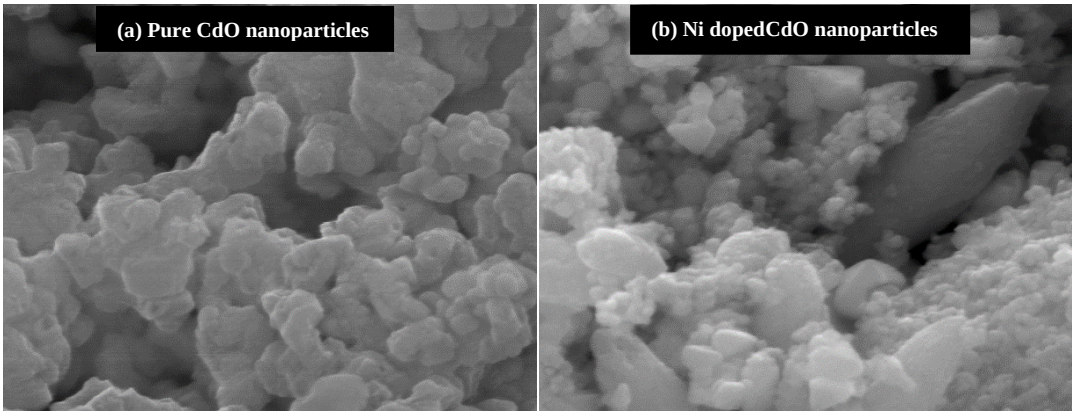

Fig.2. SEM images of Pure and Nidoped CdO Nanoparticles

C. Raman Spectroscopy

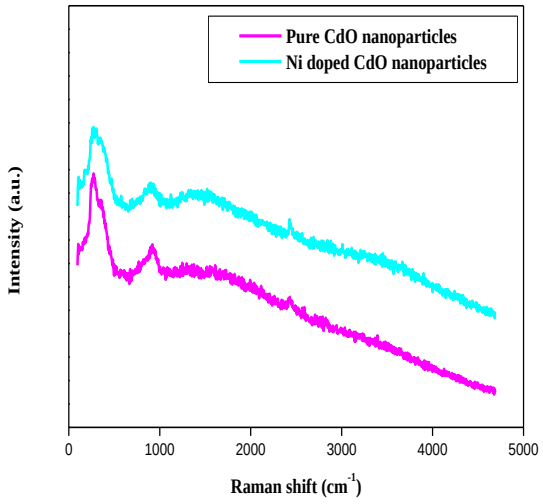

Fig.3. Raman Spectra of Pure and Ni doped CdO Nanoparticles

Fig.3 shows the Raman spectra of pure and doped samples. Shift and change in intensity of the peaks isobserved in the spectrum of doped sample. Some additional peaks appeared in the spectrum of doped sample which are red-shifted and are due to the incorporation of Ni ion into the pure sample.All the peaks observed can be assigned as transverse optical (TO) and longitudinal optical (LO) modes of cubic CdO nanostructures which arise due to stress induced by surface effects in nanostructures. These two modes in CdO nanostructures may occur due to the second-order Raman scattering found in CdO. obtained for CdO nanoparticles prepared using thermal decomposition method by C. Sagi Rani et al. [17]. The doped sample exhibits emission peaks with PL intensity higher than that of the pure cadmium oxide nanoparticles. The green emission peak at 520 nm might have originated from the oxygen vacancies on the surface of CdO [16].

These results are similar to the Raman results obtained in CdO-SnO_2 nanocomposites synthesized by Kapil Sirohi et al. [15].

D. PL Studies

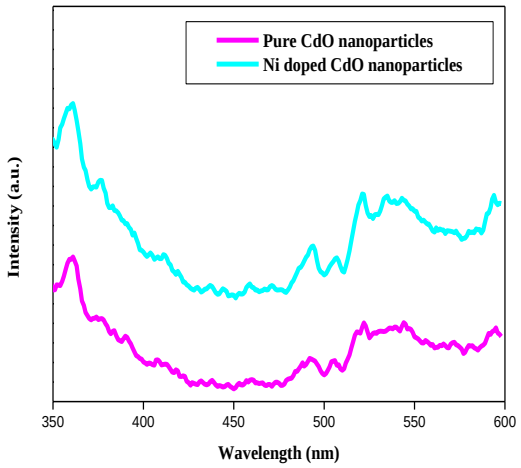

Fig.4. PL Emission Spectra of Pure and Ni dopedCdO Nanoparticles

The PL Emission spectra of pure and Ni doped CdO samples (Fig.4)exhibit a strong Ultra-Violet emission band near 361 nm and weak bands are detected in the visible region. The same type of emission spectrum is

E. UV Spectroscopy

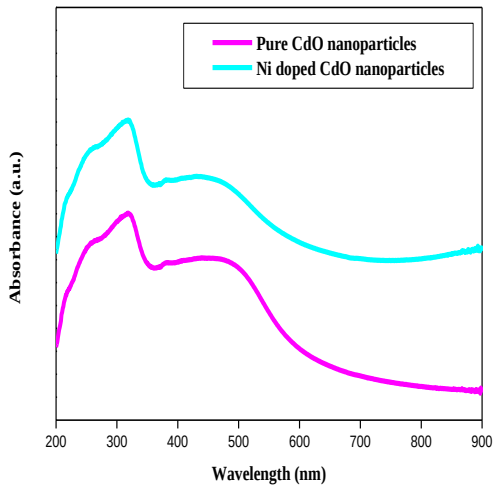

Fig.5. UV Absorption Spectra of Pure and Ni doped CdO Nanoparticles

The samples exhibit absorption bands below 400 nm as shown in Fig.5. The absorption bands of the pure and Ni doped CdO nanoparticles shows a blue shift which is due to the quantum confinement of developed nanoparticles. This optical phenomenon indicates that these nanoparticles show quantum size effect. The results of CdO nanoparticles is similar to the results obtained by Kapil Sirohiet al. [15]whereCdO-SnO_2 nanocomposites are prepared by hydrothermal method and J. Saranya et al. [18] where the absorption bands are observed in the same range.

The energy gap is found to be around 3.89eVfor pure and Ni doped CdO nanoparticlesusing the formula $E_g = hc/\lambda_{max}$, where h is the planck's constant, c is the speed of light in vacuum and λ_{max} is the wavelength corresponding to the maximum absorption used to calculate the bandgap [19].The optical bandgap of the samples is found to increase when compared to bulk CdO. This is in agreement with K. M. Prabu et al. [20] where CdO nanoparticles are prepared by precipitation method.

IV. CONCLUSION

Ni doped CdO nanoparticles are prepared successfully using co-precipitation method. The PXRD results show that when a dopant is added to pure CdO nanoparticles, the average grain size gets decreased. Both the samples exhibit face centered cubic lattice. The FESEM images indicate that the produced Ni doped nanoparticles are in the form of rods. The Raman spectra confirm the presence of TO and LO modes in CdO which is due to the stress induced by surface effects in nanostructures. The blue-green emission in the PL spectra indicate that the prepared nanoparticles are at nanoscale. UV spectra show that the samples exhibit absorption bands below 400 nm which shows that there is a blue shift due to the quantum size effect in the prepared nanoparticles. These results demonstrate that Ni dopedCdO nanoparticles are synthesized with good surface and size characteristics that is suitable for antibacterial applications. Such nanoscale particles can be tested against pathogenic gram-positive and gram-negative bacterial strains.

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