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Research Article

SYNTHESIS AND CHARACTERIZATION OF STRUCTURAL AND OPTICAL PROPERTIES OF NI-DOPED ZINC SULFIDE NANOPARTICLES

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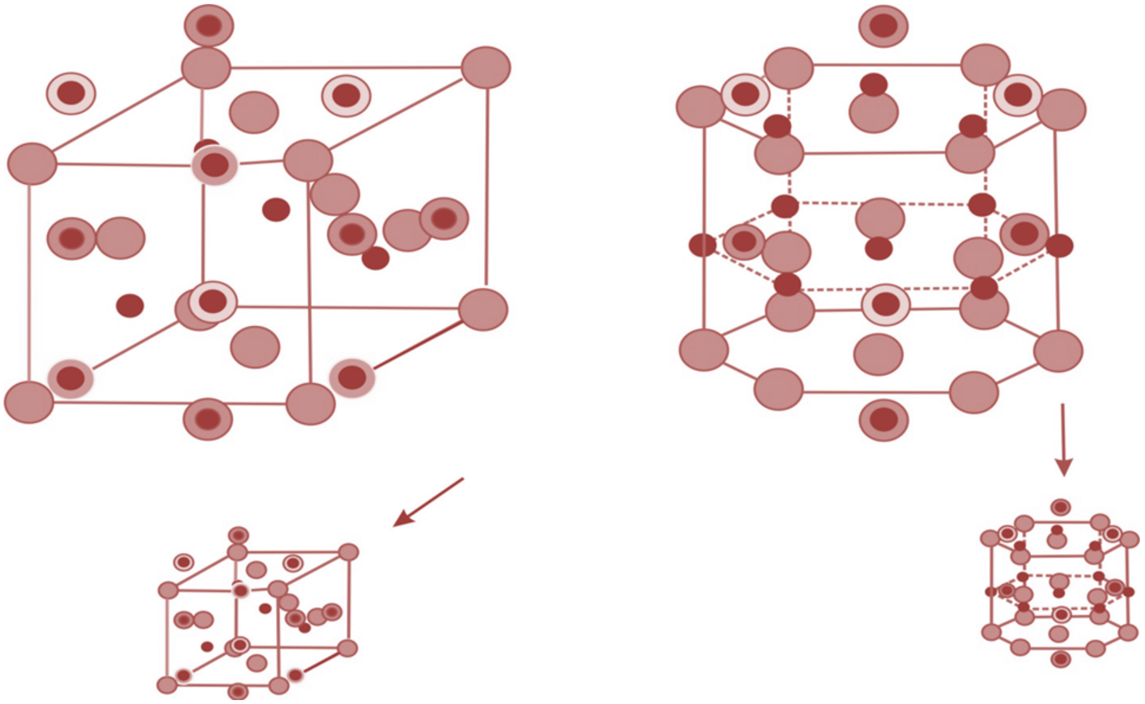
ABSTRACT

The band-gaps of wide band gap metal sulfide semiconductors such as ZnS, are significantly reduced when doped with transition metal ions Ni^{2+}.The new composite materials offer promising and versatile applications in spintronic devices, solar cells and other optoelectronic devices, and in photonics etc. It has led to substantial modifications in methods of synthesis for ZnS nanoparticles. In this research work, we have synthesized ZnS nanoparticles via simple chemical precipitation method. ZnS nanoparticles have been characterized using UV-visible spectra and Raman spectroscopy. For morphological studies we have used scanning electron microscopy (SEM). The optical band gap has been evaluated from UV-vis-nir absorption spectrum of the particles. Raman spectroscopy is used to study the rotational, vibrational and other modes of the sample, as we are interested to reveal properties of nanoclusters treating as those as nano-molecules. We correlate the variations in properties with their structures. Our investigations confirm formation of large single crystals (nanomolecules) yielding resonant Raman peaks. It is further confirmed from SEM images of the samples. Nanoparticles have special properties other than bulk. Their surface energy contributions are entirely different from their bulk counterparts and play dominant role in its stability. Thus, we assign a special phase for them as “Nanophase”. The phenomenon of nano-cluster (aggregates) formation of nickel atoms via nucleation is also confirmed for high doping concentrations of nickel, which results into inverse trend for band-gap.

Keywords: Chemical precipitation method, UV-vis-nir Spectrum, Raman Spectrum, SEM, Nanomolecules, Nano-aggregates, Quantum Confinement Effect.

1. INTRODUCTION

Zinc sulphide (II-IV semiconducting material), is chemically stable among wide band gap (3.70eV for the cubic zinc blend phase and 3.77eV for the hexagonal wurtzite phase at 300K) materials having large exciton binding energy (40eV). It has a wide range of applications such as optical sensors, solid-state solar window layer, photoconductor, phosphorous, and catalysts etc. It is white-to yellow- colored powder in crystalline form, and typically exists in cubic form also known as zinc blende or sphalerite. The cubic form is more stable. The hexagonal form is also known as both synthetic semiconducting material and as well as mineral wurtzite semiconductor. The cubic form has a band gap of 3.91eV. The refractive index of zinc blende is 2.36 and that of wurtzite is 2.35. Sphalerite transforms into wurtzite 1020°C [1, 2]. The density of nickel is 8.9gm/$cm^{-3}$and the melting and boiling points of pure Ni are 200°C and 1453°C. Nickel is silvery in color. Heat and electricity are well conducted by this malleable and ductile metal, which is hard but pliable. Fig. (1a) and Fig. (1b) show zinc blende and wurtzite structure of ZnS, respectively. Nickel dissolves gradually in dilute acid but, like iron, becomes passive when treated with nitric acid. Good mechanical qualities and resistance to numerous corrosive environments make this metal a suitable choice for a variety of applications. Curie temperature and electrical conductivity of pure nickel are extremely high [3, 4]. At room temperature, cubic ZnS has been regarded as an outstanding semiconductor. It also exhibits ferro-magnetism. However, the doping ability of ZnS with the transition metals like Nickel (Ni), Cobalt (Co), Manganese (Mn), Iron (Fe) have received considerable attention due to variations in its optical and magnetic properties. Zinc sulfide nanoparticles doped with nickel ions have gained special attraction due to their high electric-luminescence. These results can be explained on the basis of the interaction of s-p electron-holes of the host (ZnS) and 3d electrons of impurity (Ni) under the condition of quantum confinements. Nanowires and nanobelts made of ZnS have also been successfully used as biosensors in a number of biological researches. These sensors can also be used in vivo imaging and for therapeutics objectives [5]. Doping is performed by adding the dopant into the reaction mixture. Dopant nanomaterials contribute significantly to the fields of electronics, photonics, optics, and medicine [6, 7].


(a) **(b)**

Here the light pink dots represent Zn atoms, the dark spots in pink represent S atoms and dots with shells represent the dopant atoms; here Ni atoms.

Fig. 1: Symbolic structures of (a) Zinc blende and (b) wurtzite structure of ZnS.

ZnS nanoparticles have a significant band gap due to their high surface-to-volume ratio. Doping semi-conducting nanocrystals with desired functional properties is essential for the manufacturing and commercialization of nanoscale devices. Electrons and holes interact with the dopant, which is a center of impurities. The presence of an impurity pushes the central recombination process of surface states, increasing the radiative efficiency. One of the most relevant materials for research in the area of semiconducting nanocrystals, are ZnS nanoparticles doped with transition metal ions, which indicate for a new class of luminous materials. Doping concentrations of one dopant atom per 10^5 atoms are commonly utilized. Doping of semiconductors with impurities, produces impurity centers, which interact with electrons and holes, causing mid-gap states moved outside the band gap region. Doping, on the other hand, has no effect on the absorption spectrum, but the emission intensity is greatly enhanced due to the recombination process. ZnS is a promising new material for UV detectors. ZnS nanocrystals have high photostability, continuous absorption spectra, and have controllable narrow emissions in chemical sensors, which can be exploited for biological imaging and single-particle tracking investigations. Biosensors containing ZnS nanoparticles have been used to identify biological species without the need of labels, in real time, and with high sensitivity. In fluorescence-based labeling applications, ZnS QDs work as luminous inorganic fluorophores with the potential to overcome the functional limits of organic dyes. Nanoparticles must be highly luminous in order to be considered as a good candidate for biosensors. CdSe/ZnS core-shell QDs coupled with enzymes have recently been employed to detect hyperglycemia. The QDs have also been used as acceptors in the oxidation/reduction reactions that occur when glucose is converted into gluconic acid. The QD systems have a superior design, high degree of flexibility, low cost, and high level of sensitivity [8]. In the present investigation we doped nickel into zinc sulphide nanoparticles using three different nickel concentrations 0.2M, 0.3M, and 0.5M. Since the co-precipitation method is simple and low-cost method, we have used it for the synthesis of nickel doped ZnS nanoparticles. The main objective of this paper is to synthesize and characterize Ni doped ZnS nanoparticles [9].

2. MATERIAL AND METHODS

2.1. Synthesis and Characterization

ZnS nanoparticles have been synthesized using zinc acetate [Zn $(CH_3COO)_2$] metal precursor, nickel acetate [Ni $(CH_3COO)_2$] sodium sulphide [Na_2S] and distilled water. All of the chemicals were purchased from Sigma-Aldrich. The deionized water has been used as the solvent for preparing all the solutions. 0.2M aqueous solutions of zinc acetate and nickel acetate were prepared separately, by dissolving the appropriate amount of nickel acetate and zinc acetate by weight in 200ml deionized water, and likewise a 0.2M sodium sulfide solution is also prepared in 200ml deionized water. The aqueous solution of sodium sulfide [Na_2S] was added drop wise into the mixed solution of zinc acetate and nickel acetate at room temperature; a green-yellow colored solution is obtained. Stirring is done until homogeneous solutions are achieved in each case. The latter one is allowed to precipitate. The greenish precipitate was further washed several times with distilled water. Thereafter the precipitate was dried, and thoroughly ground using mortar to obtain the sample in the form of a fine powder. Finally, the dark grey/black colored Ni^{2+} doped ZnS nanoparticles are obtained. It is then collected in a sample bottle for characterization.

For characterization, we use UV-vis-nir absorption spectroscopy and Raman spectroscopy. UV-vis-nir absorption spectroscopy is highly useful in identifying nanomaterials. Raman spectroscopy is based on a phenomenon, in which the incident photons may lose or gain energy by the interactions with vibration and rotation modes of molecules of the samples with extremely high accuracy [10]. Raman spectroscopy offers detailed information on chemical structure, phases and polymorphs, crystalline nature, and molecular interaction. This is a chemical investigation tool and is non-destructive [11, 12]. SEM (scanning electron microscopy) is used to create images of surfaces (morphology) by scanning the surface with a highly focused ray of electrons. SEM analysis confirms the morphology (texture), chemical content, crystal structure, and orientation of the material surface of the sample [13].

3. RESULTS AND DISCUSSION

3.1. UV-Visible Absorption Spectra

UV-visible absorption spectra are extremely useful for detecting nanomaterials. Fig.2 depicts the optical absorption spectra of ZnS for Ni nanoparticles with nickel concentrations of 0.2M, 0.3M, and 0.5M, respectively. Understanding the behavior of semi-conductor nanoparticles requires an understanding of the optical absorption. The optical excitations of electrons across the band gaps are strongly allowed for the wavelengths matching band gap, thus producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge. Fig. (2a) shows that the absorption edge of the samples is red shifted with increasing dopant concentration for lower and moderate values. For higher concentration it again decreases. The values of band-gaps corresponding to 0.2 M, 0.3 M and 0.5 M are 3.31 eV, 3.16 eV and 4.05 eV, respectively. This may be accounted on the basis of strong sp-d exchange interaction between the ZnS bonded electrons and the localized d spins associated with Ni^{2+} ions. The absorption spectra of ZnS nanoparticles were recorded with a UV-visible spectrophotometer in the range of 300nm-500nm. ZnS nanoparticles suggest for a red shift with respect to the bulk values arising from the quantum confinement effect of the nanoparticles. The distinct absorption peaks appear at 374.25 nm, 392.60 nm and 306.02 nm corresponds to 0.2M, 0.3M, and 0.5M Ni doped ZnS nanoparticles, respectively. The absorption edge wavelengths calculated by drawing tangents on the curves are as shown in the Fig. (2b). Band-gaps are calculated using the relation, $\Delta E = h\nu = \frac{hc}{\lambda}$. The estimated band gap of 0.2M, 0.3M and 0.5M Ni-doped ZnS nanoparticles are found to be 3.31 eV, 3.16 eV and4.05 eV, respectively. Doping Ni increases particle size with increase in concentration of Ni for low and moderate doping conditions, whereas for higher concentrations, corresponding to 0.5 M solution, the trend is opposite. That can be accounted only on the basis of saturation in doping and formation of clusters (aggregates) of nickel atoms rather than Ni atoms getting into the ZnS nanocrystals. This decreasing trend of band gap after doping Ni in ZnS has been also reported [14] but the opposite case for higher doping concentration(s) has not been reported yet. Not only that, resonant Raman peaks obtained in our work, is of greater interest, because it represents special characteristics of nanophase.

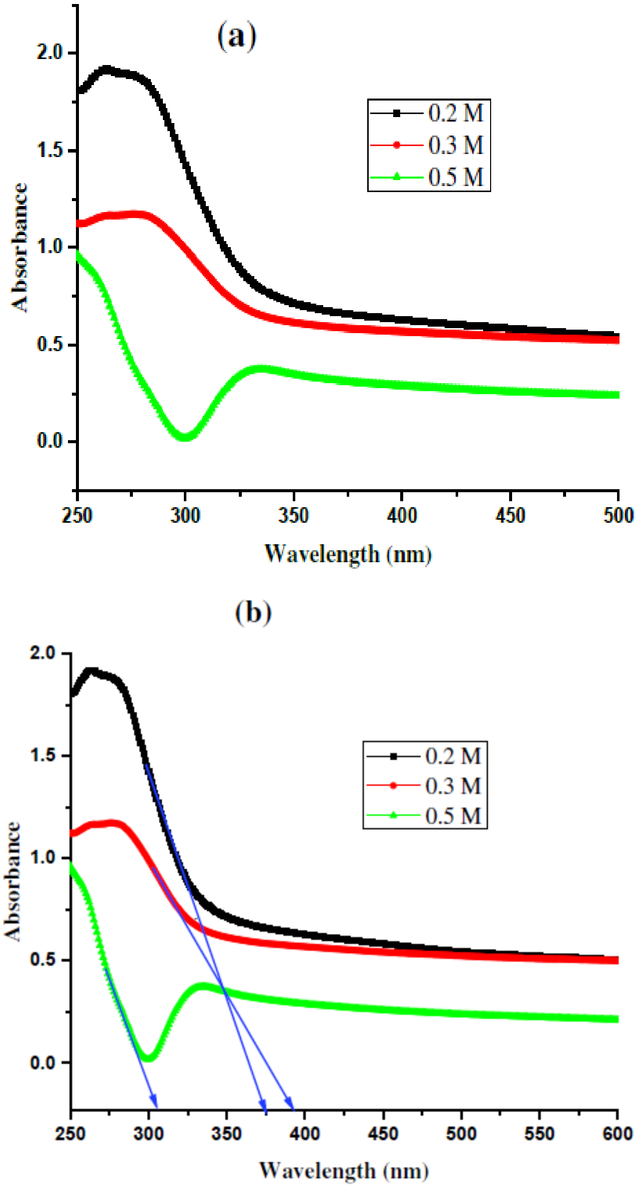


Fig. 2: (a) Absorption spectra and (b) enlarged absorption spectra of 0.2M, 0.3M and 0.5M Nickel doped ZnS nanoparticles.

3.2. Raman Analysis

Raman spectroscopy is a spectroscopic technique used to determine the vibrational modes of a molecule, while rotational modes and low-frequency modes of a system can also be investigated. Raman spectroscopy is often used to generate a structural fingerprint that can be used to identify molecules. Raman spectroscopy is enabled by the inelastic scattering of phonons and other excitations in the system, which causes the energy of the laser photons to be shifted up and down [15, 16]. The wavelengths of photons emitted after passing through the sample have shorter and longer wavelengths apart of the original wavelengths. It is a useful technique for studying lattice disorder, crystal defects, and dopant incorporation in the host lattice. The use of Raman spectroscopy is commonly not used for characterizing nanoparticles [17]. But we have studied it with the presumption that nanoparticles can also be treated as nanomolecules, provided that they are formed well, Nanoparticles have special properties other than bulk. Their surface energy contributions are entirely different from their bulk counterparts and play dominant role in its stability [18]. Thus, we may assign a special phase to them as "Nanophase". We have observed prominent peaks with relatively very high intensities, which indicate for the formation of large size single crystals resulting into in phase vibrations. The cumulative contributions from the in-phase vibrations also indicate for the high purity of the nanocrystals, because impurity may result into anharmonic and out of phase vibrations damping the intensity [19, 20].

The Raman spectra of 0.2M, 0.3M, and 0.5M Ni doped ZnS nanoparticles at room temperatures upon illumination with 532 nm wavelength radiation are as shown in Figs.3-5). Fig. (3) shows the highest Raman peak at 217.657cm^{-1}, the second-highest peak at 152.8771 cm^{-1}, and the third highest peak at 472.1948cm^{-1} for 0.2M Ni doped ZnS nanoparticle. Fig. 4 shows an increment in Raman shifting with increased intensities for the case of 0.3M Ni doped ZnS nanoparticles. For 0.3M Ni doped ZnS nanoparticles, sharp peaks occur at 136.1917cm^{-1}, 151.2099 cm^{-1}, 220.7666 cm^{-1}, 475.4113 cm^{-1}as shown in Fig. (4). Fig. 5 shows the Raman spectrum of 0.5M Ni doped ZnS nanoparticles. The highest Raman peak occurs at 217.657 cm^{-1}, the second-highest peak at 473.8032 cm^{-1}and the third highest peak at 152.8771 cm^{-1} for the case of 0.5M doping. Thus, Raman shifting shows the variations in vibrational modes of ZnS nanoparticles. Thus, the structural and optical properties can be finely tuned with ease by doping Ni into ZnS nanocrystals.

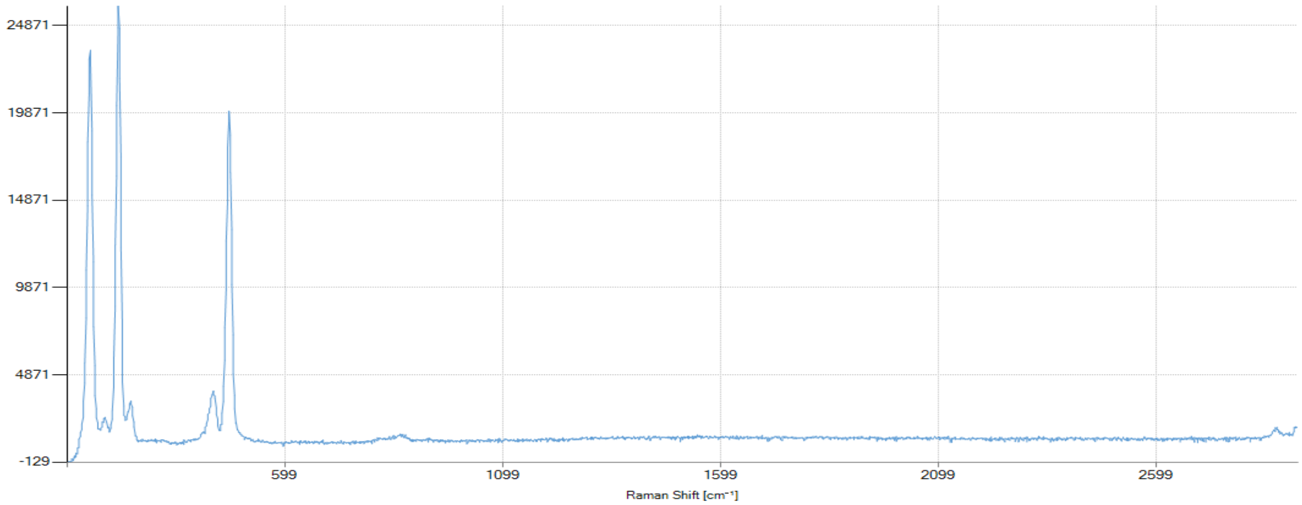


Fig. 3: Raman spectra of 0.2MNi doped ZnS nanoparticles

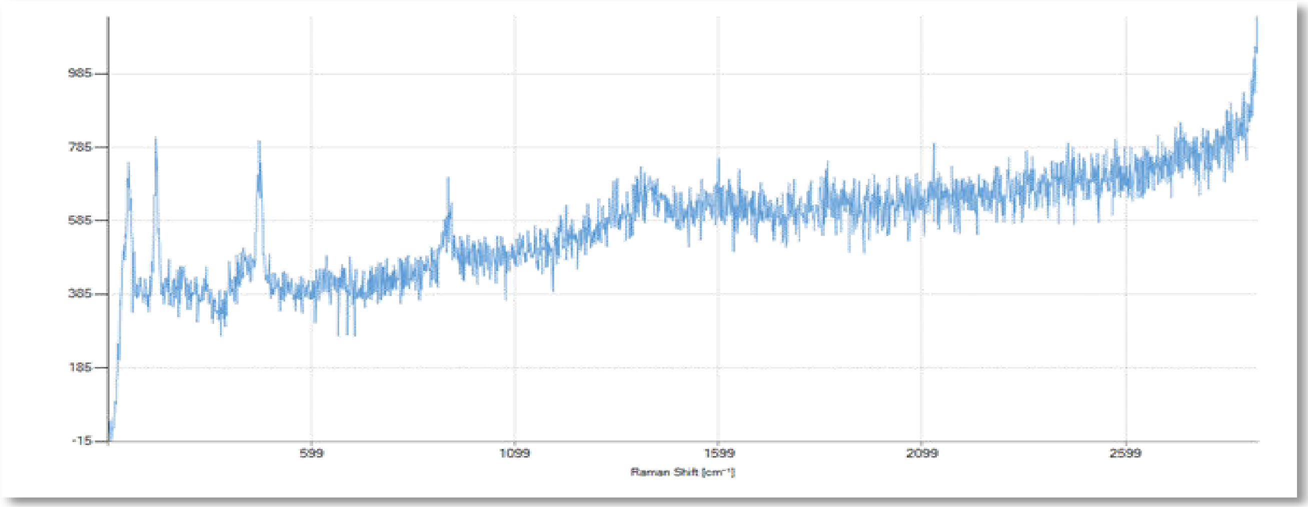


Fig. 4: Raman spectra of 0.3M Ni doped ZnS nanoparticles

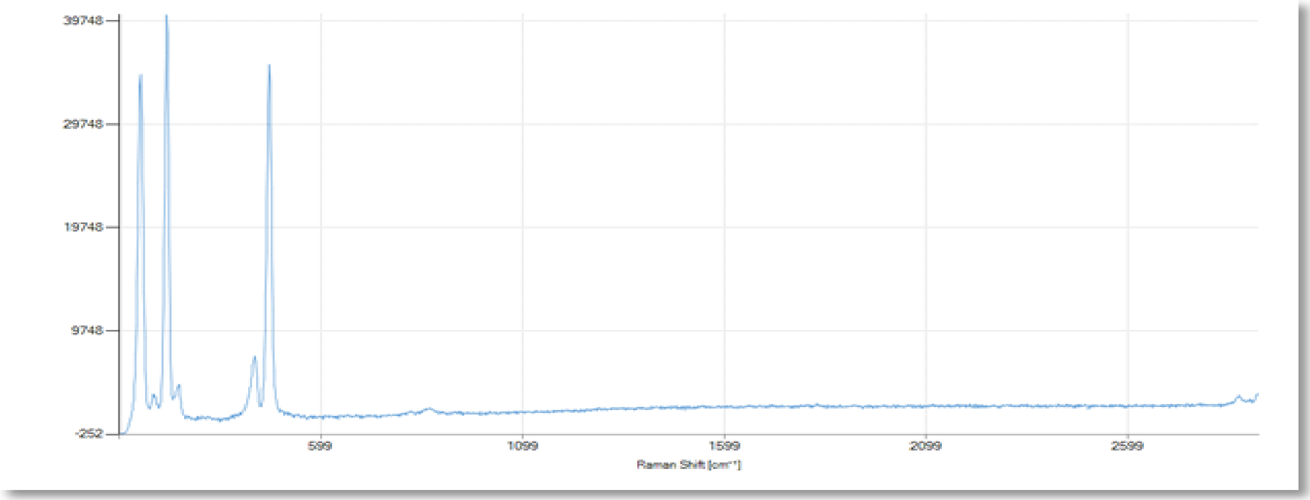
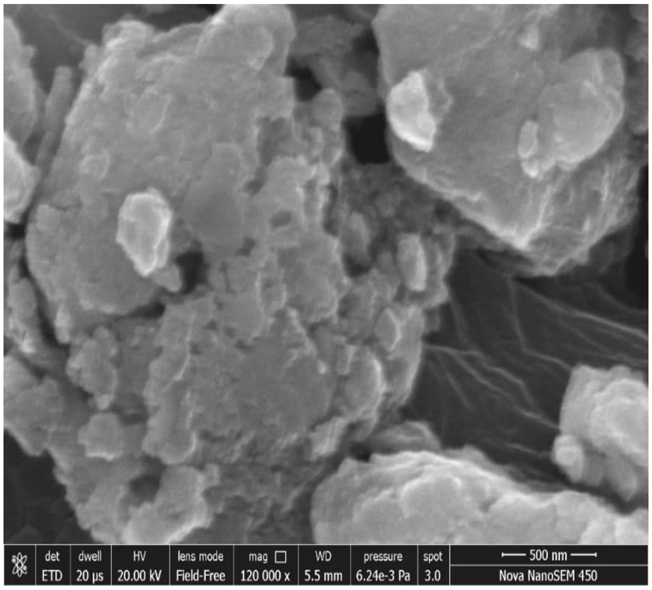


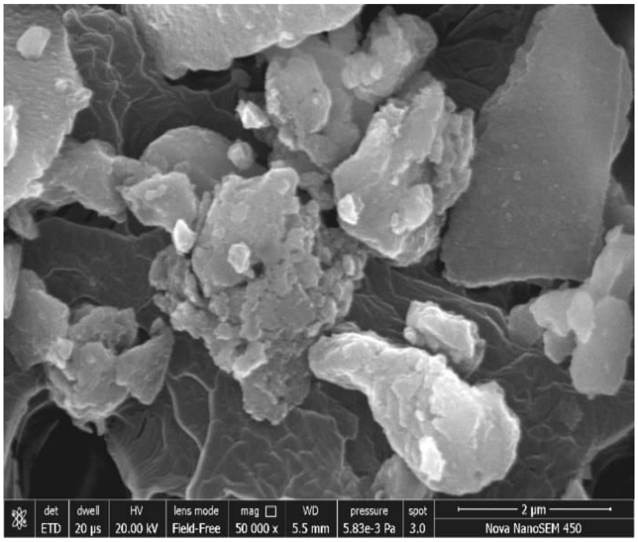
Fig. 5: Raman spectra of 0.5M Ni doped ZnS nanoparticles

3.3. Scanning Electron Microscopy (SEM) Analysis

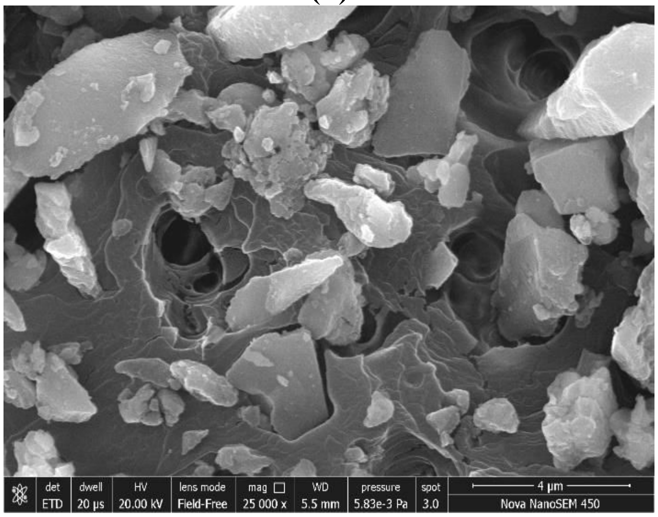
The surface morphology of Ni doped ZnS nanoparticles were studies by scanning electron microscopy (SEM) analysis. It is observed that the sample exhibit both regular and irregular morphologies. Formation of smooth large surfaces indicates for the formation of large single crystal. The periodicity gets broken at the grains boundary because of impurity atoms which enter into form of small traces of impurities in the samples, though we have used research grade chemical purity higher than 98-99%. Fig. (6a) clearly indicates for the formation of nano-aggregates. It also indicates for the formation of thin sheet-like structures one over another as can be observed at the dark plateaus. Fig. (6b) further confirms the formation of thin micron size sheets with thickness ~ 100 nm. It is important to note that the electron confinements in 0D (i.e. quantum dots), 1D (i.e. quantum wire) and 2D (i.e. nano-sheets/films) show drastically different chemical, electrical, opto-electronic and magnetic properties because of electron confinement. Their uniquely tailored size-dependent functional properties have attracted to variety of novel applications in recent past. Fig. (6c) also confirms for the formation of micron size single large crystals, which indeed support the explanation given for the resonant peaks in its Raman spectra. We have argued for distinct macromolecular behavior for these nano-structures and thus consider it as imprint of "Nanophase". Fig. (6d) further explores the formation of anisotropic large single crystals.



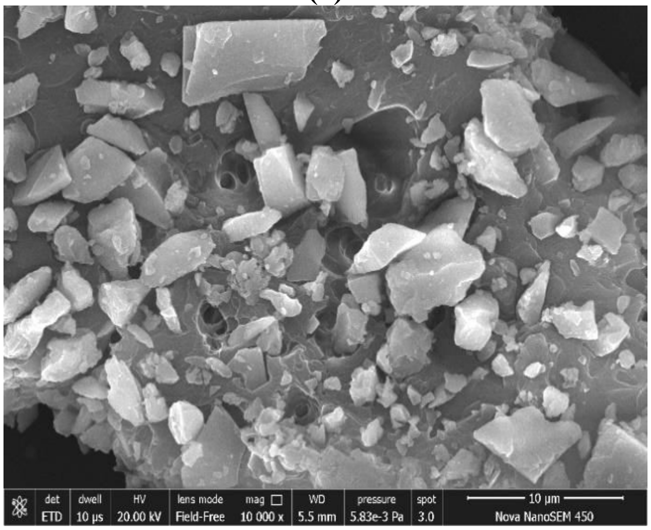
(a)



(b)



(c)



(d)

Fig. 6: (a-d) SEM images of 0.2M Ni doped ZnS nanoparticles in different magnifications (Bars of 500 nm, 2 µ, 4 µ and 10 µ are used to show the scale)

4. CONCLUSION

Chemical precipitation was used to create Ni-doped ZnS nanoparticles with varying nickel concentrations at room temperature. This method is well suited for the large-scale synthesis of Ni^{2+}doped ZnS nanoparticles in atmospheric conditions without using high-cost equipment. UV spectra revealed that the absorption bands for nanocomposites get red shifted from their corresponding bulk values because of quantum confinement of charged particles and carriers. The resonant Raman peaks are shifted and this suggests for the structure dependent variations in vibrational modes of ZnS nanoparticles. After doping nickel its optical properties can be finely tuned. The band gap decreases after doping 0.2M, 0.3M, but becomes high for higher concentrations as 0.5 M Ni doped ZnS nanoparticles because of self-aggregation of nickel atom. Formation of large (anisotropic) single crystals and thin nano-sheets of micron sizes have been reported using SEM, which have distinct properties owing to the electron confinement and can be used in many vital applications.

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Conflict of interest

None declared

Source of funding

None declared

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