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Structural, Optical and Magnetic Properties of Nickel Oxide Nanoparticles: A Review

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ABSTRACT

A comparative literature review related to pure NiO and doped (TM – Transition Metal) NiO nanoparticles is summarized in this article. Different synthesis procedures and results of characterization techniques like X- Ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX), Fourier Transform Infrared Spectroscopy (FTIR), UV-vis Spectra, Photoluminescence (PL) have been reported. Their observed Optical, Structural, electrical and magnetic properties are also stated accordingly. Effect of different doping of TM series like Cu, Zn, Mn, Fe, Nd, Co and rare earth metals like Yttrium and Gadolinium are also reported in this paper. Method of synthesis include both chemical and physical methods like Co-precipitation, low temperature hydrothermal method, thermal decomposition, composite hydroxide, wet chemical method, chemical precipitation, sol-gel method and solid state reaction method.

Keywords : *Nickel oxide, Nanoparticles, Magnetic properties, Optical properties, Structural properties*

1. Introduction:

Nanoparticles are solid colloidal particles ranging from 1 to 1000 nm in diameter. Nanoparticles have a lower concentration of point defects than bulk materials because of their small size. NiO (Nickel oxide) is an important TM oxide with cubic lattice structure and shows antiferromagnetic property. [1] Pure NiO is a Mott-Hubbard insulator below Neel temperature (523 K), in its bulk form.[1,2] It is p-type semiconducting material with a bandgap of about 3.5eV to 4 eV. Nickel nanoparticles are difficult to synthesize as they get easily oxidized. [1] Also NiO nanoparticles have attracted greater attention because of their optical, structural, magnetic, electrical properties which are used in variety of applications. [3] It is used in making electrical ceramics like thermistors, plastics, glass, used in temperature sensors and also as counter electrodes. This article discusses various synthesis methods and characterization results of Pure NiO and how it is less expensive, more environmentally friendly, and performs well. [4] Because of quantum size and surface effects, these nanoparticles have electrical, optical, and magnetic properties distinct from bulk NiO particles. [5] Different synthesis methods and characterization results of Pure NiO and various TM doped NiO nanoparticles are compared in this article.

2. Synthesis

The methods of preparation/synthesis play a vital role in producing different sizes of nanoparticles and have various intrinsic properties. The synthesis methods used for formation of NiO doped nanoparticles are –

a) Co-precipitation method [2,4–9]
b) Hydrothermal method [10]
c) Sol-gel method [3]
d) Wet chemical method [11,12]
e) Composite Hydroxide Mediated (CHM) [13]
f) Thermal degradation method [1]

As different dopants and precursors are used, a few methods are briefly described. As a result, a general overview of synthesis is provided.

The co-precipitation method is thought to be the simplest and least expensive method for controlling the size and morphology of nanoparticles. The starting materials / precursors were taken in stoichiometric proportions and dissolved in Double Distilled Water (DDW) or Deionised water. They were stirred at some particular temperature (depending upon the chemicals used) for few hours. After stirring, the sample was washed using DDW, twice or thrice to remove the impurities/by-products. Finally, the washed samples were calcined or kept in a muffle furnace at a particular temperature for few hours. The product yielded were nanoparticles. [2, 4–9]

Thermal degradation was realised to be faster, less expensive, and more environmentally friendly than other methods. Using this method, one can obtain nanoparticles of various sizes and shapes, and these differences influence their properties and applications. [1]

All of the precursors were taken in stoichiometric proportions and stirred separately for some time before being added to a gel in the Sol-gel method. These sol-gel mixtures were now stirred together and stored for heating/annealing. The dried powder was then placed in a muffle furnace for a few hours to produce the desired product. [3]

A similar Synthesis procedure was observed for other methods too.

3. Characterization results & Discussion

For different dopants, different characterization techniques were preferred. The most common characterization techniques were X-Ray Diffraction (XRD) to know the phase formation of the yield product. Apart from this, Energy Dispersive X-Ray (EDAX) was too used to know about any impurities in the product formed. Transmission Electron Microscopy (TEM) was used to know about average particle size & morphology of nanoparticles formed. Also, Scanning Electron Microscopy (SEM), Fourier Transform InfraRed Spectroscopy (FTIR), UV-Vis spectra, and other magnetic characterization techniques were used.

Structural, Optical and Magnetic properties are described below in detail.

3.1 Structural Properties

XRD – It provides the information of crystalline phase of the material. [10] All papers confirmed that the Pure NiO and TM doped NiO nanoparticles show FCC phase formation (according to JCPDS). All the peaks were indexed as (111), (200), (222), (220), (311). Information of crystallite size is known from the diffraction width. As the width decreases, the particle size increases. [10]

TEM – Crystalline size, shape and morphology were assured from this characterization technique. [5] In case of pure NiO, the average size of nanoparticles were found to be in the range of 12 nm to 35 nm whereas for TM doped NiO nanoparticle the average size of nanoparticles was in the range of 8 nm to 23 nm. It was observed that as the doping concentration of the dopants increases, the crystalline size decreased. [6] Almost all papers have reported high crystallinity of Ni nanoparticles except Zn doped which shows the small crystallinity as compared to XRD this is because of the reaction solution aging. [5]

EDAX – This technique is usually used to identify the elemental composition of materials. [14] All papers confirmed that there was no other element/ compound shown except the starting materials. No additional peaks except starting materials were observed; irrespective of synthesis procedure.

SEM – To know about surface morphology, this technique is used.Doped NiO confirms that nanoparticles formed were spherical in shape. Pure NiO show rod shaped nanoparticles [4,9]. Few papers too reported agglomeration of particles and were depending on synthesis method used; for instance in sol-gel method. [3]

3.2 Optical Properties

FTIR – Fourier Transform Infrared Spectroscopy (FTIR) is used to know about the molecular composition of the materials. Formation of pure NiO and TM doped NiO was confirmed using FTIR spectra. [5] It was observed that for Nd doped NiO, the sample is free from defects induced by oxygen deficiency.

UV-Visible Spectra & Optical band gap – This technique is used to know how much a chemical substance absorbs light [15]. According to the papers, mostly all samples exhibit strong UV absorption along with visible.[7] Generally, it was observed that the Optical band gap was reduced for mostly all samples upon substation with TM cations, as compared to pure NiO and contributed to shift in fermi level towards conduction band and indicate the presence of oxygen vacancies.[7,13] In case of Fe doped NiO, the optical band gap was found more than the pure NiO, due to quantum confinement effect. [11]

Photoluminescence (PL) –This technique is used to know about the sample purity and crystallite quality. It was seen that the PL intensity varied with increase in dopant concentration. [6] Also, the existence of Ni vacancies detected in PL spectra indicated p-type characteristic of nanoparticles. [2]

3.3 Magnetic Properties –

The magnetic properties of the material strongly depends upon particle size, shape and crystallinity. [11] On introducing dopants, the magnetic properties enhanced. [4,5] It was seen that on TM doped NiO, the net magnetization was more as compared to pure NiO [4,11]. If we increase the dopant concentration, then the magnetization decreases for higher concentration [10]. There was no proof of Room temperature ferromagnetism on doping NiO, thus the results indicate that the preparation method has great effect on magnetic properties [10]. It was also observed that for undoped NiO shows superparamagnetic property at room temperature whereas doped NiO shows ferromagnetic property [16-17]. Higher saturation magnetization is a beneficial & has great advantage to biomedical application [5].

4. Conclusion

Different synthesis approaches and their characterization techniques are mentioned in this article as review for different NiO doped nanoparticles & Pure (undoped) NiO nanoparticles. From characterization techniques it can be seen that, for all chemical routes, the nanoparticle facilitates to lessen the crystallite size and broadly has a range between 8 nm to 35nm. Phase formation (FCC) of nanoparticles is homogenous & uniform. Many results also confirmed spherical shape of nanoparticles. Further addition of dopants or substitutes can alter the size of particles. Almost all papers have pronounced use of characterization technique such as TEM, XRD, FTIR, UV Vis Spectra, EDAX. PL analysis confirmed that the prepared material has high purity.

Cu and Zn doped NiO shows spherical formation of nanoparticles via co precipitation method whereas in wet chemical process it shows nanoflakes morphology. From magnetic properties, it was seen that the net magnetization increases as doping increases. Also it was observed that undoped NiOshows superparamagnetic property at room temperature whereas doped NiO shows ferromagnetic property. Among all doped elements, Fe doped NiO shows high saturation magnetization. As far as applications are concerned, NiO nanoparticles are used as catalyst, lithium ion microbatteries, electrochromic materials, as materials for gas / temperature sensors and plenty of more.

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