Synthesis and characterization of Cadmium doped Nickel Oxide nanoparticles

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Abstract: Nanoparticles or nanocrystals made of metals, semiconductors, or oxides are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other properties. Nanoparticles have been used as quantum dots and as chemical catalysts such as nanomaterial-based catalysts. Recently, a range of nanoparticles are extensively investigated for biomedical applications including tissue engineering, drug delivery, biosensor. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nanoscale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface Plasmon resonance in some metal particles and superparamagnetism in magnetic materials. In this paper we have synthesized Cadmium Doped Nickel Oxide nano particle by co precipitation method. Finally we find the size of the nano particle in the range of 30.6nm. We have used only 4% of doping. The size of nano particle is characterized by XRD. And by comparing the pure form of Nickle Oxide with Cadmium doped Nickel Oxide and we get that some more peak of impurity (Cadmium) as (100), (101) and it also increase the intensity of the peak of Nickel Oxide, and by the PL spectrum we see the result of doping, and see the effect of wavelength on the material. UV Visible spectrum shows that absorption capacity of Nickel Oxide has been enhanced because of Cadmium Doping. And it shows the Cadmium doped Nickel Oxide shows more absorption at 270 nm FTIR spectrum shows the absorption capacity in infrared light that how much absorption is possible in wavelength that is below to red light. we find that there is significant changes in the property of Nickel Oxide nano particle this nano particle will simplifies the human beings by improving the property of Nickel Oxide Nano material by improving their strength. It has been clear that there is more percentage of doping regired to enhance the more property of Nickel Oxide.

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Introduction

Nanotechnology as defined by size is naturally very broad, including fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro fabrication, molecular engineering, etc.^[4] The associated research and applications are equally diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale.

Scientists currently debate the future implications of nanotechnology. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in nanomedicine, nanoelectronics, biomaterials energy production, and products. On the consumer other hand. nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterials, and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted.

Nickel oxide:

Nickel oxide is the chemical compound with the formula NiO. It is notable as being the only well-characterized oxide of nickel (although nickel (III) Ni2O3 and NiO 2 have been claimed⁰. The mineralogical form of NiO, bunsenite, is very rare. It is classified as a basic metal oxide. Several million kilograms are produced in varying quality annually, mainly as an intermediate in the production of nickel alloys.

NiO can be prepared by multiple methods. Upon heating above 400 °C, nickel powder reacts with oxygen to give NiO. In some commercial processes, green nickel oxide is made by heating a mixture of nickel powder and water at 1000 °C, the rate for this reaction can be increased by the addition of NiO. The simplest and most successful method of preparation is through pyrolysis of a nickel (II) compounds such as the hydroxide, nitrate, and carbonate, which yield a light green powder. Synthesis from the elements by heating the metal in oxygen can yield grey to black powders which indicates nonstoichiometry.

Structure

NiO adopts the NaCl structure, with octahedral Ni (II) and O^{2^-} sites. The conceptually simple structure is commonly known as the rock salt structure. Like many other binary metal oxides, NiO is often non-stoichiometric, meaning that the Ni:O ratio deviates from 1:1. In nickel oxide this non-stoichiometry is accompanied by a colour change, with the stoichiometrically correct NiO being green and the non-stoichiometric NiO being black.



Fig.1.1 NiO Structure

About 4000 tons of chemical grade NiO are produced annually. Black NiO is the precursor to nickel salts, which arise by treatment with mineral acids. NiO is a versatile hydrogenation catalyst.

Heating nickel oxide with either hydrogen, carbon, or carbon monoxide reduces it to metallic nickel. It combines with the oxides of sodium and potassium at high temperatures (>700 °C) to form the corresponding nickelate. Nickel oxide reacts with chromium (III) oxide in a basic moist environment to form nickel chromate:Zinc, cadmium, and mercury are generally excluded from the transition metals as they have the electronic configuration [$]d^{10}s^2$, with no incomplete *d* shell. In the oxidation state +2 the ions have the electronic configuration d¹⁰. However, these elements can exist in other oxidation states, including the +1 oxidation state, as in the diatomicion Hg2+.

2. The group 12 elements Zn, Cd and Hg may therefore, under certain rules, be classed as posttransition metals in this case. However, it is often convenient to include these elements in a discussion of the transition elements. For example, when discussing the crystal field stabilization energy of first-row transition elements, it is convenient to also include the elements calcium and zinc, as both Ca2+ and Zn2+ have a value of zero against which the value for other transition metal ions may be compared. Another example occurs in the Irving-Williams series of stability constants of complexes.

The recent (though disputed and so far not reproduced independently) synthesis of mercury (IV) fluoride (HgFhas been taken by some to reinforce the view that the group 12 elements should be considered transition metals,^[14] but some authors still consider this compound to be exceptional.

Characteristic properties

There are a number of properties shared by the transition elements that are not found in other elements, which results from the partially filled d shell. These include.

• the formation of compounds whose colour is due to d-d electronic transitions.

• the formation of compounds in many oxidation states, due to the relatively low energy gap between different possible oxidation states.

• the formation of many paramagnetic compounds due to the presence of unpaired d electrons. A few compounds of main group elements are also paramagnetic (e.g. nitric oxide, oxygen).

Experimental:

In materials science, the sol-gel process, the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation. Removal of the remaining liquid (solvent) phase requires a **drving** process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing.



Fig.2.2 Flowchart of the synthesis process of Cd doped Nickle

The precursor sol can be either deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses,

fibers, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres). The solgel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product.

Beer-Lambert Law

The Beer-Lambert law (also called the Beer-Lambert-Bouguer law or simply Beer's law) is the linear relationship between absorbance and concentration of an absorber of electromagnetic radiation. The general Beer-Lambert law is usually written as:

 $\mathbf{A} = \mathbf{a}_{\lambda} \cdot \mathbf{b} \cdot \mathbf{c}$

where A is the measured absorbance, a_{λ} is a wavelength-dependent absorptivity coefficient, b is the path length, and c is the analyte concentration. When working in concentration units of molarity, the Beer-Lambert law is written as:

 $\mathbf{A} = \mathbf{e}_{\mathbf{l}} \cdot \mathbf{b} \cdot \mathbf{c}$

where e_1 is the wavelength-dependent molar absorptivity coefficient with units of M^{-1} cm⁻¹. The λ subscript is often dropped with the understanding that a value for ε is for a specific wavelength. If multiple species that absorb light at a given wavelength are present in a sample, the total absorbance at that wavelength is the sum due to all absorbers:

 $\mathbf{A} = (\mathbf{c}_1 \cdot \mathbf{b} \cdot \mathbf{c}_1) + (\mathbf{e}_2 \cdot \mathbf{b} \cdot \mathbf{c}_2) + \dots$

where the subscripts refer to the molar absorptivity and concentration of the different absorbing species that are present.

Theory

Experimental measurements are usually made in terms of transmittance (T), which is defined as:

 $T = P/P_{Po}$

where P is the power of light after it passes through the sample and P_o is the initial light power. The relation between A and T is:

 $A = -\log (T) = -\log (P/_{Po})$

The figure shows the case of absorption of light through an optical filter and includes other processes that decreases the transmittance such as surface reflectance and scattering.



Fig 3.4 Process diagram of lambert Beer law

In analytical applications we often want to measure the concentration of an analyte independent of the effects of reflection, solvent absorption, or other interferences. The figure to the right shows the two transmittance measurements that are necessary to use absorption to determine the concentration of an analyte in solution. The top diagram is for solvent only and the bottom is for an absorbing sample in the same solvent. In this example, P_s is the source light power that is incident on a sample, P is the measured light power after passing through the analyte, solvent, and sample holder, and P_o is the measured light power after passing through only the solvent and sample holder. The measured transmittance in this case is attributed to only the analyte.

Depending on the type of instrument, the reference measurement (top diagram) might be made simultaneously with the sample measurement (bottom diagram) or a reference measurement might be saved on computer to generate the full spectrum.

Modern absorption instruments can usually display the data as either transmittance, %transmittance, absorbance. or An unknown concentration of an analyte can be determined by measuring the amount of light that a sample absorbs and applying Beer's law. If the absorptivity coefficient is not known, the unknown concentration can be determined using a working curve of absorbance versus concentration

Photo excitation

In general, three different excitation conditions are distinguished: resonant, quasi-resonant, and nonresonant. For the resonant excitation, the central energy of the laser corresponds to the lowest exciton resonance of the quantum well. No or only a negligible amount of the excess energy is injected to the carrier system. For these conditions, coherent processes contribute significantly to the spontaneous emission. The decay of polarization creates excitations directly. The detection of PL is challenging for resonant excitation as it is difficult to discriminate contributions from the excitation, i.e., stray-light and diffuse scattering from surface roughness. Thus, speckle and resonant Rayleigh-scattering are always superimposed to the incoherent emission.

In case of the non-resonant excitation, the structure is excited with some excess energy. This is the typical situation used in most PL experiments as the excitation energy can be discriminated using a spectrometer or an optical filter. One has to distinguish between quasi-resonant excitation and barrier excitation.



Fig 3.6 Photo luminescence

For quasi-resonant conditions, the energy of the excitation is tuned above the ground state but still below the barrier absorption edge, for example, into the continuum of the first sub band. The polarization decay for these conditions is much faster than for resonant excitation and coherent contributions to the quantum well emission are negligible. The initial temperature of the carrier system is significantly higher than the lattice temperature due to the surplus energy of the injected carriers. Finally, only the electron-hole plasma is initially created. It is then followed by the formation of excitations.

In case of barrier excitation, the initial carrier distribution in the quantum well strongly depends on the carrier scattering between barrier and the well.

4.1: XRD Analysis

XRD pattern provided information about crystalline phase of the nanoparticles as well as the crystallite size. A considerable broadening of diffraction peaks is the characteristic feature of the xray diffraction patterns of films and ultra-dispersed powders of cadmium sulfide. This broadening of the diffraction peaks is associated with the small sizes of particles in powders.

Fig 4.1, and 4.2 shows the XRD pattern of sample pure NiO, and Cadmium doped Nickel Oxide respectively. X-ray diffraction studies confirmed that the synthesized materials were NiO cubic phase and Cadmium doped Nickel Oxide the entire diffraction peak agreed with the reported JCPDS data. It was found that the Cadmium doped Nio Oxide nanoparticles are identified as β - Cadmium doped Nickel Oxide, which belong to the cubic crystal system. The XRD pattern of a typical Cadmium doped Nickel Oxide sample exhibits peaks at 20 values of, 33.72,38.601,42.6,52.6,53.6,63.1 can be readily indexed as (111), (200), (220), (311) and (222) crystal planes of the bulk Ca doped NiO as well as pure NiO respectively. All the reflection can be indexed to face centered cubic (fcc) NiO phase with lattice constant (a):40175 A. The broadening of the diffraction peak provides information about crystallite size. As the width increases, the particle size decreases and vice versa (Banerjee et al., 2000).





Fig.4.2 X-ray pattern cadmium Doped Nickel Oxide

Calculation of particle size for highest peak:-

Scherer's Equation D=Kλ/βcosQ

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1. Particle size for Cd doped NiO
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D =0.9 \times 1.54 / (0.28 \times \cos 21.56) (0.0174)
D=30.6 nm
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2. Particle Size for pure NiO
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 $D = 0.9 \times 1.54 / (0.24 \times 0.0174 \times \cos 21.56)$

D=35.6 nm

Sample	FWHM (A^0)	Peak No	2θ (degree)	h k l	Inter planar spacing d values (A^0)		Phase	Grain Size (nm)
					Observed d (A)	Standard d (A)	1 nase	
NiO		1	37.28	111	2.40	2.45	cubic	
	0.24	2	43.50	2 00	2.07	2.121	Cubic	35.56
		3	62.52	220	1.48	1.7621	cubic	
		4	75.65	311	1.25	1.52	Cubic	
		5	79.09	222	1.21	1.47	Cubic	
		1	37.83	111	2.37	2.45	Cubic	
Cd doped NiO	0.28	2	43.71	2 00	2.06	2.06935	Cubic	30.26
		3	63.09	220	1.477	1.76531	Cubic	
		4	75.47	311	1.257	1.52	Cubic	
		5	79.66	222	1.202	1.47	cubic	

Table 4.1 for caluating paricle size

4.3Photo luminance Analysis Of Cadmium Doped Nickel Oxide:-.

particles under 350 nm wavelength excitation at room temperature. The NiO sample with a higher crystallinity and larger particle size shows a stronger band band PL emission at 434 nm.

Figure 4.3 given below shows the PL spectra of PURE NiO and Cadmium doped Nickel Oxide nano



Fig 4.3 photo luminescence Spectrum of cadmium doped nickel oxide and nickel oxide

The stronger the band band PL intensity of NiO the higher the recombination of particles, phovoinduced electron-hole pair. The deeply traped holes are more or less localized at deep traps, exhibit a lower oxidizing potential, and prefer to react with physically adsorbed substance. Heat treatment may result in a slight deviation from NiO stoichimetry and the cation vacancy oxygen trapping in the NiO lattice leads two shoulder peaks at 496 and 540 nm in green emission band confirmed of such defects in NiO lattice. nickel vacancies can be produced due to the charge transfer As seen in the figure 4.3 all the sample showed the excitation PL emission band at 2.86eV (434nm) resultin from the surface oxygen vacancies of NiO. black emission in PL spectrum with a strong band centred at 434nm confirmed the presence of Cd doped NiO nano particles and no impurity peaks were observed. PL intensity enhanced with increasing dopant concentration.

4.3 UV –VIS Analysis of cadmium doped Nickel Oxide:-

Fig 4.4 shows the UV Vis Spectrum of pure NiO and Cadmium doped NiO nano particles. The absorption spectra of pure NiO and Cd doped NiO nanoparticles were recorded using Vis-Cary 5E model spectrometer in the wavelength range 200 - 900 nm by dissolving the nano samples in deionised water. The spectra were recorded for IR, visible and UV region. From the absorption peak, the optical band gaps were calculated and the natures of transitions were also identified. The spectra are shown in Fig. 4.4. From the spectra, it is evident that the absorbance is not registered due to its excellent optical behaviour from 300 nm to 900 nm. Negligible absorption in the region between 300 to 900 nm is an added advantage, as it is the key requirement for nanomaterials having NLO properties. Energy band gap (Eg) of materials is related to absorption coefficient (α) or (α hv) = A (hv – Eg) where 'A' is a constant, 'hv' is the photon energy, 'Eg' the band gap and 'n' is an index which assumes the values of 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the absorption $n = \frac{1}{2}$ is taken for an allowed direct transition. The extrapolation of the straight line gives the value of the energy band gap. The energy bandgaps for NiO and Cd doped NiO nanoparticles were found to be.25 and.28 eV. From the data it clear that the shift in the band gap..



Fig 4.4 UV Vis Analysis of Cadmium doped Nickle Oxide

4.4 FTIR Analysis of Cadmium doped Nickel Oxide:-

Fig 4.5 and 4.6 shows the FTIR spectra of pure NiO and Cd doped NiO respectively In this spectrum we see that transmittance is varying with the wave number. there is band arouse 3363.18 1/cm was due to

-O-H stretching Vibration. The Bands centred at 2295.2,2521.32 due to -C-H stretching and bending vibration. The band at 1170.25,1085.76,1001.12, and 732.05 can be due to CN stretching Vibrations. The bands observed at 1463.45 is due to C-C stretching and 1620.21 is due to NH bending vibrations.



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Conclusion

In this project we have synthesized Cadmium Doped Nickel Oxide nano particle by co precipitation method. Finally we find the size of the nano particle in the range of 30.6nm. We have used only 4% of doping. The size of nano particle is characterized by XRD. And by comparing the pure form of Nickle Oxide with Cadmium doped Nickel Oxide and we get that some more peak of impurity (Cadmium) as (100), (101) and it also increase the intensity of the peak of Nickel Oxide. and by the PL spectrum we see the result of doping. and see the effect of wavelength on the material.

UV Visible spectrum shows that absorption capacity of Nickel Oxide has been enhanced because of Cadmium Doping. And it shows the Cadmium doped Nickel Oxide shows more absorption at 270 nm

FTIR spectrum shows the absorption capacity in infrared light that how much absorption is possible in wavelength that is below to red light.

I find that there is significant changes in the property of Nickel Oxide nano particle this nano particle will simplifies the human beings by improving the property of Nickel Oxide Nano material by improving their strength.

It has been clear that there is more percentage of doping reqired to enhance the more property of Nickel Oxide.

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