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A comparative analysis of structural, optical and photocatalytic properties of ZnO and Ni doped ZnO nanospheres prepared by sol-gel method

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ABSTRACT

$Zn_{1-x}Ni_xO$ (x=0, 0.5) nanoparticles were successfully prepared by sol gel method. Structural analysis was performed by XRD confirming phase purity and crystalline wurtzite structure. Surface morphology of nanosystems was performed by Scanning Electron Microscopy (SEM) and High Resolution Transmission Emission Microscopy (TEM) .Due to doping of ZnO nanoparticles the absorption shifted towards the visible region from UV region .The absorption increases on doping in the visible region.The Photocatalytic activity of both the doped and undoped ZnO was analysed via degradation of Methylene Blue. The Methylene Blue decomposition rate of pure ZnO and Nickel doped ZnO nanoparticles were studied under UV – Visible region. In the visible region both pure and doped ZnO decomposed Methylene Blue.This confirms the potential application of ZnO Nanoparticles for removal of harmful dyes from waste water and drinking water.The doping has a pronounced effect on the photocatalytic activity of nanoparticles. The degradation rate of the dye increased in case of Ni doped ZnO nanospheres. Copyright © 2012 VBRI Press.

Keywords: Nanoparticles; photocatalyst; HRTEM; SEM; SAED; degradation.

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Introduction

Semiconductor metal oxides especially ZnO with a wide band gap (3.37 eV) [**1**] and large exciton binding energy(60 MeV) [**1, 2**], n-type conductivity, high isoelectric point (9.5) [**3**] and environment friendly have been used extensively for purpose of applications as microbial inhibition, photo catalysis, solar cells, removal of heavy metals [**4, 5**], gas sensors [**6**]. The nanospheres are prepared by sol gel route. The sol gel method is extensively used for synthesis of advanced ceramics and nanoparticles. As the band gap lies in UV region, ZnO absorbs UV light with wavelength equal or less than 385 nm. However for photo catalytic applications, photo catalysts as ZnO should also absorb in visible region as solar spectrum contains 46% visible, 47% IR and 5-7% of UV light [**7**]. For this the band gap has to be narrowed which can be achieved by doping with transition metal ions [**8, 9**]. The surface area and surface defects play an eminent role in photocatalytic activity of semiconductor metal oxides. The modification of surface area or variation in surface defects can affect the optical and electronic properties. Various metal oxides have been used as photocatalytic agents. .ZnO has emerged to be efficient catalyst for water detoxification because it generates H_2O_2 more efficiently [**10**] and has high surface activity [**11**]. Nanoparticles viz. TiO_2 have also been used in

degradation of dyes [**12**] also possess high photocatalytic efficiency [**13**]. However ZnO proves to be a better photocatalyst than TiO_2 due to its higher efficiency of generation and mobility of photoinduced electrons as well as holes [**14**].

The surface area and surface defects play an eminent role in photo catalytic activities of metal oxides. The doping with a transition metal ion increases the surface defects [**15**]. This can presumably shift the absorption towards visible region. The enhancement in optical absorption in surface defects by doping with Ag ion [**15**] make us proceed in study of photo catalytic property in undoped and doped ZnO nanoparticles. To improve the photo catalytic activities we doped ZnO with Ni and carried out the photo catalytic degradation of methylene blue dye. As a pollutant we have used methylene blue, which is a hazardous dye as it causes shock, hyper tension, cyanosis, jaundice, quadriplegia, and tissue necrosis.

Experimental

Synthesis of doped and undoped ZnO nanoparticles

For the synthesis of $Zn_{1-x}Ni_xO$ (x = 0, 0.5), appropriate amounts of Zn $(NO_3)_2$ (Merck, 99.9%) and Ni $(NO_3)_2$ (Merck, 99.9%) of Analytical Reagent grade were mixed and dissolved in water. In the next step the mixture was put into citric acid with constant stirring. The pH of the solution was kept at 7.0 by adding liquid ammonia solution. The solution then was dried at 80 ^{0}C to obtain a gel. The powder was then grinded and the powders were sintered at 600 ^{0}C for 2 h.

Characterization

The Phase purity and crystalline size of ZnO and Ni doped ZnO nanoparticles were determined by an XPERT-PRO X-ray diffractometer using Cu *Kα* radiation. The phase structure was determined by XRD. To study the morphological properties of ZnO and doped ZnO nanoparticles was done by using a Scanning Electron Microscope (SEM) QUANTA250 FEI D9393. Morphology was also studied by High Resolution Transmission Electron Microscopy (TEM) and SAED TEM also using PHILIPS CM200 Transmission Electron Microscope. FTIR spectra were recorded by using a Nicolet 5700 FTIR spectrophotometer from 400 to 4000 cm^{-1} by the KBr pellet method.

Photocatalytic activity /optical activity

The optical and photocatalytic properties of the samples were investigated by measuring the UV and Visible light absorption at room temperature using a Systronics double beam spectrophotometer 2202. For the measurement of optical properties 2 mg each of ZnO and Ni doped samples were added to 5 ml of water separately and were exposed to UV and Visible light.The photocatalytic activities of doped and undoped samples were evaluated by measuring photodegradation of Methylene Blue (MB) dye in water in visible region. 1.5 x 10^{-4} M solution of Methylene Blue was prepared in water and 50 mg of ZnO was added to it .Then the solution was kept in dark for five hours. The above sample was then exposed to UV and Visible light. After that solution was kept in sunlight with constant stirring and absorbance was noted after fixed intervals of time. Similar procedure was repeated with Ni doped ZnO nanoparticles.

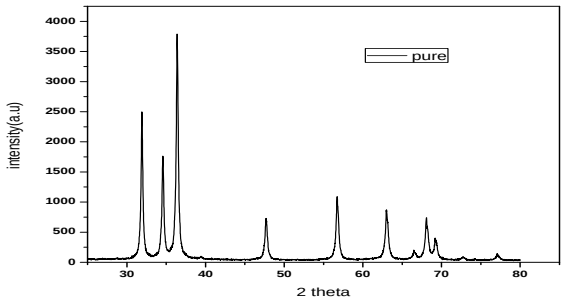

Fig. 1. XRD pattern of ZnO nanoparticles.

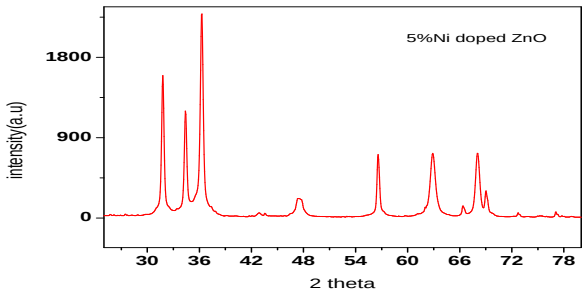

Fig. 2. XRD pattern of Ni doped ZnO nanoparticles.

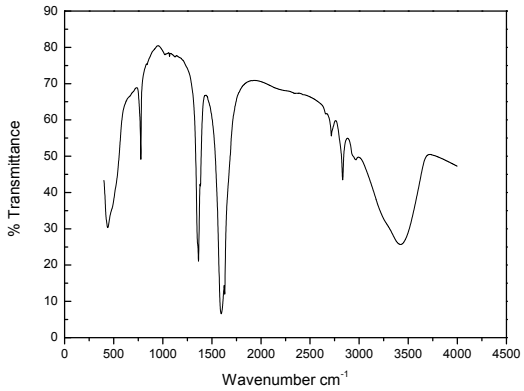

Fig. 3. FTIR pattern of pure ZnO nanoparticles.

Results and discussion

XRD analysis

XRD patterns of the ZnO and Ni doped ZnO nano-crystalline sample are shown in **Fig. 1** and **2**, respectively. It reveals that, there is no change in the wurtzite structure of ZnO after Ni doping. The spectra for pure ZnO nanoparticles show the broad peaks at the positions of 31.5661, 34.4417, 36.2883, 47.6271, 56.6760, 62.7747, 66.2951, 67.7269, 69.1416 &72.5094, which are in good agreement with the standard JCPDS file for ZnO and can be indexed as the hexagonal wurtzite structure of ZnO

having space group P63mc. The average particle size calculated is found to be 21 nm.

FTIR analysis

FTIR spectra of ZnO as shown in **Fig. 3** has a strong absorption band at 432.0 cm^{-1} which is *v*(Zn—O) stretching frequency. The *v*(COO) is represented by minor absorption at 1384.6 cm^{-1}. Likewise peaks at 3401.3 cm^{-1} and 1561.9 cm^{-1} represents *v*(OH) and *v*(C=O) stretching modes respectively.

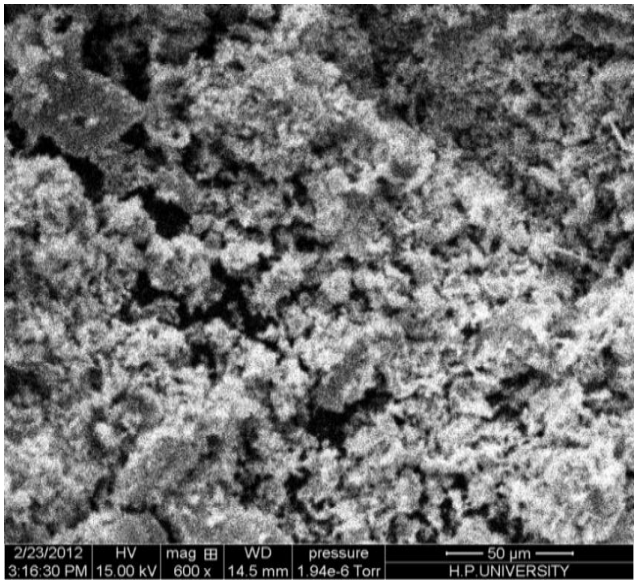

Fig. 4. SEM image of Ni doped ZnO nanoparticles.

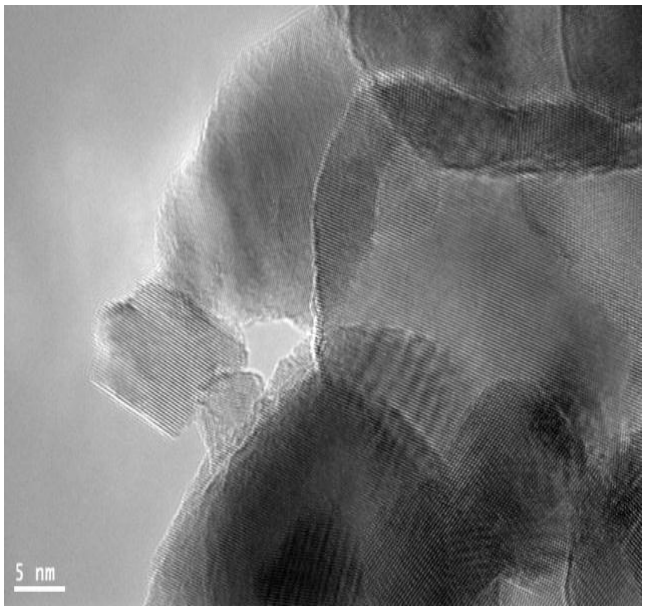

Fig. 5. HRTEM of Ni doped ZnO showing nearly spherical shape of Ni doped ZnO nanoparticles.

SEM analysis

Fig. 4 represents the surface of the prepared Ni doped ZnO nano-crystalline sample. It reveals that there is large in homogeneity at the surface with a lot of particle agglomeration. The particles are nearly spherical.

TEM analysis

High Resolution TEM clearly indicates the lattice fringes as shown by the arrows indicating clear crystalline structure that is further supported by SAED pattern by the formation of clear rings. It is also clear from pictures that particles are roughly spherical with particle size of 21nm which supports XRD data. TEM images are shown in **Fig. 5-6**.

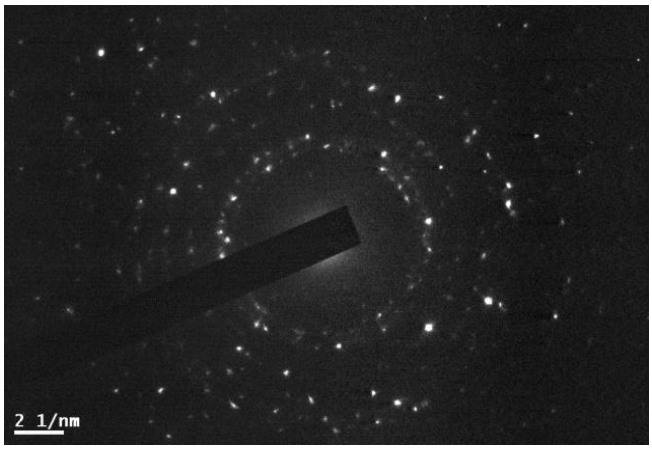

Fig. 6. Selected area electron diffraction TEM of Ni doped ZnO nanoparticles showing a perfect crystalline structure.

Photocatalytic activity and optical analysis

UV-vis spectra of both undoped and Ni doped ZnO nanoparticles showed a significant deviation in absorption intensity at the blue region with increase in doping concentration as visible in fig This can be attributed to Burstein –Moss effect [**16**].This means that the Fermi energy level merges into conduction band due to increase in carrier concentration. Hence the low energy transitions are blocked [**16**]. It is visible from figure 7 the absorbance of Ni doped ZnO nanoparticles in visible region is more than pure ZnO nanoparticles.

The band gap as calculated for pure ZnO is 3.21eV and for the Ni doped ZnO is 3.15 eV.The band gaps is calculated using the Tauc relation [**17, 18**]:

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

where α is the absorption coefficient, A is a constant and n = ½ for direct band gap semiconductor. An extrapolation of the plot of $(\alpha h\nu)^2$ vs. $h\nu$ gives the value of band gap [**19, 20**]. The large difference in the intensity of doped sample shows that Ni doped ZnO sample absorbs more visible light and so can act as a better photo catalyst under visible light irradiation. It is assumed that enhanced optical activity is due to increase in surface imperfections due to doping in ZnO nanoparticles [**11**].

The increase in absorption intensity in blue region is attributed to more pronounce doping of ZnO nanoparticles with Ni ions. Doping of ZnO with Ni adds defect sites in the vicinity of valence band and reduces the effective band gap. When UV-vis light is passed through sample the electron–hole pair is generated within the effective band gap. It means that the electron flow takes place from defect

valence state to defect conduction state. This transition requires much lower energy than band gap of ZnO.

The photocatalytic activities of undoped and Ni doped ZnO nanoparticles were carried out using UV and visible light. The photodegradation of Methylene Blue (MB) was studied in absence and presence of ZnO nanoparticles. The dye is used because of its absorption peaks in visible range. A major chunk of pollutants in contaminated water is from synthetic textile dyes and industrial dyes. Nanoparticles as metal nanoparticles as Ag and metal oxide nanoparticles as ZnO, ZnS , Fe_2O_3 have been used to study the photocatalytic degradation of various dyes viz Methyl orange [**21**] and ZnO nanoparticles have also been used to degrade dye as Rhodamine B [**22**].

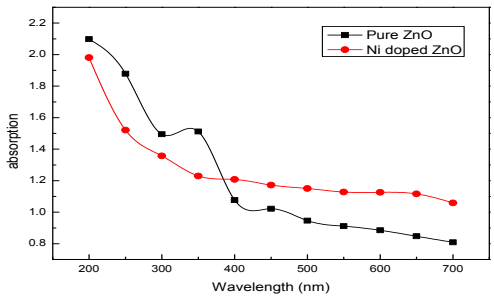

Fig. 7. UV-vis spectra of Pure ZnO and Ni doped ZnO nanoparticles.

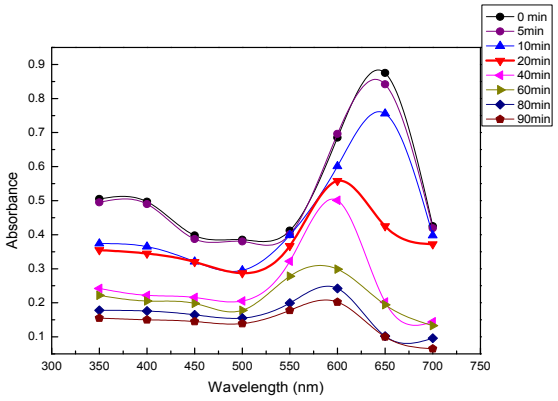

Fig. 8. Photocatalytic degradation of MB with ZnO nanoparticles in visible region.

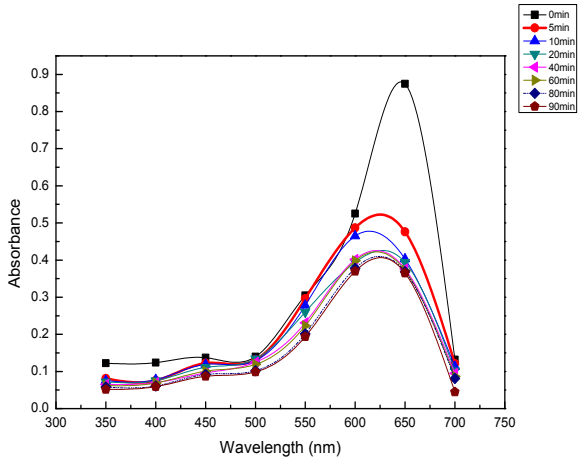

Fig. 9. Photocatalytic degradation of MB withNi doped ZnO nanoparticles with visible light.

In the UV region the undoped ZnO sample degraded the dye faster than the Ni doped ZnO nanoparticles as depicted in **Fig. 7**. The reason is being increase in surface defects on account of doping leading to enhanced absorption in the visible region. Similar effect was observed for Fe/Ni doped ZnO nanoparticles which show even more photocatalytic activity than the Ni doped ZnO nanoparticles.

Once the above samples are irradiated to visible light, electron hole pair is generated. The electron so generated disrupts the conjugation in the dye and thus the decomposition of dye and the hole so generated creates $OH^{\cdot}$ from water which again leads to degradation of dye. The mechanism is as follows:

$$ZnO + h\nu \rightarrow e^- + h^+$$

$$H_2O + h^+ \rightarrow O H\bullet + H^+$$

$$O_2 + e^- \rightarrow O_2\bullet^-$$

$$O_2\bullet^- + H^+ \rightarrow HO_2\bullet$$

$$2\ HO_2\bullet \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + O_2\bullet^- \rightarrow OH\bullet + O_2 + O$$

$$OH\bullet + MB^+ \rightarrow \text{degraded product}$$

The plot of absorption vs. wavelength at various times for the photo degradation of dye is represented in **Fig. 8 and 9**. It is visible in graph that Ni doped ZnO degrades the 50% of dye (represented by solid red curve in **Fig 8**) in just 5 minutes as compared to ZnO which takes almost 20 minutes to degrade 50% of dye (represented by solid red curve in **Fig. 9**). Hence ZnO and modified ZnO nanoparticles via doping can be used as potential photo catalytic agents for degradation of dyes and other harmful organic compounds.

Conclusion

Dye effluents from textile industries have become a serious environmental problem because of their unacceptable colour, high chemical oxygen demand and resistance to degradation. ZnO is a well-known photocatalyst. We synthesised Ni doped ZnO nanoparticles via sol gel method. The above synthesized samples proved to be more effective photocatalysts than ZnO itself. The doped ZnO nanoparticles prove to be efficient materials for degrading contaminated coloured waste water for reusing in textile industry. Hence the synthesized doped nanoparticles prove to be better agents for environmental detoxification of organic compounds, harmful dyes and some metals too from waste water.

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