Spectroscopic and fiber optic ethanol sensing properties Gd doped ZnO nanoparticles

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HIGHLIGHTS

- Simple, cost effective nanoparticles synthesis at moderate temperatures.
- Doping leads to particles growth.
- Doping leads to red shift in band gap and broad absorption in the visible range.
- Ethanol sensing increased by Gd doping into ZnO.

GRAPHICAL ABSTRACT
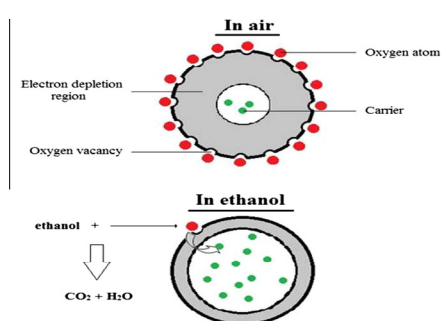
Schematic representation of clad modified fiber sensing mechanism

ARTICLE INFO

ABSTRACT

We report the structural, optical and gas sensing properties of prepared pure and Gd doped ZnO nanoparticles through solgel method at moderate temperature. Structural studies are carried out by X-ray diffraction method confirms hexagonal wurtzite structure and doping induced changes in lattice parameters is observed. Optical absorption spectral studies shows red shift in the absorption peak corresponds to band-gap from 3.42 eV to 3.05 eV and broad absorption in the visible range after Gd doping is observed. Scanning electron microscopic studies shows increase in particle size where the particle diameters increase from few nm to micrometers after Gd doping. The clad modified ethanol fiber-optic sensor studies for ethanol sensing exhibits best sensitivity for the 3% Gd doped ZnO nanoparticles and the sensitivity get lowered incase of higher percentage of Gd doped ZnO sample.

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Introduction

Metal oxide nanomaterials based gas sensors are very interesting in detection of toxic gasses whose selectivity is depend upon the sensitivity for a particular gas. Clad modified fiber optic based gas sensors using metal oxides as gas sensing medium is a well known room temperature based low cost effective sensing technique. In this type of sensors cladding portion of the fiber is replaced by the prepared metal oxide and used for gas sensing. Gas interaction with modified clad varies the intensity of the light propagating through the fiber core is the key principle in the sensing mechanism. The spectral characteristics of clad modified fiber optic sensor using metal oxide (ZnO, SnO_2, TiO_2, and WO_3) can be studied for various gasses detection such as ammonia, ethanol, and methanol [1]. ZnO as a semiconductors is a promising material due to its optical, electrical and piezoelectric properties by having large band gap (around 3.4 eV) and large exciton binding energy (60 meV). ZnO is also inexpensive, abundant in the nature, chemically stable and non toxic. Doping with appropriate elements

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in ZnO has been reported to be an excellent way to improve its properties to avail this material for device fabrications [2–10].

The spectral response of the metal oxide to these gases can be understood by the gas sensing model. Clad-modified fiber optic sensor works in evanescent wave mode. When it is partially clad-removed fiber, the amount of light leakage into cladding is lesser due to total internal reflection [11]. In case of fully clad removed fiber, light leakage onto the cladding may be higher or lower depending upon the refractive index of the cladding compared to the core [12]. Fully clad removed fiber exhibits more gas sensitivity when compare to the partially clad removed fiber. Among the various metal oxides, ZnO exhibits some vital role because of non-toxicity and low cost of preparation. Gd acts as a donor for ZnO by substituting for Zn sites. Some of the experimental result reveals that Gd doping can alter the electronic and optical properties of ZnO nanostructures [13,14]. Ethanol can be found in areas such as fuel, alcoholic beverages, medicines, varnishes and perfumes industries. At high concentrations, alcohol can be very dangerous and it is important to detect the smallest leaks. Gas sensitivity of ZnO can be enhanced by doping.

In this work we synthesized pure and Gd doped ZnO nanoparticles by using cost effective sol–gel synthesis and studied their structural, optical absorption and luminescence properties. Prepared nanomaterials are used for gas sensing using clad modified fiber optic sensor setup. Dipping technique is adopted in coating the prepared nanomaterial on the clad removed portion of the fiber and gas sensitivity and time response are studied. Dopant used in the metal oxide induced changes in gas sensitivity is discussed.

Experimental section

Pure and doped ZnO nanoparticles were synthesized by a sol–gel method. 100 ml, 0.1 M solution of Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) prepared using double distilled water (DDW) is mixed with PVP solution (1 gram dissolved in 50 ml DDW). For this mixture 100 ml, 0.1 M of NaOH was added in drop wise manner and the resultant mixture kept under continuous stirring and the temperature is maintained around 80 °C for a period of 30 min. Gd doped ZnO preparation was done in the following way: 0.003 M and 0.009 M of gadolinium nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$) were added into the 0.097 M and 0.091 M of zinc nitrate solution, respectively. Then the PVP and NaOH solutions were added to this solution in the same way stated in the procedure used for pure ZnO synthesis given above. The final solutions kept undisturbed for 24 h and the precipitates were collected by washing with ethanol and DDW followed by drying in hot air oven at 60 °C for four hours. The samples given code names as ZGd0, ZGd3 and ZGd9 based on the % of Gd concentration (0%, 3% and 9%) chosen for synthesis.

Powder X-ray diffractometry was performed at room temperature using a Rigaku Diffractometer (*Ultima III*), with Cu Kα radiation (λ = 1.54 Å). Chemical composition and surface morphology of the prepared powders were analyzed using a high resolution scanning electron microscope (SEM) with *Oxford EDAX* attachment. The optical absorption spectra were measured in the range of 200–1100 nm using *Perkin Elmer Lambda-35* UV/Vis spectrometer. The presence of chemical bonding in Gd doped ZnO nanoparticles (in KBr medium) was studied by *Nickolet iS5* FTIR (Fourier Transformed infrared) Thermo scientific Spectrometer in the range of 550–4000 cm^{-1}. The ethanol sensitivity was measured using a clad-modified fiber-optic sensor set up as previously reported [11,12].

Results and discussion

Fig. 1 shows that the XRD patterns of doped ZnO samples are similar to pure ZnO, which could be indexed to a hexagonal wurtzite structure (PCPDF card #361451). This is well agreeing with literature and our earlier reports [15,16]. No secondary phase was detected within the XRD detection limits. In order to identify influence of doping on the samples, lattice parameters 'a' and 'c' are calculated by using the formulas $a = \frac{\lambda}{\sqrt{3}\sin\theta}(h^2 + hk + k^2)$, $c = \frac{\lambda}{\sin\theta}$ [17]. Unit cell volume 'V' can be calculated by using the formula $V = \frac{\sqrt{3}a^2c}{2}$ where 'a', and 'c' are lattice parameters. An attempt for crystallite size (approximately) is carried out by using Scherrer's formula [15–17]

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where D, λ, θ, β are the mean crystallite size, X-ray wavelength, diffraction angle, FWHM of the diffraction peak respectively. The values of cell parameters, volume and average crystal size are listed in Table 1.

It is clear from the table that c-axis is increased for 3% Gd doped ZnO nanoparticles (ZGd3) from the undoped sample (ZGd0) which can attributed to the inclusion of dopant into the Zn atomic places. The increase in the values can be ascribed to the substitution of Zn^{2+} by Gd^{3+}. Indeed, later ion has a bigger ionic radius (94 pm) than the former one (74 pm). We observed that lattice parameters have negligible shift in case of high Gd doped sample (9%) where Gd enters as interstitial or formation of amorphous phase related to Gd leads to this trend. Monotonic increase in crystallite size is observed with dopant concentration supports that Gd enhances the particle growth, which is supported by our SEM observations where the particle size gets enhanced [18].

The surface morphology of the undoped and Gd doped ZnO nanoparticles are displayed in Fig. 2 along with EDAX measurements. The nanoparticles were found homogeneous, uniformly distributed and spherical in shape. These SEM studies depict increase of the particles size with increase in Gd concentration. Thus one can synthesize size variant Gd doped ZnO nanoparticles
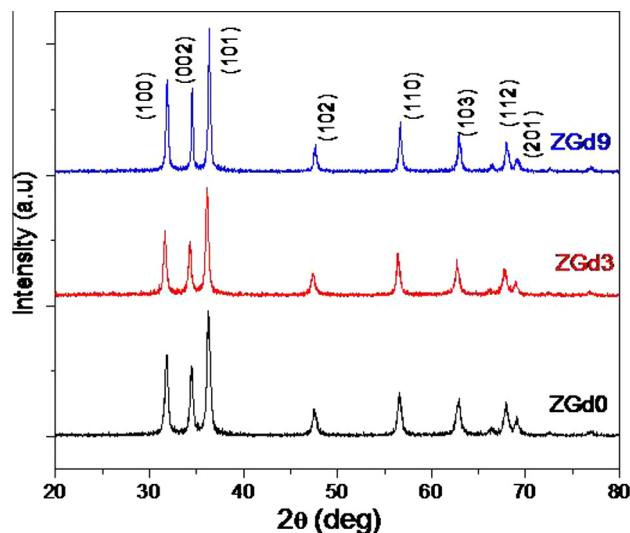

Fig. 1. XRD patterns of pure and Gd doped ZnO nanoparticles.

Table 1
Cell parameters 'a' and 'c', crystalline structure volume values (V) and average crystal size values (D) for pure and Gd doped ZnO nanoparticles.

Sample	a (Å)	c (Å)	V (Å³)	D (nm)
ZGd0	3.242	5.194	47.26	46.47
ZGd3	3.258	5.223	48.00	53.04
ZGd9	3.240	5.191	47.18	65.94