Structural Morphological Optical and Photoluminescence Properties of ZrO$_2$ Nanoparticles Synthesized by Sol-Gel Method

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Abstrsact: Zirconia(ZrO$_2$) nanoparticles with monoclinic blended structure were successfully synthesized by sol-gel methodusing zirconium (IV) acetate hydroxide as the metal precursor, polyvinylpyrrolidone as the capping agent, and deionized water asa solvent. The chemicals were mixed and stirred to form a homogeneous solution and hereafter directly underwent calcination toattain the pure nanocrystalline powder,whichwas confirmed by FTIR, UV, SEM, PL. andXRDanalyses.Thecontrol over the size and opticalproperties of nanoparticles was achieved through the molarity change in calcination temperatures from 500°C. The obtained averageparticle sizes from XRD spectra   images showed that the particle size increased with increasing calcination temperature.The optical properties which were investigated using a UV-Vis spectrophotometer showed a decrease in the band gap energy withincreasing calcination temperature due to the enlargement of the particle size. These results prove that, by eliminating dryingprocess (24 h) in the present thermal treatment method, size-controlled zirconia nanoparticles were conveniently manufacturedwith a reduction of synthesize time and energy consumption, suitable for large-scale fabrication.

Keywords; XRD, SEM, PL, UV, FTIR,

INTRODUCTION

ZrO$_2$ (zirconia) is a material of great technological importance, having good naturalcolor, high strength, transformation toughness, high chemical stability, excellent corrosion resisting, and chemical and microbial resistance [1, 2]. ZrO$_2$ is a wide band gap p-type semiconductor that exhibits abundant oxygen vacancies on its surface. The high ion exchange capacity and redox activities make it useful in catalysis [3]. ZrO$_2$ is also an important dielectric material for potential application as an insulator in transistors in future nanoelectric devices[4].ZrO$_2$has three well-defined crystal phases, that is, cubic(c-ZrO$_2$), tetragonal (t-ZrO$_2$), and monoclinic (m-ZrO$_2$),under normal atmosphere and at different temperatures [5,6].Generally, m-ZrO2 phase is thermodynamically stableup to 1100^{0}C, t-ZrO$_2$ phase exists in the temperature rangeof 1100–2370^{0}C, and the cubic phase is found at highertemperature above 2370^{0}C [8,9,10].Several techniques are available for producing zirconiananoparticles, such as sol -gel method [11], vapor phasemethod [12], pyrolysis [13], spray pyrolysis [14], hydrolysis[15], hydrothermal [16], and microwave plasma [17]. However,these methods faced many limitation factors such ascomplicated procedures, high reaction temperature, longreaction time, toxic reagents and by-products use, and highcost of production, whichmade it difficult to prepare zirconiananoparticles on a large-scale production.Thisprocess covers a verity of materials such as organic, inorganic hybrid and metallicmaterials. Nanostructured coatings developed by the sol gel techniqueprovide enhanced functional or mechanical properties as well as purity, homogeneityand improved microstructure[18,19]. It does not require vacuum and allowfabricating a large area with low cost and at low processing temperature.

Recently, sol-gel method has been used insyntheses of several nanomaterials including metals ferritenanoparticles, zincoxidenanoparticles,cadmiumOxidenanoparticles,and thermoluminescencenanomaterials. However, in the synthesis ofZrO_2nanoparticles, a solution containing metal precursorand capping mediator is directly submitted to calcination,thus eliminating the drying process and reducing the preparationtime and the energy consumption. Basically, ZrO_2 itself is an insulating direct widegap metal oxide, with an optical band gap in the range 5.0-5.85 eV [20,21]. The earliersol-gel methods for fabrication of metal oxidenanoparticles such as nanosized ZrO_2powder, a necessity forlarge-scale industrial application.The technique is relativelyenvironmentally friendly as no toxic material discharges intothe drainage system. The effect of calcination temperature onthe structural, particle size, and optical properties of ZrO_2nanoparticalsis also investigatedusing various techniques.

2. EXPERIMENTAL METHODS

2.1 Materials

$ZrOCl_2 8H_2O$ and ammonia solution (91%) were purchased from Spectrum in India. All the above mentioned chemicals are of research grade that can be used without futher purification.

2.2 Synthesis of ZrO_2 nanoparticles

The ZrO_2nanostructures were synthesized by using a very simple and low cost method.$ZrOCl_2 8H_2O$ was dissolved in distilled water in various vigorous stirring for 1Hr .Therefore ammonia solution was added into the solution drop wise while stirrin until the pH value of the solution reached 10-14. While adding the ammonia.The finally White colored precipices was containing.The $Zr(OH)_4$ precipitated was washed thoroughly with distilled water and centrifuged at 3000 rmps for 20min to remove the residuals. The process was repeated several times until the precipitate was free from any trace impurities. The Obtained $(ZrOH)_4$ precipitate was dried in a air hot oven at 100ºC for 1Hr and further calcined at 500ºC for 2Hrs resulting in the formation of (ZrO_2) nanoparticles.

2.3 Characterization of the samples

Structural analysis was carried out using X-ray diffractometry (XRD) pettometer using CuK$_\alpha$ radiation (λ= 1.5406Å) operated at 40kV and 30 mA in the wide angle region of 2θ range from 30° to 70°. Morphology and microstructure were identified by scanning electron microscope (SEM Philip XL 30). Formation of ZrO_2 phase and available molecular bonds were investigated by the FTIR absorption spectrum. To investigate the optical properties of these nanoparticles, the absorbance spectra of the samples were obtained using UV-Vis-NIR spectrophotometer.The spectral absorption spectra were recorded using UV visible spectrometer (model: Lambda 35, make Perkin) in the wave length range 300 to 1000 nm using quartz cuvettes at room temperature. The Photoluminescence (PL) Spectrum of the ZrO_2 nanoparticles dissolved in methanol has been measured using a spectrophotometer in the range of 400 to 4000 cm^{-1},(F-2500 FL Spectrophotometer, Hitachi). The Electrical conductivity study is carried out by using keithley 2636 B source meter.

3. RESULTANT DISCUSSION

3.1 Structural studies

The crystal structure in ZrO_2 nanoparticles sample with different molar concentrations is shown inFigure.1. The peak positions are in good agreement with the standard ZrO_2 (JCPDS:37-1475) . The XRD spectra of powder sample were synthesies at 0.05M, 0.1M, 0.15M and 0.2Mconcentration.

The XRD spectra of sample powder optimizedtemperature 500ºC have three resolvedpeaks at 2θ=28.216,31.5050,35.3522. which are indexed as reflection from (100) $\overline{(111)}$,(002) and (311) planes respectively.These indexed peaks corresponding to pure monoclinic phase of the ZrO_2

The crystallite size has been inferred from 2θ and the full width at half maximum(FWHM) of ($\overline{1}11$) diffraction peaks on the basis of the Scherrer's relation

$$D = \frac{K\lambda}{\beta \cos\theta}$$----------------------------- (1)

Where D is the average crystallite size(Å), K is the shape factor(0.9), λ is the wavelength of X-ray (1.5406Å) CuKα radiation , Θ is the Bragg angle and β is the corrected the line broadeningof the nanoparticles[22]. The calculated crystal size was found to increases with increase of molarity. It means that increase at higher molar concentration with decrease in FWHM of the peak. It is also evident from Table 1. for monoclinic [23] where d is the lattice spacing, a, b c and β are the lattice parameters,d is interplanar spacing,(h, k, and l) are the miller indices, θ is the angle of corresponding peakand λ is the wavelength of X-ray used (1.5406 Å). The lattice constant showed a increase with increase of molarity
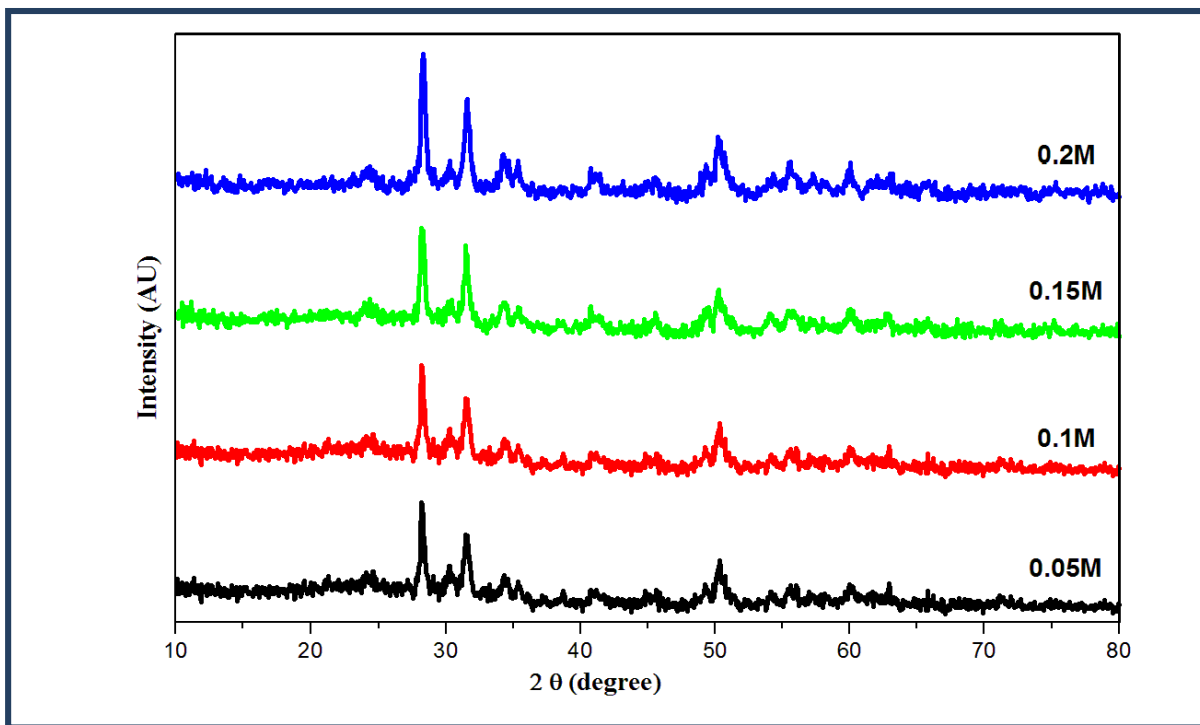

Figure.1 XRD Patterns of ZrO_2 nanoparticles for various molarity concentrations.

$$\frac{1}{d^2} = \frac{1}{sin^2\beta}\left[\frac{h^2}{a^2}-\frac{k^2 sin2\beta}{b^2}+\frac{l^2}{c^2}-\frac{2hlcos\beta}{ac}\right]$$

The structural parameters are calculated from the following equations[24],

Microstrain, $$\varepsilon = \frac{\beta cos\theta}{4}$$ --------------------- (3)

Dislocation density, $$\delta = \frac{1}{D^2}$$ --------------------- (4)

Table.1. Structural parameters of ZrO_2 nanoparticles

Molarity	2θ degree	Crystallite size(D) nm	Dislocation density δ x10^{14}lines/m^2	Microstrain ε	Lattice constants Å A	Crystal structure
0.05M	28.2161	28.97	11.915	0.0012	5.312	Monoclinic
0.10M	28.2159	34.76	8.274	0.00104	5.31	Monoclinic
0.15M	28.2779	34.76	8..271	0.0010	5.312	Monoclinic
0.20M	28.2249	34.76	8.274	0.0006	5.31	Monoclinic

β= 99.218

The lattice defects like microstrain and dislocation density showed a decreasing trend with increasing molarity which may be due to the improvement of crystallinity as well as the high orientation along (111)direction (Figure.1).

3.2. Optical study
3.2.1. Evaluation of band gap energy

Optical charactersof Zirconia (ZrO_2) nanoparticles were studied by UV absorption spectroscopy. The UV absorption spectrum of the nanoparticles as shown in Figure.2.The absorption edge was found at shorter wavelength in the UV region at 210 nm.The absorption co-efficient is calculated using the formula,

$$\alpha = \frac{2.303A}{l} \text{------------------ (5)}$$

where, A is the absorbance and l is the path length. The value of optical band gap is determined from the absorption spectra using the Tauc relation[25] ,

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

where, α is the absorption co-efficient, A is the constant having separate value for different transitions, hν is the photon energy and E_g is the band gap energy. The value of n depends upon the nature of transition. The values of n for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions are 1/2, 2, 3/2 and 3, respectively.
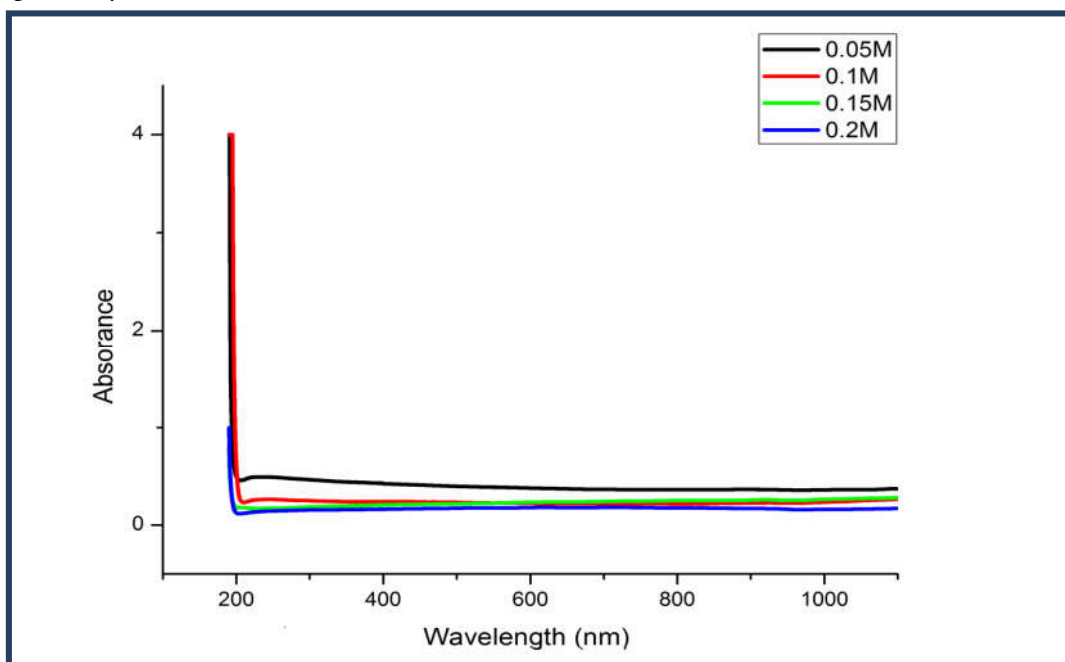

Figure. 2 Optical absorption spectra of ZrO_2 nanoparticles at various Molarities.

The band gap energies are found to be a negative number for n = 2, 3/2 and 3, and hence the relationship fitting to the ZrO_2 is n =1/2, which confirms the allowed direct transition. Figure.3 shows the curves of $(\alpha h\nu)^2$ versus hν for pure ZrO_2 nanoparticles prepared at different molarites. The E_g values are obtained by extrapolating the straight line portions of the graph to the X-axis. The measured energy band gaps from these plots are represented in Table 2. From this table, it can be observed that the E_g values varied from 4.8ev to 5.2eV for Pure ZrO_2 nanoparticles prepared at optimized temperature. The bandgap energy of semiconductors tends to decrease as the molarity is increased. An increased inters atomic spacing decreases the potential seen by the electrons in the material, which in turn reduces the size of the bandgap energy.
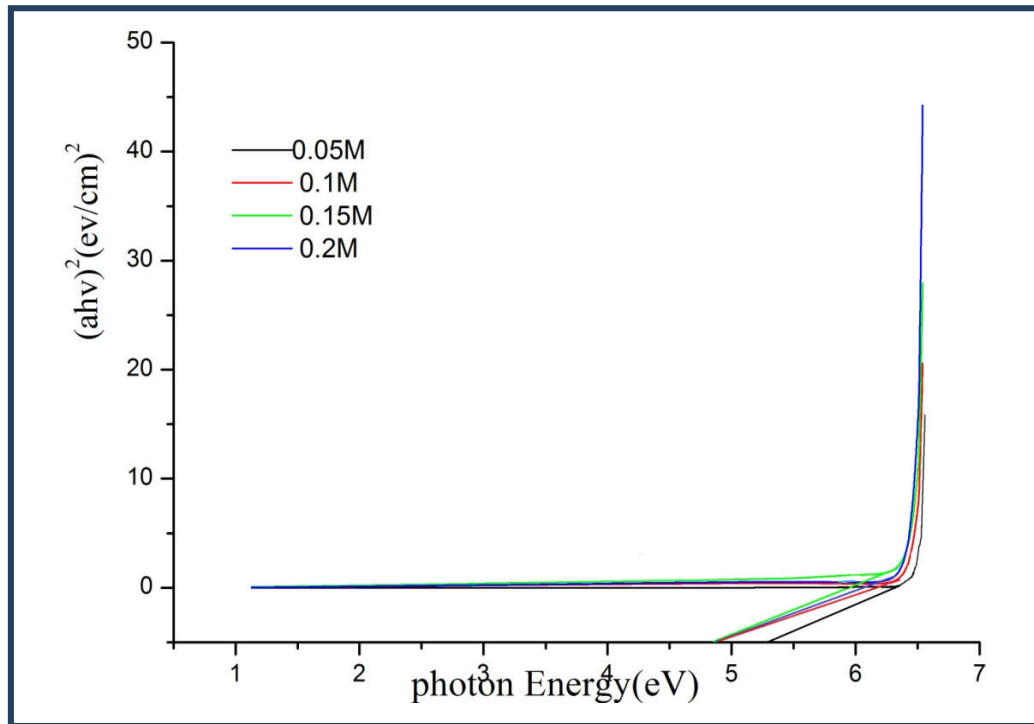

Figure. 3 The plot $(\alpha h\nu)^2$ versus hν pure ZrO_2 nanoparticle

Table. 2 Variation of absorption edges and energy band gap of ZrO_2 nanoparticles at various molarity

Molarity M	Band gap energy(eV)
0.05	5.2
0.1	4.8
0.15	4.8
0.2	4.8

3.3 Functional group analysis of ZrO_2 nanoparticles

The FTIR spectra of synthesized sample at calcined at 500 $^{\circ}$C in different molarity (0.05-0.2M) of ZrO_2 are as shown the Figure.4. The Spectrum of ZrO_2 related on the nature of materials, preparative procedures used, soild-state structure and so fouth[26]. The looking at FT-IR spectra it's clear that the ZrO_2 nanostructures still contain water molecule, since H_2O and CO_2 molecule hava property to be chemisorbed easily on the Zro_2 surface, when they exposed atmosphere [27]. The spectra were taken in the range 400- 4000 cm^{-1}. The main peaks at 470cm^{-1} due to the formation of Zr-O bonds and which the range of IR (800-400cm^{-1}) photon modes of crystalline Zroconia[28] .

The absorption band at 1552 cm^{-1} corresponds to the H-O-H bending vibration region is attributed to stretching of O-H group , characterstics of hydrated compound.
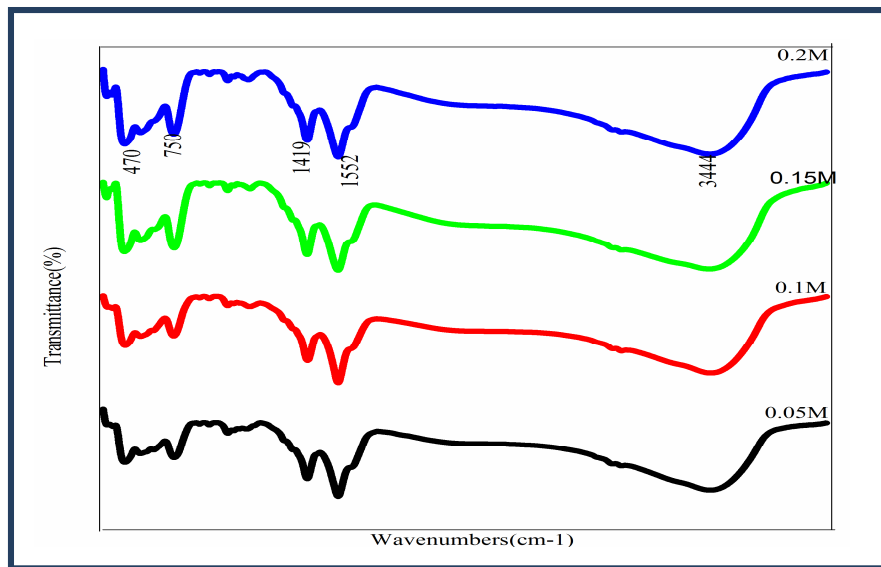

Figure. 4 FTIR spectra of ZrO$_2$ nanoparticles at various Molarities

3.4 Surface Morphlogical analysis

The Figure.5(a, b, c and d)the SEM micrographs of the surface of (ZrO$_2$)nanoparticles prepared at differentmolar concentrations. The surface morphology of the ZrO$_2$ nanoparticles is observed. But, it could not be viewed the grain size clearly. From the Figure5(a, b) one can find that, a microstructure consisted of many plateshaped crystalline particles. The microstructure formed is found to be uniform and compact which are interconnected by grains. These results suggested that, the size of the grains is large at low concentration; less than 0.1M. Further, it is reduced, when the molarity concentration is increased. There by the best uniform surface morphology is identified at 0.2M. However, the overall observation is that, the grain size is decreased and its surface becomes optically flat with increase the concentration. Pure ZrO$_2$nanoparticles appears like plate in shape of size ~1µm. All these nanoparticles present in the size range of nm.
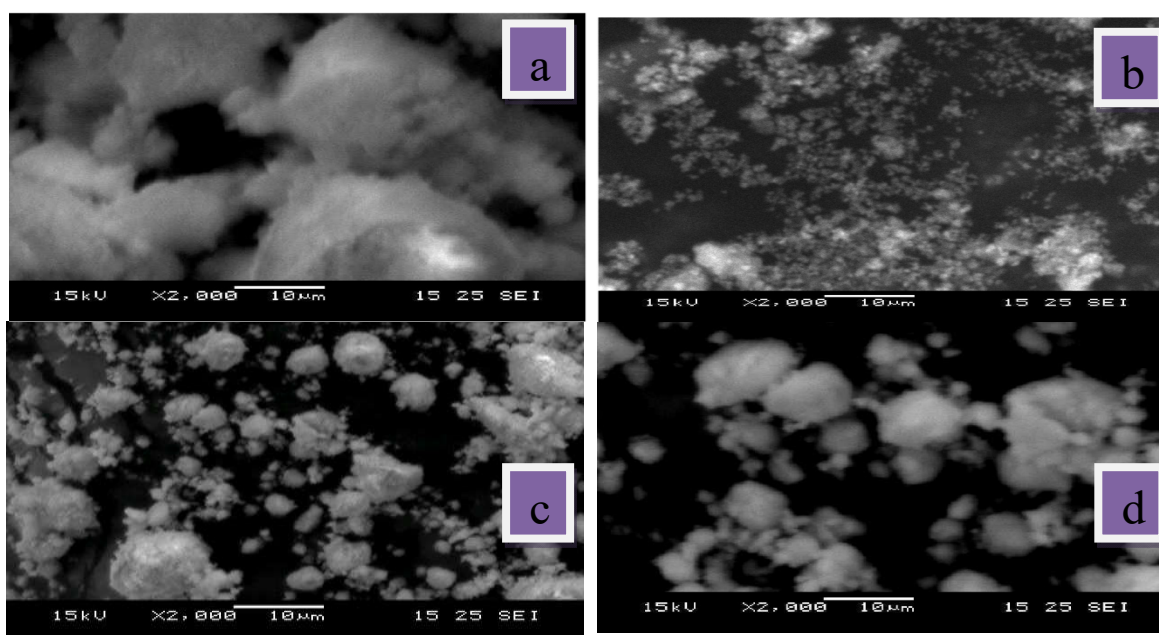

Figure.5(a-d) SEM images ofZrO$_2$ nanoparticles at different magnifications

3.5 Photoluminescence (PL)

The Photoluminescence (PL) spectra of zroconiananoparticles was recorded with a view to understand theformed nanoparticles on the emission propertiesofthematerials.Photoluminescenceemissioncurvesofthe molarity (0.05-0.2M) for zroconiananoparticals has a broad Visible emission band extending from 350 nm to 600 nm which nearly covers the entire visible range showing emission peaks for 0.15M and 0.2M at359nm,409nm,443nm,,492 nm and 518 nm are obtained. The peaks at 359 nm excitation wave length,443nm and 492nm phosphors exhibit blue. The peaks are obtained in the Figure.6. All peaks range and shift including as shown in theTable.3
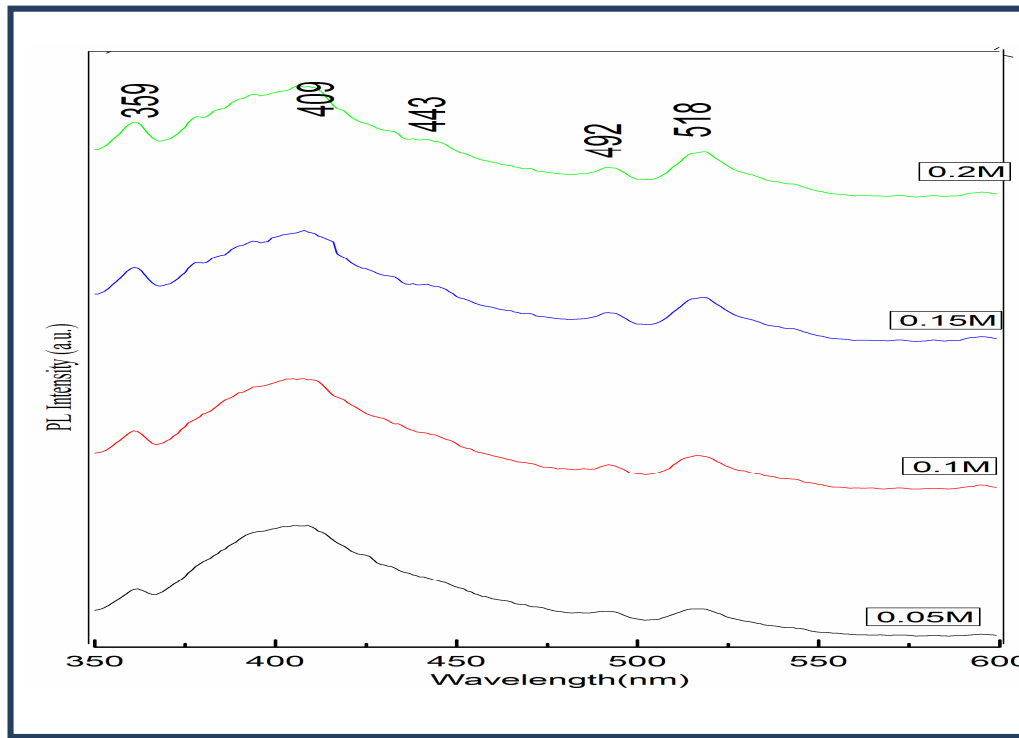

Figure. 6 The photoluminescence spectra of ZrO_2 nanoparticles at various Molarities.

Table. 3. The Photoluminescence spectra ZrO_2 nanoparticles.

Range(nm)	Colour
359-409	Green
443-492	Blue
500-596	Red /Orange

CONCLUSION

The ZrO_2 nanoparticles calcined at $500^{\circ}C$ have been prepared by a sol-gel method.The study of XRD revealed that the synthesized ZrO2 nanoparticle transformed monoclinic structure [JCPDS- NO-37 - 1475] ZrO_2nanoparticles.The Optical properties were examined by the UV-Vis absorption spectrum. The band gap value was found to be 4.8ev to 5.2ev.The PL emission of the sample covers full nearly visible range attributed to the closed level emission which can be considered to be promoted by the morphology and size of the nanoparticles formed. Considering the growth and reprocibility of the ZrO_2nanoparticles and visble emission found in the as formed sample provides better option for LED application.

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