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Synthesized and Characterization of ZrO_2 Nanoparticles

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ABSTRACT

A simple room temperature chemical route, which was based on the reaction of zirconium nitrate and hexamethylenetetramine as a starting material in aqueous medium at 576 K for 24 hr., was proposed for the synthesis of zirconium dioxide (ZrO_2) nanoparticles. The structural properties of prepared material were characterized by using X-ray diffraction and Field emission scanning electron microscopy. The optical properties of material were studied by using photoluminescence and Ultra-Violet spectroscopy. X-ray diffraction and Field emission scanning electron microscopy shows that material was crystalline with particles size in nano range. Ultra-violet spectra indicated that the as-synthesized ZrO_2 nanoparticles has a direct band gap of 4.82 eV and also is a usual value for the photo catalytic activities in UV-Vis light.

***Keyword:* zirconium nanoparticles; simple chemical route; UV-Vis spectroscopy.**

1. INTRODUCTION

Zirconium dioxide (ZrO_2) nanoparticles have attracted much research interest due to their specific electrical and optical properties. It is an important ceramic material with applications in solid oxide fuel cells, catalysts, oxygen sensors, filters and protective coating for optical mirrors [1, 2]. Pure ZrO_2 exists in three polymorphic phases at different temperatures such as monoclinic, cubic, and tetragonal. At low temperatures (below 1150 °C) the material transforms to the monoclinic structure which is a thermodynamically stable phase. At very high temperatures (>2370 °C) the material has a cubic structure. At intermediate temperatures (1150-2370 °C), it has a tetragonal structure [3]. Recently, ceramic material is of considerable interest because of their potential application in material science and commercial industries. These materials have a high specific surface area and have been extensively studied because of their distinctive properties including a high electrical and thermal conductivity, chemical stability, catalytic activity and nonlinear optical behavior [4]. Ceramic nanomaterial exhibits very interesting electrical, optical, and chemical properties, than their bulk materials [5, 6, 7]. Also various types of materials such as SnO_2 [8], TiO_2 [9] and Al_2O_3 [10] are shows interesting properties. But, these materials have some limitations (e.g., TiO_2 has a limited photo activity with the radiation provided by solar light [11]), among them, one of the most recently studied rather than reported above inorganic semiconducting materials is ZrO_2 because of its nature as n-type and it is a wideband semiconductor, with band gap in the range of 5-7 eV [12]. ZrO_2, especially at nano level is applied in various fields such as transparent optical devices, electrochemical capacitor electrodes, oxygen sensors, fuel cells, catalyst and advanced ceramics. ZrO_2 nanoparticles have been synthesized by various techniques including direct mechano-chemical and glycothermal processing, electro spinning [13, 14, 15]. Chemical route is one of the most extensively employed techniques for the preparation of metal oxide as stable, colloidal dispersions in water or organic solvents [16]. This method has been proven to have some additional advantages over the above discussed method in synthesis. The chemical route seems to be the most convenient for the synthesis of nanoparticles because of its simplicity and better control over crystallite size, efficiently control the morphology and chemical composition of prepared materials [17]. The preparation of ZrO_2 was first reported in 1997 [18]. Recently, the synthesis of ZrO_2 nanoparticles with large surface area has been described. Masoodiyeh et al [19] synthesized zirconia nanoparticles in supercritical water using hydrothermal method. The particle morphology was found to depend on the reaction temperature and pressure, pH and precursor concentration. Benfer et al [20] studied structural morphology and surface properties of ZrO_2 particles synthesized by using CVD of a liquid metal organic precursor in a flow reactor system. The structure and morphology of the zirconium is essentially preserved during extensive

thermal treatment up to 500 °C. Manoharan et al [21] synthesized zirconia phosphors nanoparticles using zirconium oxalate as precursor by a sonochemistry without the use of surfactants. These phosphors are likely to have remarkable optical applications in the fields of optoelectronic devices such as emitting UV-LEDs, UV lasers and multi-color displays. Kanade et al [22] synthesized zirconia nanoparticles by hydrothermal method using viable zirconia powder which is obtained has a stable monoclinic phase and showed spherical particle morphology. The zirconium nanoparticles using hydrothermal method in large-scale production potentially utilized for solid oxide fuel cells and other potential applications like gas sensors and electronic ceramics.
Current investigation supports that it is very necessary to synthesized and studies the zirconium nanoparticles. In the present work, ZrO_2 nanoparticles are synthesized by simple chemical route method using zirconium nitrate and hexamethylenetetramine (HMT) as starting chemical. The prepared samples was characterizes XRD techniques, PL and UU-Vis spectroscopy.

2. EXPERIMENTAL

All chemicals were used of analytical grade (SD fine, India) without further purification. The sample was prepared with deionized water of resistivity not less than 18.2 MΩ/cm. The zirconium nitrate and hexamethylenetetramine (HMT) were used for the synthesis of ZrO_2 nanoparticles. In a typical synthesis, 1 M zirconium nitrate ($ZrO(NO_3)_2 \cdot xH_2O$) was mixed with 1 M hexamethylenetetramine (HMT) in 20 ml deionized water under magnetic stirring for 45 min at room temperature. Subsequently, obtained product kept for a centrifuge operating at 3000 rpm for 28 min. After this procedure, solution was separated into two gradations. At the bottom a white layer of ZrO2 nanoparticles observed and over it more transparent and dispersed layer appeared. This centrifuged precipitate was collected through cellulose nitrate filter paper. The filtrate was dried at room temperature for 36 hours in vacuum chamber and then sintered at 550 K for 24 h. After sintering the synthesized material appears white colored powder in visible light. X-ray diffraction (XRD) patterns were recorded using a Rigaku miniflex-II diffractometer with CuKα radiation in the range 10°-70°. The ultraviolet–visible (UV–vis) spectrum recorded on Perkin Elmer UV spectrophotometer in the range 250-700 nm. Photoluminescence measurements were performed at room temperature on a Hitachi F-7000 spectrofluorometer equipped with a 450-W xenon lamp, in the range from 250-600 nm.

3. RESULTS AND DISCUSSION

The purity and crystallinity of the final product ZrO_2 nanoparticles were examined by using XRD analysis. Figure 1 show the XRD spectrum of the synthesized particles by chemical route method. The XRD spectra of the samples was recorded using a Rigaku Miniflex-II in the 2θ range from 10°-70° in steps of 0.02°. The prominent peaks appear at different 2θ position exactly indexed to the formation of this compound (PDF-01-081-1667). The sharp diffraction peaks appearing at various 2θ positions clearly confirm the prepared sample was crystalline nature. No other peaks for impurities were detected. The average crystallite sizes of the ZrO_2 nano crystallites have been calculated from diffraction by Debye-Scherrer formula:

$$D = K\lambda/\beta\cos\theta$$

Where K =0.9 is the shape factor, λ is the X-ray wavelength of CuKα radiation (0.1542 nm), θ is the Bragg angle, and β is the full-width at half-maximum (FWHM) of the respective diffraction peak (in units of radians). The average crystallite size of the ZrO2 nanoparticles was calculated to be 56 nm.

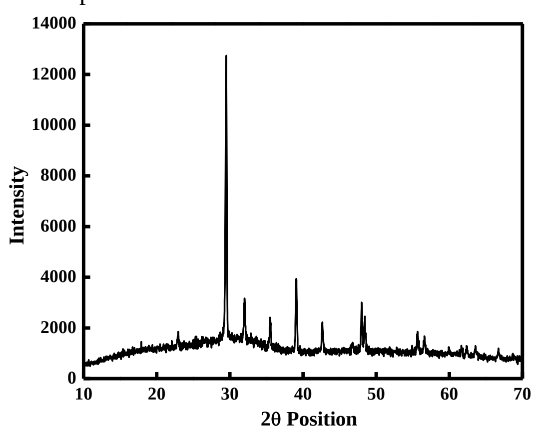

Fig- 1: XRD spectra of the ZrO2 prepared by chemical route method.

The FE-SEM image of ZrO_2 nanoparticles is shown in Fig. 2. This shows that the nanoparticles are within in nano range. The small amount of agglomeration of nanoparticles is observed in the micrograph. The average particle size is observed to be 56 nm. The average particle size estimated from XRD is in good agreement with the FE-SEM investigation. Imaging nanoparticles through electron microscopy technique is not enough to say it is in a nanoparticles state. The optical absorption is a technique that allows one to directly probe the band gap of nanoparticles. The band gap edge of a material should be blue shifted if the material is confined. This blue-shifted spectrum confirmed the formation of nanoparticles. In our case, the intense absorption is observed at 241 nm.

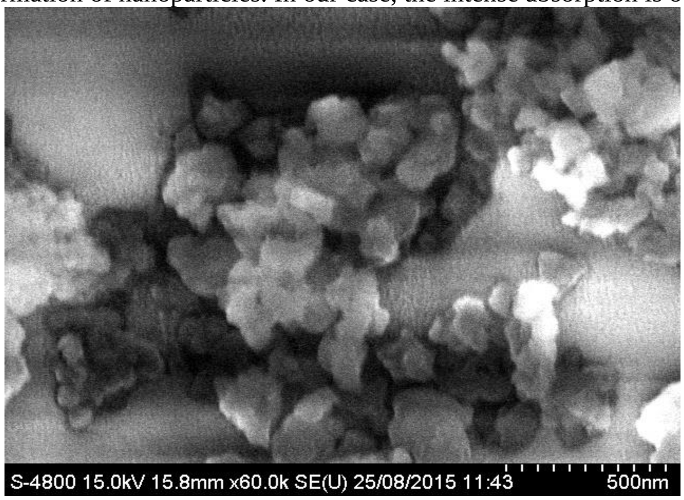

Fig- 2: FE-SEM image for ZrO_2 nanoparticles

There has been an increasing interest for the application of nanoparticles to photonics systems due to their enhanced luminescent properties, which exists due to their small size. Photoluminescence (PL) measurements were performed at room temperature on a Hitachi F-7000 spectrometer equipped with a 450-W xenon lamp, in the range from 250-600 nm, with a spectral slit width of 1 nm and photomultiplier tube (PMT) voltage of 700 V. The spectra were corrected using Rhodamine B standard by following the procedure prescribed by Hitachi. Figure 3 show the PL spectra of the synthesized ZrO_2 nanoparticles by chemical route method.

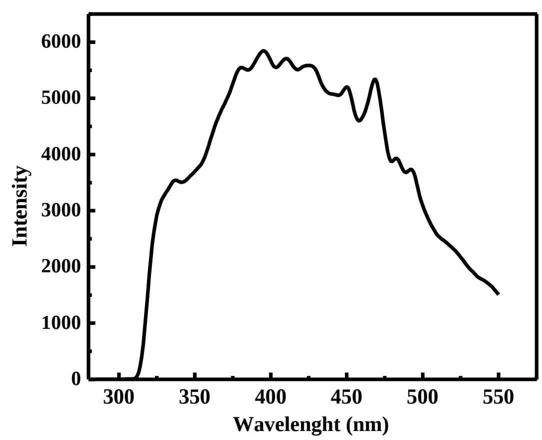

Fig- 3: PL emission spectra of the ZrO_2 prepared by chemical route method.

The spectrum shows the broad emission bands in range between 375-500 nm. This result indicates that the PL emission comes from the ZrO_2 nanoparticles. The emission bands in the ZrO_2 might be due to the transitions from the surface trap states in the conduction band to lower energy levels near to the valance band [23]. The bands observed at around 350 may be due to the presence of oxygen vacancies. It can be mentioned that the small particle size was the main reason for the broad fluorescence band [24].The most remarkable property of nanoparticles is the size evolution of the optical absorption spectra. Therefore UV-Visible absorption spectroscopy is an efficient technique to study the optical properties of nanoparticles. The UV-Vis spectrum of ZrO_2 nanoparticles prepared by the chemical route method is depicted in figure 3. The UV-Vis absorption spectrum of ZrO_2 nanoparticles was observed in region of 200-1000 nm. Inset show optical band gap of ZrO_2 nanoparticles was estimated by plotting the $(\alpha h\nu)^2$ versus hν (eV). The band gap energy of ZrO_2 nanoparticles was found to be 4.82 eV. The value of particle size and band gap of ZrO_2 clearly shows that this nanomaterial is applied in photo catalytic activities and optical devices. The UV spectrum show an absorption peaks around 241 and 302 nm. This is caused by charge transfer transitions, corresponding to the excitation of electron from valence band to the conduction band.

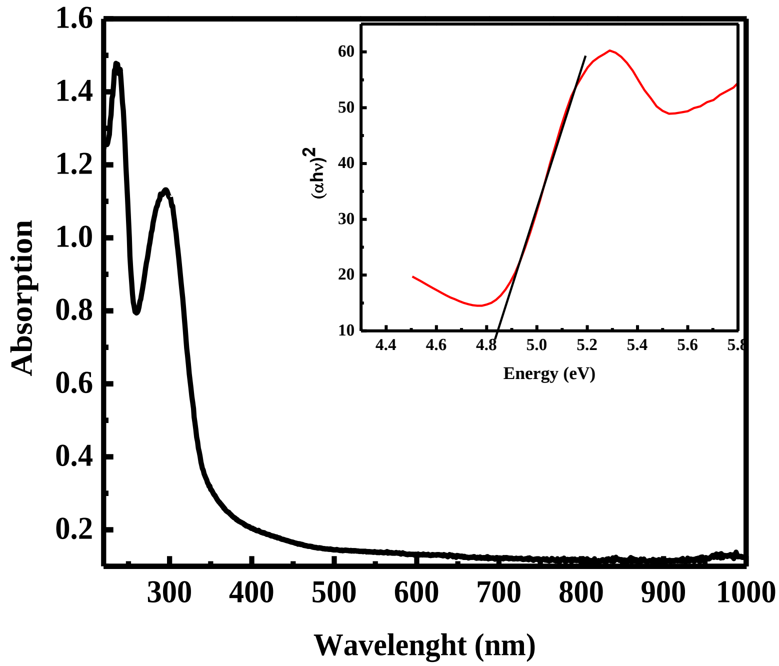

Fig-3: UV-Vis absorption spectrum of ZrO_2 nanoparticles along with optical band gap (inset).

4. CONCLUSIONS

In summary, ZrO_2 nanoparticles have been synthesized using a simple chemical route method. This product was obtained by using $ZrO(NO_3)_2{\cdot}xH_2O$ and $C_6H_{12}N_4$ as starting materials. The structural optical properties of the nanoparticles have been studied by XRD and FE-SEM while optical properties using PL and UV-Vis techniques. The nanoparticles have highly crystalline and not from other impurity peaks. An average particle size of the resulting nanoparticles was found to be 56 nm computed using XRD and FF-SEM. The optical property of the produced nanoparticles was studied by measuring absorbance and optical band gap. The estimated optical band gap energy (3.2 eV) is an accepted value for the photo catalytic activities in visible light and also for application in the solar cells and electronic devices. The chemical route method is rapid, simple, and cost effective, which can be easily extended to the preparation of other oxide nanoparticles.

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