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Synthesis & Characterization of Zirconium Oxide (ZrO_2) Nanoparticles in Hydrothermal

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Abstract: ***Heavy metals are well - known environmental pollutants owing to their toxicity, longevity in the atmosphere, and ability to accumulate in the human body via bioaccumulation. The pollution of terrestrial and aquatic ecosystems with toxic heavy metals is a major environmental concern that has consequences for public health. The paper presents the preparation and investigations of zirconium oxide (ZrO2) nanoparticles that were synthesized by hydrothermal process. The ZrO2 nanoparticles were well characterized by using different sophisticated instrumentation techniques like UV - Vis, FT - IR, XRD, TEM, EDAX, and DLS. The formation of ZrO2 NPs was primarily confirmed by its characteristic absorption band at 342 nm using UV - Visible spectroscopic hydrothermal analysis. The crystal structure was determined using X - ray diffraction. The morphology and the particle size were studied using (SEM) and (TEM). The spherical shaped particles were confirmed through the SEM analysis. The transmission electron microscopic analysis confirmed the formation of the nanoparticles with the particle size. The FT - IR and Raman spectrum ascertained the strong presence of ZrO2 nanoparticles. The optical properties were obtained from UV–visible absorption spectrum and also PL emission spectrum. The Energy Dispersive X - ray spectroscopy technique was used to identify the elemental composition of the ZrO2 Nano - particles. The dielectric constant and the dielectric loss were measured as a function of frequency and temperature.***

Keywords: Heavy metal, ZrO_2, SEM, TEM & UV - X - ray.

1. Introduction

The pollution is caused by a variety of pollutants in water, air and soil. One of the major concerned globally distributed pollutants of living environment is hazardous metals. Metals occurs naturally in the earth crust. The distribution of metals in the environmental is governed by the properties of the metal and influences of environmental factors Metals are notable for their wide environmental dispersion from such activity. Out of the 92 naturally occurring elements, approximately 30 metals and metalloids are potentially toxic to humans. Heavy metals refer to any metallic element that have relatively high density and is toxic or poisonous even at low concentration. Heavy metal is collective term which is applied to the group of metals and metalloids with atomic density greater than 4g/cm3 or 5 times or greater than water. Environment is defined as the totality of circumstances surrounding an organism or group of organisms especially the combination of external physical conditions that affect and influence the growth, development and survival of organism. Heavy metals enter the environment by the natural and anthropogenic means such as natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest or disease control agents applied to plants, air pollution fallout and a number of others (Ming – Ho, 2005). The contamination chain of heavy metals almost always follows a cyclic order i. e. Industry → Atmosphere → Soil → Water → Foods → Humans. Therefore, concern about exposures, intakes and absorption of heavy metals by humans are increasing day by day in developing world.

Nanotechnology is considered to be the most exciting research in various fields as nanomaterials possess a variety of properties. Different nanoparticles like metal and metal oxide, metal Sulphide are synthesized by both physical and chemical methods. Nanomaterials have been used in various fields such as environment, biomedical, food, and agriculture. Nanoscience is the combination of nanotechnology and chemistry dealing with the study of nanoparticles of varying sizes from nanometers.

Figure 1: Diagrammatic explanation about heavy metals in the environment

Among top - down and bottom - up methods of nanomaterials' synthesis the top - down methods like grinding and milling break the bulk material into nano - scale, while bottom - up method grows from an atom to a Nano - scale size. In addition, nanoparticles are synthesized by the different physical and chemical methods such as electrochemical technique, photochemical reduction, thermal deposition methods, chemical reduction using organic and inorganic reducing agents, evaporation - condensation methods, microwave processing, electron irradiation, gamma irradiation, micro emulsion, and laser ablation, etc. Synthesis of nanomaterials using as mentioned procedure is highly cost - effective, use of toxic chemical and hazardous bi - products. Nanostructured crystalline particles have

drawn the attention of researchers because of their wide applications made possible due to their particle size dependent properties and their scientific and industrial significance. Nano sized particles of semiconductor materials have established their usefulness in recent years because of their desirable properties and applications in various areas such as catalysts, sensors, photoelectron devices, highly functional and effectivedevices. These nanomaterials have unique thermal, structural, and electronic properties which impart them the quality of high scientific attraction in basic and applied fields. ZrO2 (zirconia) is a material of excellent technological significance, having fine natural color, high stability, high toughness, high chemical strength, desirable corrosion, chemical and microbial resistance. ZrO2 exhibits plenty of oxygen vacancies on its surface with wide band gap P - type semiconductor. The high ion exchange ability and redox movement make it useful in many catalytic processes as a catalyst. ZrO2 has been examined for potential use as an insulator in transistors for future nonelectric devices which is an important dielectric material and polymorphic compound The crystal morphology of zirconia is monoclinic, tetragonal, and cubic. To maintain the zirconia crystal phase of the unstable crystal anatomy of zirconia, the inclusion of other compositions as stabilizer agents is required at room temperature and pressure conditions. To synthesize ultrafine ceramic powders, various approaches such as sol–gel, hydrothermal, spray pyrolysis, salt - assisted aerosol decompositions, carbon nanotube template technique and reflux and emulsion precipitation have been made. The hydrothermal approach can come out with fine, high purity and stoichiometric particles of single and multi - component metal oxides. Moreover, the zirconium oxide particles with desired shape and size can be achieved, if the process circumstances such as solution pH, solute concentration, reaction temperature, reaction time, seed materials, and the type of solvent are carefully guarded. In the present investigation, the synthesis by the hydrothermal method and the characterization of ZrO2 nanoparticles are reported. The as - prepared ZrO2 nanoparticles were characterized by X - ray diffraction analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV analysis, PL, and dielectric studies

2. Experimental Procedures

2.1Synthesis of ZrO2 NPs

Zirconium Oxychloride (ZrOCl2.8H2O), Methylene blue, Rhoda mine B, reagents were purchased from Sigma Aldrich Chemical, were used for the synthesis of green catalyst ZrO2 NPs. Distilled water was used as a solvent throughout the end of the experiments and all other reagents used were of analytical grade. In a conventional synthesis, in 100 ml of distilled water 0.1 M of $ZrOCl2.8H_2O$ is dissolved with effective stirring. After a few minutes, 0.2 M of KOH is added to the above solution. Afterward, the solution formed is transferred into a stainless steel Teflon lined sterilized capacity of 100 ml and kept in an oven at 180^0C for 16hrs. To remove the soluble impurities and depress agglomeration, the resulting precipitates are cleaned with distilled water and absolute ethanol. The final product is dried for 3hrs in vacuum at 80^0C.

Characterization of ZrO2 NPs

The optical properties of ZrO2 NPs were characterized using UV - Visible spectroscopy. The obtained colloidal solution after dispersion of ZrO2 NPs powder in water for 20 min using Ultrasonic bath was studied to find out its UV - Vis characteristic absorption band. Consequently, the synthesized ZrO2 NPs powder was analyzed for their optical band gap at room temperature using a UV - Visible spectrophotometer. The X - ray diffraction (XRD) pattern of the ZrO2 powder was recorded by using a powder X - ray diffractometer (Schimadzu model: XRD 6000 using CuKa with a diffraction angle between 20^0C and 80^0C. The crystallite size was determined from the broadenings of corresponding X - ray spectral peaks by using Scherrer's formula. Scanning electron microscopy (SEM) studies were carried out on JEOL, JSM - 67001. Transmission electron microscope (TEM) image was taken using an H - 800 TEM (Hitachi, Japan) with an accelerating voltage of 100 kV. UV–Visible absorption spectrum for the samples was recorded using a Varian Cary 5E spectrophotometer in the range of 300–700 nm. The FT - IR spectrum of the ZrO2 nanoparticles was taken using an FTIR model Bruker IFS 66 W Spectrometer. The photoluminescence (PL) spectrum of the ZrO2 particles was recorded by the Perkin - Elmer lambda 900 spectrophotometer with a Xe lamp as the excitation light source. The dielectric properties of the ZrO2 nanoparticles were analyzed using a HIOKI 3532 - 50 LCR HITESTER over the frequency range 50 Hz–5 MHz.

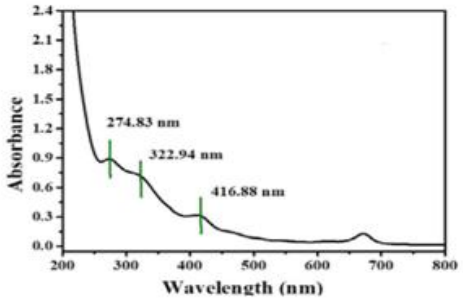


Figure 2: Absorption Vs. Wavelength plot in UV - X - ray in hydrothermal.

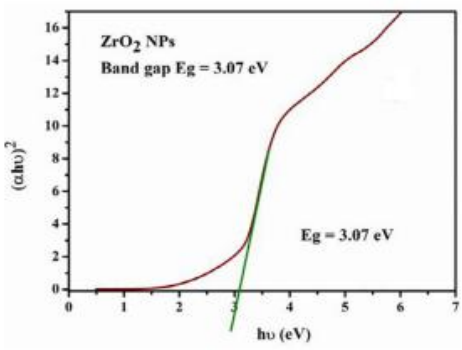
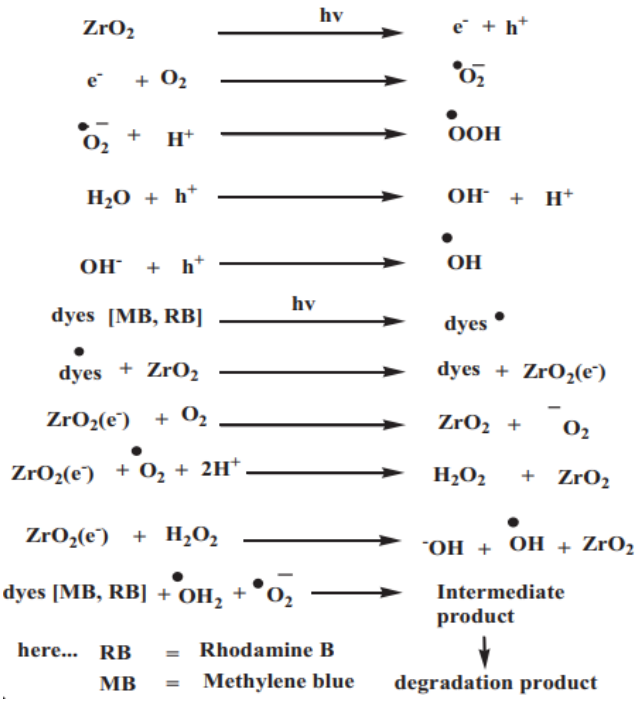


Figure 3: Cukα plot radiation plot

3. Results and discussion

The present study investigated the fabrication of ZrO2 NPs by using Cuka. X - ray diffraction (XRD) was carried out for the synthesized ZrO2 nanoparticles using instrument with CuKa radiation. The degradation ability of NPs depends on their different parameters i. e. size, shape, surface area, and

morphology. Therefore, if irradiated photon energy with the semiconducting ZrO2 NPs is greater than its bandgap energy, the electrons from the valence band are excited to conduction band and the generated holes strongly oxidize the organic molecules near the hole and generate carbon dioxide and water molecules. The photocatalytic degradation of dyes depends mainly on two factors; the main factor is the smaller size of ZrO2 NPs with large surface area and more active sites on the surfaces. The second one is low bandgap energy that strongly influences the rate of photo degradation. More significantly, after several recycles slight loss in the catalytic activity of ZrO2 NPs for dye degradation. The synthesized green catalyst ZrO2 NPs has been promising material for dye degradation studies and antioxidant activity.



From Fig.4 it can be clearly observed that the diffraction peaks appear in the pattern indicating good crystalline nature. The synthesized material displays a tetragonal structure and all the peaks are indexed. The average Nano - crystalline size (D) was calculated using the Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where k is the X - ray wavelength, h is the Bragg diffraction angle, and b is the FWHM of the XRD peak appearing at the diffraction angle h. The Scherrer formula was used to calculate the average grain size and for the most prominent peak at (101). It was found to be around 12 nm.

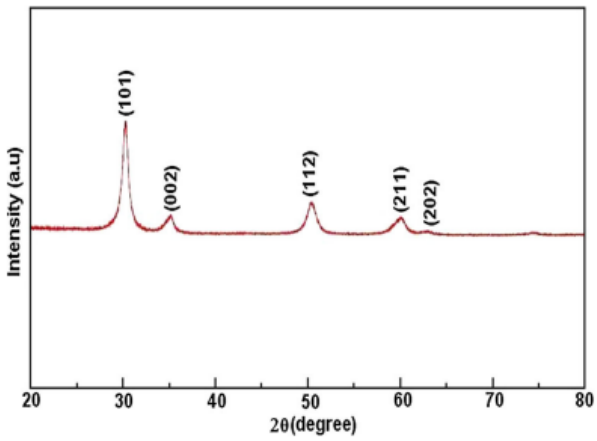


Figure 4: XRD spectrum of ZrO2 nanoparticles

3.1 Scanning electron microscopy (SEM) analysis

Figure 5 shows the SEM images of the as - prepared ZrO2 nanoparticles. Due to aggregating or overlapping of smaller particles there are some larger particles. The SEM pictures clearly exhibit that the grains are randomly distributed with smaller size and it is noticed that the particles are of homogeneous spherical shape. The image clearly indicates that the average crystalline size could be 10 nm. Figure 4 shows an elemental examination of the ZrO2 nanoparticles, in which the peaks of Zr and O are evident. The confirmation for the formation and composition of crystalline ZrO2 nanoparticles was done by quantitative analysis, which showed the Zr and O as the only elementary species present in the sample signifying the high purity and the absence of any other impurity in the sample.

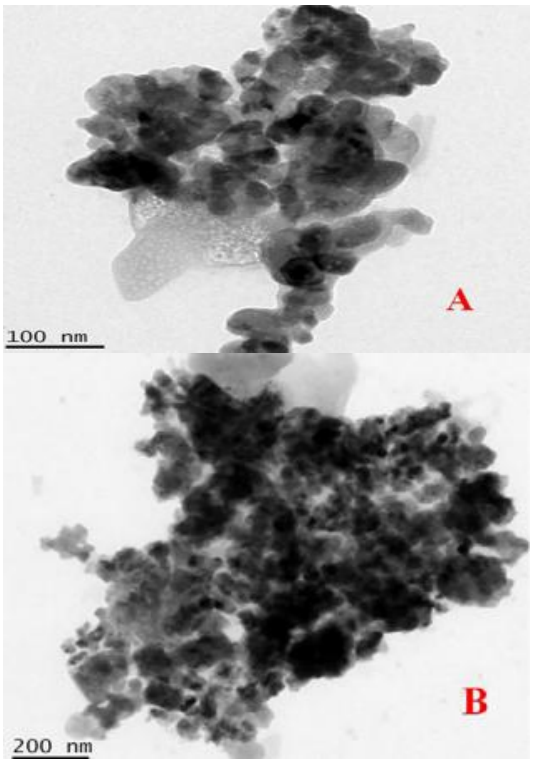


Figure 5: SEM Images of the ZrO2 nanoparticles in 100nm & 200nm.

3.2 Transmission electron microscopy (TEM)

TEM is commonly used for imaging and analytical characterization of the nanoparticles to assess the shape, size, and morphology. TEM images of the ZrO2 nanoparticles are shown in Fig.6. From the micrographs the average size of the particles was found to be &24 nm and it was directly measured from the ruler of the image.

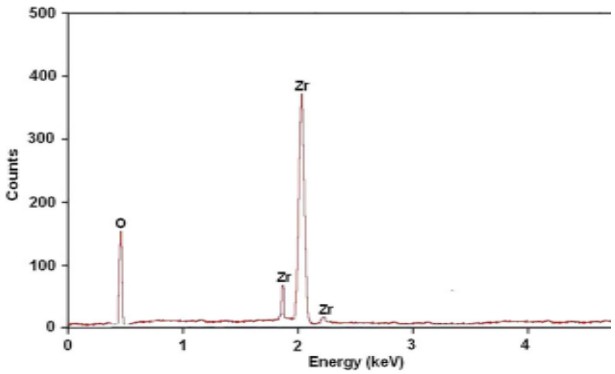


Figure 6: EDX spectrum of the ZrO2 nanoparticles

3.3 UV–visible absorption spectrum

Optical absorption measurement was also accomplished on ZrO2 nanoparticles. Figure 7 shows the deviation of the optical absorbance with the wavelength of the ZrO2 nanoparticles as prepared. The optical absorption coefficient was computed in terms of wavelength range of 300– 700 nm. It can be observed that the absorption edge is slightly red - shifted as distinguished from bulk ZrO2, thus approaching its absorption into the visible region. Hence, the samples are completely transparent at higher wavelengths. The UV spectrum exhibits an absorption peak at 320 nm which occurs due to a valence - to - conduction band.

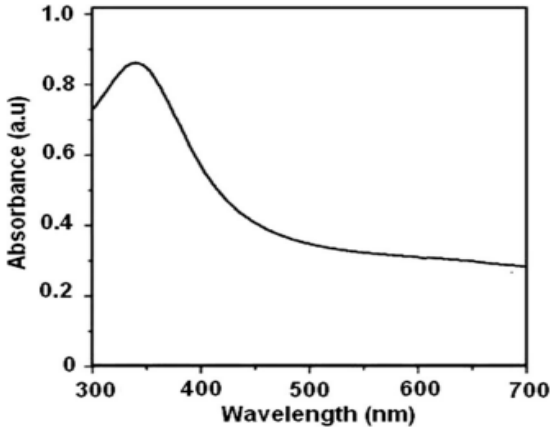


Figure 7: Optical absorption spectrum of ZrO2 NPs

4. Conclusion

We have successfully synthesized ZrO2 NPs using in Hydrothermal extract as reducing and stabilizing agent. Synthesized ZrO2 NPs were characterized by different analytical techniques such as UV - Vis, SEM, TEM, EDX. The synthesized ZrO2 NPs were crystalline with an average particles size of 25 nm. Further, the green synthesized ZrO2 NPs showed high photocatalytic activity towards remediation of environmental pollutants such as MB and Rh - B dyes. ZrO2 nanoparticles were synthesized using the hydrothermal method. The composition of ZrO2 nanoparticles was deepstated by X - ray diffraction (XRD). By using scanning and transmission electron microscopy (SEM and TEM) the size and the morphology of the samples were characterized. The size of the ZrO2 nanoparticles was distinguished using transmission electron microscopy (TEM), which also helped to determine the size of the prepared ZrO2 nanoparticles and the particle size was found to be &24 nm. The FT - IR spectrum demonstrated the strong existence of ZrO2 nanoparticles. The optical properties were examined by the UV–Vis absorption spectrum. The band gap value was found to be 5.02 eV. Room temperature photoluminescence demonstrated intrinsic defects of oxygen vacancies. The optical property of the prepared ZrO2 nanoparticles was examined by PL study and it exhibited the oxygen vacancies accompanied intrinsic defects. The dielectric constant and the dielectric loss were examined at different temperatures as a function of frequency. In addition, the synthesized ZrO2 NPs showed good antioxidant activity. Conducting education and citizen awareness programmers in the field of environment

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