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Synthesis and Characterization of ZrO₂ Nanoparticles using Microwave Assisted Method and Its Antimicrobial Activity

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ABSTRACT

Zirconium dioxide (ZrO₂) nanoparticles have been synthesized via microwave assisted method. The structural analysis was carried out using X-ray diffraction. It showed that the ZrO₂ nanoparticles exhibited monoclinic structure. The morphological studies revealed that the particles were spherical in structure and slightly agglomerated. The ZrO₂ product was investigated by FT-IR, UV, SEM and microbial activity studies.

1. Introduction

The ZrO₂ nanoparticle is very interesting and valuable material for its fundamental application based properties. The synthesized metal oxide nanoparticles vary in physical, chemical, and morphological properties and are being used in various fields as they have various applications [1]. Thermodynamically most stable form of ZrO₂ is monoclinic structure. Pure zirconia has high number of oxygen vacancies defects predominantly. The nano sized zirconia owing to large surface area has high number of oxygen vacancies at grain surface [2]. Therefore solid ZrO₂ can conduct electricity up to some extent and it is considered as p-type semiconductor. The band gap value of ZrO₂ depends upon synthesis temperature, particle size and crystalline structure. Numerous chemical methods have been reported to synthesize pure ZrO₂, such as thermal decomposition [3], sol-gel methods [4], and hydrothermal techniques [5]. The as-prepared nanoparticles were extensively characterized using X-ray diffraction, FT-IR, UV, SEM and antimicrobial activity studies.

2. Experimental Methods

2.1 Materials

All the chemicals were used as analytical grade without any further purification. Zirconium oxy nitrate and ammonia were used to prepare the nanoparticles of this work. Double distilled deionized water used in this investigation. Disc diffusion method has employed with gram negative bacteria (*Pseudomonas aeruginosa* and *Escherichia coli*) and gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*).

2.2 Synthesis

All chemicals were analytical grade (AR) and used without further purification. Zirconium oxychloride and NaOH were used for the preparation of the zirconium oxide nanoparticle. In the present work 8.6 gm of zirconium oxychloride (ZrO₂·8H₂O) was added with deionized water and stirred for homogeneous solution, during stirring NaOH solution was added till the pH value becomes 12. After that white sol has been formed. This solution kept at microwave oven with minimum temperature at 6

minute. The prepared powder filtered with deionized water and dried at 50 °C for 1 hour. This powder calcinated 600 °C for 4 hour.

2.3 Instrumentation

Powder X-ray diffraction pattern of the nanoparticles was obtained using a Rigaku Ultima IV powder X-ray diffractometer. The sample was scanned over the required range for 2θ values. The FTIR spectrum of the sample was recorded within the wavenumbers from 4000 cm⁻¹ to 400 cm⁻¹ by using Perkin Elmer Frontier FTIR. Optical properties were examined by UV-Vis spectrophotometer (UV-1800 PC Shimadzu). The antimicrobial activity was determined by disc diffusion method.

3. Results and Discussion

3.1 X-Ray Diffraction Method

Zirconium dioxide was synthesized by microwave assisted solution technique. The powder XRD pattern of the prepared ZrO₂ nanoparticles is shown in Fig. 1 which shows a strong diffraction peaks along 28.28°, 24.16°, 30.32°, 34.2°, 35.4°, 50.19°, 40.9°, 45.6°, 60.3° [6], and 65.8° with h k l values. The ZrO₂ nanoparticles show a tetragonal phase from diffraction peaks at 30.32°, 34.2°, 50.19°, and 60.3°.

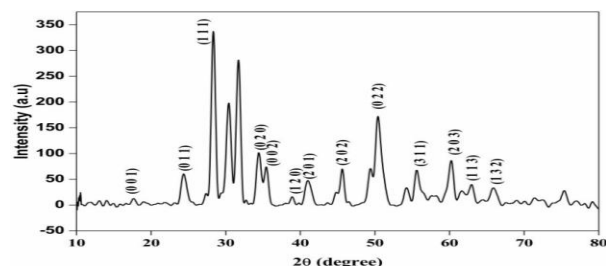


Fig. 1 XRD pattern ZrO₂ nanoparticles

From the Fig. 1, the diffraction bands were confirmed by crystalline nature. The crystalline nature was confirmed to peaks at (001), (011), (111), (020), (002), (120), (201), (202), (022), (311), (203), (113) and (132). The indexed peaks are confirmed by monoclinic structure at (002), (202), (022), (311) and (113) [7]. These both structures were confirmed by SEM images. The broad diffraction bands shows the prepared samples

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are nano sized. The ZrO₂ nanoparticle grain size was found as around 35 nm. The grain size calculated formula is given below [8],

$$D = 0.9\lambda / \beta \cos\theta,$$

where λ is incident X-ray wavelength, β is FWHM, and θ is diffraction angle. The average grain sizes of ZrO₂ nanoparticles were calculated, from the diffraction bands.

3.2 SEM Analysis

The morphology of the prepared ZrO₂ nanoparticle shows the particles are crystalline nature and looks like stony structure due to the high degree of agglomeration. Agglomeration occurred because of appropriate intermolecular attraction present between the prepared nanoparticles. From the SEM images, the particles size is found around 32 to 38 nm. This observed size was confirmed as support from XRD analysis. The particles are confirmed as a randomly spherical shape from the image. SEM measurements were carried out on ZrO₂ nanoparticles to uncover morphological differences between the two systems at the nanometer and micrometer scales. Fig. 2 shows the SEM micrograph at four different magnifications for ZrO₂ nanoparticles.

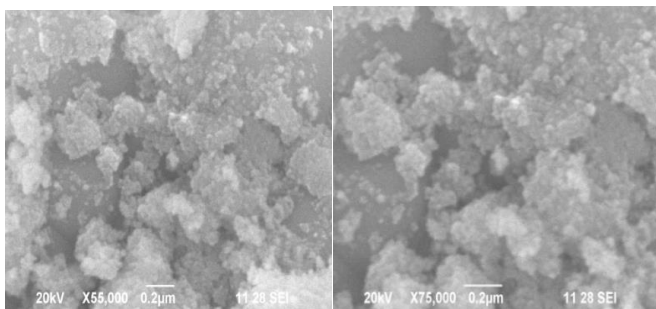


Fig. 2 SEM images of ZrO₂ nanoparticles

3.3 FTIR Characterization

The chemical structures of ZrO₂ nanoparticles are characterized by FTIR spectroscopy. FTIR study confirms the functional groups present in the prepared ZrO₂ nanoparticles. Fig. 3 shows the FTIR spectrum of the prepared sample. The weak peaks from 3000 to 3500 cm⁻¹ corresponds to the stretching vibrations of O-H on surface of ZrO₂ nanoparticle, while the peaks at 751 cm⁻¹ and 577 cm⁻¹ Zr-O₂-Zr asymmetric and Zr-O stretching modes respectively, confirms the formation of ZrO₂ phases [9]. Weak bands observed at 1642 cm⁻¹ and 3336 cm⁻¹ are explain the stretching and bending vibrations of O-H bands, show to water molecule as absorbed. The bands 1339 cm⁻¹ is confirm to absorption of nonbridging OH groups. The very sharp peaks 751 cm⁻¹ is occurred at characteristic of m-ZrO₂.

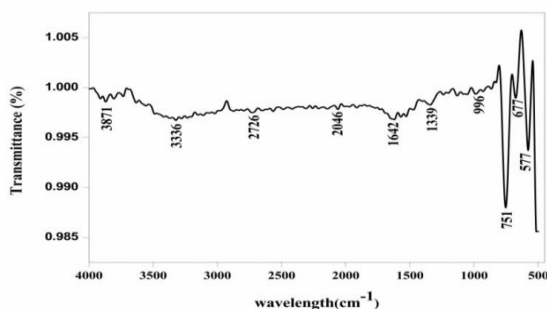


Fig. 2 FTIR spectrum of ZrO₂ nanoparticles

3.4 UV-DRS Analysis

The UV-DRS spectra of the prepared ZrO₂ nanoparticle as shown in Fig. 4. The optical band gap energy for the prepared ZrO₂ sample was determined from diffuse reflectance spectra using Kubelka Munk equation,

$$((R_{\infty}) \cdot h\nu)^2 = A(h\nu - E_g)$$

where $F(R_{\infty})$ is the Kubelka- Munk function or reemission parameter, $h\nu$ is the energy of incident photon, R_{∞} is the diffuse reflectance that is obtained from $R_{\infty} = R_{\text{sample}}/R_{\text{standard}}$, and A is a constant. The values of $((R_{\infty}) \cdot h\nu)^2$ versus $h\nu$ was plotted for the prepared sample as shown in Fig. 4. Straight line was drawn to fit the experimental curve, and was extended to cut off the $h\nu$ axis, optical band gap energy value has been determined

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of ZrO₂ nanoparticles. From the Fig. 4, the optical band gap of prepared ZrO₂ nanoparticle has been 4.9 eV.

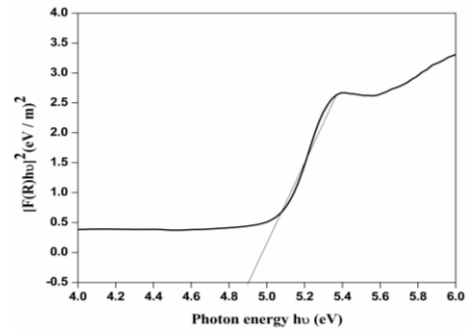


Fig. 4 UV DRS spectrum of ZrO₂ nanoparticles

3.4 Antimicrobial Activity

The antimicrobial activity of ZrO₂ was investigated against gram negative bacteria (*Pseudomonas aeruginosa* and *Escherichia coli*) and gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*), respectively. The prepared ZrO₂ nanoparticles showed a good inhibitory action against *Pseudomonas aeruginosa* (inhibition zone size of 10 mm) at the 100 µg/mL compared to other bacteria due to the negatively charged, *P. aeruginosa* cell wall readily attracting positively charged ZrO₂, and in that way inhibiting microbial actions. In addition to that the ZrO₂ nanoparticle was directly proportional to their inhibitory actions beside the tested microorganism. ZrO₂ nanoparticles have confirmed that they have possible biomedical applications.



Fig. 5 Antimicrobial activity of ZrO₂ nanoparticles

4. Conclusion

Zirconium dioxide was synthesized by microwave assisted solution technique. The indexed peaks are confirmed by monoclinic structure at (002), (202), (022), (311) and (113) the ZrO₂ nanoparticle grain size was found as around 35 nm. The morphology of the ZrO₂ nanoparticle shows the particles are crystalline nature and looks like stony structure due to the high degree of agglomeration. The SEM images, of the ZrO₂ particles size is around 32 to 38 nm. The chemical structures of ZrO₂ nanoparticle are characterized by FTIR spectroscopy. The weak peaks from 3000 to 3500 cm⁻¹ corresponds to the stretching vibrations of O-H on surface of ZrO₂ nanoparticle, while the peaks at 751 cm⁻¹ and 577 cm⁻¹ Zr-O₂-Zr asymmetric and Zr-O stretching mods respectively, confirms the formation of ZrO₂ phases. The optical band gap of prepared ZrO₂ nanoparticle has been obtained as 4.9 eV. The antimicrobial activity of ZrO₂ was investigated against gram negative bacteria (*Pseudomonas aeruginosa* and *Escherichia coli*) and gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*), respectively and leads the idea as they have possible biomedical applications.

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