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RESEARCH ARTICLE

Synthesis and Characterisation of Zirconium Oxide Nanoparticles Via the Hydrothermal Method and Evaluation of their Antibacterial Activity

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ABSTRACT:

Zirconium oxide (ZrO_2) nanoparticles were characterised and synthesised by the hydrothermal method. Products were characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-absorption spectroscopy. The crystal structure was determined by XRD. The morphology and particle size were examined via atomic force microscopy and SEM. Fourier transform infrared spectroscopy was used to prove the strong presence of ZrO_2 nanoparticles. The current research also evaluated the effectiveness of the prepared ZrO_2 nanoparticles of different concentrations as an antibacterial agent against *Staphylococcus aureus*. Results showed that the zones of inhibition increased with the increase in the concentration of ZrO_2 nanoparticles.

KEYWORDS: Zirconium Oxide, Nanoparticles, Hydrothermal, Antibacterial.

1. INTRODUCTION:

Zirconia is an element of great technological importance due to its high strength, good chemical stability, material resistance, corrosion resistance and biological and chemical resistance(1,2). Zirconia is considered a band gap p-type semiconductor that contains abundant oxygen vacancies on its surface(3). The redox activities and the high ion-exchange ability of zirconiaare important in catalytic applications(4). Zirconia manifests in three stable stages. Up to 1100°C, the monoclinic phase is the first stable phase. The first stable phase turns into the tetragonal phase as the temperature increases and remains stable until 2370°C. Afterwards, the phase turns into the cubic phase, which is considered as a fluorite type. The other two sides can be considered as structural distortions from the cubic phase(5). ZrO_2 nanoparticles are non-toxic materials and are considered as one of the most active metal oxides that contribute to many applications related to chemical catalysis(6).

ZrO_2 nanoparticles are used as pyrooptics due to their excellent optical properties and the unique sensitivity of zirconia powders. Such nanoparticles are also used in optical devices as an optical storage material in digital storage media(7). Many electronic devices use zirconium in their manufacturing processes, such as piezoelectric elements, electrodes and ion exchangers(8). ZrO_2nanoparticle alloys can also be used for space applications as alternatives to titanium in liquid rocket engines. In the field of catalysis, fuel cell technology and gas sensors(9), zirconium has been widely used in catalysis, for example, supporting Ag, Cu and Aucatalysts in methanol synthesis from $H_2$and CO_2(10), CO oxidation(11,12), water gas-shift reaction(13) and in photo catalytic reactions, such as CO_2 reduction(14).

Nanometals, such as ZrO_2 nanoparticles, are involved in many biological, industrial and environmental applications(15). In the medical and biotechnological fields, ZrO_2 nanoparticles can interfere with the natural processes of cells, such as tissue regeneration(16) and radiotherapy in treating cancer. Moreover, ZrO_2 nanoparticles are also used as drug delivery for treatment, particularly in cancer treatment(17).

ZrO_2 nanoparticles have great activity on *Fusarium oxysporum*(18), which causes plant diseases. In addition to the effectiveness of ZrO_2 nanoparticles against *Escherichia coli*, albicans fungi and *A. nigo*, ZrO_2 nanoparticles can be utilised in numerous industrial applications, such as insecticides, paints, ceramics and water treatment, and these particles exhibit great efficacy against bacteria, fungi and algae.

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Several techniques, such as the vapor-phase method(19), spray pyrolysis(20), hydrothermal method(21), hydrolysis (22), microwave plasma(23), micro-emulsion(24) and sol-gel method(25), are performed to produce ZrO_2 nanoparticles. The chemical methods of preparing zirconium nanoparticles provide new properties for the particles formed because of the quantum confinement effect. Reducing the size of the particles causes the structure of the nanoparticles to perform differently from that of a single crystal, which in turn influences the final properties(3).

An alternative and advanced study is proposed to prepare ZrO_2 nanoparticles, where the biosynthesis of nanoparticles has gained great attention due to the environmental suitability of the products in various applications in the medical and pharmaceutical fields(26, 27).

In recent years, the thermal treatment method has been applied to produce many nanomaterial's, such as zinc oxide nanoparticles(28), metal ferrite nanoparticles(29,30), cadmium oxide nanoparticles and thermo luminescence nanomaterial's(31).

The present paper was organised as follows: ZrO_2 nanoparticles were prepared via the hydrothermal method; the particles prepared were described by scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FT-IR) and UV-Visible spectroscopy. The biological activity of ZrO_2 nanoparticles was determined and utilised in the third section as an antibacterial agent.

2. MATERIALS AND METHODS:

2.1 Materials:

Zirconium oxychloride hydrate ($ZrOCl_2{\cdot}8H_2O$), ethanol and sodium hydroxide (NaOH) were supplied by Sigma-Aldrich. All chemicals were utilized as received without any further purification.

2.2 Synthesis of ZrO_2 nanoparticles:

ZrO_2 nanoparticles were prepared via the hydrothermal method. In 100mL of distilled water, 0.5M of $ZrOCl_2{\cdot}8H_2O$ was dissolved with NaOH, which was used as starting materials. At room temperature, 5 M NaOH was slowly added to the aqueous solution of $ZrOCl_2{\cdot}8H_2O$ with continuously stirring by magnetic stirrer for 30 min to obtain a zirconium hydroxide precipitate ($Zr(OH)_4$). The latter was kept in the autoclave for a few min. The sample was then run using the hydrothermal method at 180°C for 16 h. The sample was centrifuged and washed by mixture of absolute ethanol and distilled water (1:1) to remove unwanted impurities. Next, the purified sample was dried by the vacuum for 3 h at 80°C.

Reaction:

$$ZrOCl_2.\,8H_2O + NaOH \rightarrow Zr(OH)_4 + NaCl_2 + H_2O$$

$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O$$

2.3 Antibacterial activity of ZrO_2 nanoparticles:

The antibacterial activity of the prepared ZrO_2 nanoparticles was investigated against a Gram-positive bacteria strain *S. aureus* via an agar well diffusion technique(32). 20mL of Mueller-Hinton agar was aseptically distributed in petri dishes. The bacterial genera were transferred to the agar using a sterile wire loop, wells (6mm diameter) were then bored on the agar plates using a sterile tip(33). Different concentrations of the nanoparticles (25,50,100 and 200µg/mL) were used into the bored wells(34). The samples were incubated overnight at 37°C. The average diameter of inhibition zones was measured using agar well method(35). The experiments were performed in triplicate(36).

2.4 Statistical analysis:

The studied groups were compared using the *T*-test at $p<0.05$ as a significant value(37).

2.5 Material characterisation:

XRD of the ZrO_2 powder was performed using an X-ray diffractometer (Shimadzu model: XRD 6000 using CuKα radiation [λ = 1.5418 Å]). The quality of surface morphology was analysed through SEM and AFM. The FT-IR of ZrO_2 nanoparticles was obtained using an FT-IR model Bruker spectrometer.

3. RESULTS AND DISCUSSION:

3.1 XRD analysis of ZrO_2 nanoparticles:

Results of the XRD analysis of the synthesised ZrO_2 nanoparticles via the hydrothermal method using an instrument with CuKα radiation are shown in Fig. 1. The XRD peaks were consistent with the JCPDS data card 96-900-7486 of the tetragonal structure, and all the peaks were indexed. The determined peaks that corresponded to tetragonal zirconia were observed at the lattice planes of (100), (011), (110), (002) and (222) in the 2θ value: 17.33°, 24.09°, 24.54°, 33.10° and 58.26°, respectively.

Table 1. Structural parameters of ZrO_2 nanparticles as obtained from XRD analysis.

2θ(degree)	
hk1	**Observed**
100	17.33°
011	24.09°
110	24.54°
002	33.10°
222	58.26°

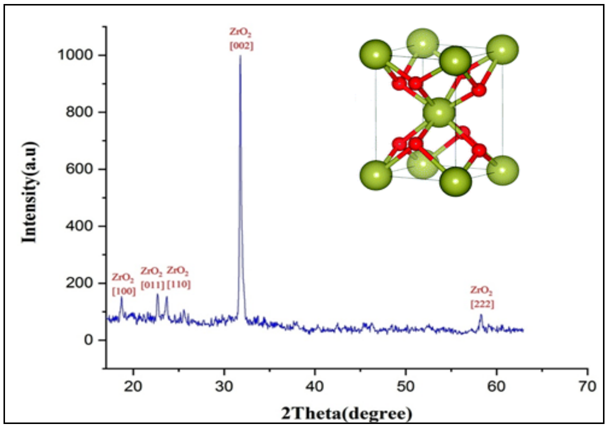
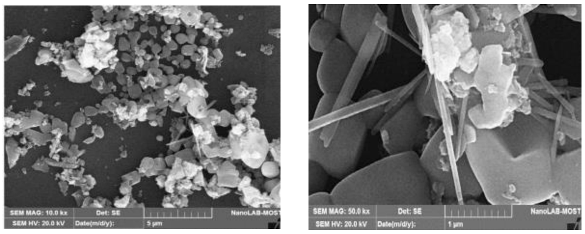


Figure 1: XRD patterns of synthesized ZrO_2 nanoparticles using hydrothermal method

3.2 SEM analysis:

Figs. 2A and B present the SEM images of the ZrO_2 synthesised via the hydrothermal method. The nanoparticles are spherical and tube-like.



A B

Figure 2: (A and B) SEM images of the ZrO_2 synthesized hydrothermal method with the different shapes

3.3 AFM analysis:

AFM was performed to analyse the morphological and size of ZrO_2 nanoparticles and the topography of the ZrO_2 surface structure. The AFM images in Fig. 3 showed that the surface structure of ZrO_2 nanoparticles was two and three-dimensional, which were grown hydrothermally. Furthermore, it was observed that the ZrO_2 nanoparticles had a small particle size distribution 73.82 nm (Fig. 4).

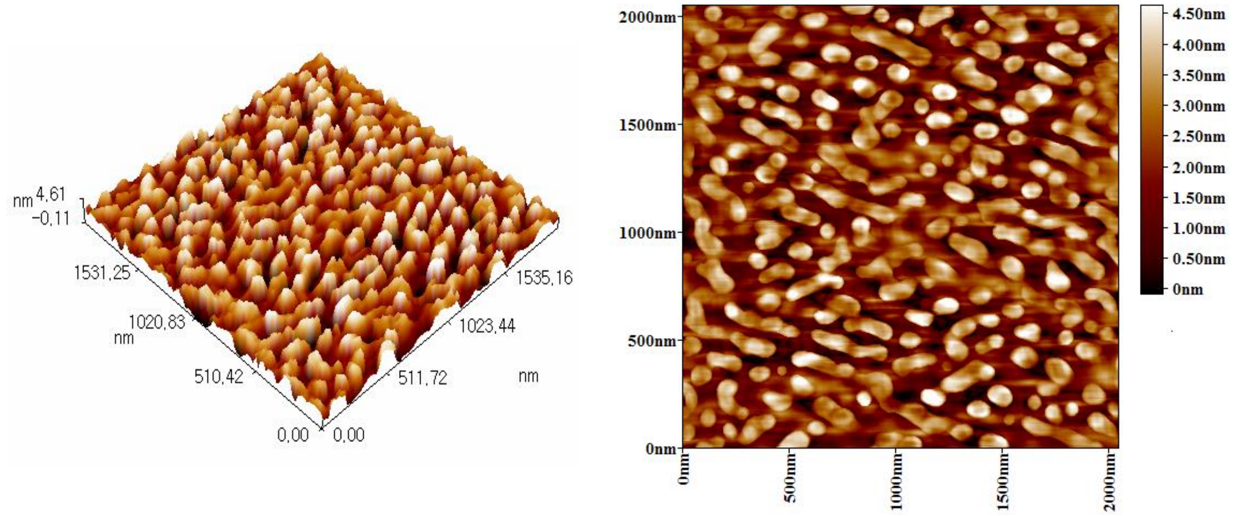


Fig. 3: AFM image of two and three- dimensional of ZrO_2 nanoparticles

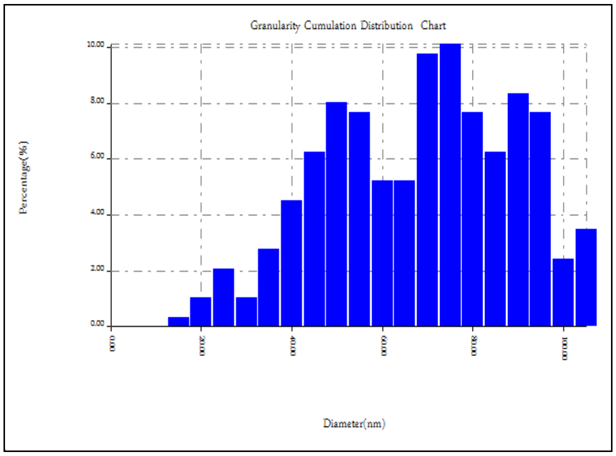


Fig. 4: The average distribution for ZrO_2nanoparticles of diameter 73.82 nm

3.4 FT-IR of ZrO_2 nanoparticles:

ZrO_2samples were identified by FT-IR spectrum in the range of 400-4000 cm^{-1}. A strong absorption with a peak at 493.74 cm^{-1} was detected due to the Zr-O vibration of the tetragonal structure, and the width of the band signified that the ZrO_2 powders were nano crystals(38). The absorption peak in the region of 1141.78cm^{-1} corresponded to the O-H bonding. Symmetric frequencies of Zr-OH were observed at 1110.92 cm^{-1}(39).

3.5 UV-Visible absorption spectrum:

Absorption measurement was performed on ZrO_2 nanoparticles. The optical absorption was obtained within the wavelength range of 200-800nm. The samples were completely transparent at higher wavelengths. The UV exhibits an absorption peak at 324nm due to a valence to conduction band.

3.6 Antibacterial activity of ZrO_2 nanoparticles:

The antibacterial activity of ZrO_2 nanoparticles against *S. aureus* bacteria was investigated via an agar well method. The zones of inhibition to different concentrations of ZrO_2 nanoparticles were measured as shown in Fig. 5. The effectiveness of ZrO_2 against the bacteria was directly proportional to the concentration of ZrO_2 nanoparticles where the maximum inhibition diameter was at a concentration of 200µg/mL. These results were consistent with those of Reference(40), who reported ZrO_2 nanoparticle activity against Gram-positive bacteria. In general, the small size of ZrO_2 nanoparticles that possess antioxidant activity and antioxidant drug effectiveness is the primary feature of penetration of the bacterial membrane. The outer membranes contained nanopores; therefore, the ZrO_2 nanoparticles was able to penetrate the cell membrane because their diameter was than that of the pores, and the result was an unrestricted mass transfer across the membranes.

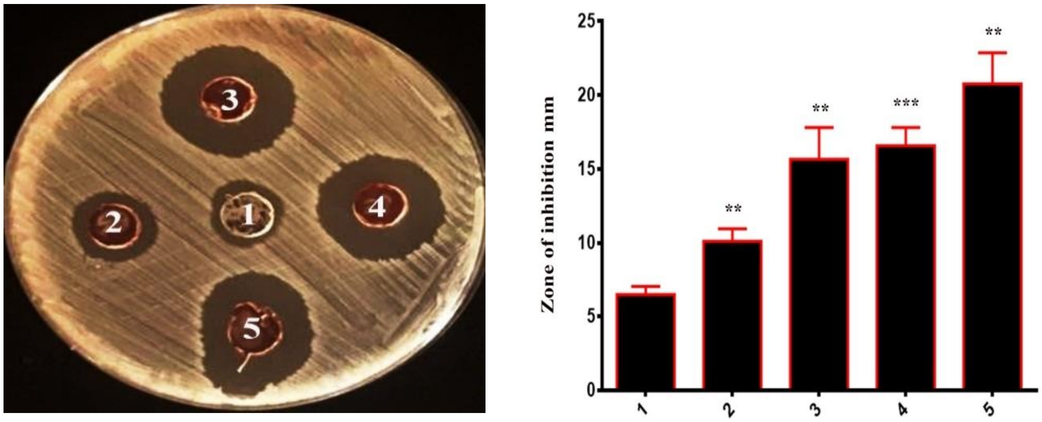


Figure 5: Anti-bacterial activity of nanoparticles against *S. aurues*. 1. negative control (DMSO). 2. Concentration 25µg/mL. 3. Concentration 50µg/mL.4. Concentration 100µg/mL. 5. Concentration 200µg/mL. The value are shown as the mean±SEM. *p<0.05, **p<0.01, and ***p<0.001.

4. CONCLUSIONS:

ZrO_2 nanoparticles were synthesised via a hydrothermal reaction using NaOH and the presence of heat. XRD results showed that the prepared nanoparticles were compatible with tetragonal zirconia. AFM, XRD and SEM analyses showed that the growth of ZrO_2 nanoparticles was limited to approximately 73nm. FT-IR analysis confirmed strong absorption peak at 473 nm due to the Zr-O vibration of the tetragonal structure and production of ZrO_2 powders as nano crystals due to the quantum confinement effect. Blue-shifted UV absorbance from the bulk ZrO_2 was achieved in the nanostructure and showed absorption peak at 324nm. The effectiveness of different concentrations of ZrO_2 nanoparticles in inhibiting *S. aureus* bacterial isolates was evaluated. The diameter of the inhibition zone reached 22mm at 200µg/mL, thereby proving the inhibitory efficacy of the ZrO_2 nanoparticles.

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